ATTACHMENT D

Testing & Monitoring Plan

Gulf Coast Sequestration, LLC (G1037)

Project Minerva, Cameron Parish
Minerva South CCS Well Nos. 001 & 002

EPA Project Id: R06-LA-0002

LDENR Appl Nos: 45031 & 45032

Date: November 2024

CERTIFICATION

Per LAC 43:VII §3603.H.1, the geoscientific aspects of the Testing and Monitoring Plan have been prepared by or under the supervision of a licensed Professional Geologist authorized to practice by and in good standing with the Louisiana Board of Professional Geoscientists. A separate certification page will be submitted with the Attachments to the Narrative that require certification.

Kaycee M. Garrett LA License No. 1325 *I, Kaycee M. Garrett, certify that I have personally examined and am familiar with the information submitted in this document and the attached documents, and that, based on my inquiry of those individuals immediately responsible for obtaining the information, I believe that the submitted information is true, accurate, and complete.*	
TESTING AND MONTORING SECTIONS (Including applicable Tables, Figures, and Appendices) Section 1 Introduction Section 2 Testing and Monitoring Requirements Section 3 Carbon Dioxide Stream Analysis Section 6 Above Confining Zone Monitoring Section 8 Reservoir Testing Section 9 Injection Zone Carbon Dioxide Plume and Pressure Extent Tracking	

Per LAC 43:VII §3603.H.2, the engineering aspects of the Narrative have been prepared by or under the supervision of a licensed Professional Engineer (PE) authorized to practice by and in good standing with the Louisiana Board Professional Engineering and Land Surveying. Since the engineering aspects of the applications have been designed by a consulting PE, the required documents will be certified once the technical review is completed by LDENR. A separate certification page will be submitted with the attachments to the Narrative that require certification.

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FACILITY INFORMATION

Facility Name: Minerva Facility

Injection Wells: Minerva South CCS Well No. 001 (MS CCS 1)
Minerva South CCS Well No. 002 (MS CCS 2)

Facility Contact: David Cook, CEO
5599 San Felipe St., Ste. 1450, Houston, Texas 77056
(713) 419-6808; dcook@gcscarbon.com

Well Locations: Sec 3, T12S, R13W, Cameron Parish, Louisiana
MS CCS 1 (NAD 1927)
Surface: 30° 02' 34.10" W, -93° 40' 20.63" N
Bottom-Hole: 30° 02' 34.10" W, -93° 40' 20.63" N
MS CCS 2 (NAD 1927)
Surface: 30° 02' 33.84" W, -93° 40' 20.48" N
Bottom-Hole: 30° 02' 13.74" W, -93° 40' 42.07" N

1 INTRODUCTION

This Testing and Monitoring Plan describes how Gulf Coast Sequestration, LLC (GCS) will monitor Project Minerva pursuant to Louisiana Administrative Code (LAC), Title 43, Chapter XVII, Section 3625.A (LAC 43:XVII §3625.A) of the Class VI UIC Regulations. In addition to demonstrating that the proposed wells are operating as planned, the carbon dioxide (CO_2) plume and pressure front are moving as predicted, and that there is no endangerment to underground sources of drinking water (USDWs), the monitoring data will be used to validate and adjust the geological models used to predict the distribution of CO_2 within the storage zone to support Area of Review (AoR) revaluations and a non-endangerment demonstration.

The scope of the Testing and Monitoring Plan is limited to the 30-year operational life of Project Minerva. Testing and monitoring activities conducted during the post injection surveillance period are discussed in the Post Injection Site Care (PISC) and Closure Plan (Attachment F). Plugging and abandonment activities for the injection wells are defined in the Injection Well Plugging Plan (Attachment E) and for the monitoring wells in the PISC and Closure Plan (Attachment F). Results of the testing and monitoring activities described below may trigger action according to the Emergency and Remedial Response Plan (Attachment G).

2 TESTING AND MONITORING REQUIREMENTS

Testing and monitoring will be conducted throughout all phases of the project for acquisition of baseline measurements and to ensure the CO_2 remains in compliance with the permitted specifications, the storage complex and injection wells are performing as expected, the CO_2 is contained and confined, and surrounding resources and USDWs are free from endangerment.

The testing and monitoring plan will be reevaluated once every 5 years after the date of

injection initiation and modified as necessary to ensure the plan is meeting expectations. If revisions to the plan are deemed necessary, supporting documentation and an amendment will be provided to the Louisiana Department of Energy and Natural Resources (LDENR) Commissioner of Conservation (Commissioner) for approval.

A summary of the testing and monitoring plan are provided in Table D.2-1. The monitoring network is shown in Figure D.2-1 with proposed AoR, the proposed injection wells, and the existing artificial penetrations. A magnetometer survey was performed over the area defined by the red dashed line in Figure D.2-1. The main objective was to identify any potential undocumented artificial penetrations that could provide pathways for vertical fluid migration within the modeled Area of Review, and to ensure that the proposed monitoring network was designed to monitor all potential risks. The results of the survey can be found in Appendix VIII-2 of the Project Minerva Narrative.

2.1 QUALITY ASSURANCE PROCEDURES

A Quality Assurance and Surveillance Plan (QASP) for all testing and monitoring activities, required pursuant to LAC 43: XVII §3625.A.11, is provided in Appendix D-I to this Testing and Monitoring Plan.

2.2 REPORTING PROCEDURES

GCS will report the results of all testing and monitoring activities to LDENR in compliance with the requirements under LAC 43: XVII §3629.A. This includes quarterly reporting regarding characteristics of the carbon dioxide stream and related data per House Bill 571. Table D.2.2-2 summarizes the monitoring activities presented in this plan and provides the monitoring frequency and reporting timeline for each activity.

2.3 COMPLIANCE AND REEVLAUATION

Per LAC 43:XVII §3625.A.10, GCS will periodically review the testing and monitoring plan to incorporate monitoring data collected under LAC 43:XVII §3625, operational data collected under LAC 43:XVII §3621, and the most recent area of review reevaluation performed under LAC 43:XVII §3615.C.2. GCS will review the testing and monitoring plan no less often than once every five years and will submit an amended testing and monitoring plan to LDENR or demonstrate to the LDENR Commissioner that no amendment to the testing and monitoring plan is needed.

If an amendment to the testing and monitoring plan is required, it will be submitted to LDENR for review. Upon approval by the LDENR Commissioner, it will be incorporated into the permit and will be subject to the permit modification requirements of LAC 43:XVII §3613, as appropriate. Amended plans or demonstrations will be submitted to the LDENR Commissioner within 12 months of the area of review revaluation; following any significant changes to the facility, such as the addition of monitoring wells or newly permitted injection wells within the area of review, on a schedule determined by the LDENR Commissioner; or when required by the LDENR Commissioner.

3 CARBON DIOXIDE STREAM ANALYSIS

GCS will sample and analyze the chemical and physical characteristics of the CO_2 stream during the operational period to yield representative data of the stream.

The anthropogenic CO_2 will be sourced from undisclosed strategic partners in the Lake Charles Industrial Corridor.

GSC has developed minimum specifications for constituents allowed in the CO_2 stream received from sources. The specifications are presented in Table D.3-1 and emitters will be required to provide evidence of compliance with the specification prior to transmission to the Minerva Facility. GCS will confirm compliance with the specifications by sampling the CO_2 steam according to the protocols provided in the following sections.

3.1 SAMPLING LOCATION AND FREQUENCY

CO_2 stream samples will be collected and analyzed quarterly. Sampling will begin on the first month of the quarter (March, June, September, December) following commencement of injection. When a proposed source is added and/or changes are made to the existing emitters CO_2 stream, GCS will conduct additional sampling outside of the sampling schedule to confirm compliance.

As demonstrated on the Process Flow Diagram for the Minerva Facility, Figure D.3.1-1, CO_2 stream sampling will be conducted at a sample port along the comingled inlet pipework to the Minerva Facility.

3.2 ANALYTICAL PARAMETERS

According to the requirements of LAC 43:XVII §3625, analysis of the CO_2 stream is required with sufficient frequency to provide data representative of its chemical and physical characteristics. The list of parameters identified for analysis of the CO_2 stream along with analytical methods are outlined in Table D.3.2-2. An equivalent method may be utilized with the prior approval of the LDENR Commissioner.

3.3 SAMPLING METHODS

Grab samples of the CO_2 stream will be obtained for analysis of gases (Table D.3.2-2). Samples will be collected by the emitter at their outlet and by GCS at the comingled inlet pipework to Minerva Facility. These grab samples will be obtained using laboratory approved sampling cylinders to collect and transport the samples. Stainless steel tubing or equivalent pressure hoses will be connected to a designated sampling port, with a regulator to control the pressure. The pressure of the CO_2 will be reduced ensuring the CO_2 is collected in the gaseous state as required by the Federal transportation regulations for shipment of compressed gases (CFR 173.301.a.8). Sample cylinders will be purged during sample collection to remove laboratory-added helium gas and ensure a representative sample. Sample containers will have a chain of custody form and will be labeled appropriately (See QASP, Appendix D-1).

3.4 LABORATORY SELECTION AND CHAIN OF CUSTODY PROCEDURES

Samples will be sent to and analyzed by a Louisiana Environmental Laboratory Accreditation Program (LELAP) accredited laboratory.

The LELAP lab will have all the necessary equipment, experience and certifications to complete the analysis.

The lab will have a chain of custody procedure that includes at a minimum the following:

- Sample date
- Sample description
- Sample type
- Relinquished/received by signature
- Sampler Name

3.5 LOCATION INFORMATION

For each CO_2 analysis, field personnel will document the time of each sample collection, a summary of all CO_2 stream analyses (including any quality assurance/quality control samples), interpret the results, note any identified changes and explain any data gaps.

3.6 REPORTING

GCS will submit the quarterly results of the CO_2 stream samples to LDENR within 30 days of the sampling event and the results will also be included in the semi-annual report of the period in which the sampling took place (LAC 43:XVII §3629.A.1.g). The report will also include any changes to the physical, chemical, and other relevant characteristics of the carbon dioxide stream from the proposed operating data.

4 CONTINUOUS RECORDING OF OPERATIONAL PARAMETERS

GCS will install and use continuous recording devices to monitor injection pressure, temperature, rate, and volume; the pressure on the annulus between the tubing and the long-string casing; and the annular volume added as required by LAC 43:XVII §3621.A.6.a.i-iv.

4.1 MONITORING EQUIPMENT, LOCATION, AND FREQUENCY

GCS will perform the activities identified in Table D.4.1-1 to monitor operational parameters and verify mechanical integrity of injection wells. Monitoring will take place at the locations and frequencies shown in the table. The general location of the devices within the injection well system is depicted on the Process Flow Diagram, Figure D.3.1-1.

Instrument specification sheets for the proposed continuous recording devices are provided in Appendix D-II. The appendix will be updated with the final technology selection upon completion of detailed design.

Except where indicated, monitoring data will be transmitted to a computerized control system that records, monitors, and controls injection processes. The system has not been

selected at this time, but examples include: Programmable Logic Controller (PLC), Supervisory Control and Data Acquisition (SCADA), or Distributed Control System (DCS). Monitoring Details

4.1.1 Injection Temperature, Pressure, Rate, and Volume/Mass

Injection temperature, pressure, rate, and volume will be measured at each injection well by volumetric flow meter(s). Each well will be equipped with primary and secondary meters. The volumetric flow meters will also be equipped with electronic pressure and temperature gauges with transmitters to continuously monitor pressure and temperature of the injection stream (Figure D.3.1-1). The data from the meter station will be collected and recorded in the computerized control system.

The computerized control system will record the volume of CO_2 and calculate the mass of CO_2 injected. The flow rate, a volumetric measurement of million standard cubic feet per day (MMscfd), will be used to determine mass over a given injection time. The metered pressure and temperature data will be used to calculate the injectate density, which will be divided into the flow rate and multiplied by injection time to determine the mass injected.

The meter will be calibrated annually for the expected flow rate range using accepted standards and will be accurate to within manufacturer's tolerances. Injection rate and pressure limitations will be implemented to ensure adherence to the maximum allowable bottomhole injection pressure. Pressure and temperature gauges will be calibrated annually.

Each wellhead will also be equipped with downhole electronic temperature and pressure gauges with transmitters to monitor both annular and injection readings.

4.1.2 Tubing-Casing Annulus Pressure Monitoring

The tubing-casing annulus pressure will be monitored continuously to ensure integrity of the downhole packer, tubing, and casing. GCS will monitor the tubing-casing pressure continuously (every 10 seconds) using a downhole electronic pressure and temperature gauge with a transmitter at the wellhead. The annulus will be filled with a non-corrosive brine with corrosion inhibitor.

The annular pressure for injection wells will be maintained with a pressure that exceeds the operating injection pressure, as stated in the injection well's Operating Plan (Project Minerva Narrative, Appendix XII). Significant changes in annular pressure could be an indication of internal or external mechanical integrity failure, provided that thermal (such as material contraction due to cooling) and pressure (such as ballooning due to increasing tubing pressure) transient effects of normal operational changes are properly diagnosed as acceptable deviations.

An initial annular pressure threshold of 5% change in pressure, that cannot be explained by changing operational conditions (e.g., injection rate, pressure, or temperature), will be utilized as an indication of mechanical integrity loss. GCS will notify LDENR if the annular pressure exceeds the threshold and cannot be maintained or stabilized after three attempts. After operation commences, GCS will conduct frequent evaluation of the pressure records

to determine if the threshold is appropriate considering the external factors that may impact operations (e.g., liquid property changes, atmospheric pressure, or pressure in the formation). Any proposed changes to the threshold will be implemented with the approval of the LDENR Commissioner.

4.1.3 Annular Fluid Volume Monitoring

When injection commences, an annulus stabilization system will be connected to the injection wells. The annulus stabilization system will be equipped with a non-corrosive brine reservoir fluid tank, a positive displacement style pump, and a reservoir fluid level gauge. The annulus stabilization system will be used to manually stabilize the annular pressure, by adding or removing annular fluid until the annular pressure normalizes. The change in volume from the annular fluid reservoir, as fluid is added or removed from the annulus, will be measured by the reservoir fluid level gauge and will be recorded by GCS.

Once normal injection operations are achieved and the annular pressure is stable, GCS will remove the annulus stabilization system and will monitor the annular pressure using the annular pressure and temperature gauge. Any future additions or removal of annular fluid to stabilize the annular pressure will be also conducted manually through the use of the portable annulus stabilization system.

4.2 REPORTING

Per LAC 43:XVII §3629.A.1, GCS will report the following values in the semi-annual submitted to LDENR and EPA:

- monthly average, maximum, and minimum values for injection pressure, flow rate and volume, and a description of any event that exceeds operating parameters for injection pressure specified in the permit;
- the monthly volume and/or mass of the carbon dioxide stream injected over the reporting period and the volume injected cumulatively over the life of the project;
- monthly average, maximum, and minimum values for the tubing-casing annular pressure, and a description of any event that exceeds operating parameters for the tubing-casing annulus pressure specified in the permit;
- monthly annulus fluid volume added; and
- a description of any event which triggers a shut-off device required by LAC 43:XVII §3621 and the response taken.

5 CORROSION MONITORING

To meet the requirements of LAC 43.XVII §3625.A.3, GCS will monitor well materials during the operation period for loss of mass, thickness, cracking, pitting, and other signs of corrosion to ensure that the well components meet the minimum standards for material strength and performance.

5.1 SURFACE MONITORING DETAILS

GCS will monitor corrosion by analyzing a corrosion loop. The loop will be constructed with the same well materials placed in contact with the carbon dioxide stream. While all efforts

will be made to operate the corrosion loop at downhole temperatures, during detailed engineering an evaluation will be made to determine the practicality and ability to simulate well conditions. Final technology selection will be completed after detailed engineering.

5.1.1 Monitoring Location and Frequency

The corrosion loops will be installed in parallel with the pipe at the surface facilities that feed CO_2 injectate to the injection wells. A process flow diagram depicting the locations is shown in Figure D.3.1-1. Material inspections will be performed by GCS personnel (or approved 3rd party contractors) on a quarterly calendar basis starting during the first month of the quarter (March, June, September, December) following commencement of injection.

5.1.2 Material Inspection

When the corrosion loop is inspected, the loop will be assessed using direct, off-line, Level 3 Non-Destructive Testing (NDT) and Non-Destructive Examination (NDE) certified inspectors and technologies including but not limited to Ultrasonic and Radiography equipment. Before injection begins, a baseline level 3 NDT/NDE inspection will be conducted. These readings will be stored and utilized to compare subsequent quarterly NDE/NDT inspections to determine cracking, pitting, or material loss. If corrosion is seen through the NDE/NDT inspection, the corrosion loop will be isolated and removed. Once removed, the corrosion loop will be sent to an International Organization for Standardization (ISO) 17025 compliant laboratory for further investigation and testing.

Thickness measurements showing a reduction in thickness greater than 20 percent of API published nominal thickness will warrant further investigation.

5.2 DOWNHOLE MONITORING DETAILS

Downhole logging data will be performed on MS CCS 1 and MS CCS 2 prior to commencing injection operations. These logs will provide a baseline casing thickness measurement to which future logs will be compared. A casing inspection logging tool will be used (which include ultrasonic imaging, magnetic flux leakage, and electromagnetic imaging) as it is proven and widely accepted within the industry for their accuracy in determining casing thickness and identifying casing corrosion.

If required, subsequent logs using the same technology will be run at a frequency specified by the LDENR Commissioner (LAC 43.XVII §3627.A.4). Results will be compared to the initial baseline log (LAC 43.XVII §3617.B.1.d.iv). Thickness measurements showing a reduction in thickness greater than 20 percent of API published nominal thickness will warrant further investigation. Additional inspection logging may be performed should the loop show excessive corrosion in excess of design-life criteria.

Alternative testing, other than those listed above, may be conducted with the written approval of the LDENR Commissioner. To obtain approval for alternative testing, GCS will submit a written request to the LDENR Commissioner, setting forth the proposed test and all technical data supporting its use.

5.3 NOTIFICATION

Per LAC 43.XVII §3617.B.6, GCS will notify the Office of Conservation at least 72 hours prior to conducting wireline logs used to monitor downhole corrosion.

5.4 REPORTING

GCS will submit the results of the wireline logs to LDENR and EPA within 30 days (or as specified by permit) (LAC 43:XVII §3629.A.2) and will include the results in the semi-annual report (LAC 43:XVII §3629.A.1.g).

GCS will submit the quarterly results of the corrosion monitoring conducted at the surface to LDENR and EPA in the semi-annual report (LAC 43:XVII §3629.A.1.g).

6 ABOVE CONFINING ZONE (ACZ) MONITORING

The goal of Above Confining Zone (ACZ) monitoring is to ensure non-endangerment of the USDW and to detect either brine or CO_2 leakage from the Injection Zone. GCS will achieve this goal by implementing monitoring methods to detect potential vertical fluid movement from the Injection Zone.

The only potential pathways for vertical fluid movement within the delineated AoR for Project Minerva are along the proposed injection wells and faults. GCS proposes to strategically install groundwater monitoring wells adjacent to these pathways to track geochemical changes that could impact the USDW in accordance with LAC 43.XVII §3625.A.4. Additionally, GCS will conduct direct monitoring of the interval above the Confining Zone using Distributed Temperature Sensing (DTS) fiber optic cables installed along MS CCS 1 and MS CCS 2 to monitor for changes in temperature as indicators of potential upward fluid migration from the Injection Zone. A summary of the ACZ monitoring strategy is provided in Table D.6-1.

6.1 ABOVE CONFINING ZONE MONITORING WELL CONSTRUCTION

Two (2) new above confining zone monitoring wells will be drilled prior to injection: Minerva South USDW Well No. 001 (MS USDW 1) and Minerva South USDW Well No. 002 (MS USDW 2).

The proposed drilling and logging procedures for MS USDW 1and MS USDW 2 are provided as Appendix D-III. GCS will submit Form UIC-25 (or its replacement), Class V Well Applications, to LDENR to for approval to drill and operate MS USDW 1 and MS USDW 2.

MS USDW 1 and MS USDW 2 will be drilled once construction of the injection wells is complete, but prior to commencement of injection.

6.1.1 Well Placement

Figure D.6.1-1 shows the locations of the proposed groundwater monitoring wells. MS USDW 1 will be sited at the Minerva South Well Pad to monitor the only known potential pathway for vertical fluid migration within the AoR.

MS USDW 2 will be sited at the well pad of Stream 34 Well No. 001 (SN 224951, Map Id 1).

GCS will convert Stream 34 Well No. 001, an existing wellbore whose bottom hole location is approximately 0.75 miles north of the Minerva South Well Pad, into an in-zone monitoring well. The converted well will be named Minerva South In-Zone Well No. 001 (MS IZ 1).

6.1.2 Monitoring Interval

The monitoring wells will be completed in the first confined sand unit below the base of the USDW. This interval corresponds to the upper sands of the Evangeline Aquifer.

6.1.3 Installation

The proposed drilling and logging procedures for MS USDW 1and MS USDW 2 are provided as Appendix D-III.

6.1.4 Operation

GCS will operate MS USDW 1 and USDW 2 in accordance with the applicable testing and integrity requirements applicable to Class V monitoring wells.

6.2 GROUNDWATER QUALITY MONITORING

6.2.1 Methods and Frequency

Table D.6-1 shows the planned monitoring methods, locations, and frequencies for groundwater quality and geochemical monitoring above the confining zone.

To meet the requirements at LAC 43.XVII §3607.C.2.e, GCS will establish a baseline geochemical dataset of groundwater quality prior to injection. After MS USDW 1 and MS USDW 2 are drilled, the groundwater sampling program will commence, and quarterly samples will be collected from each of the groundwater monitoring wells.

After injection commences, groundwater samples will be collected quarterly for the first three (3) years, and then every year in the same quarter thereafter through the operational life of the project.

6.2.2 Analytical Parameters

Table D.6.2-2 identifies the parameters that will be analyzed during groundwater monitoring and the analytical methods GCS will use.

The list of parameters may be reduced over the operational period, should it be determined during baseline sampling and/or the operational period that parameters listed in Table D.6.2-2 are no longer constituents of concern.

6.2.3 Sampling Methods

Samples will be collected using the following procedures:

- Water Level depth and elevation measurements will be taken.
- Wells will be purged such that existing water in the well is removed and fresh formation water is sampled.

- Samples will be collected by lowering clean equipment downhole. Field measurements taken for static fluid level, pH, temperature, conductance, density and dissolved oxygen.
- Samples will be preserved and sent to lab as per chain of custody procedure.

Groundwater samples will be collected following the procedures outlined in the project's QASP (Appendix D-I) during the operational and post-operational periods.

6.2.4 Accredited Laboratory/Chain of Custody and Analysis Procedures

Final laboratory selection has not been made at this time. The laboratory selected will be LELAP accredited and will meet all requirements set forth in the Testing and Monitoring Plan and the QASP (Appendix D-I). The Chain-of-Custody procedures will follow the requirements of the QASP.

The selected LELAP accredited laboratory will have all the necessary equipment, experience, and certifications to complete the analysis. Once selected, the LELAP accredited laboratory will have a chain of custody procedures that will be similar to the following:

- Sample date
- Sample description
- Sample type
- Relinquished by and received by signature
- Sampler name
- Location information

6.3 TEMPERATURE MONITORING

In addition to the required groundwater quality monitoring above the Confining Zone, GCS proposes to monitor the temperature of the intervals immediately above the Confining Zone to identify any potential upward migration of fluids from the approved Injection Zone.

A Distributed Temperature Sensing (DTS) fiber optic cable will be installed within the long-string/borehole annulus of MS CCS 1 and MS CCS 2 from surface to total depth to continuously monitor temperature. Upon completion of the injection wells, GCS will begin continuous temperature monitoring to collect baseline data prior to injection.

After injection commences, GCS will continue collecting continuous DTS data through the operational life of Project Minerva.

6.4 REPORTING

GCS will submit the results of the groundwater sampling to LDENR and EPA in the semi-annual report (LAC 43:XVII §3629.A.1.g). Analytical results will be submitted in the semi-annual report of the period in which the testing took place.

7 INJECTION WELL INTEGRITY TESTING

Per LAC 43.XVII §3627.A.2.a, §3627.A.3, and §3625.A.5, GCS will perform mechanical integrity tests (MIT) on the proposed injection wells at least once every 12 months to demonstrate internal and external integrity, using an approved method until the injection well is permanently plugged and abandoned. The primary and alternative test descriptions, the mechanical integrity demonstration, technology and frequency are summarized in Table D.7-1. The specifications for the technologies proposed to collect formation evaluation and mechanical integrity data are provided in Appendix D-IV. The appendix will be updated with the final technology selection upon selection of the vendor.

7.1 INTERNAL INTEGRITY TESTING

Although LAC 43.XVII §3625.A.5 does not prescribe demonstration of internal mechanical integrity, GCS will perform a Standard Annular Pressure Test (SAPT) test witnessed by an agent of the Office of Conservation on the proposed injection wells at least once every 12 months (LAC 43.XVII §3627.A.2.a).

GCS will also perform a SAPT after initial well construction as part of the Pre-Operational Testing Program (Attachment C) and after performing any well remedial work that involves unseating the tubing or packer (LAC 43.XVII §3627.A.2.a.i-iii).

Standard Annular Pressure Test

The SAPT is the most common means used to demonstrate mechanical integrity. This test is based on the principle that pressure applied to fluids filling a sealed vessel will persist. A well's annulus system, though closed to transfer of matter, is not closed to energy transfer because it is not isolated from transfer of heat from its surroundings, therefore an allowance for small pressure changes is necessary. The test provides an immediate demonstration of whether or not leaks, detectable by these means, exist. A discussion of the procedures for the SAPT are outlined in Appendix D-V.

7.2 EXTERNAL INTEGRITY TESTING

The approved methods to demonstrate external mechanical integrity described in LAC 43.XVII §3627.A.3.a-b include a tracer-type survey -- such as a radioactive tracer, oxygen-activation log, or similar tool -- or a temperature or noise log. However, in accordance with LAC 43.XVII §3627.A.5.a, the LDENR Commissioner may allow the use of an alternative demonstration of mechanical integrity other than those described above. The following sections outline GCS' request to use an alternative demonstration of external mechanical integrity, the technical data supporting its use, and the alternative and supplemental test technologies available should a contingent method be required.

The specifications for the technologies proposed to collect formation evaluation and mechanical integrity data are provided in Appendix D-IV. Additional information about the external mechanical integrity testing performed prior to operations can be found in the Pre-Operational Testing Program (Attachment C).

7.2.1 Primary

7.2.1.1 *Distributed Temperature Sensing (DTS)*

GCS requests to use Distributed Temperature Sensing (DTS) fiber optic cables, installed along the long-strings of MS CCS 1 and MS CCS 2, to provide continuous external mechanical integrity monitoring of the wellbores. The DTS system monitors and records the well's temperature profiles at a pre-set frequency in real time.

DTS will detect temperature changes along the wellbore if external mechanical integrity is compromised. The DTS fiber will monitor temperature throughout and above the Confining Zone, and the configuration of DTS fiber as described above, from surface to total depth, is sufficient to monitor injection wells for external mechanical integrity above the Injection Zone.

Implementation

Upon completion of MS CCS 1 and MS CCS 2 and prior to injection, a baseline temperature profile will be established. This profile represents the natural temperature gradient for each stratigraphic zone.

During the annual defined shut-in periods, the temperature profile along the length of the long-string will be compared to the baseline. Any unplanned fluid movement into the annulus or outside the casing creates a temperature anomaly when compared to the baseline cooling profile.

MIT Procedure

The procedure for using the DTS for well mechanical integrity is as follows:

1. During injection operation, record the temperature profile for 6 hours prior to shutting in well.
2. Stop injection and record temperature profile for 6 hours.
3. Evaluate data to determine if additional cooling time is needed for interpretation.
4. Start injection and record temperature profile for 6 hours.
5. Interpret Data.

Interpretation

Once the in-situ temperature is determined in the interval above the Confining Zone of MS CCS 1 and MS CCS 2, temporal changes will be analyzed by comparing the new data to previously collected data. GCS will produce and interpret time-series graphs for each well, taking into consideration the injection rate and well location.

If there are any temperature anomalies that may indicate a failure of well integrity (i.e. tubing leak or movement of fluid behind the casing), GCS will submit a Form UIC-17 Work Permit within 30 days of identification and propose to run at least one of the alternate tests described in Section 7.2.2 (Table D.7-1) or a test approved by the LDENR Commissioner.

Frequency

GCS will perform DTS MIT on each well at least once every 12 months to demonstrate

external integrity until the injection well is permanently plugged and abandoned.

7.2.2 Alternate

If the annual DTS MIT identifies any temperature anomalies that may indicate a failure of well integrity, GCS will utilize one of the following tests prescribed by the regulations to demonstrate external mechanical integrity (LAC 43.XVII §3627.A.3-4).

Background information and procedures for using the technologies proposed in the following sections are provided in Appendix D-V.

7.2.2.1 Noise Log

The use of noise logs is based on the observation that flow behind the casing in the well bore will, at some points, be turbulent. Turbulent flow causes noise which may travel significant distances along the well bore. Noise logs are appropriate where it is impractical for injection operations to be suspended for the length of time needed to allow temperature stabilization to proceed to the point at which a temperature log can be run with good results. They can also be used to locate some tubing or casing leaks.

7.2.2.2 Oxygen Activation Log

An oxygen activation log, also known as a water-flow log, is a method for detecting and measuring water flow in or around a borehole. The process involves activating oxygen with high-energy neutrons to create a nitrogen isotope, which then decays back into oxygen and emits a detectable gamma ray. Detectors placed above or below the tool count the gamma rays.

7.2.3 Supplemental

7.2.3.1 Casing Inspection Log

A casing inspection log is a record of casing thickness and integrity. This log is used to determine whether or not the casing has undergone damage. The casing inspection log identifies and quantifies corrosion damage. It identifies scale, wax, solids accumulation, and location of mechanical damage. The procedures for running the logs and presentation of the results are set by the logging company. Because the standards adopted by the logging companies are appropriate, no additional information is provided for running casing inspection logs.

7.2.3.2 Cement Bond Log

A cement bond log provides an assessment of the cement quality radially as part of well integrity and for zonal isolation, particularly the radial distribution of cement behind the casing, the casing to cement bond (traditionally known as cement bond index) and cement to formation bond in the form a variable density log (VDL). Modern cement evaluation tools provide an assessment of the cement distribution behind the casing to properly evaluate the cement quality around the circumference of the casing.

7.2.3.3 Casing Collar Locator Log

A casing collar locator log is used to precisely determine the depth of casing collars, which acts as a key reference point for correlating other logging data (like pressure or temperature) to specific locations within the wellbore. When used with other logging technologies, it ensures accurate location of potential anomalies that are identified.

7.3 NOTIFICATION

Per LAC 43.XVII §3617.B.6, GCS will notify the Office of Conservation at least 72 hours prior to conducting wireline logs or integrity tests.

7.4 REPORTING

GCS will submit the results of the wireline logs and integrity tests to LDENR and EPA within 30 days (or as specified by permit) (LAC 43:XVII §3629.A.2) and will include the results in the semi-annual report for the period in which the testing took place per (LAC 43:XVII §3629.A.1.g).

8 RESERVOIR TESTING

As described in the Pre-Operational Testing Plan (Attachment C), GCS will perform a pressure fall-off test followed by a step rate injectivity test in each well prior to operation of as required by LAC 43.XVII §3617.B.5.

During the injection phase of the wells, GCS will perform pressure fall-off tests as described below to meet the requirements of LAC 43.XVII §3625.A.6.

8.1 TESTING LOCATION AND FREQUENCY

A pressure fall-off test will be conducted prior to operations and within ±45 days of the 5-year anniversary of the startup of injection. Thereafter, a pressure fall-off test will be performed at least once every 5 years during the operational period.

8.2 TESTING DETAILS

Testing procedures will follow the methodology detailed in EPA Region 6 UIC Pressure Fall-off Testing Guideline-Third Revision (August 8, 2002) provided in Appendix D-VI.

8.3 NOTIFICATION

Per LAC 43.XVII §3617.B.6, GCS will notify the Office of Conservation at least 72 hours prior to conducting reservoir testing.

8.4 REPORTING

Per LAC 43:XVII §3629.A.1.g, GCS will submit the results of the pressure fall-off test to LDENR and EPA in the semi-annual report for the period in which the testing took place.

9 INJECTION ZONE CARBON DIOXIDE PLUME AND PRESSURE EXTENT TRACKING

GCS will employ direct and indirect methods to track the extent of the carbon dioxide plume

and the presence or absence of elevated pressure during the operation period to meet the requirements of LAC 43.XVII §3625.A.7.

Table D.9-1 presents the direct and indirect monitoring methods GCS will employ and includes the target interval, technology, locations, objectives, and frequencies for each method.

The monitoring strategy will be implemented prior to commencement of injection and will be executed throughout the life of the project. GCS will assess new technologies as they are developed and reevaluate the plan to ensure that the best site-specific methods are employed.

9.1 IN-ZONE MONITORING WELL

In-Zone monitoring wells serve a monitoring source for tracking the presence or absence of elevated pressure and CO_2 saturation within AoR. Since there are no artificial penetration within the AoR, therefore no potential pathways for fluid migration from the Injection Zone, GCS maintains that sufficient in-zone monitoring can be achieved without creating a potential pathway within the uncompromised AoR. The following section outlines how GCS proposes to conduct in-zone monitoring and the strategy for implementing it.

9.1.1 Well Location

GCS has identified Stream 34 Well No. 001 (SN 224951), an existing plugged and abandoned wellbore, as a viable candidate for conversion to an in-zone monitoring well. The bottomhole location is located outside of the AoR and approximately .75 miles north of the Minerva South well pad (Figure D.6.1-1).

As demonstrated in conversion plan provided in Appendix D-VII, GCS proposes to convert Stream 34 Well No. 001 into Minerva South In-Zone Well No. 001 (MS IZ 1) and utilize it to track the presence or absence of elevated pressure and CO_2 saturation within the Injection Zone.

9.1.2 Conversion

GCS will submit Form UIC-25 (or its replacement), Class V Well Application, to LDENR to convert Stream 34 Well No. 001 to MS IZ 1. A detailed conversion plan along with the other required documents will be submitted for approval with the Class V application. Appendix D-VII will be updated with the permit, conversion procedure, and as-drilled schematic upon approval and completion.

GCS will phase the conversion on the in-zone monitoring well no later than one year after injection commences into MS CCS 1 and MS CCS 2.

9.1.3 Monitoring Interval

MS IZ 1 will be sparsely perforated over an interval correlated to the injection interval utilized in MS CCS 1 and MS CCS 2. As the injection interval changes over the life of the project, MS IZ 1 will be perforated at the correlated injection interval, and the former perforations squeezed if necessary. A packer will be set above the perforations and completed with downhole pressure gauges on tubing. Well design will enable wireline logging, pressure

monitoring, and, if necessary, geochemical sampling of the Injection Zone.

9.1.4 Monitoring Activities

MS IZ 1 will be utilized to conduct direct monitoring of pressure and indirect monitoring of CO_2 saturation, as outlined in Table D.9-2. Sections 9.2.1 (In Situ Fluid Pressure Monitoring) and 9.3.1.4 (Pulse Neutron Logging) provide details on the monitoring activities that will be performed utilizing MS IZ 1.

9.1.5 Operation

GCS will operate MS IZ 1 in accordance with the applicable testing and integrity requirements applicable to Class V monitoring wells.

9.2 DIRECT MONITORING

9.2.1 In Situ Fluid Pressure Monitoring

GCS will track the pressure influence within the Injection Zone using the injection wells themselves and an in-zone monitoring well.

9.2.1.1 Implementation and Duration

GCS will complete the injection wells, MS CCS 1 and MS CCS 2, and in-zone monitoring well, MS IZ 1, with downhole pressure and temperature gauges connected by an electric line to a transmitter at the surface. The gauge will continuously collect pressure readings (every 10 seconds) that can be read on the transmitter at the surface. Then the pressure data will be transmitted to a computerized control system that records, monitors, and controls injection processes.

Baseline reservoir pressure data will be collected prior to injection. Injection will commence in MS CCS 1 and MS CCS 2 in succession, allowing GCS to collect pressure monitoring data from the inactive or shut-in well. As the wells are both in operation, GCS will alternately shut-in the wells annually for mechanical integrity testing. During that time, GCS will collect pressure monitoring data from the shut-in well as the active well continues injection. This will allow GCS to history-match modeled near-well pressure influence within the Injection Zone through the operational life of the injection wells.

The baseline in-situ reservoir pressure within the Injection Zone will be established after the completion of MS CCS 1 and MS CCS 2. Once operation commences, reservoir pressure data will be collected from MS IZ 1 continuously and from MS CCS 1 and MS CCS 2 during scheduled shut-ins and compared to the modeled predictions. If pressure increases greater than predicted by the current AoR model, or increases at a greater rate, it may indicate that the AoR model needs to be revised. In this case, GCS will consult with the LDENR Commissioner to determine whether an AoR revaluation is necessary.

9.2.1.2 Frequency and Reporting

In-situ pressure reading will be collected once monthly from the pressure transmitter installed in MS IZ 1 through the operational life of the project. The monthly reading will be reported in the Semi-Annual Report, along with a time-series graph for the six-month period.

Pressure data collected from MS CCS 1 and MS CCS 2 during scheduled annual shut-ins will be reported in the Semi-Annual Report, along with a time-series graph depicting the annual trend over the life of the well.

9.3 INDIRECT MONITORING

Indirect monitoring methods are geophysical techniques used to infer and interpret changes in subsurface properties without direct access to a monitored reservoir. Unlike direct monitoring methods, indirect methods rely on detecting changes in physical properties such as seismic velocities, acoustic impedance, or electromagnetic characteristics. These changes often result from variations in fluid composition, pressure, temperature, or other factors within the subsurface. Indirect monitoring is particularly valuable in projects involving subsurface CO_2 storage, as it provides continuous and comprehensive monitoring capabilities over large areas and at various depths simultaneously.

The specifications for the proposed technologies used to conduct indirect plume monitoring are provided in Appendix D-VIII. The appendix will be updated with the final instrument selection should a different vendor be selected for construction.

9.3.1 Plume Monitoring Methods

Four indirect monitoring methods will be used to define the extent of the modeled plume for Project Minerva:

- Walk-Away Vertical Seismic Profile (WA VSP)
  - Surface sources arranged in lines intersecting MS CCS 1; wellbore fiber optic cable receiver (distributed acoustic sensing, DAS) in MSCCS 1
- 3D Distributed Acoustic Sensing Vertical Seismic Profile (3D DAS VSP)
  - Surface sources arranged in a grid array with wellbore fiber optic cable receiver (distributed acoustic sensing, DAS) in MS CCS 1
- 2D Seismic Survey
  - Surface sources and surface receivers arranged in lines intersecting MS CCS 1
- Wireline logging in MS IZ 1
  - Pulsed neutron (PN) logging

A seismic baseline will be acquired before injection begins using WA VSP, 3D DAS VSP, and 2D seismic surveys simultaneously. Once injection commences, WA VSP will serve as the primary plume monitoring method for at least 10 years (or until its coverage is surpassed by the leading edge of the plume) and will be supplemented, as necessary, with 3D DAS VSP and/or 2D seismic surveys. Rock physics and VSP feasibility studies were completed to confirm that indirect seismic monitoring of injected CO_2 will be effective at Project Minerva (Appendix D-IX and Appendix D-X).

The following sections provide details of each monitoring method and the rationale for the integrated monitoring program.

9.3.1.1 Walk Away Vertical Seismic Profile (WA VSP)

WA VSP is a seismic survey technique in which seismic receivers are placed inside a well, and a seismic source is progressively moved farther away from the well ("walked away") in a linear or specific pattern (Figure D.9.3-1). GCS plans to utilize distributed acoustic sensing (DAS) technology to receive seismic signals (Appendix D-VIII), rather than discrete geophones. GCS will install the DAS fiber optic cable along the long-string of MS CCS 1. Vertical well design and DAS fiber optic cable was selected for MS CCS1 to:

- Optimize the receiver-sensor signal
- Maximize vertical seismic resolution
- Maximize lateral seismic monitoring coverage

WA VSPs are particularly useful for monitoring CO_2 plumes in CCS projects because they provide high-resolution imaging, enabling detection of subtle changes in the subsurface over time. When a CO_2 plume migrates, it changes the rock's properties, such as density and velocity. Repeated capture of WA VSPs over the life of the project allows the detection of these changes. This process is called time-lapse (4D) seismic monitoring and is a cost-efficient and effective tool.

The advantages that WA VSPs offer are the following:

- High sensitivity to changes near the wellbore – optimum method for tracking CO_2 plume fronts over time, in multiple completion intervals
- Ability to monitor complex geological structures like faults or stratigraphic traps
- Flexibility in implementation over time; acquisition layout, timing and frequency can easily be adapted to effectively track CO_2 in the subsurface
- Allows for focused monitoring, with the flexibility to adapt and decide whether a larger-scale 3D DAS VSP is necessary, optimizing both cost and data acquisition frequency
- Can be combined with 2D seismic lines – signals from the sources used in 2D seismic surveys can also be recorded by the DAS cable to capture a WA VSP

Acquisition Layout

When GCS conducts the baseline 3D DAS VSP survey (described in Section 9.2.1.2), it will provide a full 3D seismic snapshot of the subsurface at the time before CO_2 injection starts. This initial survey serves as a reference point for all subsequent WA VSPs.

GCS proposes to perform WA VSP surveys by placing the seismic sources along six seismic lines intersecting MS CCS 1 at 30-degree angles from each other (Figure D.9.3-2). This layout will detect CO_2 plume migration in multiple azimuthal directions, across all injection intervals within the Injection Zone.

Seismic sources will be progressively "walked away" (the lines will be extended) with each successive seismic shoot, as necessary, to ensure that the CO_2 plume is fully monitored. This will occur up to the coverage limit of the WA VSP. A VSP feasibility study indicates that

fully coverage is possible up to at least the modeled 10-year CO_2 plume but may continue up to the 20-year modeled plume. Preoperational field testing will further refine the feasibility study outputs. Operational data will be critical in optimizing WA VSP acquisition layout.

Implementation

A DAS fiber optic cable will be cemented behind casing, down to the base of the long-string, and will act as the seismic receiver. A seismic source (typically a vibrator truck, an air-gun, or dynamite) will be moved/placed along surface locations on the six seismic lines surrounding the well. Signals will be received by the DAS fiber optic cable and processed into a WA VSP outputs for each seismic line.

GCS will optimize the implementation of WA VSPs throughout the life of the project as seismic data is collected, analyzed and used to improve the reservoir simulation model. Optimizations may include shortening or lengthening seismic lines in certain orientations, adding additional seismic lines or modifying the frequency of WA VSPs.

Processing

The WA VSP processing sequence can be summarized in key grouped steps as follows:

- **Data QC and Geometry Setup**: First, data quality is verified by ensuring proper signal recording and geometry setup. Receiver and source locations are linked to well trajectories, ensuring accurate spatial information for processing.
- **Amplitude and Wavefield Processing**: An amplitude recovery function is normally applied to separate upgoing and down-going wavefields to focus on primary reflections. Furthermore, techniques like f-k filtering and deconvolution are used to isolate the key signals from noise and multiples.
- **First-Break Picking, Velocity Model, and Static corrections**: The first arrivals are picked to apply static corrections, which adjust for near-surface variations. These picks are also used to refine the velocity model, critical for time-to-depth conversion and further seismic imaging.
- **Migration and Stacking**: Once static corrections are applied, the data is migrated using techniques like Kirchhoff or Reverse Time Migration (RTM) to position reflectors accurately in the subsurface. RTM is a prestack two-way wave-equation migration for accurate imaging in and below areas with both great structural and velocity complexities. The method is based on directly solving the wave equation in the time domain (rather than the frequency domain). RTM can accurately handle any variation in subsurface material properties and has no limit in imaging steep dips. RTM is not based on ray tracing and hence can be performed in situations where Kirchhoff ray-based migration breaks down (Figure D.9.3-3). RTM has a proven track record for generating final images and is increasingly used for refining structural boundaries during velocity model building.
- **Final Imaging and Interpretation**: The final seismic image is generated and

interpreted. Since the objective is for CO_2 monitoring, time-lapse comparisons may be made with baseline surveys to track changes in the subsurface, like the movement of the CO_2 plume based on amplitude changes (AVO/AVA).

This sequence ensures accurate subsurface imaging in depth and is particularly useful in dynamic monitoring situations like CO_2 sequestration.

Frequency

A WA VSP baseline will be recorded along the full length of all lines defined in Figure D.9.3-2, before injection begins.

The frequency of the WA VSP monitoring is planned as follows:

- **Year 0 through 5**: WA VSPs will be repeated at least 4 times along all seismic lines. The number of sources and length of the seismic lines will be designed to ensure full CO_2 plume coverage during this period. The 4th WA VSP will occur at year 4.5, to provide 6 months for acquisition, processing and integration into the required 5 year AoR reevaluation. If necessary, more frequent WA VSP monitoring may be carried out, or a 3D DAS VSP may be shot to provide more detailed coverage.
- **Year 5 through 10**: WA VSPs will be repeated at least once along all seismic lines. The number of sources and length of the seismic lines will be designed to ensure full CO_2 plume coverage during this period. The WA VSP will occur at year 9.5, to provide 6 months for acquisition, processing and integration into the required 10 year AoR reevaluation. If necessary, more frequent WA VSP monitoring may be carried out, or a 3D DAS VSP may be shot to provide more detailed coverage.
- **Year 10 through Year 30**: WA VSPs will be repeated at least every 5 years until coverage is determined to be insufficient to monitor CO_2 migration across the full Injection Zone (currently estimated at between 10 and 20 years). After this, WA VSPs will be acquired concurrently with 2D seismic surveys every 5 years until the end of operations (~year 30). 2D seismic will extend coverage and WA VSPs will continue to provide high resolution CO_2 monitoring within the VSP coverage area.

Duration

Based on the reservoir simulation model prediction and the VSP feasibility study (Appendix D-IX), the WA VSP coverage is anticipated to be effective for an area consistent with at least the 10-year plume and potentially up to 20 years (Figure D.9.3-2). Beyond this period, the plume's dispersion and attenuation of seismic signals may reduce the effectiveness of VSP, necessitating complementary monitoring techniques or additional surveys. GCS anticipates using WA VSP as the primary monitoring method through year 10 of the project, and possibly longer, depending on the movement of the CO_2 within the proposed AoR.

Once the CO_2 plum has moved outside of the VSP coverage area, GCS will layer the WA VSP with a 2D seismic survey. While lower in resolution compared to the VSPs, the 2D seismic survey will provide broader coverage and will be essential in understanding the long-term migration of the CO_2 plume over a larger area. Repeating the 2D seismic lines will help detect

any far-field plume migration that could potentially intersect faults or other structural features, providing an additional layer of assurance in containment. Once 2D seismic surveys are implemented along with WA VSPs as the primary plume monitoring method, they will be acquired every five years prior to the re-evaluation period through the operational life of the project.

Contingency

When significant anomalies or deviations from the expected CO_2 migration path are observed in the WA VSPs, it signals that a supplemental, more detailed monitoring survey may be needed. In such cases, GCS will perform a 3D DAS VSP survey which will provide a higher-resolution, full-volume view of the CO_2 plume, allowing for a precise re-evaluation of the plume's extent and behavior.

9.3.1.2 3D DAS VSP

A 3D DAS VSP is an advance borehole seismic survey technique used to create a three-dimensional high-resolution image of the subsurface around the well with higher vertical resolution than conventional 3D seismic data. In a traditional 3D VSP, seismic sources are positioned at various locations on the surface surrounding the well, and the seismic waves generated by these sources are recorded by receivers placed inside the well at multiple depths (Figure D.9.3-4). In the 3D DAS VSP, the DAS fiber optic cable will be used as a dense array of acoustic receivers to capture the seismic data along the wellbore (Figure D.9.3-2). Acquiring a 3D DAS VSP for Project Minerva will result in enhanced spatial resolution, data coverage, and operational efficiency, enabling real-time, cost-effective, and comprehensive subsurface imaging.

MS CCS 1 will be equipped with DAS fiber optic cables along the length of the long-string casing. A VSP feasibility study was conducted for Project Minerva, which included ray-trace modelling (seismic technique used to simulate how seismic waves propagate through the subsurface). The study concluded that a VSP operated via MS CCS 1 will offer the highest quality and longest-range seismic coverage and that installing DAS along MS CCS 2 does not add any extra benefit to the monitoring program.

A technical report was prepared by Ikon Science detailing the technical workflow followed to understand the elastic changes in the surface that can be expected during sequestration, specifically focused on monitoring the CO_2 plume (Appendix D-X). The workflow details the rock physics model (including fluid substitution, forward modelling, and seismic feasibility studies), petro-elastic model, and a comprehensive breakdown for the baseline survey design, acquisition, processing and interpretation/analysis.

Acquisition Layout

The chosen seismic acquisition company will provide sources to cover an approximate area of 11.4 km2 (~2,817 acres). Provisionally, the sources are planned to be placed on a 500 feet by 500 feet grid, totaling approximately 1,350 source points, each placed at 100 feet deep (Figure D.9.3-2). These parameters will result in a high spec 3D DAS VSP that can account for repeatability and is fit for 4D monitoring. Optimization and finalization of all parameters

are subject to field testing to be carried out once MS CCS 1 has been constructed. The key steps in the acquisition layout are as follows:

- **Well Preparation and DAS Fiber Deployment**: The DAS fiber-optic cable will be installed the wellbore of MS CCS 1 from surface to a predetermined total depth (TD). This cable is permanently installed to ensure continuous seismic recording along the wellbore during the project's lifecycle.
- **Seismic Source Deployment**: Seismic sources will be deployed at carefully selected locations to ensure comprehensive coverage of the subsurface around the well, allowing for 3D imaging (Figure D.9.3-5).
- **Seismic Data Acquisition**: Once the seismic source is activated, the resulting seismic waves travel through the subsurface, reflecting off various geological layers before being recorded by the DAS system. The fiber-optic cable in the wellbore captures these reflected waves, providing a continuous and highly detailed seismic record along the well. DAS technology enables the recording of data at fine spatial intervals, typically every meter or less, along the wellbore.
- **3D Coverage and Azimuthal Sampling**: The strategic placement of seismic sources around the well ensures that the subsurface is illuminated from multiple angles and azimuths. This multi-azimuthal coverage is crucial for creating a comprehensive 3D image of the subsurface, capturing variations in geological structures and fluid distributions that may not be visible with a single azimuth.

Implementation

The implementation begins with the deployment of the DAS optic fiber cable, which will be integrated with the well completion equipment for MS CCS 1. Once the cable is placed, a seismic source will be moved/placed in multiple surface locations in a grid pattern surrounding the well. Source type will be specified during field testing, after MS CCS 1 has been constructed. Sources will be selected to optimize seismic imaging and minimize surface impact.

The seismic signals generated by the source will be recorded by the DAS system as they travel through the subsurface and reflect off geological formations, including the CO_2 plume. The fiber optic cable will capture the strain induced by the passing of seismic waves, which will then be converted into seismic data. The recorded data provides a detailed 3D image of the subsurface, allowing for the monitoring of the CO_2 plume's size, shape, and migration over time.

GCS will optimize the implementation of the 3D VSP once a preoperational field study is completed and throughout the life of the project as seismic data is collected, analyzed and used to improve the reservoir simulation model. Optimizations may include modifications to the number, layout and type of source.

Processing

Once the 3D DAS VSP data is acquired, it will undergo a series of processing steps to convert

the raw seismic recordings into usable subsurface images. The processing workflow typically includes the following steps:

- **Data Pre-processing**: The initial step involves quality control and pre-processing of the raw DAS data. Noise reduction techniques are applied to remove unwanted signals, such as ambient noise and instrument-related artifacts. Deconvolution is then performed to eliminate the source signature, enhancing the resolution of the seismic data.
- **Wavefield Separation**: The DAS VSP data includes both upgoing and down-going seismic waves. Wavefield separation is performed to isolate the upgoing waves, which are used for subsurface imaging. This step also involves the removal of multiples and other types of coherent noise that could interfere with the interpretation of the seismic signal.
- **Velocity Model Building**: Accurate imaging of the subsurface requires a detailed velocity model, which is derived from the direct arrivals (down-going waves) recorded by the DAS system. This velocity model is essential for time-to-depth conversion and ensures that the seismic reflections are accurately positioned within the subsurface.
- **Imaging and Migration**: The processed DAS VSP data will be migrated to create a 3D image of the subsurface. Migration algorithms correct for the effects of dipping layers and complex geological structures, relocating seismic events to their true spatial positions. This process results in a higher-resolution 3D images that accurately reflect the subsurface geology.
- **Amplitude Preservation and AVO/AVA Analysis**: Throughout the processing workflow, care is taken to preserve the true amplitude of the seismic reflections. This is particularly important for AVO/AVA analysis, where changes in reflection amplitude with offset or angle provide insights into the rock properties and fluid content within the reservoir.
- **Final Data Interpretation**: The processed 3D DAS VSP data is then ready for interpretation. 3D images undergo a full geophysical analysis to identify geological features, monitor fluid movements, and assess the effectiveness of reservoir management strategies. The high resolution and azimuthal coverage of 3D DAS VSP data make it a powerful tool for detailed subsurface characterization and monitoring.

This comprehensive workflow ensures that the 3D DAS VSP data is accurately processed and interpreted, providing valuable insights into the subsurface for applications such as CO_2 storage monitoring, reservoir characterization, and enhanced oil recovery.

Frequency

The initial 3D DAS VSP baseline survey will be conducted before CO_2 injection begins, establishing a reference state of the subsurface. Subsequent 3D DAS VSP surveys will be implemented if the other indirect monitoring techniques (WA VSP and 2D seismic) do not offer the information needed to track the plume. Any necessary surveys will be acquired at least 6 months prior to re-evaluation deadlines (year 5 and 10).

Duration

Based on the reservoir simulation model prediction and the VSP feasibility study (Appendix D-IX), the 3D DAS VSP coverage is anticipated to be effective for up to at least 10 years after injection commences, and possibly up to 20 years (Figure D.9.3-2). Beyond this period, the plume's dispersion and attenuation of seismic signals may reduce the effectiveness of the 3D DAS VSP, necessitating complementary monitoring techniques or additional surveys.

Contingency

When significant anomalies or deviations from the expected CO_2 migration path are observed outside of the coverage area of the 3D DAS VSPs, a 2D seismic survey will be initiated to track the plume beyond the extent of coverage.

9.3.1.3 2D Seismic Survey

Surveys along six conventional 2D seismic lines will be acquired at various times throughout the injection period of Project Minerva. These lines are designed in a star pattern, radiating outward from MS CCS 1, with each line spaced 30 degrees apart (Figure D.9.3-2). This configuration ensures comprehensive 360-degree coverage, allowing for thorough monitoring of the CO_2 plume's migration and distribution across the AoR. The length of the lines vary based on the shape of the modeled plume and may be optimized over the life of the project, as necessary.

2D seismic monitoring has been selected as it has a relatively low impact to the surface, as compared to 3D seismic surveys, or VSP networks requiring additional wells in wetland areas.

In the context of monitoring the CO_2 plume for the Project Minerva, especially when combined with a central VSP, acquiring 2D seismic lines can offer significant advantages. While the VSPs around the well will provide detailed imaging around the wellbore, the 2D seismic lines will complement this data by offering focused insights along specific azimuths. The following points outline some of the key reasons why GCS decided to acquire conventional 2D seismic data as part of the integrated CO_2 monitoring program:

- **Complementary coverage and enhanced imaging**: Seismic lines arranged in a star pattern intersecting at MS CCS 1, provide focused imaging along specific azimuths and will complement any VSP survey acquired by offering insight along key directions.
- **Cost-effectiveness**: 2D seismic has a lower acquisition cost compared to other remote sensing techniques; however, it also brings advantages such as less time and resources for acquisition, lower long-term cost, especially for ongoing monitoring programs where multiple surveys might be needed over time.
- **Flexibility and rapid deployment**: 2D seismic surveys can be more quickly designed, acquired, and processed compared to other seismic surveys such as 3Ds. This allows GCS to have the capacity for rapid responses to unexpected changes in the CO_2 plume or other subsurface conditions.

- **Simpler data processing and interpretation**: Processing 2D seismic data is generally less complex and less computationally demanding than 3D seismic data. This can lead to faster turnaround times for interpretation and decision-making. Furthermore, the simplicity of 2D seismic lines allows for a straightforward interpretation of specific geological features.
- **Lower surface impact**: Protection of wetland environments is a key priority.

Acquisition Layout

The six 2D seismic lines will be designed in a star-shaped arrangement, radiating outward, from MS CCS 1 with approximately 3,000 source points, each one at a depth of 100 feet. The appropriate number and layout of surface receivers will be determined in field testing. Each line will be spaced 30 degrees apart, covering the full 360-degrees around the well. This symmetrical distribution ensures complete azimuthal coverage, allowing for detailed imaging of the subsurface across multiple directions. This layout is particularly important for capturing potential anisotropies in the reservoir and detecting any lateral variations in the CO_2 plume. The acquisition layout consists of the following main steps:

- **Layout design**: The survey consists of six 2D seismic lines arranged in a star pattern, radiating outward from MS CCS 1 and spaced 30 degrees apart (Figure D.9.3-2). This configuration provides comprehensive 360-degree coverage around the well, ensuring thorough subsurface imaging. The lines vary in length between 4 and 6 miles based on the shape of the modeled plume and any potential risk areas.
- **Source and receiver positioning**: Detailed planning was undertaken to determine the optimal placement of seismic sources and receivers along each line. The length of the lines and the spacing of the sources/receivers are carefully designed to achieve the desired subsurface resolution and coverage. However, field tests are needed to fine tune the final acquisition parameters.
- **Deployment of seismic sources**: Mobilize seismic source equipment such as vibrators, dynamite, or air-guns, depending on the specific requirements of the survey area and environmental considerations. For Project Minerva, vibrators won't be an option due to surface conditions (wetlands), therefore, different type of sources will be tested in the field following the state's regulations.
- **Seismic data acquisition**: Seismic sources along the 6 lines are activated either sequentially or simultaneously, depending on the acquisition strategy defined in the field. The generated seismic waves travel through the subsurface and reflect off geological layers. As the seismic waves are reflected back to the surface, they are recorded by the receivers positioned along the 2D seismic lines. This process is repeated along all six lines to gather comprehensive data on the subsurface structures.
- **Quality control and monitoring**: Conduct real-time quality control to ensure that the recorded data meets the required standards. This involves monitoring signal strength, noise levels, and other key parameters.

- **Demobilization**: Once data acquisition is complete, retrieve all seismic sources and receivers from the field. Conduct site restoration to minimize any environmental impact from the survey activities, returning the area to its pre-survey condition.

Implementation

GCS will implement the survey with precise positioning of seismic sources along each of the six 2D seismic lines. The sources will sequentially activated/detonated at multiple predetermined points along each line. The seismic waves generated by the sources travel through the subsurface, reflecting off geological layers, and are captured by the surface receivers placed along the conceptual lines. The data acquisition process is carefully synchronized to ensure that each source activation and subsequent data recording are accurately time-stamped, facilitating high-quality data processing.

GCS will optimize the implementation of 2D seismic throughout the life of the project as seismic data is collected, analyzed and used to improve the reservoir simulation model. Optimizations may include shortening or lengthening seismic lines in certain orientations, adding additional seismic lines or modifying the frequency of 2D seismic acquisition.

Processing

The processing of data acquired from the six 2D lines around MS CCS 1 is a crucial step in transforming raw seismic data into actionable insights. This process aims to generate high-resolution images of the subsurface, enabling detailed monitoring of the CO_2 plume's migration and distribution within the reservoir. A standard processing sequence involves the following steps:

- **Data pre-processing**: Perform initial quality control checks and apply noise reduction techniques to clean up the raw seismic data. This step is crucial for enhancing the clarity of the recorded signals. Apply deconvolution to remove the source signature and improve the resolution of the seismic data. This helps in distinguishing between different subsurface features.
- **Velocity analysis and model building**: Use recorded seismic data to build an accurate velocity model of the subsurface. This model is essential for converting seismic travel times to depth, which is crucial for accurate subsurface imaging. Use the velocity model to convert the seismic data from the time domain to the depth domain, aligning the seismic reflections with their true subsurface positions.
- **Imaging and stacking**: Sort the seismic data into common midpoint gathers, where traces that share the same subsurface reflection point are aligned. This process enhances signal quality by improving the coherence of reflections. Follow by stacking the sorted data to enhance signal strength and suppress noise. This step is crucial for generating a clearer and more reliable image of the subsurface structures. Finish by applying migration algorithms to correct for the effects of dipping layers and other complex subsurface structures. Migration relocates seismic events to their true spatial positions, resulting in a more accurate subsurface image.
- **Amplitude preservation and analysis**: Ensure that true seismic amplitudes are

preserved throughout the processing steps. This is particularly important for AVO/AVA analysis, which relies on accurate amplitude information to interpret changes in subsurface rock properties and fluid content.

— **Final imaging and interpretation**: Generate final seismic images from the processed data. These images will be used for detailed interpretation of the subsurface, including the identification of geological features and monitoring changes in the reservoir.

Frequency

The initial 2D surveys will be conducted as part of the baseline data collection before CO_2 injection begins but after the injector well has been drilled. This baseline serves as a reference for subsequent monitoring surveys.

2D seismic surveys will be implemented once CO_2 migration moves outside of the VSP coverage. Once this occurs, surveys will be shot at least every 5 years during the testing and monitoring period.

Duration

After the CO_2 plume leaves the VSP coverage area, 2D seismic surveys will be used as the primary monitoring method. GCS anticipates this will begin 10 to 20 years after injection commences and will continue through the operational life of the project.

As discussed in Section 9.2.2 (Integrated Plume Monitoring Program), the implementation plan has been designed to be flexible, allowing for adjustments in survey frequency and scope based on real-time data and evolving site conditions.

Contingency

If there are significant anomalies or deviations of the CO_2 migration path that cannot be resolved using 2D seismic surveys, GCS will explore alternate technologies to track the plume.

9.3.1.4 Pulsed Neutron Logging

GCS will utilize Pulsed Neutron (PN) logging to monitor CO_2 saturation changes in subsurface reservoirs. A down-hole tool is used to produce PN logs, whose primary output is the “Sigma” curve. The tool distinguishes fluids based on neutron capture rates. CO_2-rich zones exhibit distinct behavior due to their large Sigma contrast with saline formation waters. The specifications for the PN logging tool is provided in Appendix D-VIII.

In addition to the Sigma curve, PN logs provide a secondary measurement—the hydrogen index ratio (Ratio) obtained from gamma-ray counts (Kennedy, Dance, Hawkes, Lenuik, & Nickel, 2018). The Ratio can be used to determine the suitability of the Sigma curve for monitoring CO_2 movement. The Ratio shows slightly better repeatability than the Sigma curve and will be used to monitor CO_2 saturation changes (Kennedy, Dance, Hawkes, Lenuik, & Nickel, 2018).

Implementation

GSC will conduct time-lapsed PN logging at MS IZ 1 to monitor for CO_2 saturation in the perforated interval. Since MS IZ 1 is located outside of the modeled stabilized CO_2 plume, the CO_2 residual gas saturation should not exceed 20%.

Interpretation

As measured CO_2 saturation data is collected at MS IZ 1, it will be compared to the predicted data from the model. As appropriate, re-evaluation of the model, or further investigation of the downhole conditions will be performed to ensure that no major deviation from the expected behavior of the plume front is experienced.

Frequency and During

PN logging of MS IZ 1 will be conducted annually for the first four years, and every two years thereafter through the operational life of Project Minerva.

9.3.2 Integrated Plume Monitoring Program

The proposed monitoring program aims to combine WA VSP, 3D DAS VSP, and 2D seismic surveys to track CO_2 plume movement over the life of Project Minerva. The three seismic techniques chosen, complemented by advanced analytical approaches such as AVO/AVA and seismic inversions, will provide a comprehensive framework for understanding the plume's behavior in real-time and ensuring containment within the storage formation.

Initial Baseline Survey Integration

WA VSP, 3D DAS VSP, and 2D seismic surveys will be acquired simultaneously as part of the baseline before injection begins. This baseline dataset will serve as a crucial reference for detecting changes in the subsurface over time.

WA VSPs, recorded in the same direction as the 2D seismic survey lines, will provide mid-range imaging that bridges the gap between the near-well and regional coverage. By taking advantage of the DAS fiber in MS CCS 1, these VSPs can deliver time-lapse imaging in specific directions of interest at a relatively low cost.

The 3D DAS VSP will provide high-resolution, near-wellbore imaging, allowing for detailed characterization of geological features close to the injection well. This method will capture the initial geometry of key structural elements such as faults and stratigraphic layers, setting a reliable benchmark for subsequent monitoring.

2D seismic survey acquired along lines in a star pattern will provide regional coverage away from the well, offering insights into the broader subsurface structure, in particular after VSP coverage is no longer sufficient.

Role of AVO/AVA and Inversions in Integration

AVO/AVA analysis will be used to extract amplitude variations with offset and/or angle, which are highly sensitive to changes in fluid content, porosity, and lithology. AVO attributes can help distinguish between the CO_2 plume and the surrounding brine-saturated rock, making them a critical tool for monitoring the plume's evolution. This technique can be applied to both WA VSPs and 2D seismic surveys to detect fluid movement away from the

wellbore.

Inversion techniques will be employed to convert seismic data into physical property models, such as acoustic impedance and shear impedance. Inversions will be particularly valuable in identifying subtle changes in reservoir properties caused by CO_2 injection. By applying inversion to both the 3D DAS VSP and 2D seismic data, the results will help track changes in the reservoir and identify zones of potential leakage or migration pathways, particularly around faults.

Elastic and rock physics inversions will also be key in interpreting WA VSPs, which will likely be shot more frequently due to their cost-effectiveness. These inversions can help quantify changes in the elastic properties of the subsurface over time, providing critical information on how the CO_2 is behaving Appendix D-X.

Temporal Monitoring and Walk-Away VSP as the Primary Tool

After the baseline acquisition, the WA VSPs will be the primary monitoring method. At the 5-year re-evaluation period, GCS will reassess the frequency of WA VSP acquisition and as the plume migrates towards the extent of the usable coverage area.

The WA VSPs will provide time-lapse data, which will be compared against the baseline to track changes in the plume and assess containment.

Reshooting the 3D VSP: Decision-Making Based on Walk-Away VSP Results

If the WA VSPs indicate unexpected CO_2 migration or potential leakage pathways GCS may decide to reshoot the 3D VSP for higher-resolution imaging. A 3D VSP reshoot would provide a more detailed update on the near-wellbore region and clarify areas of concern.

Post Year 10 Monitoring with Walk-Away VSPs and 2D Seismic Surveys

The VSP coverage area is anticipated to be effective through at least year 10 of the project. Currently, the 3D DAS VSP coverage area is consistent with the modeled plume at year 10 (Figure D.9.3-2). Outside of this coverage area, the VSP will no longer be as effective due to its limited repeatability and capacity. At this point, the WA VSP layered with a 2D seismic survey will become the primary monitoring tools for tracking the plume. While lower in resolution compared to the 3D DAS VSPs, the 2D lines will provide broader coverage and will be essential in understanding the long-term migration of the CO_2 plume over a larger area. Repeating the 2D seismic lines will help detect any far-field plume migration that could potentially intersect faults or other structural features, providing an additional layer of assurance in containment. Once 2D seismic surveys are implemented along with WA VSPs as the primary plume monitoring methods, they will be acquired every five years prior to the re-evaluation period through the operational life of the project.

Complementary Value of Each Method

The 3D DAS VSP offers high-resolution imaging around the well, capturing fine details of the reservoir and faults. The 2D seismic lines offer broader regional coverage, making them valuable for detecting long-range plume migration. The WA VSPs combine mid-range resolution and cost-efficiency, allowing for frequent monitoring in key directions.

By integrating these methods and applying advanced interpretation techniques, the monitoring program will ensure effective tracking of the CO_2 plume, with flexibility in decision-making based on real-time data.

9.4 NOTIFICATION

Per LAC 43.XVII §3617.B.6, GCS will notify the Office of Conservation at least 72 hours prior to conducting the PN logging in MS IZ 1.

9.5 REPORTING

Per LAC 43:XVII §3629.A.1.g, GCS will report the results of the proposed direct and indirect monitoring events in the semi-annual report submitted to LDENR and EPA. Direct results will be submitted in the semi-annual report for the period in which the monitoring took place. Due to the post-processing time associated with the proposed indirect methods, results will be submitted in the semi-annual report following the period in which the monitoring took place.

10 REFERENCES

Kennedy, M., Dance, T., Hawkes, C., Lenuik, A., & Nickel, E. (2018). Interpreting CO_2 Saturation Changes from Pulsed Neutron Logs at the Aquistore Site. *GHGT-14*. Melbourne, Australia.

Table D.2-1 Overview of Testing and Monitoring Program for Project Minerva

Monitoring Type (Regulatory Requirement)	Monitoring and Testing Description	Target Structure/Project Area	Location in Plan
Carbon Dioxide Stream Analysis (LAC 43:XVII §3625.A.1)	Compositional and isotopic analysis of the injected CO_2 stream	Sampled at comingled inlet pipework to Minerva Facility	Section 3
Continuous Recording of Operational Parameters (LAC 43:XVII §3625.A.2)	Downhole pressure/temperature gauges with surface transmitters and a flowmeter installed at the wellhead with alarms Downhole pressure/temperature gauges between tubing and casing annulus with transmitter at the surface	Surface-to-reservoir (injection well)	Section 4
Corrosion Monitoring of Wellbore Materials (LAC 43:XVII §3625.A.3)	Flow-through corrosion monitoring loop for periodic corrosion monitoring	Well infrastructure	Section 5
Above Confining Zone Monitoring (LAC 43:XVII §3625.A.4)	Sampling from groundwater wells completed in the first confined sand unit immediately below the base of the USDW DTS Monitoring	Near-surface environment, USDW(s) Zone above the confining zone (subsurface)	Section 6
Injection Well Integrity Testing (LAC 43:XVII §3625.A.5)	Standard Annular Pressure Test	Internal well infrastructure	Section 7
	DTS Monitoring, or alternate log/test	External well infrastructure	
Reservoir Testing (LAC 43:XVII §3625.A.6)	Pressure Fall-off test to characterize the injection reservoir and completion condition	Reservoir performance	Section 8
Injection Zone Plume and Pressure Extent Tracking (LAC 43:XVII §3625.A.7)	Pressure Monitoring	Storage reservoir and primary sealing formation	Section 9
	Walk-Away Vertical Seismic Profile (VSP), 3D Distributed Acoustic Sensing (DAS) VSP, 2D Seismic Survey, Pulse Neutron (PN) Logging	Storage reservoir	

Table D.2.2-2 Project Minerva Monitoring and Reporting Frequencies

Activity	Monitoring Frequency	Report to LDENR
CARBON DIOXIDE STREAM ANALYSIS		
CO_2 Stream Characterization	Quarterly	– Within 30 days of analysis – Semi-annual report following analyses
CONTINUOUS RECORDING OF OPERATIONAL PARAMETERS		
Injection pressure, injection rate, injection volume, pressure on the annulus, and annulus fluid level	Continuous	Semi-annual report (Monthly average values)
CORROSION MONITORING		
Corrosion Loop	Quarterly	Semi-annual report following collection
Casing Inspection Log (or equivalent)	As Required	– Within 30 days of logging – Semi-annual report following test
ABOVE CONFINING ZONE MONITORING		
Groundwater quality monitoring	– Quarterly, first 3 years – Annually, until end of ops	Semi-annual report following testing
INJECTION/MONITORING WELL MITS		
Injection/Monitoring Well Internal/External MITs	Annual and sooner if needed	– Within 30 days of test – Semi-annual report following test
Injection/Monitoring Well Workovers	As needed	– Within 30 days of workover – Semi-annual report following workover
RESERVOIR TESTING		
Pressure fall-off testing	Every 5 years	Semi-annual report following test
INJECTION ZONE CARBON DIOXIDE PLUME AND PRESSURE FRONT TRACKING		
Pressure front tracking	Monthly	Semi-annual report (Monthly average values)
Plume tracking (Seismic)	– Annually, first 4 years – Every 5 years, until end of ops	Semi-annual report following survey
Plume tracking (Pulse Neutron Logging)	– Annually, first 4 years – Every 2 years, until end of ops	Semi-annual report following logging

Table D.3-1 Project Minerva CO_2 Stream Specifications

Component	Concentration
Carbon Dioxide (CO_2)	> 97% vol
Water (H_2O)	< 630 ppmv
Total non-condensable gases*	< 3% vol
Oxygen (O_2)	< 0.1% vol
Methane (CH_4)	< 1.5% vol
Hydrogen Sulfide (H_2S)	< 50 ppmv
Mercury (Hg)	< 1 ppbv

*including N_2, Ar, O_2, CO, H_2, CH_4, C_2H_6

Table D.3.2-2 CO_2 Stream Analytical Parameters and Methods

Parameter	Analytical Methods[1]
Carbon Dioxide (CO_2)	ISBT[2] 2.0 Caustic absorption Zahm-Nagel ALI method SAM 4.1 subtraction method (GC/DID) GC/TCD
Water (H_2O)	ISBT 3.0
Oxygen (O_2)	ISBT 4.0 (GC/DID) GC/TCD
Nitrogen (N_2)	ISBT 4.0 (GC/DID) GC/TCD
Hydrogen Sulfide (H_2S)	ISBT 14.0 (GC/SCD)
Argon (Ar)	ISBT 4.0 (GC/DID) GC/TCD
Sulfur dioxide (SO_2)	ISBT 14.0 (GC/SCD)
Methane (CH_4)	ISBT 10.1 (GC/FID)
Total hydrocarbons (C_2H_6, C_3H_8+)	ISBT 10.1 (GC/FID)
Hydrogen (H_2)	ISBT 4.0 (GC/DID) GC/TCD
Carbon Monoxide (CO)	ISBT 5.0 (Colorimetric) ISBT 4.0(GC/DID)
Nitrogen Oxides (any (NO_x)	ISBT 7.0 Colorimetric
δC_{13} and C_{14}	Isotope ratio mass spectrometry Measured once and when a significant new source is added. Used for attribution during monitoring.

Note

[1] An equivalent method may be employed with the prior approval of the UIC Program Director

[2] International Society of Beverage Technologists (ISBT) Carbon Dioxide Guidelines MBAA TQ vol. 39, no. 1, 2002, pp. 32-35 as cited in ISO/TR 27921:2020(en). Carbon dioxide capture, transportation, and geological storage —Cross Cutting Issues —CO_2 stream composition

Table D.4.1-1 Operating Parameters Measured with Continuous Recording Devices

Parameter	Device(s)	Location	Min Sampling Frequency[1]	Min Recording Frequency[2]
Annular Pressure and Temperature	Electronic pressure & temperature (P/T) gauge in the annulus	Downhole gauge with transmitter at the wellhead	Continuous	30 seconds
Annular Fluid Volume	Fluid level gauge	Annular Fluid Reservoir	Continuous	Manual
	Electronic P/T gauge in the annulus	Downhole gauge with transmitter at the wellhead	Continuous	30 seconds
Injection Pressure	Electronic volumetric flow meter with pressure measurement	Meter with transmitter at wellhead	Continuous	30 seconds
Injection Rate	Electronic volumetric flow meter with rate measurement	Meter with transmitter at wellhead	Continuous	30 seconds
Injection Volume/Mass	Electronic volumetric flow meter with P/T measurement	Meter with transmitter at wellhead	Continuous	30 seconds
Downhole Pressure	Downhole P/T gauge run on tubing	Downhole gauge with transmitter at the wellhead	Continuous	30 seconds
Downhole Temperature	Downhole P/T gauge run on tubing	Downhole gauge with transmitter at the wellhead	Continuous	30 seconds

Note

(1) Sampling frequency refers to how often the monitoring device obtains data from the well for a particular parameter. For example, a recording device might sample a pressure transducer monitoring injection pressure once every two seconds and save this value in memory.

(2) Recording frequency refers to how often the sampled information gets recorded to digital format (such as a computer hard drive or a cloud-based Data Historian). Recorded data in the Data Historian will be compressed after specified durations. For example, the data from the injection pressure transducer might be recorded to a hard drive once every 30 seconds. Once stored, the recorded data will remain available at the 30 second interval for 5 days. After 5 days, the recorded data will be compressed, averaged (except for any discrepancies), and stored at 1-minute intervals for a year. After 1 year, the data will be compressed, averaged, and stored at 5-minute intervals for 5 years. After 5 years, the data will be compressed, averaged, and stored at 1 hour intervals throughout the life of the project.

Table D.6-1 Above Confining Zone Monitoring Summary

Monitoring Activity	Target Formation	Monitoring Well	Monitoring Location(s)	Monitoring Interval	Frequency
GROUNDWATER MONITORING					
Groundwater sampling	Evangeline Aquifer	Minerva South USDW Well No. 001	Minerva South Injection Well Pad	First confined sand unit below the base of the USDW (>1,800 ft below ground level (bgl))	– Baseline dataset prior to injection – Quarterly for the first 3 years after injection commences – After 3 years, annually until injection operations conclude – Unscheduled samples will be collected if an incident occurs
		Minerva South USDW Well No. 002	Stream 34 Well No. 001 (MS IZ 1) Well Pad		
FLUID MOVEMENT MONITORING					
DTS monitoring	Miocene Sands	Minerva South CCS Well No. 001	Minerva South Injection Well Pad	Interval above Confining Zone	Continuous – Min. Sampling Frequency (1): 10 sec – Min. Recording Frequency (2): 30 sec
		Minerva South CCS Well No. 002			

Notes

(1) Sampling frequency refers to how often the monitoring device obtains data from the well for a particular parameter. For example, a recording device might sample a pressure transducer monitoring injection pressure once every two seconds and save this value in memory.

(2) Recording frequency refers to how often the sampled information gets recorded to digital format (such as a computer hard drive). For example, the data from the injection pressure transducer might be recorded to a hard drive once every minute.

Table D.6.2-2 Groundwater Analysis Parameters and the Analytical Methods

Parameters	Analytical Methods [1]
FIELD MEASUREMENTS	
Dissolved Oxygen (field)	APHA 2005
Specific Conductance (field)	APHA 2510
Temperature (field)	Thermocouple
Water Density (field)	Oscillating body method
Static Water Level	Sounder
pH (field)	EPA 150.1
LABORATORY ANALYSIS	
Cations (Al, Ba, Mn, As, Cd, Cr, Cu, Pb, Sb, Se, Zn, Tl)	SW846 6010/6020
Cations (Ca, Fe, K, Mg, Na, Si)	SW846 6010/6020
Anions (Br, Cl, F, NO3, SO4)	SM 300
Dissolved CO_2	Coulometric titration, ASTM D513-11
Dissolved CH_4 (Methane)	SM 6211 B or 6211 C
Hydrogen Sulfide (H_2S)	ISBT 14.0 (GC/SCD)
Total Dissolved Solids (TDS)	Gravimetry; Method 2540 C
Oxygen, Argon, and Hydrogen	ISBT 4.0 (GC/DID) GC/TCD
Alkalinity	Method 2320B

Notes

[1] Or similar method

- The listed analytical methods may be revised based on input from the laboratories selected to do the work, and field instruments used during a given event.
- Field duplicates to be collected at rate of 10% (1 for every 10 samples) or 1 per event.
- MS/MSDs to be collected at a rate of 5% (1 for every 20 samples) or 1 per event.
- Field blanks and equipment blanks will be collected as per the QASP, Appendix D-I.

Table D.7-1 Injection Well Integrity Testing Summary

	Test Description	Mechanical Integrity	Technology	Frequency
PRIMARY	Distributed Temperature Sensing (DTS)	External	Wellbore annulus using fiber optic sensing	Annual
	Standard Annular Pressure Test	Internal	Annular Pressure Test at the wellhead	Annual
ALTERNATE	Oxygen Activation Log	External	Wireline well logging	Contingency
	Noise Log	External	Wireline well logging	Contingency
SUPPLEMENTAL	Casing Inspection Log	Internal/External	Wireline well logging	As Required
	Cement Bond Log	External	Wireline well logging	As Required
	Casing Collar Locator Log	External	Wireline well logging	As Required

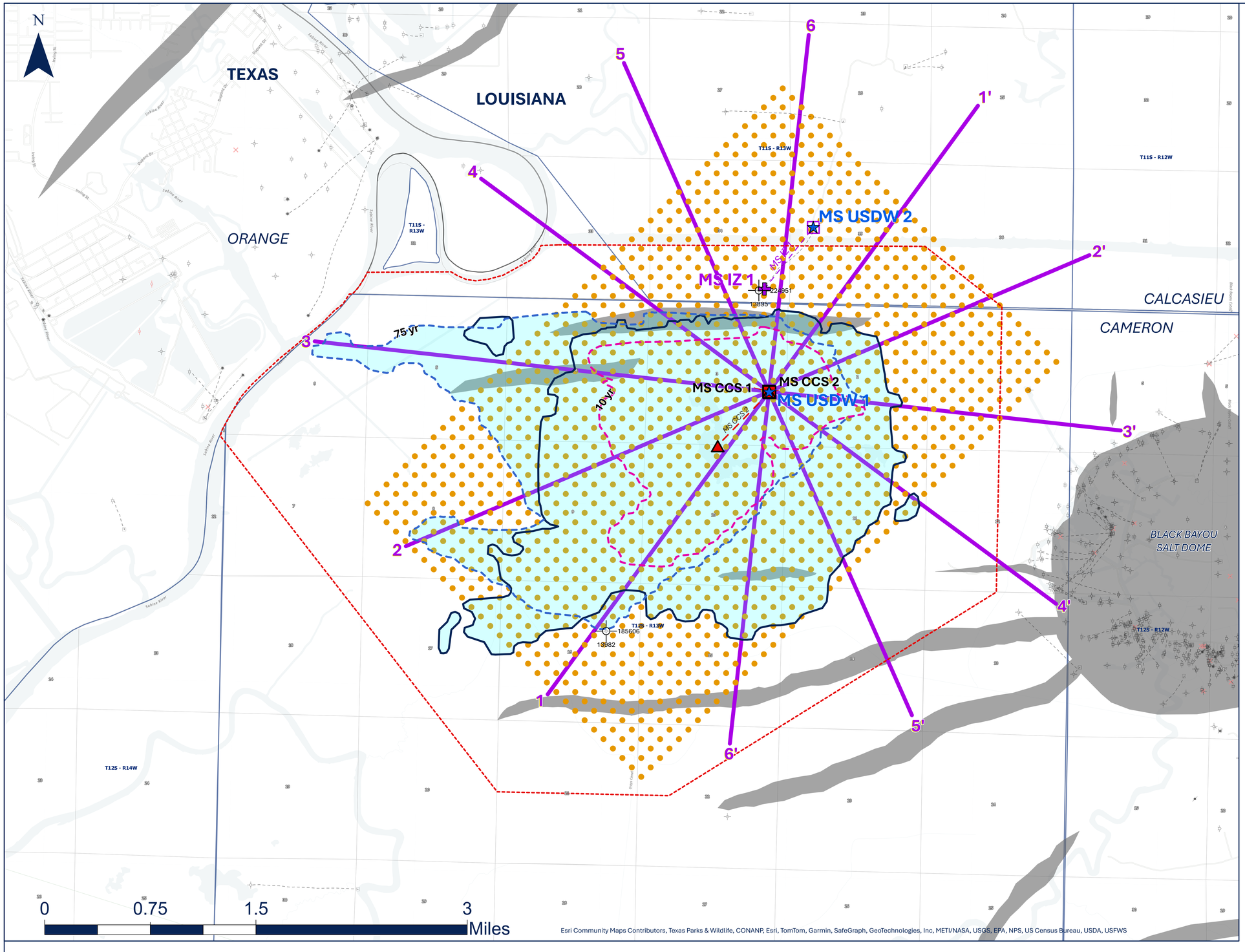
Table D.9-1 Direct and Indirect Methods for Pressure and CO_2 Plume Tracking

Monitoring Target	Target Interval	Monitoring Technology	Monitoring Location(s)	Frequency	Objective
DIRECT					
Pressure	Injection Zone	Pressure Gauge	– MS IZ 1 – MS CCS 1 or MS CCS 2	– Monthly – Annually	Monitor pressure influence from injection
INDIRECT					
Plume	Injection Zone	Walk-Away VSP	– DAS receiver in MS CCS 1 – Sources at surface, along seismic lines	– Baseline before injection – At least 4 times through year 4.5[1] – Reevaluate frequency after 4th shoot; no less than every 5 years – At least every 5 years from approx. year 9.5[1] through year 29.5[1] or until coverage is insufficient for monitoring	– Define the edge of the plume and ensure it remains within the permitted AoR.
		3D DAS VSP	– DAS receiver in MS CCS 1 – Sources at surface in 500 x 500 foot grid	– Baseline before injection – As needed thereafter	
		2D Seismic Survey	– Sources and receivers at surface along seismic lines	– Baseline before injection – Every 5 years from when VSP coverage becomes insufficient (approx. year 10-20 through year 30)	
		Pulse Neutron Capture Logging	– MS IZ 1	– Annually through year 4; – Every 2 years thereafter	– Monitor carbon dioxide saturation within the injection zone

Note 1: Seismic acquisition will occur at least 6 months prior to any required AoR resubmission to account for fieldwork and processing time.

Table D.9-2 In-Zone Monitoring Well Summary

Monitoring Activity	Monitoring Instrument	Target Formation	Frequency	Objective
DIRECT MONITORING				
Pressure Extent	Downhole Pressure and Temperature Gauge	Injection Zone	Monthly	Monitor pressure influence from injection
INDIRECT MONITORING				
CO_2 Plume Extent	Pulse Neutron Capture logging tool	Injection Zone	Annually through year 4; Every 2 years thereafter	Monitor carbon dioxide saturation within the injection zone



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FIGURE D.2-1
Monitoring Network for Project Minerva

MAP LEGEND

- 3D VSP Sources
- Injector Bottom Hole
- Injector Well Pad
- Injector Schematic Well Trajectory
- Walk-away VSP / 2D Seismic Line
- Magnetic Survey Flight Area
- 10 yr CO2 Plume
- Max Extent of Stable CO2 Plume
- Max Extent of Pressure Front
- Delineated Area of Review
- Top Upper Frio Faults
- PLSS Townships & Ranges
- PLSS Sections
- SONRIS Parishes

Monitoring Wells

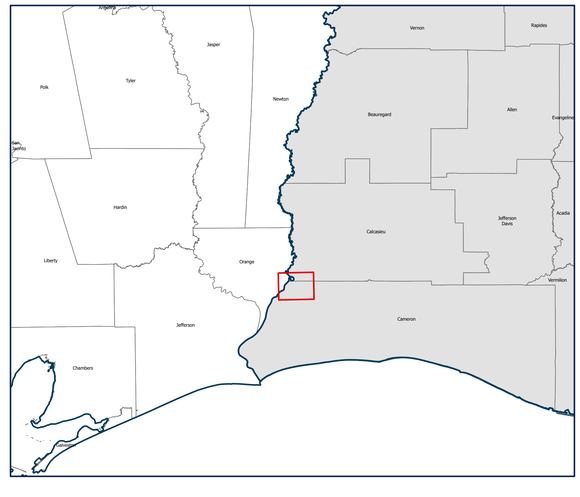
- In-Zone Bottom Location
- In-Zone Surface Location
- USDW Monitoring Well (Vertical)
- In-Zone Well Trajectory

Well Status

- Other
- Active - Producing
- Drilled
- Dry & Plugged
- Inactive
- Orphan
- Permit Expired
- Plugged & Abandoned
- Reverted
- Shut In
- Temporarily Abandoned
- Unable to Locate
- Surface Location
- Well Trajectory

Well Labels

Serial Number
Total Depth (TVDSS)
Monitoring Well Name



MAP DETAILS

PREPARED BY	R WENCEL	**DATE**	11/4/2024 2:10 PM
APPROVED BY	K GARRETT	**DATE**	11/XX/2024
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PAGE SIZE	A0 (46.81 W X 33.11 H)		

SPATIAL REFERENCE

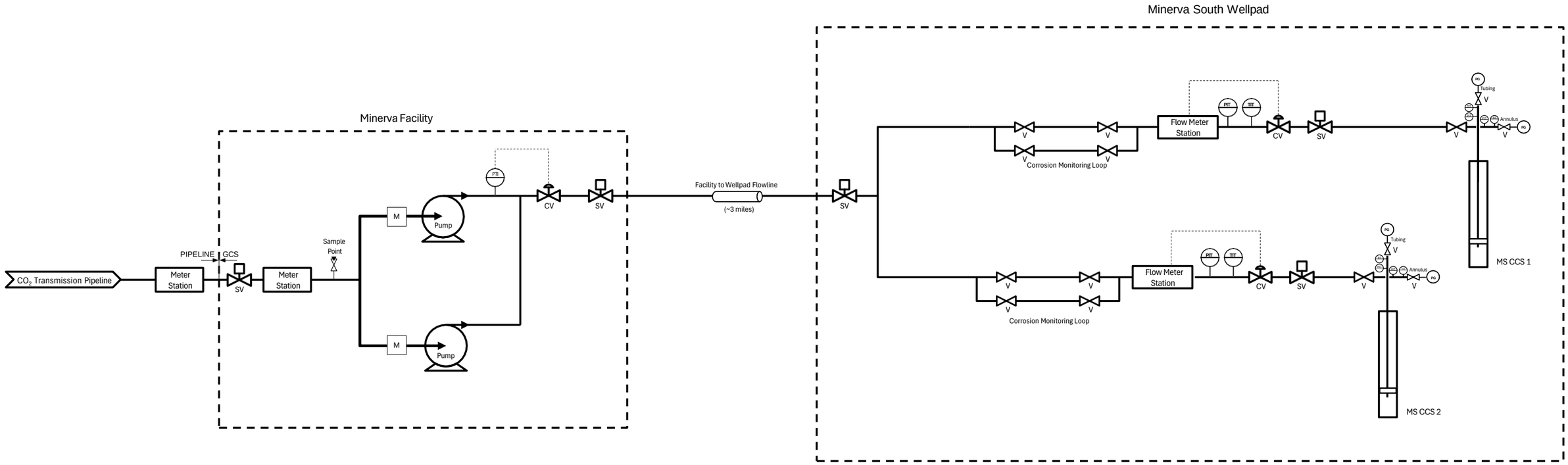
PCS	NAD 1927 State Plane Louisiana South (FIPS 1702)
GCS	GCS North American 1927
DATUM	North American 1927
PROJECTION	Lambert Conformal Conic

PROJECT MINERVA DETAILS

WELLS	Minerva South CCS Well Nos. 001 and 002
LOCATION	Cameron Parish, Louisiana
EPA PROJECT ID	R06-LA-0002
LDENR APPL NOS	45031 & 45032

LOUISIANA BOARD OF PROFESSIONAL GEOSCIENTISTS
KAYCEE GARRETT
1325
Est. 2011

Figure D.3.1-1 Process Flow Diagram of Project Minerva Operations



Key

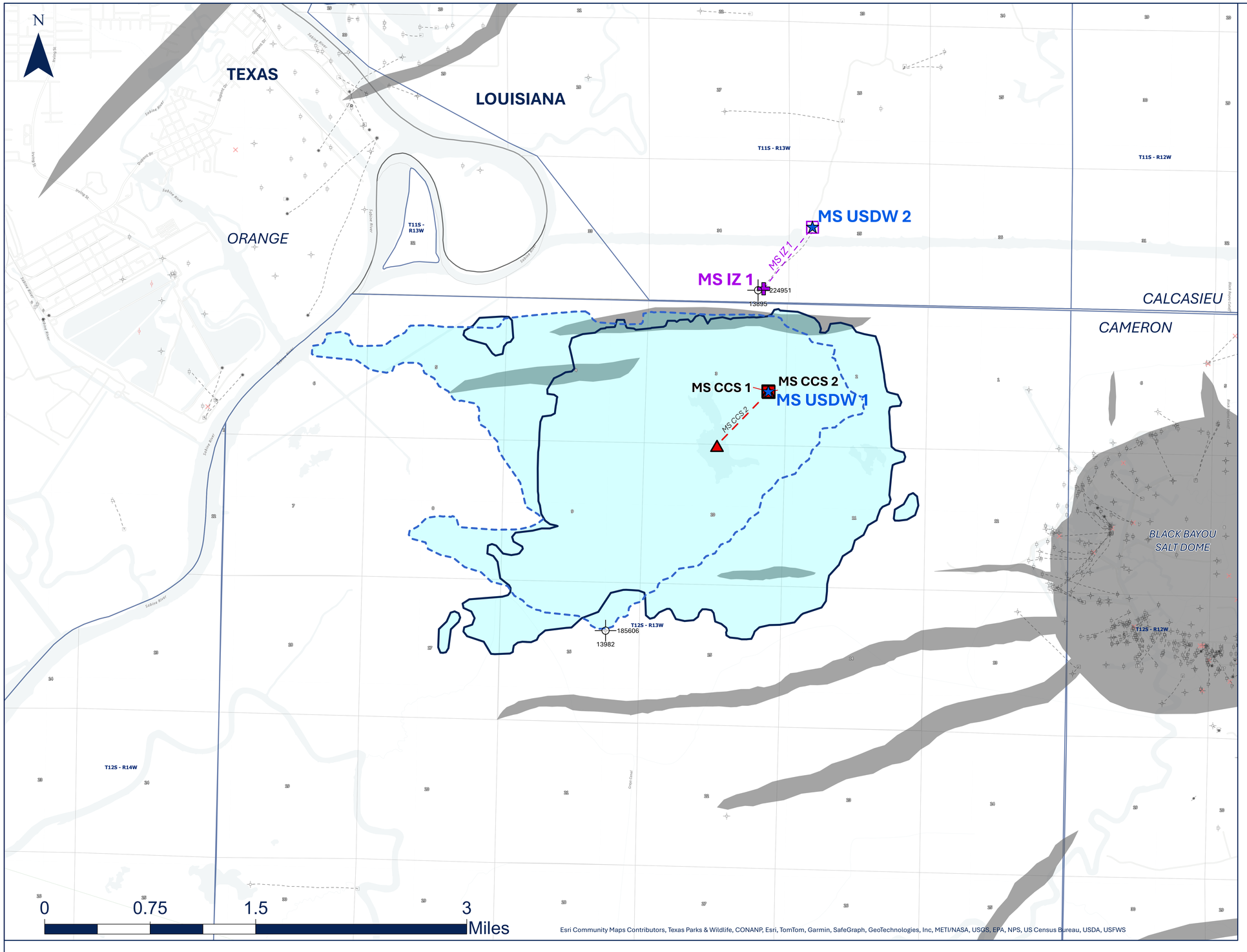
CV	Control Valve
M	Meter
PG	Pressure Gauge
PIT	Pressure Indicating Transmitter
SV	Safety Valve
TIT	Temperature Indicating Transmitter
V	Valve
.....	Control Loop

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Minerva South CCS Well Nos. 001 & 002	
Project: **Minerva**	Project ID: **R06-LA-0002**
Location: **Cameron Parish, LA**	LDENR Appl No: **45031 & 45032**



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FIGURE D.6.1-1
Above-Zone and In-Zone Monitoring Well Locations

MAP LEGEND

- Injector Bottom Hole
- Injector Well Pad
- Injector Schematic Well Trajectory
- Max Extent of Stable CO2 Plume
- Max Extent of Pressure Front
- Delineated Area of Review
- Top Upper Frio Faults
- PLSS Townships & Ranges
- PLSS Sections
- SONRIS Parishes

Monitoring Wells

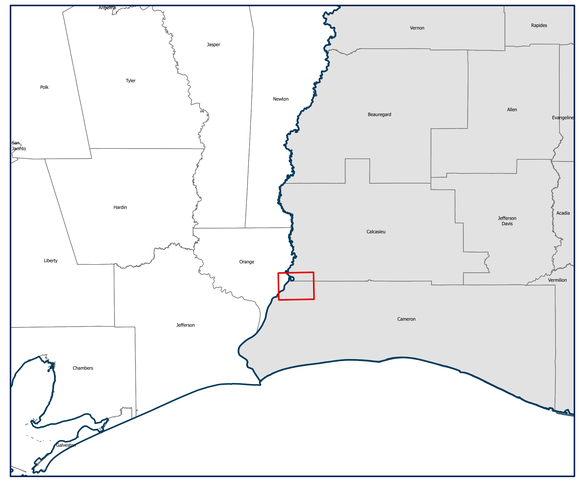
- In-Zone Bottom Location
- In-Zone Surface Location
- USDW Monitoring Well (Vertical)
- In-Zone Well Trajectory

Well Status

- Other
- Active - Producing
- Drilled
- Dry & Plugged
- Inactive
- Orphan
- Permit Expired
- Plugged & Abandoned
- Reverted
- Shut In
- Temporarily Abandoned
- Unable to Locate
- Surface Location
- Well Trajectory

Well Labels

Serial Number
Total Depth (TVDSS)
Monitoring Well Name



MAP DETAILS

PREPARED BY	R WENCEL	**DATE**	11/4/2024 2:11 PM
APPROVED BY	K GARRETT	**DATE**	11/XX/2024
MAP SCALE	1:16,000		
PAGE SIZE	A0 (46.81 W X 33.11 H)		

SPATIAL REFERENCE

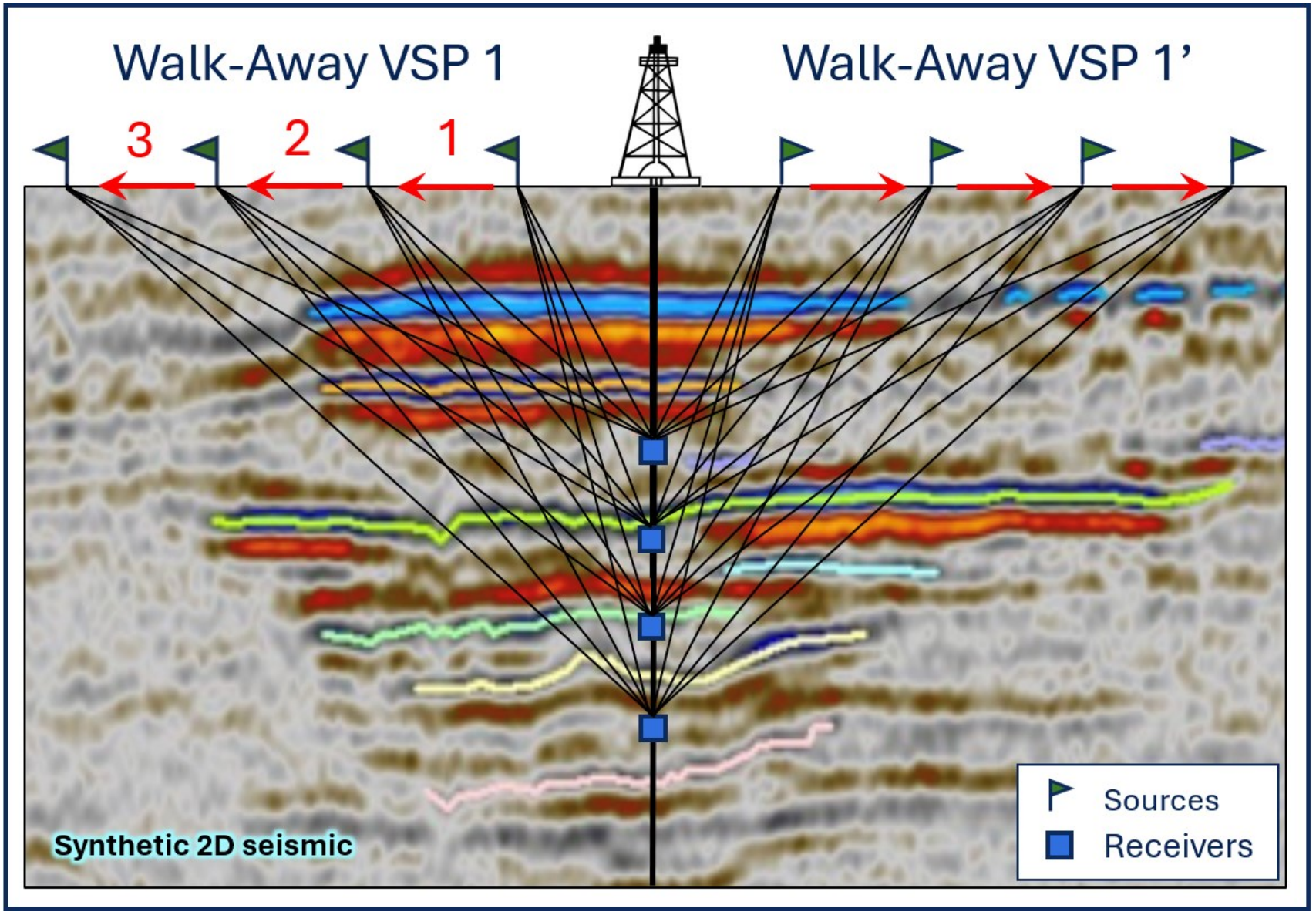
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GCS	GCS North American 1927
DATUM	North American 1927
PROJECTION	Lambert Conformal Conic

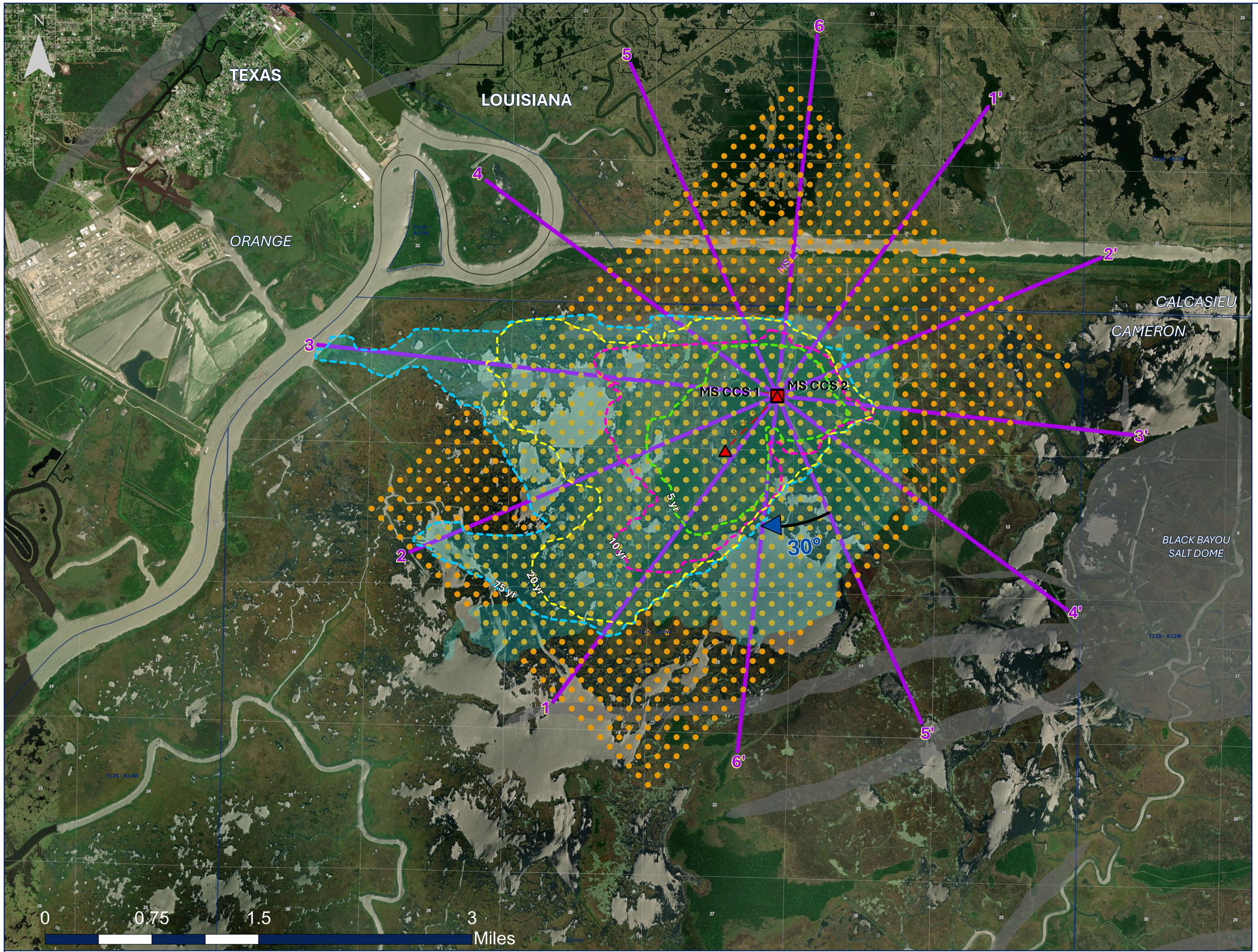
PROJECT MINERVA DETAILS

WELLS	Minerva South CCS Well Nos. 001 and 002
LOCATION	Cameron Parish, Louisiana
EPA PROJECT ID	R06-LA-0002
LDENR APPL NOS	45031 & 45032

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Figure D.9.3-1 Schematic Demonstrating Walk-Away VSP Design



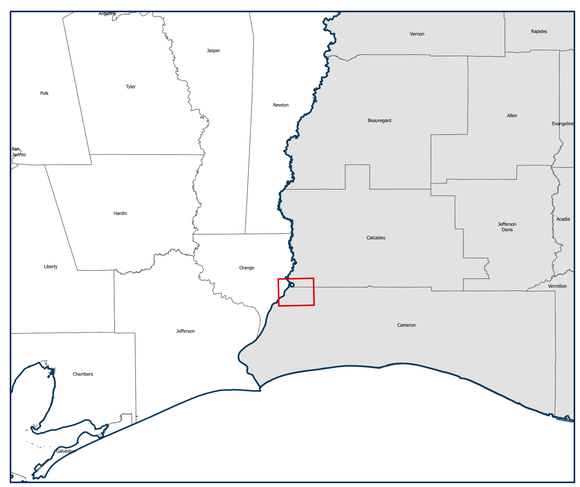


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FIGURE D.9.3-2
Indirect Monitoring-Acquisition Layout at Project Minerva

MAP LEGEND

- 3D VSP Sources
- Injector Bottom Hole
- Injector Well Pad
- Injector Schematic Well Trajectory
- Walk-away VSP / 2D Seismic Line
- 5 Year CO2 Plume
- 10 Year CO2 Plume
- 20 Year CO2 Plume
- Max Extent of Stable CO2 Plume (Year 75)
- Delineated Area of Review
- Top Upper Frio Faults
- PLSS Townships & Ranges
- PLSS Sections
- SONRIS Parishes



MAP DETAILS

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APPROVED BY	K GARRETT	**DATE**	11/XX/2024
MAP SCALE	1:16,000		
PAGE SIZE	A0 (46.81 W X 33.11 H)		

SPATIAL REFERENCE

PCS	NAD 1927 State Plane Louisiana South (FIPS 1702)
GCS	GCS North American 1927
DATUM	North American 1927
PROJECTION	Lambert Conformal Conic

PROJECT MINERVA DETAILS

WELLS	Minerva South CCS Well Nos. 001 and 002
LOCATION	Cameron Parish, Louisiana
EPA PROJECT ID	R06-LA-0002
LDENR APPL NOS	45031 & 45032

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Figure D.9.3-3 Flow Chart Illustrating Ray Trace Model Workflow

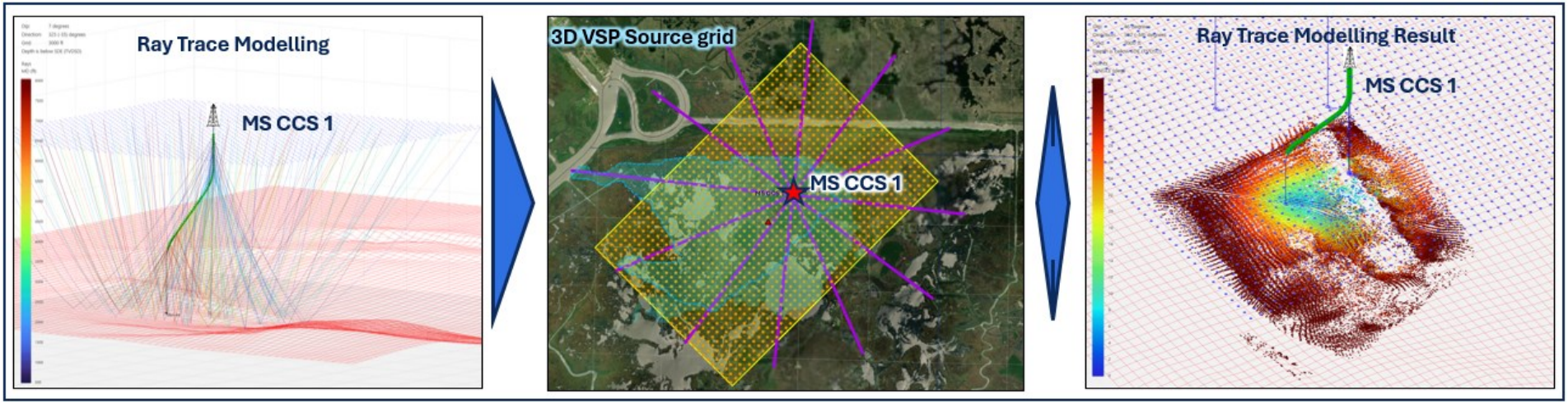


Figure D.9.3-4 Comparison of Conventional Seismic Data and 3D VSP

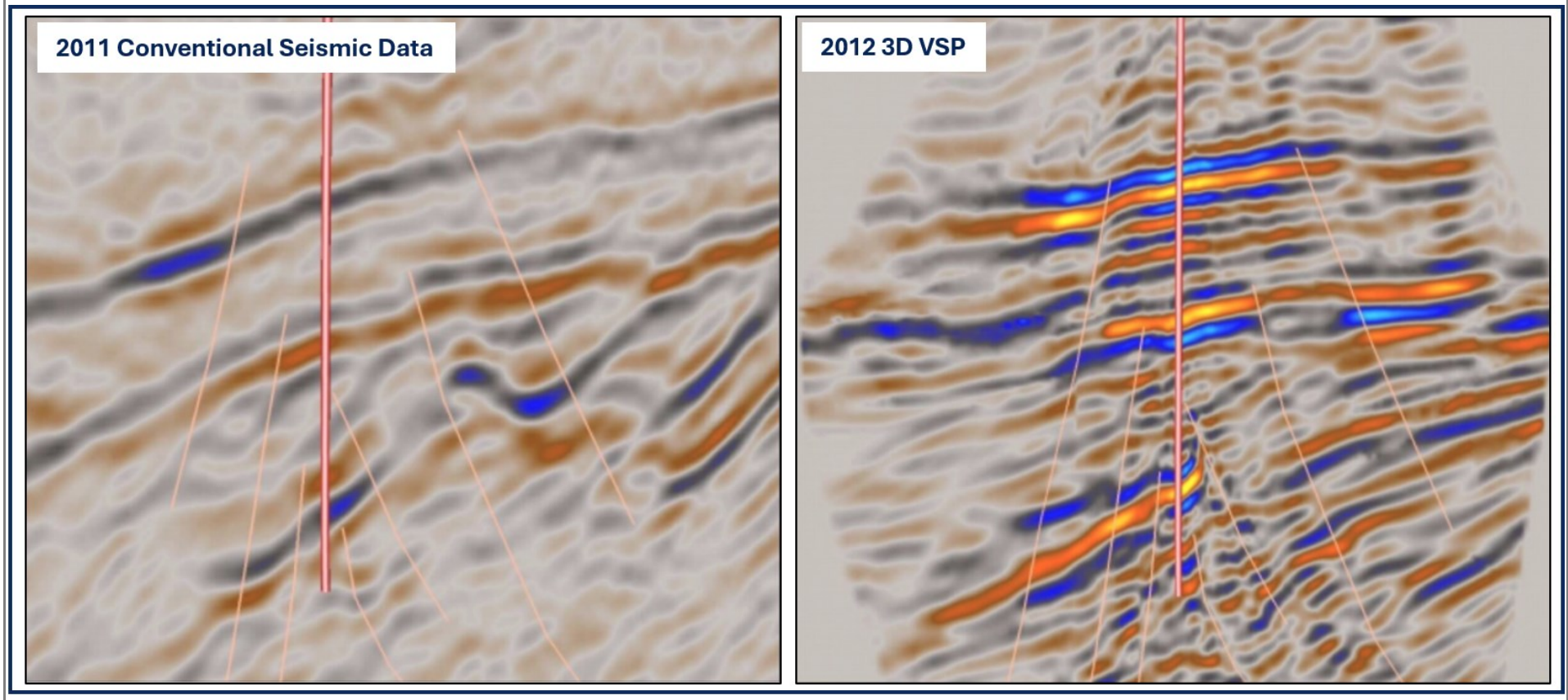
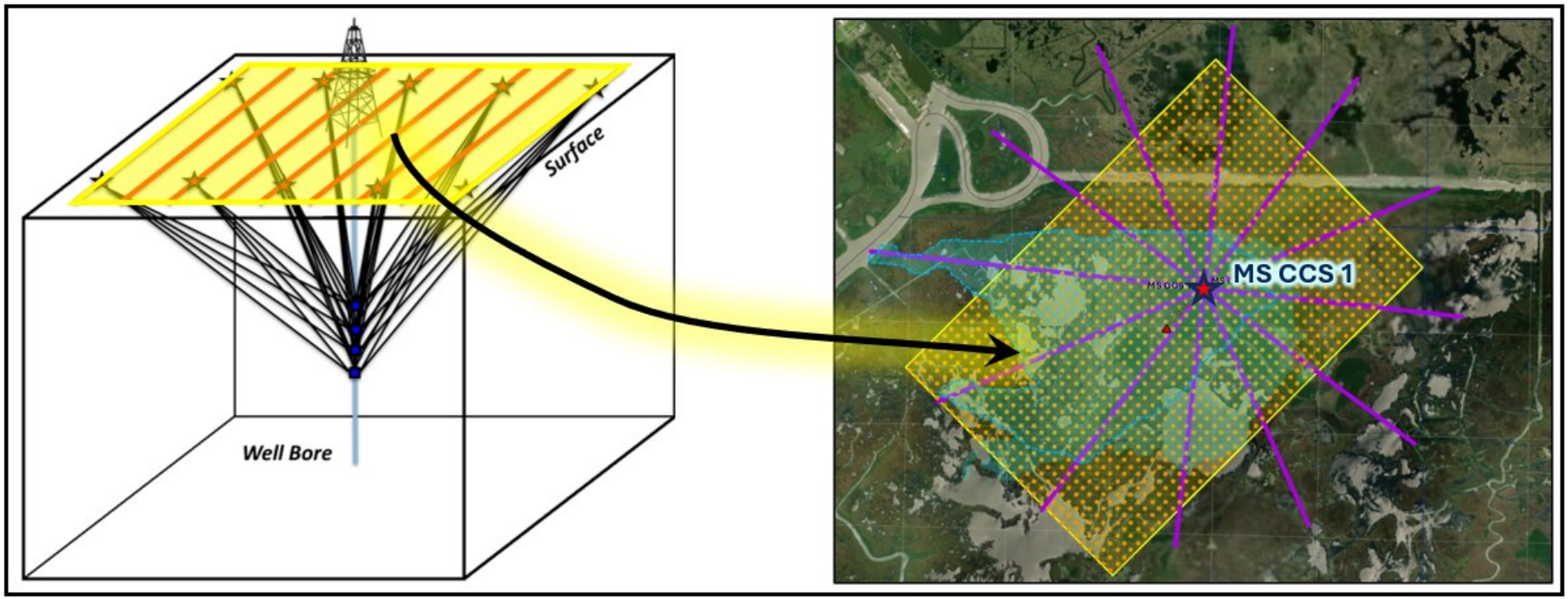


Figure D.9.3-5 3D DAS VSP Acquisition Layout



APPENDIX D-I

Quality Assurance and Surveillance Plan (QASP)

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ATTACHMENT

Attachment D.I-1	EPA 540-R-20-005, Sampler's Guide: Contract Laboratory Program Guidance for Field Samplers

TITLE AND APPROVAL SHEET

This Quality Assurance and Surveillance Plan (QASP) is approved for use and implementation at Project Minerva. The signatures below denote the approval of this document and intend to abide by the procedures outlined within it.

Signature	Date
DAVID COOK	
CHIEF EXECUTIVE OFFICER	

Signature	Date
INSERT TYPED NAME	
INSERT TITLE	

Signature	Date
INSERT TYPED NAME	
INSERT TITLE	

FACILITY INFORMATION

Facility Name: Minerva Facility

Injection Wells: Minerva South CCS Well No. 001 (MS CCS 1)
Minerva South CCS Well No. 002 (MS CCS 2)

Facility Contact: David Cook, CEO
5599 San Felipe St., Ste. 1450, Houston, Texas 77056
(713) 419-6808; dcook@gcscarbon.com

Well Locations: Sec 3, T12S, R13W, Cameron Parish, Louisiana
MS CCS 1 (NAD 1927)
Surface: 30° 02' 34.10"W, -93° 40' 20.63"N
Bottom-Hole: 30° 02' 34.10"W, -93° 40' 20.63"N
MS CCS 2 (NAD 1927)
Surface: 30° 02' 33.84"W, -93° 40' 20.48"N
Bottom-Hole: 30° 02’ 13.74”W, -93° 40' 42.07"N

1 INTRODUCTION

This Quality Assurance and Surveillance Plan (QASP) describes how Gulf Coast Sequestration, LLC (GCS) will monitor Project Minerva pursuant to LAC 43.XVII §3625.A.11. Monitoring will be used to demonstrate that Minerva South CCS Well Nos. 001 and 002 (MS CCS 1 and MS CCS 2) are operating as planned, the CO_2 plume and pressure front are moving as predicted, and that there is no endangerment to USDW. Additionally, the monitoring data will be used to validate and adjust the simulation model used to predict the distribution of the CO_2 within the Injection Zone to support Area of Review (AoR) re-evaluations and a non-endangerment demonstration.

2 DISTRIBUTION LIST

The participants of the project presented in Table D.I.2-1 will receive the completed QASP and all future updates for the duration of the project. Annual updates of the distribution list will be provided, contingent on staff changes occurring in the preceding 12 months. The GCS Site Manager will be responsible for ensuring that all those on the distribution list will receive the most current copy of the approved QASP. Names and contact details are provided for those positions on the distribution list that have currently been filled. GCS will provide an update to the UIC Director once all positions have been filled, prior to project construction.

3 PROJECT/TASK ORGANIZATION

3.1 KEY INDIVIDUALS AND RESPONSIBILITIES

Project Minerva is led by GCS and includes the participation of several subcontractors. The testing and monitoring responsibilities will be shared between GCS and designated subcontractors. Key individuals will be appointed before project construction begins; contact details will be provided to the UIC Director at that time.

Designated responsibilities will include:

GCS Field Engineering and HSE

- CO_2 stream analysis surface sampling
- Continuous recording of operational parameters
- Corrosion monitoring
- In-zone monitoring - pressure front tracking

Oilfield Service and Equipment Consultants (Baker Hughes)

- In-zone monitoring – Pulse Neutron logging
- VSP in-direct monitoring of CO_2 plume
- External mechanical integrity testing (MIT) of injection and monitoring wells
- Pressure fall-off testing of injection wells

Environmental Consultants (TetraTech)

- Above confining zone groundwater sampling and monitoring

3.2 INDEPENDENCE FROM PROJECT QUALITY ASSURANCE (QA) MANAGER AND DATA GATHERING

The majority of the physical samples collected, and data gathered as part of the Testing and Monitoring Plan will be analyzed, processed, or witnessed by third parties independent from and outside of the project management structure. The term “third parties” is used to refer to any consultancies, contractors, vendors or other businesses contracted to carry out sample collection and analysis, on behalf of GCS. "Third parties” will be given a copy of the QASP within the scope of work during the request for proposal process. GCS will issue an updated copy of the QASP to the Louisiana Department of Energy and Natural Resources (LDENR) Commissioner of Conservation (Commissioner) detailing selected third parties once they have been chosen and prior to commencement of work.

3.3 QASP RESPONSIBILITY

GCS is responsible for maintaining and distributing an official, approved QASP. GCS will review, no less than every five years, the QASP and consult with the Commissioner to determine whether changes to the plan are warranted.

3.4 ORGANIZATIONAL CHART FOR KEY PROJECT PERSONNEL

Figure D.I.3.4-1 shows the organization structure of the project. GCS will provide the Commissioner with a contact list of individuals fulfilling these roles.

4 PROBLEM DEFINITION/BACKGROUND

4.1 REASONING

The primary goal of the Testing and Monitoring Plan is to ensure that the geologic storage

project is operating as permitted and is not endangering USDWs. In compliance with LAC 43.XVII §3625, this QASP was developed and is provided as Appendix D-I of Attachment D, Testing and Monitoring Plan.

4.2 REASONS FOR INITIATING THE PROJECT

The goal of Project Minerva is to demonstrate the ability of the upper Frio Formation to accept and retain industrial-scale volumes of CO_2 for permanent geologic storage thus reducing atmospheric concentrations of CO_2.

4.3 REGULATORY INFORMATION, APPLICABLE CRITERIA, ACTION LIMITS

The Class VI rule requires owners or operators of Class VI wells to perform several types of activities during the lifetime of the project to ensure that the injection well maintains mechanical integrity, that fluid migration and the extent of pressure elevation are within the limits described in the permit application, and that USDWs are not endangered. These monitoring activities include CO_2 stream analysis, continuous recording of operational parameters, corrosion monitoring, above confining zone monitoring, MITs, pressure fall-off testing, and tracking of the CO_2 plume and associated pressure changes.

This appendix to the Testing and Monitoring Plan details both the measurements that will be taken as well as the steps to ensure that the quality of all the data can be used with confidence in making decisions during the life of the project, based on requirements stipulated in “EPA Requirements for Quality Assurance Project Plans” (EPA QA R-5).

5 PROJECT/TASK DESCRIPTION

5.1 SUMMARY OF WORK TO BE PERFORMED

Table D.I.5.1-1 provides a summary of the testing and monitoring activities planned for Project Minerva. The monitoring activities can be divided into the following monitoring categories to achieve objectives at defined locations:

- CO_2 stream monitoring;
- Injection and integrity monitoring; and
- Subsurface monitoring.

5.2 GEOGRAPHIC LOCATIONS

Figure D.I.5.2-1 illustrates the locations of the Testing and Monitoring Plan activities and elements.

5.3 RESOURCE AND TIME CONSTRAINTS

Project Minerva’s Area of Review (AoR) encompasses land primarily owned/leased by GCS. There are no additional resources or time constraints identified for the Testing and Monitoring Plan based on property ownership issues.

6 QUALITY OBJECTIVES AND CRITERIA

The overall objective of the QASP is to provide the standards and procedures necessary to validate the overall integrity of the sampling methods discussed in the Testing and Monitoring Plan and ensure the results of sampling and testing will meet the characterization and non-endangerment goals of Project Minerva. The QASP is the mechanism by which the Commissioner has confidence in the rigor of the Testing and Monitoring Plan.

In the following sections, GCS has addressed the applicable quality assurance criteria for the equipment and measurements associated with each of the monitoring areas. An instrumentation summary is provided as Table D.I.6-1.

6.1 CO_2 STREAM MONITORING

Grab samples of the CO_2 stream will be obtained for analysis of gases (Table D.I.6.1-1). Samples will be collected at each emitter's outlet and at the comingled inlet pipework to GCS facilities. These grab samples will be obtained using laboratory approved sampling cylinders to collect and transport the samples. Stainless steel tubing or equivalent pressure hoses will be connected to a designated sampling port, with a regulator to control the pressure. The pressure of the CO_2 will be reduced ensuring the CO_2 is collected in the gaseous state as required by the Federal transportation regulations for shipment of compressed gases (CFR 173.301.a.8). Sample cylinders will be purged during sample collection to remove laboratory-added helium gas and ensure a representative sample. Sample containers will have a chain of custody form and will be labeled appropriately. Samples will be sent to and analyzed by a Louisiana Environmental Laboratory Accreditation Program (LELAP) accredited laboratory.

Once the LELAP laboratory is selected, Table D.I.6.1-1 will be updated with the laboratory informed detection limit/range, typical precisions, and QC requirements for each parameter.

6.2 INJECTION AND INTEGRITY MONITORING

Injection and integrity monitoring requires equipment used to monito injection temperature, pressure, rate, and volume; the downhole temperature and pressure in the tubing and tubing-casing annulus of the injection and monitoring wells; and the mechanical integrity logs and tests performed to ensure internal and external integrity of the injection and in-zone monitoring wells. Table D.I.6.2-1 provides a summary of the operating parameters for MS CCS 1 and MS CCS 2 that will be measured with continuous recording devices.

6.2.1 Injection Temperature, Pressure, Rate, and Volume Monitoring

Injection temperature, pressure, rate, and volume will be measured at each injection well by volumetric flow meter(s). Each well will be equipped with primary and secondary meters. The volumetric flow meters will also be equipped with electronic pressure and temperature gauges with transmitters to continuously monitor pressure and temperature of the injection stream. The data from the meter station will be collected and recorded in the computerized control system.

GCS is working with vendors to determine the most appropriate flow meter for Project Minerva. The specification sheet of an example flow meter is provided in Appendix D-II of the Testing and Monitoring Plan. The specifications for the example flow meter are summarized in Table D.I.6.2-2 and will be updated with the final values upon completion of detailed design.

6.2.2 Temperature and Pressure Wellbore Monitoring

The injection wells, MS CCS 1 and MS CCS 2, and the in-zone monitoring well, Minerva South In-Zone Well No. 001 (MS IZ 1), will be equipped with the following instrumentation to monitor pressure at the surface and temperature/pressure downhole:

- Wellhead Tubing Pressure Gauge
- Wellhead Annulus Pressure Gauge
- Downhole Annulus Pressure and Temperature Gauge with Transmitter at Surface
- Downhole Pressure and Temperature Gauge with Transmitter at Surface

GCS is still working with vendors to determine the most appropriate gauges and tools for Project Minerva. The specification sheets of an example wellhead pressure gauge and a downhole pressure and temperature gauge are provided in Appendix D-II of the Testing and Monitoring Plan. The specifications, for the example of gauges are summarized in Table D.I.6.2-2 and will be updated with the final values upon completion of detailed design.

6.2.3 Mechanical Integrity Logging and Testing

External mechanical integrity will be demonstrated using the following technologies:

- Primary
  - Distributed Temperature Sensing (DTS)
- Alternate
  - Noise Log
  - Oxygen Activation Log
- Supplemental
  - Casing Inspection Log
  - Cement Bond Log
  - Casing Collar Locator Log

GCS will use DTS fiber optic cables installed from surface to total depth of MS CCS 1 and MS CCS 2 as the primary method to demonstrate external mechanical integrity. GCS will employ one of the alternate test technologies should a contingent method be required. Supplemental technologies may be required in conjunction with the primary or alternate technologies.

A summary of the logging technologies with their specifications are provided as Table D.I.6.2-3. The specifications are based on a service provider whose specification sheets for

each technology are provided as Appendix D-IV of the Testing and Monitoring Plan. Should a different service provider be selected, the table and appendix will be updated with the required information.

Data comparability expresses the confidence with which one data set can be compared to another. The data sets to be generated by this project will be very comparable to future data sets because of the use of standard methods and the level of QA/QC effort.

6.2.4 Corrosion Monitoring

GCS will monitor corrosion by analyzing a corrosion loop. The loop will be constructed with the same well materials placed in contact with the carbon dioxide stream.

When the corrosion loop is inspected, the loop will be assessed using direct, off-line, Level 3 Non-Destructive Testing (NDT) and Non-Destructive Examination (NDE) certified inspectors and technologies including but not limited to Ultrasonic and Radiography equipment.

Ultrasonic testing utilizes sound waves whose frequencies (50 kHz - 50 MHz) are above the audible range for the human ear. The piezo-electric effect of the ultrasonic transducer makes it possible to transmit and receive from within the equipment. The instrument makes it possible to inspect the internal structure of the equipment, and to detect variable thickness changes, welds, cracks, voids, delamination and other types of material or structural defects.

Radiography can be performed utilizing either X-rays or gamma rays. Both are forms of electromagnetic radiation. The difference between various forms of electromagnetic energy is related to the wavelength. X-rays and gamma rays have the shortest wavelength, and this property leads to the ability to penetrate, travel through, and exit various materials such as carbon steel and other metals. This testing method allows operators to inspect many types of manufactured components that can be examined to verify the internal structure and integrity of the specimen.

Final technology selection will be completed after detailed engineering. The QASP will be updated with the equipment specifications for the chosen technology.

6.3 SUBSURFACE MONITORING

6.3.1 Above Confining Zone Groundwater Monitoring

The quality assurance criteria for evaluating the integrity of groundwater sampling protocol include: (1) performance/measurement, (2) precision, (3) bias, (4) representativeness, (5) completeness, (6) and comparability.

Performance/Measurement Criteria

Groundwater monitoring will be conducted prior to injection to establish a baseline, during the operational lifetime of the project, and during the 50-year post injection site care and site closure (PISC) period. Above Confining Zone (ACZ) monitoring wells (MS USDW 1 and MS USDW 2) will be used to collect water-quality samples from the first confined sand unit below the base of the Underground Source of Drinking Water (USDW). All the groundwater

analytical and field monitoring parameters and outputs are listed in Table D.I.6.3-1. The list of analytes may be reassessed periodically and adjusted to include or exclude analytes based on their effectiveness to the overall monitoring program goals.

Precision

For groundwater sampling, data accuracy will be assessed by the collection and analysis of field blanks to test sampling procedures and matrix spikes to test lab procedures. Field blanks will be taken no less than one per sampling event to spot check for sample bottle contamination. Laboratory assessment of analytical precision will be the responsibility of the individual laboratories per their standard operating procedures.

Bias

Field blanks assess potential bias from the combined processes of sample handling, processing, and laboratory analysis. A field blank is prepared in the field by filling a clean container with deionized water and appropriate preservative, if any, using the same techniques as the specific sampling activity being undertaken. A field equipment blank is a sample of analyte-free media that has been used to rinse common sampling equipment to detect potential bias introduced through the usage of the sampling apparatus.

Laboratory bias is determined through the analysis of laboratory control samples and limit of quantitation check samples prepared in the sample matrix (e.g., laboratory grade water, sand, commercially available tissue) using verified and known amounts of all target analytes and by then calculating percent recovery of those analytes. Results are compared to control limits and used during evaluation of analytical performance.

Laboratory assessment of analytical bias will be the responsibility of the individual laboratories per their SOPs and analytical methodologies.

Representativeness

For groundwater sampling, data representativeness expresses the degree to which data accurately and precise represents a characteristic of a sample population, parameter variations at a sampling point, a process condition, or an environmental condition. The sampling network has been designed to provide data representative of site conditions. For results of individual groundwater sample analysis, representativeness will be estimated by ion and mass balances. Ion balances with ±10% error or less will be considered valid. A mass balance assessment will be used in cases where the ion balance is greater than ±10% to help determine the source of error. For a sample and its duplicate, if the relative percent difference is greater than 10%, the sample may be considered non-representative.

Completeness

For groundwater sampling, data completeness is a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under normal conditions. It is anticipated that data completeness of 90% for groundwater sampling will be acceptable to meet monitoring goals. For direct pressure and temperature measurements, it is expected that data will be recorded no less than 90% of the time.

Comparability

Data comparability expresses the confidence with which one data set can be compared to another. The data sets to be generated by this project will be very comparable to future data sets because of the use of standard methods and the level of QA/QC effort. If historical groundwater quality data becomes available from other sources, their applicability to the project and level of quality will be assessed prior to use with data gathered on this project.

6.3.2 Direct Monitoring

GCS will track the pressure influence within the Injection Zone by utilizing the injection wells themselves and an in-zone monitoring well, MS IZ 1. The wells will be equipped with a downhole electronic pressure and temperature gauge on the tubing with an electric line connected to a transmitter at the wellhead. The gauge will continuously collect pressure readings (every 10 seconds) that can be read on the transmitter at the surface. Then the pressure data will be transmitted to a computerized control system that records, monitors, and controls injection processes.

The baseline in-situ reservoir pressure within the Injection Zone will be established after the completion of MS CCS 1 and MS CCS 2. Once operation commences, reservoir pressure data will be recorded from MS IZ 1 monthly and from MS CCS 1 and MS CCS 2 during scheduled shut-ins and compared to the modeled predictions. If pressure increases greater than predicted by the current AoR model, or increases at a greater rate, it may indicate that the AoR model needs to be revised. In this case, GCS will consult with the LDENR Commissioner to determine whether an AoR revaluation is necessary.

The specification sheet of an example downhole pressure and temperature gauge is provided in Appendix D-II of the Testing and Monitoring Plan. The specifications for the example gauge are summarized in Table D.I.6.2-2 and will be updated with the final values upon completion of detailed design.

6.3.3 Indirect Monitoring

Four indirect monitoring methods will be used to define the extent of the modeled plume for Project Minerva:

- Walk-Away Vertical Seismic Profile (WA VSP)
- 3D Distributed Acoustic Sensing Vertical Seismic Profile (3D DAS VSP)
- 2D Seismic Survey
- Pulsed neutron logging (PNL)

Seismic Surveys

A seismic baseline will be acquired before injection begins using WA VSP, 3D DAS VSP, and 2D seismic surveys simultaneously.

WA VSP and 3D DAS VSP utilize distributed acoustic sensing (DAS) technology installed along MS CCS 1 to receive seismic signals emitted from a source. 2D seismic surveys will utilize geophones to receive seismic signals emitted from a source. Sources include

downhole air guns, vibrators, or non-disruptive explosives. The specifications for the proposed DAS and geophone technologies used to conduct indirect plume monitoring are provided in Appendix D-VIII.

Once injection commences, WA VSP will serve as the primary plume monitoring method for approximately 10 years (or until its coverage is surpassed by the leading edge of the plume) and will be supplemented, as necessary, with 3D DAS VSP and/or 2D seismic surveys. After approximately 10 years, 2D seismic surveys will serve as the primary plume monitoring method. These surveys will be conducted along seismic lines or grids described in Section 9.2 (Indirect Monitoring) in the Testing and Monitoring Plan (Attachment D).

Appendix D-IX of the Testing and Monitoring Plan (Attachment D) defines the feasibility of implementing a VSP at Project Minerva.

Logging

GCS will utilize Pulsed Neutron logging (PNL) to monitor CO_2 saturation changes in the Injection Zone. GSC will conduct time-lapsed PN logging at MS IZ 1 to monitor for CO_2 saturation in the perforated interval. Since MS IZ 1 is located outside of the modeled stabilized CO_2 plume, the CO_2 residual gas saturation should not exceed 20%. The specifications for PNL used in the in-zone monitoring well to conduct indirect plume monitoring are provided in Appendix D-VIII.

PN logging of MS IZ 1 will be conducted annually for the first four years, and every two years thereafter through the operational life of Project Minerva. GCS will continue monitoring MS IZ 1 during the post injection surveillance period defined in the Post Injection Site Care and Closure Plan (Attachment F).

Data comparability expresses the confidence with which one data set can be compared to another. The data sets to be generated by this project will be very comparable to future data sets because of the use of standard methods and the level of QA/QC effort. Direct pressure, temperature, and logging measurements will be directly comparable to previously obtained data.

7 SPECIALIZED TRAINING AND CERTIFICATIONS

7.1 SPECIALIZED TRAINING AND CERTIFICATIONS

The geophysical survey equipment and wireline logging tools will be operated by trained, qualified, and certified personnel, according to the service company which provides the equipment. The collected data will be processed and analyzed according to industry standards. No specialized certifications are required for personnel conducting groundwater sampling, but field sampling will be conducted by trained personnel. Groundwater sampling will be conducted by personnel trained to understand and follow the specific project sampling procedures outlined in this appendix. Upon request GCS will provide the agency with all laboratory SOPs developed for the specific parameter using the appropriate standard method. Each laboratory technician conducting the analysis on the samples will be trained in the SOP developed for each standard method. GCS will include the

technician's training certification with the annual report.

7.2 TRAINING PROVIDER AND RESPONSIBILITY

Training for personnel will be provided by GCS or by the subcontractor responsible for the data collection activity.

8 DOCUMENTATION AND RECORDS

8.1 REPORT FORMAT AND PACKAGE INFORMATION

Reporting will follow the outlines contained within the Testing and Monitoring Plan and will contain all required project data, as specified by the UIC Class VI permit. Data will be provided in electronic or other formats as required by the Commissioner.

8.2 OTHER PROJECT DOCUMENTS, RECORDS, AND ELECTRONIC FILES

Other documents, records, and electronic files such as, well logs, test results, or other data will be provided as required by the Commissioner.

8.3 DATA STORAGE AND DURATION

All data and project records will be stored electronically on secure servers and will have routine backups. Reporting will be retained for 10 years after it is collected pursuant to LAC 43:XVII§3625.A.1-9.

8.4 QASP DISTRIBUTION RESPONSIBILITY

GCS will be responsible for ensuring that all those on the distribution list will receive the most current copy of the approved QASP.

9 DATA GENERATION AND ACQUISITION

This plan will establish a standardized program for data acquisition and validation methods. The program will verify that collected data are reasonable, processed and analyzed correctly, and free of errors. Peer reviews or third-party consultants may serve as a QC mechanism. Issues identified during a peer review will be addressed and corrected by the data owner. Errors identified in the data via validation will be corrected, and affected users will be notified. Corrective actions will be taken to ensure the impact of any error is fully addressed.

9.1 SAMPLING PROCESS DESIGN

9.1.1 CO_2 Stream Monitoring

Design Strategy

GCS will analyze the CO_2 stream during the operation period to determine its chemical and physical characteristics and to meet the requirements of LAC 43:XVII§3625.A.1. See Section 3.0 (Carbon Dioxide Stream Analysis) of the Testing and Monitoring Plan (Attachment D) for further information.

Type and Number of Samples/Test Runs

CO_2 gas stream composition will be analyzed on a quarterly basis to ensure it meets the system specification. This is outlined in Attachment D (Testing and Monitoring Plan).

Site/Sampling Locations

CO_2 stream sampling will be conducted at a sample port along the comingled inlet pipework to the Minerva Facility.

Sampling Site Contingency

All infrastructure required to implement CO_2 stream analysis and corrosion monitoring will be located on GCS-controlled land, with guaranteed site access. All related facilities will be constructed in a way that allows access during inclement weather.

Activity Schedule

Analyzed on a quarterly basis.

9.1.2 Corrosion Monitoring

Design Strategy

To meet the requirements of LAC 43:XVII§3625.A.3, GCS will monitor well materials during the operation period for loss of mass, thickness, cracking, pitting, and other signs of corrosion to ensure that the well components meet the minimum standards for material strength and performance.

GCS will monitor corrosion by analyzing a corrosion loop. Final technology selection will be completed after detailed engineering.

Type and Number of Samples/Test Runs

The corrosion loop will be analyzed on a quarterly basis starting during the first month of the calendar quarter (i.e., March, June, September, December) following commencement of injection. This is outlined in Attachment D (Testing and Monitoring Plan).

Site/Sampling Locations

The corrosion loop will be installed in parallel with the pipe at the surface facilities that feed CO_2 injectate to the injection wells. The corrosion loop will be located downstream of all process compression/dehydration/pumping equipment and designed to monitor each injection well independently.

Sampling Site Contingency

All infrastructure required to implement CO_2 stream analysis and corrosion monitoring will be located on GCS-controlled land, with guaranteed site access. All related facilities will be constructed in a way that allows access during inclement weather.

Activity Schedule

Corrosion coupons will be analyzed quarterly.

9.1.3 Above Confining Zone Groundwater Monitoring

This section is focused on fluid sampling above the confining zone. GCS proposes to drill and complete two ACZ monitoring wells, MS USDW 1 and MS USDW 2, in the first confined sand below the lowermost USDW (Attachment D – Testing and Monitoring Plan). The following section does not address monitoring methods that do not gather physical samples (e.g., logging, seismic monitoring, and pressure/temperature monitoring).

Fluid sampling is planned to include an extensive set of chemical parameters to establish aqueous geochemical reference data. Parameters will include selected constituents that: (1) have primary and secondary EPA drinking water maximum contaminant levels, (2) are the most responsive to interaction with CO_2 or brine, (3) are needed for quality control, and (4) may be needed for geochemical modeling. The full set of parameters is given in Table D.I.6.3-1.

A baseline will be established via testing every 4 months for at least 12 months before the commencement of injection. Following commencement of injection monitoring, monitoring scope may shift to a subset of indicator parameters that are (1) the most responsive to interaction with CO_2 or brine and (2) are needed for quality control. Implementation of a reduced set of parameters would be done in consultation with the LDENR. Isotopic analyses will be performed on baseline samples to the degree that the information helps verify a condition or establish an understanding of non-project related variations. For non-baseline samples, isotopic analyses may be reduced in all monitoring wells if a review of the historical project results or other data determines that further sampling for isotopes is unneeded. During any period where a reduced set of analytes is used, if statistically significant trends are observed that are the result of unintended CO_2 or brine migration, the analytical list would be expanded to the full set of monitoring parameters.

Fluid samples will be analyzed using a laboratory meeting the requirements under the LELAP. All other samples will be analyzed by the operator or a third-party laboratory. Dissolved CO_2 will be analyzed by methods consistent with Test Method B of ASTM D 513-06, “Standard Test Methods for Total and Dissolved Carbon Dioxide in Water” or equivalent. Isotopic analysis will be conducted using established methods.

Design Strategy

GCS will conduct groundwater quality and geochemical monitoring in the first confined sand unit below the lowermost USDW (Evangeline aquifer). This will be achieved using two groundwater monitoring wells, Minerva South USDW Well No. 001 (MS USDW 1), located at the Minerva South Well Pad, and Minerva South USDW Well No. 002 (MS USDW 2) located at the well pad of the in-zone monitoring well (see Figure D.I.5.2-1).

Mixing models will be constructed to identify trends and constituents that would be diagnostic of either brine or CO_2 leakage into USDW. The baseline monitoring will be completed prior to year three and will be used to 1) modify and optimize the groundwater program to the parameters that are most diagnostic and 2) design a response program such that if an incident of leakage of CO_2 or brine into groundwater occurs, GCS will be ready to assess, report and remediate the area impacted by the leakage.

Throughout the life of the project (injection and post-injection period) monitoring of the ACZ interval will be used for early leakage detection. Fluid sampling in combination with pressure monitoring will be used to determine if leakage is occurring via any pathways through the Confining Zone (faults or artificial penetrations).

Following the three-year characterization and response-planning period, the sampling frequency at the two water wells will be decreased annually during the remaining injection period and every five years during the post-injection monitoring period. This data will be used to demonstrate non-endangerment of the USDW or initiate an immediate project shutdown if a leak of CO_2 is detected.

The number and location of USDW monitoring wells will be adapted to ensure effective monitoring and non-endangerment of the USDW over the injection and post-injection monitoring period. Monitoring data collected during the injection period will be used to history-match the simulation model and define if and where any additional USDW water wells are required.

Type and Number of Samples/Test Runs

Table D.I.6.3-1 shows the planned monitoring methods, logic behind selecting locations, and frequencies for ACZ groundwater quality and geochemical monitoring in the Evangeline Aquifer. Seasonal sampling including field parameters, dissolved and free gases, and water level monitoring will be conducted four times a year for 3 years for characterization, after which sampling frequency will be decreased and targeted to chemical species that are indicative of leakage. Refer to Section 6 (Above Confining Zone Monitoring) of the Testing and Monitoring Plan (Attachment D) for further details.

Site/Sampling Locations

Summarized in Figure D.I.5.2-1.

Sampling Site Contingency

For above zone water sampling, all wells will be drilled on GCS-controlled land and have been assessed for wellsite access. The preliminary locations of these wells are mapped in Figure D.I.5.2-1. No problems of site inaccessibility are anticipated. If inclement weather makes site access difficult, sampling schedules will be reviewed, and alternative dates may be selected that would still meet permit-related conditions.

Activity Schedule

Sampled quarterly for 3 years to detect seasonal variations and to establish a baseline, then annually, or if an incident occurs.

Continuous temperature monitoring along with the proposed injection wells will be used to detect anomalies attributed to leakage from the Injection Zone. If leakage detected, additional sampling will be added as necessary to ensure non-endangerment of the USDW.

Critical/Informational Data

During ACZ water sampling and analytical efforts, detailed field and laboratory

documentation will be taken. Documentation will be recorded in field and laboratory forms and notebooks. Critical information will include time and date of activity, person/s performing activity, location of activity (wellfield sampling) or instrument (lab analysis), field or laboratory instrument calibration data, field parameter values. For laboratory analyses, much of the critical data is generated during the analysis and provided to end users in digital and printed formats. Noncritical data may include appearance and odor of the sample, problems with well or sampling equipment, and weather conditions.

Sources of Variability

Potential sources of variability related to monitoring activities include:

- Natural variation in fluid quality, formation pressure and temperature and seismic activity,
- Variation in fluid quality, formation pressure and temperature, and seismic activity due to project operations,
- Changes in recharge due to rainfall, drought, and snowfall,
- Changes in instrument calibration during sampling or analytical activity,
- Different staff collecting or analyzing samples,
- Differences in environmental conditions during field sampling activities,
- Changes in analytical data quality during life of project, and
- Data entry errors related to maintaining project database.

Activities to eliminate, reduce, or reconcile variability related to monitoring activities include:

- Collecting baseline data to observe and document natural variation in monitoring parameters,
- Evaluating data in a timely manner after collecting to observe anomalies in data that can be addressed by being resampled or reanalyzed,
- Conducting statistical analysis of monitoring data to determine whether variability in a data set is the result of project activities or natural variation,
- Maintaining weather-related data using on-site weather monitoring data or data collected near project site (such as from local airports),
- Checking instrument calibration before, during and after sampling or sample analysis,
- Thoroughly training staff,
- Conducting laboratory quality assurance checks using third party reference materials, and/or blind, and/or replicate sample checks, and
- Developing a systematic review process of data that can include sample-specific

data quality checks (i.e., cation/anion balance for aqueous samples).

9.2 SAMPLING METHODS

Logging, geophysical monitoring, and pressure/temperature monitoring do not apply to this section and are omitted. The field sampling protocols defined herein are in line with the EPA 540-R-20-005, Sampler's Guide: Contract Laboratory Program Guidance for Field Samplers (Attachment D.I-1).

9.2.1 Sampling Standard Operating Procedures (SOPs)

Groundwater samples will be collected primarily using a low-flow sampling method consistent with (ASTM International, 2005c). If a flow-through cell is not used, field parameters will be measured in grab samples. Groundwater wells will be purged to ensure samples are representative of formation water quality. Static water levels in each well will be determined using an electronic water level indicator before any purging or sampling activities begin. Dedicated pumps (e.g., bladder pumps) will be installed in each monitoring well to minimize potential cross contamination between wells. Groundwater pH, temperature, specific conductance, and dissolved oxygen will be monitored in the field using portable probes and a flow-through cell consistent with standard methods (APHA, 2005) given sufficient flow rates and volumes. Field chemistry probes will be calibrated at the beginning of each sampling day according to equipment manufacturer procedures using standard reference solutions. When a flow-through cell is used, field parameters will be continuously monitored and will be considered stable when three successive measurements made three minutes apart fall within the stabilization parameters.

After field parameters have stabilized, samples will be collected. Samples requiring filtration will be filtered through 0.45 µm flow-through filter cartridges as appropriate and consistent with . Prior to sample collection, filters will be purged with a minimum of 100 mL of well water (or more if required by the filter manufacturer). For alkalinity and total CO_2 samples, efforts will be made to minimize exposure to the atmosphere during filtration, collection in sample containers, and analysis.

9.2.2 In-situ Monitoring

Groundwater chemistry monitoring parameters can be found in Table D.I.6.3-1.

9.2.3 Continuous Monitoring

GCS will install and use continuous recording devices to monitor, as required per LAC 43:XVII§3621.A.6.a.i-iv, §3627.A.2.a-b, and §3625.A.2, the CO_2 mass delivered to Project Minerva at the transfer point, the volume and temperature of CO_2 allocated to each well, the pressure at the wellhead, the pressure on the injection tubing, the pressure at the wellhead on the annulus between the tubing and the long string casing, and the annulus fluid volume added. Injection pressure and temperature will be continuously measured at the surface via real-time pressure/temperature (P/T) instruments installed at the primary meter station and at the allocation meters at each wellhead. Pressure will be measured using electronic pressure gauges with analog data transmitters, installed at the primary meter station and at each allocation meter/wellhead. Temperature will be measured similarly using electronic

temperature sensors with data transmitters installed in close proximity to the pressure gauges both at the primary meter station and at each allocation station.

9.2.4 Sample Homogenization, Composition, Filtration

Mixing of the sample is necessary to create a representative sample media. It is extremely important that solid samples be mixed as thoroughly as possible to ensure that the sample is as representative as possible of the sample location. The mixing technique will depend on the physical characteristics of the solid material (e.g., particle size, moisture content, etc.). The mixing container will be large enough to hold the sample volume and accommodate the procedures without spilling. Both the mixing container (generally a bowl or tray) and the mixing implement will be properly decontaminated before use. Samples will be homogenized according to procedures listed in the project-specific sampling and analysis plan (EPA 540-R-20-005 (Attachment D.I-1) or equivalent).

9.2.5 Sample Containers and Volumes

The analytical protocol(s) to be used for sample analysis often requires the use of a particular type of sample container. The type of container also may depend on the sample matrix and analysis. The use of borosilicate glass containers, which are inert to most materials, is recommended. Conventional polyethylene is recommended when sampling for metals because of the lower cost and absorption rate of metal ions. Using the wrong container may result in breakage, gathering of an insufficient volume needed to perform sample analysis, or interference of the container material with the analysis. Therefore, the correct sample containers for each sampling event will be identified using Sample Container Type Specifications as outlined in EPA 540-R-20-005 (Attachment D.I-1) or equivalent.

9.2.6 Sample Preservation

Degradation of some contaminants may occur naturally. Some water samples will require chemical preservation for certain analytes before the samples are shipped to the laboratory. Any visible reaction between the sample and added chemical preservative will be noted in the field record. Water samples will be preserved and immediately cooled to 4°C (±2°C) upon collection, and samples should remain cooled until the time of analysis (the water samples will not be frozen). Preservation techniques will align with EPA 540-R-20-005 (Attachment D.I-1) or equivalent.

9.2.7 Cleaning/Decontamination of Sampling Equipment

Dedicated pumps will be installed in each ACZ monitoring well to minimize potential cross contamination between wells. GCS is still in the process of determining the types of pumps that will be utilized. These pumps will remain in each well throughout the project period except for maintenance. Prior to installation, the pumps will be cleaned on the outside with a non-phosphate detergent. Pumps will be rinsed a minimum of three times with deionized water and a minimum of 1 liter of deionized water will be pumped through pump and sample tubing. Individual clean pumps and tubing will be placed in plastic garbage bags for transport to the field for installation. All field glassware (pipets, beakers, filter holders, etc.)

are cleaned with tap water to remove any loose dirt, washed in a dilute nitric acid solution, and rinsed three times with deionized water before use.

9.2.8 Support Facilities

For sampling of groundwater, the following are required: air compressor, vacuum pump, generator, multi-electrode water quality sonde, analytical meters (pH, specific conductance, etc.). Field activities are usually completed in field vehicles and portable laboratory trailers located on site. Field gauges will be removed from the injection well and verification well utilizing existing standard industry tools and equipment. Deployment and retrieval of verification well gauges will be done using procedures and equipment recommended by the vendor, subcontractor, or is standard per industry practice. Sampling tubing, connectors and valves required to sample the CO_2 gas stream will be supplied by the analytical lab providing the sampling containers. Sampling will occur within the existing CO_2 compression building. Similarly, corrosion coupons will be removed from the CO_2 injection line within the existing CO_2 compression building.

9.2.9 Corrective Action, Personnel, and Documentation

Field staff will be responsible for properly testing equipment and performing corrective actions on broken or malfunctioning field equipment. If corrective action cannot be taken in the field, then the equipment will be returned to the manufacturer for repair or replaced. Significant corrective actions affecting analytical results will be documented in field notes. Sample holding times will be consistent with those described in (APHA, 2005; ASTM International, 2005a; Wood, 1976). Once the samples are analyzed, the laboratory will be responsible for disposing of the containers and residues properly.

9.3 SAMPLING HANDLING AND CUSTODY

9.3.1 Maximum Hold Time/Time Before Retrieval

Daily shipment of samples to laboratories will be the preferred method whenever possible. If samples cannot be shipped daily, they will be properly preserved and maintained to meet ASTM Method D6517-00 (or equivalent) temperatures, holding times, and custody requirements (ASTM International, 2005a; ASTM International, 2005b; ASTM International, 2005c). The technical holding times are the maximum time allowed between a sample collection and the completion of the sample extraction and/or analysis. In contrast, contractual holding times are the maximum lengths of time that a laboratory can hold the sample prior to extraction and/or analysis. Samples will be processed, packaged, and shipped to the contracted laboratory, following standard sample handling and chain-of-custody guidance (EPA 540-R-20-005 (Attachment D.I-1), or equivalent). Once the samples are analyzed, the laboratory will be responsible for disposing of the containers and residues properly.

9.3.2 Sample Transportation

Samples will be shipped to a LELAP accredited laboratory with chain-of-custody documentation. Shipping and handling shall be in accordance with laboratory recommendations for the specific analytical method. The contracted laboratory will employ

EPA-approved or other industry standard analytical methods and have a documented QA/QC program in place.

9.3.3 Sampling Documentation

Collected samples will be properly documented for analysis in order to uniquely identify each sample and ensure adequate chain-of-custody procedures. If sampling on privately owned property, the property owner will be provided with a receipt for samples collected and removed from that owner's property. These types of documentation help ensure proper sample identification and provide additional chain-of-custody records.

9.3.4 Sample Identification

The use of a sample label, sample tag, or field operations will record documenting information such as daily activities, equipment and materials used, personnel involved, site security, etc. may also be utilized.

9.3.5 Sample Chain-of-Custody Record

For groundwater samples, chain-of-custody will be documented using a standardized form. A typical form is shown in Figure D.I.9.3-1, and it or a similar form will be used to document all groundwater sampling. Copies of the form will be provided to the person/lab receiving the samples as well as the person/lab transferring the samples. These forms will be retained and archived to allow simplified tracking of sample status. The chain-of -custody form and record keeping are the responsibility of groundwater sampling personnel.

9.4 ANALYTICAL METHODS

9.4.1 Analytical SOPs

Analytical SOPs are referenced in Table D.I.9.4-1. Other laboratory specific SOPs utilized by the laboratory will be determined after a contract laboratory has been selected. Upon request GCS will provide the agency with all laboratory SOPs developed for the specific parameter using the appropriate standard method. Each laboratory technician conducting the analysis on the samples will be trained in the standard methods for each SOP developed.

9.4.2 Equipment/Instrumentation Needed

Equipment and instrumentation are specified in the individual analytical methods referenced in Table D.I.9.4-1.

9.4.3 Method Performance Criteria

Non-standard method performance criteria are not anticipated for this project.

9.4.4 Analytical Failure

Each laboratory conducting analyses in Table D.I.9.4-1 will be responsible for analytical failure according to their SOPs.

9.4.5 Sample Disposal

Each laboratory conducting the analyses will be responsible for appropriate sample disposal.

9.4.6 Laboratory Turnaround

Laboratory turnaround will vary by laboratory, but generally turnaround of verified analytical results within one month will be suitable for project needs.

9.4.7 Method Validation for Nonstandard Methods

Nonstandard methods are not anticipated for this project. If nonstandard methods are needed or proposed in the future, the LDENR will be consulted on additional appropriate actions to be taken.

9.5 QUALITY CONTROL

As part of the quality control (QC) process during testing and surveillance, most of the samples collected and the data gathered will be analyzed, processed, validated, or witnessed by third parties independent of the operations staff. For specialized data such as seismicity and DTS, Project Minerva will have additional support from the providers of the selected technologies in quality control, verification of the data, and system calibration.

QC of the sampling and results will follow the protocols established in the standard analytical method used for testing. The operator reserves the right to audit the laboratory procedures and protocols to validate that the methods are being followed and the results are accurate.

9.5.1 QC activities

9.5.1.1 Blanks

Trip blanks for QA/QC purposes will be collected and used to validate test results and ensure samples are free of contamination.

9.5.1.2 Duplicates

For each water sampling round, a duplicate water sample is collected from a well from a rotating schedule, yet to be determined. Duplicate samples are collected from the same source immediately after the original sample in different sample containers and processed as all other samples. Duplicate samples are used to assess sample heterogeneity and analytical precision.

9.5.2 Exceeding Control Limits

If the sample analytical results exceed control limits (i.e., ion balances > ±10%), further examination of the analytical results will be done by evaluating the ratio of the measured total dissolved solids (TDS) to the calculated TDS (i.e., mass balance) per American Public Health Association (APHA) method (or equivalent) (APHA, 2005). The method indicates which ion analyses should be considered suspect based on the mass balance ratio. Suspect ion analyses are then reviewed in the context of historical data and interlaboratory results, if available. Suspect ion analyses are then brought to the attention of the analytical

laboratory for confirmation and/or reanalysis. The ion balance is recalculated, and if the error is still not resolved, suspect data are identified and may be given less importance in data interpretations.

9.5.3 Calculating Applicable QC Statistics

9.5.3.1 Charge Balance

Titration methods will be based on standard protocols from Standard Methods 2320B-2011. Laboratories shall have standard operating procedures for the analytical methods performed.

The analytical results are evaluated to determine correctness of analyses based on anion-cation charge balance calculation. Because all potable waters are electrically neutral, the chemical analyses should yield equally negative and positive ionic activity. The anion-cation charge balance will be calculated using the formula:

$$\%\, difference = 100 \frac{\sum cations - \sum anions}{\sum cations + \sum anions} \quad \text{Equation -1}$$

where the sums of the ions are represented in milliequivalents (meq) per liter and the criteria for acceptable charge balance is ±10%.

9.5.3.2 Mass Balance

The ratio of the measured TDS to the calculated TDS will be calculated in instances where the charge balance acceptance criteria are exceeded using the formula:

$$1.0 < \frac{measured\ TDS}{calculated\ TDS} < 1.2 \quad \text{Equation 16.4.2-1}$$

Equation 3.4.2-2 is an example equation, where the anticipated values are between 1.0 and 1.2.

9.5.3.3 Outliers

Outliers may result from random variation or may indicate something scientifically interesting. In any event, we typically do not want to simply delete the outlying observation. However, if the data contains significant outliers, we may need to consider the use of robust statistical techniques, which may include: (1) Probability Plots, (2) Box Plots, (3) Dixon's test, and (4) Rosner's test. The EPA-1989 outlier test may also be used as another screening tool to identify potential outliers.

9.6 INSTRUMENT/EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE

Logging-tool equipment will be maintained as per the wireline industry best practices.

For groundwater sampling, field equipment will be maintained, factory serviced, and factory calibrated per manufacturer's recommendations. Spare parts that may be needed during sampling will be included in supplies on-hand during field sampling.

For all laboratory equipment, testing, inspection and maintenance will be the responsibility of the analytical laboratory per standard practice, method-specific protocol, or LELAP

requirement.

9.7 INSTRUMENT/EQUIPMENT CALIBRATION AND FREQUENCY

All field equipment will be visually inspected and tested prior to use. Spare instruments, batteries, etc., will be stored in the field support trailer.

Pressure gauges used to conduct fall-off tests will be calibrated in accordance with the manufacturers' recommendations. In lieu of removing the injection tubing to recalibrate the downhole pressure gauges, their accuracy will be demonstrated by comparison with a second pressure gauge with current certified calibration, which will be lowered into the well to the same depth as the permanent downhole gauge. Calibration curves for the downhole gauge, based on annual calibration checks using the second calibration gauge, can be used for the fall-off test. These calibration curves (showing all historic pressure deviations) will accompany the fall-off test data.

During laboratory analysis, the calibration, testing, maintenance, and inspection of laboratory equipment shall be the responsibility of the contracted analytical laboratory. Equipment calibration shall be in accordance with the approved method-specific protocols for the analytical method and the laboratory's QA program. The laboratory QA program shall be reviewed and approved prior to the contract award.

9.7.1 Calibration and Frequency of Calibration

Equipment used for field sampling will be calibrated, serviced, and maintained according to the manufacturer's recommendations.

9.7.2 Calibration Methodology

Equipment used for field sampling will be calibrated, serviced, and maintained according to the manufacturer's recommendations.

9.7.3 Calibration Resolution and Documentation

Equipment used for field sampling will be calibrated, serviced, and maintained according to the manufacturer's recommendations.

9.8 INSPECTION/ACCEPTANCE FOR SUPPLIES AND CONSUMABLES

Both field operations and laboratory operations need supplies and consumables. The focus of this section is the management of laboratory and field sampling supplies and consumables. For information on the actual field/lab supplies and consumables needed for any specific method, see the reference method in 40 CFR Part 50, the general guidance methods and technical assistance documents on AMTIC and the manufacturer's operations manuals. From this information, monitoring organizations, as part of the QASP requirements, will develop specific SOPs for its monitoring and analytical methods. One section of the SOPs requires a listing of the acceptable supplies and consumables for the method. Pollutant parameters are measured using electronic (e.g., continuous emission monitors, FTIRs, etc.), wet chemical techniques, or physical methods. Chemical analysis always involves the use of consumable supplies that must be replaced on a schedule

consistent with their stability and with the rate at which samples are taken. Currently used physical methods require adequate supplies of chemicals for operation for three months so that the supplier can comply with the delivery schedules. In some cases, analytical reagents for specific air contaminants deteriorate rapidly and need protective storage. The following information may be helpful when considering the use of these consumable items. Much of the information presented below is derived from the document *Quality Assurance Principles for Analytical Laboratories* from (Garfield, Klesta, & Hirsch, 2000).

9.9 NONDIRECT MEASUREMENTS

9.9.1 Data Sources

For time lapse seismic surveys, repeatability is paramount for accurate differential comparison. Therefore, to ensure survey quality, the locations for the shots and acquisition methodology of sequential surveys will be consistent. Once these surveys are conducted, they will be compared to a baseline survey to track and monitor plume development.

9.9.2 Relevance to Project

Time lapse seismic surveys will be used to track changes in the CO_2 plume in the subsurface. Processing and comparing subsequent surveys to a baseline will allow project managers to monitor plume growth, as well as to ensure that the plume does not move outside of the intended storage reservoir. Numerical modeling will be used to predict the CO_2 plume growth and migration over time by combining the processed seismic data with the existing geologic model. In-zone pressure monitoring data will be used in numerical modeling to predict plume and pressure front behavior and confirm the plume stage within the AoR.

9.9.3 Acceptance Criteria

Following standard industry practices will ensure that the gathered seismic data will be used for accurate modeling and monitoring. Similar ground conditions shot points located within tolerable limits, functional geophones, and similar seismic input signal will be used from survey to survey to ensure repeatability. When processing seismic data, several QA checks will be done in accordance with industry standards including reformatting to structured files, geometry application, amplitude compensation, predictive deconvolution, elevation statics correction, root mean square (RMS) amplitude gain, velocity analysis every 1.24 miles (2 km), normal moveout (NMO) correction application using picked velocities, common midpoint (CMP) stacking, random noise attenuation, and instantaneous gain.

9.9.4 Resources/Facilities Needed

GCS will subcontract all necessary resources and facilities for the seismic monitoring, in-zone pressure monitoring, and groundwater sampling.

9.9.5 Validity Limits and Operating Conditions

For seismic surveys and numerical modeling, intraorganizational checks between trained and experienced personnel will ensure that all surveys and numerical modeling are conducted conforming to standard industry practices.

9.10 DATA MANAGEMENT

9.10.1 Data Management Scheme

GCS will be responsible for ensuring that all electronic and hard copy data, forms and logs are accounted for, properly completed and stored in project files.

Documentation will be sufficient that a third party can reproduce the results from the raw data. This requires that all necessary information will be documented, and that the documents are organized and maintained such that the information may be practically retrieved and made use of.

Documentation will consist of instrument and other digital files, hard copy field log sheets, calibration certificates, laboratory reports, etc. All of these documents will ultimately be stored in electronic form; however, hard copy log sheets will be retained on file. An electronic data package will be compiled containing project documentation sufficient to allow a third party to reproduce the results and organized in such a manner that this may be done without undue effort.

9.10.2 Recordkeeping and Tracking Practices

All reports, submittals and notifications will be submitted to both the EPA and the LDENR. All records will be retained by GCS throughout the life of the project and for 10 years following site closure. Data on the nature and composition of all injected fluids collected will be retained as well for 10 years after site closure. The records will be delivered to the UIC Program Director after the retention period if required by the director. Monitoring data as described in the Testing and Monitoring Plan will be retained for 10 years after it is collected. Well plugging reports, post-injection site care data and the site closure report itself will be retained for 10 years following site closure.

9.10.3 Data Handling Equipment/Procedures

GCS will be responsible for ensuring that all electronic and hard copy data, forms and logs are accounted for, properly completed and stored in project files. All data and project records will be stored electronically on secure servers and will have routine backups. Reporting will comply with Class VI UIC requirements.

9.10.4 Responsibility

GCS will be responsible for ensuring that all electronic and hard copy data, forms and logs are accounted for, properly completed and stored in project files. All data and project records will be stored electronically on secure servers and will have routine backups. Reporting will comply with Class VI UIC requirements.

9.10.5 Data Archival and Retrieval

GCS will be responsible for ensuring that all electronic and hard copy data, forms and logs are accounted for, properly completed and stored in project files. All data and project records will be stored electronically on secure servers and will have routine backups. Reporting will comply with Class VI UIC requirements. All reports, submittals and notifications will be retained by GCS throughout the life of the project and for ten (10) years

following site closure. Data on the nature and composition of all injected fluids collected will be retained as well for ten (10) years after site closure. The records will be delivered to the UIC Program Director after the retention period if required by the director. Monitoring data as described in the Testing and Monitoring Plan will be retained for 10 years after it is collected. Well plugging reports, post-injection site care data and the site closure report itself will be retained for ten (10) years following site closure.

9.10.6 Hardware and Software Configurations

All GCS and vendor hardware and software configurations will be appropriately interfaced.

9.10.7 Checklists and Forms

Checklists and forms will be procured and generated as necessary.

10 ASSESSMENT AND OVERSIGHT

10.1 ACTIVITIES TO BE CONDUCTED

Assessments of each of the QASP elements:

- CO_2 stream analysis surface sampling
- Continuous recording of operational parameters
- Corrosion monitoring
- External MIT
- ACZ monitoring
- Pressure fall-off testing
- In zone CO_2 plume and pressure from tracking

After completion of sample analysis, results will be reviewed for QC criteria as noted in Section 1.4 (Quality Objectives and Criteria). If the data quality fails to meet criteria set in Section 1.4, samples will be reanalyzed, if still within holding time criteria. If outside of holding time criteria, additional samples may be collected, or sample results may be excluded from data evaluations and interpretations. Evaluation for data consistency will be performed according to procedures described in *Statistical Analysis of Groundwater Monitoring Data at RCRA Facilities* a USEPA Unified Document (USEPA, 2009).

10.2 RESPONSIBILITY FOR CONDUCTING ASSESSMENTS

GCS or its designated subcontractors gathering data will be responsible for conducting their internal assessments. All stop work orders will be handled internally within individual organizations.

10.3 ASSESSMENT REPORTING

GCS will coordinate reporting of assessments.

10.4 CORRECTIVE ACTION

All corrective action affecting only an individual organization's data collection responsibility

should be addressed, verified, and documented by the individual project managers and communicated to the other project managers as necessary. Corrective actions affecting multiple organizations should be addressed by all members of the project leadership and communicated to other members on the distribution list for the QASP. Assessments may require integration of information from multiple monitoring sources across organizations (operational, in-zone monitoring, above-zone monitoring) to determine whether correction actions are required and/or the most cost-efficient and effective action to implement. GCS will coordinate multi-organization assessments and corrective actions as warranted.

10.5 REPORTS TO MANAGEMENT

10.5.1 QA Status Reports

QA status reports should not be needed. If any testing or monitoring techniques are changed, the QASP will be reviewed and updated as appropriate in consultation with LDENR. Revised QASPs will be distributed by GCS to the full distribution list at the beginning of this appendix.

11 DATA VALIDATION AND USABILITY

11.1 DATA REVIEW, VERIFICATION, AND VALIDATION

11.1.1 Criteria for Accepting, Rejecting, or Qualifying Data

As part of the QC process, during testing and surveillance, most of the samples collected and data gathered will be analyzed, processed, validated, or witnessed by third parties independently, outside of the operator staff.

For specialized data such as seismicity, the project will have additional support from the provider of the selected technologies to perform QC and verification of the data as well as calibration of the systems as needed.

All LDENR-reportable data will be formatted appropriately and uploaded to the GSDT at the required frequency.

11.2 VERIFICATION AND VALIDATION METHODS

11.2.1 Data Verification and Validation Processes

The project will establish a standardized program to validate the data and acquisition methods. The program will verify that collected data are reasonable, were processed and analyzed correctly, and are free of errors. Peer reviews or third-party consultant will be used as a QC mechanism to verify the information.

11.2.2 Data Verification and Validation Responsibility

If an error is identified in data under validation, in addition to correcting the error, affected work products and management decisions will be identified, affected users will be notified, and corrective actions will be coordinated to an extent of the error's impact is fully addressed.

11.2.3 Issue Resolution Process and Responsibility

GCS or its designee will overview the data handling, management, and assessment process. Contractors involved in these processes will consult with GCS to determine actions required to resolve issues.

11.2.4 Checklist, Forms, and Calculations

Checklists and forms will be developed specifically to meet permit requirements. These will be detailed as site-specific design advances.

11.3 RECONCILIATION WITH USER REQUIREMENTS

11.3.1 Evaluation of Data Uncertainty

Statistical software will be used to determine data consistency using methods consistent with the Commissioner's guidance.

11.3.2 Data Limitations Reporting

The organization-level project managers will be responsible for ensuring that data developed by their respective organizations is presented with the appropriate data-use limitations. GCS will use the current operating procedure on the use, sharing, and presentation of results and/or data for Project Minerva. This procedure has been developed to ensure quality, internal consistency and facilitate tracking and record keeping of data end users and associated publications.

12 REFERENCES

APHA. (2005). *Standard Methods for the Examination of Water and Wastewater, Volume 21* (Vol. 21). (A. D. Eaton, & M. A. Franson, Eds.) American Public Health Association.

ASTM International. (2005a). Standard Guide for Field Preservation of Groundwater Samples: Designation: D6517 – 00 (Reapproved 2005). *ASTM Standard Methods*, 5.

ASTM International. (2005b). Standard Guide for Field Filtration of Ground-Water Samples: Designation: D 6564 – 00 (Reapproved 2005). *ASTM Standard Methods*, 6.

ASTM International. (2005c). Standard Guide for Purging Methods for Wells Used for Ground-Water Quality Invesetigations: Designation: D 6452 – 99 (Reapproved 2005). *ASTM Standard Methods*, 6.

Garfield, F. M., Klesta, E., & Hirsch, J. (2000). *Quality Assurance Principles for Analytical Laboratories* (3rd Edition ed.). Gaithersburg: AOAC International; Association of Official Analytical Chemist.

USEPA. (2009). *Unified Documnet: Statistical Analysis of Groundwater Monitoring Data at RCRA Facilities*. US Environmental Protection Agency.

Wood, W. W. (1976). Chapter D2: Guidelines for Collection and Field Analysis of Ground-Water Samples for Selected Unstable Constituents. In U. S. Survey, *Techniques of Water-Resources Investigations of the United States Geological Survey* (p. 24). Alexandria: United States Geological Survey.

Table D.I.2-1 QASP Distribution List

Title	Name	Phone	Email	Address
Chief Executive Officer	David Cook	1 (713) 419-6808	dcook@gcscarbon.com	5599 San Felipe Dr., Suite 1450 Houston, Texas 77056
Field Manager	David Richard			2417 Shell Beach Dr. Lake Charles, LA 70601
Site Manager	TBD	TBD	TBD	2417 Shell Beach Dr. Lake Charles, LA 70601
24-7 Control Room Operations	TBD	TBD	TBD	5599 San Felipe Dr., Suite 1450 Houston, Texas 77056
Safety Manager	MaryEllen Roberson	1 (713) 997-3296	mroberson@gcscarbon.com	5599 San Felipe Dr., Suite 1450 Houston, Texas 77056
Audit/Risk Manager	TBD	TBD	TBD	5599 San Felipe Dr., Suite 1450 Houston, Texas 77056

Table D.I.5.1-1 Summary of Testing and Monitoring

Activity	Location(s)	Method	Analytical Technique	Lab/ Custody	Purpose
CO_2 STREAM MONITORING					
Carbon Dioxide Stream Analysis	Comingled inlet pipework to Minerva facility	Sampling Port	Standard gas analysis at lab	Provided by lab	Monitor injectate for accounting
INJECTION AND INTEGRITY MONITORING					
Injection Pressure	Distributed meters at MS CCS 1 & 2	Electronic volumetric flow meter with P/T measurement	Direct measurement	NA	Pressure of CO2 stream
Injection Rate	Distributed meters at MS CCS 1 & 2	Electronic volumetric flow meter with P/T measurement	Direct measurement	N/A	Rate of injection
Injection Volume/Mass	Distributed meters at MS CCS 1 & 2	Electronic volumetric flow meter with pressure & temperature (P/T) measurement	Volume measurements	NA	Volume of CO2 distributed to each well; calculation of mass
Annular Pressure/Temperature	Downhole gauge with transmitter at each wellhead	Electronic P/T gauge in the annulus	Direct measurement	NA	Pressure maintenance in tubing-casing annulus
Annular Volume	Downhole gauge with transmitter at each wellhead	Electronic P/T gauge in the annulus	Calculated measurement	NA	Pressure maintenance in tubing-casing annulus
Downhole Pressure/ Temperature	Downhole gauge with transmitter at each wellhead of MS CCS 1 & 2, MS IZ 1	Downhole P/T gauge run on tubing	Direct measurement	NA	P/T downhole near injection zone
Wellhead Pressure	Pressure gauge on the tubing and annulus of MS CCS 1 & 2, MS IZ 1	Surface pressure gauge at the wellhead	Direct measurement	NA	Wellhead pressure safety
External Mechanical Integrity	MS CCS 1 & 2	DTS fiber optic cables installed in the wellbore annulus	Direct Continuous monitoring	NA	Detect fluid or pressure migration from the injection zone and leakage in casing
Wireline Logging	Conducted at each injection well	Injection profile log	Provided by vendor	NA	Demonstrate External Mechanical Integrity
Corrosion Monitoring	Corrosion Loop	Non-Destructive Testing: Ultrasonic and Radiography equipment	ASTM G1-03	NA	Monitor system integrity
SUBSURFACE MONITORING					
Above Confining Zone Monitoring	MS USDW 1 & 2	Water sampling	Laboratory analysis	Provided by lab	Document groundwater chemistry
	MS CCS 1 & 2	DTS fiber optic cables installed along the long-string	Direct measurement	NA	Monitor for fluid migration from the injection zone
Pressure Fall-Off Testing	MS CCS 1 & 2	EPA Region 6 UIC Pressure Falloff Testing Guideline-Third Revision (August 8, 2002)	Direct Measurement	NA	Assess injectivity
Pressure Front Tracking (Direct)	MS IZ 1, MS CCS 1 & 2	Downhole P/T gauge run on tubing	Direct measurement	NA	In-zone pressure tracking
CO_2 Plume Tracking (Indirect)	MS CCS 1	Walk Away VSP	VSP	NA	Defining the edge of the plume and ensuring it remains within the permitted AoR.
	MS CCS 1	Vertical seismic profile (VSP)	VSP	NA	
	MS CCS 1	2D Seismic Lines	2D Seismic	NA	
	MS IZ 1	PN logs	Wireline logging	NA	Monitor carbon dioxide saturation

Table D.I.6-1 Instrumentation Summary

Instrument Type	Monitoring Location	Monitoring Target	Data Collection Location(s)	Explanation
CO_2 STREAM MONITORING				
Sampling port	CO_2 Stream	Monitor injectate for accounting	Collection at sampling port; analysis via lab	Identify unacceptable impurities, CO_2 accounting
INJECTION AND INTEGRITY MONITORING				
Electronic volumetric flow meter with pressure & temperature (P/T) measurement	MS CCS 1 & 2	Monitor injectate for each well	Computerized control system	Injection volume, rate, and pressure (with mass and density calculations) for surveillance and input to models
Wellhead pressure gauge on tubing	MS CCS 1 & 2, MS IZ 1	Pressure in injection well tubing	Manual reading of gauge	Safety and compliance
Wellhead pressure gauge on annulus	MS CCS 1 & 2, MS IZ 1	Pressure in annulus	Manual reading of gauge	Safety and compliance
Annulus pressure & temperature gauge	MS CCS 1 & 2	Pressure and temperature in tubing-casing annulus	Computerized control system	Monitoring, safety, and compliance
Downhole pressure & temperature gauge	MS CCS 1 & 2	Pressure and temperature in injection interval	Computerized control system	Monitoring, safety, and compliance
DTS fiber optic cable	MS CCS 1 & 2	Surface to Total Depth	Computerized control system	Well integrity
Ultrasonic and Radiography equipment	MS CCS 1 & 2	Corrosion of materials of construction	Loop	Safety and compliance, Well Integrity
SUBSURFACE MONITORING				
Dedicated pump & groundwater level monitoring system	MS USDW 1 & 2	Evangeline Aquifer	Environmental data storage	Installed system or relocated to each of the wells
Downhole pressure & temperature gauge	MS IZ 1	Injection Zone – Pressure	Computerized control system	Track lateral pressure front
Pulse Neutron logging	MS IZ 1	Injection Zone - Plume	Wireline Log	Monitor carbon dioxide saturation within the injection zone
DAS fiber optic cable	MS CCS 1	Surface to Total Depth	Dedicated server, designed as part of VSP array	CO2 Plume Tracking
Walk-Away VSP	MS CCS 1	Injection Zone – Plume	DAS in MS CCS 1 Sources along seismic lines in star pattern	Define the edge of the plume and ensure it remains within the permitted AoR.
3D DAS VSP	MS CCS 1	Injection Zone - Plume	DAS in MS CCS 1 Sources along 500 x 500 foot Grid	Define the edge of the plume and ensure it remains within the permitted AoR.
2D Seismic Lines	Surface	Injection Zone - Plume	Sources and receivers along seismic lines in star pattern	Define the edge of the plume and ensure it remains within the permitted AoR.

Table D.I.6.1-1 Summary of Analytical Parameters for CO_2 Stream

Parameter	Analytical Methods[1]
Carbon Dioxide (CO_2)	ISBT[2] 2.0 Caustic absorption Zahm-Nagel ALI method SAM 4.1 subtraction method (GC/DID) GC/TCD
Water (H_2O)	ISBT 3.0
Oxygen (O_2)	ISBT 4.0 (GC/DID) GC/TCD
Nitrogen (N_2)	ISBT 4.0 (GC/DID) GC/TCD
Hydrogen Sulfide (H_2S)	ISBT 14.0 (GC/SCD)
Argon (Ar)	ISBT 4.0 (GC/DID) GC/TCD
Sulfur dioxide (SO_2)	ISBT 14.0 (GC/SCD)
Methane (CH_4)	ISBT 10.1 (GC/FID)
Total hydrocarbons (C_2H_6, C_3H_8+)	ISBT 10.1 (GC/FID)
Hydrogen (H_2)	ISBT 4.0 (GC/DID) GC/TCD
Carbon Monoxide (CO)	ISBT 5.0 (Colorimetric) ISBT 4.0(GC/DID)
Nitrogen Oxides (any (NO_x)	ISBT 7.0 Colorimetric
δC_{13} and C_{14}	Isotope ratio mass spectrometry Measured once and when a significant new source is added. Used for attribution during monitoring.

Note

[1] An equivalent method may be employed with the prior approval of the Commissioner

[2] International Society of Beverage Technologists (ISBT) Carbon Dioxide Guidelines MBAA TQ vol. 39, no. 1, 2002, pp. 32-35 as cited in ISO/TR 27921:2020(en). Carbon dioxide capture, transportation, and geological storage —Cross Cutting Issues —CO_2 stream composition

Table D.I.6.2-1 Summary of Operational Parameters Measured with Continuous Recording Devices

Parameter	Device(s)	Location
Annular Pressure and Temperature	Electronic pressure & temperature (P/T) gauge in the annulus with transmitter at the surface	Downhole gauge with transmitter at the wellhead
Annular Fluid Volume	Fluid level gauge	Annular Fluid Reservoir
	Electronic P/T gauge in the annulus with	Downhole gauge with transmitter at the wellhead
Injection Pressure	Electronic volumetric flow meter with pressure measurement	Meter with transmitter at wellhead
Injection Rate	Electronic volumetric flow meter with rate measurement	Meter with transmitter at wellhead
Injection Volume/Mass	Electronic volumetric flow meter with P/T measurement	Meter with transmitter at wellhead
Downhole Pressure	Downhole P/T gauge run on tubing	Downhole gauge with transmitter at the wellhead
Downhole Temperature	Downhole P/T gauge run on tubing	Downhole gauge with transmitter at the wellhead

Table D.I.6.2-2 Continuous Recording Device Specifications

Parameter	Value
VOLUMETRIC FLOW METER	
Calibrated working flow rate range	1 - 33 ft/s (0.3 -10 m/s)
Initial flow rate accuracy	< ± 0.15% of measured volume
Flow rate resolution	0.01 m/s
Flow rate zero stability	< 0.003 ft/s (0.0009 m/s)
DOWNHOLE PRESSURE AND TEMPERATURE GUAGE (Reservoir & Annulus)	
Calibrated working pressure range	200 - 10,000 psi
Pressure accuracy	±0.015% 1.5 psi (at full scale)
Pressure resolution	0.0001
Pressure drift stability	±0.02% full scale, 2.0 psi/year
Calibrated working temperature range	77 to 302°F (25 to 302°C)
Temperature accuracy	0.27°F (0.15°C)
Temperature resolution	0.0001°F
Temperature drift stability	0.018°F (<0.01°C) per year
Temperature rating	-99.4 to 302°F (-73 to 302°C)
Instrument calibration frequency	Annual
WELLHEAD PRESSURE GUAGE (Tubing & Annulus)	
Calibrated working pressure range	10-20,000 psi
Pressure accuracy	0.05% full scale accuracy
Pressure resolution	0.001
Pressure drift stability	Limit of 5% full scale for pressure stability

Table D.I.6.2-3 Representative Logging and Testing Tool Specifications

Fiber Optic Cable	Maximum acquisition rate	Minimum spatial resolution	Minimum sampling interval	Sensing /Operating temperature range	Maximum distance range
MECHANICAL INTEGRITY MONITORING					
Distributed Temperature Sensing (DTS)	3.3 sec	~3.3 ft (1.0 m)	1.08 ft (.33 m)	0 – 573°F/300°C	~12.5 mi (20+ km)
PLUME MONITORING					
Distributed Acoustic Sensing (DAS)	10 kHz	~4.9 ft (1.5 m)	1.08 ft (.33 m)	0°C to +40°C / 32°F to +104°F	12 – 50 (EBF) mi (20 – 80 (EBF) km)

Log	Logging speed	Vertical resolution	Investigation	Temperature rating	Pressure rating
MECHANICAL INTEGRITY LOGGING					
Noise Log	0.5 sec	16 bit	10 ms	350°F	20,000 psi
Oxygen Activation Log	2 ft/min	Point of Measurement	12 in	350°F	20,000 psi
Casing Inspection Log	160 ft/min	Point of Measurement	5.5-9.425 in	350°F	15,000 psi
Cement Bond Log	Up to 9 m/min (29.52 ft/min)	3 in	Casing & Cement Interface	350°F for 30 min	20,000 psi
Casing Collar Locator Log	45m/min	Point of Measurement	20 in	400°F for 30 min	20,000 psi
PLUME MONITORING					
Pulsed Neutron Capture Log	2 ft/min	Point of Measurement	12 in	350°F	20,000 psi

Table D.I.6.3-1 Groundwater Analysis Parameters and the Analytical Methods

Parameters	Analytical Methods[1]
FIELD MEASUREMENTS	
Dissolved Oxygen (field)	APHA 2005
Specific Conductance (field)	APHA 2510
Temperature (field)	Thermocouple
Water Density (field)	Oscillating body method
Static Water Level	Sounder
pH (field)	EPA 150.1
LABORATORY ANALYSIS	
Cations (Al, Ba, Mn, As, Cd, Cr, Cu, Pb, Sb, Se, Zn, Tl)	SW846 6010/6020
Cations (Ca, Fe, K, Mg, Na, Si)	SW846 6010/6020
Anions (Br, Cl, F, NO3, SO4)	SM 300
Dissolved CO_2	Coulometric titration, ASTM D513-11
Isotopes δ13C of DIC	Isotope ratio mass spectrometry
Dissolved CH_4 (Methane)	SM 6211 B or 6211 C
Hydrogen Sulfide (H_2S)	ISBT 14.0 (GC/SCD)
Total Dissolved Solids (TDS)	Gravimetry; Method 2540 C
Oxygen, Argon, and Hydrogen	ISBT 4.0 (GC/DID) GC/TCD
Alkalinity	Method 2320B

Notes:

[1] Or similar method

- The listed analytical methods may be revised based on input from the laboratories selected to do the work, and field instruments used during a given event.
- Field duplicates to be collected at rate of 10% (1 for every 10 samples) or 1 per event.
- MS/MSDs to be collected at a rate of 5% (1 for every 20 samples) or 1 per event.
- Field blanks and equipment blanks will be collected as per Section 6.3 of the QASP, Appendix I.

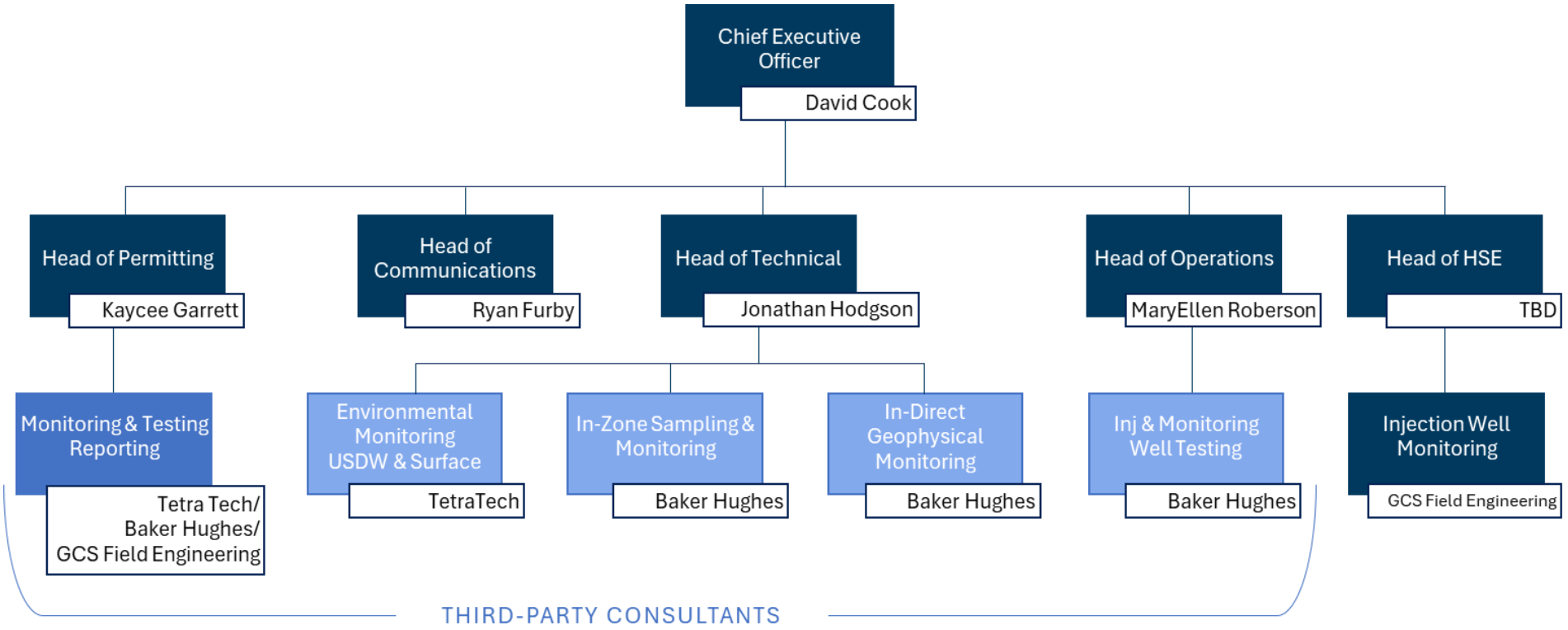
Table D.I.9.4-1 Summary of Analytical Standard Operating Procedures (SOPs)

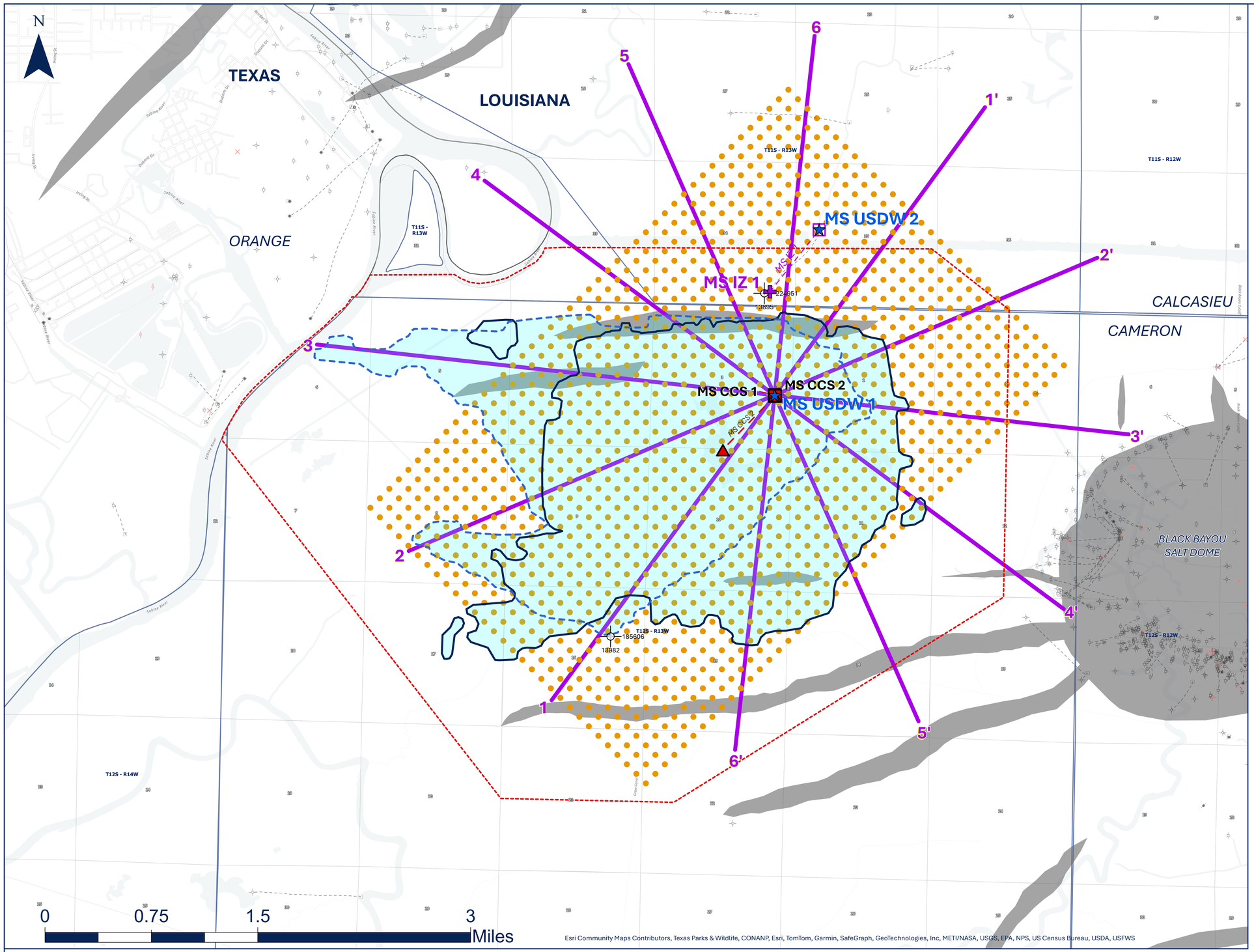
Parameters	Analytical Methods[1]	Detection Limit/ Range	Typical Precisions	QC Requirements
Cations Al, Ba, Mn, As, Cd, Cr, Cu, Pb, Sb Se, & Tl	ICP-MS, EPA Method 6020	0.001 to 0.1 mg/L (analyte, dilution and matrix dependent)	±15%	Daily calibration; blanks, duplicates and matrix spikes at 10% or greater frequency
Cations Ca, Fe, K, Mg, Na, & Si	ICP-OES, EPA Method 6010B	0.005 to 0.5 mg/L (analyte, dilution and matrix dependent)	±15%	Daily calibration; blanks, duplicates and matrix spikes at 10% or greater frequency
Anions Br, Cl, F, NO3, & SO4	Ion Chromatography, EPA Method 300.0	0.02 to 0.13 mg/L (analyte, dilution and matrix dependent)	±15%	Daily calibration; blanks and duplicates at 10% or greater frequency
Dissolved CO_2	Coulometric titration, ASTM D513-11	25 mg/L	±15%	Duplicate measurement; standards at 10% or greater frequency
Isotopes δ13C of DIC	Isotope ratio mass spectrometry[2]	12.2 mg/L HCO3 for δ13C	±0.15‰ for δ13C	10% duplicates; 4 standards/batch
TDS	Gravimetry, APHA 2540C	12 mg/L	±10%	Balance calibration, duplicate analysis
Water Density (field)	Oscillating body method	0.0000 to 2.0000	±0.0002 g/mL	Duplicate measurements
Alkalinity	APHA 2320B	4 mg/L	±3 mg/L	Duplicate analysis
pH (field)	EPA 150.1	2 to 12 pH units	±0.2 pH unit	User calibration per manufacturer recommendation
Specific conductance (field)	APHA 2510	0 to 200 mS/cm	±1% of reading	User calibration per manufacturer recommendation
Temperature (field)	Thermocouple	-5 to 50°C	±0.2°C	Factory calibration

Notes

1 An equivalent method may be employed with the prior approval of the Commissioner.
2 Gas evolution technique by Atekwana and Krishnamurthy (1998), with modifications made by Hackley et al. (2007)

Figure D.I.3.4 GCS Organizational Chart





Gulf Coast Sequestration, LLC (G1037)
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(713) 997-3145 | www.gcscarbon.com

FIGURE D.I.5.2-1
Monitoring Network for Project Minerva

MAP LEGEND

- 3D VSP Sources
- Injector Bottom Hole
- Injector Well Pad
- Injector Schematic Well Trajectory
- Walk-away VSP / 2D Seismic Line
- Magnetic Survey Flight Area
- Max Extent of Stable CO2 Plume
- Max Extent of Pressure Front
- Delineated Area of Review
- Top Upper Frio Faults
- PLSS Townships & Ranges
- PLSS Sections
- SONRIS Parishes

Monitoring Wells

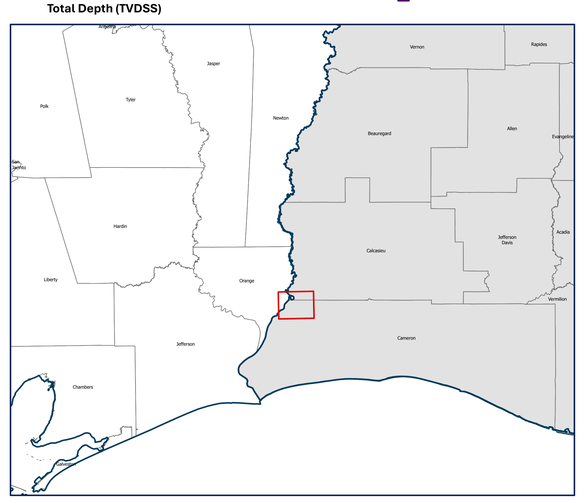
- In-Zone Bottom Location
- In-Zone Surface Location
- USDW Monitoring Well (Vertical)
- In-Zone Well Trajectory

Well Status

- Other
- Active - Producing
- Drilled
- Dry & Plugged
- Inactive
- Orphan
- Permit Expired
- Plugged & Abandoned
- Reverted
- Shut In
- Temporarily Abandoned
- Unable to Locate
- Surface Location
- Well Trajectory

Well Labels

Serial Number
Total Depth (TVDSS)
Monitoring Well Name



MAP DETAILS

PREPARED BY	R WENCEL	**DATE**	11/4/2024 4:14 PM
APPROVED BY	K GARRETT	**DATE**	11/XX/2024
MAP SCALE	1:16,000		
PAGE SIZE	A0 (46.81 W X 33.11 H)		

SPATIAL REFERENCE

PCS	NAD 1927 State Plane Louisiana South (FIPS 1702)
GCS	GCS North American 1927
DATUM	North American 1927
PROJECTION	Lambert Conformal Conic

PROJECT MINERVA DETAILS

WELLS	Minerva South CCS Well Nos. 001 and 002
LOCATION	Cameron Parish, Louisiana
EPA PROJECT ID	R06-LA-0002
LDENR APPL NOS	45031 & 45032

LOUISIANA BOARD OF PROFESSIONAL GEOSCIENTISTS
KAYCEE GARRETT
1325
Est. 2011

Chain of Custody Record

TAT(Check One): ☒ Standard ☐ 24hr ☐ 48hr ☐ 72hr ☐ Other____
(Additional charges may apply for rush TAT. If not specified, standard TAT will apply)

Order ID:_____

Client Name: _____

Address: _____ Phone: _____

_____ Email: _____

Contact Name: _____ P.O. Info:_____

Project Name: _____

Address: _____

_____

Regulatory ID (SDWA/Permit #): _____

Comments:

STL Sample Number	Sample Description / Site ID:	Date Sampled	Time Sampled	Samplers Initials	Test(s) Requested:	Bottle Quantity	See Codes Below				Comments / Field Data:
							Matrix	Sample Type	Bottle Type	Preservative	

Relinquished By:	Count	Date: / Time:	Temp ºC: _____
Received By:		Date: / Time:	Temp ºC: _____ Acceptable: Y / N
Relinquished By:		Date: / Time:	Temp ºC: _____ Acceptable: Y / N
Received in Lab By:		Date: / Time:	Temp ºC: _____ Acceptable: Y / N

Sample Conditions

- Submitted with COC? Y / N
- Number of containers match number on COC? Y / N
- All containers in tact? Y / N
- Tests within holding times? Y / N
- 40 mL VOA vials free of headspace? Y / N

Matrix Key

- NPW = Non-Potable Water
- Solid = Raw Sludge, Dewatered sludge, soil, etc. (reported as mg/kg)
- PW = Potable Water (not for SDWA compliance)
- SDWA = Safe Drinking Water Act Potable Sample

Sample Type Key

- G = Grab
- C = Composite
- 8HC = 8 Hr. Composite
- 24HC = 24 Hr. Composite

SDWA Sample Types

- D=Distribution
- E=Entry Point
- R=Raw
- C=Check
- S=Special
- M=Maximum Residence

Bottle Type Key

- P = Plastic
- G = Glass
- GA = Glass Amber
- VOA = 40mL G or GA
- PP = Sterile Polypropylene
- PS = Sterile Polystyrene
- HDPE = High Density Polyethylene
- O = Other

Preservative Key

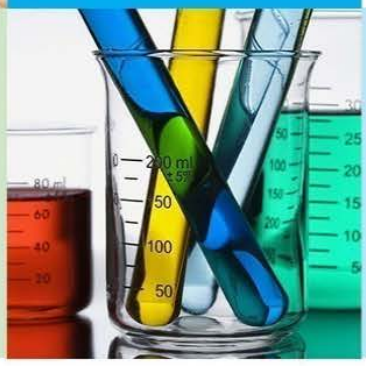
- A = Ascorbic Acid
- C = HCl
- H = HNO_3
- N = Sodium Thiosulfate
- OH = NaOH
- S = H_2SO_4
- O = Other
- NA = None Required

United States Environmental Protection Agency

Sampler's Guide



Contract Laboratory Program Guidance for Field Samplers



Office of Superfund Remediation and Technology Innovation (OSRTI)
United States Environmental Protection Agency (EPA)
Washington, DC 20460

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LIST OF ACRONYMS

ARO	Aroclor
ASB	Analytical Services Branch
BTEX	Benzene, Toluene, Ethylbenzene, and Xylene
CBC	Chlorinated Biphenyl Congener
CDD	Chlorinated Dibenzo-*p*-dioxins
CDF	Chlorinated Dibenzofurans
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CLP	Contract Laboratory Program
CLPSS	Contract Laboratory Program Support System
COC	Chain of Custody
CRQL	Contract Required Quantitation Limit
CVAA	Cold Vapor Atomic Absorption
CWA	Clean Water Act
DMC	Deuterated Monitoring Compound
DOT	Department of Transportation
DQO	Data Quality Objectives
EPA	United States Environmental Protection Agency
ERT	Environmental Response Team (EPA)
ET	Eastern Time
FSP	Field Sampling Plan
GC/MS	Gas Chromatograph/Mass Spectrometer or Gas Chromatography/Mass Spectrometry
GPS	Global Positioning System
HAZWOPER	Hazardous Waste Operations and Emergency Response
HASP	Health and Safety Plan
HCN	Hydrocyanic Acid
HTML	Hypertext Markup Language
IATA	International Air Transport Association
IC	Ion Chromatography
ICP-AES	Inductively Coupled Plasma - Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma - Mass Spectrometry
MA	Modified Analysis
MS	Matrix Spike
MSD	Matrix Spike Duplicate
NIOSH	National Institute for Occupational Safety and Health
NPL	National Priorities List
OLEM	Office of Land and Emergency Management
OSC	On-scene/On-site Coordinator
OSHA	Occupational Safety and Health Administration
OSRTI	Office of Superfund Remediation and Technology Innovation
PCBs	Polychlorinated Biphenyls
PE	Performance Evaluation
PHMSA	Pipeline and Hazardous Materials Safety Administration
ppb	Parts-Per-Billion (e.g., µg/L or µg/kg)
PPE	Personal Protective Equipment

ppm	Parts-Per-Million (e.g., mg/L or mg/kg)
ppt	Parts-Per-Trillion (e.g., ng/L or ng/kg)
PRP	Potentially Responsible Party
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl Chloride
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QATS	Quality Assurance Technical Support
QC	Quality Control
RPM	Remedial Project Manager
RSCC	Regional Sample Control Coordinator
SAM	Site Assessment Manager
SAP	Sampling and Analysis Plan
SARA	Superfund Amendments and Reauthorization Act
SDG	Sample Delivery Group
SIM	Selected Ion Monitoring
SMC	System Monitoring Compound
SMO	Sample Management Office
SOP	Standard Operating Procedure
SOW	Statement of Work
SPLP	Synthetic Precipitation Leaching Procedure
SPP	Site Project Plan
SVOA	Semivolatile Organic Analyte
TCLP	Toxicity Characteristic Leaching Procedure
TIFSD	Technology Innovation and Field Services Division
TOC	Total Organic Carbon
TR/COC	Traffic Report/Chain of Custody
UN	United Nations
UPS	United Parcel Service
USCG	United States Coast Guard
USDA	United States Department of Agriculture
VOA	Volatile Organic Analyte
XML	eXtensible Markup Language

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1.0 INTRODUCTION



The *Contract Laboratory Program Guidance for Field Samplers* (also referred to as the *Sampler's Guide*) describes the organizational roles and responsibilities for those who plan and conduct environmental sample collection for analysis through the U.S. Environmental Protection Agency (EPA) Contract Laboratory Program (CLP).

The following lists the sections of this Guide:

- Section 1, *Introduction*, introduces the structure and purpose of this document.
- Section 2, *General Sampling Information*, describes the general activities associated with environmental sampling.
- Section 3, *CLP Statements of Work*, describes the Statements of Work (SOWs) that define the requirements for CLP sampling.
- Section 4, *CLP Sample Documentation*, lists the types of documentation used to track CLP samples.
- Section 5, *The Scribe Documentation Software Tool*, provides information about Scribe, a software tool used to create sample documentation.
- Section 6, *CLP Sample Containers*, describes the types of containers required for CLP samples.
- Section 7, *CLP Sample Collection*, describes the process by which CLP samples are collected.
- Section 8, *CLP Sample Transportation and Shipping*, outlines the requirements for the packing and shipping of CLP samples.
- Section 9, *Sampler Resources*, provides links to additional information for sampling organizations.

The following lists the appendices of this Guide:

- Appendix A, *Functions within a Sampling Project*, describes the functions within a sampling project which are taken from the Quality Assurance Project Plan (QAPP) requirements.
- Appendix B, *General CLP Sample Collection Guidelines for Aqueous VOA Samples*, provides guidelines for Volatile Organic Analyte (VOA) water samples.
- Appendix C, *CLP Sample Collection Guidelines for Soil VOA Samples by SW-846 Method 5035A, TCLP Extraction by EPA SW-846 Method 1311, and SPLP Extraction by EPA SW-846 Method 1312* provides guidelines for VOA soil samples.
- Appendix D, *CLP Sample Collection Requirements by Analysis Type*, contains the sample collection requirements by SOW.
- Appendix E, *Sampling Techniques and Considerations*, recommends sampling techniques.
- Appendix F, *International Shipping*, contains information regarding shipping samples to laboratories outside the United States.
- Appendix G, *Sampling Checklists*, contains checklists used to help the sampler ensure that all necessary steps are completed.
- Appendix H, *Glossary*, provides definitions for terms used in this document.



If the field sampling team is planning to use the CLP, they should use this Guide to develop the Site Project Plan (SPP), QAPP, and Field Sampling Plan (FSP) documents.

1.1 Overview of the CLP

The CLP is a national network of EPA personnel, commercial laboratories, and support contractors whose fundamental mission is to provide environmental sample collection and analysis under the Superfund program. The Superfund program was established under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) of 1980 and presently exists under the Superfund Amendments and Reauthorization Act (SARA) of 1986. The CLP is directed by the EPA Analytical Services Branch (ASB) of the Technology Innovation and Field Services Division (TIFSD) within the Office of Superfund Remediation and Technology Innovation (OSRTI) under the Office of Land and Emergency Management (OLEM).

The primary responsibility of the CLP is to provide analytical data of known and documented quality to CLP customers through its routine and modified chemical analytical services. The CLP provides a framework that allows data to be produced in a cost-effective and efficient manner. In addition, the CLP has established strict Quality Control (QC) procedures and detailed documentation requirements to ensure the consistent quality of the data. Current CLP data users include the EPA Regions, other EPA Headquarters programs, State and Tribal governments, and other Federal agencies.

1.1.1 Key Participants within the CLP Sampling Process

In coordinating Superfund sampling efforts, ASB is supported by the Sample Management Office (SMO) contractor, Regional Sample Control Coordinators (RSCCs), Site Assessment Managers (SAMs), On-scene/On-site Coordinators (OSCs), and Remedial Project Managers (RPMs). Samplers may work directly with the RSCC, and/or an OSC from the Site Support Personnel during a sampling event. Refer to Table 1-1 for a description of the functions performed by key participants (functions may vary by Region).

Table 1-1. Participants in the CLP Sampling Process

Participants	Responsibilities
Analytical Services Branch (ASB)	ASB directs the CLP within the TIFSD of the OSRTI in the OLEM. ASB's responsibilities include: • Development of the SOWs that define required analytical methods (including QC, detection/quantitation limits, and holding times) for the analytical services procured under the CLP • Development and implementation of policies and budgets for Superfund analytical operations • Development of information management policies and products for analytical data • Management of SMO and Quality Assurance Technical Support (QATS) contracts • National administration, evaluation, and management of the CLP • Direction of CLP Quality Assurance (QA) activities in coordination with overall OLEM QA activities To obtain the most current ASB contact list, refer to the following website: https://www.epa.gov/clp/forms/contact-us-about-superfund-analytical-services-or-contract-laboratory-program#tab-2
CLP Sample Management Office (SMO)	The contractor-operated SMO provides management, operations, and administrative support to the CLP. SMO receives Regional analytical requests, coordinates and schedules sample analyses, and tracks sample shipments. SMO also receives and checks data for completeness and compliance, processes laboratory invoices, and maintains a repository of sampling records and program data.

Table 1-1. (Continued) Participants in the CLP Sampling Process

Participants	Responsibilities
CLP Contract Laboratories	The contractor-operated laboratories within the CLP provide analytical services for the separation, detection, and quantitation of the CLP's target analytes.
Environmental Response Team (ERT)	The ERT is responsible for the development, implementation, and management of the Scribe software system. In addition, the ERT oversees the development of Scribe training webinars and on-site training.
Environmental Response Team (ERT) Support Contractors	The ERT Support Contractors provide technical and administrative support for the development, implementation, and management of the Scribe software system. In addition, the ERT Support Contractors support the development of Scribe training webinars and on-site training.
Regional Sample Control Coordinator (RSCC)	In most Regions, the RSCC coordinates sampling efforts and serves as the central point-of-contact for sampling questions and problems. The RSCC works with SMO to request analytical services and receive laboratory assignments. In addition, the RSCC's activities may include informing SMO of sample shipment, cancellations, special instructions, and sampling issues. To obtain the most current RSCC contact list, refer to the following website: https://www.epa.gov/clp/forms/contact-us-about-superfund-analytical-services-or-contract-laboratory-program#tab-3
Site Support Personnel	The Site Support Personnel consist of the EPA personnel and contractors responsible for developing the QAPP and Sampling Plan for the sampling event at the site. It includes such personnel as the sampling team, QA personnel, OSC, SAM, and RPM. In most Regions, the Site Support Personnel develop Standard Operating Procedures (SOPs) for field sampling and related procedures, and assist sampling teams in adhering to the SOPs. The sampling team determines what type(s) of CLP services will be required for a particular sampling event. The Site Support Personnel review Sampling and Analysis Plans (SAPs) prepared by sampling teams and oversee sampling teams in the field. In addition, the state or territorial environmental protection agency for the location of the site provides support for the sampling event.

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2.0 GENERAL SAMPLING INFORMATION

2.1 Goals of the Sampling Process



Once the U.S. Environmental Protection Agency (EPA) has determined that physical, chemical, and/or biological testing of a site is necessary, samples of material from the site area must be collected. The type of material that must be collected and the analytical method to be used depends upon the physical location of the site, detection level(s), site history (previous sampling), and known or unknown conditions and contaminants. Samples should be collected according to the approved project and site-specific Quality Assurance Project Plan (QAPP) and Sampling and Analysis Plan (SAP). This Guide does not define specific sampling procedures, as these depend upon individual site conditions, Regional requirements, and acceptance and performance criteria. Since Regions may have their own specific requirements for individual sampling programs, they are responsible for generating Region-specific sampling Standard Operating Procedures (SOPs). EPA personnel shall also follow the procedures in CIO 2105-P-02.0 (*EPA QA Field Activities Procedures*).

2.1.1 Follow the Required Sampling Procedures

It is imperative that samplers be aware of the minimum Contract Laboratory Program (CLP) and Regional requirements that directly impact and define how a sampling event will take place. It is important to note that the procedures and guidelines set forth in this document are considered minimum CLP requirements.

The purpose of sampling is to collect representative portions from a suspected contaminated site. Sample collection is critical to determining the presence, type, concentration, and extent of environmental contamination by hazardous substances; thus, it is a crucial part of every sampling and environmental testing effort. Sampling procedures must be consistently followed to mitigate risk of error and the expense of resampling.

Failure to follow proper sampling and shipping procedures could result in samples that are contaminated, in broken containers, mislabeled, lost during shipping, compromised due to improper preservation, or unusable because of a missed holding time. If procedures are inconsistently or improperly followed, any resultant analytical data may be inaccurate and may not be legally defensible.

2.1.2 Maintain Chain of Custody of Samples and Data

Acquiring accurate and legally defensible data is the CLP's primary objective; therefore, the samplers must collect samples according to strict sampling procedures, plans, and guidelines. The Chain of Custody (COC) Records must be generated and the sample COC maintained. EPA and

many other Federal agencies use data resulting from analytical testing of samples for the following activities:

- Site Characterization
- Source Evaluation
- Identification of Potentially Responsible Parties (PRPs)
- Remedial Design
- Assessment of response and remedial priorities
- Remedial Action
- Remedial Investigation/Feasibility Studies
- Assessment of risk to human health and the environment
- Determination of appropriate cleanup actions
- Determination of cleanup achievements

2.1.3 Field Operation Records

Samplers must maintain complete, accurate, and legible field operations records as they perform a sampling activity. The following records are included:

- Field logbooks
- Corrective Action reports
- Sampling trip reports
- Supplemental standardized forms
- Records such as maps or photographs that document each step of each activity performed in the field

Samplers must refer to their project plans for Region-specific field operations record requirements. These records are an important tool because they are considered a part of the official project file when legal issues arise.

2.1.4 Comply with Safety Procedures

Care must be taken to maintain the safety of personnel collecting and handling CLP samples. If sampling requires digging in soil, utility lines (gas, oil, cable, etc.) must be marked to prevent injury or utility outage. Samples must be handled, packed, and shipped in accordance with all applicable Federal [Occupational Safety and Health Administration (OSHA) and Department of Transportation (DOT)] regulations for hazardous materials. Refer to the Health and Safety Plan (HASP) for detailed site safety requirements.

2.2 Obtain Municipal Permits, Licenses, and Clearances

Before starting a sampling event, samplers must obtain the proper municipal permits, access to the property, and any government clearances, if required. Samplers must also contact any appropriate utility companies to ascertain where any underground pipes, cables, etc., may be located.

2.2.1 Request Access to County, State, Tribal, Military, and/or Federal Property

Proper access to perform sampling activities is important not only for legal reasons, but also to eliminate delays in work and possible refusal to allow sampling to take place. It is crucial that the appropriate permits, licenses, and clearances be secured to obtain access for sampling activities that will be performed on County, State, Tribal, military, and/or Federal property. The sampler must contact the appropriate government offices or personnel well in advance to determine what kinds of approval are required. Pre-approval may be required for specific types of sample collection such as drilling or excavation. For example, drilling on a military base requires pre-

approval. Base security may require clearances for all members of the sampling team, including subcontractors. This process may take two or more days.

2.2.2 Contact Private Property Owners

Samplers must obtain written permission from the private property owner(s) before sampling on his/her property, even if verbal permission has been granted. It is recommended that samplers obtain verbal permission prior to their arrival at the sampling location, but written permission can be obtained on the day of sampling. If a property owner refuses to grant access to his/her property, it may be necessary for the sampling organization to contact the appropriate authorities for assistance. A sampler who enters private property without permission may be subject to a charge of trespassing, and samples may be considered part of an illegal search and invalid for legal proceedings.

2.2.3 Contact Utility Companies

The sampler must contact local utility companies (e.g., power, phone, gas, cable, sanitation, etc.) at least one week prior to the sampling event to have underground cables, lines, and pipes flagged and marked. This is required by law. A national one-call directory can be found at: https://call811.com

It may be necessary to turn off the utilities (i.e., electrical wires or gas lines) in order to obtain samples. The utility service(s) disruption dates should be confirmed at least two days prior to sampling activities. Samplers should follow Regional or other appropriate program procedures for the disruption of utilities.



Pre-payment of survey fees to local utility companies may be required.

2.3 Analytical Services Request

To prepare for the sampling event, the samplers should review the “Analytical Services Request Regional Notification” for samples from the CLP. This information may be in the form of the “Analytical Services Request Regional Notification” obtained from the Sample Management Office (SMO) Contract Laboratory Program Support System (CLPSS) Portal, supplied by the Regional Sample Control Coordinator (RSCC), or in other forms of communication from the Region. Information for Modified Analyses may also be obtained from the SMO CLPSS Portal. Field team leaders should contact their RSCC, Remedial Project Manager (RPM), or On-Site Coordinator (OSC) to review this information prior to going into the field, and ensure that this information matches information in the Site Project Plan (SPP), SAP, and/or QAPP. An eXtensible Markup Language (XML) file is provided as part of the laboratory assignment from the SMO CLPSS Portal which can be used for uploading site information into Scribe.

Review the following sources of information for planning:

- **Sample information:** Provides the number of samples requested, the sample matrix, the analysis types, and if Preliminary Results are required. This information is used to determine the equipment and supplies needed for the sampling event.
- **Site location:** Determines whether there are any specific requirements for accessing/exiting the site, or for working at the site.
- **Shipping period:** Establishes the time frame during which the samples are to be shipped to the laboratory/laboratories. This helps determine when sampling should occur.
- **Laboratory information:** Specifies where the samples will be shipped.

2.3.1 Review Sample Request

Review the "Analytical Services Request Notification" and other Regional communication for the following information:

- ☐ The sample request determines some of the preparatory activities for the sampling event.
- ☐ Review and evaluate the sample request to determine the number and types of samples to be collected.
- ☐ Review the required sample collection method(s).
- ☐ Review decontamination procedures necessary for site.
- ☐ Make note of sample holding times and conditions.
- ☐ Determine Performance Evaluation (PE) and Quality Control (QC) sample requirements.
- ☐ Determine whether shipping container temperature blanks are required.

2.4 Review Project Plans

Project plans describe, in detail, the requirements for the sampling event. All field team members should be familiar with the applicable project plans prior to beginning field sampling. These plans may include the following documents.

2.4.1 Site Project Plan (SPP)

The SPP describes the requirements for any activity taking place at the site. It contains information such as site history, potential contaminants, topographical information, etc. that may be integrated into the QAPP.

2.4.2 Health and Safety Plan (HASP)

The HASP describes the measures necessary to maintain the health and safety of the sampling team during the sampling event. It can include topics such as the following:

- Organization structure
- Job hazard analysis
- Site control
- Training
- Medical surveillance
- Personal protective equipment (PPE)
- Exposure monitoring
- Thermal stress
- Decontamination
- Emergency response
- Location of and directions to the nearest Emergency Room or hospital
- Standard Operating Procedures
- Confined space operations
- Spill containment

2.4.3 Quality Assurance Project Plan (QAPP)

The QAPP describes the data quality objectives and data requirements for the project, and is used by samplers to develop any subsequent plans such as the SAP or the Field Sampling Plan (FSP). Refer to Appendix A for more information on QAPP sampling requirements.

2.5 Assemble Sampling Materials

Samplers should prepare for a sampling project by assembling the appropriate sampling materials (equipment, supplies, sample containers, packing materials, and shipping materials). The equipment and supplies must be properly cleaned, calibrated, and tested as necessary to meet the needs of the sampling project prior to sampling.

2.5.1 Equipment and Supplies

Samplers should review the project plans to determine the equipment necessary for sample collection.

The following should be obtained prior to a sampling event:

- Sample containers
- Shipping containers
- Packing material
- Reagent water for decontamination and for preparation of field/equipment blanks
- Access to the Scribe software for creating sample labels, stickers, Traffic Report/COC (TR/COC) Records, and Region-specific Scribe templates
- Custody seals
- Sampling equipment such as bowls, augers, pumps, etc.
- PPE
- Internet access (either at the time of sampling or soon after the samples are shipped)

The QAPP, the SAP, or the CLP Statement of Work (SOW) may also require field samplers to provide the following:

- Shipping container temperature blanks
- Trip blanks for Volatile Organic Analyte (VOA) analysis
- Preservation supplies (e.g., ice or acid)
- Specially prepared sample vials or bottles (e.g., VOA or hexavalent chromium)
- Utensils or equipment for handling tissue samples requested by Modified Analysis

2.6 Perform Readiness Review/Dry Run

A readiness review/dry run is a test run of the proposed sampling event. It is a recommended practice as it affords samplers a chance to review all plans, documentation software (i.e., Scribe), and equipment lists for accuracy and completeness prior to sampling activities. It also provides an opportunity to consult with sampling team members to make sure that all the elements are in place and that everyone understands their tasks before actually going out into the field. Sampling project managers should provide the readiness review or dry run dates and schedules to samplers so that they can prepare accordingly.

2.7 Assess the Status of the Site and the Team

Samplers should consider taking the following actions prior to starting a sampling event:

- ☐ Communicate personnel roles and lines of authority.
- ☐ Verify that HAZWOPER training is up to date for all field staff as required.
- ☐ Ensure that permission has been granted to enter the site and collect samples.
- ☐ Confirm that utility work has been completed (if required).
- ☐ Review local weather forecast to be aware of possible dangerous weather conditions. Ensure that sampling staff are prepared for weather conditions.

- ☐ If the sampling location is inaccessible, contact the appropriate field or Regional personnel for instructions.
- ☐ Verify that the correct sampling equipment is on site.
- ☐ Ensure that personal safety measures are in place.
- ☐ Ensure that a site HASP is in place and includes procedures for emergency medical treatment and first aid, evacuation procedures, emergency contacts, and location of emergency medical facilities.
- ☐ Identify and mark the sampling location with buoys, flags, or stakes according to the sampling plans, maps, and grids.
- ☐ Park the car/van away from the sampling site and turn off the engine. Be aware of car exhaust (BTEX) contamination to volatile organic samples through all procedures, including loading and unloading the containers during shipping.

2.8 Initiate Site Control Measures

The sampling team is responsible for implementing the necessary site control measures during the sampling event, which may include the following:

- ☐ Maintaining a log of authorized personnel entering the site.
- ☐ Preventing unauthorized persons from entering the site.
- ☐ Ensuring that any decontamination equipment or procedures to prevent sample cross-contamination required in the QAPP and/or FSP are in place and carried out.

2.9 Maintain Field Logbook

Samplers must maintain a field logbook that documents the field activities. The information in the field logbooks may be used as evidence in court. The field logbook should meet the following criteria:

- ☐ Use waterproof ink to record all entries.
- ☐ Record the date and time of all entries, and the name of the person recording the information.
- ☐ Correct all errors by drawing a line through the error, initialing and dating the error, and then adding the correct information.
- ☐ Document sampling project information such as:
  - Project name, Project ID, and location
  - Names of samplers
  - Geological observations, including maps and Global Positioning System (GPS) information
  - Atmospheric conditions
  - Field measurements
  - Sampling dates, times, locations, and sample location coordinates
- ☐ Record sampling activity information such as:
  - Sampling dates and times
  - Name(s) of person(s) recording the information
  - Sample identifications
  - Sample matrices
  - Sample descriptions (e.g., odors and/or colors)
  - Number of samples collected
  - Sampling methods/equipment
- ☐ Record any and all deviations from the sampling plan.
- ☐ Record any and all difficulties in sampling and/or any unusual circumstances.

2.10 Preventing Errors

Errors in the sampling process can result in additional costs and delayed sampling results. The following section lists some of the steps that can be taken to avoid common sampling errors.

Document samples correctly:

- ☐ Use the CLP Sample Number and SMO CLPSS Portal-generated CLP Case Number correctly (sample number on each sample).
- ☐ Submit the signed TR/COC Record with the sample(s).
- ☐ Ensure that the TR/COC Record and the sample container information match each other and are accurate.
- ☐ Accurately and legibly complete and attach a custody seal to each shipping container. The project QAPP may also require that custody seals be attached to each sample container or plastic sample bag. Refer to the project QAPP for specific instructions.

Collect and preserve samples correctly:

- ☐ Collect a sufficient volume of sample so that the laboratory can perform the requested analysis and quality controls, such as Matrix Spike (MS), Matrix Spike Duplicate (MSD), and laboratory Duplicate.
- ☐ Ensure that required preservatives have been added to samples.

Ship samples correctly:

- ☐ Pack bottles and containers to prevent breaking or spilling during shipping.
- ☐ For iced samples, evenly distribute bags/packets of ice throughout the cooler and between the sample containers to ensure that all samples are sufficiently cooled to a temperature of $\leq 6°C$, but not frozen, and include a sealed container of water to be used as a temperature blank.
- ☐ Verify that the TR/COC Records have been included prior to sealing the shipping container.
- ☐ Verify that custody seals are attached to the shipping containers.
- ☐ Ensure that the shipping containers are labeled with the designated laboratory address.
- ☐ Include shipping information for United States Department of Agriculture (USDA) Quarantine samples if applicable.
- ☐ If samples are to be shipped internationally, assemble the required additional paperwork or customs authorizations. Refer to Appendix F, International Shipping, for additional information.
- ☐ Upload the electronic TR/COC Record as soon as possible after shipping.

Communicate effectively:

- ☐ It is extremely important that all parties involved in a sampling event remain in contact during the sampling process.
- ☐ The key elements of communication for a sampling event include the relationship between the RSCC, SMO, the samplers in the field, and the laboratories that will be accepting the samples.
- ☐ In instances where there are any changes to the sampling event due to a cancellation or an increase or decrease in the number of samples to be shipped, the sampler should contact the RSCC as soon as possible. The RSCC will work with SMO to resolve any potential capacity, availability, or overbooking issues with the CLP laboratories.

2.11 Exiting the Site

The following activities should be performed before leaving the sampling site:

- ☐ Ensure that all equipment has been collected and removed.
- ☐ Follow Regional guidance regarding decontamination and doffing of PPE, if used.
- ☐ Follow Regional guidance for waste removal and disposal.
- ☐ Ensure that all sampling personnel have cleared the site.
- ☐ If sampling on private property, provide a sample receipt to the property owner for all samples collected and removed from the site.

3.0 CLP STATEMENTS OF WORK

The overall requirements for sample collection, analysis, and handling under the Contract Laboratory Program (CLP) are described in the CLP Statements of Work (SOWs).

3.1 The CLP SOWs

The CLP SOWs are available on the U.S. Environmental Protection Agency (EPA) website at: https://www.epa.gov/clp/superfund-clp-analytical-statements-work-sows. Table 3-1 lists the CLP SOWs.

Table 3-1. CLP Statements of Work

Statement of Work	Analysis Types	Matrix Types
High Resolution	Chlorinated Dibenzo-*p*-Dioxins (CDDs) and Chlorinated Dibenzofurans (CDFs) Chlorinated Biphenyl Congeners (CBCs)	Soil, sediment, biosolids, oil, sludge, ash, tissue, water, and wipe
Organic/Inorganic	Trace Volatile Organic Analytes (Trace VOAs) Trace VOAs Selected Ion Monitoring (SIM) Volatile Organic Analytes (VOAs) Semivolatile Organic Analytes (SVOAs) SVOAs SIM Pesticides Aroclors Metals by Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP - AES), Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) Mercury by Cold Vapor Atomic Absorption (CVAA) Spectrometry Cyanide by Spectrophotometry Anions by Ion Chromatography (IC)* Hexavalent Chromium by IC* Total Organic Carbon (TOC)*	Soil, sediment, water, Toxicity Characteristic Leaching Procedure (TCLP)/ Synthetic Precipitation Leaching Procedure (SPLP) leachate , waste, and wipe

*Anions, Hexavalent Chromium, and TOC will be available by Modified Analysis (MA).

3.2 CLP Sample Definition

A CLP sample is defined as a discrete portion of material to be analyzed from one location for each individual or set of analyses.

A sample consists of all sample aliquots (portions), provided that the analyses are all requested from the same CLP analytical program:

- for each individual or set of analytical methods
- from one location
- for one sample matrix
- for one laboratory

3.2.1 Mixed-matrix Samples

In some instances, a mixed-matrix sample which contains either a supernate (for a sediment/soil sample) or a precipitate (for a water sample) may be collected. The decisions made with regard to the different matrices in such samples can have profound impacts on data usability. In this event, samplers should consult their sampling plans and/or discuss the required procedures with the Remedial Project Manager (RPM), On-Site Coordinator (OSC), or designee.

In general, it is recommended that two individual samples be collected by separating the aqueous layer from the solid/precipitate layer at the point of collection if possible. If the phases or layers cannot be separated effectively in the field at the point of collection, direction should be provided to the receiving laboratory to separate the layers under controlled conditions. In this case, additional sample numbers will be needed for the separate phases. They should be assigned two different sample IDs (e.g., Sample IDs ABC124 and ABC125 for Sample ID ABC123), along with notes in the field sample log and in the Special Instructions section of the Chain of Custody (COC) Record, indicating that the sample IDs are derived or related to the same sample. Refer to Section 5.1.5, Using Scribe for Mixed-matrix Samples, for information on how to use the Scribe software to track mixed-matrix samples.

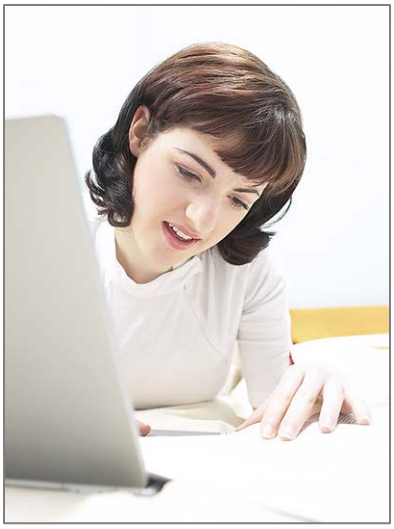


When samples are collected from several locations to form a composite sample, the sample should be assigned either a number from one of the locations used during collection, or a unique number that represents the composite sample, for tracking purposes. The numbering scheme used internally at a sampling event for identifying composite samples should also be documented appropriately (e.g., in the field logbooks).

3.3 CLP Analyses

CLP analysis is generally used for Superfund sites and includes the target analytes. The matrices can be water, leachates derived from the TCLP or SPLP, soil, sediment, waste, wipe, or tissue (non-human) for high resolution analyses. Additional matrices requested under Modified Analysis (MA) for inorganics and organics may include oil, sludge, ash, construction waste, biosolids, or tissue (non-human).

4.0 CLP SAMPLE DOCUMENTATION



The U.S. Environmental Protection Agency (EPA) Contract Laboratory Program (CLP) is required to produce accurate and legally defensible data. Therefore, in order to produce legally defensible data, control of the samples must be maintained to ensure that the samples accurately represent the site and location from which they were collected. Sample documents are tools that allow EPA to maintain the chain of custody of the samples from collection, through shipping, to analysis. The documentation also associates the sample to the sample data. Samplers should review their site-specific project plans and Quality Assurance Project Plans (QAPPs) to determine other types of documentation that must be completed for a sampling project. The following section describes the documents used to maintain the chain of custody and the tools used to create these documents.

The following table summarizes CLP sample documentation.

Table 4-1. CLP Sample Documentation Tracking

Type	Source	Purpose
CLP Sample Number	Assigned by sampling software (Scribe); ranges are supplied by the Regional Sample Control Coordinator (RSCC)	Identifies sample data. Associates the sample to the sample data.
CLP Case Number	Generated by the Sample Management Office (SMO) Contract Laboratory Program Support System (CLPSS) Portal	Identifies groups of samples collected during a single sampling event.
Traffic Report/Chain of Custody (TR/COC) Record	Created in Scribe	Tracks chain of custody of the sample and sample data.
Custody seals	Supplied by the RSCC or field sampling team	Maintains sample integrity; may indicate sample tampering or contamination if broken.
Sample labels	Created in Scribe	Affixed to the sample container to identify an individual sample.
Field operations records (as necessary)	Created and maintained by sampling team	Maintains a record of activities at the site.
Shipping container label (to the laboratory)	Carrier standard form	Used by the carrier to ship the samples to the laboratory.
Shipping container return label (return from the laboratory)	Carrier standard form	Used by the carrier to have the laboratory return the container to the Region.

The documentation required by a Region for a sampling event is outlined in project plans such as the QAPP, Sampling and Analysis Plan (SAP), and Field Sampling Plan (FSP).



EPA recommends that a dedicated field team member be responsible for all sample documentation steps, including reviewing laboratory scheduling information, creating sample labels and TR/COC Records in Scribe, maintaining a field operations log, and relinquishing control of the samples to the laboratory. This person should be identified in the Site Project Plan (SPP) or QAPP.

Under no circumstances should the site name or address appear on any documentation that is sent to the laboratory (for the CLP).

4.1 CLP Sample Numbers

A sample number is a number that is unique per sampling location and identifies each CLP sample. It is used to track samples throughout the sampling and analytical processes, and is recorded on several types of sample and sample documentation (e.g., TR/COC Records and sample labels).

Table 4-2. CLP Sample Number Letter Codes

Region	Letter Code
1	A
2	B
3	C
4	D
5	E
6	F
7	G
8	H
9	Y
10	J

According to the CLP guidelines, each individual inorganic water sample may be analyzed for total metals or filtered metals, but not both. Therefore, water samples collected for total metal and filtered metal analyses from the same sampling location must be assigned separate and unique CLP Sample Numbers. Samples for Toxicity Characteristic Leaching Procedure (TCLP) and Synthetic Precipitation Leaching Procedure (SPLP) may also require separate CLP Sample Numbers.

4.1.1 Requesting Sample Numbers

CLP Sample Numbers are created in Scribe with ranges supplied by the RSCC. The sampler should request a range of sample IDs from the RSCC. Once the initial number is entered into Scribe, the software will auto-generate the additional sample numbers required for the project. Do not re-use CLP sample numbers, as this may create difficulties for Laboratory Information Management Systems.

4.2 CLP Case Numbers

SMO CLPSS Portal-generated Case Numbers are used to track groups of samples from a sampling event throughout the sampling and analytical processes, and are recorded on several types of sample and sample documentation (e.g., TR/COC Records, sample labels). Samplers should correctly assign the Case Number to the appropriate sample bottle or container. CLP Case Numbers are obtained from the “Analytical Services Request Regional Notification” in the Access Assignment Information task in the SMO CLPSS Portal. Samplers should correctly assign the Case Number to the appropriate sample bottle or container.

4.3 CLP TR/COC Records

A TR/COC Record is used as physical evidence of sample custody and as a permanent record for each sample collected. A chain of custody record documents the exchange and transportation of samples from the field to the laboratory.

To meet CLP sample documentation and chain of custody requirements, samplers must attach a separate, signed TR/COC Record to each container shipped. The sampler should consider TR/COC documentation needs when shipping directly from the site.

- ☐ The TR/COC Record must document each sample within the shipping container.
- ☐ The Carrier Name and Airbill Number should be on each COC.
- ☐ Each TR/COC Record **must be signed by the designated field sampler**, documenting that they have relinquished control of the samples.
- ☐ TR/COC Records should be separated and shipped in the containers with the samples listed on them. Attach the TR/COC Record to the inside of the lid of the shipping container. Samples may not be shipped in a container without the corresponding TR/COC Record. This practice maintains the chain of custody for all samples in case of incorrect shipment.
- ☐ The electronic TR/COC Record should be uploaded as soon as possible after shipping.

If more than one TR/COC Record is used for the samples within one shipping container, all of the records must have complete header information and original signatures. Samplers are responsible for the care and custody of samples from the time of collection to the time of shipment to the laboratories for analysis. A sample is considered under custody if the following conditions are met:

- It is in possession or in view after being in possession
- It was in possession and then secured or sealed to prevent tampering
- It was in possession when placed in a secured area

Each time the custody of samples is turned over to another person, the TR/COC Record must be signed off by the former custodian and accepted by the new custodian.

4.4 Chain of Custody Seals

A chain of custody seal is any adhesive label or tape that can be used to seal a sample bottle, container, plastic bag, or shipping container. In the event that a container is opened or tampered with, the seal will be broken. The custody seal is used to maintain the chain of custody, as well as guard against possible sample contamination or tampering during shipping.

- ☐ Custody seals must be placed on each shipping cooler or container, and if required by the project's QAPP or FSP, on each sample bottle, container, or bag (as appropriate).
- ☐ The CLP does not provide custody seals. Custody seals should be obtained from the RSCC or supplied by site personnel.

4.5 Sample Labels

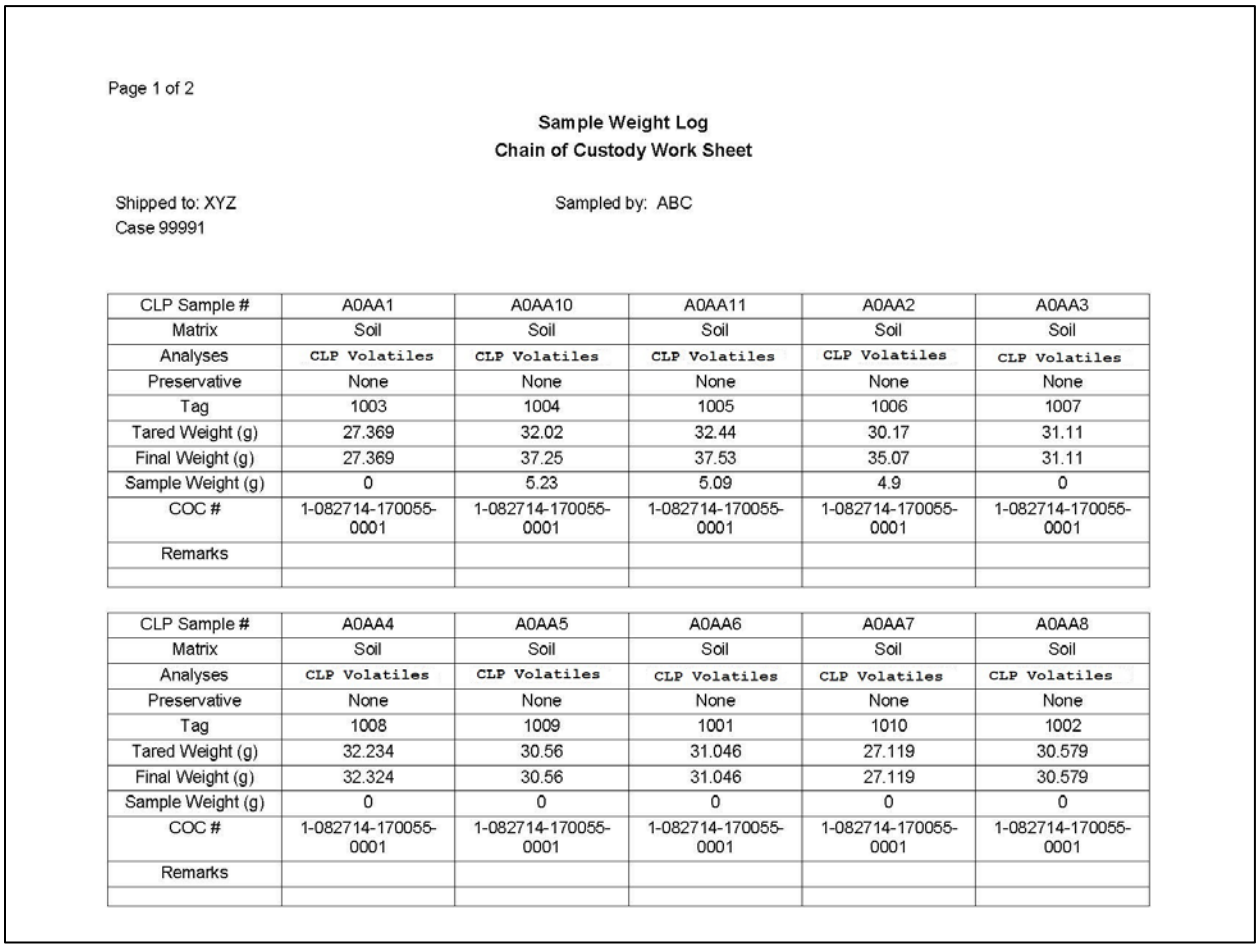
A sample label is a sticker that is attached to a sample bottle or container that contains a field sample or quality control (QC) sample.

- ☐ Sample labels are affixed to each sample container as samples are collected in the field or prior to going in the field.
- ☐ A sample label must contain, at a minimum, the sample number so that the sample can be associated with, and listed on, the associated TR/COC Record.

- Sample labels should also include the required analysis, CLP Case Number, and preservative used (to eliminate confusion at the laboratory). Samplers should refer to their site-specific project plans for Region-specific sample label requirements.
- Site information (e.g., address, site ID) should not be included on the sample label or container.
- Sample tags are NOT required by the CLP.

4.6 Sample Weight Logs

A sample weight log (Figure 4-1) identifies the tared, sample, and final weights per bottle for soil samples for Volatile Organic Analyte (VOA) analysis. In order to support the SOW requirements for VOAs, samplers should enter tared and final weights per bottle in the sample weight log. Sample weight logs are mandatory for VOA soil samples.



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Sample Weight Log
Chain of Custody Work Sheet

Shipped to: XYZ
Case 99991

Sampled by: ABC

CLP Sample #	A0AA1	A0AA10	A0AA11	A0AA2	A0AA3
Matrix	Soil	Soil	Soil	Soil	Soil
Analyses	CLP Volatiles	CLP Volatiles	CLP Volatiles	CLP Volatiles	CLP Volatiles
Preservative	None	None	None	None	None
Tag	1003	1004	1005	1006	1007
Tared Weight (g)	27.369	32.02	32.44	30.17	31.11
Final Weight (g)	27.369	37.25	37.53	35.07	31.11
Sample Weight (g)	0	5.23	5.09	4.9	0
COC #	1-082714-170055-0001	1-082714-170055-0001	1-082714-170055-0001	1-082714-170055-0001	1-082714-170055-0001
Remarks					

CLP Sample #	A0AA4	A0AA5	A0AA6	A0AA7	A0AA8
Matrix	Soil	Soil	Soil	Soil	Soil
Analyses	CLP Volatiles	CLP Volatiles	CLP Volatiles	CLP Volatiles	CLP Volatiles
Preservative	None	None	None	None	None
Tag	1008	1009	1001	1010	1002
Tared Weight (g)	32.234	30.56	31.046	27.119	30.579
Final Weight (g)	32.324	30.56	31.046	27.119	30.579
Sample Weight (g)	0	0	0	0	0
COC #	1-082714-170055-0001	1-082714-170055-0001	1-082714-170055-0001	1-082714-170055-0001	1-082714-170055-0001
Remarks					

Figure 4-1. Scribe Sample Weight Log

5.0 THE SCRIBE DOCUMENTATION SOFTWARE TOOL



The U.S. Environmental Protection Agency (EPA) Analytical Services Branch (ASB) requires samplers to use the Scribe software to create documentation for all Contract Laboratory Program (CLP) sampling efforts. The EPA recommends that a dedicated member of the sampling team be trained in the Scribe software, and be responsible for all uses of Scribe including the sample labels and the Traffic Report/Chain of Custody (TR/COC) Records at the sampling location. For assistance with obtaining or using the Scribe software, contact the Environmental Response Team (ERT) Software Support Help Desk at 800-999-6990 from 9:00 AM – 5:00 PM ET. For additional information regarding Scribe use and training materials, refer to the following website: https://response.epa.gov/scribe. Scribe allows users to create one or more sampling projects, enter data, and create sample documents for that project. Some of the capabilities of Scribe include:

- Tracking sample numbers and Case Numbers
- Associating analysis information to sample numbers
- Creating sample labels
- Setting label size and printing labels
- Selecting sample numbers to add to the chain of custody record
- Printing chain of custody records
- Filtering lists of samples
- Exporting sample data in the following formats: text file (.txt, .csv), spreadsheet (.xls, .wb3), HTML (.htm), XML (.xml), or QuickMap (.kml, .kmz)

The Scribe software tool allows users to track samples electronically. It can be downloaded at no charge from the EPA On-Scene Coordinator (OSC) website at https://www.ertsupport.org/downloads.htm

5.1 Setting Up a Sampling Event in Scribe

Scribe allows the sampler to enter much of the information prior to the event in order to facilitate processing on the day of the event. The following sections describe how to set up the sampling event in Scribe.

5.1.1 Set Up Project

The initial step when using Scribe is to set up the project as follows:

- ☐ Access the Scribe **New Project Wizard** to set up the sampling project.
- ☐ Enter the project **Site Name**, **Site #**, and **Region #** (required).
- ☐ Enter additional project information, if available. The eXtensible Markup Language (XML) file for the Case can be imported from the Sample Management Office (SMO) Contract Laboratory Program Support System (CLPSS) Portal and will customize the analysis and lab lists.

5.1.2 Create Analysis Types

The analysis types to be used for the sampling event must be defined for the project. Refer to the site sampling plan to determine which analyses are to be used.

- Use the **Analyses** table to display a list of all the analysis types available.
- Only analyses with the Program Type of "CLP," such as "CLP ICP-AES Metals," or "CLP Semivolatiles" should be selected for CLP Cases.
- If the required analysis type is missing, it can be added manually using the **Add** button.

5.1.3 Set Default Sample Number Information

Set up the default values for sample number. This allows the samplers to let the system increment sample numbers, rather than hand entering each one.

- Select **File→Options→CLP/Tag Settings** to display the **CLP/Tag Settings** window.
- Enter the new default values and click **OK**.

5.1.4 Indicate Modified Analysis (MA) on Scribe COC Records

When completing a TR/COC Record in Scribe, indicate an MA as follows:

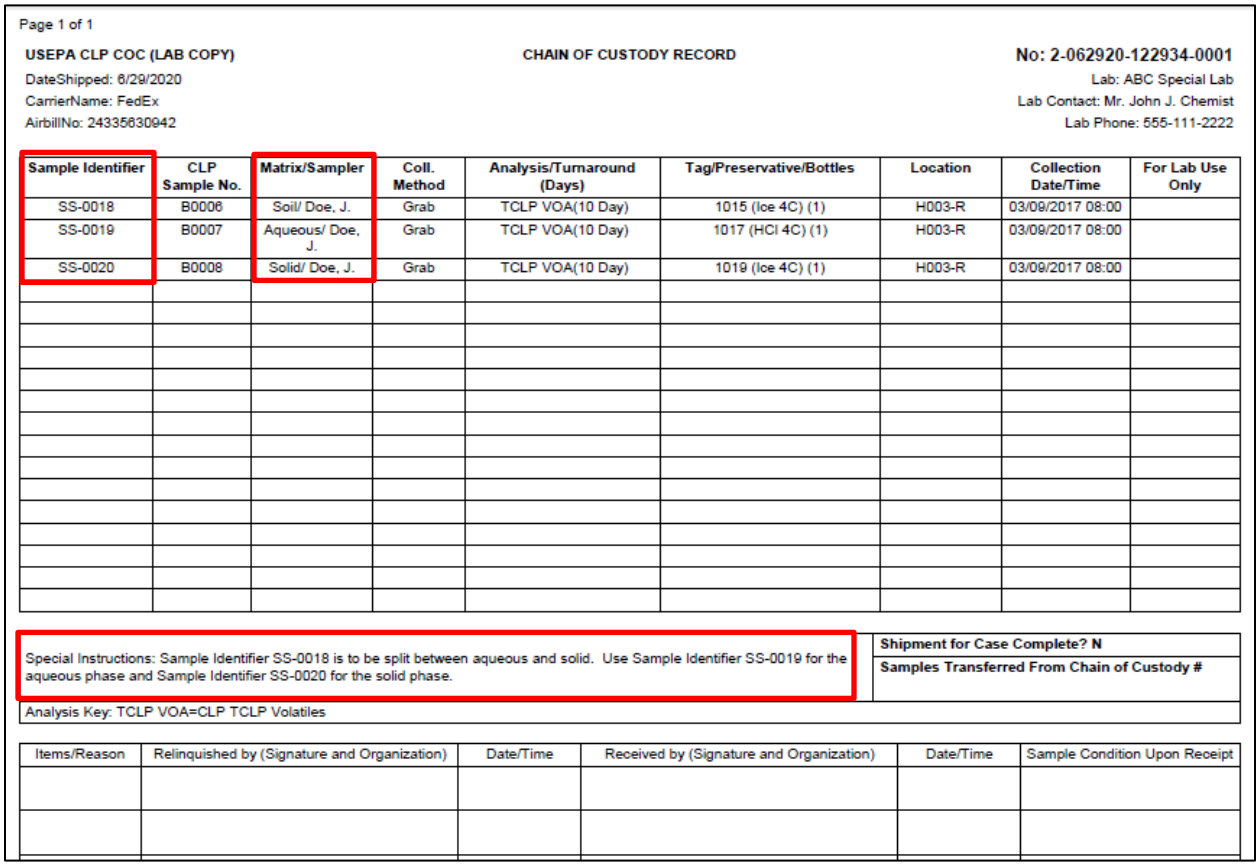
- Identify the samples that will be analyzed using (a) CLP MA(s) by creating a new analysis within the Scribe Analyses table or at the time of entering the Analyses for the sample.
- The MA analysis should contain the Modification Reference Number within the name assigned to the analysis. For example, if a Region submits an MA for an additional analyte, and the SMO assigns the Modification Reference Number 3001.0, the Scribe Analyses could be named "CLP VOA by MA 3001.0.". The associated abbreviation for this analysis could be "VOA MA".

5.1.5 Using Scribe for Mixed-matrix Samples

The Scribe **LinkSampleNo** field links the original sample to the split samples and numbers. Use this field to link to the sample IDs used for the different sample phases as follows:

- Add two (2) additional samples in Scribe indicating in the matrix field which one is the liquid/aqueous phase and which one is the solid phase (i.e., ABC124 and ABC125).
- Tie the two additional samples to the original sample number using the "LinkSampleNo" field.
  - **In Scribe**, in the **Samples** tab, click the **View** button; the **Select Columns** drop-down menu displays. Put a checkmark next to **LinkSampleNo** to make that column visible.
  - Add the "parent" or the original field sample # in the **LinkSampleNo** column (i.e., ABC123).
  - **On the COC Record**, indicate in the **Special Instructions** which of the two new sample numbers the laboratory is to use for the liquid/aqueous phase and which sample number is to be used for the solid phase.

An example of a Scribe COC Record with mixed-matrix samples is shown in Figure 5-1.



Page 1 of 1

USEPA CLP COC (LAB COPY) **CHAIN OF CUSTODY RECORD** **No: 2-062920-122934-0001**

DateShipped: 6/29/2020
CarrierName: FedEx
AirbillNo: 24335630942

Lab: ABC Special Lab
Lab Contact: Mr. John J. Chemist
Lab Phone: 555-111-2222

Sample Identifier	CLP Sample No.	Matrix/Sampler	Coll. Method	Analysis/Turnaround (Days)	Tag/Preservative/Bottles	Location	Collection Date/Time	For Lab Use Only
SS-0018	B0006	Soil/ Doe, J.	Grab	TCLP VOA(10 Day)	1015 (Ice 4C) (1)	H003-R	03/09/2017 08:00	
SS-0019	B0007	Aqueous/ Doe, J.	Grab	TCLP VOA(10 Day)	1017 (HCl 4C) (1)	H003-R	03/09/2017 08:00	
SS-0020	B0008	Solid/ Doe, J.	Grab	TCLP VOA(10 Day)	1019 (Ice 4C) (1)	H003-R	03/09/2017 08:00	

Special Instructions: Sample Identifier SS-0018 is to be split between aqueous and solid. Use Sample Identifier SS-0019 for the aqueous phase and Sample Identifier SS-0020 for the solid phase.

Shipment for Case Complete? N

Samples Transferred From Chain of Custody #

Analysis Key: TCLP VOA=CLP TCLP Volatiles

Items/Reason	Relinquished by (Signature and Organization)	Date/Time	Received by (Signature and Organization)	Date/Time	Sample Condition Upon Receipt

Figure 5-1. Scribe Mixed-Matrix Samples

5.2 Scribe CLP Analysis Codes

The following table lists the analysis codes used for CLP samples in Scribe.

Table 5-1. Scribe CLP Analysis Codes

Analysis Name	Abbreviation
Aroclors	
CLP Aroclors	ARO
High Resolution	
CLP 12 Toxic Congeners	12 Toxic CBCs
CLP 209 Congeners	209 CBCs
CLP Dioxins/Furans	CDD/CDF
Inorganics	
CLP Aluminum	Al
CLP Anions (F, Cl, Br, SO4, NO3, NO2, PO4)	Anions
CLP Anions (F, Cl, Br, SO4)	Anions 28Day
CLP Anions (NO3, NO2, PO4)	Anions 48Hour
CLP Antimony	Sb
CLP Arsenic	As
CLP Barium	Ba
CLP Beryllium	Be

Table 5-1. (Continued) Scribe CLP Analysis Codes

Analysis Name	Abbreviation
CLP Cadmium	Cd
CLP Calcium	Ca
CLP Chromium	Cr
CLP Cobalt	Co
CLP Copper	Cu
CLP Cyanide	CN
CLP Hardness	Hardness
CLP Hexavalent Chromium	Cr+6
CLP ICP-AES Metals	ICP-AES
CLP ICP-MS Metals	ICP-MS
CLP Iron	Fe
CLP Lead	Pb
CLP Magnesium	Mg
CLP Manganese	Mn
CLP Mercury	Hg
CLP Nickel	Ni
CLP Potassium	K
CLP Selenium	Se
CLP Silver	Ag
CLP Sodium	Na
CLP SPLP Aluminum	SPLP Al
CLP SPLP Antimony	SPLP Sb
CLP SPLP Arsenic	SPLP As
CLP SPLP Barium	SPLP Ba
CLP SPLP Beryllium	SPLP Be
CLP SPLP Cadmium	SPLP Cd
CLP SPLP Calcium	SPLP Ca
CLP SPLP Chromium	SPLP Cr
CLP SPLP Cobalt	SPLP Co
CLP SPLP Copper	SPLP Cu
CLP SPLP Cyanide	SPLP CN
CLP SPLP ICP-AES Metals	SPLP ICP-AES
CLP SPLP Iron	SPLP Fe
CLP SPLP Lead	SPLP Pb
CLP SPLP Magnesium	SPLP Mg
CLP SPLP Manganese	SPLP Mn
CLP SPLP Mercury	SPLP Hg
CLP SPLP Nickel	SPLP Ni
CLP SPLP Potassium	SPLP K
CLP SPLP Selenium	SPLP Se
CLP SPLP Silver	SPLP Ag
CLP SPLP Sodium	SPLP Na

Table 5-1. (Continued) Scribe CLP Analysis Codes

Analysis Name	Abbreviation
CLP SPLP Thallium	SPLP Tl
CLP SPLP Vanadium	SPLP V
CLP SPLP Zinc	SPLP Zn
CLP TCLP Arsenic	TCLP As
CLP TCLP Barium	TCLP Ba
CLP TCLP Cadmium	TCLP Cd
CLP TCLP Chromium	TCLP Cr
CLP TCLP ICP-AES Metals	TCLP ICP-AES
CLP TCLP Lead	TCLP Pb
CLP TCLP Mercury	TCLP Hg
CLP TCLP Selenium	TCLP Se
CLP TCLP Silver	TCLP Ag
CLP Thallium	Tl
CLP Total Organic Carbon Water	TOC Water
CLP Total Organic Carbon Soil	TOC Soil
CLP Vanadium	V
CLP Zinc	Zn
Organics	
CLP PAH+PCP	PAH
CLP PAH+PCP by SIM	PAH SIM
CLP Semivolatiles	SVOA
CLP SPLP Semivolatiles	SPLP SVOA
CLP SPLP Volatiles	SPLP VOA
CLP TCLP Semivolatiles	TCLP SVOA
CLP TCLP Volatiles	TCLP VOA
CLP Trace Volatiles	TVOA
CLP Trace Volatiles by SIM	TVOA SIM
CLP Volatiles	VOA
Pesticides	
CLP Pesticides	PEST
CLP SPLP Pesticides	SPLP PEST
CLP TCLP Pesticides	TCLP PEST



To avoid issues with interpretation, ensure that Total Metals and Dissolved Metals are labeled with separate sample IDs.

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6.0 CLP SAMPLE CONTAINERS

The analytical protocol(s) for sample analysis often requires the use of a specific type of sample container. The type of container will also depend on the sample matrix.

It is recommended that samplers use borosilicate glass containers which are inert to most materials when sampling for pesticides and/or other organics, and for Total Organic Carbon (TOC). Borosilicate glass is also recommended for sampling soils for metals. Conventional polyethylene is recommended when sampling for metals and anions in water because of the lower cost and absorption rate of metal ions.



Have extra containers readily available for each sampling event in case of breakage, loss, or contamination.

Containers procured for a sampling event are usually pre-cleaned and shipped ready for use from the manufacturer to the sampling site. Regardless of the type of container used, samplers must ensure that the containers have been analyzed or certified clean to levels below concern for the project based on the specifications in the Quality Assurance Project Plan (QAPP). Certificates must be kept on record. These containers must meet the U.S. Environmental Protection Agency (EPA) container type specifications listed in Tables D-1 through D-4 in Appendix D.



Samplers should document the lot numbers for every lot of cleaned containers used for each project and maintain corresponding certificates of analysis on file and available upon request.

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7.0 CLP SAMPLE COLLECTION

Samplers should determine the types of samples or aliquots to be collected, the volume required for each aliquot, and the preservation requirements by referring to the Site Project Plan (SPP) and Contract Laboratory Program (CLP) sample requirements tables in Appendix D. The following sections describe the types of samples that may be required to be collected.



7.1 Requesting the Scheduling of the Laboratory

Samplers must request that the Regional Sample Control Coordinator (RSCC) schedule the laboratory to be used for the analysis. This should be done as far in advance of the sampling event as possible.

- If one or more Modified Analysis (MA) will be required, scheduling requests should be submitted at least four weeks prior to the start of the sampling event to allow the solicitation process to be completed.
- Samplers should provide information regarding the number of samples, analyses, etc. and if Saturday delivery is likely. If known, additional information regarding weekly shipping frequency is helpful to include.
- When scheduling a sampling event that will last for more than one week, it is recommended that the sampler contact the RSCC (or designee) on a weekly basis to provide updates. Communication between the sampler, the RSCC (or designee), and the Sample Management Office (SMO) is important as it ensures better availability of laboratory capacity.
- If the time frame or number of samples for a sampling event changes, the RSCC and SMO should be notified as soon as possible to maintain capacity at the scheduled laboratory.
- The Region should contact the Analytical Services Branch (ASB) in advance if it is suspected that the samples may contain asbestos.



The CLP has the capability to schedule sampling on an emergency basis; however, the sampler must contact the RSCC (or designee) to obtain details regarding how to handle such a situation.

7.2 Preparing for the Shipping of Samples

Once the samples are collected, they will be shipped to the CLP laboratory for analysis. Samplers must have the necessary shipping supplies on site.

7.2.1 Procure Shipping Supplies

Samplers should refer to the appropriate project plans to determine the types of samples that will be collected during the sampling project to determine the necessary packaging materials to have at the site for all pertinent sample container types and sample matrices.

Samplers should also obtain the appropriate shipping paperwork (e.g., shipping forms required by the delivery service).



The CLP strongly discourages the use of vermiculite and cat litter as sources for packing material. These materials interfere with labeling and documentation and are difficult to remove from sample containers and shipping containers.

7.2.2 Laboratory Assignment Notification

Prior to beginning fieldwork, the samplers may either download an "Analytical Services Request Regional Notification" file via the Access Assignment Information task in the SMO Contract Laboratory Program Support Services (CLPSS) Portal, or obtain it from the RSCC.



The "Analytical Services Request Regional Notification" applies only to activities being performed under the CLP Statements of Work (SOWs).

7.2.3 Verify Laboratory Shipping Information

Samplers should verify the laboratory contact information, including the following:

- Laboratory name
- Laboratory address
- Contact name
- Laboratory phone number

This information, which is provided on the "Analytical Services Request Regional Notification", is used to complete both the Traffic Report/Chain of Custody (TR/COC) Records and shipping paperwork such as address labels and airbills. This file may be accessed through the SMO CLPSS Portal, or can be obtained from the RSCC prior to sampling.

7.2.4 Obtain Shipping Company Information

Samplers should also verify the shipping company information, including the following:

- Company name
- Telephone number
- Account number
- Pickup schedule



Additional guidance will be provided by the U. S. Environmental Protection Agency (EPA) if samples are to be shipped internationally. Also, see Appendix F, International Shipping.

7.2.5 Prepare Sample Container Return Documentation

CLP laboratories must routinely return sample shipping containers to the appropriate sampling office within 14 calendar days following receipt of shipment from the sampler. To ensure that empty sample shipping containers are returned to the appropriate sampling office, samplers must complete the applicable container documentation and work with Regional personnel and government agencies to provide a cost-effective mechanism for this process. The sampling container return documentation should be prepared in advance and provided to samplers before field activities begin.

The sampler (not the CLP laboratory) is responsible for the cost of the return or disposal of the container and should also include shipping airbills bearing the sampler's account number, as well as a return address, to allow for container return.

To maintain consistency across shipping container transportation programs, samplers should proceed as follows:

- Minimize the use of multiple transportation carriers.
- Use multiple-copy labels so the laboratory and the sampling team can each retain a copy for their records.
- Prepare labels in advance so that the laboratory can simply affix a completed shipping label on the container.
- Include third-party billing information (i.e., their shipping account number) on labels so the laboratory will not be billed by the transportation carrier.
- Confirm that the laboratory has been notified of the transportation carrier being used.
- Include the SMO CLPSS Portal-generated CLP Case Number on the return information.

7.3 Collecting Samples

The CLP requirements for sample volumes, preservation, and contractual holding times are defined by the applicable CLP SOWs, and outlined in the tables in Appendix D.

Samplers should follow the sample collection requirements for analyses as provided in the following tables in Appendix D:

- Organic methods (Tables D-1 and D-2)
- Inorganic methods (Table D-3)
- High Resolution methods for Dioxins/Furans and Chlorinated Biphenyl Congeners (CBCs) (Table D-4).

For an explanation of the various sample types and the requirements for collecting and submitting each particular type, refer to Table 7-1.

Table 7-1. Sample Types and CLP Submission Requirements

Sample Type	Purpose	Collection[1]	CLP Sample Number
Field Sample	To analyze for target analytes of interest	Collect from areas that are known or suspected to be contaminated. Collect at the frequency specified in the Quality Assurance Project Plan (QAPP) and Sampling and Analysis Plan (SAP).	Assign CLP Sample Numbers to the sample.
Field Duplicate	To check reproducibility of laboratory and field procedures To indicate non-homogeneity	Collect from areas that are known or suspected to be contaminated. Collect at the frequency specified in the QAPP and SAP.	Assign two separate (unique) CLP Sample Numbers (i.e., one number to the field sample and one to the duplicate). Submit single blind to the laboratory.

Table 7-1. (Continued) Sample Types and CLP Submission Requirements

Sample Type	Purpose	Collection[1]	CLP Sample Number
Field Blank	To check cross-contamination during sample collection, preservation, and shipment, as well as in the laboratory Also to check sample containers and preservatives	Collect for each group of samples of similar matrix at the frequency specified in the QAPP and SAP. Organics - Use water (demonstrated to be free of the contaminants of concern). Inorganics - Use metal-free (deionized or distilled) water or a single clean wipe.	Assign separate CLP Sample Numbers to the field blanks. Submit single blind to the laboratory.
Filter Blank	To check contamination of samples from filtering procedure	Collect when water samples are filtered by filtering blank water using the same procedure and filtering equipment that is used for samples. Use blank water (water demonstrated to be organic-free, deionized or distilled for inorganics) and collect into sample containers.	Assign separate CLP Sample Numbers to the filter blanks. Submit single blind to the laboratory.
Temperature Blank	To provide an accurate measurement of field sample temperature upon arrival to the laboratory Also to establish whether the temperature range has been maintained while in transit	Collect for each shipping container with the frequency specified in the QAPP and SAP.	Ship together with samples from the field to the laboratory. A CLP Sample Number is not required.
Trip Blank [Volatile Organic Analyte (VOA) analysis Only]	To check contamination of VOA samples during handling, storage, and shipment from field to laboratory	Prior to going into the field, prepare and seal one trip blank sample per shipment per matrix. Trip blanks should be matched with respect to matrix and volume of the preservatives used. Prepare trip blank samples with the same preservatives and reagent water used for the corresponding samples. Carry each through the same sampling and handling protocols used for field samples. Aqueous trip blank samples should be prepared using water demonstrated to be free of the contaminants of concern (deionized water is appropriate). Place one trip blank sample for each matrix in each container used to ship VOA samples.	Assign separate CLP Sample Numbers to the trip blanks. Submit single blind to the laboratory.
Equipment Blank or Rinsate Blank	To check field decontamination procedures	Collect when sampling equipment is decontaminated and reused in the field or when a sample collection vessel (bailer or beaker) will be used. Use blank water (water demonstrated to be organic-free, deionized or distilled for inorganics) and pour rinse water into the sample containers.	Assign separate CLP Sample Numbers to the equipment blanks/rinsate. Submit single blind to the laboratory.

Table 7-1. (Continued) Sample Types and CLP Submission Requirements

Sample Type	Purpose	Collection[1]	CLP Sample Number
Matrix Spike (MS) and Matrix Spike Duplicate (MSD) (Organic Analysis Only)	To check accuracy and precision of organic analyses in specific sample matrices	Collect from areas that are known or suspected to be contaminated. MS/MSD are optional per Regional direction.	Assign the same CLP Sample Number to the field sample and the extra volume for MS/MSD. Identify the sample designated for MS/MSD on the TR/COC Record.
Matrix Spike (MS) and Laboratory Duplicate (Inorganic Analysis Only)	To check accuracy and precision of inorganic analyses in specific sample matrices	Collect from areas that are known or suspected to be contaminated. It is recommended that MS and Duplicates be collected in the first round of sampling and included in the first shipment of samples to the laboratory.	Assign the same CLP Sample Number to the field sample and extra volume (if collected). Identify the sample(s) designated for MS and Duplicates on the TR/COC Record.
Performance Evaluation (PE) Samples	Specially-prepared Quality Control (QC) samples used to evaluate a laboratory's analytical proficiency	The PE samples contain analytes with concentrations unknown to the laboratory. Designated Regional or authorized personnel (depending on Regional policy) arrange for Case-specific CLP PE samples to be prepared and shipped by the Quality Assurance Technical Support (QATS) contractor. The PE samples can be shipped to the site, or shipped per Regional direction. QATS provides the appropriate preparation instructions and chain of custody materials.	Samplers must order PE samples and ship them to the laboratory if required by the Region. Assign separate CLP Sample Numbers to the PE samples. Include PE ampule numbers on the TR/COC Record.

[1] Consult Regional or Project Manager Guidance for field QC sample frequencies; laboratory QC sample frequencies are generally fixed in the laboratory contracts or specified in analytical methods.

7.3.1 Field QC Samples

Field QC samples are designed to assess variability of the media being sampled and to detect contamination and sampling errors in the field. The types of field QC samples that are generally collected include the following:

- Field duplicates
- Field blanks (such as equipment, trip, or rinse blanks)

Unless otherwise instructed, field duplicate samples should remain "blind" to the laboratory (i.e., they should have separate CLP Sample Numbers).

7.3.2 Laboratory QC Samples

A laboratory QC sample is an additional analysis of a field sample, as required by the laboratory's contract. There are three types of such samples:

- MS (for organic and inorganic samples)
- MSD (for organic samples only)
- Duplicates (for inorganic samples only)

Samplers should observe the following guidelines when collecting laboratory QC samples:

☐ Follow Regional guidance regarding the collection of laboratory QC samples.

- Regarding Gas Chromatography/Mass Spectrometry (GC/MS) organic analyses, a Region may decide to reference Deuterated Monitoring Compounds (DMCs) rather than MS/MSD for accuracy and precision.

- ☐ Wipe samples do not require laboratory QC samples.
- ☐ When laboratory QC is scheduled for CLP analyses, samplers should select one sample per matrix per Sample Delivery Group (SDG). An SDG closes when 20 samples are received for a Case or one week (3 days for 7-day turnaround samples) has elapsed, whichever comes first. Designate MS/MSD for Pesticides, Aroclors, and GC/MS analyses as directed. For GC/MS, MS/MSD are optional per Regional direction. Designate MS and laboratory Duplicate for metals, mercury, cyanide, anions, hexavalent chromium, and Total Organic Carbon (TOC). Samplers should not select a field blank or a PE Sample for laboratory QC.
- ☐ Designated samples should be identified on the TR/COC Record; the sample(s) designated for laboratory QC should be noted in "Sample Type" column.
- ☐ QC samples should be shipped in the same container as the field samples when possible.



Field QC samples should not be designated as laboratory QC samples.



In the event of multiple sample shipments during a sampling event, it is recommended that the sampler submit laboratory QC samples in the first sample shipment, and as necessary in subsequent shipments to meet laboratory contract requirements.

7.4 Recording Samples

Samplers must use Scribe to record the samples that are collected. To record the samples:

- ☐ Access the Scribe **Sampling** tab to select the type of sampling (Water Sampling, Soil/Sediment Sampling, Wipe Sampling).
- ☐ Enter the detailed information for the sample. Include laboratory analysis for each sample; see tabs for sample details and for analysis.
- ☐ When all information has been entered, click the **Close** button at the bottom of the page to save the entries and close the window.

Refer to Table 5-1 for the CLP analysis codes.

For assistance while using the Scribe software, contact the Environmental Response Team (ERT) Software Support Help Desk at 800-999-6990 from 9:00 AM – 5:00 PM ET. Refer to the following website for information on the use and training of Scribe:
https://response.epa.gov/site/site_profile.aspx?site_id=ScribeGIS

7.4.1 Hardcopy Recording

In the event that Scribe is unavailable, samplers must have backup hardcopy Scribe TR/COC Records. This should be done only in cases of power/equipment failure, and not as a matter of routine during a sampling event.

7.5 Meeting Volume, Preservation, and Holding Time Requirements

Samplers should refer to Tables D-1 through D-4 in Appendix D to obtain the specific sample volumes to be collected, the preservation needed for those samples, and the technical holding times under which they must submit samples to the scheduled CLP laboratory.

7.5.1 Collect Required Sample Volumes

Samplers should ensure that a sufficient volume is collected for each sample. If the sample volume does not meet the requirement set by the project plan, the laboratory may not be able to analyze the sample correctly. Questions regarding collecting lesser volumes than those listed in Tables D-1 through D-4 in Appendix D should be directed to ASB.

Refer to Appendix B for information regarding the collection of aqueous VOA samples. When collecting samples for VOA in soils, samplers must use the SW-846 Method 5035A guidelines included in Appendix C.



If tissue samples are homogenized or processed, it should be performed at a sample processing facility under clean room conditions to reduce potential contamination. Tissue samples should be packed and cooled on ice immediately. Tissue samples should never be sent on Friday for Monday delivery.

7.5.2 Preserve Samples

Without preservation, some samples (e.g., VOAs) may degrade to the point that they will not provide accurate results for the site. The sampler must chemically preserve some water samples for certain analytes prior to shipping them to the laboratory.

Samplers should observe the following procedures:

- ☐ Note any visible reaction between the sample and added chemical preservative in the field record.
- ☐ Preserve and immediately cool all organic, cyanide, hexavalent chromium, and anions (nitrate, nitrite, orthophosphate, and sulfate) water samples to ≤ 6°C, but not frozen, upon collection.
- ☐ Keep samples cooled until shipping (do not freeze water samples).
- ☐ Preservation techniques vary among Regions, so samplers should obtain Region-specific instructions and review the appropriate project plans and Standard Operating Procedures (SOPs).
- ☐ Refer to Appendix B for information regarding the collection of VOA water samples.

7.5.3 Ship Samples within Holding Times

There are two types of holding times: technical and contractual.

- **The technical holding time** is the maximum amount of time allowed between sample collection and the completion of sample extraction and/or analysis.
- **The contractual holding time** is the maximum amount of time that the CLP laboratory can hold a sample prior to extraction and/or analysis. The contractual holding time is the elapsed time expressed in days from the date of receipt of the sample by the laboratory until the date of its extraction and/or analysis, as specified in the applicable CLP SOW.



Contractual holding times are generally set to be two days less than the technical holding times to allow for sample packing and shipping.

Samplers should ship samples to scheduled CLP laboratories as soon as possible after collection.

- Ship samples daily to CLP laboratories whenever possible.
- Samples for certain anions (nitrate, nitrite, and orthophosphate) must ship the same day to meet holding times.
- If samples cannot be shipped on a daily basis, they must be properly preserved and maintained to meet CLP-specified temperatures, holding times, and custody requirements.
- Uploading the electronic TR/COC Record is mandatory and should be performed as soon as possible after shipping.



If samplers are shipping samples after 5:00 PM ET, they should notify the RSCC (or designee) and SMO by 8:00 AM ET on the following business day. When making a Saturday delivery, samplers should notify the RSCC (or designee) and SMO as soon as possible so that SMO will receive the delivery information (including shipping airbill information) by 3:00 PM ET on the Friday prior to delivery. Uploading the electronic TR/COC Record to the SMO CLPSS Portal sends a notification to SMO and to the laboratory that the samples have been shipped.

7.6 Completing the Documentation

The sample documentation required is defined by the project plan. It is highly recommended that samplers provide documentation, even if the Region does not require it.

In general, samplers must complete the following documentation for the samples collected:

- CLP Sample Number (on the sample container or bottle)
- Sample label
- Chain of custody seals (as appropriate)
- TR/COC Record
- Field operations records (as necessary)



Under no circumstances should the site name or address appear on any documentation being sent to the laboratory, unless the laboratory is a Regional EPA laboratory.

An example of a packaged sample is shown in Figure 7-1.

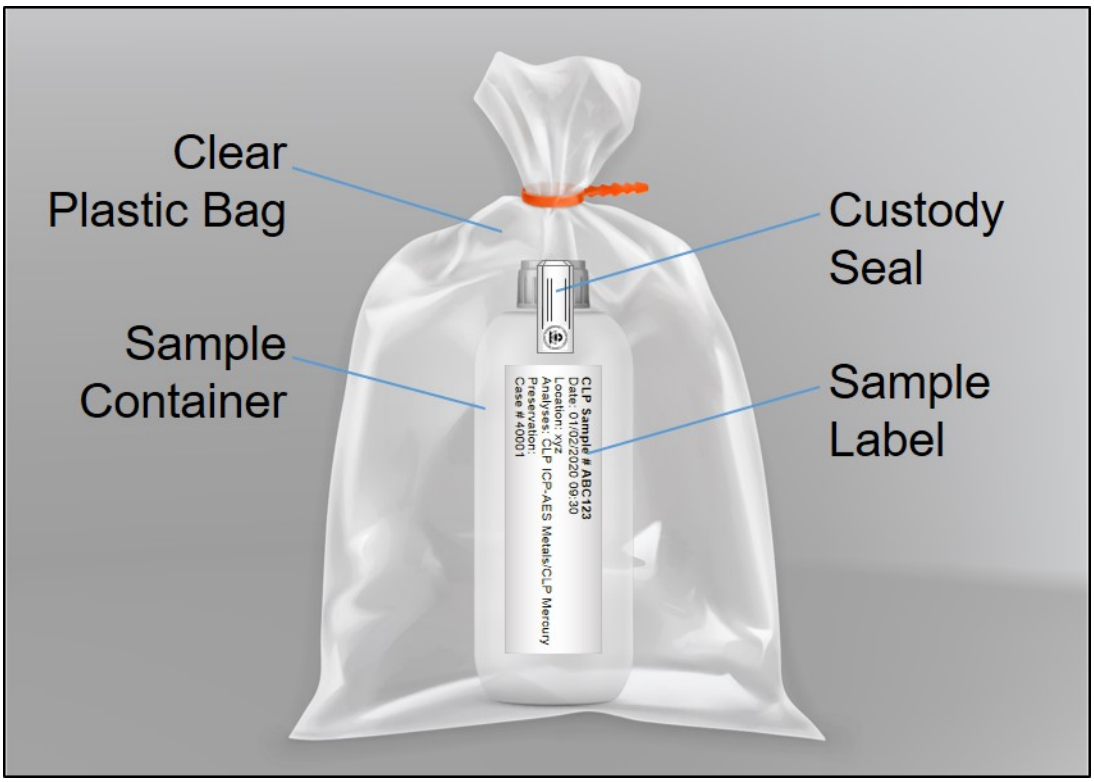


Figure 7-1. Packaged Sample with Identification and Chain of Custody Documentation (Excluding TR/COC Record)

7.6.1 Record and Label the Samples

The sample labels created in Scribe must be affixed to each sample container. A sample label contains the following information:

- Associated CLP Sample Number (either written or pre-printed)
- SMO CLPSS Portal-generated CLP Case Number
- Preservative used
- Analysis
- Additional information such as the location or the date/time of collection

Samplers should record and label the samples collected as follows:

- ☐ Using Scribe, select the **Sampling** tab to select the type of matrix (e.g., Soil/Sediment, Water Sampling).
- ☐ Access the Scribe **Sample Details** page to enter the analysis method, CLP Sample Number, and SMO CLPSS Portal-generated CLP Case Number for each sample.
- ☐ Enter samples associated with an MA by using the MA analysis previously created in Scribe. If the MA does not exist, refer to Section 5.1.2, Create Analysis Types, to create the analysis type for the MA.
- ☐ Print the sample label and place it on the sample container or bottle.
- ☐ If handwriting a sample label, complete the information using waterproof ink, place the label on the outside of the sample bottle or container, then cover the label with clear packaging tape to protect it and maintain legibility.
- ☐ Avoid wrinkles in the tape and labels.
- ☐ Sample tags are NOT required by the CLP.
- ☐ Refer to Figure 7-1 for an example of sample label placement.

Use the following guidelines for these special conditions:

- **Water samples collected for total metals and filtered metals analyses from the same sampling location** - must assign separate (unique) CLP Sample Numbers.
- **Tared VOA sample vials** - must not attach labels to tared VOA sample vials.

7.6.2 Complete the COC Records in Scribe

Samplers should use the Scribe format for CLP projects. Complete the Scribe COC Record as follows:

Access the Scribe COC Page

- Select the **Chain of Custody** link under the **Sample Management** header. The ***Chain of Custody*** page displays.

Create the COC Record

- Click the **Add a Chain of Custody** button at the bottom of the page. The ***COC Details*** pop-up window displays.
- Enter the information for the COC, including selecting the **CLP format** (Inorganic, Organic, or High Resolution).

  Note: It is important that the correct **COC Format** is selected when the COC Record is created. The user should choose the CLP format for the type of samples being submitted, as shown in Figure 7-2.

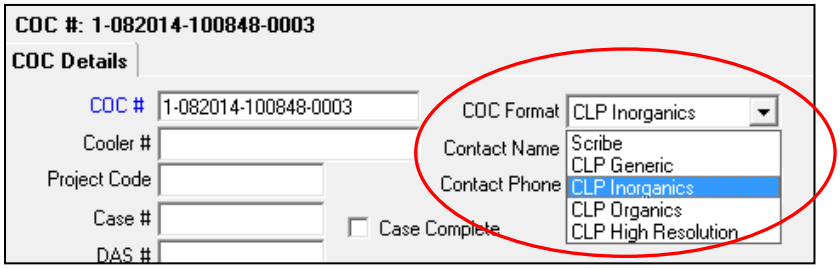


Figure 7-2. COC Details Pop-up Window

- Ensure that the **Case #** is also filled in. (If it was entered in the CLP/Tag Settings, it will automatically be filled in.)

Assign Samples to the COC Record

- Assign samples to the **COC Record** (it will filter based on selected COC format SOW).
- Ensure that all sample information has been entered.
- Enter any additional information, such as sampler name, matrix, and preservation.
- Indicate any samples that will be analyzed using an MA.
- Scribe generates a laboratory and a Regional copy of the COC Record (see Figures 7-3 and 7-4).

Print the COC Record

- Print the **COC Record** by selecting either the **Lab Copy** or **Region Copy**. There will be a QC check; ensure that all information is filled in.
- Print as many copies of the **COC Record** as is necessary.
- Sign and submit original copies of the **COC Record**.



Sampler information, etc., is not added when creating the COC Record; it is added when editing the sample itself.

7.6.3 Making Manual Edits to Printed Scribe COC Records

If a Scribe COC Record has been printed and deletions or edits need to be made, samplers must use the following procedures:

- If making a deletion, delete the incorrect information in Scribe, reprint the COC Record, and discard the original.
- If making an addition, enter the new information in Scribe, reprint the COC Record, and discard the original.
- If corrections occur after shipment, adhere to the Regional procedures and guidelines for handling hardcopy COC Records.

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USEPA CLP COC (LAB COPY) | **CHAIN OF CUSTODY RECORD** | **No: 2-010614-124708-0001**

DateShipped: 1/3/2020 | Lab: EPA Labs

CarrierName: FedEx | Case #: 21490 | Lab Contact: John Smith

AirbillNo: ABC12345 | Cooler #: | Lab Phone:

Sample Identifier	CLP Sample No.	Matrix/Sampler	Coll. Method	Analysis/Turnaround (Days)	Tag/Preservative/Bottles	Location	Collection Date/Time	For Lab Use Only
12345-0001	B0AA0	Soil/ EPA	Grab	SVOA(21)/PR, SVOA 1723.3(21)/PR, PEST(21), ARO(21), VOA(21), VOA MA(21)	(0 C), (0 C), (0 C), (0 C), (0 C), (0 C) (6)	ABC	01/03/2020 08:00	
12345-0002	B0AA1	Soil/ EPA	Grab	ARO(21), PEST(21), SVOA(21)	(0 C), (0 C), (0 C), (0 C) (4)	ABC	01/03/2020 08:00	
12345-0003	B0AA2	Soil/ EPA	Grab	ARO(21), PEST(21), SVOA(21)	(0 C), (0 C), (0 C), (0 C) (4)	DEF	01/03/2020 09:00	
12345-0004	B0AA3	Soil/ EPA	Grab	ARO(21), PEST(21), SVOA(21)	(0 C), (0 C), (0 C), (0 C) (4)	GHI	01/03/2020 10:00	
12345-0005	B0AA4	Soil/ EPA	Grab	ARO(21), PEST(21), SVOA(21)	(0 C), (0 C), (0 C), (0 C) (4)	JKL	01/03/2020 11:00	
12345-0006	B0AA5	Soil/ EPA	Grab	SVOA(21), SVOA 1723.3(21), PEST(21), ARO(21), VOA MA(21)	(0 C), (0 C), (0 C), (0 C), (0 C), (0 C) (6)	DEF	01/03/2020 09:00	
12345-0007	B0AA6	Soil/ EPA	Grab	SVOA(21), SVOA 1723.3(21), PEST(21), ARO(21), VOA MA(21)	(0 C), (0 C), (0 C), (0 C), (0 C), (0 C) (6)	GHI	01/03/2020 10:00	
12345-0008	B0AA7	Soil/ EPA	Grab	ARO(21), PEST(21), SVOA(21)	(0 C), (0 C), (0 C), (0 C) (4)	JKL	01/03/2020 11:00	

Sample(s) to be used for Lab QC: 12345-0001, 12345-0001, 12345-0001, 12345-0001, 12345-0001, 12345-0001

Shipment for Case Complete? Y

Samples Transferred From Chain of Custody #

Analysis Key: SVOA=CLP Semivolatiles, SVOA 1723.3=CLP SVOA MA 1723.3, PEST=CLP Pesticides, ARO=CLP Aroclors, VOA=CLP Volatiles, VOA MA=CLP VOA (MA 1722.4)

Items/Reason	Relinquished by (Signature and Organization)	Date/Time	Received by (Signature and Organization)	Date/Time	Sample Condition Upon Receipt

Figure 7-3. Scribe Chain of Custody Record (Laboratory Copy)

Page 1 of 1

USEPA CLP COC (REGION COPY)
DateShipped: 1/3/2020
CarrierName: FedEx
AirbillNo: ABC12345

CHAIN OF CUSTODY RECORD
Field Sampler's Guide
Case #: 21490
Cooler #:

No: 2-010614-124708-0001
Lab: EPA Labs
Lab Contact: John Smith
Lab Phone:

Sample Identifier	CLP Sample No.	Matrix/Sampler	Coll. Method	Analysis/Turnaround (Days)	Tag/Preservative/Bottles	Location	Collection Date/Time	Sample Type
12345-0001	B0AA0	Soil/ EPA	Grab	SVOA(21)/PR, SVOA 1723.3(21)/PR, PEST(21), ARO(21), VOA(21), VOA MA(21)	(0 C), (0 C), (0 C), (0 C), (0 C), (0 C) (6)	ABC	01/03/2020 08:00	Lab QC
12345-0002	B0AA1	Soil/ EPA	Grab	ARO(21), PEST(21), SVOA(21)	(0 C), (0 C), (0 C), (0 C) (4)	ABC	01/03/2020 08:00	Field Sample
12345-0003	B0AA2	Soil/ EPA	Grab	ARO(21), PEST(21), SVOA(21)	(0 C), (0 C), (0 C), (0 C) (4)	DEF	01/03/2020 09:00	Field Sample
12345-0004	B0AA3	Soil/ EPA	Grab	ARO(21), PEST(21), SVOA(21)	(0 C), (0 C), (0 C), (0 C) (4)	GHI	01/03/2020 10:00	Field Sample
12345-0005	B0AA4	Soil/ EPA	Grab	ARO(21), PEST(21), SVOA(21)	(0 C), (0 C), (0 C), (0 C) (4)	JKL	01/03/2020 11:00	Field Sample
12345-0006	B0AA5	Soil/ EPA	Grab	SVOA(21), SVOA 1723.3(21), PEST(21), ARO(21), VOA MA(21)	(0 C), (0 C), (0 C), (0 C), (0 C), (0 C) (6)	DEF	01/03/2020 09:00	Field Sample
12345-0007	B0AA6	Soil/ EPA	Grab	SVOA(21), SVOA 1723.3(21), PEST(21), ARO(21), VOA MA(21)	(0 C), (0 C), (0 C), (0 C), (0 C), (0 C) (6)	GHI	01/03/2020 10:00	Field Sample
12345-0008	B0AA7	Soil/ EPA	Grab	ARO(21), PEST(21), SVOA(21)	(0 C), (0 C), (0 C), (0 C) (4)	JKL	01/03/2020 11:00	Field Sample

Sample(s) to be used for Lab QC: 12345-0001, 12345-0001, 12345-0001, 12345-0001, 12345-0001, 12345-0001

Shipment for Case Complete? Y

Samples Transferred From Chain of Custody #

Analysis Key: SVOA=CLP Semivolatiles, SVOA 1723.3=CLP SVOA MA 1723.3, PEST=CLP Pesticides, ARO=CLP Aroclors, VOA=CLP Volatiles, VOA MA=CLP VOA (MA 1722.4)

Items/Reason	Relinquished by (Signature and Organization)	Date/Time	Received by (Signature and Organization)	Date/Time	Sample Condition Upon Receipt

Figure 7-4. Scribe Chain of Custody Record (Region Copy)

7.6.4 Complete and Attach Custody Seals

Custody seals are usually pre-printed stickers that are signed (or initialed) and dated by the samplers after sample collection and placed on sample bottles or containers and/or shipping containers (see Figure 7-5).

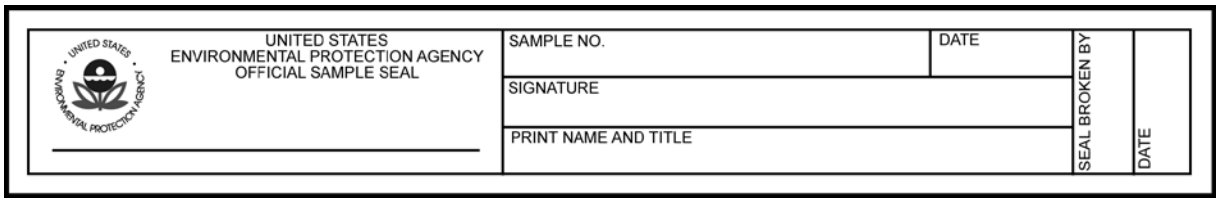


Figure 7-5. Custody Seal

The custody seal documents the individual who sealed the sample container and verifies that the sample has not been tampered with. Custody seals can also be used to maintain custody of other items such as envelopes.

The use and type of custody seals can vary by Region or collecting organization. Samplers should obtain the appropriate custody seals and specific instructions for their use from the RSCC. Note that some Regions require the sampling team to provide their own custody seals.

- Custody seals shall be placed in such a manner that they will break if the sample bottle or container, or the shipping cooler or container is tampered with or opened after leaving custody of the samplers.
- Custody seals should never be placed directly onto a coring tool used as a transport device (e.g., 5 g Sampler) or tared, 40 mL closed-system vials. The seals must be placed on the bag for the coring tool used as a transport device, or on the bag used to enclose the vials. Refer to Table 8-1 for details.

Instructions for completing and attaching a custody seal are included in Table 7-2.

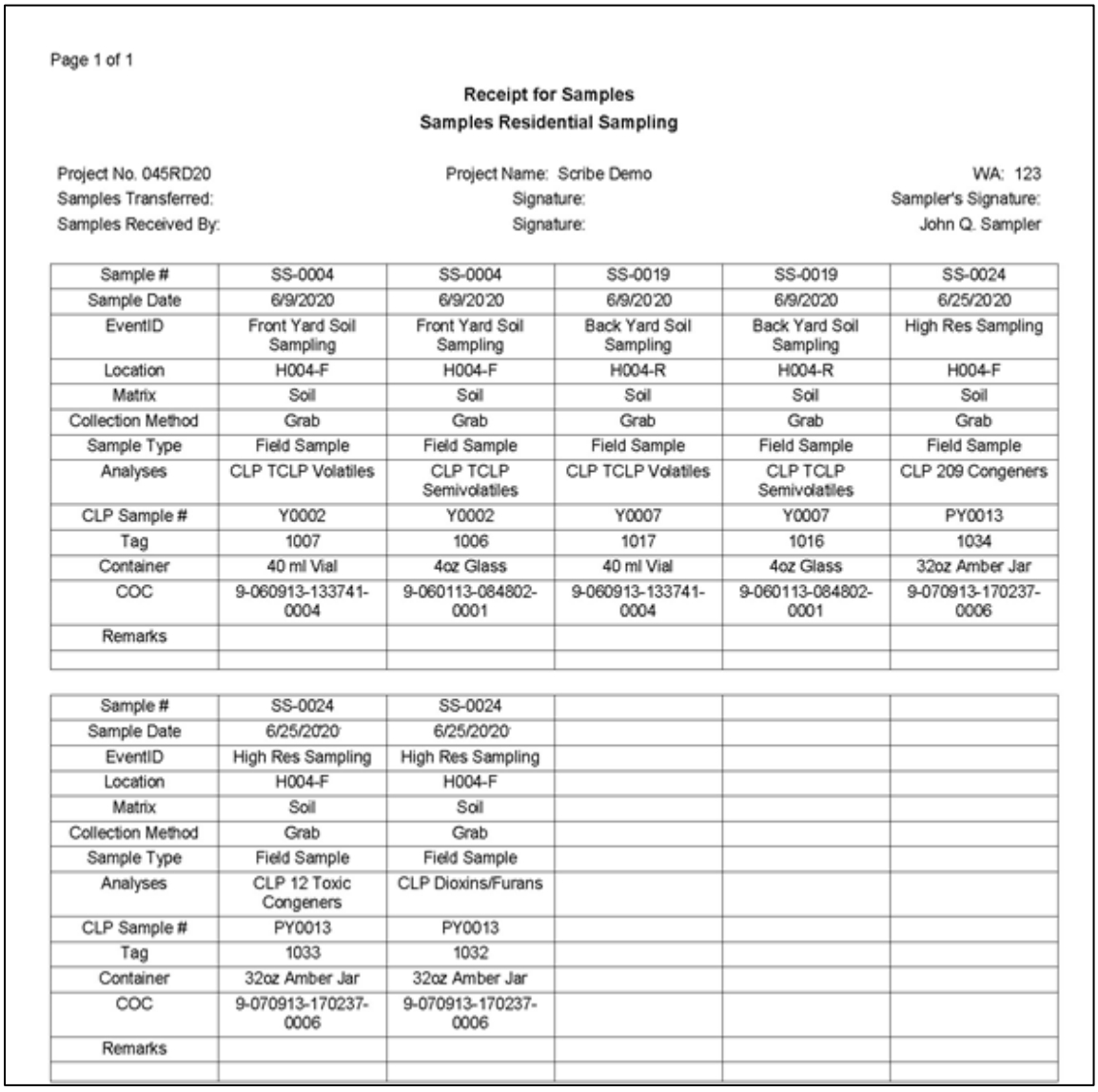
Table 7-2. Completing and Attaching a Custody Seal

Step	Action	Important Notes
1	Record the CLP Sample Number.	The space for the CLP Sample Number does not need to be completed on custody seals being placed on the opening of a shipping container, only on those being placed on the opening of sample bottles or containers.
2	Record the month, day, and year of sample collection.	
3	Sign the seal in the signature field.	
4	Print your name and title in the “Print Name and Title” field.	
5	Place the custody seal over the edge of the sample bottle or container such that it will break if tampered with.	Custody seals can be placed directly on any sample container except for coring tools used as a transport device (e.g., 5 g Samplers) and tared VOA bottles. If packing coring tools used as a transport device or tared VOA bottles, place them in a clear plastic bag and place the custody seal on the outside of the bag.
6	If possible, cover the custody seal with clear plastic tape to protect it.	Take special care to not place the protective tape over the seal in such a way that it can be removed and then re-attached without signs of tampering.

7.7 Providing a Sample Receipt

After samples have been collected on private property, the sampler should prepare a receipt for these samples and provide it to the property owner. This step is especially important when sampling on private property since the analytical results from these samples could be used during future litigation, and the receipt will serve as proof that the owner granted approval for the removal of the samples from the property. An example of a sample receipt created using Scribe is shown in Figure 7-6.

Detailed instructions for generating a Sample Receipt Report are included in Exercise 9 - Section K of the "V 3.10.1 Scribe Training Guide.PDF" which can be obtained from this download: https://response.epa.gov/sites/ScribeGIS/files/Scribe%20V310%20Student%20Files.zip



Page 1 of 1

Receipt for Samples
Samples Residential Sampling

Project No. 045RD20 | Project Name: Scribe Demo | WA: 123
Samples Transferred: | Signature: | Sampler's Signature:
Samples Received By: | Signature: | John Q. Sampler

Sample #	SS-0004	SS-0004	SS-0019	SS-0019	SS-0024
Sample Date	6/9/2020	6/9/2020	6/9/2020	6/9/2020	6/25/2020
EventID	Front Yard Soil Sampling	Front Yard Soil Sampling	Back Yard Soil Sampling	Back Yard Soil Sampling	High Res Sampling
Location	H004-F	H004-F	H004-R	H004-R	H004-F
Matrix	Soil	Soil	Soil	Soil	Soil
Collection Method	Grab	Grab	Grab	Grab	Grab
Sample Type	Field Sample	Field Sample	Field Sample	Field Sample	Field Sample
Analyses	CLP TCLP Volatiles	CLP TCLP Semivolatiles	CLP TCLP Volatiles	CLP TCLP Semivolatiles	CLP 209 Congeners
CLP Sample #	Y0002	Y0002	Y0007	Y0007	PY0013
Tag	1007	1006	1017	1016	1034
Container	40 ml Vial	4oz Glass	40 ml Vial	4oz Glass	32oz Amber Jar
COC	9-060913-133741-0004	9-060113-084802-0001	9-060913-133741-0004	9-060113-084802-0001	9-070913-170237-0006
Remarks					

Sample #	SS-0024	SS-0024			
Sample Date	6/25/2020	6/25/2020			
EventID	High Res Sampling	High Res Sampling			
Location	H004-F	H004-F			
Matrix	Soil	Soil			
Collection Method	Grab	Grab			
Sample Type	Field Sample	Field Sample			
Analyses	CLP 12 Toxic Congeners	CLP Dioxins/Furans			
CLP Sample #	PY0013	PY0013			
Tag	1033	1032			
Container	32oz Amber Jar	32oz Amber Jar			
COC	9-070913-170237-0006	9-070913-170237-0006			
Remarks					

Figure 7-6. Sample Receipt Created Using the Scribe Software

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8.0 CLP SAMPLE TRANSPORTATION AND SHIPPING

The sampling organization is not only responsible for the transportation and shipping of the Contract Laboratory (CLP) samples to the scheduled recipient laboratory that will be performing the analysis, but it is also responsible for complying with all applicable packaging, labeling, and shipping requirements. Samplers should review the applicable project plans to be aware of all State, Federal, Department of Transportation (DOT), and International Air Transport Association (IATA) regulations governing environmental and hazardous sample packaging.



8.1 Providing Shipment Notification

Some Regions may require that samplers notify their Regional Sample Control Coordinator (RSCC) (or designee) when samples are shipped, while other Regions may allow samplers to contact the Sample Management Office (SMO) directly to provide shipping notification. It is recommended that the electronic Chain of Custody (COC) Record be submitted through the Contract Laboratory Program Support System (CLPSS) (aka "the SMO CLPSS Portal") as soon as possible after shipping. Submitting the COC Record electronically sends a notification to SMO and to the laboratory that the samples have been shipped. It is recommended that samplers contact the RSCC to verify if such notification is necessary. If samplers are shipping samples after 5:00 PM ET, they should notify the RSCC (or designee) and SMO by 8:00 AM ET on the following business day.

It is strongly recommended that samplers provide shipping notification to the RSCC even if they have received approval to directly notify SMO so that the Region is aware of any changes in the final number and timing of samples delivered.

8.2 Packing and Shipping Samples

After collecting the samples, it is important that the samplers properly package them for shipment and ensure that the samples are sent to the appropriate laboratory without delay. Prompt and proper packaging of samples will achieve the following:

- Protect the integrity of samples from changes in composition or concentration caused by bacterial growth or degradation from increased temperatures.
- Reduce the chance of leaking or breaking of sample containers that would result in loss of sample volume, loss of sample integrity, and exposure of personnel to toxic substances.
- Help ensure compliance with shipping regulations.

A single CLP sample may be contained in several different bottles and vials. For example, one water sample may consist of all containers needed for three of the analytical analyses available under this service [i.e., Semivolatile Organic Analyte (SVOA) analysis, Pesticide analysis, and Aroclor analysis], even though the analyses are collected in separate containers. Therefore, the analysis to be performed and the matrix type will determine the type of container(s) that will be used, as well as the volume that should be collected for that particular sample analysis.

8.2.1 Inventory of Samples and Documentation

Samplers should inventory the contents of shipping containers against the corresponding Traffic Report/Chain of Custody (TR/COC) Records when packing samples for shipment to laboratories. Check for the following:

- Ensure that the correct number of containers has been collected for each analysis of the samples.
- Confirm that the required Performance Evaluation (PE) and Quality Control (QC) samples and temperature blanks are included in the shipment.
- Verify that the correct sample numbers and analyses have been assigned to each sample.

8.2.2 Shipping Regulations

Sample shipping personnel are legally responsible for ensuring that sample shipments comply with all applicable shipping regulations. Verify that the following shipping regulations are adhered to if any of the following conditions apply to the samples:

Note: Field Samplers are legally required to know sample characteristics before shipping.

- **Foreign soil movement** - Follow U.S. Department of Agriculture (USDA) soil quarantine and shipping requirements, providing soil permits or required soil import agreements to the laboratory for completion.
- **Chlorinated Dibenzo-*p*-Dioxin (CDD) and Chlorinated Dibenzofuran (CDF)** - Refer to the High Resolution Superfund Method Statement of Work (SOW) for specific information on the safety and handling requirements for samples potentially containing CDD/CDF.
- **Radiological** - Samples suspected to be radioactive must be screened; follow the instructions from the Analytical Services Branch (ASB) Program Manager. Radioactive/Radiological samples are NOT accepted by the CLP.
- **Dry ice** - If dry ice is used to ship tissue samples, follow DOT and IATA regulations. Refer to the Code of Federal Regulations (49 CFR 173.217) classifying dry ice as Hazard Class 9 *UN 1845* (Hazardous Material) and IATA Dangerous Goods regulations or DOT regulations and U.S. Environmental Protection Agency (EPA) guidelines. Refer to Appendix C for detailed shipping guidelines when using SW-846 Method 5035A to preserve and ship frozen samples.



When shipping from remote locations, dry ice may be used with water ice for the purpose of keeping the water ice from melting. Wrap the dry ice in newspaper and place above any water ice. Never place dry ice in an air-tight container.

Access more transportation and shipping information using the following websites:



Dangerous goods regulations
IATA website
https://www.iata.org/en/programs/cargo

DOT/Pipeline and Hazardous Materials Safety Administration (PHMSA)
https://www.phmsa.dot.gov/phmsa-regulations

The nature of the samples collected determines the type of shipping materials to be used.

Refer to the project plan to determine which type of shipping container should be used for each type of sample collected during the sampling event.

8.2.3 Shipping Temperature

Samples must be stored under conditions that maintain sample integrity.

- Samples requiring cold preservation should be placed in shipping containers or other suitable containers with ice to reduce the temperature as soon as possible after collection.
- Ideally, all samples should be shipped the day of collection for overnight delivery to the laboratory.
- If samples requiring cold preservation cannot be shipped on the day of collection, the sample temperature should be maintained at ≤ 6°C, but not frozen, until they are shipped to the laboratory.

8.2.4 Pack Shipping Containers

Packing shipping containers correctly will prevent sample containers from breaking and leaking. Pack shipping containers according to the instructions outlined in Table 8-1.

Table 8-1. Packing Samples for Shipment

Step	Action	Important Notes
1	Seal all drain holes in the shipping container, both inside and out, to prevent leakage in the event of sample breakage.	
2	Check all lids/caps to make sure the samples are tightly sealed and will not leak.	
3	Wipe loose soil residue from containers.	
4	Seal samples in a clear plastic bag.	Custody seals can be placed directly on any sample container except for coring tools used as a transport device (e.g., 5 g Samplers) and tared Volatile Organic Analyte (VOA) bottles. If packing coring tools used as a transport device or tared VOA bottles, place them in a clear plastic bag and affix the custody seal to the outside of the bag.
5	Fully chill those samples that require chilling to ≤ 6°C (but not frozen) prior to placing in the container with suitable packing materials.	
6	It is recommended that samplers line shipping containers with non-combustible, absorbent packing material prior to placing samples in the shipping container.	The CLP strongly discourages the use of vermiculite and cat litter as sources for packing material. These materials interfere with labeling and documentation and are difficult to remove from sample containers and shipping containers.
7	Place samples in CLEAN, sealed, watertight shipping containers (e.g., metal or hard plastic coolers).	
8	Conduct an inventory of the contents of the shipping cooler/container against the corresponding TR/COC Record(s).	
9	Cover samples in double-bagged ice to prevent water damage to packing materials.	Do NOT pour loose ice directly into the sample container. The ice is used to maintain the temperature of the samples in the shipping cooler.
10	It is recommended that a temperature blank be included each shipping container in a location which will allow for easy access by the laboratory upon opening the shipping container.	The temperature blank is generally a 40 mL vial filled with water and labeled “temperature blank” but does not have a CLP Sample Number.
11	Ensure that the site name or other site-identifying information does not appear on any documentation being sent to the laboratory.	

Table 8-1. (Continued) Packing Samples for Shipment

Step	Action	Important Notes
12	Label the outside of the shipping container with any instructions for handling, such as, “This end up,” “Do not Tamper With,” or "Environmental Laboratory Samples."	
13	If shipping samples containing methanol as a preservative (e.g., samples to be analyzed by SW-846 Method 5035A), use a label to indicate the presence of methanol, the United Nations (UN) identification number for methanol (UN 1230), and Limited Quantity.	

VOA soil samples must be placed on their side prior to being placed on ice. Vials are placed on their side so that the septum is wet on the inside, thereby preventing vapor leaks around it, in case any bubbles form. Also, in case the samples freeze, the water will expand into the flexible septum rather than breaking the vial.

8.2.5 Include Required Paperwork

☐ Attach the necessary paperwork to the shipping cooler or container. All paperwork must be placed in a plastic bag or pouch and then secured to the underside of the shipping container lid (Figure 8-1).

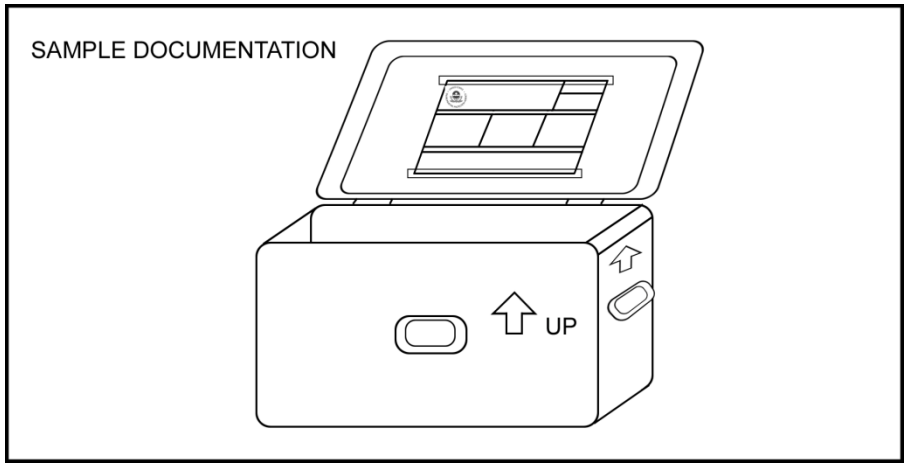


Figure 8-1. Sample Shipping Container with Attached TR/COC Record, PE Sample Instructions (if applicable), and Container Return Documentation

Required paperwork includes:

- TR/COC Records
- Sample weight logs (Figure 4-1), if required for VOA samples
- PE instruction sheets if PE samples are included in the container
- Shipping container return instructions and/or airbills

Contact the RSCC (or designee) for specific paperwork requirements.

8.2.6 Label and Seal Sample Shipping Containers

After packing the samples in the shipping containers, samplers must carefully secure the top and bottom of the containers with tape, place return address labels clearly on the outside of the container, and attach the required chain of custody seals (Figure 8-2).

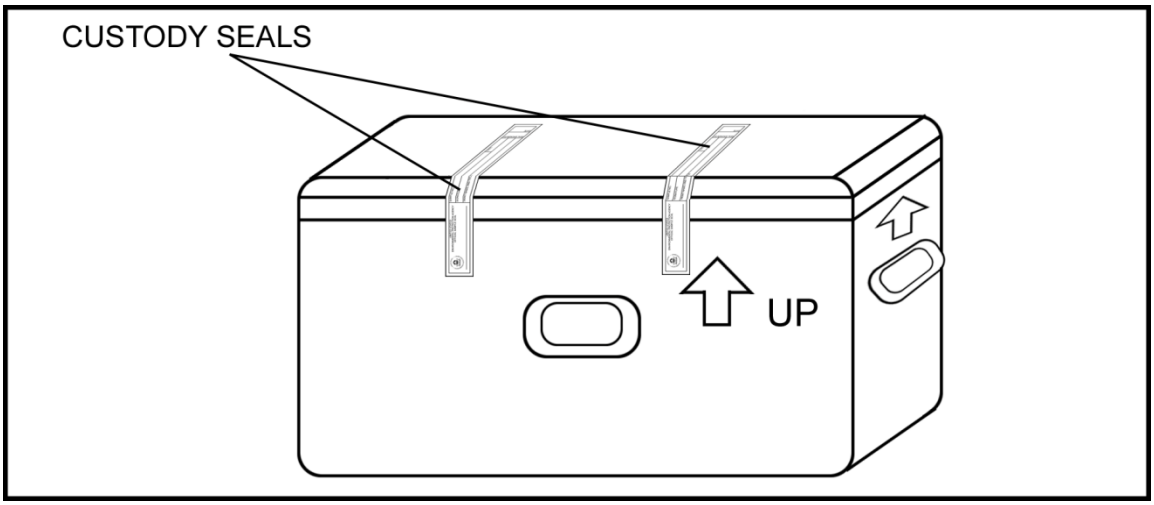


Figure 8-2. Shipping Container with Custody Seals

Use the following guidelines to label shipping containers:

- When shipping more than one container to a laboratory, samplers should mark each container as "1 of 2," "2 of 2," etc.
- An airbill, addressed to the Sample Custodian of the receiving laboratory, must be completed for each container shipped. Samplers should receive the correct name, address, and telephone number of the laboratory to which they must ship samples from the RSCC or the SMO CLPSS Portal.
- To avoid delays in analytical testing, it is critical that for samples associated with multiple types of analyses the correct containers with the correct types of samples are sent to the correct laboratory. For example, inorganic samples may be shipped to one laboratory for analysis, while organic samples may need to be shipped to another laboratory.
- Confirm the shipping company's hours of operation, shipping schedule, and pick-up/drop-off requirements.

8.2.7 Overnight Delivery

It is imperative that samples be sent via overnight delivery. Delays due to longer shipment times may result in missed technical holding times or temperatures rising above the preservation limit, which may destroy sample integrity or require the re-collection of samples for analysis.

8.2.8 Saturday Delivery

Samplers should notify the RSCC (or designee) and SMO as soon as possible when shipping samples for Saturday delivery, so that the delivery information is received by 3:00 PM ET on the Friday prior to delivery.

8.2.9 Shipment Notification

Samplers should upload shipment information to the SMO CLPSS Portal and report all sample shipments to the RSCC (or designee) on the day shipping is completed. **Under no circumstances**

should the sampler contact the laboratory directly. If samplers are shipping samples after 5:00 PM ET, they should notify the RSCC (or designee) or SMO by 8:00 AM ET on the following business day. Samplers should receive the name, phone number, and email address of the appropriate SMO coordinator to notify from the Region/RSCC. Samplers should be aware if the Region requires them to notify the RSCC (or designee) and SMO of sample shipment.

Samplers should provide the following information to the RSCC (or designee):

- Name, phone number, and email address at which they can be reached (preferably closest on-site phone number if still in the field)
- SMO CLPSS Portal-generated Case Number
- Number, matrix and analysis types of samples shipped, and MA number (if required)
- Name of laboratory (or laboratories) to which the samples were shipped
- Airbill number(s)
- Date of shipment
- Case status (i.e., whether or not the Case is complete)
- Problems encountered, special comments, or any unanticipated issues
- Information for the next anticipated shipment



For Saturday delivery, samplers should notify the RSCC (or designee) and SMO as soon as possible so that SMO will receive the delivery information (including shipping airbill information) by 3:00 PM ET on the Friday prior to delivery. Uploading the electronic COC to the SMO CLPSS Portal sends a notification to SMO and to the laboratory that the samples have been shipped.

8.2.10 Uploading the Electronic COC

The electronic COC Record must be uploaded to the SMO CLPSS Portal as soon as possible after sample shipment. The following is an overview of the steps used to upload the electronic COC Record:

☐ Using **Scribe**:

- Under **Sample Management**, click on the **Chain of Custody** link.
- Click the **Export** button on the top of the menu bar.
- Select the **COC XML File (.xml)** option.
- Select the **COC(s)** to be exported.
- Make sure that the **CLP Region Copy COC XML Template** is checked.
- Click **OK**.
- Provide a **filename** for the exported XML file. Per CLP guidance, the XML file name must reference the Region #, Case Number, and the date.
- Click the **Save** button.

☐ Using the SMO **CLPSS Portal**:

- Select the **Submit Chain of Custody** task.
- **Select** the COC file to upload.
- Enter any **comments** associated with the COC file.
- **Submit** the file; CLPSS provides a confirmation page.
- **Print or download** a copy of the submission summary to keep as a record of the submission.



For a detailed description of how to create and upload electronic COC Record files using Scribe and the SMO CLPSS Portal, refer to each system's user documentation.

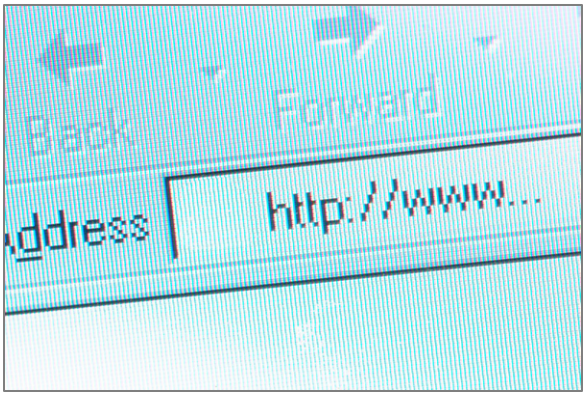
8.2.11 Return of Sample Shipping Containers

CLP laboratories must routinely return sample shipping containers within 14 calendar days following shipment receipt. Therefore, the sampler should also include container return instructions with each shipment. Note that the **samplers** (not the CLP laboratory) are responsible for the costs of return or disposal of these containers and should include shipping airbills bearing the sampler's account number, as well as a return address. **Samplers should use the least expensive return shipping option possible.**

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9.0 SAMPLER RESOURCES

This Guidance document provides a summary of the many resources used to define and manage the sampling process. Samplers may need to refer to the original source documents or websites for further information or clarification. The resources cited herein are listed in this section.



9.1 List of Resources

Table 9-1 provides a list of the resources available to samplers and referenced throughout this Guidance document.

Table 9-1. Resources for Samplers

Resource	Location
U. S. Environmental Protection Agency (EPA) Contract Laboratory Program (CLP) Statements of Work (SOWs)	https://www.epa.gov/clp/superfund-clp-analytical-statements-work-sows
Scribe Software Support	https://ertsupport.org/scribe
Contract Laboratory Program Support System (CLPSS)	https://smoclpss.com/uaa/login
EPA Environmental Response Team (ERT) User Manual for Scribe Contract Laboratory Program (CLP) Sampling	http://www.epaosc.org/sites/ScribeGIS/files/Scribe%20CLP%20User%20Guide.pdf
CLP Guidance Documents	https://www.epa.gov/clp/superfund-clp-analytical-services-guidance-documents-documents
Department of Transportation (DOT) Pipeline and Hazardous Materials Safety Administration (PHMSA) regulations	https://www.phmsa.dot.gov/phmsa-regulations
Use of Dry Ice - Federal Regulations (49CFR 173.217) classified dry ice as Hazard Class 9 *UN 1845* (Hazardous Material).	https://www.gpo.gov/fdsys/pkg/CFR-2004-title49-vol2/xml/CFR-2004-title49-vol2-sec173-217.xml
International Air Transport Association (IATA) transportation regulations	https://www.iata.org
United States Department of Agriculture (USDA) Regulated Organisms and Soil Permits	https://www.aphis.usda.gov/plant_health/permits/organism/soil/
Common Ground Alliance - marking for underground utilities	https://call811.com

Table 9-1. (Continued) Resources for Samplers

Resource	Location
Water Sampling Requirements of Dissolved Metals determinations	***EPA Method SW-846 3005A – Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA or ICP Spectroscopy, Section 2.2:*** Dissolved Metals - The sample is filtered through a 0.45-µm filter at the time of collection and the liquid phase is then acidified at the time of collection with nitric acid. Samples for dissolved metals do not need to be digested as long as the acid concentrations have been adjusted to the same concentration as in the standards. https://www.epa.gov/sites/production/files/2015-12/documents/3005a.pdf
	Clean Water Act (CWA), §136.3 Identification of test procedures. Table II – Required Containers, Preservation Techniques, and Holding Times Footnote 7: For dissolved metals, filter grab samples within 15 minutes of collection and before adding preservatives. For a composite sample collected with an automated sampler (e.g., using a 24-hour composite sampler; see 40 CFR 122.21(g)(7)(i) or 40 CFR Part 403, Appendix E), filter the sample within 15 minutes after completion of collection and before adding preservatives. If it is known or suspected that dissolved sample integrity will be compromised during collection of a composite sample collected automatically over time (e.g., by interchange of a metal between dissolved and suspended forms), collect and filter grab samples to be composited (footnote 2) in place of a composite sample collected automatically. https://www.federalregister.gov/documents/2017/08/28/2017-17271/clean-water-act-methods-update-rule-for-the-analysis-of-effluent
EPA Method SW-846 5035A - Closed-System Purge-and-Trap Extraction for Volatile Organics in Soil and Waste Samples	https://www.epa.gov/sites/production/files/2015-12/documents/5035a_r1.pdf.
NIOSH/OSHA/USCG/EPA Occupational Safety and Health Guidance Manual for Hazardous Waste Site Activities	https://www.osha.gov/Publications/complinks/OSHG-HazWaste/4agency.html
The Roles of Project Managers and Laboratories in Maintaining the Representativeness of Incremental and Composite Soil Samples, EPA/OSWER 9200.1-117FS	https://www.clu-in.org/download/char/RolesofPMsandLabsinSubsampling.pdf

9.2 For More Information

For additional information regarding the CLP or this Guidance document, refer to the Superfund Analytical Services/Contract Laboratory Program website at: https://www.epa.gov/clp

APPENDIX A FUNCTIONS WITHIN A SAMPLING PROJECT

The following table describes Quality Assurance Project Plan (QAPP) sampling requirements based on *EPA Requirements for Quality Assurance Project Plans* (EPA QA/R-5).

Table A-1. QAPP Requirements

Functions Within a Sampling Project	Elements of that Function
Project Management	
Project/Task Organization	Identifies the individuals or organizations participating in the project and defines their specific roles and responsibilities.
Problem Definition/Background	States the specific problem to be solved or decision to be made and includes sufficient background information to provide a historical and scientific perspective for each particular project.
Project/Task Description	Describes the activities to be performed and the schedule for implementation to include: • Measurements to be made during the course of the project. • Applicable technical, regulatory, or program-specific quality standards, criteria, or objectives. • Any special personnel and equipment requirements; assessment tools needed. • A work schedule and any required project and quality records, including types of reports needed.
Quality Objectives and Criteria	Describes the project quality objectives and measurement performance criteria.
Special Training/Certification	Ensures that any specialized training required for modified field sampling techniques, field analyses, laboratory analyses, or data validation should be specified.
Documents and Records	• Itemizes the information and records that must be included in the data report package and specifies the desired reporting format for hardcopy and electronic forms, when used. • Identifies any other records and/or documents applicable to the project such as audit reports, interim progress reports, and final reports that will be produced. • Specifies or references all applicable requirements for the final disposition of records and documents, including location and length of retention period.
Data Generation and Acquisition	
Sampling Process Design (Experimental Design)	• Describes the experimental design or data collection design for the project. • Classifies all measurements as critical or non-critical.
Sampling Methods	• Describes the procedures for collecting samples and identifies sampling methods and equipment. Includes any implementation requirements, support facilities, sample preservation requirements, and materials needed. • Describes the process for preparing and decontaminating sampling equipment to include the disposal of decontamination by-products, selection and preparation of sample containers, sample volumes, preservation methods, and maximum holding times for sampling, preparation, and/or analysis. • Describes specific performance requirements for the method. • Addresses the actions to be taken when a failure in sampling occurs, which party is responsible for corrective action, and how the effectiveness of the corrective action shall be determined and documented.

Table A-1. (Continued) QAPP Requirements

Functions Within a Sampling Project	Elements of that Function
Sample Handling and Custody	• Describes the requirements and provisions for sample handling and custody in the field, transport, and laboratory, taking into account the nature of the samples, the maximum allowable sample holding times before extraction and analysis, and the available shipping options and schedules. • Includes examples of sample labels, custody forms, and sample custody logs.
Analytical Methods	• Identifies the analytical methods and equipment required, including sub-sampling or extraction methods, waste disposal requirements (if any), and specific method performance requirements. • Identifies analytical methods by number, date, and regulatory citation (as appropriate). If a method allows the user to select from various options, the method citations should state exactly which options are being selected. • Addresses the actions to be taken when a failure in the analytical system occurs, who is responsible for corrective action, and how the effectiveness of the corrective action shall be determined and documented. • Specifies the laboratory turnaround time needed, if important to the project schedule. • Specifies whether a field sampling and/or laboratory analysis Case Narrative is required to provide a complete description of any difficulties encountered during sampling or analysis.
Quality Control (QC)	• Identifies required measurement QC checks for both the field and laboratory. • States the frequency of analysis for each type of QC check, and the spike analyte sources and levels. • States or references the required control limits for each QC check and the corrective action(s) required when control limits are exceeded and how the effectiveness of the corrective action shall be determined and documented. • Describes or references the procedures to be used to calculate each of the QC statistics.
Instrument/Equipment Testing, Inspection, and Maintenance	• Describes how inspections and acceptance testing of environmental sampling and measurement systems and their components will be performed and documented. Identifies and discusses the procedure by which final acceptance will be performed by independent personnel. • Describes how deficiencies are to be resolved and when re-inspection will be performed. • Describes or references how periodic preventative and corrective maintenance of measurement or test equipment shall be performed. • Identifies the equipment and/or system requiring periodic maintenance. • Discusses how the availability of spare parts identified in the operating guidance and/or design specifications of the systems will be assured and maintained.
Instrument/Equipment Calibration and Frequency	• Identifies all tools, gauges, instruments, and other sampling, measuring, and test equipment used for data collection activities affecting quality that must be controlled, and at specific times, calibrated to maintain performance within specified limits. • Identifies the certified equipment and/or standards used for calibration. • Describes or references the calibration procedures to be conducted using certified equipment and/or standards with known valid relationships to nationally recognized performance standards. If no such standards exist, documents the basis for calibration. • Indicates how records of calibration shall be maintained and traced to the instrument.
Inspection/Acceptance of Supplies and Consumables	• Describes how and by whom supplies and consumables shall be inspected and accepted for use in the project. • States acceptance criteria for such supplies and consumables.

Table A-1. (Continued) QAPP Requirements

Functions Within a Sampling Project	Elements of that Function
Non-direct Measurements	• Identifies all the types of data needed for project implementation or decision-making that are obtained from non-measurement sources (e.g., computer databases, programs, literature files, historical databases). • Describes the intended use of data. • Defines the acceptance criteria for the use of such data in the project. • Specifies any limitations on the use of the data.
Data Management	• Describes the project data management scheme, tracing the data path from generation in the field or laboratory to their final use or storage. • Describes or references the standard record-keeping procedures, document control system, and the approach used for data storage and retrieval on electronic media.

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APPENDIX B GENERAL CLP SAMPLE COLLECTION GUIDELINES FOR AQUEOUS VOA SAMPLES



Regional guidance and/or specific Project Plan requirements will supersede the guidelines listed below.

Collect the following:

- At least four 40 mL glass containers with polytetrafluoroethylene (PTFE)-lined septa and open top screw-caps that are filled to capacity with no air bubbles, preserved to a pH of 2 with HCl, and cooled to ≤ 6°C, but not frozen, immediately after collection. DO NOT FREEZE THE SAMPLES.

Regular Samples	4 vials (40 mL filled to capacity with no headspace or air bubbles)
Regular Samples Requiring Quality Control (QC) Analysis	4 vials for Sample (40 mL filled to capacity with no headspace or air bubbles) 2 vials for Matrix Spike (MS) (40 mL filled to capacity with no headspace or air bubbles) 2 vials for Matrix Spike Duplicate (MSD) (40 mL filled to capacity with no headspace or air bubbles)

- If Selected Ion Monitoring (SIM) analysis is requested, at least two additional 40 mL glass containers with PTFE-lined septa and open top screw-caps that are filled to capacity with no air bubbles, preserved to a pH of 2 with HCl, and cooled to ≤ 6°C, but not frozen, immediately after collection.

Regular Samples With SIM Analysis	4 vials for Sample (40 mL filled to capacity with no headspace or air bubbles) 2 vials (40 mL filled to capacity with no headspace or air bubbles)

Test for Carbonates, Residual Chlorine, Oxidants, and Sulfides:

- It is important that samplers obtain Regional guidance when testing and ameliorating for:
  - Carbonates;
  - Residual chlorine (e.g., municipal waters or industrial waste waters that are treated with chlorine prior to use or discharge); or
  - Oxidants.
- Volatile Organic Analyte (VOA) samples containing carbonates react with the acid preservative causing effervescence (due to formation of carbon dioxide), which can cause loss of volatile analytes.
- Residual chlorine present in VOA samples can continue to react with dissolved organic matter. This continuous reaction may lead to inaccurate quantitation of certain analytes present in the sample at the time of collection.
- Residual chlorine and oxidants present in VOA samples can cause degradation of certain volatile analytes (e.g., styrene).

Perform the following for *Pre-Preserved* Vials:

1. Pour the sample slowly down the edge of the sample vial to avoid excess aeration or agitation of the sample during filling.
2. Fill the vial completely so that a reverse (convex) meniscus is present and ensure that there are no air bubbles present (either in the body or especially at the top of the vial).
3. Place the septum on the vial so that the PTFE side is in contact with the sample, and then firmly tighten the cap.

4. Gently flip the vial a few times to ensure that the sample is mixed with the acid preservative.
5. While holding the vial inverted, gently tap the sample to check for air bubbles (either in the body or especially at the top of the inverted vial).
6. If air bubbles are present, discard the sample and select a new vial in which to collect a new sample. Repeat Steps 1 - 5 above.
7. Do NOT mix or composite samples for VOAs.
8. Cool sample to a temperature of ≤ 6°C, but not frozen. Samplers should begin the cooling process in the field as samples are being collected. Double-bagged ice should be used. DO NOT FREEZE WATER SAMPLES.
9. Immediately transfer the vial to the sample shuttle (device that contains a "set" of VOA vials) once it has been collected. Do NOT allow ice to touch the vials.

Perform the Following for *Empty* Vials:

1. Rinse the vial with sample water prior to actual sample collection and preservation.



Regions vary in their approach to pre-rinsing and/or re-using sample vials (e.g., some Regions do not recommend pre-rinsing and/or re-use of pre-cleaned containers using sample water). Be sure to follow Regional guidance.

2. Add 1-2 mL of acid preservative to the vial. Check to ensure that the sample requires a preservative (follow Regional guidance).
3. Pour the sample slowly down the edge of the sample vial to avoid excess aeration and agitation of the sample.
4. Fill the vial completely so that a reverse (convex) meniscus is present and ensure that there are no air bubbles present (either in the body or especially at the top of the vial).
5. Place the septum on the vial so that the PTFE side is in contact with the sample, and then firmly tighten the cap.
6. Gently flip the vial a few times to ensure that the sample is mixed with the acid preservative.
7. While holding the vial inverted, gently tap the vial to check for air bubbles (either in the body or especially at the top of the vial).
8. If an air bubble is present that is larger than ~6 mm (pea size), discard the sample and collect a new sample using the same sample vial. Repeat Steps 1 - 7 above.
9. Check the re-collected sample for air bubbles. If there are air bubbles after three consecutive attempts to eliminate air bubbles by the addition of sample water, the entire sample and sample vial should be discarded and a new sample collected without preservative. Note the absence of preservative due to the impact on holding time.
10. Do NOT mix or composite samples for VOAs.
11. Cool sample to a temperature of ≤ 6°C, but not frozen. Samplers should begin the cooling process in the field as samples are being collected. Double-bagged ice should be used. DO NOT FREEZE WATER SAMPLES.
12. Immediately transfer the vial to the sample shuttle (device which contains a "set" of VOA vials) once it has been collected. Do NOT allow ice to touch the vials.

Things to Remember:

- Samples should be shipped as soon as possible, preferably on the same day as sample collection to avoid exceeding sample holding times. If overnight transit is not possible, samples should be maintained at ≤ 6°C, but not frozen, until they are shipped to the laboratory.
- If samples are not preserved (a requirement for certain analyses), the technical holding time is shortened to 7 days.

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APPENDIX C CLP SAMPLE COLLECTION GUIDELINES FOR SOIL VOA SAMPLES BY SW-846 METHOD 5035A, TCLP EXTRACTION BY EPA METHOD SW-846 METHOD 1311, AND SPLP EXTRACTION BY EPA SW-846 METHOD 1312

A. Preferred Options for the Contract Laboratory Program (CLP) are Options 1, 2, 3, and 4:

This analytical method employs sample vials that are filled and weighed in the field and never opened during the analytical process. For this reason, sampling personnel should be equipped with a portable balance capable of weighing to 0.01g.



Soil samples must be placed on their side prior to being frozen or placed on ice. Vials are placed on their side so that the septum is wet on the inside, thereby preventing vapor leaks around it, in case any bubbles form. Also, in case the samples freeze, the water will expand into the flexible septum rather than breaking the vial. Dry ice or field freezers are the only options.

Option 1.

Closed-system Vials:

Container - tared or preweighed 40 mL Volatile Organic Analyte (VOA) Analysis vial containing a magnetic stir bar.

Collect 5 g of soil per vial (iced or frozen in the field). Check the pre-tared weight of the (dry) Volatile Organic Analyte (VOA) vials prior to departure for the sampling event under controlled conditions. Weigh vials and soil samples to the nearest 0.01 g. This check is to ensure that the original weight was properly recorded.

Regular Samples	3 Vials - Dry (5 g soil per vial) 1 Vial - Dry (filled with soil, no headspace) 4 Total Vials
Regular Samples Requiring Quality Control (QC) Analysis	11 Vials - Dry (5 g soil per vial) 1 Vial - Dry (filled with soil, no headspace) 12 Total Vials

Option 2.

Closed-system Vials Containing Water:

Container - tared or pre-weighed 40 mL VOA vial containing a magnetic stir bar and 5 mL water.

Collect 5 g of soil per vial (iced or frozen in the field). Weigh vials and soil samples to the nearest 0.01 g.

Regular Samples	3 Vials with water added (5 g soil and 5 mL water per vial) 1 Vial - Dry (filled with soil, no headspace) 4 Total Vials (3 with water and 1 dry)
Regular Samples Requiring QC Analysis	11 Vials with water added (5 g soil and 5 mL water per vial) 1 Vial - Dry (filled with soil, no headspace) 12 Total Vials (11 with water and 1 dry)

Option 3.

Container - 5 g Samplers or equivalent and coring tool used as a transport device.



All samples should be iced or frozen in the field and bagged individually.

Regular Samples	3 Samplers (5 g soil per Sampler) 1 Vial - Dry (filled with soil, no headspace) 4 Total (3 Samplers and 1 Vial)
Regular Samples Requiring QC Analysis	11 Samplers (5 g soil per Sampler) 1 Vial - Dry (filled with soil, no headspace) 12 Total (11 Samplers and 1 Vial)

Option 4.

Closed-system Vials:

Container - tared or preweighed 40 mL VOA vial.

Collect 25 g of soil per vial (iced or frozen in the field). Check the pre-tared weight of the (dry) VOA vials prior to departure for the sampling event under controlled conditions. Weigh vials and soil samples to the nearest 0.01 g. This check is to ensure that the original weight was properly recorded.

Regular Samples	6 Vials - Dry (25 g soil per vial)

B. Options 5, 6, and 7 are NOT preferred options for the CLP:

Option 5.

Closed-system Vials:

Container - tared or preweighed 40 mL VOA vial containing a magnetic stir bar and preservative.

Collect 5 g of soil per vial and add Sodium bisulfate ($NaHSO_4$) preservative (5 mL water + 1 g $NaHSO_4$) - iced in the field.

Caution: **This option is NOT a Preferred Option for the CLP because:**

$NaHSO_4$ preservation creates low pH conditions that will cause the destruction of certain CLP target analytes (e.g., vinyl chloride, trichloroethene, trichlorofluoromethane, cis- and trans-1,3-dichloropropene). Projects requiring the quantitation of these analytes should consider alternative sample preservation methods. $NaHSO_4$ also cannot be used on carbonaceous soils. Check the soil before using this method of collection! Soils can be checked by placing a test sample in a clean vial, then adding several drops of $NaHSO_4$ solution. If the soil bubbles, use Option 5b and note this issue on the Traffic Report/Chain of Custody (TR/COC) Record.

Option 5a. Samples preserved in the field

Regular Samples	3 Vials with $NaHSO_4$ preservative added (5 g soil per vial) 1 Vial - Dry (filled with soil, no headspace) 4 Total Vials (3 with $NaHSO_4$ preservative and 1 without)
Regular Samples Requiring QC Analyses	6 Vials with $NaHSO_4$ preservative added (5 g soil per vial) 2 Vials - Dry (filled with soil, no headspace) 8 Total Vials (6 with $NaHSO_4$ and 2 without)

Option 5b. Samples to be preserved by the laboratory (No $NaHSO_4$ preservative is added to these samples in the field).

Regular Samples	3 Vials - Dry (5 g soil per vial) 1 Vial - Dry (filled with soil, no headspace) 4 Total Vials
Regular Samples Requiring QC Analyses	6 Vials - Dry (5 g soil per vial) 2 Vials - Dry (filled with soil, no headspace) 8 Total Vials

Option 6.

Methanol Preservation (medium-level analysis only):

Container - tared or pre-weighed 40 mL VOA vials containing 5 mL methanol.

Collect 5 g of soil per vial (iced in the field).

Caution: **This is NOT a preferred option for the CLP because:**

Samples preserved with methanol can only be analyzed by the medium-level method. Low-level Contract Required Quantitation Limits (CRQLs) cannot be achieved when samples are preserved in this manner. If this soil option is used, then samples for low-level analysis by one of the other options should also be collected and accompany the medium-level soil.

Additional problems associated with use of methanol as a preservative in the field include:

- Possible contamination of the methanol by sampling-related activities (e.g., absorption of diesel fumes from sampling equipment);
- Leakage of methanol from the sample vials during shipping, resulting in loss of VOAs prior to analysis.

Regular Samples	2 Vials (5 g soil and 5 mL methanol per vial) 1 Vial - Dry (filled with soil, no headspace) 3 Total Vials (2 with methanol and 1 dry)
Regular Samples Requiring QC Analyses	6 Vials (5 g soil and 5 mL methanol per vial) 1 Vial -Dry (filled with soil, no headspace) 7 Total Vials (6 with methanol and 1 dry)



If shipping samples that contain methanol as a preservative, a shipping label must be used to indicate the presence of methanol. This label must also contain the United Nations (UN) identification number for methanol (UN 1230), and indicate Limited Quantity. Refer to http://www.phmsa.dot.gov for additional information about the safe shipping of methanol.

Option 7.

Glass Containers filled with sample - No Headspace:

Container - 4 oz. Glass Jars.

Glass container filled with soil with no headspace and iced.

Caution: This is NOT a preferred option for the CLP because:

Samples collected in this manner lose most of their volatile analytes prior to analysis when the sample containers are opened and sub-sampled in the laboratory. This option is only available when required by the Region.

Regular Samples	2 Glass Jars (4 oz.) filled with sample, no headspace 1 Vial - Dry (filled with soil, no headspace) 3 Total Containers
Regular Samples Requiring QC Analyses	2 Glass Jars (4 oz.) filled with sample, no headspace 1 Vial - Dry (filled with soil, no headspace) 3 Total Containers

C. Caution:

1. Extreme care should be taken to ensure that frozen or iced samples do not break during shipment.
2. Before adding soil to pre-weighed vials containing a stir bar, weigh the vials to confirm the tared weight. If the weight varies by more than 0.1 g, record the new weight on the label and the sample documentation. Do NOT add labels to these vials once the tared weight has been determined or confirmed.

D. Dry Samples:

Collect in a dry 40 mL VOA vial (or a 4 oz. wide mouth jar) with no headspace. No water, $NaHSO_4$, or methanol is added to this sample. This sample is collected to determine moisture content; therefore, it does not need to be tared or have a stir bar.

E. Iced or Frozen Samples:

1. Iced means cooled to $\leq 6°C$, but not frozen, immediately after collection.
2. Frozen means cooled to $< -7°C$ immediately after collection.
3. Dry ice is not a long-term freezing agent and may contaminate samples.

F. Sample Delivery:

The CLP strongly recommends that all samples arrive at the laboratory by close of business the next day following sample collection.

G. Notes:

1. For Options 2, 5, and 6, check the weight of the pre-tared VOA vials plus liquid in the field due to the possibility that liquid may have leaked out during packing, transit, or deployment in the field just prior to sampling. This check is to ensure that the original weight is properly recorded.
2. For Option 5, samples can be preserved with $NaHSO_4$ either:
   - In the field; or
   - The samplers must evaluate whether $NaHSO_4$ would be compatible with the sample prior to requesting the laboratory to add it to the sample.

3. Regional Quality Assurance Project Plans (QAPPs) may require the use of Option 6. Note that this option is for medium-level analysis ONLY.
4. If water, methanol, or $NaHSO_4$ preservative is added to the vials in the field, a field blank containing the appropriate preservative used in the vials should be sent to the laboratory for analysis.

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APPENDIX D CLP SAMPLE COLLECTION REQUIREMENTS BY ANALYSIS TYPE

The following tables (D-1 through D-4) specify the number of containers of each type necessary for each analysis based on the sampling methodology and QC requirements.

Table D-1. Sample Collection Requirements for CLP Organics [Volatile Organic Analytes (VOAs) Only]

Analysis	Matrix	Sample Type	Container Type[1]	Closure[2]	Minimum Number of Containers Needed				Minimum Volume/Mass[3]	Important Notes	Preservative[4]	Technical Holding Time[5]
					with Water	Dry	% Moisture	TOTAL				
VOAs	Water	Samples Only	40 mL amber or clear glass vial, 24 mm neck finish.	Polypropylene or phenolic, open-top screw-cap, 1.5 cm opening, 24-400 size.	-	-	-	**4**	Fill to capacity	Containers/vials must be filled to capacity with no headspace or air bubbles. Refer to Appendix B for samples requiring QC analyses. If amber containers are not available, the samples should be protected from light.	Preserve to a pH of 2 with HCl and cool to ≤ 6°C, but not frozen, immediately after collection. DO NOT FREEZE water samples.	14 days
		Samples with SIM			-	-	-	**6**				
		Samples with Matrix Spike (MS)/MS Duplicate (MSD)[6]			-	-	-	**8**				
	Soil/ Sediment	Samples Only	**OPTION 1** Closed-system 40 mL amber or clear glass vial containing magnetic stirrer, 24 mm neck finish.	Polypropylene or phenolic, open-top screw-cap, 1.5 cm opening, 24-400 size.	-	3	1	**4**	5g	Place samples on side prior to being iced.[7] Refer to Appendix C for samples requiring QC analyses.	Frozen to < -7°C **OR** Iced to ≤ 6°C, but not frozen.	14 days **OR** 48 hours (unpreserved)[7]
		Samples with MS/MSD[6]			-	11	1	**12**				
		Samples Only	**OPTION 2** Closed-system 40 mL amber or clear glass vial containing magnetic stirrer, 24 mm neck finish and 5 mL water.	Polypropylene or phenolic, open-top screw-cap, 1.5 cm opening, 24-400 size.	3	-	1	**4**	5 g	Place samples on side prior to being iced.[7] Refer to Appendix C for samples requiring QC analyses.	Frozen to < -7°C **OR** Iced to ≤ 6°C, but not frozen.	14 days **OR** 48 hours (unpreserved)[7]
		Samples with MS/MSD[6]			11	-	1	**12**				

Table D-1. (Continued) Sample Collection Requirements for CLP Organics [Volatile Organic Analytes (VOAs) Only]

Analysis	Matrix	Sample Type	Container Type[1]	Closure[2]	Minimum Number of Containers Needed				Minimum Volume/Mass[3]	Important Notes	Preservative[4]	Technical Holding Time[5]
					with Water	Dry	% Moisture	TOTAL				
		Samples Only	**OPTION 3** Coring tool used as a transport device.		-	3	1	**4**	5 g	Refer to Appendix C for samples requiring QC analysis. Place samples on side prior to being iced.[7]	Frozen to < -7°C **OR** Iced to ≤ 6°C, but not frozen.	14 days (frozen) **OR** 48 hours (iced)[7]
		Samples with MS/MSD[6]			-	11	1	**12**				
		Samples for TCLP/SPLP Only	**OPTION 4** Closed-system 40 mL amber or clear glass vial 24 mm neck finish.	Polypropylene or phenolic, open-top screw-cap, 1.5 cm opening, 24-400 size.	-	6	-	**6**	150 g[8]	Place samples on side prior to being iced.[7]	Iced to ≤ 6°C but not frozen.	14 days

Notes

1 Vials for soil analysis are typically pre-labeled and tared. Vials for water analysis are not pre-labeled or tared.

2 Septums for VOA vials 24 mm disc of Polytetrafluoroethylene (PTFE) bonded to silicone for a total thickness of 0.100 - 0.125 in.

3 Minimum volume/mass to be collected in order to ensure sample analysis can be performed. Collect additional volume for MS/MSD samples to allow for sufficient volume for these analyses in the event sample volume is lost as a result of sample containers breaking, leaking, or laboratory accidents.

4 Check Regional guidance regarding use of acid as a preservative of samples that may contain carbonates, residual chlorine, and other oxidants.

5 Technical holding time is calculated from the time of sample collection to sample extraction, and determined as 14 days for preserved (frozen or iced) samples and 48 hours for non-preserved (iced) samples.

6 For Gas Chromatograph/Mass Spectrometer (GC/MS) organic analyses, a Region may decide to reference Deuterated Monitoring Compounds (DMCs) rather than MS/MSD for accuracy and precision.

7 Vials are placed on their side so that the septum is wet on the inside, thereby preventing vapor leaks around it, in case any bubbles form. Also, in case samples freeze, the water will expand into the flexible septum rather than breaking the vial.

8 Samples with low solids content that are scheduled for Toxicity Characteristic Leaching Procedure (TCLP) or Synthetic Precipitation Leaching Procedure (SPLP) may require up to 1000 mL total volume.

Table D-2. Sample Collection Requirements for CLP Organics [Semivolatile Organic Analytes (SVOAs), Pesticides, and Aroclors]

Analysis	Matrix	Sample Type	Container Type	Closure	Minimum Volume/Mass[1]	Important Notes	Preservative/ Collection	Technical Holding Time[2]
SVOAs	Water[3]	Samples Only	1 L amber round glass bottle, 33 mm pour-out neck finish.	Polypropylene or phenolic cap, 33-430 size; 0.015 in. PTFE liner.	2 L (per Test)	If amber containers are not available, the samples should be protected from light.	Cool all samples to ≤ 6°C, but not frozen, immediately after collection. DO NOT FREEZE water samples.	7 days
		Samples with SIM			2 L			
		Samples with MS/MSD			5 L			
		Samples with SIM with MS/MSD			5 L			
	Soil/ Sediment/ Waste[4]	Samples Only	One 8 oz. short, wide mouth, straight-sided, glass jar, 70 mm neck finish or two 4 oz. tall, wide mouth, straight-sided, glass jar, 48 mm neck finish.	Polypropylene or phenolic cap, 70-400 size; 0.015 in. PTFE liner. Or Polypropylene or phenolic cap, 48-400 size; 0.015 in. PTFE liner.	150 g		Cool all samples to ≤ 6°C, but not frozen, immediately after collection.	14 days
		Samples with SIM						
		Samples with MS/MSD	Two 8 oz. short, wide mouth, straight-sided, glass jars, 70 mm neck finish or three 4 oz. tall, wide mouth, straight-sided, glass jar, 48 mm neck finish.		300 g			
		Samples with SIM with MS/MSD						
		Samples for Only TCLP/SPLP	Two 8 oz. short, wide mouth, straight-sided, glass jars, 70 mm neck finish or four 4 oz. tall, wide mouth, straight-sided, glass jar, 48 mm neck finish.		450 g			

Table D-2. (Continued) Sample Collection Requirements for CLP Organics [Semivolatile Organic Analytes (SVOAs), Pesticides, and Aroclors]

Analysis	Matrix	Sample Type	Container Type	Closure	Minimum Volume/Mass[1]	Important Notes	Preservative/ Collection	Technical Holding Time[2]
Pesticides	Water[3, 5]	Samples Only	1 L amber round glass bottle, 33 mm pour-out neck finish.	Polypropylene or phenolic cap, 33-430 size; 0.015 in. PTFE liner.	2 L	If amber containers are not available, the samples should be protected from light.	Cool all samples to ≤ 6°C, but not frozen, immediately after collection. DO NOT FREEZE water samples.	7 days
		Samples with MS/MSD			5 L			
	Soil/ Sediment/ Waste[4]	Samples Only	One 8 oz. short, wide mouth, straight-sided, glass jar, 70 mm neck finish or two 4 oz. tall, wide mouth, straight-sided, glass jar, 48 mm neck finish.	Polypropylene or phenolic cap, 70-400 size; 0.015 in. PTFE liner. Or Polypropylene or phenolic cap, 48-400 size; 0.015 in. PTFE liner.	150 g		Cool all samples to ≤ 6°C, but not frozen, immediately after collection.	14 days
		Samples with MS/MSD	Two 8 oz. short, wide mouth, straight-sided, glass jars, 70 mm neck finish or three 4 oz. tall, wide mouth, straight-sided, glass jar, 48 mm neck finish.		300 g			
		Samples for Only TCLP/SPLP	Two 8 oz. short, wide mouth, straight-sided, glass jars, 70 mm neck finish or four 4 oz. tall, wide mouth, straight-sided, glass jar, 48 mm neck finish.		450 g			
	Wipes	Samples Only	20 mL glass vial.	Polypropylene or phenolic cap, PTFE liner.	1 wipe			14 days
Aroclors	Water[3, 5]	Samples Only	1 L amber round glass bottle, 33 mm pour-out neck finish.	Polypropylene or phenolic cap, 33-430 size; 0.015 in. PTFE liner.	2 L	If amber containers are not available, the samples should be protected from light.	Cool all samples to ≤ 6°C, but not frozen, immediately after collection. DO NOT FREEZE water samples.	7 days
		Samples with MS/MSD			5 L			
	Soil/ Sediment/ Waste[4]	Samples Only	One 8 oz. short, wide mouth, straight-sided, glass jar, 70 mm neck finish or two 4 oz. tall, wide mouth, straight-sided, glass jar, 48 mm neck finish.	Polypropylene or phenolic cap, 70-400 size; 0.015 in. PTFE liner. Or Polypropylene or phenolic cap, 48-400 size; 0.015 in. PTFE liner.	150 g		Cool all samples to ≤ 6°C, but not frozen, immediately after collection.	14 days
		Samples with MS/MSD	Two 8 oz. short, wide mouth, straight-sided, glass jars, 70 mm neck finish or three 4 oz. tall, wide mouth, straight-sided, glass jar, 48 mm neck finish.		300 g			
	Wipes	Samples Only	20 mL glass vial.	Polypropylene or phenolic cap, PTFE liner.	1 wipe			14 days

Table D-2. (Continued) Sample Collection Requirements for CLP Organics [Semivolatile Organic Analytes (SVOAs), Pesticides, and Aroclors]

Notes

1 Minimum volume/mass to be collected in order to ensure sample analysis can be performed.

2 This technical holding time is calculated from the time of sample collection to sample extraction. Sample extracts are to be analyzed within 40 days of extraction. It is recommended that samplers ship samples to the laboratory on the same day that they are collected, or as soon as possible thereafter.

3 An aqueous sample for SVOA analysis would require the field sampler to collect at least 2 L for field samples and at least 3 L for the MS and MSD samples for a total volume of 5 L. If Pesticide or Aroclor MS/MSD analyses are required for the same sample, only two extra 1 L bottles of each sample would be needed, for a total of seven bottles (which includes samples and MS/MSD for both methods). Collect additional volume for MS/MSD samples to allow for sufficient volume for these analyses in the event sample volume is lost as a result of sample containers breaking, leaking, or laboratory accidents.

4 If one or two extractable analyses are required for soil/sediment, only a single 8 oz. or two 4 oz. jars are required. If three extractable analyses are required, two 8 oz. or four 4 oz. jars are required. The number of jars should be doubled if MS/MSD is required.

5 Samplers must test for chlorine in aqueous samples in the field upon collection. Refer to the Sampling and Analysis Plan (SAP) and Appendix E of this document for guidance.

Table D-3. Sample Collection Requirements for CLP Inorganics

Analysis	Matrix	Sample Type	Container Type	Closure	Minimum Volume/ Mass[1]	Important Notes	Preservative/ Collection[2]	Technical Holding Time[3]
Metals/ICP-AES, Metals/ICP-MS, and/or Mercury/CVAA	Water	Samples Only	0.5 L high density polyethylene, cylinder-round bottle, 28 mm neck finish.	Polyethylene cap, ribbed, 28-410 size; F217 polyethylene liner.	0.5 L	DO NOT FREEZE water samples.	Acidify to pH < 2 with HNO_3 immediately after collection.[4]	6 months for all metals except Mercury (28 days)
		Samples with MS/Duplicate			1 L			
	Soil/ Sediment/ Waste[5]	Samples Only	One 8 oz. short, wide mouth, straight-sided, glass jar, 70 mm neck finish.	Polypropylene or phenolic cap, 70-400 size; 0.015 in. PTFE liner.	Fill to capacity		Cool to ≤ 6°C, but not frozen, immediately after collection.	6 months
		Samples with MS/Duplicate						
		Samples for Only TCLP/SPLP	Two 8 oz. short, wide mouth, straight-sided, glass jars, 70 mm neck finish.					
Metals/ICP-AES[6]	Wipe	Samples Only	1 qt. polymer zip-top bag.	Has self-closing mechanism.	N/A		Store at room temperature.	6 months
Cyanide/ Spectrophotometric Determination	Water	Samples Only	0.5 L high density polyethylene, cylinder-round bottle, 28 mm neck finish.	Polyethylene cap, ribbed, 28-410 size; F217 polyethylene liner.	0.5 L	DO NOT FREEZE water samples.	To neutralize residual chlorine, add 0.6 g ascorbic acid for each liter of sample collected, immediately upon collection.[7] Add NaOH until pH > 10 and cool to ≤ 6°C, but not frozen, immediately after collection.	14 days
		Sample with MS/Duplicate			1 L			
	Soil/ Sediment/ Waste[5]	Samples Only	One 8 oz. short, wide mouth, straight-sided, glass jar, 70 mm neck finish.	Polypropylene or phenolic cap, 70-400 size; 0.015 in. PTFE liner.	Fill to capacity		Cool to ≤ 6°C, but not frozen, immediately after collection.	14 days
		Samples with MS/Duplicate						
		Samples for SPLP						

Table D-3. (Continued) Sample Collection Requirements for CLP Inorganics

Analysis	Matrix	Sample Type	Container Type	Closure	Minimum Volume/ Mass[1]	Important Notes	Preservative/ Collection[2]	Technical Holding Time[3]
Anions/Ion Chromatography (IC)[8]	Water	Samples Only	125 mL high density polyethylene, cylinder-round bottle, 28 mm neck finish.	Polyethylene or polypropylene cap, ribbed.	125 mL	DO NOT FREEZE water samples.	For the analysis of nitrate, nitrite, orthophosphate, and sulfate cool to ≤ 6°C, but not frozen, immediately after collection. Do not allow samples for orthophosphate to be held at room temperature more than 12 hours.	48 hours for nitrate, nitrite, and orthophosphate. 28 days for bromide, chloride, fluoride, and sulfate.
		Samples with MS/Duplicate			250 mL			
	Soil	Samples Only	One 8 oz. short, wide mouth, straight-sided, glass jar, 70 mm neck finish.	Polypropylene or phenolic cap, 70-400 size; 0.015 in. PTFE liner.	Fill to capacity		Cool to ≤ 6°C, but not frozen, immediately after collection.	48 hours for nitrate, nitrite, and orthophosphate. 28 days for bromide, chloride, fluoride, and sulfate.
		Samples with MS/Duplicate						
Hexavalent Chromium/Ion Chromatography (IC)[8]	Water	Samples Only	125 mL high density polyethylene or polypropylene, cylinder-round bottle, 28 mm neck finish.	Polyethylene or polypropylene cap, ribbed.	125 mL	DO NOT FREEZE water samples.	Cool to ≤ 6°C, but not frozen, immediately after collection. Field filter. Preserve to pH > 8 using either liquid preservative [NH_4OH/$(NH_4)_2SO_4$ 1 mL per 100 mL sample] or solid mix [13.3 mg Na_2CO_3/10.5 mg $NaHCO_3$/33 mg $(NH_4)_2SO_4$ per sample].	28 days
		Samples with MS/Duplicate			250 mL			
Total Organic Carbon (TOC)[8]	Water	Samples Only	125 m L round glass bottle, 22 mm pour-out neck finish.	Polypropylene or phenolic cap, PTFE liner.	125 mL	DO NOT FREEZE water samples.	Acidify to pH < 2 with H_2SO_4 or H_3PO_4 immediately after collection and cool to ≤ 6°C, but not frozen.	28 days
		Samples with MS/Duplicate			250 mL			
	Soil	Samples Only	4 oz. (120 mL) tall, wide mouth, straight-sided, amber glass jar, 48 mm neck finish.	Polypropylene or phenolic cap, 48-400 size; 0.015 in. PTFE liner.	Fill to capacity		Cool to ≤ 6°C, but not frozen, immediately after collection.	28 days
		Samples with MS/Duplicate						

Table D-3. (Continued) Sample Collection Requirements for CLP Inorganics

Notes

1 Minimum volume/mass to be collected in order to ensure sample analysis can be performed.
2 Check Regional guidance regarding use of acid as a preservative of samples that may contain carbonates, residual chlorine, and other oxidants.
3 This technical holding time is calculated from the time of sample collection to sample analysis.
4 Water samples collected for total metal and filtered metal analyses from the same sampling location must be assigned separate (unique) CLP Sample Numbers.
5 Only one 8 oz. jar is needed for soil/sediment when all metals (including mercury) and cyanide analyses are required for soil/sediment samples. Collect more than one jar when TCLP or SPLP are scheduled.
6 Wipe materials have varied from laboratory tissues (e.g., Kimwipes®) to pre-moistened “baby wipes” from the nearest store.
7 Samplers must test for sulfide and oxidizing agents (e.g., chlorine) in aqueous samples in the field upon collection. Refer to the SAP for guidance. Sulfides adversely affect the analytical procedure. The following can be done to test for and neutralize sulfides. Place a drop of the sample on lead acetate test paper to detect the presence of sulfides. If sulfides are present, treat 25 mL more of the sample than that required for the cyanide determination with powdered cadmium carbonate or lead carbonate. Yellow cadmium sulfide or black lead sulfide precipitates if the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper. Filter the solution through a dry filter paper into a dry beaker, and from the filtrate measure the sample to be used for analysis. Avoid a large excess of cadmium carbonate and a long contact time in order to minimize a loss by complication or occlusion of cyanide on the precipitated material. Sulfide removal should be performed in the field, if practical, prior to pH adjustment with NaOH.
8 Analyses available through Modified Analysis only.

Table D-4. Sample Collection Requirements for CLP Chlorinated Dibenzo-*p*-Dioxins/Chlorinated Dibenzofurans (CDDs/CDFs) and Chlorinated Biphenyl Congeners (CBCs)

Analysis	Matrix	Container Types	Closure	Minimum Volume/Mass[1]	Important Notes	Preservative	Technical Holding Time[2]
CDD/CDF and CBC	Water[3]	1 L amber round glass bottle, 33 mm pour-out neck finish.	Polypropylene or phenolic cap, 33-430 size; 0.015 in. PTFE liner.	2L	If amber containers are not available, the samples should be protected from light.	Cool all samples to ≤ 6°C, but not frozen, immediately after collection. DO NOT FREEZE water samples. If residual chlorine is present, add 80 mg sodium thiosulfate/L of water. If pH is greater than 9, adjust to 7-9 with sulfuric acid.	1 year
	Soil/Sediment/Oil/ Sludge Ash/Biosolids	8 oz. short, wide mouth, straight-sided, glass jar, 70 mm neck finish or 4 oz. (120 mL) tall, wide mouth, straight-sided, amber glass jar, 48 mm neck finish.	Polypropylene or phenolic cap, 70-400 size; 0.015 in. PTFE liner. Or Polypropylene or phenolic cap, 48-400 size; 0.015 in. PTFE liner.	Fill to capacity	If amber containers are not available, the samples should be protected from light.	Cool all samples to ≤ 6°C, but not frozen, immediately after collection.	
	Tissue	Heavy duty aluminum foil as transport device. 8 oz. short, wide mouth, straight-sided, glass jar, 70 mm neck finish or 4 oz. (120 mL) tall, wide mouth, straight-sided, amber glass jar, 48 mm neck finish.	Polypropylene or phenolic cap, 70-400 size; 0.015 in. PTFE liner. Or Polypropylene or phenolic cap, 48-400 size; 0.015 in. PTFE liner.	20 g for each analytical method	If amber containers are not available, the samples should be protected from light.	Cool all samples to ≤ 6°C, or freeze immediately after collection.	

Notes

1 Minimum volume/mass to be collected in order to ensure sample analysis can be performed.

2 This technical holding time is calculated from the time of sample collection to sample extraction. Sample extracts are to be analyzed within 1 year of extraction when sample extracts are stored under the appropriate conditions. It is recommended that samplers ship samples to the laboratory on the same day that they are collected, or as soon as possible thereafter.

3 Samplers must test for chlorine in aqueous samples in the field upon collection. Refer to the SAP for guidance.

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APPENDIX E SAMPLING TECHNIQUES AND CONSIDERATIONS

During a sampling event, samplers are expected to follow prescribed sampling techniques. Samplers should also be aware of any special sampling considerations, contaminant issues, and sample compositing and mixing methods that could affect their sampling efforts.



Regional guidance will take precedence over any of the techniques and considerations listed below.

1. General Sampling Techniques

Information regarding surface water, groundwater, sediment, soil, and surface wipe sampling can be found in many documents including, but not limited to, the following sources:

- *Compendium of ERT Surface Water and Sediment Sampling Procedures*, EPA/540/P-91/005
- *Compendium of ERT Soil Sampling and Surface Geophysics Procedures*, EPA/540/P-91/006
- *Compendium of ERT Groundwater Sampling Procedures*, EPA/540/P-91/007
- *The Roles of Project Managers and Laboratories in Maintaining the Representativeness of Incremental and Composite Soil Samples*, EPA/OSWER 9200.1-117FS
- *Lead in Surface Wipe Samples*, NIOSH Method 9100, August 15, 1994
- *Elements on Wipes*, NIOSH Method 9102, March 15, 2003
- *Surface Wipe Sampling Procedure*, IH75190, Brookhaven National Laboratory, Industrial Hygiene Group, May 10, 2011

When working with potentially hazardous materials, samplers should follow U.S. Environmental Protection Agency (EPA) and Occupational Health and Safety Administration (OSHA) requirements, specific health and safety procedures, and Department of Transportation (DOT) requirements.

2. Special Sampling Considerations

Samplers should refer to the Regional Standard Operating Procedures (SOPs) to obtain specific procedures for proper collection and preservation of samples in the field. For additional guidance regarding sampling for Volatile Organic Analytes (VOAs) Analysis in soil and water, see Appendices B and C. Samplers should obtain Regional guidance when testing and ameliorating for:

- Carbonates in VOA soil and water samples
- Residual chlorine in VOA soil and water samples, or in aqueous cyanide samples
- Oxidants in VOA soil and water samples
- Sulfides and oxidizing agents in aqueous cyanide samples

3. Contaminant Sampling

Certain analytes can be detected in the parts-per-billion (ppb) and/or parts-per-trillion (ppt) range. Extreme care MUST be taken to prevent cross-contamination of these samples. The following precautions should be taken when trace contaminants are a concern:

- Disposable gloves should be worn for each different location sampled.
- When collecting both surface water and sediments, surface water samples should be collected first to reduce the chance of sediment dispersal into the surface water, and the resulting loss of surface water sample integrity.

- Sampling should occur progressively, from the least to the most contaminated area, if this information is known to the sampling team.
- Samplers should use equipment constructed of polytetrafluoroethylene (PTFE), stainless steel, or glass that has been properly pre-cleaned for the collection of samples for trace organic and/or inorganic analyses. Equipment constructed of plastic or polyvinyl chloride (PVC) should NOT be used to collect samples for trace organic analyte analyses.
- Equipment constructed of stainless steel should NOT be used to collect samples for trace metals analyses.

4. Sample Compositing

Sample compositing is a site-specific activity that must be conducted according to the Sampling and Analysis Plan (SAP). Compositing is typically used for large sites to improve the precision (i.e., lower the variance) of the estimated average contaminant concentrations. **Samples for VOA analysis should NOT be composited to minimize loss of analytes.**

Composite samples consist of a series of discrete grab samples that are mixed together to characterize the average composition of a given material. The discrete samples are usually of equal volume, but may be weighted to reflect an increased flow or volume. Nevertheless, all discrete samples must be collected in an identical manner and the number of grab samples forming a composite should be consistent. There are several compositing techniques that may be required, such as:

- Flow-proportioned - Collected proportional to the flow rate during the compositing period by either a time-varying/constant volume or a time-constant/varying volume method. This technique is usually associated with wastewater or storm water runoff sampling.
- Time - Composed of a varying number of discrete samples collected at equal time intervals during the compositing period. This technique is typically used to sample wastewater and streams, and in some air sampling applications.
- Areal - Collected from individual grab samples collected in an area or on a cross-sectional basis. Areal composites are comprised of equal volumes of grab samples where all grabs are collected in an identical manner. This technique is typically used for estimating average contaminant concentrations in soils or sediments. It is also useful when contaminants are present in nugget form (i.e., TNT chunks, lead shot, etc.), thus exhibiting large differences in concentration over a small sample area.
- Vertical - Collected from individual grab samples taken from a vertical cross section. Vertical composites are comprised of equal volumes of grab samples where all grab samples are collected in an identical manner. Examples would include vertical profiles of a soil borehole or sediment columns.
- Volume - Collected from discrete samples whose aliquot volumes are proportional to the volume of sampled material. Volume composites are usually associated with hazardous waste bulking operations where the sample represents combined or bulked waste.

When compositing solid or tissue samples (i.e., sediment, soil, or sludge) for analysis of analytes present in trace quantities, use a stainless steel or PTFE bowl and spatula as applicable.

5. Sample Mixing and Homogenizing

Mixing of the sample for the remaining parameters is necessary to create a representative sample media. It is extremely important that solid samples be mixed as thoroughly as possible to ensure that the sample is representative of the sample location. Refer to the project-specific SAP for instructions on removal of any extraneous materials (e.g., leaves, sticks, rocks, etc.). The mixing technique will depend on the physical characteristics (e.g., particle size, moisture content, etc.) of the solid material. For example, grinding and homogenization of tissue is easier when it is partially frozen. The mixing container should be large enough to hold the sample volume and accommodate the procedures without spilling. Both the mixing container (generally a bowl or tray) and the mixing implement should be properly decontaminated before use. Samples should be homogenized

according to procedures listed in the project-specific SAP. Table E-1 provides a brief procedure for mixing a soil sample with a small particle size (less than 1/4 in.) and filling sample containers in the field.

Table E-1. Mixing a Sample and Filling Sample Containers

Step	Action
1	Roll the contents of the compositing container to the middle of the container and mix.
2	Quarter the sample and move to the sides of the container.
3	Mix each quarter individually, then combine and mix OPPOSITE quarters, then roll to the middle of the container.
4	Mix the sample once more, and then quarter the sample again.
5	Mix each quarter individually, then combine and mix ADJACENT corners, then roll to the middle of the container. The goal is to achieve a consistent physical appearance before sample containers are filled.
6	Flatten piled material into an oblong shape.
7	Using a flat-bottomed scoop, collect a strip of soil across the entire width of the short axis and place it into a sample container.
8	Repeat Step 7 at evenly-spaced intervals until the sample containers are filled.
9	Record the approximate quantity of each subsample in the field logbook.

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APPENDIX F INTERNATIONAL SHIPPING

The following section provides information on shipping Contract Laboratory Program (CLP) samples to laboratories outside the United States.

F.1 United Parcel Service (UPS) Procedure for Shipping to Canada

1. Introduction

Samplers should refer to the Standard Operating Procedure (SOP) for the responsibilities and procedures for shipping to Canadian laboratories. The following sections detail the export shipping process.

2. Overview

UPS will provide pick-up and delivery service for small package (weighing less than 150 lbs. each) shipments to laboratories in Canada.

3. Contact Information

UPS Strategic Support for Government Accounts	https://www.ups.com/us/en/services/government.page
UPS International Customer Service	www.ups.com/international
Preferred Customer Associate Team	https://www.ups.com/us/en/help-support-center.page?

4. Customs Broker

The laboratory should be notified of each shipment so they know to contact their customs broker to have the shipment released. Otherwise, shipments may be held in customs. Laboratories may also act as their own broker.

5. Product Profile

Service Level – EPA receives government pricing for shipments via UPS *Worldwide Express Saver* service. This service provides guaranteed delivery within 1 – 3 business days, by end of day, to Canada. The maximum weight per package is 150 lbs. (70 kg), maximum length is 108 in. (270 cm) per package and the maximum dimensions are 165.0 in. (419.10 cm) per package, length and girth combined.

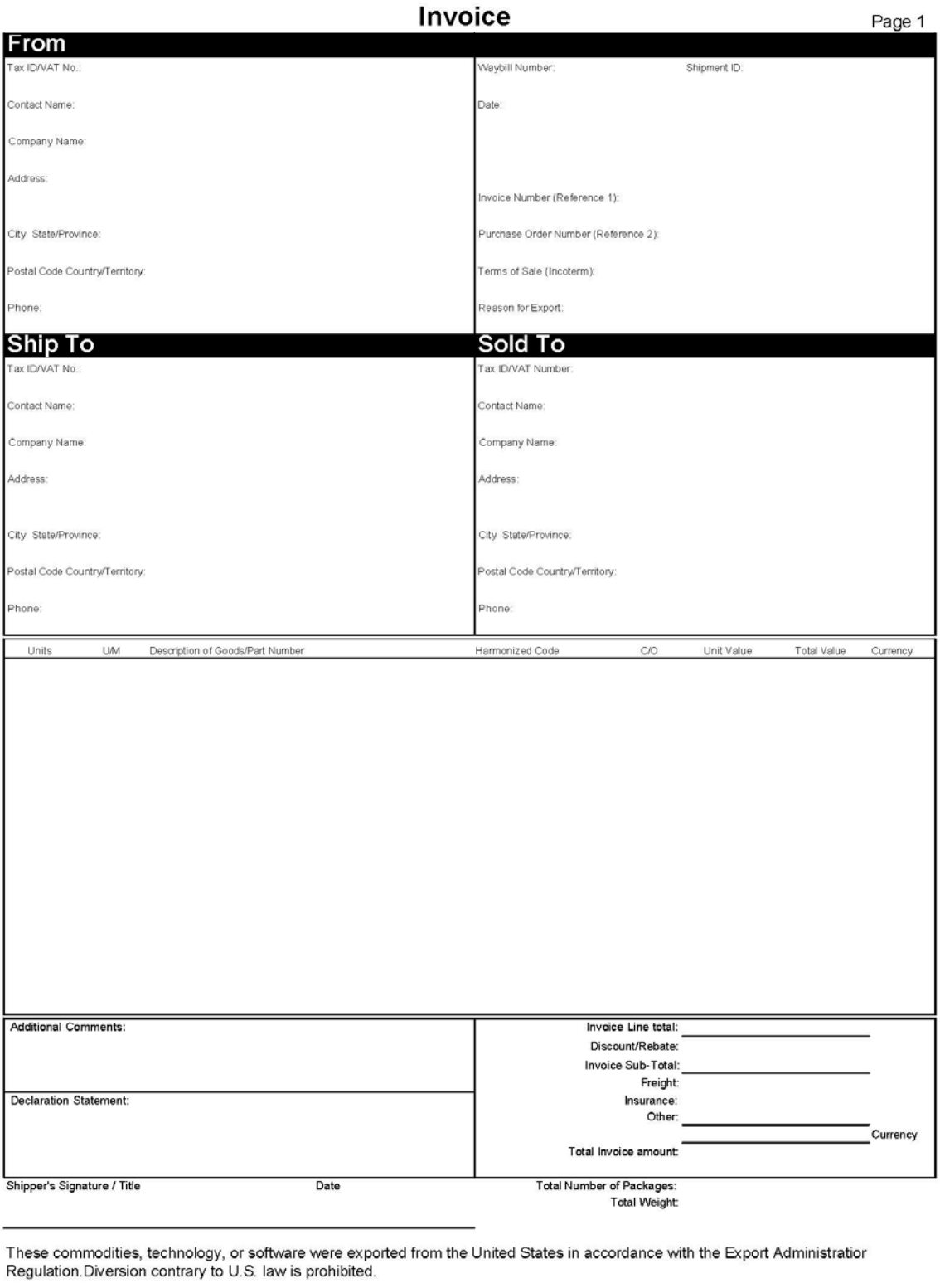
6. Commercial Invoice

A commercial invoice form (see Figure F-1) is used for all shipments containing non-documents. It is the primary document used for importation control, valuation, and duty determination. This document identifies the items in the shipments.

The form should include:

- Complete name and address information for both shipper and consignee
- Phone numbers for shipper and consignee
- Terms of Sale (Incoterm)
- Reason for export
- A complete description of the item
- Type of item
- Item use
- Harmonized Tariff Codes, if known

- Country of origin (where manufactured) for each commodity
- Number of units, unit value, and total value (purchase price) of each item
- Number of packages and total weight
- Shipper’s signature and date
- A nominal or fair market value must be stated for items of no commercial value



Invoice

Page 1

From

Tax ID/VAT No.:

Contact Name:

Company Name:

Address:

City State/Province:

Postal Code Country/Territory:

Phone:

Waybill Number: Shipment ID:

Date:

Invoice Number (Reference 1):

Purchase Order Number (Reference 2):

Terms of Sale (Incoterm):

Reason for Export:

Ship To

Tax ID/VAT No.:

Contact Name:

Company Name:

Address:

City State/Province:

Postal Code Country/Territory:

Phone:

Sold To

Tax ID/VAT Number:

Contact Name:

Company Name:

Address:

City State/Province:

Postal Code Country/Territory:

Phone:

Units	U/M	Description of Goods/Part Number	Harmonized Code	C/O	Unit Value	Total Value	Currency

Additional Comments:

Declaration Statement:

Invoice Line total:

Discount/Rebate:

Invoice Sub-Total:

Freight:

Insurance:

Other:

Currency

Total Invoice amount:

Shipper's Signature / Title Date

Total Number of Packages:

Total Weight:

These commodities, technology, or software were exported from the United States in accordance with the Export Administratior Regulation.Diversion contrary to U.S. law is prohibited.

Figure F-1. Commercial Invoice Template

7. Packing with Coolants and Refrigerants (Dry Ice)

Coolants and refrigerants are used to keep temperature-sensitive items cold or frozen while in transit. Dry ice (frozen carbon dioxide) and ice are the most common types of coolant/refrigerants used for transportation.

International Air Shipments Containing Dry Ice

International Air shipments containing dry ice require the shipper to have a UPS International Special Commodities contract. For additional information, please contact the UPS Hazardous Materials Support Center at 1-800-554-9964, or visit our online UPS Guide for Shipping International Dangerous Goods.

https://www.ups.com/us/en/help-center/packaging-and-supplies/special-care-shipments/international-dangerous-goods/shippers-responsibilities.page

International Dry Ice Packages Shipped via Air Service Require the Following Under International Air Transport Association (IATA):

- Process through WorldShip 2019, CampusShip, or compliant software
- An acceptance audit is performed
- Mark the outer carton with:
  - The words “Dry Ice” of “Carbon Dioxide, Solid” and “UN 1845”
  - The amount of dry ice contained in the package in kg
  - Class 9 Diamond label

Requirements for Preparing Dry Ice Shipments:

- Fill any empty space in the shipping container with appropriate packing material to prevent product movement during transit.
- Wrap temperature-sensitive products in two watertight plastic bags or use absorbent material along with a plastic liner.
- Avoid shipping temperature-sensitive products over the weekend.
- Wrap the refrigerant in paper or another carton to slow the sublimation rate and prevent excess space when using dry ice.
- Do not place the refrigerant at the bottom of the package because cold air will not circulate.
- Do not seal the inner insulated container when using dry ice. Venting is required to allow some carbon dioxide gas to escape the package.

* UPS CampusShip is a web-based, UPS-hosted shipping solution that helps to increase efficiency and reduce costs.

8. Additional Information

Common items that may be hazardous require the shipper to have a UPS International Special Commodities contract. For additional information, contact the UPS Hazardous Materials Support Center at 1-800-554-9964, or visit the online UPS Guide for Shipping International Dangerous Goods.

Descriptions that Indicate Dangerous Goods – watch for any of the following descriptions that could indicate Dangerous Goods or Hazardous Materials:

- Acidic
- Caustic
- Combustible Communicable
- Compressed Gas
- Corrosive
- Explosive
- Flammable
- Infectious
- Inflammable

- Poison
- Radioactive
- Refrigerated
- Toxic
- Volatile

Note: The above is only a sampling of terms which should prompt further questions about a shipment.

9. Tools and Resources

UPS Global

Access UPS Global website to get up-to-date information on everything international, including information on how to prepare an international shipment, track your package, and import/export country regulations and international forms.

Processing International Package using UPS CampusShip

https://www.ups.com/media/en/CampusShip_shipping_QuickStart_Guide.pdf

Step-by-Step Instructions for International Shipping

Step 1. Verify That The Commodity Can Be Shipped

Determine if service restrictions apply to either the United States or Canada.

Check for Embargoed/Suspended Service

Verify that your commodity can be shipped to or from the United States and Canada.

Check List of UPS Export Prohibited Articles

Step 2. Select an International Service If price and time are your primary considerations in selecting an international service, use the Service Comparison tool on UPS CampusShip to find the guaranteed delivery time and price of every service available to and from the United States and Canada.

Step 3. Select an International Billing Option

UPS offers flexible international billing options. Select the applicable option.

Learn More About International Billing Options

Step 4. Create Required Documentation

Determine the export documentation required for the shipment and complete each form.

Learn How to Create Documentation

Step 5. Prepare The Shipment

Use UPS International Shipping Basics to learn more about preparing your shipment.

Learn What Packing Materials to Use for Your International Shipment

Identify Specific Weight and Size Limitations Convert the Weight, Length, Area, and Volume of Your Shipment

Decide whether to declare a value for high value items. If the value of the goods exceeds $100.00 (USD), declare a higher value, up to $50,000.00 (USD) per package. For packages that exceed the maximum declared value, a waiver must be obtained. Refer to the applicable terms and conditions of service for additional limits and restrictions.

Learn More About Declared Value

Step 6. Ship The Package

Use UPS CampusShip or Internet Shipping on ups.com to prepare the international shipping label and the international forms required for certain shipments.

Step 7. Get The Shipment to UPS

In instances where automatic pickup has not been scheduled, UPS On-Call Pickup® may be requested to pick up all ground, air, and international shipments from any location. UPS On-Call Pickup can be scheduled at ups.com or by calling 1-800-PICK-UPS® for same day or future day pickup. Packages can also be shipped from UPS locations including The UPS Store®.

Find Locations

Step 8. Check Shipment Status

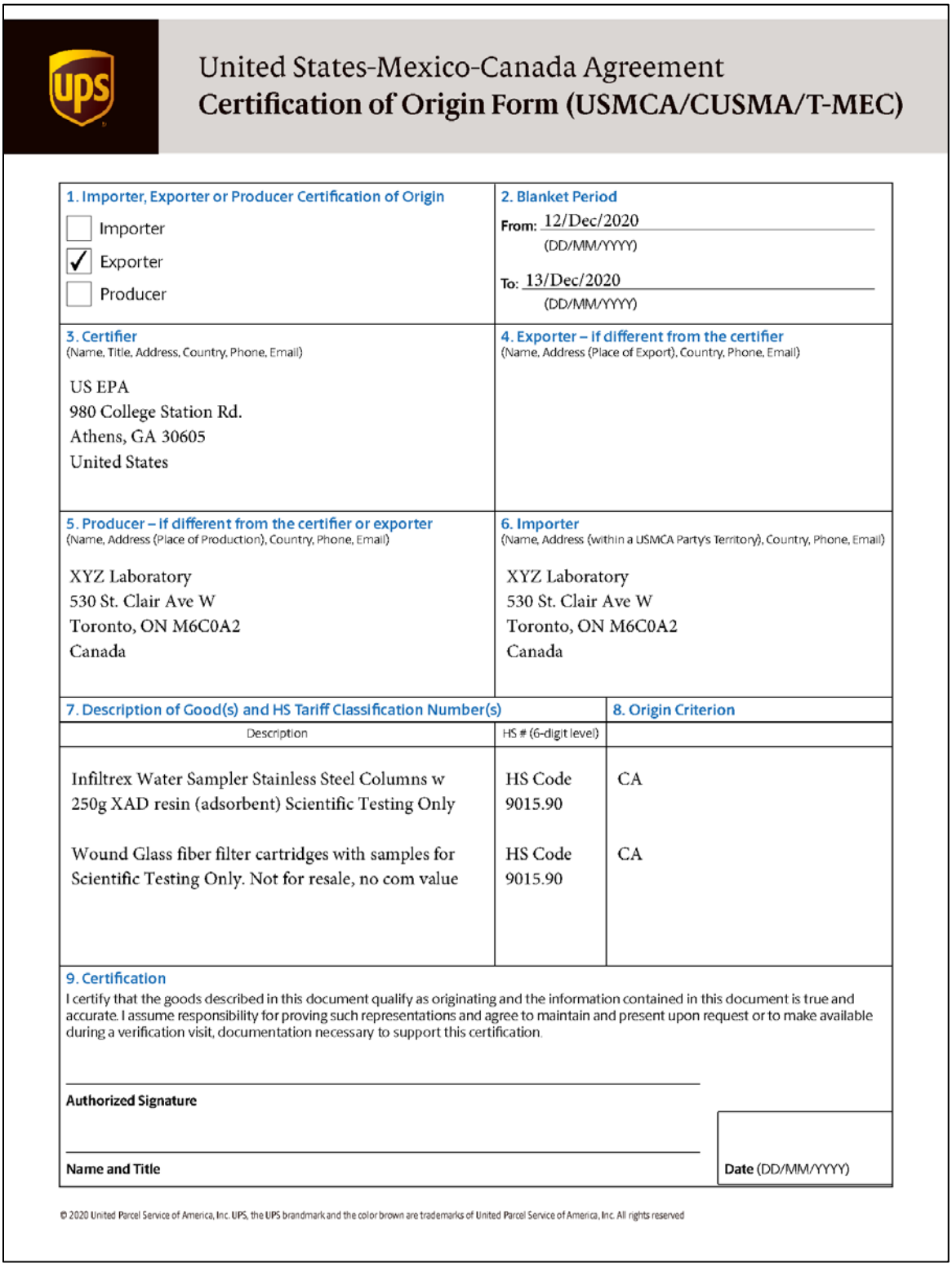
Since each UPS package is assigned a unique tracking number, shipment information is easily accessible. Tracking information is always available at ups.com, by e-mail, and through optional services.

Track Your Shipment

Learn About More Ways to Track

F.2 Completed Customs Forms Example

Shipping samples to an international laboratory requires the completion of a customs form. The following is an example of a correctly completed customs form for shipment to a laboratory in Canada.



United States-Mexico-Canada Agreement
Certification of Origin Form (USMCA/CUSMA/T-MEC)

1. Importer, Exporter or Producer Certification of Origin

- ☐ Importer
- ☑ Exporter
- ☐ Producer

2. Blanket Period

From: 12/Dec/2020 (DD/MM/YYYY)

To: 13/Dec/2020 (DD/MM/YYYY)

3. Certifier
(Name, Title, Address, Country, Phone, Email)

US EPA
980 College Station Rd.
Athens, GA 30605
United States

4. Exporter – if different from the certifier
(Name, Address (Place of Export), Country, Phone, Email)

5. Producer – if different from the certifier or exporter
(Name, Address (Place of Production), Country, Phone, Email)

XYZ Laboratory
530 St. Clair Ave W
Toronto, ON M6C0A2
Canada

6. Importer
(Name, Address (within a USMCA Party's Territory), Country, Phone, Email)

XYZ Laboratory
530 St. Clair Ave W
Toronto, ON M6C0A2
Canada

7. Description of Good(s) and HS Tariff Classification Number(s)

Description	HS # (6-digit level)	8. Origin Criterion
Infiltrex Water Sampler Stainless Steel Columns w 250g XAD resin (adsorbent) Scientific Testing Only	HS Code 9015.90	CA
Wound Glass fiber filter cartridges with samples for Scientific Testing Only. Not for resale, no com value	HS Code 9015.90	CA

9. Certification

I certify that the goods described in this document qualify as originating and the information contained in this document is true and accurate. I assume responsibility for proving such representations and agree to maintain and present upon request or to make available during a verification visit, documentation necessary to support this certification.

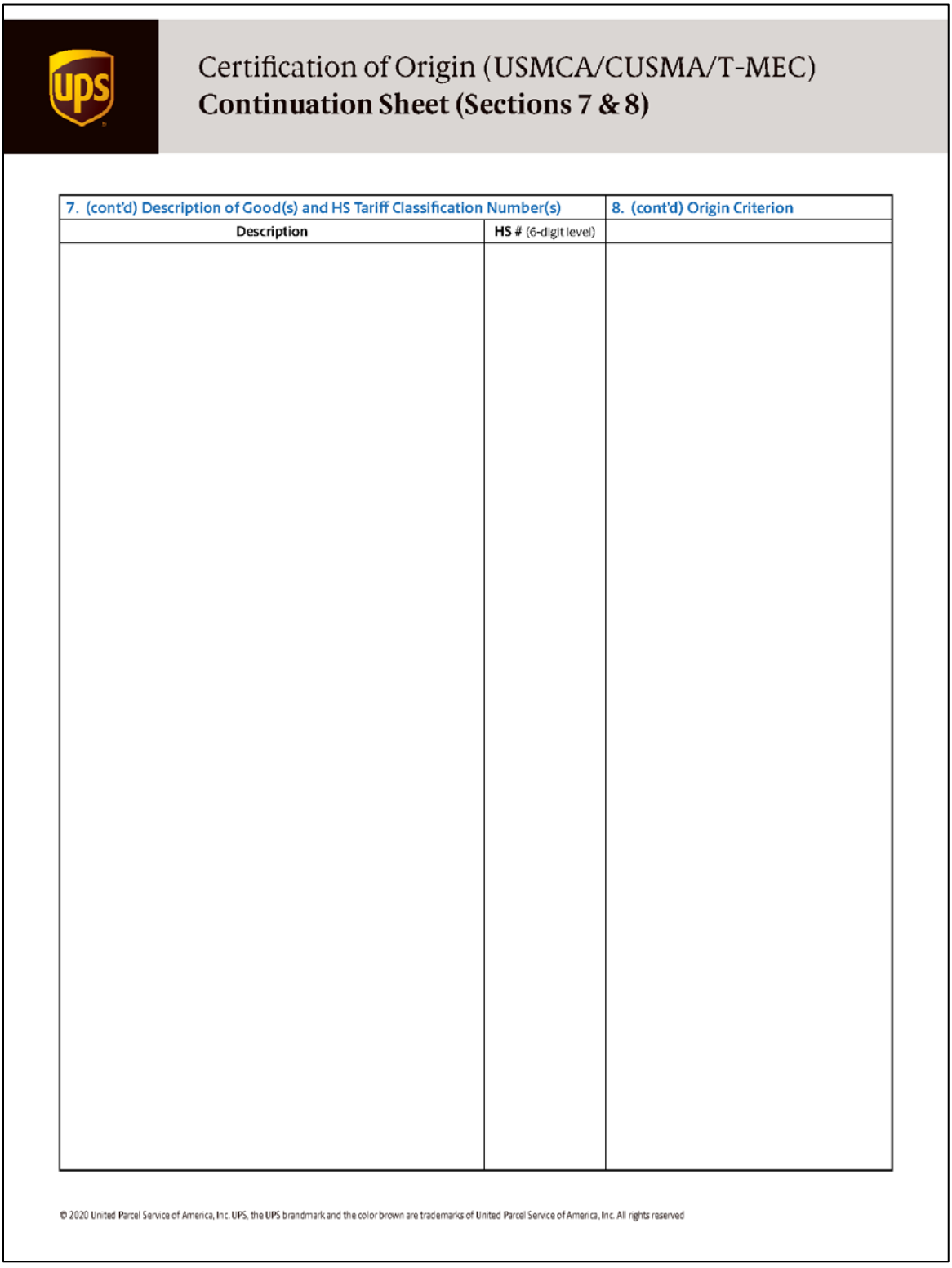
Authorized Signature

Name and Title

Date (DD/MM/YYYY)

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Figure F-2. International Shipping Form (1 of 3)

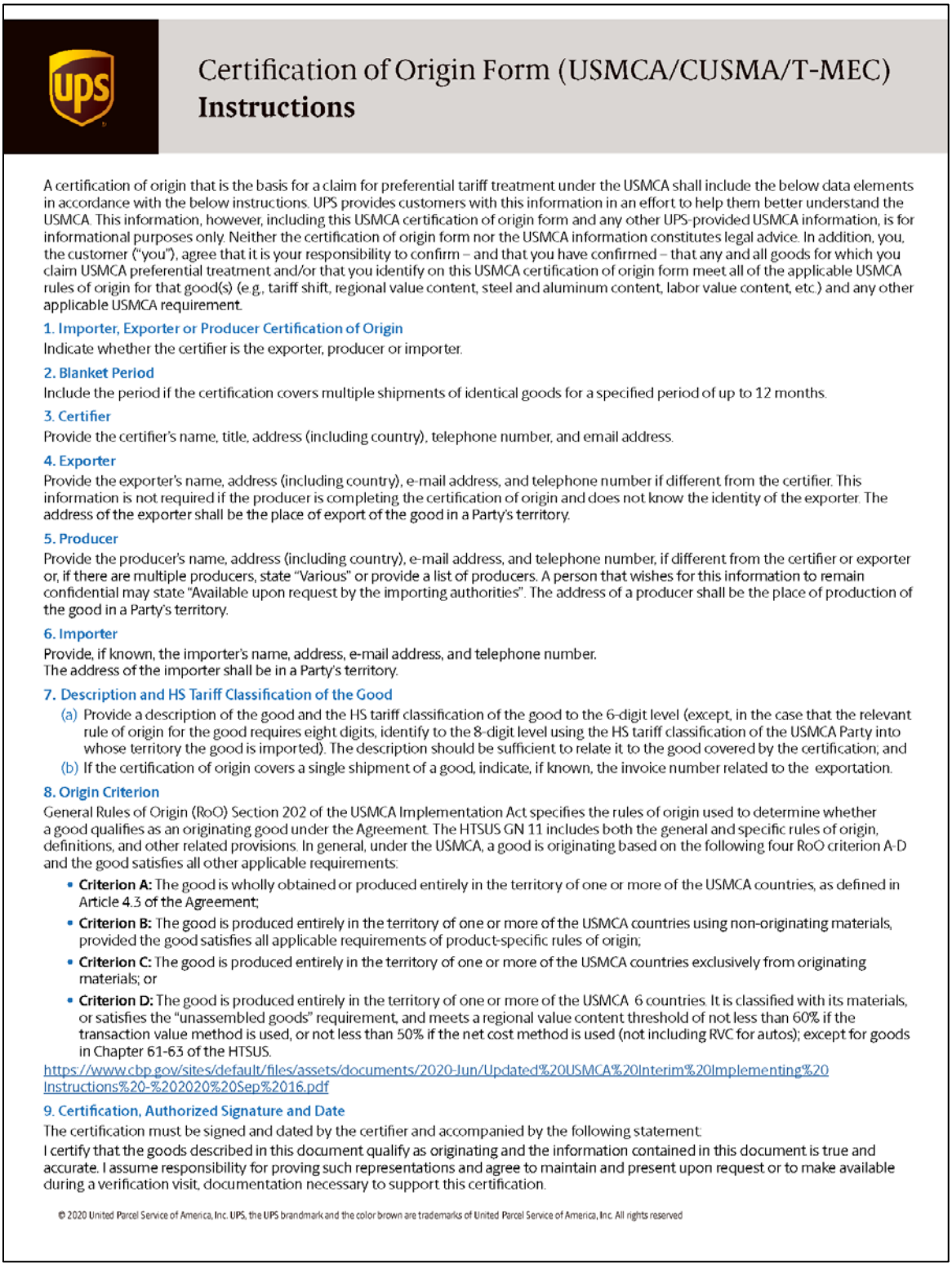


Certification of Origin (USMCA/CUSMA/T-MEC)
Continuation Sheet (Sections 7 & 8)

7. (cont'd) Description of Good(s) and HS Tariff Classification Number(s)		8. (cont'd) Origin Criterion
Description	**HS #** (6-digit level)	

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Figure F-3. International Shipping Form (2 of 3)



Certification of Origin Form (USMCA/CUSMA/T-MEC) Instructions

A certification of origin that is the basis for a claim for preferential tariff treatment under the USMCA shall include the below data elements in accordance with the below instructions. UPS provides customers with this information in an effort to help them better understand the USMCA. This information, however, including this USMCA certification of origin form and any other UPS-provided USMCA information, is for informational purposes only. Neither the certification of origin form nor the USMCA information constitutes legal advice. In addition, you, the customer ("you"), agree that it is your responsibility to confirm – and that you have confirmed – that any and all goods for which you claim USMCA preferential treatment and/or that you identify on this USMCA certification of origin form meet all of the applicable USMCA rules of origin for that good(s) (e.g., tariff shift, regional value content, steel and aluminum content, labor value content, etc.) and any other applicable USMCA requirement.

1. Importer, Exporter or Producer Certification of Origin

Indicate whether the certifier is the exporter, producer or importer.

2. Blanket Period

Include the period if the certification covers multiple shipments of identical goods for a specified period of up to 12 months.

3. Certifier

Provide the certifier's name, title, address (including country), telephone number, and email address.

4. Exporter

Provide the exporter's name, address (including country), e-mail address, and telephone number if different from the certifier. This information is not required if the producer is completing the certification of origin and does not know the identity of the exporter. The address of the exporter shall be the place of export of the good in a Party's territory.

5. Producer

Provide the producer's name, address (including country), e-mail address, and telephone number, if different from the certifier or exporter or, if there are multiple producers, state "Various" or provide a list of producers. A person that wishes for this information to remain confidential may state "Available upon request by the importing authorities". The address of a producer shall be the place of production of the good in a Party's territory.

6. Importer

Provide, if known, the importer's name, address, e-mail address, and telephone number.
The address of the importer shall be in a Party's territory.

7. Description and HS Tariff Classification of the Good

(a) Provide a description of the good and the HS tariff classification of the good to the 6-digit level (except, in the case that the relevant rule of origin for the good requires eight digits, identify to the 8-digit level using the HS tariff classification of the USMCA Party into whose territory the good is imported). The description should be sufficient to relate it to the good covered by the certification; and

(b) If the certification of origin covers a single shipment of a good, indicate, if known, the invoice number related to the exportation.

8. Origin Criterion

General Rules of Origin (RoO) Section 202 of the USMCA Implementation Act specifies the rules of origin used to determine whether a good qualifies as an originating good under the Agreement. The HTSUS GN 11 includes both the general and specific rules of origin, definitions, and other related provisions. In general, under the USMCA, a good is originating based on the following four RoO criterion A-D and the good satisfies all other applicable requirements:

- **Criterion A:** The good is wholly obtained or produced entirely in the territory of one or more of the USMCA countries, as defined in Article 4.3 of the Agreement;
- **Criterion B:** The good is produced entirely in the territory of one or more of the USMCA countries using non-originating materials, provided the good satisfies all applicable requirements of product-specific rules of origin;
- **Criterion C:** The good is produced entirely in the territory of one or more of the USMCA countries exclusively from originating materials; or
- **Criterion D:** The good is produced entirely in the territory of one or more of the USMCA 6 countries. It is classified with its materials, or satisfies the "unassembled goods" requirement, and meets a regional value content threshold of not less than 60% if the transaction value method is used, or not less than 50% if the net cost method is used (not including RVC for autos); except for goods in Chapter 61-63 of the HTSUS.

https://www.cbp.gov/sites/default/files/assets/documents/2020-Jun/Updated%20USMCA%20Interim%20Implementing%20Instructions%20-%202020%20Sep%2016.pdf

9. Certification, Authorized Signature and Date

The certification must be signed and dated by the certifier and accompanied by the following statement:

I certify that the goods described in this document qualify as originating and the information contained in this document is true and accurate. I assume responsibility for proving such representations and agree to maintain and present upon request or to make available during a verification visit, documentation necessary to support this certification.

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Figure F-4. International Shipping Form (3 of 3)

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APPENDIX G SAMPLING CHECKLISTS

Table G-1. Personnel Preparation Checklist

(Page 1 of 2)

Personnel Briefing	Yes	No	Comments
1. Did you review sampling team responsibilities and identify individual(s) responsible for corrective actions?			
2. Did you ensure that you have met the appropriate personal safety and protection requirements?			
3. Did you identify sampling locations and receive permission to access them, as appropriate?			
4. Did you contact the appropriate utility companies PRIOR to the start of sampling?  By law, utility companies must be contacted prior to the start of digging/sampling so that any underground utilities (gas lines, water lines, electrical lines, etc.) can be marked. A list of one-call centers for each state may be found at: https://call811.com			
5. If sampling on private property, do you have sample receipts to provide to the property owner for all samples collected and removed from the property?			
6. Have you determined the number and type of samples to be collected?			
7. Did you review sample collection methods?			
8. Have you reviewed sample container requirements?			
9. Did you review decontamination requirements, procedures, and locations?			
10. Did you determine holding times and conditions?			
11. Did you determine Performance Evaluation (PE) and Quality Control (QC) sample requirements?			
12. Have you obtained shipping container temperature blanks, if required?			
13. Did you review sample label requirements?			
14. Did you review Traffic Report/Chain of Custody (TR/COC) Record and custody seal requirements?			
15. Have you obtained the laboratory name, shipping addresses, and telephone number?			
16. Did you review shipping container return instructions?			
17. Have you obtained shipping company information (name, telephone number, account number, and pickup schedule)?			
18. Have you obtained shipping schedules?			
19. Did you review shipment reporting requirements and the appropriate contact names and telephone numbers for reporting?			

Table G-1. (Continued) Personnel Preparation Checklist

(Page 2 of 2)

Personnel Briefing	Yes	No	Comments
20. Have you included any sampler comments regarding sampling issues (e.g., low volumes, matrix, suspected concentrations based on field measurements)?			

Table G-2. General Sample Collection Checklist

(Page 1 of 1)

General Sample Collection	Yes	No	Comments
1. Did you identify and mark the sampling location with buoys, flags, or stakes according to the sampling plans, maps, and grids?			
2. If the sampling location is inaccessible, did you contact the appropriate field or Regional personnel for instructions?			
3. Did you use the correct sampling equipment?			
4. Did you follow the correct decontamination procedures?			
5. Did you follow the correct collection procedures?			
6. Did you use the correct sample containers for each sample collected?			
7. Did you use certified clean containers for all samples? Are certificates kept on record?			
8. Did you use certified clean water for all field, trip, equipment, and rinsate blanks? Are certificates kept on record?			
9. Did you collect the correct volume for each sample?			
10. Did you collect the correct type of sample, including primary samples and QC samples?			
11. Did you properly preserve each sample collected?			
12. Did you correctly document and label each sample with all necessary information?  Under no circumstances should the site name or address appear on any documentation being sent to the laboratory, unless the laboratory is a Regional U.S. Environmental Protection Agency (EPA) laboratory.			
13. If sampling on private property, did you provide a sample receipt to the owner of the property for all samples collected and removed from the property?			

Table G-3. Completing Field Logbook Checklist

(Page 1 of 1)

Completing Field Logbook	Yes	No	Comments
1. Did you use waterproof ink when writing in the field logbook?			
2. Did you document sampling project information such as: • Project name, Project ID, and location • Names of samplers • Geological observations, including maps • Atmospheric conditions • Field measurements • Sampling dates, times, and locations?  Under no circumstances should the site name or address appear on any documentation being sent to the laboratory, unless the laboratory is a Regional EPA laboratory.			
3. Did you record sampling activity information such as: • Sampling dates and times • Sample identifications • Sample matrices • Sample descriptions (e.g., odors and/or colors) • Number of samples collected • Sampling methods/equipment • Description of QC samples?			
4. Did you document any and all deviations from the sampling plan?			
5. Did you document any and all difficulties in sampling and/or any unusual circumstances?			
6. Were all errors corrected by crossing a line through the error, initialing the error, dating the error, and then adding the correct information?			

Table G-4. Completing Handwritten Sample Labels Checklist

(Page 1 of 1)

Completing Handwritten Sample Labels	Yes	No	Comments
1. Did the Regional Sample Control Coordinator (RSCC) provide Contract Laboratory Program (CLP) Sample Numbers and Sample Management Office (SMO) Contract Laboratory Program Support System (CLPSS) Portal-generated CLP Case Numbers?			
2. If additional CLP Sample Numbers were needed, did you contact the appropriate Regional personnel?			
3. Were the CLP Sample Numbers and SMO CLPSS Portal-generated CLP Case Numbers on the labels correct?			
4. Were samples uniquely numbered and designated to only one sample?  Samples collected for total metal and filtered metal analyses must receive separate, unique, CLP Sample Numbers.			
5. Were QC samples numbered accordingly?			
6. Were the specific requirements followed for total and filtered metals analysis, QC and PE samples, and SW-846 Method 5035A?			
7. Were all temperature blanks labeled with “TEMPERATURE BLANK”?			
8. Was a sample label containing the CLP Sample Number, SMO CLPSS Portal-generated CLP Case Number, location, concentration, preservative, and the analysis, attached to each sample bottle or container as the sample was collected?  Under no circumstances should the site name or address appear on any documentation being sent to the laboratory, unless the laboratory is a Regional EPA laboratory.			
9. Was clear tape placed over the sample labels to protect the labels from moisture and to help the labels adhere to the sample bottle?  Use only CLEAR tape over the sample labels and avoid wrinkles in the tape and the sample labels.			
10. Were all errors corrected by drawing a line through the error, initialing and dating the error, and then adding the correct information?			

Table G-5. Completing Handwritten Custody Seals Checklists

(Page 1 of 1)

Completing Custody Seals	Yes	No	Comments:
1. If required for the project, did you sign and date the custody seal?			
2. Did you attach a completed custody seal to the sample bottle, container, or plastic bag, placing the seal over the cap or lid of each sample bottle or container or on the bag opening such that it will be broken if the sample bottle, container, or bag is opened or tampered with?			
3. As appropriate, did you attach the completed custody seal to the sample shipping container or cooler, placing the seal such that it will be broken if the container or cooler is opened or tampered with?			
4. Were all errors corrected by crossing a line through the error, initialing and dating the error, and then adding the correct information?			

Table G-6. Packing Sample Container Checklist

(Page 1 of 1)

Packing Sample Container	Yes	No	Comments
1. Did you follow all State, Federal, Department of Transportation (DOT), and International Air Transportation Association (IATA) regulations governing the packaging of environmental and hazardous samples?  If samples contain methanol preservation (e.g., samples to be analyzed by SW-846 Method 5035A), refer to the packaging instructions in Appendix C.			
2. Were all CLP Sample Numbers, SMO CLPSS Portal-generated CLP Case Numbers, analyses, labels, and custody seals attached to the correct sample containers?			
3. Is Modified Analysis indicated if requested?			
4. Was an inventory conducted of CLP Sample Numbers, SMO CLPSS Portal-generated CLP Case Numbers, analyses, and containers, and verified against the TR/COC Records?			
5. Were the correct number and type of PE and QC samples collected?			
6. Were all sample containers sealed in clear plastic bags with the sample label and tag (if applicable) visible through the packaging?			
7. Was suitable absorbent packing material placed around the sample bottles or containers?			
8. Were the outsides of metal containers labeled properly with the CLP Sample Number, SMO CLPSS Portal-generated CLP Case Number, and the analysis of the sample inside?			

Table G-7. Packing Shipping Container Checklist

(Page 1 of 2)

Packing Shipping Container	Yes	No	Comments
1. Were shipping samples in a clean waterproof metal or hard plastic ice chest, cooler, or container in good condition?			
2. Were all non-applicable labels from previous shipments removed from the container?			
3. Were all inside and outside drain plugs closed and covered with suitable tape (e.g., duct tape)?			
4. Was the inside of the shipping container lined with plastic (e.g., large heavy-duty garbage bag)?			
5. Was the lined shipping container packed with non-combustible absorbent packing material?			
6. Were sample containers placed in the shipping container in an upright position not touching one another?			
7. Was a shipping container temperature blank included in the cooler?			
8. Did the documentation in the cooler only address the samples in that container?			
9. Was the site name absent from all documentation?  Under no circumstances should the site name or address appear on any documentation being sent to the laboratory, unless the laboratory is a Regional EPA laboratory.			
10. Was there sufficient packing material around and in between the sample bottles to avoid breakage during transport?			
11. If required, was double-bagged ice placed on top and around sample bottles to keep the samples cold at ≤ 6°C?  Do not pack loose ice into the cooler.			
12. Was the top of the plastic liner fastened and secured with tape?			
13. Was a completed custody seal placed around the top of the fastened plastic liner (if required by the Region)?			
14. Were all sample documents enclosed within the shipping container (e.g., TR/COC Record, PE instructions, and container return instructions) in a waterproof plastic bag?			
15. Was the plastic bag, containing the documentation, taped to the underside of the lid?			
16. Were shipping container return instructions and airbills taped to the underside of the cooler lid?			
17. Was the return address of the shipping container written with permanent ink on the underside of the lid?			
18. Was tape placed around the outside of the entire container and over the hinges?			
19. Were the completed custody seals placed over the top edge of the container so the container cannot be opened without breaking the seals?			
20. Was the return address label attached to the top left corner of the container lid?			

Table G-7. Packing Shipping Container Checklist

(Page 2 of 2)

Packing Shipping Container	Yes	No	Comments
21. Were instructional labels attached to the top of the container, as necessary (e.g., "This End Up," "Do Not Tamper With," or "Environmental Laboratory Samples")?			
22. Have all U.S. DOT regulations been met for the shipment when shipping hazardous samples?			
23. If shipping samples containing methanol as a preservative (e.g., samples to be analyzed by SW-846 Method 5035A), was a label used to indicate the presence of methanol, the United Nations (UN) identification number for methanol (UN 1230), and Limited Quantity?			

Table G-8. Shipping & Reporting CLP Samples Checklist

(Page 1 of 1)

Shipping CLP Samples	Yes	No	Comments:
1. Did you follow all State, Federal, DOT, and IATA regulations governing the shipment of environmental and hazardous samples?			
2. Was a separate airbill filled out for each container being shipped?			
3. Was the airbill filled out completely, including correct laboratory name, address, and telephone number, identification of recipient as "Sample Custodian," and appropriate delivery option (e.g., overnight or Saturday)?			
4. Was the completed airbill attached to the top of the container with the correct laboratory address?			
5. If more than one container was being shipped to the same laboratory, were they marked as "1 of 2," "2 of 2," etc.?			
6. Were the samples being shipped "overnight" through a qualified commercial carrier?			
7. Did you export the electronic COC XML file from Scribe?			
8. Did you upload the electronic COC XML file using the Submit Chain of Custody task in the SMO CLPSS Portal?			
Reporting CLP Samples	**Yes**	**No**	**Comments:**
1. Did you contact the RSCC (or designee) and the Contract Laboratory Program Sample Management Office (SMO) on the same day samples were shipped?			
2. If the samples were shipped after 5:00 PM Eastern Time (ET), were they reported to the RSCC (or designee) and to SMO by 8:00 AM ET the following business day?			
3. Did you notify the RSCC (or designee) and SMO so that SMO will receive the delivery information (including shipping airbill information) by 3:00 PM ET on Friday for sample shipments that will be delivered to the laboratory on Saturday?			
4. Did you provide the RSCC (or designee) or the SMO CLPSS Portal with: • Your name, phone number, email address, and Region number; • Case Number of the project; • Modified Analysis Number, if requested; • Exact number of samples, matrix(ces), and type of analysis; • Laboratory(ies) to which the samples were shipped; • Carrier name and airbill number; • Date of shipment; • Date of next shipment; and • Any other information pertinent to the shipment?			

APPENDIX H GLOSSARY

Analyte -- The specific compound, mixture, element, or ion an analysis seeks to determine.

Analytical Services Branch (ASB) -- The branch of the Technology Innovation and Field Services Division (TIFSD) of the United States Environmental Protection Agency's (EPA's) Office of Superfund Remediation and Technology Innovation (OSRTI) responsible for the overall management of the Contract Laboratory Program (CLP) under the Office of Land and Emergency Management (OLEM).

Aroclor -- Polychlorinated biphenyls (PCBs) or a class of organic compounds with 1 to 10 chlorine atoms attached to biphenyl and a general chemical formula of $C_{12}H_{10-x}Cl_x$. PCBs, commercially produced as complex mixtures containing multiple isomers at different degrees of chlorination, were marketed in North America under the trade name Aroclor.

Case -- A finite, usually predetermined, number of samples collected over a given time period from a particular site. Case Numbers are assigned by the Sample Management Office (SMO). A Case consists of one or more Sample Delivery Groups (SDGs).

Chlorinated Dibenzo-*p*-Dioxin/Chlorinated Dibenzofuran (CDD/CDF) -- A group of organic compounds of tetra- through octa-chlorinated dibenzo-*p*-dioxins (CDDs) and dibenzofurans (CDFs).

Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) -- First authorized by Congress in December 1980, and amended in 1986, CERCLA provided broad Federal authority to respond directly to the release or possible release of hazardous substances that may endanger human health or the environment. CERCLA also established a Trust Fund to provide for cleanup when no responsible party could be identified; hence, CERCLA is commonly referred to as "Superfund."

Congener -- Individual compound belonging to a group or class of compounds with a similar general structure.

Contract Laboratory Program (CLP) -- Supports the EPA's Superfund effort by providing a range of state-of-the-art chemical analytical services of known and documented quality. This program is directed by the Analytical Services Branch (ASB) of the Technology Innovation and Field Services Division (TIFSD) Office of the Superfund Remediation and Technology Innovation (OSRTI) of the EPA.

Custody Seal -- An adhesive label or tape that is used to seal a sample bottle or container that maintains chain of custody and that will break if the sample bottle or container is opened or tampered with.

Cyanide (Total) -- Cyanide ion and complex cyanides converted to hydrocyanic acid (HCN) by reaction in a reflux system of a mineral acid in the presence of magnesium ion.

Data Quality Objectives (DQO) -- Qualitative and quantitative statements that clarify technical and quality objectives, define the appropriate type of data, and specify tolerable levels of potential decision errors that will be used as the basis for establishing the quality and quantity of data needed to support decisions.

Data Validation -- Data validation is based on Region-defined criteria and limits, professional judgment of the data validator, and (if available) the Quality Assurance Project Plan (QAPP) and Sampling and Analysis Plan (SAP).

Deuterated Monitoring Compound (DMC) -- Compounds added to every Gas Chromatograph/Mass Spectrometer (GC/MS) calibration standard, blank, and sample to evaluate the efficiency of the extraction/purge-and-trap procedures, and the performance of the GC/MS systems. DMCs are isotopically labeled (deuterated) analogs of native target compounds. DMCs are not expected to be naturally detected in the environmental media.

Duplicate -- Quality Control (QC) sample required by the laboratory's contract to check the accuracy and precision of inorganic analyses. It is a second aliquot of the same sample to determine the precision of the method.

Equipment Blank -- A sample used to check field decontamination procedures. See Field Blank.

Field Blank -- Any sample that is submitted from the field and identified as a blank. A field blank is used to check for cross-contamination during sample collection, sample shipment, and in the laboratory. A field blank includes trip blanks, rinsate blanks, bottle blanks, equipment blanks, preservative blanks, decontamination blanks, etc.

Field Duplicate -- A duplicate sample generated in the field, not in the laboratory. Checks reproducibility of laboratory and field procedures and indicates non-homogeneity.

Field QC Sample -- Any QC samples submitted from the field to the laboratory. Examples include, but are not limited to, field blanks, field duplicates, and field spikes.

Field Sample -- Primary sample material collected from the field from which other samples, such as duplicates or split samples are derived. A field sample can be prepared in the field and sent for analysis in one or multiple containers, and is identified by a unique EPA sample number.

Field Sampling Plan (FSP) -- Developed to outline the actual steps and requirements pertaining to a particular sampling event, and explains, in detail, each component of the event to all involved samplers.

Holding Time -- The elapsed time expressed in hours, days, or months from the date of collection of the sample until the date of its analysis.

> **Contractual** -- The maximum length of time that the CLP laboratory can hold samples prior to extraction and/or analysis, as specified in the CLP analytical services Statements of Work (SOWs).
>
> **Technical** -- The maximum length of time that samples may be held from time of collection to time of preparation and/or analysis and still be considered valid.

Laboratory Blank -- See Method Blank.

Laboratory Duplicate -- A sample required by the laboratory's contract to check the precision of inorganic analyses.

Laboratory QC Sample -- An additional volume of an existing sample, as required by the laboratory's contract, used to detect contamination or error in the laboratory's practices.

Matrix -- The predominant material of which a sample to be analyzed is composed. Matrix is not synonymous with phase (liquid or solid).

Matrix Spike (MS) -- QC sample required by the laboratory's contract to check the accuracy of organic and inorganic analyses. It is an aliquot of a sample (water or soil) that is fortified (spiked) with known quantities of a specific analyte and subjected to the entire analytical procedure to indicate the appropriateness of the method for the matrix by measuring recovery. See Matrix Spike Duplicate.

Matrix Spike Duplicate (MSD) -- QC sample required by the laboratory's contract to check the accuracy and precision of organic analyses. It is a second aliquot of the same matrix as the Matrix Spike (MS) that is spiked to determine the precision of the method. See Matrix Spike.

Method Blank -- An analytical control consisting of all reagents, internal standards and surrogate standards (or DMCs for GC/MS organic analysis), that is carried throughout the entire analytical procedure. The method blank is used to define the level of laboratory, background, and reagent contamination, also referred to as laboratory blank when defining the level of laboratory contamination.

Modified Analysis (MA) -- A contractual document with modified Statement of Work (SOW) requirements that append to the SOW. All contract and analytical SOW requirements remain in effect unless explicitly modified.

Performance Evaluation (PE) Sample -- A sample of known composition to the EPA; however, it is unknown to the Contractor and is provided to evaluate Contractor performance.

Pesticides -- Substances intended to repel, kill, or control any species designated a "pest," including weeds, insects, rodents, fungi, bacteria, and other organisms. Under the CLP, only organochlorine pesticides are analyzed (e.g., DDT, Dieldrin, Endrin, etc.).

Polychlorinated Biphenyls (PCBs) -- A group of toxic, persistent chemicals used in electrical transformers and capacitors for insulating purposes, and in gas pipeline systems as a lubricant. The sale and new use of PCBs were banned by law in 1979.

Quality Assurance (QA) -- An integrated system of management activities involving planning, implementation, assessment, reporting, and quality improvement to ensure that a process, item, or service is of the type and quality needed and expected by the customer.

Quality Assurance Project Plan (QAPP) -- Document written to meet requirements outlined in the document *EPA Guidance for Quality Assurance Project Plans* (EPA QA/R-5). Prepared in advance of field activities and used by samplers to develop any subsequent plans such as the Sampling and Analysis Plan (SAP) or the Field Sampling Plan (FSP).

Quality Control (QC) -- The overall system of technical activities that measures the attributes and performance of a process, item, or service against defined standards to verify that they meet the stated requirements established by the customer; operational techniques and activities that are used to fulfill requirements for quality.

Regional Sample Control Coordinator (RSCC) -- In most Regions, coordinates sampling efforts and serves as the central point of contact for sampling questions and problems. Also assists in coordinating the level of Regional sampling activities to correspond with the monthly projected demand for analytical services.

Regional Site Manager -- Coordinates the development of data quality objectives and oversees project-specific remedial or removal contractors, State officials, or private parties conducting site sampling efforts.

Rinsate Blank -- A sample used to check decontamination procedures. Also see Field Blank.

Sample -- A discrete portion of material to be analyzed that is contained in single or multiple containers, and identified by a unique sample number.

Sample Delivery Group (SDG) -- A unit within a sample Case that is used to identify a group of samples for delivery. An SDG is defined by the following, whichever is most frequent:

- Each Case of field samples received; or
- Each 20 field samples (excluding PE samples) within a Case; or
- Each 7 calendar day period (3 calendar day period for 7-day turnaround) during which field samples in a Case are received (said period beginning with the receipt of the first sample in the SDG).

In addition, all samples and/or sample analyses assigned to an SDG must have been scheduled under the same contractual turnaround time. Preliminary Results have no impact on defining the SDG. Sample may be assigned to SDGs by matrix (e.g., all soil samples in one SDG, all water samples in another) at the discretion of the laboratory.

Sample Label -- An identification label attached to a sample bottle or container to identify the sample.

Sample Management Office (SMO) -- A Contractor-operated facility operated under the SMO contract, awarded and administered by the EPA.

Sample Number -- A unique number used to identify and track a sample. This number can be recorded on a sample label or written on the sample bottle or container using indelible ink.

Sampling and Analysis Plan (SAP) -- A document that explains how samples are to be collected and analyzed for a particular sampling event.

Scribe -- A stand-alone Windows-based desktop application that samplers can use to automatically create and generate sample documentation prior to and during sampling events.

Semivolatile Organic Analyte (SVOA) -- A compound amenable to analysis by extraction of the sample using an organic solvent.

Standard Operating Procedure (SOP) -- A written document that details the method for an operation, analysis, or action with thoroughly prescribed techniques and steps, and that is officially approved as the methods for performing certain routine or repetitive tasks.

Statement of Work (SOW) -- A document that specifies how laboratories analyze samples under a particular Contract Laboratory Program (CLP) analytical program.

Superfund -- The program operated under the legislative authority of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and Superfund Amendments and Reauthorization Act (SARA), that funds and carries out EPA removal and remedial activities at hazardous waste sites. These activities include establishing the National Priorities List (NPL), investigating sites for inclusion on the list, determining their priority, and conducting and/or supervising cleanup and other remedial actions.

Superfund Amendments and Reauthorization Act (SARA) -- The 1986 amendment to the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA).

Traffic Report/Chain of Custody (TR/COC) Record -- A record that is functionally similar to a packing slip that accompanies a shipment of goods. Used as physical evidence of sample custody and functions as a permanent record for each sample collected.

Trip Blank -- A sample used to check for contamination during sample handling and shipment from field to laboratory. Also see Field Blank.

Volatile Organic Analyte (VOA) -- A compound amenable to analysis by the purge-and-trap technique. Used synonymously with the term purgeable compound.

Part 1000 INTRODUCTION

1010 INTRODUCTION

1010 A. Scope and Application of Methods

The procedures described in these standards are intended for the examination of waters of a wide range of quality, including water suitable for domestic or industrial supplies, surface water, ground water, cooling or circulating water, boiler water, boiler feed water, treated and untreated municipal or industrial wastewater, and saline water. The unity of the fields of water supply, receiving water quality, and wastewater treatment and disposal is recognized by presenting methods of analysis for each constituent in a single section for all types of waters.

An effort has been made to present methods that apply generally. Where alternative methods are necessary for samples of different composition, the basis for selecting the most appropriate method is presented as clearly as possible. However, samples with extreme concentrations or otherwise unusual compositions or characteristics may present difficulties that preclude the direct use of these methods. Hence, some modification of a procedure may be necessary in specific instances. Whenever a procedure is modified, the analyst should state plainly the nature of modification in the report of results.

Certain procedures are intended for use with sludges and sediments. Here again, the effort has been to present methods of the widest possible application, but when chemical sludges or slurries or other samples of highly unusual composition are encountered, the methods of this manual may require modification or may be inappropriate.

Most of the methods included here have been endorsed by regulatory agencies. Procedural modification without formal approval may be unacceptable to a regulatory body.

The analysis of bulk chemicals received for water treatment is not included herein. A committee of the American Water Works Association prepares and issues standards for water treatment chemicals.

Part 1000 contains information that is common to, or useful in, laboratories desiring to produce analytical results of known quality, that is, of known accuracy and with known uncertainty in that accuracy. To accomplish this, apply the quality assurance methods described herein to the standard methods described elsewhere in this publication. Other sections of Part 1000 address laboratory equipment, laboratory safety, sampling procedures, and method development and validation, all of which provide necessary information.

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1010 B. Statistics

1. Normal Distribution

If a measurement is repeated many times under essentially identical conditions, the results of each measurement, x, will be distributed randomly about a mean value (arithmetic average) because of uncontrollable or experimental error. If an infinite number of such measurements were to be accumulated, the individual values would be distributed in a curve similar to those shown in Figure 1010:1. The left curve illustrates the Gaussian or normal distribution, which is described precisely by the mean, μ, and the standard deviation, σ. The mean, or average, of the distribution is simply the sum of all values divided by the number of values so summed, i.e., $\mu = (\sum_i x_i)/n$. Because no measurements are repeated an infinite number of times, an *estimate* of the mean is made, using the same summation procedure but with n equal to a finite number of repeated measurements (10, or 20, or. . .). This estimate of μ is denoted by $\bar{x}$. The standard deviation of the normal distribution is defined as $\sigma = [\sum(x-\mu)^2/n]^{1/2}$. Again, the analyst can only estimate the standard deviation because the number of observations made is finite; the estimate of σ is denoted by s and is calculated as follows:

$$s = [\Sigma(x-\bar{x})^2/(n-1)]^{1/2}$$

The standard deviation fixes the width, or spread, of the normal distribution, and also includes a fixed fraction of the values making up the curve. For example, 68.27% of the measurements lie between $\mu \pm 1\sigma$, 95.45% between $\mu \pm 2\sigma$, and 99.70% between $\mu \pm 3\sigma$. It is sufficiently accurate to state that 95% of the values are within $\pm 2\sigma$ and 99% within $\pm 3\sigma$. When values are assigned to the $\pm\sigma$ multiples, they are confidence limits. For example, 10 ± 4 indicates that the confidence limits are 6 and 14, while values from 6 to 14 represent the confidence interval.

Another useful statistic is the standard error of the mean, σ_μ, which is the standard deviation divided by the square root of the number of values, or $\sigma/\sqrt{n}$. This is an estimate of the accuracy of the mean and implies that another sample from the same population would have a mean within some multiple of this. Multiples of this statistic include the same fraction of the values as stated above for σ. In practice, a relatively small number of average values is available, so the confidence intervals of the mean are expressed as $\bar{x} \pm ts/\sqrt{n}$ where t has the following values for 95% confidence intervals:

n	*t*
2	12.71
3	4.30

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n	*t*
4	3.18
5	2.78
10	2.26
∞	1.96

The use of *t* compensates for the tendency of a small number of values to underestimate uncertainty. For $n > 15$, it is common to use $t = 2$ to estimate the 95% confidence interval.

Still another statistic is the relative standard deviation, σ/μ, with its estimate s/x, also known as the coefficient of variation (*CV*), which commonly is expressed as a percentage. This statistic normalizes the standard deviation and sometimes facilitates making direct comparisons among analyses that include a wide range of concentrations. For example, if analyses at low concentrations yield a result of 10 ± 1.5 mg/L and at high concentrations 100± 8 mg/L, the standard deviations do not appear comparable. However, the percent relative standard deviations are 100 (1.5/10) = 15% and 100 (8/100) = 8%, which indicate the smaller variability obtained by using this parameter.

2. Log-Normal Distribution

In many cases the results obtained from analysis of environmental samples will not be normally distributed, i.e., a graph of the data will be obviously skewed, as shown at right in Figure 1010:1, with the mode, median, and mean being distinctly different. To obtain a nearly normal distribution, convert the results to logarithms and then calculate *x* and *s*. The antilogarithms of these two values are estimates of the geometric mean and the geometric standard deviation, x_g and s_g.

3. Rejection of Data

Quite often in a series of measurements, one or more of the results will differ greatly from the other values. Theoretically, no result should be rejected, because it may indicate either a faulty technique that casts doubt on all results or the presence of a true variant in the distribution. In practice, reject the result of any analysis in which a known error has occurred. In environmental studies, extremely high and low concentrations of contaminants may indicate the existence of areas with problems or areas with no contamination, so they should not be rejected arbitrarily.

An objective test for outliers has been described.[1] If a set of data is ordered from low to high: $x_L, x_2 \ldots x_H$, and the average and standard deviation are calculated, then suspected high or low outliers can be tested by the following procedure. First, calculate the statistic *T* :

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$$T = (x_H - \bar{x})/s \text{ for a high value, or}$$
$$T = (\bar{x} - x_L)/s \text{ for a low value.}$$

Second, compare the value of T with the value from Table 1010:I for either a 5% or 1% level of significance. If the calculated T is larger than the table value for the number of measurements, n, then the x_H or x_L is an outlier at that level of significance.

Further information on statistical techniques is available elsewhere.[2,3]

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1010 C. Glossary

1. Definition of Terms

The purpose of this glossary is to define concepts, not regulatory terms; it is not intended to be all-inclusive.

Accuracy—combination of bias and precision of an analytical procedure, which reflects the closeness of a measured value to a true value.

Bias—consistent deviation of measured values from the true value, caused by systematic errors in a procedure.

Calibration check standard—standard used to determine the state of calibration of an instrument between periodic recalibrations.

Confidence coefficient—the probability, %, that a measurement result will lie within the confidence interval or between the confidence limits.

Confidence interval—set of possible values within which the true value will lie with a specified level of probability.

Confidence limit—one of the boundary values defining the confidence interval.

Detection levels—Various levels in increasing order are:

Instrumental detection level (IDL)—the constituent concentration that produces a signal greater than five times the signal/ noise ratio of the instrument. This is similar, in many respects, to ‘‘critical level’’ and ‘‘criterion of detection.’’ The latter level is stated as

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1.645 times the *s* of blank analyses.

Lower level of detection (LLD)—the constituent concentration in reagent water that produces a signal 2(1.645)*s* above the mean of blank analyses. This sets both Type I and Type II errors at 5%. Other names for this level are ‘‘detection level’’ and ‘‘level of detection’’ (LOD).

Method detection level (MDL)—the constituent concentration that, when processed through the complete method, produces a signal with a 99% probability that it is different from the blank. For seven replicates of the sample, the mean must be 3.14*s* above the blank where *s* is the standard deviation of the seven replicates. Compute MDL from replicate measurements one to five times the actual MDL. The MDL will be larger than the LLD because of the few replications and the sample processing steps and may vary with constituent and matrix.

Level of quantitation (LOQ)/minimum quantitation level (MQL)—the constituent concentration that produces a signal sufficiently greater than the blank that it can be detected within specified levels by good laboratories during routine operating conditions. Typically it is the concentration that produces a signal 10*s* above the reagent water blank signal.

Duplicate—usually the smallest number of replicates (two) but specifically herein refers to duplicate samples, i.e., two samples taken at the same time from one location.

Internal standard—a pure compound added to a sample extract just before instrumental analysis to permit correction for inefficiencies.

Laboratory control standard—a standard, usually certified by an outside agency, used to measure the bias in a procedure. For certain constituents and matrices, use National Institute of Standards and Technology (NIST) Standard Reference Materials when they are available.

Precision—measure of the degree of agreement among replicate analyses of a sample, usually expressed as the standard deviation.

Quality assessment—procedure for determining the quality of laboratory measurements by use of data from internal and external quality control measures.

Quality assurance—a definitive plan for laboratory operation that specifies the measures used to produce data of known precision and bias.

Quality control—set of measures within a sample analysis methodology to assure that the process is in control.

Random error—the deviation in any step in an analytical procedure that can be treated by standard statistical techniques.

Replicate—repeated operation occurring within an analytical procedure. Two or more analyses for the same constituent in an extract of a single sample constitute replicate extract analyses.

Surrogate standard—a pure compound added to a sample in the laboratory just before processing so that the overall efficiency of a method can be determined.

Type I error—also called alpha error, is the probability of deciding a constituent is present when

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it actually is absent.

Type II error—also called beta error, is the probability of not detecting a constituent when it actually is present.

1020 QUALITY ASSURANCE

1020 A. Introduction

This section applies primarily to chemical analyses. See Section 9020 for quality assurance and control for microbiological analyses.

Quality assurance (QA) is the definitive program for laboratory operation that specifies the measures required to produce defensible data of known precision and accuracy. This program will be defined in a documented laboratory quality system.

The laboratory quality system will consist of a QA manual, written procedures, work instructions, and records. The manual should include a quality policy that defines the statistical level of confidence used to express the precision and bias of data, as well as the method detection limits. Quality systems, which include QA policies and all quality control (QC) processes, must be in place to document and ensure the quality of analytical data produced by the laboratory and to demonstrate the competence of the laboratory. Quality systems are essential for any laboratory seeking accreditation under state or federal laboratory certification programs. Included in quality assurance are quality control (Section 1020B) and quality assessment (Section 1020C). See Section 1030 for evaluation of data quality.

1. Quality Assurance Planning

Establish a QA program and prepare a QA manual or plan. Include in the QA manual and associated documents the following items[1-4]: cover sheet with approval signatures; quality policy statement; organizational structure; staff responsibilities; analyst training and performance requirements; tests performed by the laboratory; procedures for handling and receiving samples; sample control and documentation procedures; procedures for achieving traceability of measurements; major equipment, instrumentation, and reference measurement standards used; standard operating procedures (SOPs) for each analytical method; procedures for generation, approval, and control of policies and procedures; procedures for procurement of reference materials and supplies; procedures for procurement of subcontractors' services; internal quality control activities; procedures for calibration, verification, and maintenance of instrumentation and equipment; data-verification practices including interlaboratory comparison and proficiency-testing programs; procedures to be followed for feedback and corrective action whenever testing discrepancies are detected; procedures for exceptions that permit departure from documented policies; procedures for system and performance audits and reviews; procedures for assessing data precision and accuracy and determining method detection limits;

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procedures for data reduction, validation, and reporting; procedures for records archiving; procedures and systems for control of the testing environment; and procedures for dealing with complaints from users of the data. Also define and include the responsibility for, and frequency of, management review and updates to the QA manual and associated documents.

On the title page, include approval signatures and a statement that the manual has been reviewed and determined to be appropriate for the scope, volume, and range of testing activities at the laboratory,[4] as well as an indication that management has made a commitment to assure that the quality systems defined in the QA manual are implemented and followed at all times.

In the QA manual, clearly specify and document the managerial responsibility, authority, quality goals, objectives, and commitment to quality. Write the manual so that it is clearly understood and ensures that all laboratory personnel understand their roles and responsibilities.

Implement and follow chain-of-custody procedures to ensure that chain of custody is maintained and documented for each sample. Institute procedures to permit tracing a sample and its derivatives through all steps from collection through analysis to reporting final results to the laboratory's client and disposal of the sample. Routinely practice adequate and complete documentation, which is critical to assure data defensibility and to meet laboratory accreditation/certification requirements, and ensure full traceability for all tests and samples.

Standard operating procedures (SOPs) describe the analytical methods to be used in the laboratory in sufficient detail that a competent analyst unfamiliar with the method can conduct a reliable review and/or obtain acceptable results. Include in SOPs, where applicable, the following items[2-5]: title of referenced, consensus test method; sample matrix or matrices; method detection level (MDL); scope and application; summary of SOP; definitions; interferences; safety considerations; waste management; apparatus, equipment, and supplies; reagents and standards; sample collection, preservation, shipment, and storage requirements; specific quality control practices, frequency, acceptance criteria, and required corrective action if acceptance criteria are not met; calibration and standardization; details on the actual test procedure, including sample preparation; calculations; qualifications and performance requirements for analysts (including number and type of analyses); data assessment/data management; references; and any tables, flowcharts, and validation or method performance data. At a minimum, validate a new SOP before use by first determining the MDL and performing an initial demonstration of capability using relevant regulatory guidelines.

Use and document preventive maintenance procedures for instrumentation and equipment. An effective preventive maintenance program will reduce instrument malfunctions, maintain more consistent calibration, be cost-effective, and reduce downtime. Include measurement traceability to National Institute of Standards and Technology (NIST) Standard Reference Materials (SRMs) or commercially available reference materials certified traceable to NIST SRMs in the QA manual or SOP to establish integrity of the laboratory calibration and measurement program. Formulate document-control procedures, which are essential to data defensibility, to cover the complete process of document generation, approval, distribution, storage, recall, archiving, and disposal. Maintain logbooks for each test or procedure performed

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with complete documentation on preparation and analysis of each sample, including sample identification, associated standards and QC samples, method reference, date/time of preparation/analysis, analyst, weights and volumes used, results obtained, and any problems encountered. Keep logbooks that document maintenance and calibration for each instrument or piece of equipment. Calibration procedures, corrective actions, internal quality control activities, performance audits, and data assessments for precision and accuracy (bias) are discussed in Section 1020B and Section 1020C.

Data reduction, validation, and reporting are the final steps in the data-generation process. The data obtained from an analytical instrument must first be subjected to the data reduction processes described in the applicable SOP before the final result can be obtained. Specify calculations and any correction factors, as well as the steps to be followed in generating the sample result, in the QA manual or SOP. Also specify all of the data validation steps to be followed before the final result is made available. Report results in standard units of mass, volume, or concentration as specified in the method or SOP. Report results below the MDL in accordance with the procedure prescribed in the SOP. Ideally, include a statement of uncertainty with each result. See references and bibliography for other useful information and guidance on establishing a QA program and developing an effective QA manual.

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1020 B. Quality Control

Include in each analytical method or SOP the minimum required QC for each analysis. A good quality control program consists of at least the following elements, as applicable: initial demonstration of capability, ongoing demonstration of capability, method detection limit determination, reagent blank (also referred to as method blank), laboratory-fortified blank (also referred to as blank spike), laboratory-fortified matrix (also referred to as matrix spike), laboratory-fortified matrix duplicate (also referred to as matrix spike duplicate) or duplicate sample, internal standard, surrogate standard (for organic analysis) or tracer (for radiochemistry), calibration, control charts, and corrective action, frequency of QC indicators, QC acceptance criteria, and definitions of a batch. Section 1010 and Section 1030 describe calculations for evaluating data quality.

1. Initial Demonstration of Capability

The laboratory should conduct an initial demonstration of capability (IDC) at least once, by each analyst, before analysis of any sample, to demonstrate proficiency to perform the method and obtain acceptable results for each analyte. The IDC also is used to demonstrate that modifications to the method by the laboratory will produce results as precise and accurate as results produced by the reference method. As a minimum, include a reagent blank and at least four laboratory-fortified blanks (LFBs) at a concentration between 10 times the method detection level (MDL) and the midpoint of the calibration curve or other level as specified in the method.

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Run the IDC after analyzing all required calibration standards. Ensure that the reagent blank does not contain any analyte of interest at a concentration greater than half the MQL or other level as specified in the method. See Section 1010C, for definition of MQL. Ensure that precision and accuracy (percent recovery) calculated for the LFBs are within the acceptance criteria listed in the method of choice. If no acceptance criteria are provided, use 80 to 120% recovery and ≤20% relative standard deviation (RSD), as a starting point. If details of initial demonstration of capability are not provided in the method of choice, specify and reference the method or procedure used for demonstrating capability.

2. Ongoing Demonstration of Capability

The ongoing demonstration of capability, sometimes referred to as a ‘‘laboratory control sample or laboratory control standard,’’ ‘‘quality control check sample,’’ or ‘‘laboratory-fortified blank,’’ is used to ensure that the laboratory remains in control during the period when samples are analyzed, and separates laboratory performance from method performance on the sample matrix. See ¶ 5 below for further details on the laboratory-fortified blank. Preferably obtain this sample from an external source (not the same stock as the calibration standards). Analyze QC check samples on a quarterly basis, at a minimum.

3. Method Detection Level Determination and Application

Determine the method detection level (MDL) for each analyte of interest and method to be used before data from any samples are reported, using the procedure described in Section 1030C. As a starting point for determining the concentration to use in MDL determination, use an estimate of five times the estimated detection limit. Perform MDL determinations as an iterative process. If calculated MDL is not within a factor of l0 of the value for the known addition, repeat determinations at a more suitable concentration. Conduct MDL determinations at least annually (or other specified frequency) for each analyte and method in use at the laboratory. Perform or verify MDL determination for each instrument. Perform MDL determinations over a period of at least 3 d for each part of the procedure. Calculate recoveries for MDL samples. Recoveries should be between 50 and 150% and %RSD values ≤ 20% or repeat the MDL determination. Maintain MDL and IDC data and have them available for inspection.

Apply the MDL to reporting sample results as follows:

- Report results below the MDL as ‘‘not detected.’’
- Report results between the MDL and MQL with qualification for quantitation.
- Report results above the MQL with a value and its associated error.

4. Reagent Blank

A reagent blank or method blank consists of reagent water (See Section 1080) and all reagents that normally are in contact with a sample during the entire analytical procedure. The reagent blank is used to determine the contribution of the reagents and the preparative analytical steps to error in the measurement. As a minimum, include one reagent blank with each sample set (batch) or on a 5% basis, whichever is more frequent. Analyze a blank after the daily

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calibration standard and after highly contaminated samples if carryover is suspected. Evaluate reagent blank results for the presence of contamination. If unacceptable contamination is present in the reagent blank, identify and eliminate source of contamination. Typically, sample results are suspect if analyte(s) in the reagent blank are greater than the MQL. Samples analyzed with an associated contaminated blank must be re-prepared and re-analyzed. Refer to the method of choice for specific acceptance criteria for the reagent blank. Guidelines for qualifying sample results with consideration to reagent blank results are as follows:

- If the reagent blank is less than the MDL and sample results are greater than the MQL, then no qualification is required.
- If the reagent blank is greater than the MDL but less than the MQL and sample results are greater than the MQL, then qualify the results to indicate that analyte was detected in the reagent blank.
- If the reagent blank is greater than the MQL, further corrective action and qualification is required.

5. Laboratory-Fortified Blank

A laboratory-fortified blank is a reagent water sample to which a known concentration of the analytes of interest has been added. A LFB is used to evaluate laboratory performance and analyte recovery in a blank matrix. As a minimum, include one LFB with each sample set (batch) or on a 5% basis, whichever is more frequent. The definition of a batch is typically method-specific. Process the LFB through all of the sample preparation and analysis steps. Use an added concentration of at least 10 times the MDL, the midpoint of the calibration curve, or other level as specified in the method. Prepare the addition solution from a different reference source than that used for calibration. Evaluate the LFB for percent recovery of the added analytes. If LFB results are out of control, take corrective action, including re-preparation and re-analysis of associated samples if required. Use the results obtained for the LFB to evaluate batch performance, calculate recovery limits, and plot control charts (see ¶ 12 below). Refer to the method of choice for specific acceptance criteria for the LFB.

6. Laboratory-Fortified Matrix

A laboratory-fortified matrix (LFM) is an additional portion of a sample to which known amounts of the analytes of interest are added before sample preparation. The LFM is used to evaluate analyte recovery in a sample matrix. As a minimum, include one LFM with each sample set (batch) or on a 5% basis, whichever is more frequent. Add a concentration of at least 10 times the MRL, the midpoint of the calibration curve, or other level as specified in the method to the selected sample(s). Preferably use the same concentration as for the LFB to allow the analyst to separate the effect of matrix from laboratory performance. Prepare the LFM from a reference source different from that used for calibration. Make the addition such that sample background levels do not adversely affect the recovery (preferably adjust LFM concentrations if the known sample is above five times the background level). For example, if the sample contains the analyte of interest, make the LFM sample at a concentration equivalent to the concentration found in the

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known sample. Evaluate the results obtained for LFMs for accuracy or percent recovery. If LFM results are out of control, take corrective action to rectify the effect or use another method or the method of standard addition. Refer to the method of choice for specific acceptance criteria for LFMs until the laboratory develops statistically valid, laboratory-specific performance criteria. Base sample batch acceptance on results of LFB analyses rather than LFMs alone, because the matrix of the LFM sample may interfere with the method performance.

7. Laboratory-Fortified Matrix Duplicate/Duplicate Sample

A LFM duplicate is a second portion of the sample described in ¶ 6 above to which a known amount of the analyte of interest is added before sample preparation. If sufficient sample volume is collected, this second portion of sample is added and processed in the same way as the LFM. If sufficient sample volume is not collected to analyze a LFM duplicate, use an additional portion of an alternate sample to obtain results for a duplicate sample to gather data on precision. As a minimum, include one LFM duplicate or one duplicate sample with each sample set (batch) or on a 5% basis, whichever is more frequent. Evaluate the results obtained for LFM duplicates for precision and accuracy (precision alone for duplicate samples). If LFM duplicate results are out of control, take corrective action to rectify the effect or use another method or the method of standard addition. If duplicate results are out of control, reprepare and reanalyze the sample and take additional corrective action as needed (such as reanalysis of sample batch). Refer to the method of choice for specific acceptance criteria for LFM duplicates or duplicate samples until the laboratory develops statistically valid, laboratory-specific performance criteria. If no limits are included in the method of choice, calculate preliminary limits from initial demonstration of capability. Base sample batch acceptance on results of LFB analyses rather than LFM duplicates alone, because the matrix of the LFM sample may interfere with the method performance.

8. Internal Standard

Internal standards (IS) are used for organic analyses by GC/MS, some GC analyses, and some metals analyses by ICP/MS. An internal standard is an analyte included in each standard and added to each sample or sample extract/digestate just before sample analysis. Internal standards should mimic the analytes of interest but not interfere with the analysis. Choose an internal standard having retention time or mass spectrum separate from the analytes of interest and eluting in a representative area of the chromatogram. Internal standards are used to monitor retention time, calculate relative response, and quantify the analytes of interest in each sample or sample extract/digestate. When quantifying by the internal standard method, measure all analyte responses relative to this internal standard, unless interference is suspected. If internal standard results are out of control, take corrective action, including reanalysis if required. Refer to the method of choice for specific internal standards and their acceptance criteria.

9. Surrogates and Tracers

Surrogates are used for organic analyses; tracers are used for radiochemistry analyses. Surrogates and tracers are used to evaluate method performance in each sample. A surrogate

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standard is a compound of a known amount added to each sample before extraction. Surrogates mimic the analytes of interest and are compound(s) unlikely to be found in environmental samples, such as fluorinated compounds or stable, isotopically labeled analogs of the analytes of interest. Tracers are a different isotope of the analyte or element of interest. Surrogates and tracers are introduced to samples before extraction to monitor extraction efficiency and percent recovery in each sample. If surrogate or tracer results are out of control, take corrective action, including repreparation and reanalysis if required. Refer to the method of choice for specific surrogates or tracers and their acceptance criteria, until the laboratory develops statistically valid, laboratory-specific performance criteria.

10. Calibration

a. Instrument calibration: Perform instrument calibration, as well as maintenance, according to instrument manual instructions. Use instrument manufacturer's recommendations for calibration. Perform instrument performance checks, such as those for GC/MS analyses, according to method or SOP instructions.

b. Initial calibration: Perform initial calibration with a minimum of three concentrations of standards for linear curves, a minimum of five concentrations of standards for nonlinear curves, or as specified by the method of choice. Choose a lowest concentration at the reporting limit, and highest concentration at the upper end of the calibration range. Ensure that the calibration range encompasses the analytical concentration values expected in the samples or required dilutions. Choose calibration standard concentrations with no more than one order of magnitude between concentrations.

Use the following calibration functions as appropriate: response factor for internal standard calibration, calibration factor for external standard calibration, or calibration curve. Calibration curves may be linear through the origin, linear not through the origin, or nonlinear through or not through the origin. Some nonlinear functions can be linearized through mathematical transformations, e.g., log. The following acceptance criteria are recommended for the various calibration functions.

If response factors or calibration factors are used, the calculated %RSD for each analyte of interest must be less than the method-specified value. When using response factors (e.g., for GC/MS analysis), evaluate the performance or sensitivity of the instrument for the analyte of interest against minimum acceptance values for the response factors. Refer to the method of choice for the calibration procedure and acceptance criteria on the response factors or calibration factors for each analyte.

If linear regression is used, use the minimum correlation coefficient specified in the method. If the minimum correlation coefficient is not specified, then a minimum value of 0.995 is recommended. Compare each calibration point to the curve and recalculate. If any recalculated values are not within the method acceptance criteria, identify the source of outlier(s) and correct before sample quantitation. Alternately, a method's calibration can be judged against a reference method by measuring the method's ''calibration linearity'' or %RSD among the ''response

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factors'' at each calibration level or concentration.[2]

Use initial calibration, with any of the above functions (response factor, calibration factor, or calibration curve), for quantitation of the analytes of interest in samples. Use calibration verification, described in the next section, only for checks on the initial calibration and not for sample quantitation, unless otherwise specified by the method of choice. Perform initial calibration when the instrument is set up and whenever the calibration verification criteria are not met.

c. Calibration verification: Calibration verification is the periodic confirmation by analysis of a calibration standard that the instrument performance has not changed significantly from the initial calibration. Base this verification on time (e.g., every 12 h) or on the number of samples analyzed (e.g., after every 10 samples). Verify calibration by analyzing a single standard at a concentration near or at the midpoint of the calibration range. The evaluation of the calibration verification analysis is based either on allowable deviations from the values obtained in the initial calibration or from specific points on the calibration curve. If the calibration verification is out of control, take corrective action, including reanalysis of any affected samples. Refer to the method of choice for the frequency of calibration verification and the acceptance criteria for calibration verification.

11. QC Calculations

The following is a compilation of equations frequently used in QC calculations.

a. Initial calibrations:

Relative response factor (RRF):

$$RRF(x) = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x}$$

where:

RRF = relative response factor,
A = peak area or height of characteristic ion measured,
C = concentration,
is = internal standard, and
x = analyte of interest.

Response factor (RF):

$$RF(x) = \frac{A_x}{C_x}$$

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where:

RF = response factor,
A = peak area or height,
C = concentration, and
x = analyte of interest.

Calibration factor (CF):

$$CF = \frac{\text{peak area (or height) of standards}}{\text{mass injected}}$$

Relative standard deviation (%RSD):

$$\%\ RSD = \frac{s}{\bar{x}} \times 100\%$$

$$s = \sqrt{\sum_{i=1}^{n} \frac{(x_i - \bar{x})^2}{(n-1)}}$$

where:

s = standard deviation,
n = total number of values,
x_i = each individual value used to calculate mean, and
x = mean of n values.

b. Calibration verification:

% Difference (%D) for response factor:

$$\%\ D = \frac{\overline{RF_i} - RF_c}{RF_i} \times 100\%$$

where:

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$\overline{RF_i}$ = average RF or RRF from initial calibration, and
RF_c = relative RF or RRF from calibration verification standard.

% Difference (%D) for values:

$$\%D = \frac{\text{true value} - \text{found value}}{\text{true value}} \times 100\%$$

% Recovery:

$$\%\ \text{Recovery} = \frac{\text{found value}}{\text{true value}} \times 100\%$$

c. Laboratory-fortified blank (laboratory control sample):

$$\%\ \text{Recovery} = \frac{\text{found value}}{\text{true value}} \times 100\%$$

d. Surrogates:

$$\%\ \text{Recovery} = \frac{\text{quantity measured}}{\text{quantity added}} \times 100\%$$

e. Laboratory-fortified matrix (LFM) sample (matrix spike sample):

$$\%\ \text{Recovery} = \frac{(\text{LFM sample result} - \text{sample result})}{\text{known LFM added concentration}} \times 100\%$$

f. Duplicate sample:

Relative percent difference (RPD):

$$RPD = \frac{(\text{sample result} - \text{duplicate result})}{(\text{sample result} + \text{duplicate result})/2} \times 100\%$$

g. Method of standards addition:

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$$\text{Sample concentrations} \times \text{mg/L} = \frac{S_2 \times V_1 \times C}{(S_1 - S_2) \times V_2}$$

where:

C = concentration of the standard solution, mg/L,
S_1 = signal for fortified portion,
S_2 = signal for unfortified portion,
V_1 = volume of standard addition, L, and
V_2 = volume of sample portion used for method of standard addition, L.

12. Control Charts

Two types of control charts commonly used in laboratories are as follows: accuracy or means charts for QC samples, including reagent blanks, laboratory control standards, calibration check standards, laboratory fortified blanks, laboratory fortified matrices, and surrogates; and precision or range charts, %RSD or relative percent difference (RPD), for replicate or duplicate analyses. These charts are essential tools for quality control. Computer-generated and maintained lists or databases with values, limits, and trending may be used as an alternate to control charts.

a. Accuracy (means) chart: The accuracy chart for QC samples is constructed from the average and standard deviation of a specified number of measurements of the analyte of interest. The accuracy chart includes upper and lower warning levels (WL) and upper and lower control levels (CL). Common practice is to use ±2*s* and ±3*s* limits for the WL and CL, respectively, where *s* represents standard deviation. These values are derived from stated or measured values for reference materials. The number of measurements, *n* or *n*-1, used to determine the standard deviation, *s*, is specified relative to statistical confidence limits of 95% for WLs and 99% for CLs. Set up an accuracy chart by using either the calculated values for mean and standard deviation or the percent recovery. Percent recovery is necessary if the concentration varies. Construct a chart for each analytical method. Enter results on the chart each time the QC sample is analyzed. Examples of control charts for accuracy are given in Figure 1020:1.

b. Precision (range) chart: The precision chart also is constructed from the average and standard deviation of a specified number of measurements of the analyte of interest. If the standard deviation of the method is known, use the factors from Table 1020:I to construct the central line and warning and control limits as in Figure 1020:2. Perfect agreement between replicates or duplicates results in a difference of zero when the values are subtracted, so the baseline on the chart is zero. Therefore for precision charts, only upper warning limits and upper control limits are meaningful. The standard deviation is converted to the range so that the analyst need only subtract the two results to plot the value on the precision chart. The mean range is computed as:

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$$\overline{R} = D_2 s$$

the control limit as

$$CL = \overline{R} \pm 3s(R) = D_4 \overline{R}$$

and the warning limit as

$$WL = \overline{R} \pm 2s(R) = \overline{R} \pm 2/3(D_4 \overline{R} - \overline{R})$$

where:

D_2 = factor to convert s to the range (1.128 for duplicates, as given in Table 1020:I),
$s(R)$ = standard deviation of the range, and
D_4 = factor to convert mean range to $3s(R)$ (3.267 for duplicates, as given in Table 1020:I).

A precision chart is rather simple when duplicate analyses of a standard are used (Figure 1020:2). For duplicate analyses of samples, the plot will appear different because of the variation in sample concentration. If a constant relative standard deviation in the concentration range of interest is assumed, then R, D_4R etc., may be computed as above for several concentrations, a smooth curve drawn through the points obtained, and an acceptable range for duplicates determined. Figure 1020:3 illustrates such a chart. A separate table, as suggested below the figure, will be needed to track precision over time.

More commonly, the range can be expressed as a function of the relative standard deviation (coefficient of variation). The range can be normalized by dividing by the average. Determine the mean range for the pairs analyzed by

$$\overline{R} = (\Sigma R_i)/n$$

and the variance (square of the standard deviation) as

$$s_R^2 = (\Sigma R_i^2 - n\overline{R}^2)/(n - 1)$$

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Then draw lines on the chart at $R + 2s_R$ and $R + 3s_R$ and, for each duplicate analysis, calculate normalized range and enter the result on the chart. Figure 1020:4 is an example of such a chart.

c. Chart analyses: If the warning limits (WL) are at the 95% confidence level, 1 out of 20 points, on the average, would exceed that limit, whereas only 1 out of 100 would exceed the control limits (CL). Use the following guidelines, based on these statistical parameters, which are illustrated in Figure 1020:5 :

Control limit—If one measurement exceeds a CL, repeat the analysis immediately. If the repeat measurement is within the CL, continue analyses; if it exceeds the CL, discontinue analyses and correct the problem.

Warning limit—If two out of three successive points exceed a WL, analyze another sample. If the next point is within the WL, continue analyses; if the next point exceeds the WL, evaluate potential bias and correct the problem.

Standard deviation—If four out of five successive points exceed 1*s*, or are in decreasing or increasing order, analyze another sample. If the next point is less than 1*s*, or changes the order, continue analyses; otherwise, discontinue analyses and correct the problem.

Trending—If seven successive samples are on the same side of the central line, discontinue analyses and correct the problem.

The above considerations apply when the conditions are either above or below the central line, but not on both sides, e.g., four of five values must exceed either +1*s* or –1*s*. After correcting the problem, reanalyze the samples analyzed between the last in-control measurement and the out-of-control one.

Another important function of the control chart is assessment of improvements in method precision. In the accuracy and precision charts, if measurements never or rarely exceed the WL, recalculate the WL and CL using the 10 to 20 most recent data points. Trends in precision can be detected sooner if running averages of 10 to 20 are kept. Trends indicate systematic error; random error is revealed when measurements randomly exceed warning or control limits.

13. QC Evaluation for Small Sample Sizes

Small sample sizes, such as for field blanks and duplicate samples, may not be suitable for QC evaluation with control charts. QC evaluation techniques for small sample sizes are discussed elsewhere.[3]

14. Corrective Action

Quality control data outside the acceptance limits or exhibiting a trend are evidence of unacceptable error in the analytical process. Take corrective action promptly to determine and eliminate the source of the error. Do not report data until the cause of the problem is identified and either corrected or qualified. Example data qualifiers are listed in Table 1020:II. Qualifying data does not eliminate the need to take corrective actions, but allows for the reporting of data of known quality when it is either not possible or practical to reanalyze the sample(s). Maintain

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records of all out-of-control events, determined causes, and corrective action taken. The goal of corrective action is not only to eliminate such events, but also to reduce repetition of the causes.

Corrective action begins with the analyst, who is responsible for knowing when the analytical process is out of control. The analyst should initiate corrective action when a QC check exceeds the acceptance limits or exhibits trending and should report an out-of-control event to the supervisor. Such events include QC outliers, hold-time failures, loss of sample, equipment malfunctions, and evidence of sample contamination. Recommended corrective action to be used when QC data are unacceptable are as follows:

- Check data for calculation or transcription error. Correct results if error occurred.
- Check to see if sample(s) was prepared and analyzed according to the approved method and SOP. If it was not, prepare and/or analyze again.
- Check calibration standards against an independent standard or reference material. If calibration standards fail, reprepare calibration standards and/or recalibrate instrument and reanalyze affected sample(s).
- If a LFB fails, reanalyze another laboratory-fortified blank.
- If a second LFB fails, check an independent reference material. If the second source is acceptable, reprepare and reanalyze affected sample(s).
- If a LFM fails, check LFB. If the LFB is acceptable, qualify the data for the LFM sample or use another method or the method of standard addition.
- If a LFM and the associated LFB fail, reprepare and reanalyze affected samples.
- If reagent blank fails, analyze another reagent blank.
- If second reagent blank fails, reprepare and reanalyze affected sample(s).
- If the surrogate or internal standard known addition fails and there are no calculation or reporting errors, reprepare and reanalyze affected sample(s).

If data qualifiers are used to qualify samples not meeting QC requirements, the data may or may not be usable for the intended purposes. It is the responsibility of the laboratory to provide the client or end-user of the data with sufficient information to determine the usability of qualified data.

15. References

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1020 C. Quality Assessment

Quality assessment is the process used to ensure that quality control measures are being performed as required and to determine the quality of the data produced by the laboratory. It includes such items as proficiency samples, laboratory intercomparison samples, and performance audits. These are applied to test the precision, accuracy, and detection limits of the methods in use, and to assess adherence to standard operating procedure requirements.

1. Laboratory Check Samples (Internal Proficiency)

The laboratory should perform self-evaluation of its proficiency for each analyte and method in use by periodically analyzing laboratory check samples. Check samples with known amounts of the analytes of interest supplied by an outside organization or blind additions can be prepared independently within the laboratory to determine percent recovery of the analytes of interest by each method.

In general, method performance will have been established beforehand; acceptable percent recovery consists of values that fall within the established acceptance range. For example, if the acceptable range of recovery for a substance is 85 to 115%, then the analyst is expected to achieve a recovery within that range on all laboratory check samples and to take corrective action if results are outside of the acceptance range.

2. Laboratory Intercomparison Samples

A good quality assessment program requires participation in periodic laboratory intercomparison studies. Commercial and some governmental programs supply laboratory intercomparison samples containing one or multiple constituents in various matrices. The frequency of participation in intercomparison studies should be adjusted relative to the quality of results produced by the analysts. For routine procedures, semi-annual analyses are customary. If failures occur, take corrective action and analyze laboratory check samples more frequently until acceptable performance is achieved.

3. Compliance Audits

Compliance audits are conducted to evaluate whether the laboratory meets the applicable requirements of the SOP or consensus method claimed as followed by the laboratory. Compliance audits can be conducted by internal or external parties. A checklist can be used to document the manner in which a sample is treated from time of receipt to final reporting of the result. The goal of compliance audits is to detect any deviations from the SOP or consensus method so that corrective action can be taken on those deviations. An example format for a

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checklist is shown in Table 1020:III.

4. Laboratory Quality Systems Audits

A quality systems audit program is designed and conducted to address all program elements and provide a review of the quality system. Quality systems audits should be conducted by a qualified auditor(s) who is knowledgeable about the section or analysis being audited. Audit all major elements of the quality system at least annually. Quality system audits may be conducted internally or externally; both types should occur on a regular scheduled basis and should be handled properly to protect confidentiality. Internal audits are used for self-evaluation and improvement. External audits are used for accreditation as well as education on client requirements and for approval of the end use of the data. Corrective action should be taken on all audit findings and its effectiveness reviewed at or before the next scheduled audit.

5. Management Review

Review and revision of the quality system, conducted by laboratory management, is vital to its maintenance and effectiveness. Management review should assess the effectiveness of the quality system and corrective action implementation, and should include internal and external audit results, performance evaluation sample results, input from end user complaints, and corrective actions.

6. Bibliography

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1030 DATA QUALITY

1030 A. Introduction

The role of the analytical laboratory is to produce measurement-based information that is technically valid, legally defensible, and of known quality. Quality assurance is aimed at optimizing the reliability of the measurement process. All measurements contain error, which may be systematic (with an unvarying magnitude) or random (with equal probability of being positive or negative and varying in magnitude). Determination of the systematic and random error components of an analytical method uniquely defines the analytical performance of that

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method.[1] Quality control (QC) procedures identify and control these sources of error.

1. Measures of Quality Control

Random error (precision) and systematic error (bias) are two routine indicators of measurement quality used by analysts to assess validity of the analytical process. Precision is the closeness of agreement between repeated measurements. A measurement has acceptable precision if the random errors are low. Accuracy is the closeness of a measurement to the true value. A measurement is acceptably accurate when both the systematic and random errors are low. QC results outside the acceptance limits, as set by the data quality objectives, are evidence of an analytical process that may be out of control due to determinant errors such as contaminated reagents or degraded standards.

2. Measurement Error and Data Use

Measurement error, whether random or systematic, reduces the usability of laboratory data. As a measured value decreases, its relative error (e.g., relative standard deviation) may increase and its usable information decrease. Reporting tools, such as detection or quantitation limits, frequently are used to establish a lower limit on usable information content.

Laboratory data may be used for such purposes as regulatory monitoring, environmental decision-making, and process control. The procedures used to extract information for these different purposes vary and may be diametrically opposed. For example, a measurement for regulatory monitoring may be appropriately qualified when below the detection level because the error bar is relatively large and may preclude a statistically sound decision. Data collected over a period of time, however, may be treated by statistical methods to provide a statistically sound decision even when many of the data are below detection levels.[2]

3. The Analyst's Responsibility

The analyst must understand the measures of quality control and how to apply them to the data quality objectives of process control, regulatory monitoring, and environmental field studies. It is important that the quality objectives for the data be clearly defined and detailed before sample analysis so that the data will be technically correct and legally defensible.

4. Reference

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1030 B. Measurement Uncertainty

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Standard Methods for the Examination of Water and Wastewater

1. Introduction

Even with the fullest possible extent of correction, every measurement has error that is ultimately unknown and unknowable. The description of this unknown error is ‘‘measurement uncertainty.’’

Reporting uncertainty along with a measurement result is good practice, and may spare the user from making unwarranted or risky decisions based only on the measurement.

Whereas measurement error (E) is the actual, unknown deviation of the measurement (M) from the unknown true value (T), measurement uncertainty (U) is the state of knowledge about this unknown deviation, and is often expressed as U, as in $M \pm U$. U may be defined as an uncertainty expression.[1,2] This section concerns the definition of U, how to compute it, a recommendation for reporting uncertainty, the interpretation and scope of uncertainty, and other ways of expressing measurement uncertainty.

2. Error

A measurement can be related to the unknown true value and unknown measurement error as follows:

$$M = T + E$$

This is a simple additive relationship. There are other plausible relationships between M and E, such as multiplicative or arbitrary functional relationships, which are not discussed here.

Because E is unknown, M must be regarded as an uncertain measurement. In some practical situations, a value may be treated as known. T^* may be, for example, a published reference value, a traceable value, or a consensus value. The purpose of the substitution may be for convenience or because the measurement process that produced T^* has less bias or variation than the one that produced M. For example, based on the average of many measurements, a vessel might be thought to contain $T^* = 50$ µg/ L of salt in water. It then may be sampled and routinely measured, resulting in a reported concentration of $M = 51$ µg/L. The actual concentration may be $T = 49.9$ µg/L, resulting in $E = 51 - 49.9 = 1.1$ µg/L.

To generalize the nature of uncertainty, measurement error may be negligible or large in absolute terms (i.e., in the original units) or relative terms (i.e., unitless, $E \div T$ or T^*). The perceived acceptability of the magnitude of an absolute error depends on its intended use. For example, an absolute error of 1.1 µg/L may be inconsequential for an application where any concentration over 30 µg/L will be sufficient. However, if it is to be used instead as a standard for precision measurement (e.g., of pharmaceutical ingredients), 1.1 µg/L too much could be unacceptable.

3. Uncertainty

Reported measurement uncertainty will contain the actual measurement error with a stated

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level of confidence. For example, if $M \pm U$ is presented as a 95% confidence interval, approximately 95% of the time, the measurement error E will fall within the range of $\pm U$.

4. Bias

Bias is the systematic component of error. It is defined as the signed deviation between the limiting average measured value and the true value being measured as the number of measurements in the average tends to infinity and the uncertainty about the average tends to zero. For example, the reason the T = 49.9 µg/L salt solution is thought to be T^* = 50 µg/L could be a bias, B = 0.1 µg/L. The ''leftover'' error, 1.1 – 0.1 = 1.0 µg/L, is the random component. This random component (also called stochastic error) changes with each measurement. The bias is fixed, and may be related to the laboratory method used to produce T^*. Usually, a recognized method will be used to produce or certify the traceable standard, a sample with a certificate stating the accepted true value T^*. The method may be the best method available or simply the most widely accepted method. It is chosen to have very low error, both bias and random. Such a traceable standard may be purchased from a standards organization such as NIST.

5. Bias and Random Variation

Measurement error, E, (and measurement uncertainty) can be split into two components, random and systematic:

$$E = Z + B$$

Random error, Z, is the component of the measurement error that changes from one measurement to the next, under certain conditions. Random measurement errors are assumed to be independent and have a distribution, often assumed to be Gaussian (i.e., they are normally distributed). The normal distribution of Z is characterized by the distribution mean, µ, and standard deviation, σ_E. In discussion of measurement error distribution, µ is assumed to be zero because any non-zero component is part of bias, by definition. The population standard deviation, σ_E, can be used to characterize the random component of measurement error because the critical values of the normal distribution are well known and widely available. For example, about 95% of the normal distribution lies within the interval $\mu \pm 2\sigma_E$. Hence, if there is no measurement bias, and measurement errors are independent and normally distributed, $M \pm 2\sigma_E$ (95% confidence, assumed normal) is a suitable way to report a measurement and its uncertainty. More generally, normal probability tables and statistical software give the proportion of the normal distribution and thus the % confidence gained that is contained within $\pm k\sigma_E$ for any value of scalar k.

Usually, however, the population standard deviation, σ_E, is not known and must be estimated by the sample standard deviation, s_E. This estimate of the standard deviation is based on multiple observations and statistical estimation. In this case, the choice of the scalar k must be based not

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on the normal distribution function, but on the Student's *t* distribution, taking into account the number of degrees of freedom associated with s_E.

Systematic error (*B*) is all error that is not random, and typically is equated with bias. Systematic error also can contain outright mistakes (blunders) and lack of control (drifts, fluctuations, etc.).[3] In this manual, the terms ''systematic error'' and ''bias'' are used interchangeably.

Systematic uncertainty often is more difficult to estimate and make useful than is random uncertainty. Knowledge about bias is likely to be hard to obtain, and once obtained it is appropriately and likely to be exploited to make the measurement less biased. If measurement bias is known exactly (or nearly so), the user can subtract it from *M* to reduce total measurement error.

If measurement bias is entirely unknown, and could take on any value from a wide but unknown distribution of plausible values, users may adopt a worst-case approach and report an extreme bound, or they may simply ignore the bias altogether. For example, historical data may indicate that significant interlaboratory biases are present, or that every time a measurement system is cleaned, a shift is observed in QC measurements of standards. In the absence of traceable standards, it is hard for laboratory management or analysts to do anything other than ignore the potential problem.

The recommended practice is to conduct routine QA/QC measurements with a suite of internal standards. Plot measurements on control charts, and when an out-of-control condition is encountered, recalibrate the system with traceable standards. This permits the laboratory to publish a boundary on bias, assuming that the underlying behavior of the measurement system is somewhat predictable and acceptably small in scale in between QA/QC sampling (e.g., slow drifts and small shifts).

6. Repeatability, Reproducibility, and Sources of Bias and Variation

a. Sources and measurement: The sources of bias and variability in measurements are many; they include sampling error, sample preparation, interference by matrix or other measurement quantities/qualities, calibration error variation, software errors, counting statistics, deviations from method by analyst, instrument differences (e.g., chamber volume, voltage level), environmental changes (temperature, humidity, ambient light, etc.), contamination of sample or equipment (e.g., carryover and ambient contamination), variations in purity of solvent, reagent, catalyst, etc., stability and age of sample, analyte, or matrix, and warm-up or cool-down effects, or a tendency to drift over time.

The simplest strategy for estimating typical measurement bias is to measure a traceable (known) standard, then compute the difference between the measured value *M* and the known value *T*, assumed to be the true value being measured.

$$M - T = B + Z$$

The uncertainty in the measurement of the traceable standard is assumed to be small,

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although in practice there may be situations where this is not an appropriate assumption. If random measurement uncertainty is negligible (i.e., $Z \approx 0$), the difference, $M - T$, will provide an estimate of bias (B). If random uncertainty is not negligible, it can be observed and quantified by making a measurement repeatedly on the same test specimen (if the measurement process is not destructive). This may be part of a QA/QC procedure.

b. Repeatability: As quantified by the repeatability standard deviation (σ_{RPT}), repeatability is the minimal variability of a measurement system obtained by repeatedly measuring the same specimen while allowing *no* controllable sources of variability to affect the measurement. Repeatability also can be obtained by pooling sample standard deviations of measurements of J different specimens, as follows:

$$\sigma_{RPT} = \sqrt{\frac{1}{J} \cdot \sum_{i=1}^{J} \sigma_{RPT,i}^{2}}$$

Repeatability also is called ‘‘intrinsic measurement variability,’’ and is considered an approximate lower boundary to the measurement standard deviation that will be experienced in practice. The repeatability standard deviation sometimes is used to compute uncertainty intervals, $\pm U$, that can be referred to as ultimate instrument variability, based on the Student's t distribution function ($\pm U = \pm k s_{RPT}$).

Common sense and application experience demonstrate that repeatability is an overly optimistic estimate to report as measurement uncertainty for routine measurement. In routine use, measurements will be subject to many sources of bias and variability that are intentionally eliminated or restrained during a repeatability study. In routine use, uncertainty in both bias (B) and variability (Z) are greater.

c. Reproducibility: As quantified by the reproducibility standard deviation (σ_{RPD}), reproducibility is the variability of a measurement system obtained by repeatedly measuring a sample while allowing (or requiring) selected sources of bias or variability to affect the measurement. With σ_{RPD}, provide list of known applicable sources of bias and variability, and whether or not they were varied.

Barring statistical variation (i.e., variation in estimates of variability, such as the noisiness in sample standard deviations), the reproducibility standard deviation always is greater than the repeatability standard deviation, because it has additional components. Typically, one or more of the following is varied in a reproducibility study: instrument, analyst, laboratory, or day. Preferably design a study tailored to the particular measurement system (see 1030B.7). If the sample is varied, compute reproducibility standard deviations separately for each sample, then pool results if they are homogeneous. Treat factors varied in the study as random factors and assume them to be independent normal random variables with zero mean. However, this

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assumption often can be challenged, because the sample and possibly the target populations may be small (they may even be identical), and there may be a question of ‘‘representativeness.’’ For example, six laboratories (or analysts, or instruments) may report usable measurements out of a total population of twenty capable of doing tandem mass spectrometry for a particular analyte and matrix. It is hard to know how representative the six are of the twenty, especially after a ranking and exclusion process that can follow a study, and whether the biases of the twenty are normally distributed (probably not discernible from six measurements, even if the six are representative).

It may be more appropriate to treat each factor with few, known factor values (i.e., choices such as laboratories) as fixed factors, to use the statistical term. Fixed factors have fixed effects. That is, each laboratory has a different bias, as might each analyst, each instrument, and each day, but these biases are not assumed to have a known (or knowable) distribution. Therefore, a small sample cannot be used to estimate distribution parameters, particularly a standard deviation. For example, assuming that variables are random, normal, and have zero mean may be inappropriate in an interlaboratory round-robin study. It must be assumed that every laboratory has some bias, but it is difficult to characterize the biases because of laboratory anonymity, the small number of laboratories contributing usable data, and other factors.

Because of these concerns about assumptions and the potential ambiguity of its definition, do not report reproducibility unless it is accompanied with study design and a list of known sources of bias and variability and whether or not they were varied.

7. Gage Repeatability and Reproducibility, and the Measurement Capability Study

Combining the concepts of repeatability and reproducibility, the Gage Repeatability and Reproducibility (Gage R&R) approach has been developed.[4] It treats all factors as random (including biases), and is based on the simplest nontrivial model:

$$Z = Z_{RPT} + Z_L$$

where:

Z_{RPT} = normally distributed random variable with mean equal to zero and variance equal to σ_{RPT}^2, and

Z_L = normally distributed random variable with mean equal to zero and with the variance of the factor (e.g., interlaboratory) biases, σ_L^2.

The overall measurement variation then is quantified by

$$\sigma_E = \sigma_{RPD} = \sqrt{\sigma_{RPT}^2 + \sigma_L^2}$$

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Estimates for σ_{RPT} and σ_{RPD} usually are obtained by conducting a nested designed study and analyzing variance components of the results. This approach can be generalized to reflect good practice in conducting experiments. The following measurement capability study (MCS) procedure is recommended. The objective of such studies is not necessarily to quantify the contribution of every source of bias and variability, but to study those considered to be important, through systematic error budgeting.

To perform a measurement capability study to assess measurement uncertainty through systematic error budgeting, proceed as follows:

Identify sources of bias and variation that affect measurement error. This can be done with a cause-and-effect diagram, perhaps with source categories of: equipment, analyst, method (i.e., procedure and algorithm), material (i.e., aspects of the test specimens), and environment.

Select sources to study, either empirically or theoretically. Typically, study sources that are influential, that can be varied during the MCS, and that cannot be eliminated during routine measurement. Select models for the sources. Treat sources of bias as fixed factors, and sources of variation as random factors.

Design and conduct the study, allowing (or requiring) the selected sources to contribute to measurement error. Analyze the data graphically and statistically (e.g., by regression analysis, ANOVA, or variance components analysis). Identify and possibly eliminate outliers (observations with responses that are far out of line with the general pattern of the data), and leverage points (observations that exert high, perhaps undue, influence).

Refine the models, if necessary (e.g., based on residual analysis), and draw inferences for future measurements. For random effects, this probably would be a confidence interval; for fixed effects, a table of estimated biases.

8. Other Assessments of Measurement Uncertainty

In addition to the strictly empirical MCS approach to assessing measurement uncertainty, there are alternative procedures, discussed below in order of increasing empiricism.

a. Exact theoretical: Some measurement methods are tied closely to exact first-principles models of physics or chemistry. For example, measurement systems that count or track the position and velocity of atomic particles can have exact formulas for measurement uncertainty based on the known theoretical behavior of the particles.

b. Delta method (law of propagation of uncertainty): If the measurement result can be expressed as a function of input variables with known error distributions, the distribution of the measurement result sometimes can be computed exactly.

c. Linearized: The mathematics of the delta method may be difficult, so a linearized form of $M = T + E$ may be used instead, involving a first-order Taylor series expansion about key variables that influence E:

$$(M + \delta M) = T + \delta M/\delta G_1 + \delta M/\delta G_2 + \delta M/\delta G_3 + ...$$

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for sources G_1, G_2, G_3, etc. of bias and variation that are continuous variables (or can be represented by continuous variables). The distribution of this expression may be simpler to determine, as it involves the linear combination of scalar multiples of the random variables.

d. Simulation: Another use of the delta method is to conduct computer simulation. Again assuming that the distributions of measurement errors in input variables are known or can be approximated, a computer (i.e., Monte Carlo) simulation can obtain empirically the distribution of measurement errors in the result. Typically, one to ten thousand sets of random deviates are generated (each set has one random deviate for each variable), and the value of M is computed and archived. The archived distribution is an empirical characterization of the uncertainty in M.

e. Sensitivity study (designed experiment): If the identities and distributions of sources of bias and variation are known and these sources are continuous factors, but the functional form of the relationship between them and M is not known, an empirical sensitivity study (i.e., MCS) can be conducted to estimate the low-order coefficients ($\delta M/\delta G$) for any factor G. This will produce a Taylor series approximation to the δM, which can be used to estimate the distribution of δM, as in ¶ c above.

f. Random effects study: This is the nested MCS and variance components analysis described in ¶ 7 above.

g. Passive empirical (QA/QC-type data): An even more empirical and passive approach is to rely solely on QA/QC or similar data. The estimated standard deviation of sample measurements taken on many different days, by different analysts, using different equipment, perhaps in different laboratories can provide a useful indication of uncertainty.

9. Statements of Uncertainty

Always report measurements with a statement of uncertainty and the basis for the statement.

Develop uncertainty statements as follows:[4-6]

Involve experts in the measurement principles and use of the measurement system, individuals familiar with sampling contexts, and potential measurement users to generate a cause-and-effect diagram for measurement error, with sources of bias and variation (‘‘factors’’) identified and prioritized. Consult literature quantifying bias and variation. If needed, conduct one or more measurement capability studies incorporating those sources thought to be most important. In some cases, Gage R&R studies may be sufficient. These studies will provide ‘‘snapshot’’ estimates of bias and variation.

Institute a QA/QC program in which traceable or internal standards are measured routinely and the results are plotted on X and R control charts (or equivalent charts). React to out-of-control signals on the control charts. In particular, re-calibrate using traceable standards when the mean control chart shows a statistically significant change. Use the control charts, relevant literature, and the MCSs to develop uncertainty statements that involve both bias and variation.

10. References

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1030 C. Method Detection Level

1. Introduction

Detection levels are controversial, principally because of inadequate definition and confusion of terms. Frequently, the instrumental detection level is used for the method detection level and *vice versa*. Whatever term is used, most analysts agree that the smallest amount that can be detected above the noise in a procedure and within a stated confidence level is the detection level. The confidence levels are set so that the probabilities of both Type I and Type II errors are acceptably small.

Current practice identifies several detection levels (see 1010C), each of which has a defined purpose. These are the instrument detection level (IDL), the lower level of detection (LLD), the method detection level (MDL), and the level of quantitation (LOQ). Occasionally the instrument detection level is used as a guide for determining the MDL. The relationship among these levels is approximately IDL:LLD:MDL:LOQ = 1:2:4:10.

2. Determining Detection Levels

An operating analytical instrument usually produces a signal (noise) even when no sample is present or when a blank is being analyzed. Because any QA program requires frequent analysis of blanks, the mean and standard deviation become well known; the blank signal becomes very precise, i.e., the Gaussian curve of the blank distribution becomes very narrow. The IDL is the constituent concentration that produces a signal greater than three standard deviations of the mean noise level or that can be determined by injecting a standard to produce a signal that is five times the signal-to-noise ratio. The IDL is useful for estimating the constituent concentration or amount in an extract needed to produce a signal to permit calculating an estimated method detection level.

The LLD is the amount of constituent that produces a signal sufficiently large that 99% of

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the trials with that amount will produce a detectable signal. Determine the LLD by multiple injections of a standard at near zero concentration (concentration no greater that five times the IDL). Determine the standard deviation by the usual method. To reduce the probability of a Type I error (false detection) to 5%, multiply *s* by 1.645 from a cumulative normal probability table. Also, to reduce the probability of a Type II error (false nondetection) to 5%, double this amount to 3.290. As an example, if 20 determinations of a low-level standard yielded a standard deviation of 6 μg/L, the LLD is 3.29 × 6 = 20 μg/L.[1]

The MDL differs from the LLD in that samples containing the constituent of interest are processed through the complete analytical method. The method detection level is greater than the LLD because of extraction efficiency and extract concentration factors. The MDL can be achieved by experienced analysts operating well-calibrated instruments on a nonroutine basis. For example, to determine the MDL, add a constituent to reagent water, or to the matrix of interest, to make a concentration near the estimated MDL.[2] Prepare and analyze seven portions of this solution over a period of at least 3 d to ensure that MDL determination is more representative than measurements performed sequentially. Include all sample processing steps in the determination. Calculate the standard deviation and compute the MDL. The replicate measurements should be in the range of one to five times the calculated MDL. From a table of the one-sided *t* distribution select the value of *t* for 7 – 1 = 6 degrees of freedom and at the 99% level; this value is 3.14. The product 3.14 times *s* is the desired MDL.

Although the LOQ is useful within a laboratory, the practical quantitation limit (PQL) has been proposed as the lowest level achievable among laboratories within specified limits during routine laboratory operations.[3] The PQL is significant because different laboratories will produce different MDLs even though using the same analytical procedures, instruments, and sample matrices. The PQL is about five times the MDL and represents a practical and routinely achievable detection level with a relatively good certainty that any reported value is reliable.

3. Description of Levels

Figure 1030:1 illustrates the detection levels discussed above. For this figure it is assumed that the signals from an analytical instrument are distributed normally and can be represented by a normal (Gaussian) curve.[4] The curve labeled B is representative of the background or blank signal distribution. As shown, the distribution of the blank signals is nearly as broad as for the other distributions, that is $\sigma_B = \sigma_I = \sigma_L$. As blank analyses continue, this curve will become narrower because of increased degrees of freedom.

The curve labeled I represents the IDL. Its average value is located $k\sigma_B$ units distant from the blank curve, and *k* represents the value of *t* (from the one-sided *t* distribution) that corresponds to the confidence level chosen to describe instrument performance. For a 95% level and $n = 14$, $k = 1.782$ and for a 99% limit, $k = 2.68$. The overlap of the B and I curves indicates the probability of not detecting a constituent when it is present (Type II error).

The curve at the extreme right of Figure 1030:1 represents the LLD. Because only a finite

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number of determinations is used for calculating the IDL and LLD, the curves are broader than the blank but are similar, so it is reasonable to choose $\sigma_I = \sigma_L$. Therefore, the LLD is $k\sigma_I + k\sigma_L = 2k\sigma_L$ from the blank curve.

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1030 D. Data Quality Objectives

1. Introduction

Data quality objectives are systematic planning tools based on the scientific method. They are used to develop data collection designs and to establish specific criteria for the quality of data to be collected. The process helps planners identify decision-making points for data collection activities, to determine the decisions to be made based on the data collected, and to identify the criteria to be used for making each decision. This process documents the criteria for defensible decision-making before an environmental data collection activity begins.

2. Procedure

The data quality objective process comprises the stages explained in this section.

a. Stating the issue: Sometimes the reason for performing analyses is straightforward, e.g., to comply with a permit or other regulatory requirement. However, at times the reason is far more subjective; e.g., to gather data to support remedial decisions, or to track the changes in effluent quality resulting from process changes. A clear statement of the reason for the analyses is integral to establishing appropriate data quality objectives; this should include a statement of how the data are to be used, e.g., to determine permit compliance, to support decisions as to whether additional process changes will be necessary, etc.

b. Identifying possible decisions and actions: Initially, express the principal study question. For example: Is the level of contaminant A in environmental medium B higher than regulatory

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level C? This example is relatively straightforward.

Other questions may be more complex, for example: How is aquatic life affected by discharges into receiving waters by publicly owned treatment works (POTWs)? Break such a question down into several questions that might then be used to develop several decisions; organize these questions in order of consensus priority of all participating parties.

Identify alternative actions, including the no-action alternative, that could result from the various possible answers to the principal study questions.

In the first example above, if the level of contaminant in the environmental medium is higher than the regulatory level, some cleanup or treatment action may be indicated. If it is lower, the no-action alternative may be indicated, or the study team may wish to look at other environmental media and regulatory levels.

Finally, combine the principal study question with alternative actions into a decision statement. For the first example, the decision statement might be: Determine whether the mean level of contaminant A in environmental medium B exceeds the regulatory level C and requires remediation.

A multi-tiered decision statement might be: . . . if not, determine whether the maximum level of contaminant A in environmental medium D exceeds the regulatory level E and requires remediation.

c. Identifying inputs: Identify the information needed to make the necessary decision. Inputs may include measurements (including measurements of physical and chemical characteristics), data sources (historical), applicable action levels, or health effects concerns.

Identify and list the sources of information: previous data, historical records, regulatory guidance, professional judgment, scientific literature, and new data. Evaluate qualitatively whether any existing data are appropriate for the study. Existing data will be evaluated quantitatively later. Identify information needed to establish the action level. Define the basis for setting the action levels: they may be based on regulatory thresholds or standards or may be derived from issue-specific considerations, such as risk analysis. Determine only the criteria that will be used to set the numerical value. The actual numerical action level is determined later.

Confirm that the appropriate measurement methods exist to provide the necessary data. Assure that there are analytical methods for the parameters or contaminants of interest, and that they are appropriate for the matrix to be sampled. Consider the samples to be collected and the analytical methods to determine the potential for matrix interferences for each method. Assure that the limits of the method (e.g., detection limit, quantitation limit, reporting limit) are appropriate for the matrix (e.g., drinking water, wastewater, groundwater, leachate, soil, sediment, hazardous waste) and the parameter to be measured. Ensure that a laboratory is available to perform the analyses; determine its capacity, turn-around time, data product, and cost. Include this information as input to the decision-making process.

d. Identifying study limits: Identify both the geographical area and the time frame to which the decision will apply. Also define the scale of decision-making. Identify the smallest, most appropriate subsets of the total population for which decisions will be made. These subsets could

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be based on spatial or temporal boundaries. For example, while spatial boundaries of the issue may be a 300-acre site, samples may be collected from, and decisions made for, each square of a grid made up of 50-ft squares drawn on a site map. Also, while temporal boundaries of the issue may be identified (as the duration of storm events), samples may be collected at, and decisions made for, 2-h increments during a storm event. A decision resulting from this type of study might be to construct a stormwater bypass structure that would carry the first flow, which might contain the highest nutrient load, but would not necessarily carry the peak flow.

Identify any practical constraints on data collection. Identify any logistical issues that might interfere with the data-collection process, including seasonal conditions, daily variations, meteorological conditions, access conditions, availability of personnel, time, equipment, project budget, regulatory limits, appropriate analytical methods, matrix interferences, detection limits, reporting limits, site access limitations, and expertise.

e. Developing a decision rule: Define the parameter of interest, specify an action level, and integrate outputs from the previous data quality objective process steps into a single statement that describes a logical basis for choosing among alternative actions. A decision rule may be worded as follows, substituting case-specific information for the underlined words:

If *the factor of interest* within *the scale of decision making* is greater than *the action level*, then take *alternative action A*; otherwise take *alternative action B.*

The factor of interest is a descriptive measure (such as an instantaneous value, a mean, a median, or a proportion) that specifies the characteristic (such as calcium level in water, PCB level in soil, radon level in air) that the decision-maker would like to know about the statistical population affected by the potential decision (such as rivers or streams within a specific watershed, the specified depth of soil within a site boundary, or in basements or crawlspaces within a metropolitan area).

The scale of decision-making is the smallest, most appropriate subset for which separate decisions will be made (such as each stream segment/river mile or each square of a grid identified on a site map, or each section of township X, range Y of county Z).

The action level is a measurement threshold value of the parameter of interest that provides the criterion for choosing among alternative actions (such as a stream standard to protect aquatic life, a published regulatory standard, or a health-effects-related level).

Alternative action A is the alternative of choice if the action level is exceeded (such as initiate non-point-source controls, initiate cleanup of the soil to a specified depth, or distribute technical information to property owners). Noncompliance with the action level is the alternative hypothesis. (Either alternative action can be labeled A without making the decision rule any less valid.)

Alternative action B is the alternative of choice if the action level is not exceeded (such as continue routine monitoring, leave the soil in place, or provide a summary of the data collection activity to potential developers). Compliance with the action level is the null hypothesis that is generally the no-action alternative or baseline condition. Either alternative action can be labeled B without making the decision rule any less valid.

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f. Specifying limits on decision errors: Establish limits on the decision error that the decision-maker will tolerate. Use these limits to establish performance goals for design of the data collection activity. Base limits on the consequences of making a wrong decision.

Decision-makers are interested in knowing the true state of some feature of the environment. Environmental data can be only an estimate of this true state; decisions therefore are based on environmental data that are in some degree of error. The goal is to develop a data-collection design that reduces the chances of making a decision error to a level that is acceptable to the decision-maker. Sources of uncertainty include sample design error and measurement error; when combined, they represent the total study error.

Sample design error refers to the error inherent in using a portion of a population to represent the whole population. It is not practical, for example, to measure and record the concentration of an analyte at every point in a stream on a continuous basis; instead, measure analyte concentration at well-defined locations and time intervals to represent this analyte concentration continuum.

Measurement error refers to the error inherent in the measurement process. A measurement system does not measure, on a molecular level, the amount of an analyte in a sample; it measures an indicator of the amount of an analyte in a sample. This indicator might be the amount of a specific wavelength of light absorbed by a sample, the change in conductivity of a solution containing the analyte, or the amount of an analyte, in a gaseous or ionized form, that passes through a membrane.

Use data to choose between the one condition of the environment (the null hypothesis, H_0) and an alternative condition (the alternative hypothesis, H_a). A decision error occurs when the decision-maker rejects the null hypothesis when it is true (false-positive decision error) or fails to reject the null hypothesis when it is false (false-negative decision error).*#(1)

The null hypothesis usually is treated as the baseline condition that is presumed to be true in the absence of strong evidence to the contrary. Either condition may be selected as the null hypothesis, but if the null hypothesis is chosen carefully, it provides a way to guard against making the decision error that the decision-maker considers to have the more undesirable consequences.

While the possibility of a decision error never can be totally eliminated, it can be controlled by various means, including collecting a large number of samples (to control sampling design error), analyzing individual samples several times, or using more precise laboratory methods (to control measurement error). Better sampling designs also can be developed to collect data that more accurately represent the population of interest. Every study will use a different method of controlling decision errors, depending on the source of the largest components of total decision error in the data set and the ease of reducing those error components.

Reducing the probability of making decision errors generally increases study costs. In many cases, however, it is not necessary to control decision error within very small limits to meet the decision-maker's needs. If the consequences of decision errors are minor, a reasonable decision could be made on the basis of relatively crude data. If, on the other hand, consequences of

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decision errors are severe, the decision-maker will want to control sampling design and measurements within very small limits.

Factors used to judge data quality include precision, bias, representativeness, completeness, and comparability. Precision, bias, and completeness can be applied to the measurement (field and laboratory) system. Most analytical laboratories have systems to quantify these factors. Laboratory precision can be estimated through the analysis of laboratory replicates. Laboratory bias can be estimated by the analysis of standards, known additions, and performance evaluation (PE) samples. There is no common system in place to estimate field bias. A combination of field and laboratory completeness can be estimated through comparison of the number of analytical results provided by the laboratory with the number of analytical results specified in the sample design. Laboratory representativeness and comparability involve the analytical method used and the performance of the laboratory as compared to the performance of other laboratories (PE studies), which are not commonly quantified.

Precision, bias, representativeness, completeness, and comparability can be applied to the sample design: Precision would indicate how precisely this sample design reflects the total population. Bias would indicate how accurately this sample design reflects the total population. Representativeness would indicate to what extent the sample design is representative of the total population. Completeness would indicate how well the sample design reflects the complete population. Comparability would indicate the similarity of the sample design to other sample designs for similar situations. None of these usually is measured.

While data quality factors provide some insight into sample measurement errors, they do not provide any indication of sample design errors. These errors are additive, so that if precision were ±90%, bias were ±90%, and representativeness were ±90%, combined uncertainty could be up to ±27%:

$$(100\% \times 0.1) + (90\% \times 0.1) + (81\% \times 0.1) = 10\% + 9\% + 8\% = 27\%$$

Because most errors are not quantifiable, a study usually is designed with a balance between acceptable decision errors and acceptable study cost.

g. Optimizing the design for collection: Identify the most resource-effective design for the study that will achieve the data quality objectives (DQOs). Use statistical techniques to develop alternative data collection designs and evaluate their efficiency in meeting the DQOs. To develop the optimal study design, it may be necessary to work through this step more than once after revisiting previous steps of the process.

Review the DQO outputs and existing environmental data, develop general data collection design alternatives, and formulate the mathematical expressions needed to solve the design issue for each data collection design alternative. Develop the following three mathematical expressions:

- A method for testing the statistical hypothesis and a sample size formula that corresponds to the method (e.g., Student's *t* test),

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- A statistical model that describes the relationship of the measured value to the ‘‘true’’ value. Often the model will describe the components of error or bias believed to exist in the measured value, and
- A cost function that relates the number of samples to the total cost of sampling and analysis.

Select the optimal sample size that satisfies the DQOs for each data collection design alternative. Using the mathematical expressions specified above, calculate the optimal sample size that satisfies the DQOs. If no design will meet the limits on decision errors within the budget or other constraints, relax one or more constraints by, for example, increasing the budget for sampling and analysis, increasing the width of the region of uncertainty, increasing the tolerable decision error rates, relaxing other project constraints such as the schedule, or changing the boundaries; it may be possible to reduce sampling and analysis costs by changing or eliminating subgroups that will require separate decisions.

Select the most resource-effective data collection design that satisfies all of the DQOs and document the operational details and theoretical assumptions of the selected design in the sampling and analysis plan.

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1030 E. Checking Correctness of Analyses

The following procedures for checking correctness of analyses are applicable specifically to water samples for which relatively complete analyses are made.[1] These include pH, conductivity, total dissolved solids (TDS), and major anionic and cationic constituents that are indications of general water quality.

The checks described do not require additional laboratory analyses. Three of the checks require calculation of the total dissolved solids and conductivity from measured constituents. Sum concentrations (in milligrams per liter) of constituents to calculate the total dissolved solids are as follows:

$$\text{Total dissolved solids} = 0.6\,(\text{alkalinity}^{*}\#(2)) + Na^{+} + K^{+} + Ca^{2+} + Mg^{2+} + Cl^{-} + SO_4^{2-} + SiO_3^{2-} + NO_3^{-} + F^{-}$$

Calculate electrical conductivity from the equation:

$$G = \lambda C - (k_1\lambda + k_2)\,(C)^{3/2}$$

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where:

G = conductivity of salt solution,
C = concentration of salt solution,
λ = equivalent conductance of salt solution at infinite dilution,
k_1, k_2 = constants for relaxation of ion cloud effect and electrophoretic effect relative to ion mobility.[1]

1. Anion-Cation Balance[2]

The anion and cation sums, when expressed as milliequivalents per liter, must balance because all potable waters are electrically neutral. The test is based on the percentage difference defined as follows:

$$\% \text{ difference} = 100 \frac{\Sigma \text{ cations} - \Sigma \text{ anions}}{\Sigma \text{ cations} + \Sigma \text{ anions}}$$

and the typical criteria for acceptance are as follows:

Anion Sum *meq/L*	Acceptable Difference
0–3.0	±0.2 meq/L
3.0–10.0	± 2%
10.0–800	5%

2. Measured TDS = Calculated TDS[2]

The measured total dissolved solids concentration should be higher than the calculated one because a significant contributor may not be included in the calculation. If the measured value is less than the calculated one, the higher ion sum and measured value are suspect; the sample should be reanalyzed. If the measured solids concentration is more than 20% higher than the calculated one, the low ion sum is suspect and selected constituents should be reanalyzed. The acceptable ratio is as follows:

$$1.0 < \frac{\text{measured TDS}}{\text{calculated TDS}} < 1.2$$

3. Measured EC = Calculated EC

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If the calculated electrical conductivity (EC) is higher than the measured value, reanalyze the higher ion sum. If the calculated EC is less than the measured one, reanalyze the lower ion sum. The acceptable ratio is as follows:

$$0.9 < \frac{\text{calculated EC}}{\text{measured EC}} < 1.1$$

Some electrical conductivity values for ions commonly found in water are given in Table 1030:I.

4. Measured EC and Ion Sums

Both the anion and cation sums should be $^1/_{100}$ of the measured EC value. If either of the two sums does not meet this criterion, that sum is suspect; reanalyze the sample. The acceptable criteria are as follows:

$$100 \times \text{anion (or cation) sum, meq/L} = (0.9–1.1)\ \text{EC}$$

5. Calculated TDS to EC Ratio

If the ratio of calculated TDS to conductivity falls below 0.55, the lower ion sum is suspect; reanalyze it. If the ratio is above 0.7, the higher ion sum is suspect; reanalyze it. If reanalysis causes no change in the lower ion sum, an unmeasured constituent, such as ammonia or nitrite, may be present at a significant concentration. If poorly dissociated calcium and sulfate ions are present, the TDS may be as high as 0.8 times the EC. The acceptable criterion is as follows:

$$\text{calculated TDS/conductivity} = 0.55–0.7$$

6. Measured TDS to EC Ratio

The acceptable criteria for this ratio are from 0.55 to 0.7. If the ratio of TDS to EC is outside these limits, measured TDS or measured conductivity is suspect; reanalyze.

A more complete exposition[3] of the above quality-control checks has been published.

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1040 METHOD DEVELOPMENT AND EVALUATION

1040 A. Introduction

Although standard methods are available from many nationally recognized sources, there may be occasions when they cannot be used or when no standard method exists for a particular constituent or characteristic. Therefore, method development may be required. Method development is the set of experimental procedures devised for measuring a known amount of a constituent in various matrices, in the case of chemical analyses; or a known characteristic (e.g., biological or toxicological) of various matrices.

1040 B. Method Validation

Whether an entirely new method is developed by accepted research procedures or an existing method is modified to meet special requirements, validation by a three-step process is required: determination of single-operator precision and bias, analysis of independently prepared unknown samples, and determination of method ruggedness.

1. Single-Operator Characteristics

This part of the validation procedure requires determining the method detection level (MDL) as in Section 1030; the bias of the method, i.e., the systematic error of the method; and the precision obtainable by a single operator, i.e., the random error introduced in using the method. To make these determinations, analyze at least 7 but preferably 10 or more portions of a standard at each of several concentrations in each matrix that may be used. Use one concentration at, or slightly above, the MDL and one relatively high so that the range of concentrations for which the method is applicable can be specified.

The use of several concentrations to determine bias and precision will reveal the form of the relationship between these method characteristics and the concentration of the substance, the characteristic toxicity of the substance, or the biological factor of interest. This relationship may be constant, linear, or curvilinear and is a significant characteristic of the method that should be explained clearly. Table 1040:I shows calculation of precision and bias for a single concentration in a single matrix from eight replicate analyses of a standard with a known concentration of 1.30 mg/L.

The bias is 0.49/8 = 0.06 mg/L and the precision is the square root of $0.2335/(8-1) = \sqrt{0.03336}$, or 0.18 mg/L (note that this is similar to the calculation for standard deviation).

2. Analysis of Unknown Samples

This step in the method validation procedure requires analysis of independently prepared standards where the value is unknown to the analyst. Analyze each unknown in replicate by

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following the standard operating procedure for the method. The mean amount recovered should be within three standard deviations (*s*) of the mean value of the standard but preferably within 2 *s*.

Obtain the unknowns from other personnel in the analyst's laboratory using either purchased analytical-grade reagents or standards available from National Institute of Standards and Technology (NIST). If available for the particular constituent, performance evaluation samples from EPA-Cincinnati are particularly useful.

3. Method Ruggedness

A test of the ruggedness, i.e., stability of the result produced when steps in the method are varied, is the final validation step. It is especially important to determine this characteristic of a method if it is to be proposed as a standard or reference method. A properly conducted ruggedness test will point out those procedural steps in which rigor is critical and those in which some leeway is permissible.

The Association of Official Analytical Chemists[1] has suggested a method for this test in which eight separate analyses can be used to determine the effect of varying seven different steps in an analytical procedure. To illustrate, suppose the effect of changing the factors in Table 1040:II is to be determined. To make the determination, denote the nominal factors by capital letters A through G and the variations by the corresponding lower-case letters. Then set up a table of the factors as in Table 1040:III.

If combination 1 is analyzed, the result will be s. If combination 2 is analyzed, the result will be t, and so on until all eight combinations have been analyzed. To determine the effect of varying a factor, find the four results where the factor was nominal (all caps) and the four where it was varied (all lower case) and compare the averages of the two groups. For example, to compare the effect of changing C to c, use results (s + u + w + y)/4 and (t + v + x + z)/4. Calculate all seven pairs to get seven differences, which can then be ranked to reveal those with a significant effect on the results. If there is no outstanding difference, calculate the average and standard deviation of the eight results s through z. The standard deviation is a realistic estimate of the precision of the method. This design tests main effects, not interactions.

4. Equivalency Testing

After a new method has been validated by the procedures listed above, it may be prudent to test the method for equivalency to standard methods, unless none exist. This requires analysis of a minimum of three concentrations by the alternate and by the standard method. If the range of concentration is very broad, test more concentrations. Once an initial set of analyses (five or more) has been made at each chosen concentration, apply the following statistical steps:[2]

1. Test the distribution of data for normality and transform the data if necessary (Section 1010B).
2. Select an appropriate sample size based on an estimate of the standard deviation.[3]

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3. Test the variances of the two methods using the F-ratio statistic.
4. Test the average values of the two methods using a Student-*t* statistic.

An explanation of each of these steps with additional techniques and examples has been published.[4] Because the number of analyses can be very large, the calculations become complex and familiarity with basic statistics is necessary. A listing of standard, reference, and equivalent methods for water analysis is available.[5]

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1040 C. Collaborative Testing

Once a new or modified method has been developed and validated it is appropriate to determine whether the method should be made a standard method. The procedure to convert a method to standard status is the collaborative test.[1] In this test, different laboratories use the standard operating procedure to analyze a select number of samples to determine the method's bias and precision as would occur in normal practice.

In planning for a collaborative test, consider the following factors: a precisely written standard operating procedure, the number of variables to be tested, the number of levels to be tested, and the number of replicates required. Because method precision is estimated by the standard deviation, which itself is the result of many sources of variation, the variables that affect it must be tested. These may include the laboratory, operator, apparatus, and concentration range.

1. Variables

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Test at least the following variables: Laboratory—Involve at least three different laboratories, although more are desirable to provide a better estimate of the standard deviation; Apparatus—Because model and manufacturer differences can be sources of error, analyze at least two replicates of each concentration per laboratory; Operators—To determine overall precision, involve at least six analysts with not more than two from each laboratory; Levels—If the method development has indicated that the relative standard deviation is constant, test three levels covering the range of the method. If it is not constant, use more levels spread uniformly over the operating range.

If matrix effects are suspected, conduct the test in each medium for which the method was developed. If this is not feasible, use appropriate grades of reagent water as long as this is stipulated in the resulting statement of method characteristics.

2. Number of Replicates

Calculate the number of replicates after the number of variables to be tested has been determined by using the formula:

$$r > 1 + (30/P)$$

where:

r = number of replicates and
P = the product of several variables.

The minimum number of replicates is two. As an example, if three levels of a substance are to be analyzed by single operators in six laboratories on a single apparatus, then P is calculated as follows:

$$P = 3 \times 1 \times 6 \times 1 = 18$$

and the number of replicates is

$$r > 1 + (30/18) > 2.7 \text{ or } r = 3.$$

3. Illustrative Collaborative Test

Send each of five laboratories four concentrations of a compound (4.3, 11.6, 23.4, and 32.7 mg/L) with instructions to analyze in triplicate using the procedure provided. Tabulate results as shown in Table 1040:IV below (the results for only one concentration are shown). Because there are no obviously aberrant values (use the method in Section 1010B to reject outliers), use all the data.

Calculate the average and standard deviation for each laboratory; use all 15 results to calculate a grand average and standard deviation. The difference between the average of each laboratory and the grand average reveals any significant bias, such as that shown for Laboratories 1 and 3. The difference between the grand average and the known value is the

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method bias, e.g., 33.0 – 32.7 = 0.3 mg/L or 0.9%. The relative standard deviation of the grand average (1.5 mg/L) is 4.5%, which is the method precision, and the *s* for each laboratory is the single-operator precision.

As noted in Table 1040:IV, the sum of the deviations from the known value for the laboratories was 1.3, so the average deviation (bias) was 1.3/5 = 0.26, rounded to 0.3, which is the same as the difference between the grand average and the known value.

For all four unknowns in this test, the percentage results indicated increasing bias and decreasing precision as the concentration decreased. Therefore, to describe the method in a formal statement, the precision would be given by a straight line with the formula $y = mx + b$; where y is the relative standard deviation, m is the slope of the line, x is the concentration, and b is the relative standard deviation at concentration = 0. The values found from the collaborative test are shown in Table 1040:V.

These results indicate that the method is acceptable. However, concentrations of less than about 10 mg/L require greater care in analysis.

4. Reference

1. YOUDEN, W.J. & E.H. STEINER. 1975. Statistical Manual of the AOAC. Assoc. Official Analytical Chemists, Washington, D.C.

1050 EXPRESSION OF RESULTS

1050 A. Units

This text uses the International System of Units (SI) and chemical and physical results are expressed in milligrams per liter (mg/L). See Section 7020D for expression of radioactivity results. Record only the significant figures. If concentrations generally are less than 1 mg/L, it may be more convenient to express results in micrograms per liter (µg/L). Use µg/L when concentrations are less than 0.1 mg/L.

Express concentrations greater than 10 000 mg/L in percent, 1% being equal to 10 000 mg/L when the specific gravity is 1.00. In solid samples and liquid wastes of high specific gravity, make a correction if the results are expressed as parts per million (ppm) or percent by weight:

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$$\text{ppm by weight} = \frac{\text{mg/L}}{\text{sp gr}}$$

$$\%\text{ by weight} = \frac{\text{mg/L}}{10\,000 \times \text{sp gr}}$$

In such cases, if the result is given as milligrams per liter, state specific gravity.

The unit equivalents per million (epm), or the identical and less ambiguous term milligram-equivalents per liter, or milliequivalents per liter (me/L), can be valuable for making water treatment calculations and checking analyses by anion-cation balance.

Table 1050:I presents factors for converting concentrations of common ions from milligrams per liter to milliequivalents per liter, and vice versa. The term milliequivalent used in this table represents 0.001 of an equivalent weight. The equivalent weight, in turn, is defined as the weight of the ion (sum of the atomic weights of the atoms making up the ion) divided by the number of charges normally associated with the particular ion. The factors for converting results from milligrams per liter to milliequivalents per liter were computed by dividing the ion charge by weight of the ion. Conversely, factors for converting results from milliequivalents per liter to milligrams per liter were calculated by dividing the weight of the ion by the ion charge.

1050 B. Significant Figures

1. Reporting Requirements

To avoid ambiguity in reporting results or in presenting directions for a procedure, it is the custom to use ‘‘significant figures.’’ All digits in a reported result are expected to be known definitely, except for the last digit, which may be in doubt. Such a number is said to contain only significant figures. If more than a single doubtful digit is carried, the extra digit or digits are not significant. If an analytical result is reported as ‘‘75.6 mg/L,’’ the analyst should be quite certain of the ‘‘75,’’ but may be uncertain as to whether the ‘‘.6’’ should be .5 or .7, or even .4 or .8, because of unavoidable uncertainty in the analytical procedure. If the standard deviation were known from previous work to be ±2 mg/L, the analyst would have, or should have, rounded off the result to ‘‘76 mg/L’’ before reporting it. On the other hand, if the method were so good that a result of ‘‘75.61 mg/L’’ could have been conscientiously reported, then the analyst should not have rounded it off to 75.6.

Report only such figures as are justified by the accuracy of the work. Do not follow the all-too-common practice of requiring that quantities listed in a column have the same number of figures to the right of the decimal point.

2. Rounding Off

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Round off by dropping digits that are not significant. If the digit 6, 7, 8, or 9 is dropped, increase preceding digit by one unit; if the digit 0, 1, 2, 3, or 4 is dropped, do not alter preceding digit. If the digit 5 is dropped, round off preceding digit to the nearest even number: thus 2.25 becomes 2.2 and 2.35 becomes 2.4.

3. Ambiguous Zeros

The digit 0 may record a measured value of zero or it may serve merely as a spacer to locate the decimal point. If the result of a sulfate determination is reported as 420 mg/L, the report recipient may be in doubt whether the zero is significant or not, because the zero cannot be deleted. If an analyst calculates a total residue of 1146 mg/L, but realizes that the 4 is somewhat doubtful and that therefore the 6 has no significance, the answer should be rounded off to 1150 mg/L and so reported but here, too, the report recipient will not know whether the zero is significant. Although the number could be expressed as a power of 10 (e.g., 11.5×10^2 or 1.15×10^3), this form is not used generally because it would not be consistent with the normal expression of results and might be confusing. In most other cases, there will be no doubt as to the sense in which the digit 0 is used. It is obvious that the zeros are significant in such numbers as 104 and 40.08. In a number written as 5.000, it is understood that all the zeros are significant, or else the number could have been rounded off to 5.00, 5.0, or 5, whichever was appropriate. Whenever the zero is ambiguous, it is advisable to accompany the result with an estimate of its uncertainty.

Sometimes, significant zeros are dropped without good cause. If a buret is read as ‘‘23.60 mL,’’ it should be so recorded, and not as ‘‘23.6 mL.’’ The first number indicates that the analyst took the trouble to estimate the second decimal place; ‘‘23.6 mL’’ would indicate a rather careless reading of the buret.

4. Standard Deviation

If, for example, a calculation yields a result of 1449 mg/L or 1451 mg/L with a standard deviation of ±100 mg/L, report as 1449 ± 100 mg/L or 1451 ± 100 mg/L, respectively. Ensure that the number of significant figures in the standard deviation is not reduced if the value is 100 ± 1. This could cause incorrect rounding of data to 1400 or 1500 mg/L, respectively.

5. Calculations

As a practical operating rule, round off the result of a calculation in which several numbers are multiplied or divided to as few significant figures as are present in the factor with the fewest significant figures. Suppose that the following calculations must be made to obtain the result of an analysis:

$$\frac{56 \times 0.003\,462 \times 43.22}{1.684}$$

A ten-place calculator yields an answer of ‘‘4.975 740 998.’’ Round off this number to ‘‘5.0’’

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because one of the measurements that entered into the calculation, 56, has only two significant figures. It was unnecessary to measure the other three factors to four significant figures because the ‘‘56’’ is the ‘‘weakest link in the chain’’ and limits accuracy of the answer. If the other factors were measured to only three, instead of four, significant figures, the answer would not suffer and the labor might be less.

When numbers are added or subtracted, the number that has the fewest decimal places, not necessarily the fewest significant figures, puts the limit on the number of places that justifiably may be carried in the sum or difference. Thus the sum

```
  0.0072
 12.02
  4.0078
 25.9
4886
4927.9350
```

must be rounded off to ‘‘4928,’’ no decimals, because one of the addends, 4886, has no decimal places. Notice that another addend, 25.9, has only three significant figures and yet it does not set a limit to the number of significant figures in the answer.The preceding discussion is necessarily oversimplified. The reader is referred to mathematical texts for more detailed discussion.

1060 COLLECTION AND PRESERVATION OF SAMPLES

1060 A. Introduction

It is an old axiom that the result of any testing method can be no better than the sample on which it is performed. It is beyond the scope of this publication to specify detailed procedures for the collection of all samples because of varied purposes and analytical procedures. Detailed information is presented in specific methods. This section presents general considerations, applicable primarily to chemical analyses. See appropriate sections for samples to be used in toxicity testing and microbiological, biological, and radiological examinations.

The objective of sampling is to collect a portion of material small enough in volume to be transported conveniently and yet large enough for analytical purposes while still accurately representing the material being sampled. This objective implies that the relative proportions or concentrations of all pertinent components will be the same in the samples as in the material being sampled, and that the sample will be handled in such a way that no significant changes in composition occur before the tests are made.

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Frequently the objective of sampling and testing is to demonstrate whether continuing compliance with specific regulatory requirements has been achieved. Samples are presented to the laboratory for specific determinations with the sampler being responsible for collecting a valid and representative sample. Because of the increasing importance placed on verifying the accuracy and representativeness of data, greater emphasis is placed on proper sample collection, tracking, and preservation techniques. Often, laboratory personnel help in planning a sampling program, in consultation with the user of the test results. Such consultation is essential to ensure selecting samples and analytical methods that provide a sound and valid basis for answering the questions that prompted the sampling and that will meet regulatory and/or project-specific requirements.

This section addresses the collection and preservation of water and wastewater samples; the general principles also apply to the sampling of solid or semisolid matrices.

1. General Requirements

Obtain a sample that meets the requirements of the sampling program and handle it so that it does not deteriorate or become contaminated or compromised before it is analyzed.

Ensure that all sampling equipment is clean and quality-assured before use. Use sample containers that are clean and free of contaminants. Bake at 450°C all bottles to be used for organic-analysis sampling.

Fill sample containers without prerinsing with sample; prerinsing results in loss of any pre-added preservative and sometimes can bias results high when certain components adhere to the sides of the container. Depending on determinations to be performed, fill the container full (most organic compound determinations) or leave space for aeration, mixing, etc. (microbiological and inorganic analyses). If a bottle already contains preservative, take care not to overfill the bottle, as preservative may be lost or diluted. Except when sampling for analysis of volatile organic compounds, leave an air space equivalent to approximately 1% of the container volume to allow for thermal expansion during shipment.

Special precautions (discussed below) are necessary for samples containing organic compounds and trace metals. Because many constituents may be present at low concentrations (micrograms or nanograms per liter), they may be totally or partially lost or easily contaminated when proper sampling and preservation procedures are not followed.

Composite samples can be obtained by collecting over a period of time, depth, or at many different sampling points. The details of collection vary with local conditions, so specific recommendations are not universally applicable. Sometimes it is more informative to analyze numerous separate samples instead of one composite so that variability, maxima, and minima can be determined.

Because of the inherent instability of certain properties and compounds, composite sampling for some analytes is not recommended where quantitative values are desired (examples include oil and grease, acidity, alkalinity, carbon dioxide, chlorine residual, iodine, hexavalent chromium, nitrate, volatile organic compounds, radon-222, dissolved oxygen, ozone,

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temperature, and pH). In certain cases, such as for BOD, composite samples are routinely required by regulatory agencies. Refrigerate composite samples for BOD and nitrite.

Sample carefully to ensure that analytical results represent the actual sample composition. Important factors affecting results are the presence of suspended matter or turbidity, the method chosen for removing a sample from its container, and the physical and chemical changes brought about by storage or aeration. Detailed procedures are essential when processing (blending, sieving, filtering) samples to be analyzed for trace constituents, especially metals and organic compounds. Some determinations can be invalidated by contamination during processing. Treat each sample individually with regard to the substances to be determined, the amount and nature of turbidity present, and other conditions that may influence the results.

Carefully consider the technique for collecting a representative sample and define it in the sampling plan. For metals it often is appropriate to collect both a filtered and an unfiltered sample to differentiate between total and dissolved metals present in the matrix. Be aware that some metals may partially sorb to filters. Beforehand, determine the acid requirements to bring the pH to <2 on a separate sample. Add the same relative amount of acid to all samples; use ultrapure acid preservative to prevent contamination. Be sure that the dilution caused by acidifying is negligible or sufficiently reproducible for a dilution correction factor. When filtered samples are to be collected, filter them, if possible, in the field, or at the point of collection before preservation with acid. Filter samples in a laboratory-controlled environment if field conditions could cause error or contamination; in this case filter as soon as possible. Often slight turbidity can be tolerated if experience shows that it will cause no interference in gravimetric or volumetric tests and that its influence can be corrected in colorimetric tests, where it has potentially the greatest interfering effect. Sample collector must state whether or not the sample has been filtered.

Make a record of every sample collected and identify every bottle with a unique sample number, preferably by attaching an appropriately inscribed tag or label. Document sufficient information to provide positive sample identification at a later date, including the unique sample identification number, the name of the sample collector, the date, hour, exact location, and, if possible, sample type (e.g., grab or composite), and any other data that may be needed for correlation, such as water temperature, weather conditions, water level, stream flow, post-collection conditions, etc. If space for all pertinent information for label or attached tag is insufficient, record information in a bound sample log book at the sampling site at the time of sample collection. Use waterproof ink to record all information (preferably with black, non-solvent-based ink). Fix sampling points by detailed description in the sampling plan, by maps, or with the aid of stakes, buoys, or landmarks in a manner that will permit their identification by other persons without reliance on memory or personal guidance. Global positioning systems (GPS) also are used and supply accurate sampling position data. Particularly when sample results are expected to be involved in litigation, use formal ‘‘chain-of-custody’’ procedures (see ¶ B.2 below), which trace sample history from collection to final reporting.

Before collecting samples from distribution systems, flush lines with three to five pipe

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volumes (or until water is being drawn from the main source) to ensure that the sample is representative of the supply, taking into account the volume of pipe to be flushed and the flow velocity. If the distribution system volume is unavailable, flush with tap fully open for at least 2 to 3 min before sampling. An exception to these guidelines, i.e., collecting a first draw sample, is when information on areas of reduced or restricted flow is desired or when samples for lead in drinking water are being collected.

Although well pumping protocols depend on the objectives of an investigation and other factors such as well characteristics and available equipment, a general rule is to collect samples from wells only after the well has been purged sufficiently (usually with three to ten well volumes) to ensure that the sample represents the groundwater. Purging stagnant water is critical. Sometimes it will be necessary to pump at a specified rate to achieve a characteristic drawdown, if this determines the zones from which the well is supplied; record purging rate and drawdown, if necessary. By using methods with minimal drawdown, purging volumes can be reduced significantly.

When samples are collected from a river or stream, observed results may vary with depth, stream flow, and distance from each shore. Selection of the number and distribution of sites at which samples should be collected depends on study objectives, stream characteristics, available equipment, and other factors. If equipment is available, take an integrated sample from top to bottom in the middle of the main channel of the stream or from side to side at mid-depth. If only grab or catch samples can be collected, preferably take them at various points of equal distance across the stream; if only one sample can be collected, take it in the middle of the main channel of the stream and at mid-depth. Integrated samples are described further in ¶ B.1*c* below.

Rivers, streams, lakes, and reservoirs are subject to considerable variations from normal causes such as seasonal stratification, diurnal variations, rainfall, runoff, and wind. Choose location, depth, and frequency of sampling depending on local conditions and the purpose of the investigation.

Use the following examples for general guidance. Avoid areas of excessive turbulence because of potential loss of volatile constituents and of potential presence of denser-than-air toxic vapors. Avoid sampling at weirs if possible because such locations tend to favor retrieval of lighter-than-water, immiscible compounds. Generally, collect samples beneath the surface in quiescent areas and open sampling container below surface with the mouth directed toward the current to avoid collecting surface scum unless oil and grease is a constituent of interest; then collect water at the surface. If composite samples are required, ensure that sample constituents are not lost during compositing because of improper handling of portions being composited. If samples will be analyzed for organic constituents, refrigerate composited portions. Do not composite samples for VOC analysis because some of the components will be lost through volatilization.

2. Safety Considerations

Because sample constituents may be toxic, take adequate precautions during sampling and sample handling. Toxic substances can enter through the skin and eyes and, in the case of

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vapors, also through the lungs. Ingestion can occur via direct contact of toxic materials with foods or by adsorption of vapors onto foods. Precautions may be limited to wearing gloves or may include coveralls, aprons, or other protective apparel. Often, the degree of protection provided by chemical protective clothing (CPC) is specific for different manufacturers and their product models[1]; ensure that the clothing chosen will offer adequate protection. Always wear eye protection (e.g., safety glasses with side shields or goggles). When toxic vapors may be present, sample only in well-ventilated areas, or use an appropriate respirator or self-contained breathing apparatus. In a laboratory, open sample containers in a fume hood. Never have food in the laboratory, near samples, or near sampling locations; always wash hands thoroughly before handling food.[2]

Always prohibit eating, drinking, or smoking near samples, sampling locations, and in the laboratory. Keep sparks, flames, and excessive heat sources away from samples and sampling locations. If flammable compounds are suspected or known to be present and samples are to be refrigerated, use only specially designed *explosion-proof* refrigerators.[2]

Collect samples safely, avoiding situations that may lead to accidents. When in doubt as to the level of safety precautions needed, consult a knowledgeable industrial hygienist or safety professional. Samples with radioactive contaminants may require other safety considerations; consult a health physicist.

Label adequately any sample known or suspected to be hazardous because of flammability, corrosivity, toxicity, oxidizing chemicals, or radioactivity, so that appropriate precautions can be taken during sample handling, storage, and disposal.

3. References

1. FORSBERG K. & L.H. KEITH. 1998. Instant Gloves and CPC Database. Instant Reference Sources, Inc. Austin, Tex.
2. WATER POLLUTION CONTROL FEDERATION. 1986. Removal of Hazardous Wastes in Wastewater Facilities—Halogenated Organics. Manual of Practice FD-11, Water Pollution Control Fed., Alexandria, Va.

1060 B. Collection of Samples

1. Types of Samples

a. Grab samples: Grab samples are single samples collected at a specific spot at a site over a short period of time (typically seconds or minutes). Thus, they represent a ‘‘snapshot’’ in both space and time of a sampling area. Discrete grab samples are taken at a selected location, depth, and time. Depth-integrated grab samples are collected over a predetermined part or the entire depth of a water column, at a selected location and time in a given body of water.

A sample can represent only the composition of its source at the time and place of

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collection. However, when a source is known to be relatively constant in composition over an extended time or over substantial distances in all directions, then the sample may represent a longer time period and/or a larger volume than the specific time and place at which it was collected. In such circumstances, a source may be represented adequately by single grab samples. Examples are protected groundwater supplies, water supplies receiving conventional treatment, some well-mixed surface waters, but rarely, wastewater streams, rivers, large lakes, shorelines, estuaries, and groundwater plumes.

When a source is known to vary with time, grab samples collected at suitable intervals and analyzed separately can document the extent, frequency, and duration of these variations. Choose sampling intervals on the basis of the expected frequency of changes, which may vary from as little as 5 min to as long as 1 h or more. Seasonal variations in natural systems may necessitate sampling over months. When the source composition varies in space (i.e., from location to location) rather than time, collect samples from appropriate locations that will meet the objectives of the study (for example, upstream and downstream from a point source, etc.).

The same principles apply to sampling wastewater sludges, sludge banks, and muds, although these matrices are not specifically addressed in this section. Take every possible precaution to obtain a representative sample or one conforming to a sampling program.

b. Composite samples: Composite samples should provide a more representative sampling of heterogeneous matrices in which the concentration of the analytes of interest may vary over short periods of time and/or space. Composite samples can be obtained by combining portions of multiple grab samples or by using specially designed automatic sampling devices. Sequential (time) composite samples are collected by using continuous, constant sample pumping or by mixing equal water volumes collected at regular time intervals. Flow-proportional composites are collected by continuous pumping at a rate proportional to the flow, by mixing equal volumes of water collected at time intervals that are inversely proportional to the volume of flow, or by mixing volumes of water proportional to the flow collected during or at regular time intervals.

Advantages of composite samples include reduced costs of analyzing a large number of samples, more representative samples of heterogeneous matrices, and larger sample sizes when amounts of test samples are limited. Disadvantages of composite samples include loss of analyte relationships in individual samples, potential dilution of analytes below detection levels, increased potential analytical interferences, and increased possibility of analyte interactions. In addition, use of composite samples may reduce the number of samples analyzed below the required statistical need for specified data quality objectives or project-specific objectives.

Do not use composite samples with components or characteristics subject to significant and unavoidable changes during storage. Analyze individual samples as soon as possible after collection and preferably at the sampling point. Examples are dissolved gases, residual chlorine, soluble sulfide, temperature, and pH. Changes in components such as dissolved oxygen or carbon dioxide, pH, or temperature may produce secondary changes in certain inorganic constituents such as iron, manganese, alkalinity, or hardness. Some organic analytes also may be changed by changes in the foregoing components. Use time-composite samples only for

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determining components that can be demonstrated to remain unchanged under the conditions of sample collection, preservation, and storage.

Collect individual portions in a wide-mouth bottle every hour (in some cases every half hour or even every 5 min) and mix at the end of the sampling period or combine in a single bottle as collected. If preservatives are used, add them to the sample bottle initially so that all portions of the composite are preserved as soon as collected.

Automatic sampling devices are available; however, do not use them unless the sample is preserved as described below. Composite samplers running for extended periods (weeks to months) should undergo routine cleaning of containers and sample lines to minimize sample growth and deposits.

c. Integrated (discharge-weighted) samples: For certain purposes, the information needed is best provided by analyzing mixtures of grab samples collected from different points simultaneously, or as nearly so as possible, using discharge-weighted methods such as equal-width increment (EWI) or equal discharge-increment (EDI) procedures and equipment. An example of the need for integrated sampling occurs in a river or stream that varies in composition across its width and depth. To evaluate average composition or total loading, use a mixture of samples representing various points in the cross-section, in proportion to their relative flows. The need for integrated samples also may exist if combined treatment is proposed for several separate wastewater streams, the interaction of which may have a significant effect on treatability or even on composition. Mathematical prediction of the interactions among chemical components may be inaccurate or impossible and testing a suitable integrated sample may provide more useful information.

Both lakes and reservoirs show spatial variations of composition (depth and horizontal location). However, there are conditions under which neither total nor average results are especially useful, but local variations are more important. In such cases, examine samples separately (i.e., do not integrate them).

Preparation of integrated samples usually requires equipment designed to collect a sample water uniformly across the depth profile. Knowledge of the volume, movement, and composition of the various parts of the water being sampled usually is required. Collecting integrated samples is a complicated and specialized process that must be described adequately in a sampling plan.

2. Chain-of-Custody Procedures

Properly designed and executed chain-of-custody forms will ensure sample integrity from collection to data reporting. This includes the ability to trace possession and handling of the sample from the time of collection through analysis and final disposition. This process is referred to as ‘‘chain-of-custody’’ and is required to demonstrate sample control when the data are to be used for regulation or litigation. Where litigation is not involved, chain-of-custody procedures are useful for routine control of samples.

A sample is considered to be under a person’s custody if it is in the individual’s physical possession, in the individual’s sight, secured and tamper-proofed by that individual, or secured in

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an area restricted to authorized personnel. The following procedures summarize the major aspects of chain of custody. More detailed discussions are available.[1,2]

a. Sample labels (including bar-code labels): Use labels to prevent sample misidentification. Gummed paper labels or tags generally are adequate. Include at least the following information: a unique sample number, sample type, name of collector, date and time of collection, place of collection, and sample preservative. Also include date and time of preservation for comparison to date and time of collection. Affix tags or self-adhesive labels to sample containers before, or at the time of, sample collection.

b. Sample seals: Use sample seals to detect unauthorized tampering with samples up to the time of analysis. Use self-adhesive paper seals that include at least the following information: sample number (identical with number on sample label), collector's name, and date and time of sampling. Plastic shrink seals also may be used.

Attach seal in such a way that it is necessary to break it to open the sample container or the sample shipping container (e.g., a cooler). Affix seal to container before sample leaves custody of sampling personnel.

c. Field log book: Record all information pertinent to a field survey or sampling in a bound log book. As a minimum, include the following in the log book: purpose of sampling; location of sampling point; name and address of field contact; producer of material being sampled and address, if different from location; type of sample; and method, date, and time of preservation. If the sample is wastewater, identify process producing waste stream. Also provide suspected sample composition, including concentrations; number and volume of sample(s) taken; description of sampling point and sampling method; date and time of collection; collector's sample identification number(s); sample distribution and how transported; references such as maps or photographs of the sampling site; field observations and measurements; and signatures of personnel responsible for observations. Because sampling situations vary widely, it is essential to record sufficient information so that one could reconstruct the sampling event without reliance on the collector's memory. Protect log book and keep it in a safe place.

d. Chain-of-custody record: Fill out a chain-of-custody record to accompany each sample or group of samples. The record includes the following information: sample number; signature of collector; date, time, and address of collection; sample type; sample preservation requirements; signatures of persons involved in the chain of possession; and inclusive dates and times of possession.

e. Sample analysis request sheet: The sample analysis request sheet accompanies samples to the laboratory. The collector completes the field portion of such a form that includes most of the pertinent information noted in the log book. The laboratory portion of such a form is to be completed by laboratory personnel and includes: name of person receiving the sample, laboratory sample number, date of sample receipt, condition of each sample (i.e., if it is cold or warm, whether the container is full or not, color, if more than one phase is present, etc.), and determinations to be performed.

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f. Sample delivery to the laboratory: Deliver sample(s) to laboratory as soon as practicable after collection, typically within 2 d. Where shorter sample holding times are required, make special arrangements to insure timely delivery to the laboratory. Where samples are shipped by a commercial carrier, include the waybill number in the sample custody documentation. Insure that samples are accompanied by a completed chain-of-custody record and a sample analysis request sheet. Deliver sample to sample custodian.

g. Receipt and logging of sample: In the laboratory, the sample custodian inspects the condition and seal of the sample and reconciles label information and seal against the chain-of-custody record before the sample is accepted for analysis. After acceptance, the custodian assigns a laboratory number, logs sample in the laboratory log book and/or computerized laboratory information management system, and stores it in a secured storage room or cabinet or refrigerator at the specified temperature until it is assigned to an analyst.

h. Assignment of sample for analysis: The laboratory supervisor usually assigns the sample for analysis. Once the sample is in the laboratory, the supervisor or analyst is responsible for its care and custody.

i. Disposal: Hold samples for the prescribed amount of time for the project or until the data have been reviewed and accepted. Document the disposition of samples. Ensure that disposal is in accordance with local, state, and U.S. EPA approved methods.

3. Sampling Methods

a. Manual sampling: Manual sampling involves minimal equipment but may be unduly costly and time-consuming for routine or large-scale sampling programs. It requires trained field technicians and is often necessary for regulatory and research investigations for which critical appraisal of field conditions and complex sample collection techniques are essential. Manually collect certain samples, such as waters containing oil and grease.

b. Automatic sampling: Automatic samplers can eliminate human errors in manual sampling, can reduce labor costs, may provide the means for more frequent sampling,[3] and are used increasingly. Be sure that the automatic sampler does not contaminate the sample. For example, plastic components may be incompatible with certain organic compounds that are soluble in the plastic parts or that can be contaminated (e.g., from phthalate esters) by contact with them. If sample constituents are generally known, contact the manufacturer of an automatic sampler regarding potential incompatibility of plastic components.

Program an automatic sampler in accordance with sampling needs. Carefully match pump speeds and tubing sizes to the type of sample to be taken.

c. Sorbent sampling: Use of solid sorbents, particularly membrane-type disks, is becoming more frequent. These methods offer advantages of rapid, inexpensive sampling if the analytes of interest can be adsorbed and desorbed efficiently and the water matrix is free of particulates that plug the sorbent.

4. Sample Containers

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The type of sample container used is of utmost importance. Test sample containers and document that they are free of analytes of interest, especially when sampling and analyzing for very low analyte levels. Containers typically are made of plastic or glass, but one material may be preferred over the other. For example, silica, sodium, and boron may be leached from soft glass but not plastic, and trace levels of some pesticides and metals may sorb onto the walls of glass containers.[4] Thus, hard glass containers*#(3) are preferred. For samples containing organic compounds, do not use plastic containers except those made of fluorinated polymers such as polytetrafluoroethylene (PTFE).[3]

Some sample analytes may dissolve (be absorbed) into the walls of plastic containers; similarly, contaminants from plastic containers may leach into samples. Avoid plastics wherever possible because of potential contamination from phthalate esters. Container failure due to breakdown of the plastic is possible. Therefore, use glass containers for all organics analyses such as volatile organics, semivolatile organics, pesticides, PCBs, and oil and grease. Some analytes (e.g., bromine-containing compounds and some pesticides, polynuclear aromatic compounds, etc.) are light-sensitive; collect them in amber-colored glass containers to minimize photodegradation. Container caps, typically plastic, also can be a problem. Do not use caps with paper liners. Use foil or PTFE liners but be aware that metal liners can contaminate samples collected for metals analysis and they may also react with the sample if it is acidic or alkaline. Serum vials with PTFE-lined rubber or plastic septa are useful.

In rare situations it may be necessary to use sample containers not specifically prepared for use, or otherwise unsuitable for the particular situation; thoroughly document these deviations. Documentation should include type and source of container, and the preparation technique, e.g., acid washed with reagent water rinse. For QA purposes the inclusion of a bottle blank may be necessary.

5. Number of Samples

Because of variability from analytical and sampling procedures (i.e., population variability), a single sample is insufficient to reach any reasonable desired level of confidence. If an overall standard deviation (i.e., the standard deviation of combined sampling and analysis) is known, the required number of samples for a mobile matrix such as water may be estimated as follows:[4]

$$N \geq \left(\frac{ts}{U}\right)^2$$

where:

N = number of samples,
t = Student-t statistic for a given confidence level,
s = overall standard deviation, and
U = acceptable level of uncertainty.

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To assist in calculations, use curves such as those in Figure 1060:1. As an example, if *s* is 0.5 mg/L, *U* is ± 0.2 mg/L, and a 95% confidence level is desired, approximately 25 to 30 samples must be taken.

The above equation assumes that total error (population variability) is known. Total variability consists of all sources of variability, including: the distribution of the analytes of interest within the sampling site, collection, preservation, preparation, and analysis of samples, and data handling and reporting. In simpler terms, error (variability) can be divided into sampling and analysis components. Sampling error due to population variability (including heterogeneous distribution of analytes in the environmental matrix) usually is much larger than analytical error components. Unfortunately, sampling error usually is not available and the analyst is left with only the published error of the measurement system (typically obtained by using a reagent water matrix under the best analytical conditions).

More accurate equations are available.[5] These are based on the Z distribution for determining the number of samples needed to estimate a mean concentration when variability is estimated in absolute terms using the standard deviation. The coefficient of variation (relative standard deviation) is used when variability is estimated in relative terms.

The number of random samples to be collected at a site can be influenced partly by the method that will be used. The values for standard deviation (SD) or relative standard deviation (RSD) may be obtained from each of the methods or in the literature.[6] However, calculations of estimated numbers of samples needed based only on this information will result in underestimated numbers of samples because only the analytical variances are considered, and the typically larger variances from the sampling operations are not included. Preferably, determine and use SDs or RSDs from overall sampling and analysis operations.

For estimates of numbers of samples needed for systematic sampling (e.g., drilling wells for sampling groundwater or for systematically sampling large water bodies such as lakes), equations are available[7] that relate number of samples to shape of grid, area covered, and space between nodes of grid. The grid spacing is a complex calculation that depends on the size and shape of any contaminated spot (such as a groundwater plume) to be identified, in addition to the geometric shape of the sampling grid.

See individual methods for types and numbers of quality assurance (QA) and quality control (QC) samples, e.g., for normal-level (procedural) or low-level (contamination) bias or for precision, involving sampling or laboratory analysis (either overall or individually). Estimates of numbers of QC samples needed to achieve specified confidence levels also can be calculated. Rates of false positives (Type I error) and false negatives (Type II error) are useful parameters for estimating required numbers of QC samples. A false positive is the incorrect conclusion that an analyte is present when it is absent. A false negative is the incorrect conclusion that an analyte is absent when it is present. If the frequency of false positives or false negatives desired to be detected is less than 10%, then

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$$n = \frac{\ln \alpha}{\ln (1 - Y)}$$

where:

α = (1 – desired confidence level), and
Y = frequency to detect (<10%).

If the frequency that is desirable to detect is more than 10%, iterative solution of a binomial equation is necessary.[5,8]

Equations are available as a computer program†#(4) for computing sample number by the *Z* distribution, for estimating samples needed in systematic sampling, and for estimating required number of QC samples.

6. Sample Volumes

Collect a 1-L sample for most physical and chemical analyses. For certain determinations, larger samples may be necessary. Table 1060:I lists volumes ordinarily required for analyses, but it is strongly recommended that the laboratory that will conduct the analyses also be consulted to verify the analytical needs of sampling procedures as they pertain to the goals and data quality objective of an investigation.

Do not use samples from the same container for multiple testing requirements (e.g., organic, inorganic, radiological, bacteriological, and microscopic examinations) because methods of collecting and handling are different for each type of test. Always collect enough sample volume in the appropriate container in order to comply with sample handling, storage, and preservation requirements.

7. References

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1060 C. Sample Storage and Preservation

Complete and unequivocal preservation of samples, whether domestic wastewater, industrial wastes, or natural waters, is a practical impossibility because complete stability for every constituent never can be achieved. At best, preservation techniques only retard chemical and biological changes that inevitably continue after sample collection.

1. Sample Storage before Analysis

a. Nature of sample changes: Some determinations are more affected by sample storage than others. Certain cations are subject to loss by adsorption on, or ion exchange with, the walls of glass containers. These include aluminum, cadmium, chromium, copper, iron, lead, manganese, silver, and zinc, which are best collected in a separate clean bottle and acidified with nitric acid to a pH below 2.0 to minimize precipitation and adsorption on container walls. Also, some organics may be subject to loss by adsorption to the walls of glass containers.

Temperature changes quickly; pH may change significantly in a matter of minutes; dissolved gases (oxygen, carbon dioxide) may be lost. Because changes in such basic water quality properties may occur so quickly, determine temperature, reduction-oxidation potential, and dissolved gases in situ and pH, specific conductance, turbidity, and alkalinity immediately after sample collection. Many organic compounds are sensitive to changes in pH and/or temperature resulting in reduced concentrations during storage.

Changes in the pH-alkalinity-carbon dioxide balance may cause calcium carbonate to precipitate, decreasing the values for calcium and total hardness.

Iron and manganese are readily soluble in their lower oxidation states but relatively insoluble in their higher oxidation states; therefore, these cations may precipitate or they may dissolve from a sediment, depending on the redox potential of the sample. Microbiological activity may affect the nitrate-nitrite-ammonia content, phenol or BOD concentration, or the reduction of sulfate to sulfide. Residual chlorine is reduced to chloride. Sulfide, sulfite, ferrous iron, iodide,

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and cyanide may be lost through oxidation. Color, odor, and turbidity may increase, decrease, or change in quality. Sodium, silica, and boron may be leached from the glass container. Hexavalent chromium may be reduced to trivalent chromium.

Biological activity taking place in a sample may change the oxidation state of some constituents. Soluble constituents may be converted to organically bound materials in cell structures, or cell lysis may result in release of cellular material into solution. The well-known nitrogen and phosphorus cycles are examples of biological influences on sample composition.

Zero head-space is important in preservation of samples with volatile organic compounds and radon. Avoid loss of volatile materials by collecting sample in a completely filled container. Achieve this by carefully filling the bottle so that top of meniscus is above the top of the bottle rim. It is important to avoid spillage or air entrapment if preservatives such as HCl or ascorbic acid have already been added to the bottle. After capping or sealing bottle, check for air bubbles by inverting and gently tapping it; if one or more air bubbles are observed then, if practical, discard the sample and repeat refilling bottle with new sample until no air bubbles are observed (this cannot be done if bottle contained preservatives before it was filled).

Serum vials with septum caps are particularly useful in that a sample portion for analysis can be taken through the cap by using a syringe,[1] although the effect of pressure reduction in the head-space must be considered. Pulling a sample into a syringe under vacuum can result in low bias data for volatile compounds and the resulting headspace precludes taking further subsamples.

b. Time interval between collection and analysis: In general, the shorter the time that elapses between collection of a sample and its analysis, the more reliable will be the analytical results. For certain constituents and physical values, immediate analysis in the field is required. For composited samples it is common practice to use the time at the end of composite collection as the sample collection time.

Check with the analyzing laboratory to determine how much elapsed time may be allowed between sample collection and analysis; this depends on the character of the sample and the stability of the target analytes under the conditions of storage. Many regulatory methods limit the elapsed time between sample collection and analysis (see Table 1060:I). Changes caused by growth of microorganisms are greatly retarded by keeping the sample at a low temperature (<4°C but above freezing). When the interval between sample collection and analysis is long enough to produce changes in either the concentration or the physical state of the constituent to be measured, follow the preservation practices given in Table 1060:I. Record time elapsed between sampling and analysis, and which preservative, if any, was added.

2. Preservation Techniques

To minimize the potential for volatilization or biodegradation between sampling and analysis, keep samples as cool as possible without freezing. Preferably pack samples in crushed or cubed ice or commercial ice substitutes before shipment. Avoid using dry ice because it will freeze samples and may cause glass containers to break. Dry ice also may effect a pH change in

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samples. Keep composite samples cool with ice or a refrigeration system set at 4°C during compositing. Analyze samples as quickly as possible on arrival at the laboratory. If immediate analysis is not possible, preferably store at 4°C.[1]

No single method of preservation is entirely satisfactory; choose the preservative with due regard to the determinations to be made. Use chemical preservatives only when they do not interfere with the analysis being made. When they are used, add them to the sample bottle initially so that all sample portions are preserved as soon as collected. Because a preservation method for one determination may interfere with another one, samples for multiple determinations may need to be split and preserved separately. All methods of preservation may be inadequate when applied to suspended matter. Do not use formaldehyde as a preservative for samples collected for chemical analysis because it affects many of the target analytes.

Methods of preservation are relatively limited and are intended generally to retard biological action, retard hydrolysis of chemical compounds and complexes, and reduce volatility of constituents.

Preservation methods are limited to pH control, chemical addition, the use of amber and opaque bottles, refrigeration, filtration, and freezing. Table 1060:I lists preservation methods by constituent. See Section 7010B for sample collection and preservation requirements for radionuclides.

The foregoing discussion is by no means exhaustive and comprehensive. Clearly it is impossible to prescribe absolute rules for preventing all possible changes. Additional advice will be found in the discussions under individual determinations, but to a large degree the dependability of an analytical determination rests on the experience and good judgment of the person collecting the sample. Numbers of samples required for confidence levels in data quality objectives, however, rely on statistical equations such as those discussed earlier.

3. Reference

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1080 REAGENT WATER

1080 A. Introduction

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One of the most important aspects of analysis is the preparation of reagent water to be used for dilution of reagents and for blank analysis. Reagent water is water with no detectable concentration of the compound or element to be analyzed at the detection limit of the analytical method. Reagent water should be free of substances that interfere with analytical methods. The quality of water required is related directly to the analysis being made. Requirements for water quality may differ for organic, inorganic, and biological constituents depending on the use(s) for which the water is intended.

Any method of preparation of reagent water is acceptable provided that the requisite quality can be met. Improperly maintained systems may add contaminants. Reverse osmosis, distillation, and deionization in various combinations all can produce reagent water when used in the proper arrangement. Ultrafiltration and/or ultraviolet treatment also may be used as part of the process. Section 1080 provides general guidelines for the preparation of reagent water. Table 1080:I lists commonly available processes for water purification and major classes of contaminants removed by purification.

For details on preparing water for microbiological tests, see Section 9020B.3*c*.

1080 B. Methods for Preparation of Reagent Water

1. Distillation

Prepare laboratory-grade distilled water by distilling water from a still of all-borosilicate glass, fused quartz, tin, or titanium. To remove ammonia distill from an acid solution. Remove CO_2 by boiling the water for 15 min and cooling rapidly to room temperature; exclude atmospheric CO_2 by using a tube containing soda lime or a commercially available CO_2-removing agent.*#(5)

Boiling the water may add other impurities by leaching impurities from the container. Freshly replaced filters, cartridges and resins initially can release impurities. Pretreat feedwater and provide periodic maintenance to minimize scale formation within the still. Pretreatment may be required where the feedwater contains significant concentrations of calcium, magnesium, and bicarbonate ions; it may involve demineralization via reverse osmosis or ion exchange.

2. Reverse Osmosis

Reverse osmosis is a process in which water is forced under pressure through a semipermeable membrane removing a portion of dissolved constituents and suspended impurities. Product water quality depends on feedwater quality.

Select the reverse osmosis membrane module appropriate to the characteristics of the feedwater. Obtain rejection data for contaminants in the feedwater at the operating pressure to be used in preparing reagent water. Set overall water production to make the most economical use of water without compromising the final quality of the permeate. Selection of spiral-wound or hollow fiber configurations depends on fouling potential of the feedwater. Regardless of

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configuration used, pretreatment may be required to minimize membrane fouling with colloids or particulates and to minimize introduction of chlorine, iron, and other oxidizing compounds that may degrade reverse osmosis membranes. Periodic flushing of the membrane modules is necessary.

3. Ion Exchange

Prepare deionized water by passing feedwater through a mixed-bed ion exchanger, consisting of strong anion and strong cation resins mixed together. When the system does not run continuously, recirculate product water through ion-exchange bed.

Use separate anion and cation resin beds in applications where resin regeneration is economically attractive. In such instances, position the anion exchanger downstream of the cation exchanger to remove leachates from the cation resin. Proper bed sizing is critical to the performance of the resins. In particular, set the length-to-diameter ratio of the bed in accordance with the maximum process flow rate to ensure that optimal face velocities are not exceeded and that sufficient residence time is provided.

In applications where the feedwater has significant quantities of organic matter, remove organics to minimize potential fouling of the resins. Possible pretreatments include prefiltration, distillation, reverse osmosis, or adsorption.

4. Adsorption

Adsorption is generally used to remove chlorine and organic impurities. It is accomplished typically with granular activated carbon. Efficiency of organics removal depends on the nature of the organic contaminants, the physical characteristics of the activated carbon, and the operating conditions. In general, organics adsorption efficiency is inversely proportional to solubility and may be inadequate for the removal of low-molecular-weight, polar compounds. Performance differences among activated carbons are attributable to the use of different raw materials and activation procedures. Select the appropriate activated carbon with regard to these differences. Even with optimum activated carbon, proper performance will not be attained unless the column is sized to give required face velocity and residence time at the maximum process flow rate.

Use of activated carbon may adversely affect resistivity. This effect may be controlled by use of reverse osmosis, mixed resins, or special adsorbents. To achieve the lowest level of organic contamination, use mixtures of polishing resins with special carbons in conjunction with additional treatment steps, such as reverse osmosis, natural carbons, ultraviolet oxidation, or ultrafiltration.

1080 C. Reagent Water Quality

1. Quality Guidelines

Several guidelines for reagent water quality, based on contaminant levels, are available, but the final test is the appropriateness for the analysis. Table 1080:II lists some characteristics of

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various qualities of reagent water.

High-quality reagent water, having a minimum resistivity of 10 megohms-cm, 25°C (in line), typically is prepared by distillation, deionization, or reverse osmosis treatment of feedwater followed by polishing with a mixed-bed deionizer and passage through a 0.2-µm-pore membrane filter. Alternatively treat by reverse osmosis followed by carbon adsorption and deionization. Determine quality at the time of production. Mixed-bed deionizers typically add small amounts of organic matter to water, especially if the beds are fresh. Resistivity should be >10 megohm-cm at 25°C, measured in-line. Resistivity measurements will not detect organics or nonionized contaminants, nor will they provide an accurate assessment of ionic contaminants at the microgram-per-liter level.

Medium-quality water typically is produced by distillation or deionization. Resistivity should be >1 megohm-cm at 25°C.

Low-quality water should have a minimum resistivity of 0.1 megohm-cm, and may be used for glassware washing, preliminary rinsing of glassware, and as feedwater for production of higher-grade waters.

The pH of high- or medium-quality water cannot be measured accurately without contaminating the water. Measure other constituents as required for individual tests.

High-quality water cannot be stored without significant degradation; produce it continuously and use it immediately after processing. Medium-quality water may be stored, but keep storage to a minimum and provide quality consistent with the intended use. Store only in materials that protect the water from contamination, such as TFE and glass for organics analysis or plastics for metals. Store low-quality water in materials that protect the water from contamination.

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1090 LABORATORY OCCUPATIONAL HEALTH AND SAFETY

1090 A. Introduction

1. General Discussion

Achievement of a safe and healthful workplace is the responsibility of the organization, the laboratory manager, the supervisory personnel and, finally, the laboratory personnel themselves. All laboratory employees must make every effort to protect themselves and their fellow workers by conscientiously adhering to the health and safety program that has been developed and documented specifically for their laboratory.

2. Organizing for Safety

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a. Overall program: The responsibility for establishing and enforcing a laboratory health and safety (LH&S) program ultimately rests with the laboratory director. The LH&S program must, at the minimum, address how to protect oneself from the hazards of working with biological (1090H), chemical (1090J), and radiological (1090I) agents. Such a program is a necessary component of an overall laboratory quality system that provides for the health and safety of the entire laboratory staff. As a part of the quality system, all aspects of the LH&S program must be fully documented. Laboratory personnel must be trained. The LH&S program must be fully implemented and its application audited periodically. Appropriate records of all activities must be kept to document performance, meet appropriate regulatory requirements, and document the status of the LH&S program.

In the United States, the minimum standard of practice for health and safety activities is detailed in government documents.[1,2] Each laboratory should appoint as needed a chemical hygiene officer (CHO), a biological hygiene officer (BHO), a radiological hygiene officer (RHO), and, where appropriate or desired, a LH&S committee. The CHO, the committee, and laboratory management must develop, document, and implement a ‘‘written’’ laboratory hygiene plan (LHP), or chemical hygiene plan (CHP).

b. Specific responsibilities: Specific responsibilities applicable at various levels within the organization are as follows:

1) The chief executive officer (CEO) has ultimate responsibility for LH&S within the organization and must, with other managers and supervisors, provide continuous support for the LH&S program.

2) The supervisor has primary responsibility for the LH&S program in his or her work group.

3) The biological hygiene officer (BHO) has the responsibility to work with managers, supervisors, and other employees to develop and implement appropriate biological hygiene policies and practices; monitor procurement, use, and disposal of biological agents used in the laboratory; see that appropriate audits are conducted and that records are maintained; know the current legal requirements concerning working with biological agents; and seek ways to improve the biological hygiene program.

4) The chemical hygiene officer (CHO) has the same responsibilities as the biological hygiene officer, but with respect to chemicals, and also is responsible for helping supervisors (project directors) develop precautions and adequate facilities and for keeping material safety data sheets (MSDSs) available for review.

5) The radiological hygiene officer (RHO), referred to as radiation safety officer in most regulatory language, has the same responsibilities as the chemical hygiene officer, but with respect to radiological chemicals and exposure.

6) The laboratory supervisor has overall responsibility for chemical hygiene in the laboratory, including responsibility to ensure that workers know and follow the chemical hygiene rules, that protective equipment is available and in working order, and that appropriate

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training has been provided; performs regular, formal chemical hygiene and housekeeping inspections, including routine inspections of emergency equipment, and maintenance of appropriate records; knows the current legal requirements concerning regulated substances; specifies the required levels of protective apparel and equipment needed to perform the work; and ensures that facilities and training for use of any material being ordered are adequate.

7) The project director (or a director of a specific operation) has primary responsibility for biological, chemical, and/or radiological hygiene procedures as appropriate for all operations under his or her control.

8) The laboratory worker has the responsibility for planning and conducting each operation in accordance with the institutional chemical hygiene, biological hygiene, and radiological hygiene procedures, and for developing good personal chemical, biological, and radiological hygiene habits.

3. Records

Maintain records of all accidents including ‘‘near-misses,’’ medical care audits, inspections, and training for specified time periods that depend on the nature of the requirement. Keep records on standardized report forms containing sufficient information to enable an investigator to determine who was involved, what happened, when and where it happened, and what injuries or exposures, if any, resulted. Most importantly, these records should enable the formulation of appropriate corrective actions where warranted. The standard of practice for LH&S activities requires that a log (record) be kept of those accidents causing major disability. Record not only all accidents, but also ‘‘near-misses,’’ to permit full evaluation of safety program effectiveness. Maintain a file detailing all of the recommendations for the LH&S program.

4. Information and Training[2]

The standard of practice for hazard communication or ‘‘right-to know’’ requires that employees be notified about hazards in the workplace.

Laboratory personnel must be under the direct supervision and regular observation of a technically qualified individual who must have knowledge of the hazards present, their health effects, and related emergency procedures. The supervisor must educate laboratory personnel in safe work practices at the time of initial assignment and when a new hazardous substance is introduced into the workplace. Personnel have a right to know what hazardous materials are present, the specific hazards created by those materials, and the required procedures to protect themselves against these hazards. The hazard communication standard [2] requires information and training on material safety data sheets (MSDSs), labeling, chemical inventory of all hazardous substances in the workplace, and informing contractors of hazardous substances.

Training dealing with health and safety techniques and work practices requires a concerted effort by management, and must be conducted on a routine basis by competent and qualified individuals to be effective. Records of training must be maintained.

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1090 B. Safe Laboratory Practices

Use the information, rules, work practices, and/or procedures discussed below for essentially all laboratory work with chemicals.

1. General Rules

a. Accidents and spills:

1) Eye contact—Promptly flush eyes with water for a prolonged period (minimum of 15 min) and seek immediate medical attention.

2) Ingestion—Encourage victim to drink large amounts of water.

3) Skin contact—Promptly flush affected area with water for approximately 15 min and remove any contaminated clothing. If symptoms persist after washing, seek medical attention.

4) Clean-up—Promptly clean up spills, using appropriate protective apparel and equipment and proper disposal procedures.

5) Working alone—Avoid working alone in a building; do not work alone in a laboratory if the procedures to be conducted are hazardous.

b. Vigilance: Be alert to unsafe conditions and see that they are corrected when detected.

2. Work Practices/Rules

a. Work habits: Develop and encourage safe habits, avoid unnecessary exposure to chemicals by any route, and avoid working alone whenever possible.

b. Exhaust ventilation: Do not smell or taste chemicals. Vent any apparatus that may discharge toxic chemicals (vacuum pumps, distillation columns, etc.) into local exhaust devices.

c. Glove boxes: Inspect gloves and test glove boxes before use.

d. Cold and/or warm rooms: Do not allow release of toxic substances in cold rooms and/or warm rooms, because these rooms usually have no provisions for exhausting contaminants.

e. Use/choice of chemicals: Use only those chemicals for which the quality of the available

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ventilation system is appropriate.

f. Eating, smoking, and related activities: DO NOT eat, drink, smoke, chew gum, or apply cosmetics in areas where laboratory chemicals are present. Always wash hands before conducting these activities.

g. Food storage: DO NOT store, handle, or consume food or beverages in storage areas, refrigerators, or glassware and utensils that also are used for laboratory operations.

h. Equipment and glassware: Handle and store laboratory glassware with care to avoid damage. Do not use damaged glassware. Use extra care with Dewar flasks and other evacuated glass apparatus; shield or wrap them to contain chemicals and fragments should implosion occur. Use equipment for its designed purpose only.

i. Washing: Wash areas of exposed skin well before leaving the laboratory.

j. Horseplay: Avoid practical jokes or other behavior that might confuse, startle, or distract another worker.

k. Mouth suction: Do not use mouth suction for pipetting or starting a siphon.

l. Personal protective equipment: Do not wear personal protective clothing or equipment in nonlaboratory areas. Remove laboratory coats immediately on significant contamination with hazardous materials.

m. Personal apparel: Confine long hair and loose clothing. Wear shoes at all times in the laboratory but do not wear sandals or perforated shoes.

n. Personal housekeeping: Keep work area clean and uncluttered, with chemicals and equipment properly labeled and stored. Clean up work area on completion of an operation or at the end of each day.

o. Unattended operations: Leave lights on, place an appropriate sign on the door, and provide for containment of toxic substances in the event of failure of a utility service (such as cooling water) to an unattended operation.

3. Personal Protective Equipment

Carefully plan a program addressing the need for, use of, and the training with personal protective equipment. Such a program includes seeking information and advice about hazards, developing appropriate protective procedures, and proper positioning of equipment before beginning any new operations.

a. Eye protection: Wear appropriate eye protection (this applies to all persons, including visitors) where chemicals are stored or handled. Avoid use of contact lenses in the laboratory unless necessary; if contact lenses are used, inform supervisor so that special precautions can be taken.

b. Skin protection: Wear appropriate gloves when the potential for contact with toxic chemicals exists. Inspect gloves before each use, wash them before removal, and replace periodically.

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c. Respiratory protection: Use appropriate respiratory equipment when engineering controls are unable to maintain air contaminant concentrations below the action levels, i.e., one half the permissible exposure limit (PEL)[1] or threshold limit value (TLV[7]), i.e., levels below which no irreversible health affects are expected. When work practices are used that are expected to cause routine exposures that exceed the PEL or TLV, respiratory protection is required to prevent overexposure to hazardous chemicals. If respirators are used or provided in the laboratory then the LH&S standard of practice requires that a complete respiratory protection plan (RPP) be in place. The minimum requirements for an RPP meeting the LH&S standard of practice are published.[1] Inspect respirators before use and check for proper fit.

d. Other protective equipment: Provide and use any other protective equipment and/or apparel as appropriate.

4. Engineering Controls

Fume hoods: Use the hood for operations that might result in the release of toxic chemical vapors or dust. As a rule of thumb, use a hood or other local ventilation device when working with any appreciably volatile substance with a TLV of less than 50 ppm. Confirm that hood performance is adequate before use. Open hood minimally during work. Keep hood door closed at all other times except when adjustments within the hood are being made. Keep stored materials in hoods to a minimum, and do not block vents or air flow. Provide at least an 8-cm space under and around all items used in hoods, and ensure that they are at least 15 cm from the front of the hood.

5. Waste Disposal

Ensure that the plan for each laboratory operation includes plans and training for waste disposal. Deposit chemical waste in appropriately labeled receptacles and follow all other waste disposal procedures of the Chemical Hygiene Plan (see 1090J). Do not discharge any of the following contaminants to the sewer: concentrated acids or bases; highly toxic, malodorous, or lachrymatory substances; substances that might interfere with the biological activity of wastewater treatment plants; and substances that may create fire or explosion hazards, cause structural damage, or obstruct flow. For further information on waste disposal, see Section 1100.

6. Work with Chemicals of Moderate Chronic or High Acute Toxicity

Examples of chemicals in this category include diisopropylfluorophosphate, hydrofluoric acid, and hydrogen cyanide. The following rules are intended to supplement the rules listed previously for routine laboratory operations. Their purpose is to minimize exposure to these toxic substances by any exposure route using all reasonable precautions. The precautions are appropriate for substances with moderate chronic or high acute toxicity used in significant quantities.

a. Location: Use and store these substances only in areas of restricted access with special warning signs. Always use a hood (previously evaluated to confirm adequate performance with a face velocity of at least 24 m/min) or other containment device for procedures that may result in

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the generation of aerosols or vapors containing the substance; trap released vapors to prevent their discharge with the hood exhaust.

b. Personal protection: Always avoid skin contact by use of gloves and long sleeves, and other protective apparel as appropriate. Always wash hands and arms immediately after working with these materials.

c. Records: Maintain records of the amounts of these materials on hand, amounts used, and the names of the workers involved.

d. Prevention of spills and accidents: Be prepared for accidents and spills.

Ensure that at least two people are present at all times if a compound in use is highly toxic or of unknown toxicity.

Store breakable containers of these substances in chemically resistant trays; also work and mount apparatus above such trays or cover work and storage surfaces with removable, absorbent, plastic-backed paper. If a major spill occurs outside the hood, evacuate the area; ensure that cleanup personnel wear suitable protective apparel and equipment.

e. Waste: Thoroughly decontaminate or incinerate contaminated clothing or shoes. If possible, chemically decontaminate by chemical conversion. Store contaminated waste in closed, suitably labeled, impervious containers (for liquids, in glass or plastic bottles half-filled with vermiculite).

7. Work with Chemicals of High Chronic Toxicity

Examples of chemicals in this category include (where they are used in quantities above a few milligrams, or a few grams, depending on the substance) dimethyl mercury, nickel carbonyl, benzo(a)pyrene, *N*-nitrosodiethylamine, and other substances with high carcinogenic potency. The following rules are intended to supplement the rules listed previously for routine laboratory operations.

a. Access: Conduct all transfers and work with these substances in a controlled area, i.e., a restricted-access hood, glove box, or portion of a laboratory, designated for use of highly toxic substances, for which all people with access are aware of the substances being used and necessary precautions.

b. Approvals: Prepare a plan for use and disposal of these materials and obtain the approval of the laboratory supervisor.

c. Non-contamination/decontamination: Protect vacuum pumps against contamination by scrubbers or HEPA filters and vent them into the hood. Decontaminate vacuum pumps or other contaminated equipment, including glassware, in the hood before removing them from the controlled area. Decontaminate the controlled area before routine work is resumed.

d. Exiting: On leaving a controlled area, remove any protective apparel (place it in an appropriately labeled container), and thoroughly wash hands, forearms, face, and neck.

e. Housekeeping: Use a wet mop or a vacuum cleaner equipped with a HEPA filter. Do not dry sweep if the toxic substance is a dry powder.

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f. Medical surveillance: If using toxicologically significant quantities of such a substance on a regular basis (e.g., three times per week), consult a qualified physician about desirability of regular medical surveillance.

g. Records: Keep accurate records of the amounts of these substances stored and used, the dates of use, and names of users.

h. Signs and labels: Ensure that the controlled area is conspicuously marked with warning and restricted access signs and that all containers of these substances are appropriately labeled with identity and warning labels.

i. Spills: Ensure that contingency plans, equipment, and materials to minimize exposures of people and property are available in case of accident.

j. Storage: Store containers of these chemicals only in a ventilated, limited-access area.

k. Glove boxes: For a negative-pressure glove box, ensure that the ventilation rate is at least 2 volume changes/h and the pressure drop at least 1.3 cm of water. For a positive-pressure glove box, thoroughly check for leaks before each use. In either case, trap the exit gases or filter them through a HEPA filter and then release them into the hood.

l. Waste: Ensure that containers of contaminated waste (including washings from contaminated flasks) are transferred from the controlled area in a secondary container under the supervision of authorized personnel.

8. Physical Hazards

a. Electrical: Ensure that electrical wiring, connections, and apparatus conform to the requirement of the latest National Electrical Code. Fire, explosion, power outages, and electrical shocks are all serious hazards that may result from incorrect use of electrical devices. Ground all electrical equipment or use double-insulated equipment. Use ground fault interrupter circuit breakers to the maximum extent possible. Do not locate electrical receptacles inside fume hoods, and do not use equipment near volatile flammable solvents. Use approved safety refrigerators. Disconnect electrical equipment from the power supply before service or repair is attempted and never bypass safety interlocks. Attempting to repair equipment using employees not thoroughly acquainted with electrical principles may present particularly dangerous situations.

b. Non-ionizing radiation: Non-ionizing radiation, also called electromagnetic radiation, is generally considered to be the radio frequency region of the radiation spectrum. For the purposes of dealing with personal exposures in laboratories, it also includes the microwave frequency region. Typical laboratory exposures to non-ionizing radiation usually include ultraviolet, visible, infrared, and microwave radiation.

For normal environmental conditions and for incident electromagnetic energy of frequencies from 10 MHz to 100 GHz, the radiation protection guide is 10 mW/cm^2. The radiation protection applies whether the radiation is continuous or intermittent. This means a power density of 10 mW/cm^2 for periods of 0.1 h or more, or an energy density of 1 $mW\text{-}h/cm^2$ during any 0.1-h period. These recommendations apply to both whole-body irradiation and partial body

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irradiation.

Ultraviolet radiation (UV) and lasers are used frequently. With properly constructed and operated instruments, it is not a significant hazard but can be harmful when used for controlling microorganisms in laboratory rooms or for sterilizing objects.

When using devices that generate or use non-ionizing radiation, observe the following precautions: Wear safety glasses or goggles with solid side pieces whenever there is a possibility of exposure to harmful (UV) radiation. Provide proper shielding (shiny metal surfaces reflect this energy). Shut off all these devices (UV lamps) when not in use. Post warning signs and install indicator lights to serve as a constant reminder when these types of devices are in use (UV lamps).

c. Mechanical: Shield or guard drive belts, pulleys, chain drivers, rotating shafts, and other types of mechanical power transmission apparatus. Laboratory equipment requiring this guarding includes vacuum pumps, mixers, blenders, and grinders.

Shield portable power tools. Guard equipment such as centrifuges, which have high-speed revolving parts, against ‘‘fly-aways.’’ Securely fasten equipment that has a tendency to vibrate (e.g., centrifuges and air compressors) to prevent the tendency to ‘‘walk’’ and locate them away from bottles and other items that may fall from shelves or benches because of the vibration.

d. Compressed gases: Gas cylinders may explode or ‘‘rocket’’ if improperly handled. Leaking cylinders may present an explosion hazard if the contents are flammable; they are an obvious health hazard if the contents are toxic; and they may lead to death by suffocation if the contents are inert gases. The Compressed Gas Association has published procedures governing use and storage of compressed gases. Transfer gas cylinders only with carts, hand trucks, or dollies. Secure gas cylinders properly during storage, transport, and use, and leave valve safety covers on cylinders during storage and transport. Avoid the use of adapters or couplers with compressed gas. Properly identify cylinder contents.

9. Chemical Hazards

a. General precautions: Chemical injuries may be external or internal. External injuries may result from skin exposure to caustic or corrosive substances such as acids, bases, or reactive salts. Take care to prevent accidents, such as splashes and container spills. Internal injuries may result from the toxic or corrosive effects of substances absorbed by the body. These internal injuries may result from inhalation, skin contact, or ingestion.

Table 1090:I, Table 1090:II, and Table 1090:III list PELs, TLVs, and/or short-term exposure limits and ceilings for some chemical materials specified in *Standard Methods*, as given in various published sources.[1-8] The PEL values reported in these tables are in some instances higher than the levels that some nations believe to be appropriate. Because the health and safety program should be driven by meeting best industrial hygiene practice, always use the lowest recommended exposure values when protecting human health.

In addition, pay careful attention to equipment corrosion that ultimately may lead to safety hazards from equipment failure.

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b. Inorganic acids and bases: Many inorganic acids and bases have PELs and TLVs. Table 1090:I presents PELs (based on U.S. standards) and/or TLVs as well as short-term exposure limits and ceilings for some inorganic chemicals specified in *Standard Methods*. These PELs and TLVs indicate the maximum air concentration to which workers may be exposed. Fumes of these acids and bases are severe eye and respiratory system irritants. Liquid or solid acids and bases can quickly cause severe burns of the skin and eyes. When acids are heated to increase the rate of digestion of organic materials, they pose a significantly greater hazard because fumes are produced and the hot acid reacts very quickly with the skin.

Store acids and bases separately in well-ventilated areas and away from volatile organic and oxidizable materials. Use containers (rubber or plastic buckets) to transport acids and bases.

Work with strong acids and bases only in a properly functioning chemical fume hood. Slowly add acids and bases to water (with constant stirring) to avoid spattering. If skin contact is made, thoroughly flush the contaminated area with water and seek medical attention if irritation persists. Do not wear contaminated clothing until after it has been cleaned thoroughly. Leather items (e.g., belts and shoes) will retain acids even after rinsing with water and may cause severe burns if worn. If eye contact is made, immediately flush both eyes for at least 15 min with an eye wash and seek medical attention.

c. Perchloric acid and other highly reactive chemicals: Concentrated perchloric acid reacts violently or explosively on contact with organic material and may form explosive heavy metal perchlorates. Do not use laboratory fume hoods used with perchloric acid for organic reagents, particularly volatile solvents. In addition to these hazards, perchloric acid produces severe burns when contact is made with the skin, eyes, or respiratory tract. Preferably provide a dedicated perchloric acid hood. Follow the manufacturer's instructions for proper cleaning, because exhaust ducts become coated and must be washed down regularly.

Use extreme caution when storing and handling highly reactive chemicals, such as strong oxidizers. Improper storage can promote heat evolution and explosion. Do not store strong oxidizers and reducers in close proximity.

d. Organic solvents and reagents: Most solvents specified in *Standard Methods* have PELs and/or TLVs as well as short-term exposure limits or ceilings for workplace exposures (see Table 1090:II).

Many organic reagents, unlike most organic solvents, do not have PELs/TLVs or short-term exposure limits and ceilings, but this does not mean that they are less hazardous. Table 1090:III contains PELs/TLVs or short-term exposure limits and ceilings for some reagents specified in *Standard Methods*.

Some compounds are suspect carcinogens and should be treated with extreme caution. These compounds include solvents and reagents such as benzene, carbon tetrachloride, chloroform, dioxane, perchloroethylene, and benzidine. Lists of chemicals with special hazardous characteristics are available from the Occupational Safety and Health Administration and the National Institute for Occupational Safety and Health. In the U.S., the lists of ''Regulated Carcinogens'' and of ''Chemicals Having Substantial Evidence of Carcinogenicity'' are

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especially important. Developing and following laboratory handling procedures for compounds on such authoritative lists should significantly reduce the potential for exposures.

Solvents used in the laboratory usually fall into several major categories: alcohols, chlorinated compounds, and hydrocarbons. Exposure to each of these classes of compounds can have a variety of health effects. Alcohols, in general, are intoxicants, capable of causing irritation of the mucous membranes and drowsiness. Chlorinated hydrocarbons cause narcosis and damage to the central nervous system and liver. Hydrocarbons, like the other two groups, are skin irritants and may cause dermatitis after prolonged skin exposure. Because of the volatility of these compounds, hazardous vapor concentrations can occur (fire or explosion hazard). Proper ventilation is essential.

The majority of organic reagents used in this manual fall into four major categories: acids, halogenated compounds, dyes and indicators, and pesticides. Most organic acids have irritant properties. They are predominantly solids from which aerosols may be produced. Dyes and indicators also present an aerosol problem. Handle pesticides with caution because they are poisons, and avoid contact with the skin. Wear gloves and protective clothing. The chlorinated compounds present much the same hazards as the chlorinated solvents (narcosis and damage to the central nervous system and liver). Proper labeling for the compound, including a date for disposal based on the manufacturer's recommendations, permits tracking chemical usage and disposal of outdated chemicals.

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1090 C. Laboratory Facility/Fixed Equipment

1. Facility Design

The laboratory facility must have a general ventilation system with air intakes and exhausts located to avoid intake of contaminated air, well-ventilated stockrooms and/or storerooms, laboratory hoods and sinks, miscellaneous safety equipment including eyewash fountains and safety showers, and arrangements for the disposal of wastes and samples in accordance with applicable federal, state, and local regulations.

2. Facility and Fixed Equipment Maintenance

Maintain facilities and equipment with scheduled maintenance and continual surveillance to ensure proper operation. Give special attention to the adequacy of ventilation system.

a. Facility ventilation systems:

1) The general laboratory ventilation should provide a source of air for breathing and for input to local ventilation devices such as fume hoods. Do not rely on it for protection from exposure to toxic substances used during the working day. The system should direct air flow into the laboratory from nonlaboratory areas and then exhaust the air directly to the exterior of the building in a manner that will prevent its re-entry.

2) Laboratory fume hoods—As a minimum, provide at least 1 linear m of hood space per

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worker if workers spend most of their time working with chemicals or if they work with chemical substances with PELs or TLVs less than 100 ppm. Equip each hood with a continuous monitoring device to allow convenient confirmation of adequate hood performance before each use. If this is not possible, avoid work with substances with PELs or TLVs less than 100 ppm or with unknown toxicity, or provide other types of local ventilation devices.

3) Other local ventilation devices—Provide ventilated chemical/biological cabinets, canopy hoods and instrument/work station snorkels as needed. Many local ventilation devices require a separate exhaust duct, as do canopy hoods and snorkels.

4) Special ventilation areas/devices—It may be necessary to pass exhaust air from special ventilation areas or devices such as radiological hoods, glove boxes, and isolation rooms through HEPA filters, scrubbers, or other treatment before release into regular exhaust system. Ensure that cool rooms and warm rooms have provisions for rapid escape and for escape in the event of electrical failure.

5) Ventilation system modifications—Make alteration in the ventilation system only in consultation with an expert qualified in laboratory ventilation system design. Thoroughly test changes in the ventilation system to demonstrate adequate worker protection.

b. Facility ventilation system performance: A ventilation system rate of 4 to 12 room air changes per hour is considered adequate where local exhaust ventilation devices such as fume hoods are used as the primary method of control. General ventilation system air flow should not be turbulent and should be relatively uniform throughout the laboratory, with no high-velocity or static areas; air flow into and within laboratory fume hoods should not be excessively turbulent; fume hood face velocity should be adequate for the intended use (for general-purpose fume hoods this is typically 18 to 30 m/min). The effective protection provided by a fume hood depends on a number of factors including hood location and design, and cannot be determined solely on the basis of the face velocity.

c. Facility ventilation system evaluation: Evaluate performance characteristics (quality and quantity) of the ventilation system on installation, re-evaluate whenever a change in local ventilation devices is made, and monitor routinely. Schedule such monitoring with a frequency dictated by the type, age, condition, and any accessories associated with the device, but at least annually; monitor hoods at least quarterly. Document all ventilation system checks or actions such as flow checks, calibration, alterations, repairs, maintenance, or any other action that may determine or change flow efficiency or characteristics.

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1090 D. Hazard Evaluation

1. Hazard Evaluation

Hazard evaluation refers to the assessment of whether an employee has been overexposed to a hazardous substance or if such an exposure episode is likely to occur and to what extent.

The evaluation does not require monitoring airborne concentrations of the hazardous substances involved. Such an assessment may be informal and simply involve considering, among other factors, the chemical and physical properties of the substance and the quantity of

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substance used. In addition, the exposure assessment may be sufficient to estimate the probability of an overexposure.

Specify, document, and use hazard assessment criteria. Base such criteria on the toxicity of the substances to be used, the exposure potential of the chemical procedures to be performed, and the capacity of the available engineering control systems.

In cases where continuous monitoring devices are used, include resulting exposure data in the exposure evaluation. Air monitoring *only* provides information for inhalation exposure. Other means are required to determine whether overexposure could have occurred as a result of ingestion, or dermal or eye contact.

2. Spills of Toxic or Hazardous Substances

Spills are usually the result of loss of containment due to equipment failure or breakage (uncontrolled releases). The loss of containment can result in overexposure episodes. Calculations using data from material safety data sheets, the chemical and physical properties of the substance, known laboratory air changes, and work-station air volume will allow assessment of the possibility of an overexposure episode.

3. Work Practice Assignment

Use the information calculated from these exposure assessments to develop the written work practices needed to protect the health of the employee while conducting the procedure.

4. Documentation of Hazard Assessments

Document, validate, and authenticate all hazard assessments, preferably using a standard form.

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Also see references 2 through 8, Section 1090B.10.

1090 E. Personal Protective Equipment

1. Introduction

The employer must provide and maintain personal protective equipment (PPE) in condition that is sanitary and reliable against hazards in the workplace. All PPE also must be properly designed and constructed for the work to be performed. Several general references on PPE are available.[1-3] .

It is essential to select PPE based on an assessment of the hazards[3] or potential hazards to which an employee is exposed, to insure that the correct PPE will be obtained. Use personal protective equipment only when it is not possible or feasible to provide engineering controls. Such personal protective equipment includes all clothing and other work accessories designed to create a barrier against workplace hazards.

The basic element of any personal protective equipment management program must be an in-depth evaluation of the equipment needed to protect against the hazards at the workplace. Management dedicated to the safety and health of employees must use that evaluation to set a standard operating procedure for personnel, then encourage those employees to use, maintain, and clean the equipment to protect themselves against those hazards.

Using personal protective equipment requires hazard awareness and training on the part of the user. Make employees aware that the equipment does not eliminate the hazard. If the equipment fails, exposure will occur. To reduce the possibility of failure, use equipment that is properly fitted and maintained in a clean and serviceable condition.

Selection of the proper piece of personal protective equipment for the job is important. Employers and employees must understand the equipment's purpose and its limitations. Do not alter or remove equipment even though an employee may find it uncomfortable (equipment may be uncomfortable simply because it does not fit properly).

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2. Eye Protection

The LH&S standard of practice requires the use of eye and face protective equipment[3] where there is a reasonable probability of injury prevention through its use. Employers must provide a type of protector suitable for work to be performed, and employees must use the protectors. These requirements also apply to supervisors and management personnel, and to visitors while they are in hazardous areas.

Protectors must provide adequate protection against particular hazards for which they are designed, be reasonably comfortable when worn under the designated conditions, fit snugly without interfering with the movements or vision of the wearer, and be durable, easy to disinfect and clean, and kept in good repair.

In selecting the protector, consider the kind and degree of hazard. Where a choice of protectors is given, and the degree of protection required is not an important issue, worker comfort may be a deciding factor.

Persons using corrective glasses and those who are required to wear eye protection must wear glasses with protective lenses providing optical correction, goggles that can be worn over corrective glasses without disturbing the adjustment of the glasses, or goggles that incorporate corrective lenses mounted behind the protective lenses.

When limitations or precautions are indicated by the manufacturer, transmit them to the user and observe strictly. Safety glasses require special frames. Combinations of normal wire frames with safety lenses are not acceptable.

Design, construction, testing, and use of eye and face protection must be in accordance with national standards.[4]

3. Protective Work Gloves

Match glove material to the hazard: such materials as nitrile, neoprene, natural rubber, PVC, latex, and butyl rubber vary widely in chemical resistance. What may be safe with one chemical may prove harmful with another (see Table 1090:IV and Table 1090:V). Glove thickness may be as important as glove material in some cases. Many organic reagents, unlike most organic solvents, do not have PELs/TLVs but this does not mean that they are less hazardous.

Evaluate physical properties of the glove material: In addition to chemical resistance, glove materials vary in physical toughness. Select the glove that provides the abrasion, tear, flame, and puncture resistance required for the job.

Maximize comfort and dexterity. Lined gloves absorb perspiration and help insulate the hand. Unlined gloves conform to the hand. Lighter-gauge gloves improve touch sensitivity and flexibility, heavier-gauge gloves add protection and strength.

Ensure a safe grip. Nonslip grips allow for easier and safer handling. Embossed, pebbled, etched, and dotted coatings improve grip in wet or dry working conditions.

Measure proper size and length. Loose-fitting gloves affect dexterity and can be hazardous. Tight-fitting gloves may cause hand fatigue and tend to wear out faster. Gloves should fit

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comfortably without restricting motion and they should be long enough to protect the wrist, forearm, elbow, or the entire arm, depending on the application.

4. Head Protection

Water and wastewater laboratories seldom require this kind of personal protection, but field work may require such protection.

Head injuries are caused by falling or flying objects or by bumping the head against a fixed object. Head protection, in the form of protective hats, must both resist penetration and absorb the shock of a blow. Make the shell of the hat of a material hard enough to resist the blow, and utilize a shock-absorbing lining composed of head band and crown straps to keep the shell away from the wearer's skull. Protective materials used in helmets should be water-resistant and slow burning. Helmets consist essentially of a shell and suspension. Ventilation is provided by a space between the headband and the shell. Ensure that each helmet is accompanied by instructions explaining the proper method of adjusting and replacing the suspension and headband.

Visually inspect daily all components, shells, suspensions, headbands, sweatbands, and any accessories for signs of dents, cracks, penetration or any other damage that might reduce the degree of safety originally provided.

Do not store or carry helmets on the rear window deck of an automobile because sunlight and extreme heat may adversely affect the degree of protection.

Further information is available elsewhere.[3,5]

5. Hearing Protection

Exposure to high noise levels can cause hearing loss or impairment, and it can create physical and psychological stress. There is no cure for noise-induced hearing loss, so prevention of excessive noise exposure is the only way to avoid hearing damage. Specifically designed protection is required, depending on the type of noise encountered.

Use preformed or molded ear plugs fitted individually by a professional. Waxed cotton, foam, or fiberglass wool earplugs are self-forming. When properly inserted, they work as well as most molded earplugs. Plain cotton is ineffective as protection against hazardous noise.

Some earplugs are disposable, to be used one time and then thrown away. Clean nondisposable types after each use for proper protection.

Earmuffs need to make a perfect seal around the ear to be effective. Glasses, long sideburns, long hair, and facial movements, such as chewing, can reduce protection. Special equipment is available for use with glasses or beards.

More specific information on hearing conservation is available.[3]

6. Foot and Leg Protection

According to accident reviews most workers who suffered impact injuries to the feet were not wearing protective footwear. Furthermore, most of their employers did not require them to wear safety shoes. The typical foot injury was caused by objects falling less than 1.2 m and the

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median weight was about 30 kg. Most workers were injured while performing their normal job activities at their worksites.

Safety shoes should be sturdy and have an impact-resistant toe. In some shoes, metal insoles protect against puncture wounds. Additional protection, such as metatarsal guards, may be found in some types of footwear. Safety shoes come in a variety of styles and materials, such as leather and rubber boots and oxfords.

Safety footwear is classified according to its ability to meet minimum requirements for both compression and impact test. Those requirements and testing procedures and further information may be found elsewhere.[3,6]

7. References

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2. FORSBERG, K. & S.Z. MANSDORF. 1993. Quick Selection Guide To Chemical Protective Clothing, 2nd ed. Van Nostrand Reinhold, New York, N.Y.
3. OCCUPATIONAL SAFETY AND HEALTH ADMINISTRATION. General Requirements for Personal Protective Equipment. 29 CFR 1910.132.
4. AMERICAN NATIONAL STANDARDS INSTITUTE. 1968. Design, Construction, Testing, and Use of Eye and Face Protection. ANSI Z87 1-1968, American National Standards Inst., Inc., New York, N.Y.
5. AMERICAN NATIONAL STANDARDS INSTITUTE. 1986. Safety Requirements for Industrial Head Protection. ANSI Z89.1-1986. American National Standards Inst., Inc., New York, N.Y.
6. AMERICAN NATIONAL STANDARDS INSTITUTE. 1967 & 1983. Men's Safety-Toe Footware. ANSI Z41 1-1967 & Z41-1983, American National Standards Inst., Inc., New York, N.Y.

1090 F. Worker Protection Medical Program

1. Preventive Medicine Program

The preventive medicine program should include inoculations to provide protection from tetanus and other diseases that are associated with the types of samples received and analyzed by the laboratory. The scope of this program depends on the diseases prevalent in the area where the samples originate. The program also must comply with the appropriate regulations.

2. Medical Surveillance

Routine surveillance may be indicated for anyone whose work involves routine handling of

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hazardous chemical or biological substances. Consult a qualified occupational health physician and/or toxicologist to determine whether a regular schedule of medical surveillance is indicated.

3. Environmental Monitoring

a. General: The initiation of environmental monitoring (exposure monitoring) associated with laboratory uses of hazardous chemical substances is triggered by exposures exceeding the action level (usually defined as one-half the PEL or TLV), PEL, or TLV. The employer is responsible for ensuring that employees' exposures to such substances do not exceed the PELs specified in the regulations dealing with air contaminants.[1]

b. Employee exposure determination: Determine a worker's exposure to any hazardous chemical substance if there is reason to believe that exposure levels for that substance routinely exceed the action level. Where there is no action level for a substance the worker exposure must not exceed the PEL or TLV. If the initial monitoring confirms that an employee exposure exceeds the action level, or in the absence of an action level, the PEL, the employer must immediately comply with the exposure monitoring provisions of the relevant national standard. Monitoring may be terminated in accordance with the relevant standard (if one exists) or when the exposures are found to be below the action level (one half the PEL or TLV) or in the absence of an action level, below the PEL or TLV. The workers are to be notified in accordance with national standard; if none exists, they should at least be notified within 15 working days after any monitoring results have become available to the employer, either by contacting the employee individually or by posting the results in an appropriate location accessible to employees.

4. Medical Consultation and Medical Examinations

All employees who work with hazardous chemicals should have an opportunity to receive medical attention (at no personal cost), including any follow up examinations that the examining physician determines to be necessary, under the following circumstances:

- Whenever an employee develops signs or symptoms associated with an exposure to a hazardous chemical that the employee may have been using.
- Where exposure monitoring reveals an exposure level routinely above the action level (or in the absence of an action level, the PEL or TLV). For a national regulated substance for which there are exposure monitoring and medical surveillance requirements, establish medical surveillance for the affected employee as prescribed by the particular standard.
- Whenever an uncontrolled event, such as a spill, leak, explosion, or other occurrence, takes place in the work area, resulting in the likelihood of a hazardous exposure. Provide the affected employee an opportunity for a medical consultation to determine the need for a medical examination.

All medical examinations and consultations should be performed by, or under the direct supervision of, a licensed physician, without cost to the employee or loss of pay, and at a

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reasonable time and place. Inform the physician of the identity of the hazardous chemical(s) to which the employee may have been exposed; the conditions under which the exposure occurred, including quantitative exposure data, if available; and the signs and symptoms of exposure that the employee is experiencing, if any. The employer must obtain from the examining physician a written opinion that includes any recommendation for further medical follow-up, the results of the medical examination and any associated tests, notice of any medical condition revealed during the examination that may place the employee at increased risk as a result of exposure to a hazardous chemical found in the workplace, and a statement that the employee has been informed by the physician of the results of the consultation or medical examination and any medical condition that may require further examination or treatment. The written opinion must not reveal specific findings or diagnoses unrelated to occupational exposure.

5. Reference

1. OCCUPATIONAL SAFETY AND HEALTH ADMINISTRATION. Air Contaminants. 29 CFR 1910.1000.

6. Bibliography

DOULL, J., C.D. KLAASSEN & M.O. AMDUR. 1980. Casarett and Doull's Toxicology: The Basic Science of Poisons, 2nd ed. Macmillan Publishing Co., Inc., New York, N.Y.

WILLIAMS, P.L. & J.L. BURSON. 1985. Industrial Toxicology: Safety and Health Applications in the Workplace. Van Nostrand Reinhold Co., New York, N.Y.

OCCUPATIONAL SAFETY AND HEALTH ADMINISTRATION. Access to Employee Exposure and Medical Records. 29 CFR 1910.20.

OCCUPATIONAL SAFETY AND HEALTH ADMINISTRATION. Occupational Exposure to Hazardous Chemicals in Laboratories. 29 CFR 1910.1450.

1090 G. Provisions for Work with Particularly Hazardous Substances

The information outlined in the following paragraphs meets the LH&S standard of practice[1] and also represents good industrial hygiene practices.

1. Designated Area

Wherever appropriate, the employer must establish a ‘‘designated area,’’ that is, an area that may be used for work with select carcinogens, reproductive toxins, or substances having a high degree of acute toxicity. A designated area may be the entire laboratory, an area of a laboratory, or a device such as a laboratory hood.

2. Select Carcinogen

In the U.S. a ‘‘select carcinogen’’ means any substance meeting at least one of the following criteria: the substance is regulated by OSHA as a carcinogen; it is listed under the category,

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‘‘known to be carcinogenic,’’ by the U.S. National Toxicology Program (NTP);[2] it is listed under Group 1 (carcinogenic to humans) by the International Agency for Research on Cancer (IARC);[3] or it is listed in either Group 2A or 2B by IARC[3] or under the category, ‘‘reasonably anticipated to be carcinogenic’’ by NTP,[2] and causes statistically significant tumor incidence in experimental animals after inhalation exposure of 6 to 7 h/d, 5 d/week, for significant portion of a lifetime to dosages of less than 10 mg/m^3, or after repeated skin application of less than 300 mg/kg of body weight/week, or after oral dosages of less than 50 mg/kg of body weight/d.

3. Use of Containment Devices

The work conducted and its scale must be appropriate to the physical facilities available and, especially, to the quality of ventilation.

The general laboratory ventilation system must be capable of providing air for breathing and for input to local ventilation devices. It should not be relied on for protection from toxic substances released into the laboratory, but should ensure that laboratory air is continually replaced, preventing increase of air concentrations of toxic substances during the working day, and that air flows into the laboratory from nonlaboratory areas and out to the exterior of the building.

4. References

1. OCCUPATIONAL SAFETY AND HEALTH ADMINISTRATION. Laboratory Standard. Occupational Exposure to Hazardous Chemicals in Laboratories. 29 CFR 1910.1450.
2. U.S. PUBLIC HEALTH SERVICE, NATIONAL TOXICOLOGY PROGRAM. 1980. Annual Report on Carcinogens. Dep. Health & Human Services, U.S. Government Printing Off., Washington, D.C.
3. INTERNATIONAL AGENCY FOR RESEARCH ON CANCER. (Various dates). IARC monographs on risk of chemicals to humans. World Health Org. Publications Center, Albany, N.Y.

5. Bibliography

NATIONAL INSTITUTES OF HEALTH. 1981. Guidelines for the Laboratory Use of Chemical Carcinogens. NIH Publ. No. 81-2385, U.S. Government Printing Off., Washington, D.C.

Also see Section 1090C.3.

1090 H. Biological Safety

1. Introduction

The analysis of environmental samples involves worker contact with samples that may be contaminated with agents that present microbiological hazards. The majority of these agents

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involve exposures to pathogenic microorganisms or viruses that may produce human disease by accidental ingestion, inoculation, injection, or other means of cutaneous penetration. The primary means of exposure to these microbiological hazards involves hand-mouth contact while handling the samples, contaminated laboratory materials and/or aerosols created by incubating, pipetting, centrifuging, or blending of samples or cultures. Use the following rules, work practices and/or procedures to control or minimize exposure to these agents.

2. General Rules

Do not mix dilutions by blowing air through a pipet into a microbiological culture.

When working with grossly polluted samples, such as wastewater or high-density microbial cultures, use a pipetting device attached to a pipetting bulb to prevent accidental ingestion (never pipet by mouth).

Because untreated waters may contain waterborne pathogens, place all used pipets in a jar containing disinfectant solution for decontamination before glassware washing. Do not place used pipets on table tops, on laboratory carts, or in sinks without adequate decontamination.

3. Work Practices

Good personal hygiene practices are essential to control contact exposures. Frequently disinfect hands and working surfaces. Encourage immunization of laboratory staff against tetanus and possibly typhoid and other infectious agents to minimize risk of exposure.

Provide drinking water outside the laboratory, preferably from a foot-operated drinking fountain.

Eliminate flies and other insects to prevent contamination of sterile equipment, media, samples, and bacterial cultures and to prevent spread of infectious organisms to personnel.

Observe appropriate precautions in use of laboratory equipment. Use a leakproof blender tightly covered during operation to minimize contamination. Use a centrifuge tightly covered to minimize exposure if culture-containing tubes should shatter during centrifuging. The tube breakage produces a cleanup problem and microbiological aerosols. Conduct activities such as inserting a hot loop into a flask of broth culture in a manner that eliminates or minimizes the hazards due to aerosolized microorganisms. Sterilize contaminated materials (cultures, samples, used glassware, serological discards, etc.) by autoclaving before discarding them or processing for reuse. Preferably use specially marked biohazard bags for disposal. Dispose of contaminated broken glass in a specially marked container.

4. Procedures

Quaternary ammonium compounds that include a compatible detergent, or solutions of sodium hypochlorite are satisfactory disinfectants for pipet discard jars. Use the highest concentrations recommended for these commercial products provided that this concentration does not cause a loss of markings or fogging of pipets.

Sterilize biological waste materials to eliminate all infectious substances, and sterilize all contaminated equipment or apparatus before washing, storage, or disposal, preferably by

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autoclaving. When decontaminating materials in the autoclave, heat them to at least 121°C under a pressure of 103 kPa for a minimum of 30 min. The contact time is measured from time the contact chamber reaches 121°C. If the waste is contained in bags, add water to the contents to insure wet heat. Dry heat and chemical treatment also may be used for sterilizing nonplastic items. After sterilization, the wastes can be handled safely and disposed of by conventional disposal systems in accordance with local regulations.

5. Waste Disposal

Sterilize contaminated materials by autoclaving (see ¶ 3 above) before discarding them.

If combustible materials cannot be decontaminated, burn them with special precautions; permits for burning may be required. Use temporary storage for decay or permanent storage for treating radioactive wastes when alternatives are not available. Collect contaminated combustible wastes and animal carcasses in impermeable containers for disposal by incineration.

6. Bibliography

NATIONAL INSTITUTES OF HEALTH. 1981. Guidelines for the Laboratory Use of Chemical Carcinogens. NIH Publ. No. 81-2385, U.S. Government Printing Off., Washington, D.C.

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FURR, A.K., ed. 1990. CRC Handbook of Laboratory Safety, 3rd ed. CRC Press, Inc., Boca Raton, Fla.

1090 I. Radiological Safety

1. Introduction

This section discusses ionizing radiation safety related to gas chromatography detectors and specific analytical procedures (see Table 1090:VI). Ionizing radiation includes alpha particles, beta particles, gamma rays, and X-rays. Non-ionizing radiation safety is discussed elsewhere (Section 1090B.8).

All persons are exposed to ionizing radiation. The average annual radiation dose to the whole body from cosmic, terrestrial, and internal sources, medical and dental X-rays, etc., is about 185 mrems/year (1.85 mSieverts/year). It is essential to prevent unnecessary continuous or intermittent occupational exposures, and to take steps to eliminate accidents that may result in dangerous radiation exposure.

Personnel who work in laboratories may be exposed to ionizing radiation sources using both

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procedures and instruments. Evaluate potential exposures and control the associated equipment and procedures using work practices developed to minimize and/or eliminate exposures.

Users of radioactive materials are responsible for compliance with the requirements of their national nuclear regulatory body (in the United States, the Nuclear Regulatory Commission)[1] and/or related state regulations. In addition, administrative or local requirements may apply at specific facilities. The use of ''exempt'' quantities is regulated[1] even though the facility may be exempt from specific licensing requirements.

Radionuclides are used in laboratories to develop and evaluate analytical methods, to prepare counting standards, and to calibrate detectors and counting instruments (see Part 7000). Sealed sources, such as the nickel-63 detector cell used in electron capture gas chromatograph units, also are common.

2. Exposures

a. Exposure limits and control: The LH&S standard of practice[2] does not permit the use of personal protective equipment for allowing employee exposures above the limits specified by the NRC.[1] The NRC exposure limits are the maximum permissible exposures for 40 h in any workweek of 7 consecutive days.

The exposure limits may be adjusted proportionately (upward) for a period where the exposure is less than 40 h. However, the limit must be adjusted proportionately (downward) for periods where the exposure period is greater than 40 h.

Limiting exposure to ionizing radiation includes providing engineering (physical safeguards) and administrative (procedural) controls for using radioactive materials. Engineering controls include shields, barriers, and interlocks to limit external exposure, and exhaust ventilation systems and personal protective equipment to limit internal contamination. Administrative controls include conducting periodic surveys and reviews of activities, training in the use of radioactive materials, and documented procedures (see below).

Hazards associated with the use of devices, such as X-ray diffraction apparatus or an electron microscope, can be minimized or eliminated by following the manufacturer's operating instructions and the laboratory safety procedures.

b. Monitoring procedures and equipment: Radiochemical exposure monitoring may be done by collecting and analyzing wipe samples, using portable survey instruments, and/or by collecting and analyzing air samples. More than one technique usually is required.

Survey equipment may either integrate the response over time (e.g., exposure, absorbed dose), or results may be presented as a response rate (e.g., count rate or exposure rate). Typical choices include ion chambers, G-M counters, and scintillation detectors.

Thin-windowed GM-counters are suitable for wipe samples and for monitoring skin and clothing. An alpha scintillation monitor is needed to detect alpha-emitters. An excellent discussion of monitoring techniques for radioisotopes is available.[3]

c. Facility surveys: Conduct periodic surveys to assess the effectiveness of physical and

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procedural controls. Survey procedures generally use wipe tests for removable contamination and/or portable measurement devices for locating or measuring fixed and removable radioactivity.

1) Sealed sources—Check these sources for integrity by wipe tests at least every 6 months. Electron capture detectors using ^{63}Ni or ^{3}H require counting wipes by liquid scintillation or windowless gas-flow proportional counters to measure low-energy beta radiation effectively.

2) Work and storage areas—Survey these areas periodically to assess possible contamination or external radiation fields using portable survey instruments. The frequency of the surveys is dictated by the documented contamination record for the laboratory. Usually the radioactivities presented using the methods of Part 7000 are not measurable with routine survey instruments. Therefore use blanks in the analytical process in determining the presence of low-level contamination.

3) Documentation and records—Completely document each survey, identifying the personnel involved, the location, the type, model, and serial numbers of survey instruments used, the type and energy of radiations measured, the date and time of the survey, the instrument response to a check source, the instrument background count or exposure rate, and the results of each measurement.[4]

d. Personnel surveys and monitoring: Conduct and document surveys after routine use of unsealed radionuclide sources to confirm that personnel and the work area have not been contaminated by the process. Wear monitoring devices if there is a reasonable probability of exceeding 25% of the occupational exposure dose equivalent limit. Personal monitoring devices include film badges, thermoluminescent dosimeters, and solid state electronic dosimeters. The length of time the personal monitoring badges are worn before evaluation depends on the ability of the device to integrate the exposure over long periods, the probability and magnitude of the exposure, and the need to assure that the device is available and used.

Personnel performing procedures in *Standard Methods* would not be expected to receive exposures approaching 1.25 rem/quarter and may wish to consider 3-month wear periods if dosimetry is required.

Personal (external radiation) exposure is evaluated by using a personal dosimeter, preferably the film dosimeter (badge). The dosimeter badge measures the accumulated radiation over a period of time. Pocket ionization chambers, thermoluminescent dosimeters, and thimble chambers also may be used to supplement the film dosimeter.

Whole body or gamma spectrometry radiation detectors may be used to determine the presence of radioactive substances in the body, but these instruments are expensive and require the operator to be specially trained. Evaluate equipment and supplies that have been, or are suspected to have been, in contact with radioactive substances to determine if contamination is present. Because body waste may contain radioactive contaminants evaluate it also for the presence of contamination where personal exposures have been confirmed.

3. Work Practices

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Each individual should be familiar with procedures for dealing with radiation emergencies from small spills to major accidents, depending on facility programs. Emergency procedures should include notifications required, containment methods, clean-up procedures, and survey techniques. Emergency supplies should be readily available for coping with major accidents.

Contamination is typically prevented through proper use of laboratory facilities and procedures. Procedures include the use of gloves, aprons, safety glasses, and other protective clothing to eliminate the possibility of skin contamination and transfer. Learn proper pipetting and weighing techniques before working with radioactive sources. Conduct work with unsealed radioactive sources in unobstructed work areas with adequate means of containing and absorbing potential spillage of liquids.

4. Procedures

Develop and implement a radiation safety plan and provide a copy to all persons working with radioactive materials or radiation-producing machines, and provide both lecture and practical training to all employees.

a. Safety plan elements: The recommended minimum plan should include procedures for obtaining authorization to use, order, handle, and store radionuclides; safe handling of unsealed radioactive material; safe response to radiation accidents; decontamination of personnel and facilities; personnel monitoring; laboratory monitoring; and disposal of radioactive materials.

b. Handling radioactive materials: Become knowledgeable about the hazards associated with the materials to be used. Plan work activities to minimize the time spent handling radioactive materials or in using radioactive sources. Work as far from radioactive sources as possible, use shielding appropriate for the materials to be used, and use radioactive materials only in defined work areas. Wear protective clothing and dosimeters as appropriate. Monitor work areas to ensure maximum contamination control. Minimize the accumulation of waste materials in the work area. Use appropriate personal hygiene and self-monitor after using radioactive materials and after each decontamination procedure.

c. Training of users: Train personnel working with radioactive materials in radiation safety as part of the overall occupational health program. Address at least the following topics: characteristics of ionizing radiation and radioactive contamination; radiation dose limits; environmental radiation background; acute and chronic effects; internal and external modes of exposure; basic protective measures; responsibilities of employer and employees; radiation protection program responsibilities; posting, warning signs, and alarms; radiation monitoring programs; and emergency procedures.[5]

5. Waste Disposal

Generalized disposal criteria for radioactive wastes have been developed by the U.S. National Committee on Radiation Protection and Measurements.[4] Two general philosophies govern the disposal of radioactive wastes: dilution and dispersion to reduce the concentration of radionuclide by carrier dilution or dilution in a receiving medium, and concentration and

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confinement, usually involving reduction in waste volume with subsequent storage for decay purposes.

Airborne wastes can be treated by either method. Ventilation includes discharge from hooded operations to the atmosphere. Typical radioactive gases include iodine, krypton, and xenon. Iodine can be removed by scrubbing or by reaction with silver nitrate. Noble gases can be removed by absorption; standard techniques can be used for particulate. Dilution methods are suitable for liquids with low activity. Intermediate levels may be treated by various physical-chemical processes to separate the waste into a nonradioactive portion that can be disposed of by dilution and a high-activity portion to be stored. Solid wastes may consist of equipment, glassware, and other materials. When possible, decontaminate these materials and reuse. Decontamination usually results in a liquid waste.

Dispose of all waste in conformance with the requirements of the regulatory authority having jurisdiction.

Determine the laboratory's status and obtain approval before storing, treating and/or disposing of wastes.

6. References

1. NUCLEAR REGULATORY COMMISSION. Standards for Protection Against Radiation. 10 CFR Part 20.
2. OCCUPATIONAL SAFETY AND HEALTH ADMINISTRATION. Ionizing Radiation. 29 CFR 1910.96.
3. FURR, A.K., ed. 1990. CRC Handbook of Laboratory Safety, 3rd ed. CRC Press, Inc., Boca Raton, Fla.
4. NATIONAL COUNCIL ON RADIATION PROTECTION AND MEASUREMENTS. 1976. Environmental Radiation Measurements. Rep. No. 50, National Counc. Radiation Protection & Measurements, Washington, D.C.

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1090 J. Chemical Hygiene Plan

1. Introduction

The information presented in this section describes the intent and lists the minimum requirements and critical elements of the OSHA laboratory standard.[1] This standard is performance-based and represents good industrial hygiene practice. Any organization that chooses not to follow or use the OSHA standards to meet that standard's requirements must demonstrate that the procedures it uses meet the minimum level of employee protection afforded by the OSHA standard.

Much of the information presented in the preceding subsections of 1090 was provided as guidance and should be used in developing and finalizing the laboratory chemical hygiene plan (CHP).

2. Requirements

Develop and implement a written CHP capable of protecting employees from health hazards associated with the chemicals used in the laboratory. This CHP must be capable of keeping exposures below the permissible exposure limits (PELs/TLVs) and also must be readily available to employees. The CHP must at minimum address the following elements, and must describe specific measures the employer will undertake to ensure laboratory employee protection.

a. Standard operating procedures or work practices: Include procedures and practices relevant to safety and health considerations. These are to be followed when laboratory work involves the use of hazardous chemicals. Include the information contained in MSDSs for hazardous chemicals when conducting a hazard assessment and developing work practices. Some of the guidance presented in an MSDS is intended for use in industrial settings where material is used in large quantities for a full work shift and not for the small-volume, short-duration exposures experienced in laboratories.

b. Exposure hazard criteria and procedures: These will be used to determine and implement control measures for reducing employee exposure to hazardous chemicals while conducting laboratory operations. They include engineering controls, the use of personal protective equipment, and hygiene practices. Pay particular attention to the selection of control measures for work activities that involve chemicals known to be extremely hazardous.

c. Protective equipment performance procedures: These include procedures for evaluating the performance of fume hoods and other protective equipment and specific measures to be taken to ensure proper and adequate performance of such equipment.

d. Employee information and training: This training must be timely, be refreshed periodically, evaluated for effectiveness, and documented.

e. Approval procedures: The plan must state the circumstances under which a specific laboratory operation, procedure, or activity requires prior approval before implementation.

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f. Employee medical consultation and medical examinations.

g. Safety personnel: The plan must designate personnel responsible for implementation of the CHP. This should include the formal assignment of a Chemical Hygiene Officer and, where appropriate, the establishment of a Chemical Hygiene Committee.

h. Additional employee protection: The plan should include provisions for working with particularly hazardous substances. These substances include ‘‘select carcinogens’’ (see Section 1090G.2), reproductive toxins, and substances that have a high degree of acute toxicity. Give specific consideration to establishment of a designated area, use of containment devices such as fume hoods or glove boxes, procedures for safe removal of containment waste, decontamination procedures, emergency plans and procedure (test annually as a minimum), and employer review and evaluation of the effectiveness of the CHP at least annually and updating as necessary.

3. Reference

1. OCCUPATIONAL SAFETY AND HEALTH ADMINISTRATION. Occupational Exposure to Hazardous Chemicals in Laboratories. 29 CFR 1910.1450.

1100 WASTE MINIMIZATION AND DISPOSAL

1100 A. Introduction

Waste minimization and disposal are part of integrated hazardous materials management. It is important to become familiar with federal regulations regarding the use and disposal of hazardous materials prior to their purchase, storage, and use for water and waste-water analysis. Proper management of hazardous materials will reduce the amount of hazardous waste and associated disposal costs.

1100 B. Waste Minimization

1. General Considerations

Waste minimization or pollution prevention in the laboratory is the preferred approach in managing laboratory waste. Minimizing waste makes good economic sense: it reduces both costs and liabilities associated with waste disposal. For certain hazardous-waste generators it also is a regulatory requirement.

2. Waste Minimization Methods

Waste minimization methods include source reduction, recycling, and reclamation.[1] Waste treatment, which also may be considered a form of waste minimization, is addressed in Section 1100C.

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Source reduction can be achieved through the purchase and use of smaller quantities of chemicals. While large-volume purchases may seem economical, the costs of disposing of expired-shelf-life materials also must be considered. Date chemical inventory and use oldest stock first, or if possible, use ‘‘just in time’’ material delivery. Commercial laboratories and chemical users in general can return samples or unopened chemicals to sender or supplier for recycling or disposal. Many suppliers will accept unopened containers of chemicals.

Substitute nonhazardous materials for hazardous chemicals where possible. Wherever possible use methods that do not require the use of hazardous chemicals or use micro-scale analytical methods.

Improving laboratory procedures, documentation, and training will increase awareness of waste minimization and proper disposal practices, and may allow different sections within a laboratory to share standards and stock chemicals. Evaluate hazardous materials storage and use areas for potential evaporation, spills, and leaks. Segregate waste streams where possible to keep nonhazardous waste from becoming hazardous waste through contact with hazardous waste. Segregation also facilitates treatment and disposal.

Transfer of unused stock chemicals to other areas of the laboratory where they may be used or to other institutions is a way to minimize waste.[2] Check with laboratory’s legal counsel before transferring chemicals.

Recycling/reclamation has limited potential in water and waste-water laboratories. Volumes generated are generally too small for economical reclamation and purity requirements are often too great. However, organic solvents often can be distilled and recovered for reuse and mercury and silver can be recovered.[3]

3. References

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3. HENDRICKSON, K.J., M.M. BENJAMIN, J.F. FERGUSON & L. GOEBEL. 1984. Removal of silver and mercury from spent COD test solutions. *J. Water Pollut. Control. Fed.* 56(5):468.

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1. General Considerations

Stringent penalties exist for the improper disposal of hazardous wastes. Potential criminal and civil liability exists for both organizations and individuals. Specific requirements vary by state and local jurisdiction and are subject to change. Federal requirements for hazardous waste generators and transporters and for treatment, storage, and disposal facilities (TSDFs) are found in regulations pursuant to the Resource Conservation and Recovery Act of 1976 (RCRA) as amended by the Hazardous and Solid Waste Amendments of 1984 (HSWA). Many activities, in particular treatment, storage, and disposal of hazardous wastes, require a permit or license.[1,2]

Develop a plan for the safe and legal disposal of chemical and biological substances in conjunction with the laboratory supervisor and safety coordinator. Plan should address the proper transport, storage, treatment, and disposal of hazardous waste. Properly characterize composites and document wastes. Refer to Section 1090 on Safety with regard to protective equipment in the handling of hazardous materials.

2. Waste Treatment and Disposal Methods

Treatment can be used to reduce volume, mobility, and/or toxicity of hazardous waste where expertise and facilities are available. Treatment, even on a small scale, may require a permit. Consult with federal, state, and local regulatory officials.

Waste treatment methods include thermal, chemical, physical, and biological treatment, and combinations of these methods.[1]

a. Thermal treatment: Thermal treatment methods include incineration and sterilization. They involve using high temperatures to change the chemical, physical, or biological character or composition of the waste. Incineration is often used to destroy organic solvents and is preferred for infectious wastes, although sterilization through autoclaving and/or ultraviolet light also may be allowed. Check with local health department officials.

b. Chemical treatment: Methods include chemical reaction (oxidation/reduction, neutralization, ion exchange, chemical fixation, photolysis, coagulation, precipitation) of the waste material. Neutralization of acidic or alkaline wastes is the most common form of chemical treatment. Elementary neutralization of corrosive wastes is exempt from federal RCRA permitting requirements. Before discharge of wastes to a publicly owned treatment works (POTW), ensure that they contain no pollutants (other than corrosivity) exceeding the limits set by the POTW. The oxidation of cyanide to cyanate with a strong chemical oxidant is an example of a toxicity-reducing chemical treatment.

c. Physical treatment: Methods include solidification, compaction, photo-induced reaction, distillation, flocculation, sedimentation, flotation, aeration, filtration, centrifugation, reverse osmosis, ultrafiltration, gravity thickening, and carbon or resin adsorption. Physical treatment generally reduces volume or mobility of waste materials.

d. Biological treatment: Methods include using biosolids to destroy organic compounds, composting organic-rich wastes, and using bioreactors to promote decomposition. Biological

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treatment usually is economical on a scale larger than is possible in most water and wastewater laboratories.

e. Ultimate disposal: After waste minimization and treatment, remaining waste streams require disposal. Nonhazardous wastes that cannot be treated further can be discharged as wastewater, emitted to the atmosphere, or placed on or in the ground.

With extreme caution, it may be permissible to dispose of limited quantities (at certain concentrations) of laboratory wastes to the sanitary sewer system or to evaporate volatile wastes in chemical ventilation hoods. Obtain written permission of local, state, and federal authorities to dispose of waste in this manner. With increasing regulatory constraints imposed by RCRA, the Clean Air Act, and Clean Water Act, these disposal options are becoming increasingly limited. Wastes disposed of in this manner may contact other substances in the sewer or ventilation systems and produce hazardous reactions.

Most hazardous wastes generated in laboratories must be sent off site for further treatment and disposal. Exercise extreme care in selecting a reputable waste hauler and disposal firm. Many firms will assist laboratories in packaging and manifesting ‘‘lab packs,’’ 19- to 208-L (5- to 55-gal) drums containing several smaller containers of wastes.[1] Liability does not disappear when the waste leaves the generator’s facility. Ensure that the laboratory receives a copy of the completed manifest and certificate of treatment and/or disposal. If possible, visit the disposal facility in advance to observe how it will manage a waste.

Certain wastes require special handling. As mentioned previously, incinerate infectious waste or sterilize it before disposal. Before reuse, sterilize all nondisposable equipment that has come into contact with infectious waste.

Although most water and wastewater laboratories do not work with radiochemical wastes, some do. Handle radiochemical wastes with extreme care. Generalized disposal criteria for radioactive wastes have been developed by the National Council on Radiation Protection and Measurements.[3] Low-level radioactive waste must be in solid form for final disposal on land. Some firms will process liquid radioactive wastes into solids. Adding absorbent materials to liquid radioactive wastes is not permissible. Certain states allow low-level liquid radioactive waste to be discharged to a permitted publicly owned treatment works (POTW).

Other wastes that require special handling include polychlorinated biphenyls (PCBs), dioxin/furans and their precursors, petroleum products, and asbestos. Consult with federal and state officials before disposing of these wastes.

3. References

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Radiation. 10 CFR Part 20.

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Figures

Figure 1010:1. Normal (left) and skewed (right) distributions.

Figure 1020:1. Control charts for means.

Figure 1020:2. Duplicate analyses of a standard.

Figure 1020:3. Range chart for variable concentrations.

Figure 1020:4. Range chart for variable ranges.

Figure 1020:5. Means control chart with out-of-control data (upper half).

Figure 1030:1. Detection limit relationship.

Figure 1060:1. Approximate number of samples required in estimating a mean concentration. Source: Methods for the Examination of Waters and Associated Materials: General Principles of Sampling and Accuracy of Results. 1980. Her Majesty's Stationery Off., London, England.

TABLES

TABLE 1010:I. CRITICAL VALUES FOR 5% AND 1% TESTS OF DISCORDANCY FOR A SINGLE OUTLIER IN A NORMAL SAMPLE

Number of Measurements *n*	Critical Value 5%	Critical Value 1%
3	1.15	1.15
4	1.46	1.49

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Number of Measurements *n*	Critical Value 5%	1%
5	1.67	1.75
6	1.82	1.94
7	1.94	2.10
8	2.03	2.22
9	2.11	2.32
10	2.18	2.41
12	2.29	2.55
14	2.37	2.66
15	2.41	2.71
16	2.44	2.75
18	2.50	2.82
20	2.56	2.88
30	2.74	3.10
40	2.87	3.24
50	2.96	3.34
60	3.03	3.41
100	3.21	3.60
120	3.27	3.66

Source: BARNETT, V. T. LEWIS. 1984. Outliers in Statistical Data. John Wiley Sons, New York, N.Y.

TABLE 1020:I. FACTORS FOR COMPUTING LINES ON RANGE CONTROL CHARTS

Number of Observations *n*	Factor for Central Line (D_2)	Factor for Control Limits (D_4)
2	1.128	3.267
3	1.693	2.575
4	2.059	2.282
5	2.326	2.115
6	2.534	2.004

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Source: ROSENSTEIN, M. A. S. GOLDEN. 1964. Statistical Techniques for Quality Control of Environmental Radioassays. AQCS Rep. Stat-1. Public Health Serv., Winchester, Mass.

TABLE 1020:II. EXAMPLE DATA QUALIFIERS

Symbol	Explanation
B	Analyte found in reagent blank. Indicates possible reagent or background contamination.
E	Reported value exceeded calibration range.
J	Reported value is an estimate because concentration is less than reporting limit or because certain QC criteria were not met.
N	Organic constituents tentatively identified. Confirmation is needed.
PND	Precision not determined.
R	Sample results rejected because of gross deficiencies in QC or method performance. Re-sampling and/or re-analysis is necessary.
RND	Recovery not determined.
U	Compound was analyzed for, but not detected.

* Based on U.S. Environmental Protection Agency guidelines.[1]

TABLE 1020:III. AUDIT OF A SOIL ANALYSIS PROCEDURE

	Procedure	Comment	Remarks
1.a	Sample entered into logbook	yes	lab number assigned
2.a	Sample weighed	yes	dry weight
3.a	Drying procedure followed	no	maintenance of oven not done
4a.	Balance calibrated	yes	once per year
b.	Cleaned and zero adjusted	yes	weekly
5.a	Sample ground	yes	to pass 50 mesh
6.a	Ball mill cleaned	yes	should be after each sample

.

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Procedure	Comment	Remarks
.		
.		

TABLE 1030:I. CONDUCTIVITY FACTORS OF IONS COMMONLY FOUND IN WATER

Ion	Conductivity (25°C) *μmhos/cm*	
	Per me/L	Per mg/L
Bicarbonate	43.6	0.715
Calcium	52.0	2.60
Carbonate	84.6	2.82
Chloride	75.9	2.14
Magnesium	46.6	3.82
Nitrate	71.0	1.15
Potassium	72.0	1.84
Sodium	48.9	2.13
Sulfate	73.9	1.54

TABLE 1040:I. PRECISION AND BIAS FOR A SINGLE CONCENTRATIONIN A SINGLE MATRIX

Result *mg/L*	Difference (–1.30)	Squared Difference
1.23	–0.07	0.0049
1.21	–0.09	0.0081
1.30	0.0	0.0000
1.59	0.29	0.0841
1.57	0.27	0.0729
1.21	–0.09	0.0081
1.53	0.23	0.0529
1.25	–0.05	0.0025
Sum	0.49	0.2335

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Result *mg/L*	Difference (–1.30)	Squared Difference

TABLE 1040:II. VARIATIONS IN FACTORS FOR METHOD RUGGEDNESS DETERMINATION

Factor	Nominal	Variation
Mixing time	10 min	12 min
Portion size	5 g	10 g
Acid concentration	1*M*	1.1*M*
Heat to	100°C	95°C
Hold heat for	5 min	10 min
Stirring	yes	no
pH adjust	6.0	6.5

TABLE 1040:III. FACTOR MATRIX FOR METHOD RUGGEDNESS DETERMINATION

	Combinations							
Factor value	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
A or a	A	A	A	A	a	a	a	a
B or b	B	B	b	b	B	B	b	b
C or c	C	c	C	c	C	c	C	c
D or d	D	D	d	d	d	d	D	D
E or e	E	e	E	e	e	E	e	E
F or f	F	f	f	F	F	f	f	F
G or g	G	g	g	G	g	G	G	g
Result	s	t	u	v	w	x	y	z

Source: YOUDEN, W. J. E. H. STEINER. 1975. Statistical Manual of AOAC. Assoc. Official Analytical Chemists, Washington, D.C.

TABLE 1040:IV. SAMPLE COLLABORATIVE TEST RESULTS

	Deviation

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TABLE 1040:IV. SAMPLE COLLABORATIVE TEST RESULTS

Laboratory	Result *mg/L*	Experimental *x* ± *s*	Deviation From Known	Deviation From Grand Average
1	32.7			
	35.2	34.7 ± 1.8	–2.0	–1.7
	36.3			
2	32.6			
	33.7	33.3 ± 0.6	–0.6	–0.3
	33.6			
3	30.6			
	30.6	31.2 ± 1.0	–1.5	–1.8
	32.4			
4	32.6			
	32.5	33.0 ± 0.8	–0.3	–0
	33.9			
5	32.4			
	33.4	32.6 ± 0.8	–0.1	–0.4
	32.9			
$(\sum x)/n$ = 33			$\sum$ = 1.3	$\sum$ = –0.2
s = 1.5				

TABLE 1040:V. METHOD PRECISION AND BIAS

Known Amount *mg/L*	Amount Found *mg/L*	CV (% Standard Deviation)	Bias %
4.3	4.8	12.5	11.5
11.6	12.2	10.2	5.6
23.4	23.8	5.4	1.9
32.7	33.0	4.5	0.9

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TABLE 1050:I. CONVERSION FACTORS* (Milligrams per Liter—Milliequivalents per Liter)

Ion (Cation)	me/L = mg/L×	mg/L = me/L×	Ion (Anion)	me/L = mg/L×	mg/L = me/L×
Al^{3+}	0.111 2	8.994	BO_2^-	0.023 36	42.81
B^{3+}	0.277 5	3.604	Br^-	0.012 52	79.90
Ba^{2+}	0.014 56	68.66	Cl^-	0.028 21	35.45
Ca^{2+}	0.049 90	20.04	CO_3^{2-}	0.033 33	30.00
Cr^{3+}	0.057 70	17.33	CrO_4^{2-}	0.017 24	58.00
			F^-	0.052 64	19.00
Cu^{2+}	0.031 47	31.77	HCO_3^-	0.016 39	61.02
Fe^{2+}	0.035 81	27.92	HPO_4^{2-}	0.020 84	47.99
Fe^{3+}	0.053 72	18.62	$H_2PO_4^-$	0.010 31	96.99
H^+	0.992 1	1.008	HS^-	0.030 24	33.07
K^+	0.025 58	39.10	HSO_3^-	0.012 33	81.07
			HSO_4^-	0.010 30	97.07
Li^+	0.144 1	6.941	I^-	0.007 880	126.9
Mg^{2+}	0.082 29	12.15	NO_2^-	0.021 74	46.01
Mn^{2+}	0.036 40	27.47	NO_3^-	0.016 13	62.00
Mn^{4+}	0.072 81	13.73	OH^-	0.058 80	17.01
Na^+	0.043 50	22.99	PO_4^{3-}	0.031 59	31.66
NH_4^+	0.055 44	18.04	S^{2-}	0.062 37	16.03
Pb^{2+}	0.009 653	103.6	SiO_3^{2-}	0.026 29	38.04
Sr^{2+}	0.022 83	43.81	SO_3^{2-}	0.024 98	40.03
Zn^{2+}	0.030 59	32.70	SO_4^{2-}	0.020 82	48.03

* Factors are based on ion charge and not on redox reactions that may be possible for certain of these ions. Cations and anions are listed separately in alphabetical order.

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TABLE 1060:I. SUMMARY OF SPECIAL SAMPLING AND HANDLING REQUIREMENTS*

Determination	Container†	Minimum Sample Size *mL*	Sample Type‡	
Acidity	P, G(B)	100	g	Refrigerate
Alkalinity	P, G	200	g	Refrigerate
BOD	P, G	1000	g, c	Refrigerate
Boron	P (PTFE) or quartz	1000	g, c	HNO_3 to pH <
Bromide	P, G	100	g, c	None required
Carbon, organic, total	G (B)	100	g, c	Analyze imme H_3PO_4, or H_2S
Carbon dioxide	P, G	100	g	Analyze imme
COD	P, G	100	g, c	Analyze as so refrigerate
Chloride	P, G	50	g, c	None required
Chlorine, total, residual	P, G	500	g	Analyze imme
Chlorine dioxide	P, G	500	g	Analyze imme
Chlorophyll	P, G	500	g	Unfiltered, dar Filtered, dark, (Do not store i
Color	P, G	500	g, c	Refrigerate
Specific conductance	P, G	500	g, c	Refrigerate
Cyanide				
Total	P, G	1000	g, c	Add NaOH to
Amenable to chlorination	P, G	1000	g, c	Add 0.6 g asc refrigerate
Fluoride	P	100	g, c	None required
Hardness	P, G	100	g, c	Add HNO_3 or
Iodine	P, G	500	g	Analyze imme

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Determination	Container†	Minimum Sample Size *mL*	Sample Type‡	
Metals, general	P(A), G(A)	1000	g, c	For dissolved pH <2
Chromium VI	P(A), G(A)	1000	g	Refrigerate
Copper by colorimetry*				
Mercury	P(A), G(A)	1000	g, c	Add HNO_3 to
Nitrogen				
Ammonia	P, G	500	g, c	Analyze as so refrigerate
Nitrate	P, G	100	g, c	Analyze as so
Nitrate + nitrite	P, G	200	g, c	Add H_2SO_4 to
Nitrite	P, G	100	g, c	Analyze as so
Organic, Kjeldahl*	P, G	500	g, c	Refrigerate, ac
Odor	G	500	g	Analyze as so
Oil and grease	G, wide-mouth calibrated	1000	g	Add HCl or H_2
Organic compounds				
MBAs	P, G	250	g, c	Refrigerate
Pesticides*	G(S), PTFE-lined cap	1000	g, c	Refrigerate, ac chlorine prese
Phenols	P, G, PTFE-lined cap	500	g, c	Refrigerate, ac
Purgeables* by purge and trap	G, PTFE-lined cap	2 × 40	g	Refrigerate; ac acid/L if residu
Base/neutrals acids	G(S) amber	1000	g, c	Refrigerate
Oxygen, dissolved	G, BOD bottle	300		
Electrode				Analyze imme
Winkler				Titration may b
Ozone	G	1000	g	Analyze imme

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Determination	Container†	Minimum Sample Size *mL*	Sample Type‡	
pH	P, G	50	g	Analyze imme
Phosphate	G(A)	100	g	For dissolved
Phosphorus, total	P, G	100	g, c	Add H_2SO_4 to
Salinity	G, wax seal	240	g	Analyze imme
Silica	P (PTFE) or quartz	200	g, c	Refrigerate, d
Sludge digester gas	G, gas bottle	—	g	—
Solids[9]	P, G	200	g, c	Refrigerate
Sulfate	P, G	100	g, c	Refrigerate
Sulfide	P, G	100	g, c	Refrigerate; a NaOH to pH >
Temperature	P, G	—	g	Analyze imme
Turbidity	P, G	100	g, c	Analyze same refrigerate

* For determinations not listed, use glass or plastic containers; preferably refrigerate during storage and analyze as soon as possible.
† P = plastic (polyethylene or equivalent); G = glass; G(A) or P(A) = rinsed with 1 + 1 HNO_3; G(B) = glass, borosilicate; G(S) = glass, rinsed with organic solvents or baked.
‡ g = grab; c = composite.
§ Refrigerate = storage at 4°C ± 2°C; in the dark; analyze immediately = analyze usually within 15 min of sample collection.
‖ See citation[10] for possible differences regarding container and preservation requirements. N.S. = not stated in cited reference; stat = no storage allowed; analyze immediately.
If sample is chlorinated, see text for pretreatment.

TABLE 1080:I. WATER PURIFICATION PROCESSES

	Major Classes of Contaminants*					
Process	Dissolved Ionized Solids	Dissolved Ionized Gases	Dissolved Organics	Particulates	Bacteria	P Er
Distillation	G–E†	P	G	E	E	

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	Major Classes of Contaminants*					
Process	Dissolved Ionized Solids	Dissolved Ionized Gases	Dissolved Organics	Particulates	Bacteria	P Er
Deionization	E	E	P	P	P	
Reverse osmosis	G‡	P	G	E	E	
Carbon adsorption	P	P§	G–E ‖	P	P	
Filtration	P	P	P	E	E	
Ultrafiltration	P	P	G#	E	E	
Ultraviolet oxidation	P	P	G–E**	P	G††	

Permission to use this table from C3-A2, Vol. 11, No. 13, Aug. 1991, ‘‘Preparation and Testing of Reagent Water in the Clinical Laboratory - Second Edition’’ has been granted by the National Committee for Clinical Laboratory Standards. The complete current standard may be obtained from National Committee for Clinical Laboratory Standards, 771 E. Lancaster Ave., Villanova, PA 19085.

* E = Excellent (capable of complete or near total removal), G = Good (capable of removing large percentages), P = Poor (little or no removal).

† Resistivity of water purified by distillation is an order of magnitude less than water produced by deionization, due mainly to the presence of CO_2 and sometimes H_2S, NH_3, and other ionized gases if present in the feedwater.‡ Resistivity of dissolved ionized solids in the product water depends on original feedwater resistivity.

§ Activated carbon removes chlorine by adsorption.

‖ When used in combination with other purification processes, special grades of activated carbon and other synthetic adsorbents exhibit excellent capabilities for removing organic contaminants. Their use, however, is targeted toward specific compounds and applications.

Ultrafilters have demonstrated usefulness in reducing specific feedwater organic contaminants based on the rated molecular weight cut-off of the membrane.

** 185 nm ultraviolet oxidation (batch process systems) is effective in removing trace organic contaminants when used as post-treatment. Feedwater makeup plays a critical role in the performance of these batch processors.

†† 254 nm UV sterilizers, while not physically removing bacteria, may have bactericidal or bacteriostatic capabilities limited by intensity, contact time, and flow rate.

TABLE 1080:II. REAGENT WATER SPECIFICATIONS*

Quality Parameter	High	Medium	Low
Resistivity, megohm-cm at 25°C	>10	>1	0.1

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Quality Parameter	High	Medium	Low
Conductivity, μmho/cm at 25°C	<0.1	<1	10
SiO_2, mg/L	<0.05	<0.1	<1

TABLE 1090:I. PERMISSIBLE EXPOSURE LIMITS, THRESHOLD LIMIT VALUES, SHORT-TERM EXPOSURE LIMITS, AND/OR CEILINGS FOR SOME INORGANIC CHEMICALS SPECIFIED IN *STANDARD METHODS*

Compound	Chemical Abstract No. CAS No.	PEL/TLV STEL mg/m^3
Chromic acid and chromates†‡ (as CrO_3)	7440-47-3	0.1/0.05
Chromium, soluble chromic, chromous salts (as Cr)	7440-47-3	0.5/0.5
Chromium metal and insoluble salts	7440-47-3	1/0.5
Hydrogen chloride	7647-01-0	7.5(C)/7.5(C)
Hydrogen peroxide	7722-84-1	1.4/1.4
Lead‡	7439-92-1	–/0.15
Mercury†§	7439-97-6	0.1/0.05
Nitric acid	7697-37-2	5/5.2, 10(S)
Phosphoric acid	7664-38-2	1/1, 3(S)
Potassium hydroxide	1310-58-3	–/2(C)
Silver (metal and soluble compounds, as Ag)	7440-22-4	0.01/0.1 meta
Sodium azide	26628-22-8	–/0.29(C)
Sodium hydroxide	1310-73-2	2(C)/2(C)
Sulfuric acid	7664-93-9	1/1, 3(S)

* Short-term exposure limit. See 29 CFR 1910.1028.
† (Suspect) carcinogen.
‡ Substance has a Biological Exposure Index (BEI).
§ Skin hazard.

TABLE 1090:II. PERMISSIBLE EXPOSURE LIMITS, THRESHOLD LIMIT VALUES, SHORT-TERM EXPOSURE LIMITS, AND/OR CEILINGS FOR ORGANIC SOLVENTS SPECIFIED IN *STANDARD METHODS*

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EXPOSURE LIMITS, AND/OR CEILINGS FOR ORGANIC SOLVENTS SPECIFIED IN *STANDARD METHODS*

Compound	Chemical Abstract No. CAS No.	PEL/TLV STEL(S)* c ppm (v/v
Acetic acid	64-19-7	10/10, 15(S)
Acetone	67-64-1	1000/750, 1000(S)
Acetonitrile	75-05-8	40/40, 60(S)
Benzene†‡	71-43-2	10, 25(C), 50 peak 10 mi
n-Butyl alcohol§	71-36-3	100/50(C)
tert-Butyl alcohol	75-65-0	100/100, 150(S)
Carbon disulfide‡	75-15-0	20, 30(C), 100 peak 30 m
Carbon tetrachloride†§	56-23-5	10, 25, 200 peak 5 min/4
Chloroform†	67-66-3	50(C)/10
Cyclohexanone§	108-94-1	50/50
Dioxane§ (diethylene dioxide)	123-91-1	100/25
Ethyl acetate	141-78-6	400/400
Ethyl alcohol	64-17-5	1000/1000
Ethyl ether (diethyl ether)	60-29-7	400/400, 500(S)
Ethylene glycol	107-21-1	–/50(C)
n-Hexane‡	110-54-3	100/50
Isoamyl alcohol (primary and secondary)	123-51-3	100/100, 125(S)
Isobutyl alcohol	78-83-1	100/50
Isopropyl alcohol	67-63-0	400/400, 500(S)
Isopropyl ether	108-20-3	500/250, 310(S)
Methyl alcohol§	67-56-1	200/200, 250(S)
2-Methoxyethanol§ (methyl cellosolve)	109-86-4	25/5
Methylene chloride†	75-09-2	500, 1000(C), 2000 peak
Pentane	109-66-0	1000/600, 750(S)
Perchloroethylene†‡ (tetrachloroethylene)	127-18-4	100, 200(C), 300 peak 5 200(S)
n-Propyl alcohol§	71-23-8	200/200, 250(S)
Pyridine	110-86-1	5/5
Toluene‡§	108-88-3	200, 300(C), 500 peak 1(

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Compound	Chemical Abstract No. CAS No.	PEL/TLV STEL(S)* c ppm (v/v
Xylenes‡ (*o*-, *m*-, *p*-isomers)	1330-20-7 (95-47-6, 108-38-3, 106-42-3)	100/100, 150(S)

* Short-term exposure limit. See 29 CFR 1910.1028.
† (Suspect) carcinogen.
‡ Substance has a Biological Exposure Index (BEI).
§ Skin hazard.

TABLE 1090:III. PERMISSIBLE EXPOSURE LIMITS, THRESHOLD LIMIT VALUES, SHORT-TERM EXPOSURE LIMITS, AND/OR CEILINGS FOR SOME OF THE REAGENTS SPECIFIED IN *STANDARD METHODS*

Compound	Chemical Abstract No. CAS No.	PEL/TLV STEL(S)* or (ppm (v/v)
2-Aminoethanol (ethanolamine)	141-43-5	3/3, 6(S)
Benzidine†‡	92-87-5	Confirmed human ca
Benzyl chloride	100-44-7	1/1
Chlorobenzene	108-90-7	75/10
Diethanolamine	111-42-2	–/3
Naphthalene	91-20-3	10/10, 15(S)
Oxalic acid	144-62-7	1/1 mg/m^3
Phenol‡	108-95-2	5/5
2-Chloro-6-(trichloromethyl) pyridine (nitrapyrin)	1929-82-4	
Total dust		15/10 mg/m^3
Respirable fraction		5/– mg/m^3

* Short-term exposure limit. See 29 CFR 1910.1028.
† (Suspect) carcinogen.
‡ Skin hazard.

TABLE 1090:IV. GLOVE SELECTION FOR ORGANIC CHEMICAL HANDLING

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TABLE 1090:IV. GLOVE SELECTION FOR ORGANIC CHEMICAL HANDLING

Compound	Chemical Abstract No. CAS No.	Chemical Class	Butyl Rubber	Neoprene
Ethers:		241		
Ethyl ether (diethyl ether)	60-29-7	241		
Isopropyl ether	108-20-3	241		
2-Methoxyethanol† (methyl cellosolve)	109-86-4	245	X	
Halogen compounds:		261		
Carbon tetrachloride*	56-23-5	261		
Chloroform*	67-66-3	261		
Methylene chloride	75-09-2	261		
Perchloroethylene* (tetrachloroethylene)	127-18-4	261		
Hydrocarbons:		291		
n-Hexane	110-54-3	291		
Pentane	109-66-0	291		
Benzene*	71-43-2	292		
Toluene	108-88-3	292		
Xylenes (*o*-, *m*-, *p*-isomers)	1330-20-7	292		
Hydroxyl compounds:		311		
n-Butyl alcohol	71-36-3	311	X	X
Ethyl alcohol	64-17-5	311	X	
Methyl alcohol	67-56-1	311	X	
n-Propyl alcohol	71-23-8	311		
Isoamyl alcohol	123-51-3	311		
Isobutyl alcohol	78-83-1	311	X	
Isopropyl alcohol	67-63-0	312		X
tert-Butyl alcohol (2,2-methylpropanol)	75-65-0	313	X	
Ethylene glycol	107-21-1	314	X	X
Ketones:		391		
Acetone	67-64-1	391	X	

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Compound	Chemical Abstract No. CAS No.	Chemical Class	Butyl Rubber	Neoprene
Cyclohexanone	108-94-1	391	X	
Heterocyclic compounds:		271		
Dioxane† (diethylene dioxide)	123-91-1	278	X	
Pyridine	110-86-1	271	X	
Miscellaneous organic compounds:				
Acetic acid	75-07-0	102	X	X
Ethyl acetate	141-78-6	222	X	
Acetonitrile	75-05-8	431	X	
Carbon disulfide	75-15-0	502		

* (Suspect) carcinogen.
† Skin hazard.

TABLE 1090:V. GLOVE SELECTION FOR INORGANIC CHEMICAL HANDLING

Compound	Chemical Abstract No. (CAS No.)	Chemical Class	Suit: Butyl Rubber	Suit: Natural Rubber	Suit: N
Inorganic acids:		370			
Chromic acid,* (Cr^{+6})	7440-47-3	370	X		
Hydrochloric acid, 30–70% solutions	10035-10-6	370	X	X	
Hydrochloric acid, <30% solutions	10035-10-6	370	X	X	
Nitric acid, 30–70% solutions	7697-37-2	370	X		
Nitric acid, <30% solutions	7697-37-2	370	X	X	
Phosphoric acid, >70% solutions	7664-38-2	370		X	
Phosphoric acid, 30–70% solutions	7664-38-2	370		X	
Sulfuric acid, >70% solutions	7664-93-9	370	X		
Sulfuric acid, 30–70% solutions	7664-93-9	370	X	X	
Sulfuric acid, <30% solutions	7664-93-9	370	X	X	
Inorganic bases:		380			

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Compound	Chemical Abstract No. (CAS No.)	Chemical Class	Suit: Butyl Rubber	Suit: Natural Rubber	Suit: N
Ammonium hydroxide, 30–70% solutions	7664-41-7	380	X		
Ammonium hydroxide, <30% solutions	7664-41-7	380	X		
Potassium hydroxide, 30–70% solutions	1310-58-3	380	X	X	
Sodium hydroxide, >70% solutions	1310-73-2	380			
Sodium hydroxide, 30–70% solutions	1310-73-2	380	X	X	
Inorganic salt solutions:		340			
Dichromate solutions, <30%,* (Cr^{+6})	7440-47-3	340			
Inorganic miscellaneous:					
Hydrogen peroxide, 30–70% solutions	7722-39-3	300		X	
Mercury†	7439-97-6	560			

* (Suspect) carcinogen.
† Skin hazard.

TABLE 1090:VI. PROCEDURES INVOLVING POTENTIAL EXPOSURE TO IONIZING RADIATION

Standard Methods Section	Radionuclide	Type of Radiation
Part 6000 methods: GC with electron capture detectors	^{63}Ni or ^{3}H	Low-energy beta (^{63}Ni, 17 ke
7110 Gross Alpha and Gross Beta Radioactivity	Alpha: Uranium, ^{230}Th, ^{239}Pu, ^{241}Am Beta: ^{137}Cs, ^{90}Sr	Alpha; beta and gamma; or b
7500-Cs Radioactive Cesium	^{134}Cs, ^{137}Cs	Beta, gamma
7500-I Radioactive Iodine	^{131}I	Beta, gamma
7500-Ra Radium	^{226}Ra	Alpha, beta, gamma
7500-Sr A Total Radioactive Strontium and Strontium-90	^{89}Sr, ^{90}Sr	Beta-emitters
7500-^{3}H Tritium	^{3}H	Low-energy beta (6 keV avg)

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Standard Methods Section	Radionuclide	Type of Radiation
7500-U Uranium	U series	Alpha, beta, gamma

Part 2000 PHYSICAL & AGGREGATE PROPERTIES

2010 INTRODUCTION

This part deals primarily with measurement of the physical properties of a sample, as distinguished from the concentrations of chemical or biological components. Many of the determinations included here, such as color, electrical conductivity, and turbidity, fit this category unequivocally. However, physical properties cannot be divorced entirely from chemical composition, and some of the techniques of this part measure aggregate properties resulting from the presence of a number of constituents. Others, for example, calcium carbonate saturation, are related to, or depend on, chemical tests. Also included here are tests for appearance, odor, and taste, which have been classified traditionally among physical properties, although the point could be argued. Finally, Section 2710, Tests on Sludges, includes certain biochemical tests. However, for convenience they are grouped with the other tests used for sludge.

With these minor exceptions, the contents of this part have been kept reasonably faithful to its name. Most of the methods included are either inherently or at least traditionally physical, as distinguished from the explicitly chemical, radiological, biological, or bacteriological methods of other parts.

2020 QUALITY ASSURANCE/QUALITY CONTROL

Part 2000 contains a variety of analytical methods, many of which are not amenable to standard quality-control techniques. General information on quality control is provided in Part 1000 and specific quality-control techniques are outlined in the individual methods. The following general guidelines may be applied to many of the methods in this part:

Evaluate analyst performance for each method. Determine competence by analyses of samples containing known concentrations.

Calibrate instruments and ensure that instrument measurements do not drift.

Assess the precision of analytical procedures by analyzing at least 10% of samples in duplicate. Analyze a minimum of one duplicate with each set of samples.

Determine bias of an analytical procedure in each sample batch by analysis of blanks, known additions with a frequency of at least 5% of samples, and, if possible, an externally provided

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standard.

2110 APPEARANCE*#(6)

To record the general physical appearance of a sample, use any terms that briefly describe its visible characteristics. These terms may state the presence of color, turbidity, suspended solids, organisms and their immature forms, sediment, floating material, and similar particulate matter detectable by the unaided eye. Use numerical values when they are available, as for color, turbidity, and suspended solids.

2120 COLOR*#(7)

2120 A. Introduction

Color in water may result from the presence of natural metallic ions (iron and manganese), humus and peat materials, plankton, weeds, and industrial wastes. Color is removed to make a water suitable for general and industrial applications. Colored industrial wastewaters may require color removal before discharge into watercourses.

1. Definitions

The term ‘‘color’’ is used here to mean true color, that is, the color of water from which turbidity has been removed. The term ‘‘apparent color’’ includes not only color due to substances in solution, but also that due to suspended matter. Apparent color is determined on the original sample without filtration or centrifugation. In some highly colored industrial wastewaters color is contributed principally by colloidal or suspended material. In such cases both true color and apparent color should be determined.

2. Pretreatment for Turbidity Removal

To determine color by currently accepted methods, turbidity must be removed before analysis. Methods for removing turbidity without removing color vary. Filtration yields results that are reproducible from day to day and among laboratories. However, some filtration procedures also may remove some true color. Centrifugation avoids interaction of color with filter materials, but results vary with the sample nature and size and speed of the centrifuge. When sample dilution is necessary, whether it precedes or follows turbidity removal, it can alter the measured color.

Acceptable pretreatment procedures are included with each method. State the pretreatment method when reporting results.

3. Selection of Method

The visual comparison method is applicable to nearly all samples of potable water. Pollution

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by certain industrial wastes may produce unusual colors that cannot be matched. In this case use an instrumental method. A modification of the tristimulus and the spectrophotometric methods allows calculation of a single color value representing uniform chromaticity differences even when the sample exhibits color significantly different from that of platinum cobalt standards. For comparison of color values among laboratories, calibrate the visual method by the instrumental procedures.

4. Bibliography

OPTICAL SOCIETY OF AMERICA. 1943. Committee Report. The concept of color. *J. Opt. Soc. Amer.* 33:544.

JONES, H. et al. 1952. The Science of Color. Thomas Y. Crowell Co., New York, N.Y.

2120 B. Visual Comparison Method

1. General Discussion

a. Principle: Color is determined by visual comparison of the sample with known concentrations of colored solutions. Comparison also may be made with special, properly calibrated glass color disks. The platinum-cobalt method of measuring color is the standard method, the unit of color being that produced by 1 mg platinum/L in the form of the chloroplatinate ion. The ratio of cobalt to platinum may be varied to match the hue in special cases; the proportion given below is usually satisfactory to match the color of natural waters.

b. Application: The platinum-cobalt method is useful for measuring color of potable water and of water in which color is due to naturally occurring materials. It is not applicable to most highly colored industrial wastewaters.

c. Interference: Even a slight turbidity causes the apparent color to be noticeably higher than the true color; therefore remove turbidity before approximating true color by differential reading with different color filters[1] or by differential scattering measurements.[2] Neither technique, however, has reached the status of a standard method. Remove turbidity by centrifugation or by the filtration procedure described under Method C. Centrifuge for 1 h unless it has been demonstrated that centrifugation under other conditions accomplishes satisfactory turbidity removal.

The color value of water is extremely pH-dependent and invariably increases as the pH of the water is raised. When reporting a color value, specify the pH at which color is determined. For research purposes or when color values are to be compared among laboratories, determine the color response of a given water over a wide range of pH values.[3]

d. Field method: Because the platinum-cobalt standard method is not convenient for field use, compare water color with that of glass disks held at the end of metallic tubes containing glass comparator tubes filled with sample and colorless distilled water. Match sample color with the color of the tube of clear water plus the calibrated colored glass when viewed by looking

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toward a white surface. Calibrate each disk to correspond with the colors on the platinum-cobalt scale. The glass disks give results in substantial agreement with those obtained by the platinum-cobalt method and their use is recognized as a standard field procedure.

e. Nonstandard laboratory methods: Using glass disks or liquids other than water as standards for laboratory work is permissible only if these have been individually calibrated against platinum-cobalt standards. Waters of highly unusual color, such as those that may occur by mixture with certain industrial wastes, may have hues so far removed from those of the platinum-cobalt standards that comparison by the standard method is difficult or impossible. For such waters, use the methods in Section 2120C and Section 2120D. However, results so obtained are not directly comparable to those obtained with platinum-cobalt standards.

f. Sampling: Collect representative samples in clean glassware. Make the color determination within a reasonable period because biological or physical changes occurring in storage may affect color. With naturally colored waters these changes invariably lead to poor results.

2. Apparatus

a. Nessler tubes, matched, 50-mL, tall form.

b. pH meter, for determining sample pH (see Section 4500-H).

3. Preparation of Standards

a. If a reliable supply of potassium chloroplatinate cannot be purchased, use chloroplatinic acid prepared from metallic platinum. Do not use commercial chloroplatinic acid because it is very hygroscopic and may vary in platinum content. Potassium chloroplatinate is not hygroscopic.

b. Dissolve 1.246 g potassium chloroplatinate, K_2PtCl_6 (equivalent to 500 mg metallic Pt) and 1.00 g crystallized cobaltous chloride, $CoCl_2 \cdot 6H_2O$ (equivalent to about 250 mg metallic Co) in distilled water with 100 mL conc HCl and dilute to 1000 mL with distilled water. This stock standard has a color of 500 units.

c. If K_2PtCl_6 is not available, dissolve 500 mg pure metallic Pt in aqua regia with the aid of heat; remove HNO_3 by repeated evaporation with fresh portions of conc HCl. Dissolve this product, together with 1.00 g crystallized $CoCl_2 \cdot 6H_2O$, as directed above.

d. Prepare standards having colors of 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 60, and 70 by diluting 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 6.0, and 7.0 mL stock color standard with distilled water to 50 mL in nessler tubes. Protect these standards against evaporation and contamination when not in use.

4. Procedure

a. Estimation of intact sample: Observe sample color by filling a matched nessler tube to the 50-mL mark with sample and comparing it with standards. Look vertically downward through tubes toward a white or specular surface placed at such an angle that light is reflected upward

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through the columns of liquid. If turbidity is present and has not been removed, report as ‘‘apparent color.’’ If the color exceeds 70 units, dilute sample with distilled water in known proportions until the color is within the range of the standards.

b. Measure pH of each sample.

5. Calculation

a. Calculate color units by the following equation:

$$\text{Color units} = \frac{A \times 50}{B}$$

where:

A = estimated color of a diluted sample and
B = mL sample taken for dilution.

b. Report color results in whole numbers and record as follows:

Color Units	Record to Nearest
1–50	1
51–100	5
101–250	10
251–500	20

c. Report sample pH.

6. References

1. KNIGHT, A.G. 1951. The photometric estimation of color in turbid waters. *J. Inst. Water Eng.* 5:623.
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3. BLACK, A.P. & R.F. CHRISTMAN. 1963. Characteristics of colored surface waters. *J. Amer. Water Works Assoc.* 55:753.

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RUDOLFS, W. & W.D. HANLON. 1951. Color in industrial wastes. *Sewage Ind. Wastes* 23:1125.

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CHRISTMAN, R.F. & M. GHASSEMI. 1966. Chemical nature of organic color in water. *J. Amer. Water Works Assoc.* 58:723.

GHASSEMI, M. & R.F. Christman. 1968. Properties of the yellow organic acids of natural waters. *Limnol. Oceanogr.* 13:583.

2120 C. Spectrophotometric Method

1. General Discussion

a. Principle: The color of a filtered sample is expressed in terms that describe the sensation realized when viewing the sample. The hue (red, green, yellow, etc.) is designated by the term ‘‘dominant wavelength,’’ the degree of brightness by ‘‘luminance,’’ and the saturation (pale, pastel, etc.) by ‘‘purity.’’ These values are best determined from the light transmission characteristics of the filtered sample by means of a spectrophotometer.

b. Application: This method is applicable to potable and surface waters and to wastewaters, both domestic and industrial.

c. Interference: Turbidity interferes. Remove by the filtration method described below.

2. Apparatus

a. Spectrophotometer, having 10-mm absorption cells, a narrow (10-nm or less) spectral band, and an effective operating range from 400 to 700 nm.

b. Filtration system, consisting of the following (see Figure 2120:1):

1) *Filtration flasks,* 250-mL, with side tubes.

2) *Walter crucible holder.*

3) *Glass Gooch filtering crucible with fritted disk,* pore size 40 to 60 μm.

4) *Calcined filter aid.**#(8)

5) *Vacuum system.*

3. Procedure

a. Preparation of sample: Bring two 50-mL samples to room temperature. Use one sample at the original pH; adjust pH of the other to 7.6 by using sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) of such concentrations that the resulting volume change does not exceed 3%. A standard pH is necessary because of the variation of color with pH. Remove excessive quantities of suspended materials by centrifuging. Treat each sample separately, as follows:

Thoroughly mix 0.1 g filter aid in a 10-mL portion of centrifuged sample and filter to form a

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precoat in the filter crucible. Direct filtrate to waste flask as indicated in Figure 2120:1. Mix 40 mg filter aid in a 35-mL portion of centrifuged sample. With vacuum still on, filter through the precoat and pass filtrate to waste flask until clear; then direct clear-filtrate flow to clean flask by means of the three-way stopcock and collect 25 mL for the transmittance determination.

b. Determination of light transmission characteristics: Thoroughly clean 1-cm absorption cells with detergent and rinse with distilled water. Rinse twice with filtered sample, clean external surfaces with lens paper, and fill cell with filtered sample.

Determine transmittance values (in percent) at each visible wavelength value presented in Table 2120:I, using the 10 ordinates marked with an asterisk for fairly accurate work and all 30 ordinates for increased accuracy. Set instrument to read 100% transmittance on the distilled water blank and make all determinations with a narrow spectral band.

4. Calculation

a. Tabulate transmittance values corresponding to wavelengths shown in Columns *X*, *Y*, and *Z* in Table 2120:I. Total each transmittance column and multiply totals by the appropriate factors (for 10 or 30 ordinates) shown at the bottom of the table, to obtain tristimulus values *X*, *Y*, and *Z*. The tristimulus value *Y* is *percent luminance.*

b. Calculate the trichromatic coefficients *x* and *y* from the tristimulus values *X*, *Y*, and *Z* by the following equations:

$$x = \frac{X}{X + Y + Z}$$

$$y = \frac{Y}{X + Y + Z}$$

Locate point (*x*, *y*) on one of the chromaticity diagrams in Figure 2120:2 and determine the dominant wavelength (in nanometers) and the purity (in percent) directly from the diagram.

Determine hue from the dominant-wavelength value, according to the ranges in Table 2120:II.

5. Expression of Results

Express color characteristics (at pH 7.6 and at the original pH) in terms of *dominant wavelength* (nanometers, to the nearest unit), *hue* (e.g., blue, blue-green, etc.), *luminance* (percent, to the nearest tenth), and *purity* (percent, to the nearest unit). Report type of instrument (i.e., spectrophotometer), number of selected ordinates (10 or 30), and the spectral band width (nanometers) used.

6. Bibliography

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2120 D. Tristimulus Filter Method

1. General Discussion

a. Principle: Three special tristimulus light filters, combined with a specific light source and photoelectric cell in a filter photometer, may be used to obtain color data suitable for routine control purposes.

The percentage of tristimulus light transmitted by the solution is determined for each of the three filters. The transmittance values then are converted to trichromatic coefficients and color characteristic values.

b. Application: This method is applicable to potable and surface waters and to wastewaters, both domestic and industrial. Except for most exacting work, this method gives results very similar to the more accurate Method C.

c. Interference: Turbidity must be removed.

2. Apparatus

*a. Filter photometer.**#(9)

b. Filter photometer light source: Tungsten lamp at a color temperature of 3000°C.†#(10)

c. Filter photometer photoelectric cells, 1 cm.‡#(11)

d. Tristimulus filters.§#(12)

e. Filtration system: See Section 2120C.2*b* and Figure 2120:1.

3. Procedure

a. Preparation of sample: See Section 2120C.3*a*.

b. Determination of light transmission characteristics: Thoroughly clean (with detergent) and rinse 1-cm absorption cells with distilled water. Rinse each absorption cell twice with filtered sample, clean external surfaces with lens paper, and fill cell with filtered sample.

Place a distilled water blank in another cell and use it to set the instrument at 100% transmittance. Determine percentage of light transmission through sample for each of the three tristimulus light filters, with the filter photometer lamp intensity switch in a position equivalent to 4 V on the lamp.

4. Calculation

a. Determine luminance value directly as the percentage transmittance value obtained with the No. 2 tristimulus filter.

b. Calculate tristimulus values X, Y, and Z from the percentage transmittance (T_1, T_2, T_3) for filters No. 1, 2, 3, as follows:

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$$X = T_3 \times 0.06 + T_1 \times 0.25$$

$$Y = T_2 \times 0.316$$

$$Z = T_3 \times 0.374$$

Calculate and determine trichromatic coefficients *x* and *y*, dominant wavelength, hue, and purity as in Section 2120C.4*b* above.

5. Expression of Results

Express results as prescribed in Section 2120C.5.

2120 E. ADMI Tristimulus Filter Method

1. General Discussion

a. Principle: This method is an extension of Tristimulus Method 2120D. By this method a measure of the sample color, independent of hue, may be obtained. It is based on use of the Adams-Nickerson chromatic value formula[1] for calculating single number color difference values, i.e., uniform color differences. For example, if two colors, A and B, are judged visually to differ from colorless to the same degree, their ADMI color values will be the same. The modification was developed by members of the American Dye Manufacturers Institute (ADMI).[2]

b. Application: This method is applicable to colored waters and wastewaters having color characteristics significantly different from platinum-cobalt standards, as well as to waters and wastewaters similar in hue to the standards.

c. Interference: Turbidity must be removed.

2. Apparatus

*a. Filter photometer**#(13) equipped with CIE tristimulus filters (see Section 2120D.2*d*).

b. Filter photometer light source: Tungsten lamp at a color temperature of 3000°C (see Section 2120D.2*b*).

c. Absorption cells and appropriate cell holders: For color values less than 250 ADMI units, use cells with a 5.0-cm light path; for color values greater than 250, use cells with 1.0-cm light path.

d. Filtration system: See Section 2120C.2*b* and Figure 2120:1; or a centrifuge capable of achieving 1000 × *g*. (See Section 2120B.)

3. Procedure

a. Instrument calibration: Establish curves for each photometer; calibration data for one instrument cannot be applied to another one. Prepare a separate calibration curve for each absorption cell path length.

1) Prepare standards as described in Section 2120B.3. For a 5-cm cell length prepare

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standards having color values of 25, 50, 100, 200, and 250 by diluting 5.0, 10.0, 20.0, 40.0, and 50.0 mL stock color standard with distilled water to 100 mL in volumetric flasks. For the shorter pathlength, prepare appropriate standards with higher color values.

2) Determine light transmittance (see ¶ 3*c*, below) for each standard with each filter.

3) Using the calculations described in ¶ 3*d* below, calculate the tristimulus values (X_s, Y_s, Z_s) for each standard, determine the Munsell values, and calculate the intermediate value (*DE*).

4) Using the *DE* values for each standard, calculate a calibration factor F_n for each standard from the following equation:

$$F_n = \frac{(APHA)_n\,(b)}{(DE)_n}$$

where:

$(APHA)_n$ = APHA color value for standard *n*,
$(DE)_n$ = intermediate value calculated for standard *n*, and
b = cell light path, cm.

Placing $(DE)_n$ on the X axis and F_n on the Y axis, plot a curve for the standard solutions. Use calibration curve to derive the *F* value from *DE* values obtained with samples.

b. Sample preparation: Prepare two 100-mL sample portions (one at the original pH, one at pH 7.6) as described in Section 2120C.3*a*, or by centrifugation. (NOTE: Centrifugation is acceptable only if turbidity removal equivalent to filtration is achieved.)

c. Determination of light transmission characteristics: Thoroughly clean absorption cells with detergent and rinse with distilled water. Rinse each absorption cell twice with filtered sample. Clean external surfaces with lens paper and fill cell with sample. Determine sample light transmittance with the three filters to obtain the transmittance values: T_1 from Filter 1, T_2 from Filter 2, and T_3 from Filter 3. Standardize the instrument with each filter at 100% transmittance with distilled water.

d. Calculation of color values: Tristimulus values for samples are X_s, Y_s, and Z_s; for standards X_r, Y_r, and Z_r; and for distilled water X_c, Y_c, and Z_c. Munsell values for samples are V_{xs}, V_{ys}, and V_{zs}; for standards V_{xr}, V_{yr}, and V_{zr}; and for distilled water V_{xc}, Y_{yc}, and V_{zc}.

For each standard or sample calculate the tristimulus values from the following equations:

$$X = (T_3 \times 0.1899) + (T_1 \times 0.791)$$

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$Y = T_2$

$Z = T_3 \times 1.1835$

Tristimulus values for the distilled water blank used to standardize the instrument are always:

$X_c = 98.09$

$Y_c = 100.0$

$Z_c = 118.35$

Convert the six tristimulus values (X_s, Y_s, Z_s, X_c, Y_c, Z_c) to the corresponding Munsell values using published tables 2, 3, 4†#(14) or by the equation given by Bridgeman.[3]

Calculate the intermediate value of *DE* from the equation:

$$DE = \{(0.23\ \Delta V_y)^2 + [\Delta(V_x - V_y)]^2 + [0.4\ \Delta(V_y - V_z)]^2\}^{1/2}$$

where:

$$V_y = V_{ys} - V_{yc}$$

$$\Delta(V_x - V_y) = (V_{xs} - V_{ys}) - (V_{xc} - V_{yc})$$

$$\Delta(V_y - V_z) = (V_{ys} - V_{zs}) - (V_{yc} - V_{zc})$$

when the sample is compared to distilled water.

With the standard calibration curve, use the *DE* value to determine the calibration factor *F*.

Calculate the final ADMI color value as follows:

$$\text{ADMI value} = \frac{(F)\ (DE)}{b}$$

where:

b = absorption cell light path, cm.

Report ADMI color values at pH 7.6 and at the original pH.

4. Alternate Method

The ADMI color value also may be determined spectrophotometrically, using a spectrophotometer with a narrow (10-nm or less) spectral band and an effective operating range

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of 400 to 700 nm. This method is an extension of 2120C. Tristimulus values may be calculated from transmittance measurements, preferably by using the weighted ordinate method or by the selected ordinate method. The method has been described by Allen et al.,[2] who include work sheets and worked examples.

5. References

1. MCLAREN, K. 1970. The Adams-Nickerson colour-difference formula. *J. Soc. Dyers Colorists* 86:354.
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2130 TURBIDITY*#(15)

2130 A. Introduction

1. Sources and Significance

Clarity of water is important in producing products destined for human consumption and in many manufacturing operations. Beverage producers, food processors, and potable water treatment plants drawing from a surface water source commonly rely on fluid-particle separation processes such as sedimentation and filtration to increase clarity and insure an acceptable product. The clarity of a natural body of water is an important determinant of its condition and productivity.

Turbidity in water is caused by suspended and colloidal matter such as clay, silt, finely divided organic and inorganic matter, and plankton and other microscopic organisms. Turbidity is an expression of the optical property that causes light to be scattered and absorbed rather than transmitted with no change in direction or flux level through the sample. Correlation of turbidity with the weight or particle number concentration of suspended matter is difficult because the size, shape, and refractive index of the particles affect the light-scattering properties of the suspension. When present in significant concentrations, particles consisting of light-absorbing

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materials such as activated carbon cause a negative interference. In low concentrations these particles tend to have a positive influence because they contribute to turbidity. The presence of dissolved, color-causing substances that absorb light may cause a negative interference. Some commercial instruments may have the capability of either correcting for a slight color interference or optically blanking out the color effect.

2. Selection of Method

Historically, the standard method for determination of turbidity has been based on the Jackson candle turbidimeter; however, the lowest turbidity value that can be measured directly on this device is 25 Jackson Turbidity Units (JTU). Because turbidities of water treated by conventional fluid-particle separation processes usually fall within the range of 0 to 1 unit, indirect secondary methods were developed to estimate turbidity. Electronic nephelometers are the preferred instruments for turbidity measurement.

Most commercial turbidimeters designed for measuring low turbidities give comparatively good indications of the intensity of light scattered in one particular direction, predominantly at right angles to the incident light. Turbidimeters with scattered-light detectors located at 90° to the incident beam are called nephelometers. Nephelometers are relatively unaffected by small differences in design parameters and therefore are specified as the standard instrument for measurement of low turbidities. Instruments of different make and model may vary in response.†#(16) However, interinstrument variation may be effectively negligible if good measurement techniques are used and the characteristics of the particles in the measured suspensions are similar. Poor measurement technique can have a greater effect on measurement error than small differences in instrument design. Turbidimeters of nonstandard design, such as forward-scattering devices, may be more sensitive than nephelometers to the presence of larger particles. While it may not be appropriate to compare their output with that of instruments of standard design, they still may be useful for process monitoring.

An additional cause of discrepancies in turbidity analysis is the use of suspensions of different types of particulate matter for instrument calibration. Like water samples, prepared suspensions have different optical properties depending on the particle size distributions, shapes, and refractive indices. A standard reference suspension having reproducible light-scattering properties is specified for nephelometer calibration.

Its precision, sensitivity, and applicability over a wide turbidity range make the nephelometric method preferable to visual methods. Report nephelometric measurement results as nephelometric turbidity units (NTU).

3. Storage of Sample

Determine turbidity as soon as possible after the sample is taken. Gently agitate all samples before examination to ensure a representative measurement. Sample preservation is not practical; begin analysis promptly. Refrigerate or cool to 4°C, to minimize microbiological decomposition of solids, if storage is required. For best results, measure turbidity immediately without altering the original sample conditions such as temperature or pH.

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2130 B. Nephelometric Method

1. General Discussion

a. Principle: This method is based on a comparison of the intensity of light scattered by the sample under defined conditions with the intensity of light scattered by a standard reference suspension under the same conditions. The higher the intensity of scattered light, the higher the turbidity. Formazin polymer is used as the primary standard reference suspension. The turbidity of a specified concentration of formazin suspension is defined as 4000 NTU.

b. Interference: Turbidity can be determined for any water sample that is free of debris and rapidly settling coarse sediment. Dirty glassware and the presence of air bubbles give false results. ‘‘True color,’’ i.e., water color due to dissolved substances that absorb light, causes measured turbidities to be low. This effect usually is not significant in treated water.

2. Apparatus

a. Laboratory or process nephelometer consisting of a light source for illuminating the sample and one or more photoelectric detectors with a readout device to indicate intensity of light scattered at 90° to the path of incident light. Use an instrument designed to minimize stray light reaching the detector in the absence of turbidity and to be free from significant drift after a short warmup period. The sensitivity of the instrument should permit detecting turbidity differences of 0.02 NTU or less in the lowest range in waters having a turbidity of less than 1 NTU. Several ranges may be necessary to obtain both adequate coverage and sufficient sensitivity for low turbidities. Differences in instrument design will cause differences in measured values for turbidity even though the same suspension is used for calibration. To minimize such differences, observe the following design criteria:

1) Light source—Tungsten-filament lamp operated at a color temperature between 2200 and 3000°K.

2) Distance traversed by incident light and scattered light within the sample tube—Total not to exceed 10 cm.

3) Angle of light acceptance by detector—Centered at 90° to the incident light path and not to exceed ±30° from 90°. The detector and filter system, if used, shall have a spectral peak response between 400 and 600 nm.

b. Sample cells: Use sample cells or tubes of clear, colorless glass or plastic. Keep cells scrupulously clean, both inside and out, and discard if scratched or etched. Never handle them where the instrument’s light beam will strike them. Use tubes with sufficient extra length, or with a protective case, so that they may be handled properly. Fill cells with samples and standards that have been agitated thoroughly and allow sufficient time for bubbles to escape.

Clean sample cells by thorough washing with laboratory soap inside and out followed by multiple rinses with distilled or deionized water; let cells air-dry. Handle sample cells only by

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the top to avoid dirt and fingerprints within the light path.

Cells may be coated on the outside with a thin layer of silicone oil to mask minor imperfections and scratches that may contribute to stray light. Use silicone oil with the same refractive index as glass. Avoid excess oil because it may attract dirt and contaminate the sample compartment of the instrument. Using a soft, lint-free cloth, spread the oil uniformly and wipe off excess. The cell should appear to be nearly dry with little or no visible oil.

Because small differences between sample cells significantly impact measurement, use either matched pairs of cells or the same cell for both standardization and sample measurement.

3. Reagents

a. Dilution water: High-purity water will cause some light scattering, which is detected by nephelometers as turbidity. To obtain low-turbidity water for dilutions, nominal value 0.02 NTU, pass laboratory reagent-grade water through a filter with pore size sufficiently small to remove essentially all particles larger than 0.1 μm;*#(17) the usual membrane filter used for bacteriological examinations is not satisfactory. Rinse collecting flask at least twice with filtered water and discard the next 200 mL.

Some commercial bottled demineralized waters have a low turbidity. These may be used when filtration is impractical or a good grade of water is not available to filter in the laboratory. Check turbidity of bottled water to make sure it is lower than the level that can be achieved in the laboratory.

b. Stock primary standard formazin suspension:

1) Solution I—Dissolve 1.000 g hydrazine sulfate, $(NH_2)_2 \cdot H_2SO_4$, in distilled water and dilute to 100 mL in a volumetric flask. CAUTION: *Hydrazine sulfate is a carcinogen; avoid inhalation, ingestion, and skin contact. Formazin suspensions can contain residual hydrazine sulfate.*

2) Solution II—Dissolve 10.00 g hexamethylenetetramine, $(CH_2)_6N_4$, in distilled water and dilute to 100 mL in a volumetric flask.

3) In a flask, mix 5.0 mL Solution I and 5.0 mL Solution II. Let stand for 24 h at 25 ± 3°C. This results in a 4000-NTU suspension. Transfer stock suspension to an amber glass or other UV-light-blocking bottle for storage. Make dilutions from this stock suspension. The stock suspension is stable for up to 1 year when properly stored.

c. Dilute turbidity suspensions: Dilute 4000 NTU primary standard suspension with high-quality dilution water. Prepare immediately before use and discard after use.

d. Secondary standards: Secondary standards are standards that the manufacturer (or an independent testing organization) has certified will give instrument calibration results equivalent (within certain limits) to the results obtained when the instrument is calibrated with the primary standard, i.e., user-prepared formazin. Various secondary standards are available including: commercial stock suspensions of 4000 NTU formazin, commercial suspensions of microspheres of styrene-divinylbenzene copolymer,†#(18) and items supplied by instrument manufacturers,

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such as sealed sample cells filled with latex suspension or with metal oxide particles in a polymer gel. The U.S. Environmental Protection Agency[1] designates user-prepared formazin, commercial stock formazin suspensions, and commercial styrene-divinylbenzene suspensions as ‘‘primary standards,’’ and reserves the term ‘‘secondary standard’’ for the sealed standards mentioned above.

Secondary standards made with suspensions of microspheres of styrene-divinylbenzene copolymer typically are as stable as concentrated formazin and are much more stable than diluted formazin. These suspensions can be instrument-specific; therefore, use only suspensions formulated for the type of nephelometer being used. Secondary standards provided by the instrument manufacturer (sometimes called ‘‘permanent’’ standards) may be necessary to standardize some instruments before each reading and in other instruments only as a calibration check to determine when calibration with the primary standard is necessary.

All secondary standards, even so-called ‘‘permanent’’ standards, change with time. Replace them when their age exceeds the shelf life. Deterioration can be detected by measuring the turbidity of the standard after calibrating the instrument with a fresh formazin or microsphere suspension. If there is any doubt about the integrity or turbidity value of any secondary standard, check instrument calibration first with another secondary standard and then, if necessary, with user-prepared formazin. Most secondary standards have been carefully prepared by their manufacturer and should, if properly used, give good agreement with formazin. Prepare formazin primary standard only as a last resort. Proper application of secondary standards is specific for each make and model of nephelometer. Not all secondary standards have to be discarded when comparison with a primary standard shows that their turbidity value has changed. In some cases, the secondary standard should be simply relabeled with the new turbidity value. Always follow the manufacturer’s directions.

4. Procedure

a. General measurement techniques: Proper measurement techniques are important in minimizing the effects of instrument variables as well as stray light and air bubbles. Regardless of the instrument used, the measurement will be more accurate, precise, and repeatable if close attention is paid to proper measurement techniques.

Measure turbidity immediately to prevent temperature changes and particle flocculation and sedimentation from changing sample characteristics. If flocculation is apparent, break up aggregates by agitation. Avoid dilution whenever possible. Particles suspended in the original sample may dissolve or otherwise change characteristics when the temperature changes or when the sample is diluted.

Remove air or other entrained gases in the sample before measurement. Preferably degas even if no bubbles are visible. Degas by applying a partial vacuum, adding a nonfoaming-type surfactant, using an ultrasonic bath, or applying heat. In some cases, two or more of these techniques may be combined for more effective bubble removal. For example, it may be necessary to combine addition of a surfactant with use of an ultrasonic bath for some severe

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conditions. Any of these techniques, if misapplied, can alter sample turbidity; *use with care*. If degassing cannot be applied, bubble formation will be minimized if the samples are maintained at the temperature and pressure of the water before sampling.

Do not remove air bubbles by letting sample stand for a period of time because during standing, turbidity-causing particulates may settle and sample temperature may change. Both of these conditions alter sample turbidity, resulting in a nonrepresentative measurement.

Condensation may occur on the outside surface of a sample cell when a cold sample is being measured in a warm, humid environment. This interferes with turbidity measurement. Remove all moisture from the outside of the sample cell before placing the cell in the instrument. If fogging recurs, let sample warm slightly by letting it stand at room temperature or by partially immersing it in a warm water bath for a short time. Make sure samples are again well mixed.

b. Nephelometer calibration: Follow the manufacturer's operating instructions. Run at least one standard in each instrument range to be used. Make certain the nephelometer gives stable readings in all sensitivity ranges used. Follow techniques outlined in ¶s 2*b* and 4*a* for care and handling of sample cells, degassing, and dealing with condensation.

c. Measurement of turbidity: Gently agitate sample. Wait until air bubbles disappear and pour sample into cell. When possible, pour well-mixed sample into cell and immerse it in an ultrasonic bath for 1 to 2 s or apply vacuum degassing, causing complete bubble release. Read turbidity directly from instrument display.

d. Calibration of continuous turbidity monitors: Calibrate continuous turbidity monitors for low turbidities by determining turbidity of the water flowing out of them, using a laboratory-model nephelometer, or calibrate the instruments according to manufacturer's instructions with formazin primary standard or appropriate secondary standard.

5. Interpretation of Results

Report turbidity readings as follows:

Turbidity Range *NTU*	Report to the Nearest *NTU*
0–1.0	0.05
1–10	0.1
10–40	1
40–100	5
100–400	10
400–1000	50
>1000	100

When comparing water treatment efficiencies, do not estimate turbidity more closely than specified above. Uncertainties and discrepancies in turbidity measurements make it unlikely that

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results can be duplicated to greater precision than specified.

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2150 ODOR*#(19)

2150 A. Introduction

1. Discussion

Odor, like taste, depends on contact of a stimulating substance with the appropriate human receptor cell. The stimuli are chemical in nature and the term ‘‘chemical senses’’ often is applied to odor and taste. Water is a neutral medium, always present on or at the receptors that perceive sensory response. In its pure form, water is odor-free. Man and other animals can avoid many potentially toxic foods and waters because of adverse sensory response. These senses often provide the first warning of potential hazards in the environment.

Odor is recognized[1] as a quality factor affecting acceptability of drinking water (and foods prepared with it), tainting of fish and other aquatic organisms, and esthetics of recreational waters. Most organic and some inorganic chemicals contribute taste or odor. These chemicals

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may originate from municipal and industrial waste discharges, from natural sources such as decomposition of vegetable matter, or from associated microbial activity, and from disinfectants or their products.

The potential for impairment of the sensory quality of water has increased as a result of expansion in the variety and quantity of waste materials, demand for water disposal of captured air pollutants, and increased reuse of available water supplies by a growing population. Domestic consumers and process industries such as food, beverage, and pharmaceutical manufacturers require water essentially free of tastes and odors.

Some substances, such as certain inorganic salts, produce taste without odor and are evaluated by taste testing (Section 2160). Many other sensations ascribed to the sense of taste actually are odors, even though the sensation is not noticed until the material is taken into the mouth. Because some odorous materials are detectable when present in only a few nanograms per liter, it is usually impractical and often impossible to isolate and identify the odor-producing chemical. The human nose is the practical odor-testing device used in this method. Odor tests are performed to provide qualitative descriptions and approximate quantitative measurements of odor intensity. The method for intensity measurement presented here is the *threshold odor* test, based on a method of limits.[2] This procedure, while not universally preferred,[3] has definite strengths.[4]

Sensory tests are useful as a check on the quality of raw and finished water and for control of odor through the treatment process.[2,3,5] They can assess the effectiveness of different treatments and provide a means of tracing the source of contamination.

Section 6040B provides an analytical procedure for quantifying several organic odor-producing compounds including geosmin and methylisoborneol.

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2150 B. Threshold Odor Test

1. General Discussion

a. Principle: Determine the threshold odor by diluting a sample with odor-free water until the least definitely perceptible odor is achieved. There is no absolute threshold odor concentration, because of inherent variation in individual olfactory capability. A given person varies in sensitivity over time. Day-to-day and within-day differences occur. Furthermore, responses vary as a result of the characteristic, as well as concentration, of odorant. The number of persons selected to measure threshold odor will depend on the objective of the tests, economics, and available personnel. Larger-sized panels are needed for sensory testing when the results must represent the population as a whole or when great precision is desired. Under such circumstances, panels of no fewer than five persons, and preferably ten or more, are recommended.[1] Measurement of threshold levels by one person is often a necessity at water treatment plants. Interpretation of the single tester result requires knowledge of the relative acuity of that person. Some investigators have used specific odorants, such as *m*-cresol or *n*-butanol, to calibrate a tester's response.[2] Others have used the University of Pennsylvania Smell Identification Test to assess an individual's ability to identify odors correctly.[3]

b. Application: This threshold method is applicable to samples ranging from nearly odorless natural waters to industrial wastes with threshold numbers in the thousands. There are no intrinsic difficulties with the highly odorous samples because they are reduced in concentration proportionately before being presented to the test observers.

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c. Qualitative descriptions: A fully acceptable system for characterizing odor has not been developed despite efforts over more than a century. Nevertheless, Section 2170 (Flavor Profile Analysis) specifies a set of 23 odor reference standards that may be used if qualitative descriptions are important. These descriptors can be used with the Threshold Odor Test to standardize methods for sensory analysis.

d. Sampling and storage: Collect samples for odor testing in glass bottles with glass or TFE-lined closures. Complete tests as soon as possible after sample collection. If storage is necessary, collect at least 500 mL of sample in a bottle filled to the top; refrigerate, making sure that no extraneous odors can be drawn into the sample as it cools. Do not use plastic containers.

e. Dechlorination: Most tap waters and some wastewaters are chlorinated. Often it is desirable to determine the odor of the chlorinated sample as well as that of the same sample after dechlorination. Dechlorinate with thiosulfate in exact stoichiometric quantity as described under Nitrogen (Ammonia), Section 4500-NH_3 .

f. Temperature: Threshold odor values vary with temperature. For most tap waters and raw water sources, a sample temperature of 60°C will permit detection of odors that otherwise might be missed; 60°C is the standard temperature for hot threshold odor tests. For some purposes—because the odor is too fleeting or there is excessive heat sensation—the hot odor test may not be applicable; where experience shows that a lower temperature is needed, use a standard test temperature of 40°C. For special purposes, other temperatures may be used. *Report temperature at which observations are made.*

2. Apparatus

To assure reliable threshold measurements, use odor-free glassware. Clean glassware shortly before use with nonodorous soap and acid cleaning solution and rinse with odor-free water. Reserve this glassware exclusively for threshold testing. Do not use rubber, cork, or plastic stoppers. Do not use narrow-mouth vessels.

a. Sample bottles, glass-stoppered or with TFE-lined closures.

b. Constant-temperature bath: A water bath or electric hot plate capable of temperature control of ± 1°C for odor tests at elevated temperatures. The bath must not contribute any odor to the odor flasks.

c. Odor flasks: Glass-stoppered, 500-mL (ST 32) erlenmeyer flasks, to hold sample dilutions during testing.

d. Pipets:

1) *Transfer and volumetric pipets or graduated cylinders:* 200-, 100-, 50-, and 25-mL.

2) *Measuring pipets:* 10-mL, graduated in tenths.

e. Thermometer: Zero to 110°C, chemical or metal-stem dial type.

3. Odor-Free Water

a. Sources: Prepare odor-free water by passing distilled, deionized, or tap water through

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activated carbon. If product water is not odor-free, rebuild or purify the system. In all cases verify quality of product water daily.

b. Odor-free-water generator (Figure 2150:1):*#(20) Make the PVC generator from a 2-ft length of 4-in. PVC pipe approved for use for drinking water purposes (e.g., Schedule 80, or National Water Council-approved in U.K.). Thread pipe end to accept threaded caps. Have a small threaded nipple in the cap center for water inlet or outlet. To retain the activated carbon, place coarse glass wool in top and bottom of generator. Regulate water flow to generator by a needle valve and a pressure regulator to provide the minimum pressure for the desired flow. Use activated carbon of approximately 12 to 40 mesh grain size.†#(21)

c. Generator operation: Pass tap or purified water through odor-free-water generator at rate of 100 mL/min. When generator is started, flush to remove carbon fines and discard product, or pre-rinse carbon.

Check quality of water obtained from the odor-free-water generator daily at 40 and 60°C before use. The life of the carbon will vary with the condition and amount of water filtered. Subtle odors of biological origin often are found if moist carbon filters stand idle between test periods. Detection of odor in the water coming through the carbon indicates that a change of carbon is needed.

4. Procedure

a. Precautions: Carefully select by preliminary tests the persons to make taste or odor tests. Although extreme sensitivity is not required, exclude insensitive persons and concentrate on observers who have a sincere interest in the test. Avoid extraneous odor stimuli such as those caused by smoking and eating before the test or those contributed by scented soaps, perfumes, and shaving lotions. Insure that the tester is free from colds or allergies that affect odor response. Limit frequency of tests to a number below the fatigue level by frequent rests in an odor-free atmosphere. Keep room in which tests are conducted free from distractions, drafts, and odor.[2] If necessary, set aside a special odor-free room ventilated by air that is filtered through activated carbon and maintained at a constant comfortable temperature and humidity.[4]

For precise work use a panel of five or more testers. Do not allow persons making odor measurements to prepare samples or to know dilution concentrations being evaluated. Familiarize testers with the procedure before they participate in a panel test. Present most dilute sample first to avoid tiring the senses with the concentrated sample. Keep temperature of samples during testing within 1°C of the specified temperature.

Because many raw and waste waters are colored or have decided turbidity that may bias results, use opaque or darkly colored odor flasks, such as red actinic erlenmeyer flasks.

b. Characterization: As part of the threshold test or as a separate test, direct each observer to describe the characteristic sample odor using odor reference standards (see Section 2170). Compile the consensus that may appear among testers and that affords a clue to the origin of the odorous component. The value of the characterization test increases as observers become more experienced with a particular category of odor, e.g., earthy, musty, chlorine.

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c. Threshold measurement:‡#(22) The ‘‘threshold odor number,’’ designated by the abbreviation TON, is the greatest dilution of sample with odor-free water yielding a definitely perceptible odor. Bring total volume of sample and odor-free water to 200 mL in each test. Follow dilutions and record corresponding TON presented in Table 2150:I. These numbers have been computed thus:

$$\text{TON} = \frac{A + B}{A}$$

where:

A = mL sample and
B = mL odor-free water.

1) Place proper volume of odor-free water in the flask first, add sample to water (avoiding contact of pipet or sample with lip or neck of flask), mix by swirling, and proceed as follows:

Determine approximate range of the threshold number by adding 200 mL, 50 mL, 12 mL, and 2.8 mL sample to separate 500-mL glass-stoppered erlenmeyer flasks containing odor-free water to make a total volume of 200 mL. Use a separate flask containing only odor-free water as reference for comparison. Heat dilutions and reference to desired test temperature.

2) Shake flask containing odor-free water, remove stopper, and sniff vapors. Test sample containing least amount of odor-bearing water in the same way. If odor can be detected in this dilution, prepare more dilute samples as described in ¶ 5) below. If odor cannot be detected in first dilution, repeat above procedure using sample containing next higher concentration of odor-bearing water, and continue this process until odor is detected clearly.

3) Based on results obtained in the preliminary test, prepare a set of dilutions using Table 2150:II as a guide. Prepare the five dilutions shown on the appropriate line and the three next most concentrated on the next line in Table 2150:II. For example, if odor was first noted in the flask containing 50 mL sample in the preliminary test, prepare flasks containing 50, 35, 25, 17, 12, 8.3, 5.7, and 4.0 mL sample, each diluted to 200 mL with odor-free water. This array is necessary to challenge the range of sensitivities of the entire panel of testers.

Insert two or more blanks in the series near the expected threshold, but avoid any repeated pattern. Do not let tester know which dilutions are odorous and which are blanks. Instruct tester to smell each flask in sequence, beginning with the least concentrated sample, until odor is detected with certainty.

4) Record observations by indicating whether odor is noted in each test flask. For example:

mL Sample Diluted to 200 mL	**12**	**0**	**17**	**25**	**0**	**35**	**50**

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mL Sample Diluted to 200 mL	12	0	17	25	0	35	50
Response	–	–	–	+	–	+	–

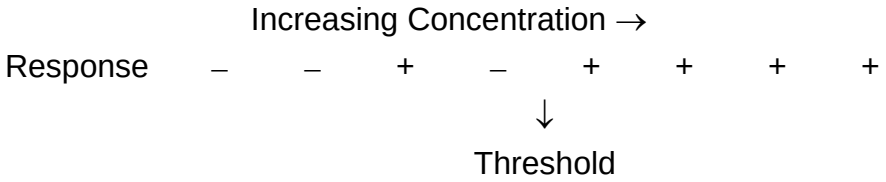
5) If the sample being tested requires more dilution than is provided by Table 2150:II, prepare an intermediate dilution consisting of 20 mL sample diluted to 200 L with odor-free water. Use this dilution for the threshold determination. Multiply TON obtained by 10 to correct for the intermediate dilution. In rare cases more than one tenfold intermediate dilution step may be required.

5. Calculation

The threshold odor number is the dilution ratio at which odor is just detectable. In the example above, 4c4), the first detectable odor occurred when 25 mL sample was diluted to 200 mL. Thus the threshold is 200 divided by 25, or 8. Table 2150:I lists the threshold numbers corresponding to common dilutions.

The smallest TON that can be observed is 1, as in the case where the odor flask contains 200 mL undiluted sample. If no odor is detected at this concentration, report ‘‘No odor observed’’ instead of a threshold number. (In special applications, fractional threshold numbers have been calculated.[6])

Anomalous responses sometimes occur; a low concentration may be called positive and a higher concentration in the series may be called negative. In such a case, designate the threshold as the point after which no further anomalies occur. For instance:



where:

– signifies negative response and
+ signifies positive response.

Occasionally a flask contains residual odor or is contaminated inadvertently. For precise testing repeat entire threshold odor test to determine if the last flask marked ‘‘ – ’’ was actually a mislabelled blank of odor-free water or if the previous ‘‘ + ’’ was a contaminated sample.

Use appropriate statistical methods to calculate the most probable average threshold from large numbers of panel results. For most purposes, express the threshold of a group as the

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geometric mean of individual thresholds.

6. Interpretation of Results

A threshold number is not a precise value. In the case of the single observer it represents a judgment at the time of testing. Panel results are more meaningful because individual differences have less influence on the result. One or two observers can develop useful data if comparison with larger panels has been made to check their sensitivity. Do not make comparisons of data from time to time or place to place unless all test conditions have been standardized carefully and there is some basis for comparison of observed intensities.

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2160 TASTE*#(23)

2160 A. Introduction

1. General Discussion

Taste refers only to gustatory sensations called bitter, salty, sour, and sweet that result from chemical stimulation of sensory nerve endings located in the papillae of the tongue and soft palate. Flavor refers to a complex of gustatory, olfactory, and trigeminal sensations resulting from chemical stimulation of sensory nerve endings located in the tongue, nasal cavity, and oral cavity.[1] Water samples taken into the mouth for sensory analysis always produce a flavor, although taste, odor, or mouth-feel may predominate, depending on the chemical substances present. Methods for sensory analysis presented herein require that the sample be taken into the mouth, that is, be tasted, but technically the sensory analysis requires evaluation of the complex sensation called flavor. As used here, taste refers to a method of sensory analysis in which

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samples are taken into the mouth but the resultant evaluations pertain to flavor.

Three methods have been developed for the sensory evaluation of water samples taken into the mouth: the flavor threshold test (FTT), the flavor rating assessment (FRA), and the flavor profile analysis (FPA) (Section 2170). The FTT is the oldest. It has been used extensively and is particularly useful for determining if the overall flavor of a sample of finished water is detectably different from a defined standard.[2] The FRA is especially valuable for determining if a sample of finished water is acceptable for daily consumption,[3] and the FPA is most useful for identifying and characterizing individual flavors in a water sample.[4]

Make flavor tests only on samples known to be safe for ingestion. Do not use samples that may be contaminated with bacteria, viruses, parasites, or hazardous chemicals, that contain dechlorinating agents such as sodium arsenite or that are derived from an unesthetic source. Do not make flavor tests on wastewaters or similar untreated effluents. Observe all sanitary and esthetic precautions with regard to apparatus and containers contacting the sample. Properly clean and sterilize containers before using them. Conduct analyses in a laboratory free from interfering background odors and if possible provide non-odorous carbon-filtered air at constant temperature and humidity. Use the procedure described in Section 2150 with respect to taste- and odor-free water to prepare dilution water and reference samples.

2. References

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2. BAKER, R.A. 1961. Taste and Odor in Water: A Critical Review. Manufacturing Chemists' Assoc., Washington, D.C.
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4. MALLEVIALE, J. & I.H. SUFFET, eds. 1987. The Identification and Treatment of Tastes and Odors in Drinking Water. American Water Works Association Research Foundation, Denver, Colo.

2160 B. Flavor Threshold Test (FTT)

1. General Discussion

Use the FTT to measure detectable flavor quantitatively. More precisely, use the method to compare the sample flavor objectively with that of specified reference water used as diluent.

The flavor threshold number (FTN) is the greatest dilution of sample with reference water yielding a definitely perceptible difference. The FTN is computed as follows:

$$\text{FTN} = \frac{A + B}{A}$$

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where:

A = sample volume, mL, and
B = reference water (diluent) volume, mL.

Table 2160:I gives the FTNs corresponding to various dilutions.

2. Procedure

a. Panel selection: Carefully select by preliminary trials interested persons to make flavor tests. Exclude insensitive persons and insure that the testers are free from colds or allergies. Familiarize testers with the procedure before they participate in a panel test, but do not let them prepare samples or know dilution concentrations being evaluated. For precise work use a panel of five or more testers.

b. Taste characterization: Have each observer describe the characteristic sample flavor of the most concentrated sample. Compile the consensus that may appear among testers. The value of characterization increases as observers become more experienced with a particular flavor category such as chlorophenolic, grassy, or musty.

c. Preliminary test: To determine approximate range of the FTN, add 200-, 50-, 12-, and 4-mL sample portions to volumes of reference water (see Section 2150) designated in Table 2160:I in separate 300-mL glass beakers to make a total of 200 mL in each beaker, and mix gently with clean stirrer. Use separate beaker containing only reference water for comparison. Keep sample temperature during testing within 1°C of specified temperature. Present samples to each taster in a uniform manner, with the reference water presented first, followed by the most dilute sample. If a flavor can be detected in this dilution, prepare an intermediate sample by diluting 20 mL sample to 200 mL with reference water. Use this dilution for threshold determination and multiply FTN obtained by 10 to correct for intermediate dilution. In rare cases a higher intermediate dilution may be required.

If no flavor is detected in the most dilute sample, repeat using the next concentration. Continue this process until flavor is detected clearly.

d. FTN determination: Based on results obtained in the preliminary test, prepare a set of dilutions using Table 2160:II as a guide. Prepare the seven dilutions shown on the appropriate line. This array is necessary to challenge the range of sensitivities of the entire panel of testers. If the sample being tested requires more dilution than is provided by Table 2160:II, make intermediate dilutions as directed in *c* above.

Use a clean 50-mL beaker filled to the 25-mL level or use an ordinary restaurant-style drinking glass for each dilution and reference sample. Do not use glassware used in sensory testing for other analyses. Between tests, sanitize containers in an automatic dishwasher supplied with water at not less than 60°C.

Maintain samples at 15± 1°C. However, if temperature of water in the distribution system is higher than 15°C, select an appropriate temperature. Specify temperature in reporting results.

Present series of samples to each tester in order of increasing concentration. Pair each

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sample with a known reference. Have tester taste sample by taking into the mouth whatever volume is comfortable, moving sample throughout the mouth, holding it for several seconds, and discharging it without swallowing. Have tester compare sample with reference and record whether a flavor or aftertaste is detectable. Insert two or more reference blanks in the series near the expected threshold, but avoid any repeated pattern. Do not let tester know which samples have flavor and which are blanks. Instruct tester to taste each sample in sequence, beginning with the least concentrated sample, until flavor is detected with certainty.

Record observations by indicating whether flavor is noted in each test beaker. For example:

mL Sample Diluted to 200 mL	6	8	12	0	17	25	35	0	50
Response	–	–	–	–	–	+	+	–	+

where:

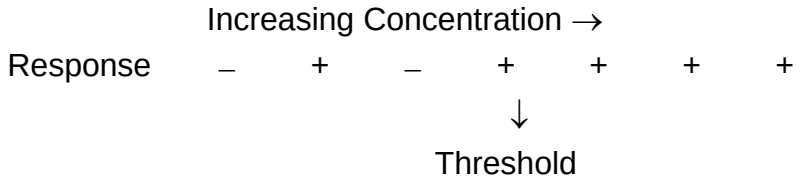
– signifies negative response and
+ signifies positive response.

3. Calculation

The flavor threshold number is the dilution ratio at which flavor is just detectable. In the example above, the first detectable flavor occurred when 25 mL sample was diluted to 200 mL yielding a threshold number of 8 (Table 2160:I). Reference blanks do not influence calculation of the threshold.

The smallest FTN that can be observed is 1, where the beaker contains 200 mL undiluted sample. If no flavor is detected at this concentration, report ‘‘No flavor observed’’ instead of a threshold number.

Anomalous responses sometimes occur; a low concentration may be called positive and a higher concentration in the series may be called negative. In such cases, designate the threshold as that point after which no further anomalies occur. The following illustrates an approach to an anomalous series (responses to reference blanks are excluded): Response:



Calculate mean and standard deviation of all FTNs if the distribution is reasonably symmetrical; otherwise, express the threshold of a group as the median or geometric mean of individual thresholds.

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4. Interpretation of Results

An FTN is not a precise value. In the case of the single observer it represents a judgment at the time of testing. Panel results are more meaningful because individual differences have less influence on the test result. One or two observers can develop useful data if comparison with larger panels has been made to check their sensitivity. Do not make comparisons of data from time to time or place to place unless all test conditions have been standardized carefully and there is some basis for comparison of observed FTNs.

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2160 C. Flavor Rating Assessment (FRA)

1. General Discussion

When the purpose of the test is to estimate acceptability for daily consumption, use the flavor rating assessment described below. This procedure has been used with samples from public sources in laboratory research and consumer surveys to recommend standards governing mineral content in drinking water. Each tester is presented with a list of nine statements about the water ranging on a scale from very favorable to very unfavorable. The tester's task is to select the statement that best expresses his or her opinion. The individual rating is the scale number of the statement selected. The panel rating for a particular sample is an appropriate measure of central tendency of the scale numbers for all testers for that sample.

2. Samples

Sample finished water ready for human consumption or use experimentally treated water if the sanitary requirements given in Section 2160A.1 are met fully. Use taste- and odor-free water as described in Section 2150 and a solution of 2000 mg NaCl/L prepared with taste- and odor-free water as criterion samples.

3. Procedure

a. Panel selection and preparation: Give prospective testers thorough instructions and trial or orientation sessions followed by questions and discussion of procedures. In tasting samples, testers work alone. Select panel members on the basis of performance in these trial sessions. Do not let testers know the composition or source of specific samples.

b. Rating test: A single rating session may be used to evaluate up to 10 samples, including the criterion samples mentioned in ¶ 2 above. Allow at least 30 min rest between repeated rating sessions.

For glassware requirements, see Section 2160B2*d*.

Present samples at a temperature that the testers will find pleasant for drinking water; maintain this temperature throughout testing. A temperature of 15°C is recommended, but in any case, do not let the test temperature exceed tap water temperatures customary at the time of the test. Specify test temperature in reporting results.

Independently randomize sample order for each tester. Instruct each to complete the following steps: 1) Taste about half the sample by taking water into the mouth, holding it for several seconds, and discharging it without swallowing; 2) Form an initial judgment on the rating scale; 3) Make a second tasting in a similar manner; 4) Make a final rating and record

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result on an appropriate data form; 5) Rinse mouth with reference water; 6) Rest 1 min before repeating Steps 1 through 5 on next sample.

c. Characterization: If characterization of flavor also is required, conduct a final rating session wherein each tester is asked to describe the flavor of each sample rated (see Section 2160B.2*b*).

4. Calculation

Use the following scale for rating. Record ratings as integers ranging from one to nine, with one given the highest quality rating. Calculate mean and standard deviation of all ratings if the distribution is reasonably symmetrical, otherwise express the most typical rating of a group as the median or geometric mean of individual ratings.

Action tendency scale:

1) I would be very happy to accept this water as my everyday drinking water.
2) I would be happy to accept this water as my everyday drinking water.
3) I am sure that I could accept this water as my everyday drinking water.
4) I could accept this water as my everyday drinking water.
5) Maybe I could accept this water as my everyday drinking water.
6) I don't think I could accept this water as my everyday drinking water.
7) I could not accept this water as my everyday drinking water.
8) I could never drink this water.
9) I can't stand this water in my mouth and I could never drink it.

5. Interpretation of Results

Values representing the central tendency and dispersion of quality ratings for a laboratory panel are only estimates of these values for a defined consuming population.

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2170 FLAVOR PROFILE ANALYSIS*#(24)

2170 A. Introduction

1. Discussion

Flavor profile analysis (FPA) is a technique for identifying sample taste(s) and odor(s). For general information on taste see Section 2160; for information on odor see Section 2150.

FPA differs from threshold odor number because the sample is not diluted and each taste or odor attribute is individually characterized and assigned its own intensity rating. The single numerical rating obtained in measuring threshold odor is controlled by the most readily perceived odorant or mixture. Sample dilution may change the odor attribute that is measured.[1,2] FPA determines the strength or intensity of each perceived taste or odor without dilution or treatment of the sample.

2. References

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2170 B. Flavor Profile Analysis

1. General Discussion

a. Principle: Flavor profile analysis uses a group of four or five trained panelists to examine the sensory characteristics of samples. Flavor attributes are determined by tasting; odor attributes (aroma) are determined by sniffing the sample. The method allows more than one flavor, odor attribute, or feeling factor (e.g., drying, burning) to be determined per sample and each attribute's strength to be measured.

Panelists must be able to detect and recognize various odors present. Flavor profile analysis requires well-trained panelists and data interpreters. Reproducibility of results depends on the training and experience of the panelists.

Initially, panelists record their perceptions without discussion. Once each individual has made an independent assessment of a sample, the panel discusses its findings and reaches a consensus.[1]

b. Interference: Fatigue (adaptation) denotes the decrease in the analyst's sensory acuity with continued exposure to stimulation.[1] Because odor mixtures are more complex than taste mixtures, olfactory adaptation is more serious.[2] Factors that can induce fatigue include odor intensity, type of odorants (some compounds such as geosmin and chlorine induce more fatigue than others), number of samples tested during a session, and rest interval between samples.[1] The rest interval also is important because it prevents carryover of odors between samples.

Background odors present during analysis affect results. Analyst illness, i.e., cold or allergy, can diminish or otherwise alter perception.

c. Application: Flavor profile analysis has been applied to drinking water sources, finished drinking water, sampling points within the drinking water treatment train, and bottled waters, and for investigating customer complaints.

d. Precautions: Some compounds are health hazards when inhaled or ingested. Do not use this method for industrial wastes or other samples suspected of containing high concentrations of hazardous compounds. Chemically analyze suspect samples to determine whether hazardous chemicals are present before making flavor profile analysis. Do not taste untreated drinking water unless it is certain that no health threat (biological or chemical) exists.

Because flavor profile analysis includes discussion during which panelists reach consensus description, avoid including on the panel a person with a dominating personality.[3] The opinions of a senior member or panel leader also may have this undesired effect.[3]

2. Apparatus[4-8]

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Reserve apparatus and glassware exclusively for flavor profile analysis. Prepare sample bottles by washing bottle and cap with detergent. Rinse 10 times with hot water. Optionally rinse with HCl (1:1). Rinse with odor-free water (see 2150B.3) at least three times. If there is residual odor, such as chalky, repeat cleaning.

Prepare 500-mL erlenmeyer flasks by either of the two methods described below provided that it imparts no odor to the sample. Make tests with freshly cleaned containers.

1) Without wearing rubber gloves wash flask with soapy water. Additionally, scrub outside of flask with scouring pad to remove body oils. Rinse 10 times with hot water and 3 times with odor-free water. To store flask add 100 to 200 mL odor-free water and stopper. Before use, rinse with 100 mL odor-free water. If there is residual odor, repeat cleaning.

2) Do not handle with rubber gloves. Before use, heat 200 mL odor-free water to boiling; lightly lay stopper over flask opening, permitting water vapor to escape. Discard boiled water and let flask cool to room temperature. If there is residual odor repeat or use cleaning alternative 1). After analyzing a sample, discard sample, rinse 10 times with hot tap water, add 200 mL odor-free water, stopper, and store.

For flasks with persistent odor use commercial cleaning mixture*#(25) or HCl (1:1).

a. Sample bottles: Glass, 1-L, with TFE-lined closure.

b. Containers for odor analysis:[4] Select container for odor analysis depending on panelists' preference, temperature of sample, and availability of container.

1) Panel preference[4-8]—Plastic cups, 7- or 8-ounce disposable, are convenient. Some panels have found that these plastic cups impart a plastic and/or floral aroma to samples. They prefer 500-mL erlenmeyer flasks with ST32 ground-glass stoppers. The panel should determine the acceptable, odor-free, test container.

2) Temperature[4]—If aroma samples are tested at 45°C, do not use plastic. If aroma samples are tested at 25°C, use the same plastic cup and sample for both aroma and flavor analysis.

3) Availability[4]—Containers must be consistently available because the panel responses may change when different containers are used.

c. Containers for flavor analysis:[4] Use either plastic disposable, e.g., polyethylene,†#(26) or glass containers. Do not use wax-lined or paper cups. If using glass containers verify that they contribute no taste to the sample. Wash glass containers as directed above.

d. Watch glasses.

e. Constant-temperature water bath capable of maintaining a temperature ± 1°C. The bath must not contribute any odor to the odor flasks or testing room.

f. Thermometer, graduated 0 to 110°C, chemical or metal-stem dial type.

g. Syringes.

h. Ice chest.

i. Odor-free testing room:[3,5] Hold flavor profile analysis sessions in a clean, well-lit quiet,

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aroma-free, and temperature-controlled room. Seat panel members around a common table to facilitate exchange of responses during discussion. Place a blackboard or easel pad in the room so that all panelists are able to see it. Preferably use an easel pad with odor-free markers (such as a wax, china marker).

j. Refrigerator capable of maintaining a temperature of 4°C.

3. Reagents

a. Odor-free water: See Section 2150B.3.

b. Crackers: Use salt- and flavor-free crackers‡#(27) to cleanse the palate during taste testing. Before tasting anything, use the crackers and taste-free water to cleanse the palate. Use crackers between samples to reduce carryover of perceptions.

c. Odor and flavor standards: Odor and flavor reference standards are being developed for use as a guide for qualitative descriptions (attributes). Aroma reference standards help panelists come to agreement on the description of specific aromas.[4-11] Table 2170:I, Table 2170:II, and Table 2170:III list some of the aroma references in use. New references are being added continually. A taste and odor wheel has been developed from these lists.[2] For odor identification and training, place several drops of stock solutions (producing moderately strong odors) onto sterile cotton in 25-mL amber-colored vials with TFE-lined caps. Standards can be stored until odor changes.

d. Taste standards: Chemicals used for taste standards are sucrose (sweet), citric acid (sour), sodium chloride (salt), and caffeine (bitter). Table 2170:IV lists the chemicals used and their concentrations for basic taste standards at ‘‘slight,’’ ‘‘moderate,’’ and ‘‘strong’’ levels.[4,5] The taste standards provide reference points for both taste and odor intensity ratings. The panelists compare the intensity of what they are smelling or tasting to the intensity of the standards they have tasted. Make taste standards available during panel training. Because the tastes from all but the sweet standard tend to overpower any subsequent tasting, use only the sweet taste standard during actual sample analysis. If the panel meets as seldom as once a week, make sweet standards available so that panelists can ‘‘recalibrate’’ themselves. Panels that meet more than once a week may not need to ‘‘recalibrate.’’ Make standards fresh each time they are used.[4]

4. Scale

The strength of a taste or odor is judged according to the following scale:

—	(odor-free)
T	(threshold)
2	(very weak)
4	(weak)
6	
8	(moderate)

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10

12 (strong)

5. Procedure

a. Sample collection: Collect sample in cleaned container. When sampling from a tap, remove all screens and aerators, minimize turbulence. Flush tap at least 5 min. Reduce flow rate during sampling. Rinse bottle with sample, then fill it to the top, with no headspace. Chill or refrigerate sample immediately and analyze as soon after collection as possible, preferably within 24 h, but no longer than 48 h.

b. Sample preparation:[4] Pour samples into properly prepared glassware or acceptable disposable containers. Analyze samples at the same temperature. Adjust sample temperatures by placing samples in a water bath 15 min before analysis. Prepare a sample for each panelist. Examine odor samples before flavor samples.

1) Odor analysis—When using 500-mL erlenmeyer flasks for odor analysis, place 200 mL sample in the flask. Make transfer carefully to avoid loss of volatile components. When plastic cups are used, place 60 mL sample in cup and cover it with a watch glass.

2) Taste analysis—Bring sample to 25°C before pouring into containers for tasting. Cover with a watch glass if samples are not tasted immediately. If samples are tested at 25°C for odor, use the same sample for flavor analysis.

c. Panelists: Carefully screen and train panelists.[8]

d. Pre-test considerations: Notify panelists well in advance of panel session so a substitute can be found if necessary. Panelists who have colds or allergic attacks the day of the panel are unacceptable; they should ask the panel coordinator to find a substitute. Panelists must not smoke or eat for 15 to 30 min before the session. Wearing cologne or perfume or washing hands with scented soap before the session is not permitted.

e. Sample analysis: The panel consists of four or five members. If fewer than four panelists are available, store the sample until a full panel can meet.

1) Odor analysis—Heat samples to proper temperature. If erlenmeyer flasks are used, sample temperature is 45°C. If plastic cups are used, sample temperature is 25°C. Give each panelist his/her own sample. If a flask is used, hold it with one hand on the bottom and the other on the stopper. Do not touch flask neck. Gently swirl (do not shake) flask in a circular manner to ensure that volatile compounds are released into the headspace. Bring flask close to nose, remove stopper, and sniff at the flask opening. Record impressions of odor attributes in the order perceived and the assessment of each attribute's intensity. If a cup is used, gently swirl on the table top for a few seconds. Remove watchglass, and keeping hands away from the cup, sniff sample and record perceptions. CAUTION: *Sniff samples only if they are known to be toxicologically safe.* For both the flask and the plastic cup method, smell all samples before going on to the taste test. Do not discuss or interact with other panelists.

2) Taste analysis—When tasting, take sample into the mouth and roll it over the entire

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surface of the tongue. Slurping enhances the odor aspect of flavor. CAUTION: *Taste only samples known to be biologically and toxicologically safe*. Do not discuss or interact with other panelists.

3) Intensity—In both taste and odor analysis, each panelist determines intensity ratings by matching intensity of the flavor or aroma perceived with the defined intensities of the basic taste standards. Initially this may be difficult. Some panels have found it helpful to make basic taste standards available throughout the analysis so that any panelist who wishes to ‘‘recalibrate’’ may do so.

4) Re-examination of samples—First impressions are most important, particularly for intensity. The intensity rating may diminish upon re-examination because of fatigue and volatility of the odorant. However, if an aroma or flavor is difficult for a panelist to describe, the panelist may go back and re-evaluate the sample before recording the results.

5) Individual results—As soon as a sample is tasted or smelled, record individual results. Information recorded includes a description of aromas or flavors perceived, their intensity, and the order in which they were perceived.

6) Rest interval—Sniff odor-free water and rest at least 2 min between samples. Fatigue is a problem[1] that can be dealt with. When samples are expected to cause fatigue, the panel leader can increase the rest interval and limit the number of samples presented. The leader also may try to arrange samples such that samples known to be fatiguing are placed near the end of the sample row. Avoid juxtaposition of such samples. Also, use taste- and odor-free blanks between samples. Five to six samples per session is the maximum.

7) Discussion—When all panelists have had an opportunity to examine the sample, hold a discussion period. Each panelist’s impression of the sample is stated and the panel leader records it to be seen by everyone. By examining the order of appearance, intensity, and description, the panel leader attempts to group responses together, soliciting comments from the panel members as to whether or not they agree. Sometimes panelists detect an aroma that they cannot describe; in the discussion they may see what another panelist called it and decide to agree with that description. With inexperienced panels, several different descriptors may be used for the same aroma. As the panel gains more experience, these differences tend to be reconciled. It is the responsibility of the panel leader to ensure that the panelists are provided with standards that duplicate the sample aromas. Descriptions that fewer than 50% of the panelists use are called ‘‘other notes’’ and are listed separately or are not included in the group results.

8) Recording panel results—Record the following: sample description; time of sampling; identity of panel member; flavor, aroma, and feeling factor descriptions; intensity rating; order of perception; range and average for each descriptor.

6. Calculation and Interpretation[1]

In early testing intensity was used to describe the strength of an odor in an ordinal scale from slight to strong.[12] If an odor was recognized, then it had an intensity. The rating scale has been modified to use numbers corresponding to the ordinal categories. Points (other than threshold) on

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the scale can be anchored by the use of taste standards. Thus a certain concentration of a taste standard is defined as a certain point on the rating scale and numerical ratings for nonthreshold intensities are anchored. Threshold ratings are not defined by any standards. Their meaning is different from that of the other ratings and they are difficult to manipulate mathematically.

Calculate averages if at least 50% of the panelists agree on a given description. If a panelist does not give that description, assign an intensity value of zero. For example:

		Intensity								
Description	Panelist					I	II	III	IV	Average
Musty	2	4	0	2	2.0					
Chlorinous	2	4	4	4	3.5					

7. Quality Control[12]

Use odor-free samples and duplicates occasionally. The odor-free sample serves to detect guessing. Duplicates check reproducibility. A standard concentration of an odor reference standard in odor-free water also can be used to check odor recognition and reproducibility of the intensity scale.

Use counterbalancing of samples so that each panelist receives the samples in a different order. This prevents error due to order effects such as fatigue, carryover, and expectation.

8. Precision and Bias

Initial studies of precision and bias have been completed.[12,13] An odor recognition and reproducibility study by untrained panelists has rated some of the odors of Table 2170:I, Table 2170:II, and Table 2170:III as poor, fair, good, or excellent.[13]

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2310 ACIDITY*#(28)

2310 A. Introduction

Acidity of a water is its quantitative capacity to react with a strong base to a designated pH. The measured value may vary significantly with the end-point pH used in the determination. Acidity is a measure of an aggregate property of water and can be interpreted in terms of specific substances only when the chemcical composition of the sample is known. Strong mineral acids, weak acids such as carbonic and acetic, and hydrolyzing salts such as iron or aluminum sulfates may contribute to the measured acidity according to the method of determination.

Acids contribute to corrosiveness and influence chemical reaction rates, chemical speciation, and biological processes. The measurement also reflects a change in the quality of the source

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water.

2310 B. Titration Method

1. General Discussion

a. Principle: Hydrogen ions present in a sample as a result of dissociation or hydrolysis of solutes react with additions of standard alkali. Acidity thus depends on the end-point pH or indicator used. The construction of a titration curve by recording sample pH after successive small measured additions of titrant permits identification of inflection points and buffering capacity, if any, and allows the acidity to be determined with respect to any pH of interest.

In the titration of a single acidic species, as in the standardization of reagents, the most accurate end point is obtained from the inflection point of a titration curve. The inflection point is the pH at which curvature changes from convex to concave or vice versa.

Because accurate identification of inflection points may be difficult or impossible in buffered or complex mixtures, the titration in such cases is carried to an arbitrary end-point pH based on practical considerations. For routine control titrations or rapid preliminary estimates of acidity, the color change of an indicator may be used for the end point. Samples of industrial wastes, acid mine drainage, or other solutions that contain appreciable amounts of hydrolyzable metal ions such as iron, aluminum, or manganese are treated with hydrogen peroxide to ensure oxidation of any reduced forms of polyvalent cations, and boiled to hasten hydrolysis. Acidity results may be highly variable if this procedure is not followed exactly.

b. End points: Ideally the end point of the acidity titration should correspond to the stoichiometric equivalence point for neutralization of acids present. The pH at the equivalence point will depend on the sample, the choice among multiple inflection points, and the intended use of the data.

Dissolved carbon dioxide (CO_2) usually is the major acidic component of unpolluted surface waters; handle samples from such sources carefully to minimize the loss of dissolved gases. In a sample containing only carbon dioxide-bicarbonates-carbonates, titration to pH 8.3 at 25°C corresponds to stoichiometric neutralization of carbonic acid to bicarbonate. Because the color change of phenolphthalein indicator is close to pH 8.3, this value generally is accepted as a standard end point for titration of total acidity, including CO_2 and most weak acids. Metacresol purple also has an end point at pH 8.3 and gives a sharper color change.

For more complex mixtures or buffered solutions selection of an inflection point may be subjective. Consequently, use fixed end points of pH 3.7 and pH 8.3 for standard acidity determinations via a potentiometric titration in wastewaters and natural waters where the simple carbonate equilibria discussed above cannot be assumed. Bromphenol blue has a sharp color change at its end point of 3.7. The resulting titrations are identified, traditionally, as ‘‘methyl orange acidity’’ (pH 3.7) and ‘‘phenolphthalein’’ or total acidity (pH 8.3) regardless of the actual method of measurement.

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c. Interferences: Dissolved gases contributing to acidity or alkalinity, such as CO_2, hydrogen sulfide, or ammonia, may be lost or gained during sampling, storage, or titration. Minimize such effects by titrating to the end point promptly after opening sample container, avoiding vigorous shaking or mixing, protecting sample from the atmosphere during titration, and letting sample become no warmer than it was at collection.

In the potentiometric titration, oily matter, suspended solids, precipitates, or other waste matter may coat the glass electrode and cause a sluggish response. Difficulty from this source is likely to be revealed in an erratic titration curve. Do *not* remove interferences from sample because they may contribute to its acidity. Briefly pause between titrant additions to let electrode come to equilibrium or clean the electrodes occasionally.

In samples containing oxidizable or hydrolyzable ions such as ferrous or ferric iron, aluminum, and manganese, the reaction rates at room temperature may be slow enough to cause drifting end points.

Do not use indicator titrations with colored or turbid samples that may obscure the color change at the end point. Residual free available chlorine in the sample may bleach the indicator. Eliminate this source of interference by adding 1 drop of 0.1*M* sodium thiosulfate ($Na_2S_2O_3$).

d. Selection of procedure: Determine sample acidity from the volume of standard alkali required to titrate a portion to a pH of 8.3 (phenolphthalein acidity) or pH 3.7 (methyl orange acidity of wastewaters and grossly polluted waters). Titrate at room temperature using a properly calibrated pH meter, electrically operated titrator, or color indicators.

Use the hot peroxide procedure (¶ 4*a*) to pretreat samples known or suspected to contain hydrolyzable metal ions or reduced forms of polyvalent cation, such as iron pickle liquors, acid mine drainage, and other industrial wastes.

Color indicators may be used for routine and control titrations in the absence of interfering color and turbidity and for preliminary titrations to select sample size and strength of titrant (¶ 4*b*).

e. Sample size: The range of acidities found in wastewaters is so large that a single sample size and normality of base used as titrant cannot be specified. Use a sufficiently large volume of titrant (20 mL or more from a 50-mL buret) to obtain relatively good volumetric precision while keeping sample volume sufficiently small to permit sharp end points. For samples having acidities less than about 1000 mg as calcium carbonate ($CaCO_3$)/L, select a volume with less than 50 mg $CaCO_3$ equivalent acidity and titrate with 0.02*N* sodium hydroxide (NaOH). For acidities greater than about 1000 mg as $CaCO_3$/L, use a portion containing acidity equivalent to less than 250 mg $CaCO_3$ and titrate with 0.1*N* NaOH. If necessary, make a preliminary titration to determine optimum sample size and/or normality of titrant.

f. Sampling and storage: Collect samples in polyethylene or borosilicate glass bottles and store at a low temperature. Fill bottles completely and cap tightly. Because waste samples may be subject to microbial action and to loss or gain of CO_2 or other gases when exposed to air,

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analyze samples without delay, preferably within 1 d. If biological activity is suspected analyze within 6 h. Avoid sample agitation and prolonged exposure to air.

2. Apparatus

a. Electrometric titrator: Use any commercial pH meter or electrically operated titrator that uses a glass electrode and can be read to 0.05 pH unit. Standardize and calibrate according to the manufacturer's instructions. Pay special attention to temperature compensation and electrode care. If automatic temperature compensation is not provided, titrate at 25 ± 5°C.

b. Titration vessel: The size and form will depend on the electrodes and the sample size. Keep the free space above the sample as small as practicable, but allow room for titrant and full immersion of the indicating portions of electrodes. For conventional-sized electrodes, use a 200-mL, tall-form Berzelius beaker without a spout. Fit beaker with a stopper having three holes, to accommodate the two electrodes and the buret. With a miniature combination glass-reference electrode use a 125-mL or 250-mL erlenmeyer flask with a two-hole stopper.

c. Magnetic stirrer.

d. Pipets, volumetric.

e. Flasks, volumetric, 1000-, 200-, 100-mL.

f. Burets, borosilicate glass, 50-, 25-, 10-mL.

g. Polyolefin bottle, 1-L.

3. Reagents

a. Carbon dioxide-free water: Prepare all stock and standard solutions and dilution water for the standardization procedure with distilled or deionized water that has been freshly boiled for 15 min and cooled to room temperature. The final pH of the water should be ≥ 6.0 and its conductivity should be <2 μmhos/cm.

b. Potassium hydrogen phthalate solution, approximately 0.05*N:* Crush 15 to 20 g primary standard $KHC_8H_4O_4$ to about 100 mesh and dry at 120°C for 2 h. Cool in a desiccator. Weigh 10.0 ± 0.5 g (to the nearest mg), transfer to a 1-L volumetric flask, and dilute to 1000 mL.

c. Standard sodium hydroxide titrant, 0.1*N:* Prepare solution approximately 0.1*N* as indicated under Preparation of Desk Reagents (see inside front cover). Standardize by titrating 40.00 mL $KHC_8H_4O_4$ solution (¶ 3*b*), using a 25-mL buret. Titrate to the inflection point (¶ 1*a*), which should be close to pH 8.7. Calculate normality of NaOH:

$$\text{Normality} = \frac{A \times B}{204.2 \times C}$$

where:

A = g $KHC_8H_4O_4$ weighed into 1-L flask,

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B = mL $KHC_8H_4O_4$ solution taken for titration, and
C = mL NaOH solution used.

Use the measured normality in further calculations or adjust to 0.1000*N*; 1 mL = 5.00 mg $CaCO_3$.

d. Standard sodium hydroxide titrant, 0.02*N:* Dilute 200 mL 0.1*N* NaOH to 1000 mL and store in a polyolefin bottle protected from atmospheric CO_2 by a soda lime tube or tight cap. Standardize against $KHC_8H_4O_4$ as directed in ¶ 3*c*, using 15.00 mL $KHC_8H_4O_4$ solution and a 50-mL buret. Calculate normality as above (¶ 3*c*); 1 mL = 1.00 mg $CaCO_3$.

e. Hydrogen peroxide, H_2O_2, 30%.

f. Bromphenol blue indicator solution, pH 3.7 indicator: Dissolve 100 mg bromphenol blue, sodium salt, in 100 mL water.

g. Metacresol purple indicator solution, pH 8.3 indicator: Dissolve 100 mg metacresol purple in 100 mL water.

h. Phenolphthalein indicator solution, alcoholic, pH 8.3 indicator.

i. Sodium thiosulfate, 0.1*M:* Dissolve 25 g $Na_2S_2O_3 \cdot 5H_2O$ and dilute to 1000 mL with distilled water.

4. Procedure

If sample is free from hydrolyzable metal ions and reduced forms of polyvalent cations, proceed with analysis according to *b*, *c*, or *d*. If sample is known or suspected to contain such substances, pretreat according to *a*.

a. Hot peroxide treatment: Pipet a suitable sample (see ¶ 1*e*) into titration flasks. Measure pH. If pH is above 4.0 add 5-mL increments of 0.02*N* sulfuric acid (H_2SO_4) (Section 2320B.3*c*) to reduce pH to 4 or less. Remove electrodes. Add 5 drops 30% H_2O_2 and boil for 2 to 5 min. Cool to room temperature and titrate with standard alkali to pH 8.3 according to the procedure of 4*d*.

b. Color change: Select sample size and normality of titrant according to criteria of ¶ 1*e*. Adjust sample to room temperature, if necessary, and with a pipet discharge sample into an erlenmeyer flask, while keeping pipet tip near flask bottom. If free residual chlorine is present add 0.05 mL (1 drop) 0.1*M* $Na_2S_2O_3$ solution, or destroy with ultraviolet radiation. Add 0.2 mL (5 drops) indicator solution and titrate over a white surface to a persistent color change characteristic of the equivalence point. Commercial indicator solutions or solids designated for the appropriate pH range (3.7 or 8.3) may be used. Check color at end point by adding the same concentration of indicator used with sample to a buffer solution at the designated pH.

c. Potentiometric titration curve:

1) Rinse electrodes and titration vessel with distilled water and drain. Select sample size and

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normality of titrant according to the criteria of ¶ 1*e*. Adjust sample to room temperature, if necessary, and with a pipet discharge sample while keeping pipet tip near the titration vessel bottom.

2) Measure sample pH. Add standard alkali in increments of 0.5 mL or less, such that a change of less than 0.2 pH units occurs per increment. After each addition, mix thoroughly but gently with a magnetic stirrer. Avoid splashing. Record pH when a constant reading is obtained. Continue adding titrant and measure pH until pH 9 is reached. Construct the titration curve by plotting observed pH values versus cumulative milliliters titrant added. A smooth curve showing one or more inflections should be obtained. A ragged or erratic curve may indicate that equilibrium was not reached between successive alkali additions. Determine acidity relative to a particular pH from the curve.

d. Potentiometric titration to pH 3.7 or 8.3: Prepare sample and titration assembly as specified in ¶ 4*c*1). Titrate to preselected end-point pH (¶ 1*d*) without recording intermediate pH values. As the end point is approached make smaller additions of alkali and be sure that pH equilibrium is reached before making the next addition.

5. Calculation

$$\text{Acidity, as mg } CaCO_3/L = \frac{[(A \times B) - (C \times D)] \times 50\,000}{\text{mL sample}}$$

where:

A = mL NaOH titrant used,
B = normality of NaOH,
C = mL H_2SO_4 used (¶ 4*a*), and
D = normality of H_2SO_4.

Report pH of the end point used, as follows: ‘‘The acidity to pH _____ = _____ mg $CaCO_3$/L.’’ If a negative value is obtained, report the value as negative. The absolute value of this negative value should be equivalent to the net alkalinity.

6. Precision and Bias

No general statement can be made about precision because of the great variation in sample characteristics. The precision of the titration is likely to be much greater than the uncertainties involved in sampling and sample handling before analysis.

Forty analysts in 17 laboratories analyzed synthetic water samples containing increments of bicarbonate equivalent to 20 mg $CaCO_3$/L. Titration according to the procedure of ¶ 4*d* gave a standard deviation of 1.8 mg $CaCO_3$/L, with negligible bias. Five laboratories analyzed two

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samples containing sulfuric, acetic, and formic acids and aluminum chloride by the procedures of ¶s 4*b* and 4*d*. The mean acidity of one sample (to pH 3.7) was 487 mg $CaCO_3$/L, with a standard deviation of 11 mg/L. The bromphenol blue titration of the same sample was 90 mg/L greater, with a standard deviation of 110 mg/L. The other sample had a potentiometric titration of 547 mg/L, with a standard deviation of 54 mg/L, while the corresponding indicator result was 85 mg/L greater, with a standard deviation of 56 mg/L. The major difference between the samples was the substitution of ferric ammonium citrate, in the second sample, for part of the aluminum chloride.

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2320 ALKALINITY*#(29)

2320 A. Introduction

1. Discussion

Alkalinity of a water is its acid-neutralizing capacity. It is the sum of all the titratable bases. The measured value may vary significantly with the end-point pH used. Alkalinity is a measure of an aggregate property of water and can be interpreted in terms of specific substances only when the chemical composition of the sample is known.

Alkalinity is significant in many uses and treatments of natural waters and wastewaters. Because the alkalinity of many surface waters is primarily a function of carbonate, bicarbonate, and hydroxide content, it is taken as an indication of the concentration of these constitutents. The measured values also may include contributions from borates, phosphates, silicates, or other bases if these are present. Alkalinity in excess of alkaline earth metal concentrations is significant in determining the suitability of a water for irrigation. Alkalinity measurements are used in the interpretation and control of water and wastewater treatment processes. Raw domestic wastewater has an alkalinity less than, or only slightly greater than, that of the water supply. Properly operating anaerobic digesters typically have supernatant alkalinities in the range of 2000 to 4000 mg calcium carbonate ($CaCO_3$)/L.[1]

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2320 B. Titration Method

1. General Discussion

a. Principle: Hydroxyl ions present in a sample as a result of dissociation or hydrolysis of solutes react with additions of standard acid. Alkalinity thus depends on the end-point pH used. For methods of determining inflection points from titration curves and the rationale for titrating to fixed pH end points, see Section 2310B.1*a*.

For samples of low alkalinity (less than 20 mg $CaCO_3$/L) use an extrapolation technique based on the near proportionality of concentration of hydrogen ions to excess of titrant beyond the equivalence point. The amount of standard acid required to reduce pH exactly 0.30 pH unit is measured carefully. Because this change in pH corresponds to an exact doubling of the hydrogen ion concentration, a simple extrapolation can be made to the equivalence point.[1,2]

b. End points: When alkalinity is due entirely to carbonate or bicarbonate content, the pH at the equivalence point of the titration is determined by the concentration of carbon dioxide (CO_2) at that stage. CO_2 concentration depends, in turn, on the total carbonate species originally present and any losses that may have occurred during titration. The pH values in Table 2320:I are suggested as the equivalence points for the corresponding alkalinity concentrations as milligrams $CaCO_3$ per liter. ‘‘Phenolphthalein alkalinity’’ is the term traditionally used for the quantity measured by titration to pH 8.3 irrespective of the colored indicator, if any, used in the determination. Phenolphthalein or metacresol purple may be used for alkalinity titration to pH 8.3. Bromcresol green or a mixed bromcresol green-methyl red indicator may be used for pH 4.5.

c. Interferences: Soaps, oily matter, suspended solids, or precipitates may coat the glass electrode and cause a sluggish response. Allow additional time between titrant additions to let electrode come to equilibrium or clean the electrodes occasionally. Do not filter, dilute, concentrate, or alter sample.

d. Selection of procedure: Determine sample alkalinity from volume of standard acid required to titrate a portion to a designated pH taken from ¶ 1*b*. Titrate at room temperature with a properly calibrated pH meter or electrically operated titrator, or use color indicators. If using color indicators, prepare and titrate an indicator blank.

Report alkalinity less than 20 mg $CaCO_3$/L only if it has been determined by the low-alkalinity method of ¶ 4*d*.

Construct a titration curve for standardization of reagents.

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Color indicators may be used for routine and control titrations in the absence of interfering color and turbidity and for preliminary titrations to select sample size and strength of titrant (see below).

e. Sample size: See Section 2310B.1*e* for selection of size sample to be titrated and normality of titrant, substituting 0.02*N* or 0.1*N* sulfuric (H_2SO_4) or hydrochloric (HCl) acid for the standard alkali of that method. For the low-alkalinity method, titrate a 200-mL sample with 0.02*N* H_2SO_4 from a 10-mL buret.

f. Sampling and storage: See Section 2310B.1 *f*.

2. Apparatus

See Section 2310B.2.

3. Reagents

a. Sodium carbonate solution, approximately 0.05*N:* Dry 3 to 5 g primary standard Na_2CO_3 at 250°C for 4 h and cool in a desiccator. Weigh 2.5 ± 0.2 g (to the nearest mg), transfer to a 1-L volumetric flask, fill flask to the mark with distilled water, and dissolve and mix reagent. Do not keep longer than 1 week.

b. Standard sulfuric acid or hydrochloric acid, 0.1*N:* Prepare acid solution of approximate normality as indicated under Preparation of Desk Reagents. Standardize against 40.00 mL 0.05*N* Na_2CO_3 solution, with about 60 mL water, in a beaker by titrating potentiometrically to pH of about 5. Lift out electrodes, rinse into the same beaker, and boil gently for 3 to 5 min under a watch glass cover. Cool to room temperature, rinse cover glass into beaker, and finish titrating to the pH inflection point. Calculate normality:

$$\text{Normality, } N = \frac{A \times B}{53.00 \times C}$$

where:

A = g Na_2CO_3 weighed into 1-L flask,
B = mL Na_2CO_3 solution taken for titration, and
C = mL acid used.

Use measured normality in calculations or adjust to 0.1000*N*; 1 mL 0.1000*N* solution = 5.00 mg $CaCO_3$.

c. Standard sulfuric acid or hydrochloric acid, 0.02*N:* Dilute 200.00 mL 0.1000*N* standard acid to 1000 mL with distilled or deionized water. Standardize by potentiometric titration of

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15.00 mL 0.05*N* Na_2CO_3 according to the procedure of ¶ 3*b*; 1 mL = 1.00 mg $CaCO_3$.

d. Bromcresol green indicator solution, pH 4.5 indicator: Dissolve 100 mg bromcresol green, sodium salt, in 100 mL distilled water.

e. Mixed bromcresol green-methyl red indicator solution:[3] Use either the aqueous or the alcoholic solution:

1) Dissolve 100 mg bromcresol green sodium salt and 20 mg methyl red sodium salt in 100 mL distilled water.

2) Dissolve 100 mg bromcresol green and 20 mg methyl red in 100 mL 95% ethyl alcohol or isopropyl alcohol.

f. Metacresol purple indicator solution, pH 8.3 indicator: Dissolve 100 mg metacresol purple in 100 mL water.

g. Phenolphthalein solution, alcoholic, pH 8.3 indicator.

h. Sodium thiosulfate, 0.1*N:* See Section 2310B.3*i*.

4. Procedure

a. Color change: See Section 2310B.4*b*.

b. Potentiometric titration curve: Follow the procedure for determining acidity (Section 2310B.4*c*), substituting the appropriate normality of standard acid solution for standard NaOH, and continue titration to pH 4.5 or lower. Do not filter, dilute, concentrate, or alter the sample.

c. Potentiometric titration to preselected pH: Determine the appropriate end-point pH according to ¶ 1*b*. Prepare sample and titration assembly (Section 2310B.4*c*). Titrate to the end-point pH without recording intermediate pH values and without undue delay. As the end point is approached make smaller additions of acid and be sure that pH equilibrium is reached before adding more titrant.

d. Potentiometric titration of low alkalinity: For alkalinities less than 20 mg/L titrate 100 to 200 mL according to the procedure of ¶ 4*c*, above, using a 10-mL microburet and 0.02*N* standard acid solution. Stop the titration at a pH in the range 4.3 to 4.7 and record volume and exact pH. Carefully add additional titrant to reduce the pH exactly 0.30 pH unit and again record volume.

5. Calculations

a. Potentiometric titration to end-point pH:

$$\text{Alkalinity, mg } CaCO_3/L = \frac{A \times N \times 50\,000}{\text{mL sample}}$$

where:

A = mL standard acid used and

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N = normality of standard acid

or

$$\text{Alkalinity, mg } CaCO_3/L = \frac{A \times t \times 1000}{\text{mL sample}}$$

where:

t = titer of standard acid, mg $CaCO_3$/mL.

Report pH of end point used as follows: ‘‘The alkalinity to pH _____ = _____ mg $CaCO_3$/L’’ and indicate clearly if this pH corresponds to an inflection point of the titration curve.

b. Potentiometric titration of low alkalinity:

Total alkalinity, mg $CaCO_3$/L

$$= \frac{(2B - C) \times N \times 50\,000}{\text{mL sample}}$$

where:

B = mL titrant to first recorded pH,
C = total mL titrant to reach pH 0.3 unit lower, and
N = normality of acid.

c. Calculation of alkalinity relationships: The results obtained from the phenolphthalein and total alkalinity determinations offer a means for stoichiometric classification of the three principal forms of alkalinity present in many waters. The classification ascribes the entire alkalinity to bicarbonate, carbonate, and hydroxide, and assumes the absence of other (weak) inorganic or organic acids, such as silicic, phosphoric, and boric acids. It further presupposes the incompatibility of hydroxide and bicarbonate alkalinities. Because the calculations are made on a stoichiometric basis, ion concentrations in the strictest sense are not represented in the results, which may differ significantly from actual concentrations especially at pH > 10. According to this scheme:

1) Carbonate (CO_3^{2-}) alkalinity is present when phenolphthalein alkalinity is not zero but is less than total alkalinity.

2) Hydroxide (OH^-) alkalinity is present if phenolphthalein alkalinity is more than half the total alkalinity.

3) Bicarbonate (HCO_3^-) alkalinity is present if phenolphthalein alkalinity is less than half the

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total alkalinity. These relationships may be calculated by the following scheme, where *P* is phenolphthalein alkalinity and *T* is total alkalinity (¶ 1*b*):

Select the smaller value of *P* or (*T* –*P*). Then, carbonate alkalinity equals twice the smaller value. When the smaller value is *P*, the balance (*T* –2*P*) is bicarbonate. When the smaller value is (*T*–*P*), the balance (2*P*–*T*) is hydroxide. All results are expressed as $CaCO_3$. The mathematical conversion of the results is shown in Table 2320:II. (A modification of Table 2320:II that is more accurate when $P \simeq {}^1/_2T$ has been proposed.[4])

Alkalinity relationships also may be computed nomographically (see Carbon Dioxide, Section 4500-CO_2). Accurately measure pH, calculate OH^- concentration as milligrams $CaCO_3$ per liter, and calculate concentrations of CO_3^{2-} and HCO_3^- as milligrams $CaCO_3$ per liter from the OH^- concentration, and the phenolphthalein and total alkalinities by the following equations:

$$CO_3^{2-} = 2P - 2[OH^-]$$

$$HCO_3^- = T - 2P + [OH^-]$$

Similarly, if difficulty is experienced with the phenolphthalein end point, or if a check on the phenolphthalein titration is desired, calculate phenolphthalein alkalinity as $CaCO_3$ from the results of the nomographic determinations of carbonate and hydroxide ion concentrations:

$$P = 1/2\ [CO_3^{2-}] + [OH^-]$$

6. Precision and Bias

No general statement can be made about precision because of the great variation in sample characteristics. The precision of the titration is likely to be much greater than the uncertainties involved in sampling and sample handling before the analysis.

In the range of 10 to 500 mg/L, when the alkalinity is due entirely to carbonates or bicarbonates, a standard deviation of 1 mg $CaCO_3$/L can be achieved. Forty analysts in 17 laboratories analyzed synthetic samples containing increments of bicarbonate equivalent to 120 mg $CaCO_3$/L. The titration procedure of ¶ 4*b* was used, with an end point pH of 4.5. The standard deviation was 5 mg/L and the average bias (lower than the true value) was 9 mg/L.[5]

Sodium carbonate solutions equivalent to 80 and 65 mg $CaCO_3$/L were analyzed by 12 laboratories according to the procedure of ¶ 4*c*.[6] The standard deviations were 8 and 5 mg/L, respectively, with negligible bias.[6] Four laboratories analyzed six samples having total alkalinities of about 1000 mg $CaCO_3$/L and containing various ratios of carbonate/bicarbonate by the procedures of both ¶ 4*a* and ¶ 4*c*. The pooled standard deviation was 40 mg/L, with negligible difference between the procedures.

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2330 CALCIUM CARBONATE SATURATION*#(30)

2330 A. Introduction

1. General Discussion

Calcium carbonate ($CaCO_3$) saturation indices commonly are used to evaluate the scale-forming and scale-dissolving tendencies of water. Assessing these tendencies is useful in corrosion control programs and in preventing $CaCO_3$ scaling in piping and equipment such as industrial heat exchangers or domestic water heaters.

Waters oversaturated with respect to $CaCO_3$ tend to precipitate $CaCO_3$. Waters undersaturated with respect to $CaCO_3$ tend to dissolve $CaCO_3$. Saturated waters, i.e., waters in equilibrium with

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$CaCO_3$, have neither $CaCO_3$-precipitating nor $CaCO_3$-dissolving tendencies. Saturation represents the dividing line between ‘‘precipitation likely’’ and ‘‘precipitation not likely.’’

Several water quality characteristics must be measured to calculate the $CaCO_3$ saturation indices described here. Minimum requirements are total alkalinity (2320), total calcium (3500-Ca), pH (4500-H^+), and temperature (2550). The ionic strength also must be calculated or estimated from conductivity (2510) or total dissolved solids (2540C) measurements. Measure pH at the system’s water temperature using a temperature-compensated pH meter. If pH is measured at a different temperature, for example in the laboratory, correct the measured pH.[1-3] In measuring pH and alkalinity, minimize CO_2 exchange between sample and atmosphere. Ideally, seal the sample from the atmosphere during measurements[4]; at a minimum, avoid vigorous stirring of unsealed samples.

There are two general categories of $CaCO_3$ saturation indices: indices that determine whether a water has a *tendency* to precipitate $CaCO_3$ (i.e., is oversaturated) or to dissolve $CaCO_3$ (i.e., is undersaturated) and indices that estimate the *quantity* of $CaCO_3$ that can be precipitated from an oversaturated water and the amount that can be dissolved by an undersaturated water. Indices in the second category generally yield more information but are more difficult to determine.

2. Limitations

It is widely assumed that $CaCO_3$ will precipitate from oversaturated waters and that it cannot be deposited from undersaturated waters. Exceptions may occur. For example, $CaCO_3$ deposition from oversaturated waters is inhibited by the presence of phosphates (particularly polyphosphates), certain naturally occurring organics, and magnesium.[5-7] These materials can act as sequestering agents or as crystal poisons. Conversely, $CaCO_3$ deposits have been found in pipes conveying undersaturated water. This apparent contradiction is caused by high pH (relative to the bulk water pH) in the immediate vicinity of certain areas (cathodes) of corroding metal surfaces. A locally oversaturated condition may occur even if the bulk water is undersaturated. A small, but significant, amount of $CaCO_3$ can be deposited.

The calculations referred to here, even the most sophisticated computerized calculations, do not adequately describe these exceptions. For this reason, do not consider saturation indices as absolutes. Rather, view them as guides to the behavior of $CaCO_3$ in aqueous systems and supplement them, where possible, with experimentally derived information.

Similarly, the effects predicted by the indices do not always conform to expectations. The relationship between the indices and corrosion rates is a case in point. Conceptually, piping is protected when $CaCO_3$ is precipitated on its surfaces. $CaCO_3$ is believed to inhibit corrosion by clogging reactive areas and by providing a matrix to retain corrosion products, thus further sealing the surfaces. Waters with positive indices traditionally have been assumed to be protective while waters with negative indices have been assumed to be not protective, or

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corrosive. The expected relationship is observed sometimes,[8,9] but not always.[10,11] Unexpected results may be due in part to limited capability to predict $CaCO_3$ behavior. Also, water characteristics not directly involved in the calculation of the indices (e.g., dissolved oxygen, buffering intensity, chloride, sulfate, and water velocity) may influence corrosion rates appreciably.[9,12-16] Thus, do not estimate corrosion rates on the basis of $CaCO_3$ indices alone.

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2330 B. Indices Indicating Tendency of a Water to Precipitate $CaCO_3$ or Dissolve $CaCO_3$

1. General Discussion

Indices that indicate $CaCO_3$ precipitation or dissolution tendencies define whether a water is oversaturated, saturated, or undersaturated with respect to $CaCO_3$. The most widely used indices are the Saturation Index (SI): the Relative Saturation (RS), also known as the Driving Force Index (DFI); and the Ryznar Index (RI). The SI is by far the most commonly used and will be described here. The RS and SI are related (see Equation 6, Section 2330D). The RI[1] has been used for many years, sometimes with good results. Because it is semi-empirical it may be less reliable than the SI.

2. Saturation Index by Calculation

SI is determined from Equation 1.

$$SI = pH - pH_s \qquad (1)$$

where:

pH = measured pH and
pH_s = pH of the water if it were in equilibrium with $CaCO_3$ at the existing calcium ion [Ca^{2+}] and bicarbonate ion [HCO_3^-] concentrations.

A positive SI connotes a water oversaturated with respect to $CaCO_3$. A negative SI signifies an undersaturated water. An SI of zero represents a water in equilibrium with $CaCO_3$.

a. Analytical solution for pH_s: Determine pH_s as follows[2]:

$$pH_s = pK_2 - pK_s + p[Ca^{2+}] + p[HCO_3^-] + 5\,pf_m \qquad (2)$$

where:

K_2 = second dissociation constant for carbonic acid, at the water temperature,
K_s = solubility product constant for $CaCO_3$ at the water temperature,

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$[Ca^{2+}]$ = calcium ion concentration, g-moles/L,
$[HCO_3^-]$ = bicarbonate ion concentration, g-moles/L, and
f_m = activity coefficient for monovalent species at the specified temperature.

In Equation 2, *p* preceding a variable designates $-\log_{10}$ of that variable.

Calculate values of pK_2, pK_s, and pf_m required to solve Equation 2 from the equations in Table 2330:I. To save computation time, values for pK_2 and pK_s have been precalculated for selected temperatures (see Table 2330:II).

Table 2330:II gives several values for pK_s. Different isomorphs of $CaCO_3$ can form in aqueous systems, including calcite, aragonite, and vaterite. Each has somewhat different solubility properties. These differences can be accommodated when computing pH_s simply by using the pK_s for the compound most likely to form. The form of $CaCO_3$ most commonly found in fresh water is calcite. Use the pK_s for calcite unless it is clear that a different form of $CaCO_3$ controls $CaCO_3$ solubility.

Estimate calcium ion concentration from total calcium measurements with Equation 3.

$$[Ca^{2+}] = Ca_t - Ca_{ip} \qquad (3)$$

where:

Ca_t = total calcium, g-moles/L, and
Ca_{ip} = calcium associated with ion pairs such as $CaHCO_3^+$, $CaSO_4^0$, and $CaOH^+$.

Calcium associated with ion pairs is not available to form $CaCO_3$.

Estimate $[HCO_3^-]$, the bicarbonate ion concentration, from Equation 4.

$$[HCO_3^-] = \frac{Alk_t - Alk_o + 10^{(pf_m - pH)} - 10^{(pH + pf_m - pK_w)}}{1 + 0.5 \times 10^{(pH - pK_2)}} \qquad (4)$$

where:

Alk_t = total alkalinity, as determined by acid titration to the carbonic acid end point, g-equivalents/L,
K_w = dissociation constant for water, at the water temperature, and
Alk_o = alkalinity contributed by NH_3^0, $H_3SiO_4^-$, HPO_4^{2-}, $B(OH)_4^-$, CH_3COO^- (acetate), HS^-, and ion pairs such as $CaHCO_3^+$ and $MgOH^+$. These contributions usually are small compared to the contributions of components normally considered (HCO_3^-, CO_3^{2-},OH^-,

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and H^+).

Calculations can be simplified. For example, in Equation 4, terms containing exponents (e.g., $10^{(pH + pf_{m-pkw})}$) usually can be neglected for waters that are approximately neutral (pH 6.0 to 8.5) with alkalinity greater than about 50 mg/L as $CaCO_3$. The terms Ca_{ip} in Equation 3 and Alk_o in Equation 4 are difficult to calculate without computers. Therefore they usually are neglected for hand calculations. The simplified version of Equation 2 under such conditions is:

$$pH_s = pK_2 - pK_s + p[Ca_t] + p[Alk_t] + 5\,pf_m$$

1) Sample calculation—The calculation is best illustrated by working through an example. Assume that calcite controls $CaCO_3$ solubility and determine the SI for a water of the following composition:

	Concentration				
Constituent	**mg**	**÷**	**mg mole**	**=**	***g-moles/L***
Calcium	152		40 000		3.80×10^{-3}
Magnesium	39		24 312		1.60×10^{-3}
Sodium	50		22 989		2.18×10^{-3}
Potassium	5		39 102		1.28×10^{-4}
Chloride	53		35 453		1.49×10^{-3}
Alkalinity (as $CaCO_3$)	130		50 000		2.60×10^{-3}*
Sulfate	430		96 060		4.48×10^{-3}
Silica (as SiO_2)	15		60 084		2.50×10^{-4}

*g-equivalents.
Water temperature = 20°C (293.2°K); pH = 9.00.

Before evaluating pf_m in Equation 2, determine the ionic strength (I) and another constant (A). Estimate ionic strength from the first equation of Table 2330:I, assuming all the alkalinity is due to bicarbonate ion. Use the alkalinity concentration (2.60×10^{-3}) and the bicarbonate charge (–1) to calculate the contribution of alkalinity to ionic strength. Assume silica is mostly H_4SiO_4. Because H_4SiO_4 has zero charge, silica does not contribute to ionic strength.

$$I = 0.5\,[4(3.80 \times 10^{-3}) + 4(1.60 \times 10^{-3}) + 2.18 \times 10^{-3} +$$

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$$1.28 \times 10^{-4} + 1.49 \times 10^{-3} + 2.60 \times 10^{-3} + 4(4.48 \times 10^{-3})]$$
$$= 2.29 \times 10^{-2} \text{ g-moles/L}$$

In the absence of a complete water analysis, estimate ionic strength from conductivity or total dissolved solids measurements (see alternative equations, Table 2330:I).

Estimate A from the equation in Table 2330:I, after first determining the dielectric constant E from the formula in the same table. Alternatively, use precalculated values of A in Table 2330:II. In Table 2330:II, $A = 0.506$ at 20°C.

Next estimate pf_m from the equation in Table 2330:I

$$pf_m = 0.506 \times \left[\frac{\sqrt{2.29 \times 10^{-2}}}{1 + \sqrt{2.29 \times 10^{-2}}} - 0.3\,(2.29 \times 10^{-2}) \right] = 0.063$$

Determine $[HCO_3^-]$ from Equation 4. Neglect Alk_o, but because the pH exceeds 8.5, calculate the other terms. From Table 2330:II, $pK_2 = 10.38$ and $pK_w = 14.16$.

$$[HCO_3^-] = \frac{2.60 \times 10^{-3} + 10^{(0.063 - 9.0)} - 10^{(9.0 + 0.063 - 14.16)}}{1 + 0.5 \times 10^{(9.0 - 10.38)}} = 2.54 \times 10^{-3} \text{ g-moles/L}$$

Therefore $p[HCO_3^-] = 2.60$.

Determine $[Ca^{2+}]$ from Equation 3. Neglect $Ca_{ip.}$

$$[Ca^{2+}] = Ca_t = 3.80 \times 10^{-3} \text{ g-moles/L}$$

Therefore $p[Ca^{2+}] = 2.42$.

From Table 2330:II, pK_s for calcite is 8.45.

Determine pH_s from Equation 2:

$$pH_s = 10.38 - 8.45 + 2.42 + 2.60 + 5\,(0.063) = 7.27$$

And finally, determine SI from Equation 1:

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$$SI = 9.00 - 7.27 = 1.73$$

The positive *SI* indicates the water is oversaturated with respect to calcite.

2) Effect of neglecting Ca_{ip} and Alk_o—If Ca_{ip} is neglected, pH_s is underestimated and *SI* is overestimated by an amount equal to $p(1 - Y_{Ca_{ip}})$, where $Y_{Ca_{ip}}$ is the fraction of total calcium in ion pairs. For example, if $Y_{Ca_{ip}} = 0.30$ then the estimate for *SI* is 0.15 units too high. Similarly, if Alk_o is neglected, *SI* is overestimated by an amount equal to $p(1-Y_{Alk_o})$, where Y_{Alk_o} is the fraction of total alkalinity contributed by species other than HCO_3^-, CO_3^{2-}, OH^-, and H^+. The effects of neglecting Ca_{ip} and Alk_o are additive.

Ca_{ip} and Alk_o may be neglected if the factors $Y_{Ca_{ip}}$ and Y_{Alk_o} are small and do not interfere with interpretation of the *SI*. The factors are small for waters of low and neutral pH, but they increase as pH values approach and exceed 9. At high pH values, however, the *SI* is typically much larger than its overestimate, so neglecting Ca_{ip} and Alk_o causes no problem. To return to the example above, when calculations were done with a computerized water chemistry code (SEQUIL) (see Table 2330:III) that considers Ca_{ip} and Alk_o, the *SI* was 1.48, i.e., 0.25 units lower than the result obtained by hand calculations. In this instance, neglecting Ca_{ip} and Alk_o did not interfere with interpreting the result. Both calculations showed the water to be strongly oversaturated.

The potential for misinterpretation is most acute in nearly-saturated waters of high sulfate concentration. Recirculating cooling water is an example. Calcium is sequestered by the robust $CaSO_4^0$ ion pair and the *SI* can be overestimated by as much as 0.3 to 0.5 units, even at neutral pH. Under these conditions, the *SI* may be thought to be zero (neither scale-forming or corrosive) when in fact it is negative.

Resolve this problem by determining pH_s using computerized water chemistry codes that consider ion pairs and the other forms of alkalinity. Section 2330D provides information about water chemistry codes. The most accurate calculations are obtained when a complete mineral analysis is provided.

An alternative but somewhat less rigorous procedure involves direct measurement of (Ca^{2+}), the calcium ion activity, with a calcium specific-ion electrode.[9] Use Equation 5 to determine $p[Ca^{2+}]$; then use $p[Ca^{2+}]$ in Equation 2.

$$p[Ca^{2+}] = p(Ca^{2+}) - 4pf_m \qquad (5)$$

This approach eliminates the need to determine Ca_{ip}. However, no equivalent procedure is available to bypass the determination of Alk_o.

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b. Graphical solutions for pH_s: Caldwell-Lawrence diagrams can be used to determine pH_s.[10-12] The diagrams are particularly useful for estimating chemical dosages needed to achieve desired water conditions. Consult the references for descriptions of how to use the diagrams; see Section 2330D for additional information about the diagrams.

3. Saturation Index by Experimental Determination

a. Saturometry: Saturometers were developed to measure the relative saturation of seawater with respect to $CaCO_3$. A water of known calcium and pH is equilibrated with $CaCO_3$ in a sealed flask containing a pH electrode. The water temperature is controlled with a constant-temperature bath. During equilibration the pH decreases if $CaCO_3$ precipitates and increases if $CaCO_3$ dissolves. When the pH stops changing, equilibrium is said to have been achieved. The initial pH and calcium values and the final pH value are used to calculate the relative saturation (RS).[13] Equation 6, Section 2330D, may then be used to determine SI.

A major advantage of this method is that the approach to equilibrium can be tracked by measuring pH, thus minimizing uncertainty about the achievement of equilibrium. The method is most sensitive in the range of minimum buffering intensity (pH 7.5 to 8.5). The calculations do not consider ion pairs or noncarbonate alkalinity, except borate. The technique has been used for *in situ* oceanographic measurements[14] as well as in the laboratory.

The saturometry calculations discussed above use K_s of the $CaCO_3$ phase assumed to control solubility. Uncertainties occur if the identity of the controlling solid is unknown. Resolve these uncertainties by measuring K_s of the controlling solid. It is equal to the $CaCO_3$ activity product, $[Ca^{2+}] \times [CO_3^{2-}]$, at equilibrium. Calculate the latter from the equilibrium pH and initial calcium, alkalinity, and pH measurements.[15]

b. Alkalinity difference technique:[16] *SI* also can be determined by equilibrating water of known pH, calcium, and alkalinity with $CaCO_3$ in a sealed, constant-temperature system. The $CaCO_3$ activity product before equilibration is determined from initial calcium, pH, and alkalinity (or total carbonate) values. The $CaCO_3$ solubility product constant (K_s) equals the $CaCO_3$ activity product after equilibration, which is determined by using the alkalinity change that occurred during equilibration. *RS* is found by dividing the initial activity product by K_s. Calculate *SI* by using Equation 6 (see Section 2330D.1). The advantage of this method is that it makes no assumptions about the identity of the $CaCO_3$ phase. However it is more difficult to determine when equilibrium is achieved with this method than with the saturometry method.

Whatever the method used, use the temperatures that are the same as the temperature of the water source. Alternatively, correct test results to the temperature of the water source.[16]

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2330 C. Indices Predicting the Quantity of $CaCO_3$ That Can Be Precipitated or Dissolved

The Calcium Carbonate Precipitation Potential (CCPP) predicts both tendency to precipitate or to dissolve $CaCO_3$ and quantity that may be precipitated or dissolved. The CCPP also is known by other names, e.g., Calcium Carbonate Precipitation Capacity (CCPC).

The CCPP is defined as the quantity of $CaCO_3$ that theoretically can be precipitated from oversaturated waters or dissolved by undersaturated waters during equilibration.[1] The amount that actually precipitates or dissolves may be less, because equilibrium may not be achieved. The CCPP is negative for undersaturated waters, zero for saturated waters, and positive for oversaturated waters.

1. Calculating CCPP

The CCPP does not lend itself to hand calculations. Preferably calculate CCPP with computerized water chemistry models and Caldwell-Lawrence diagrams (see Section 2330D).

The most reliable calculations consider ion pairs and the contribution to alkalinity of other species besides HCO_3^-, CO_3^{2-}, OH^-, and H^+. Models that do not consider these factors overestimate the amount of $CaCO_3$ that can be precipitated and underestimate the amount of $CaCO_3$ that can be dissolved.

2. Experimental Determination of CCPP

Estimate CCPP by one of several experimental techniques.

a. Saturometry: See Section 2330B. The CCPP is determined as part of the RS calculation.

b. Alkalinity difference technique: See Section 2330B. The CCPP equals the difference between alkalinity (or calcium) values of the initial and equilibrated water, when they are expressed as $CaCO_3$.

c. Marble test: The marble test[1-5] is similar to the alkalinity difference technique. The CCPP equals the change in alkalinity (or calcium) values during equilibration, when they are expressed as $CaCO_3$.

d. Enslow test: The Enslow test[5] is a continuous version of the alkalinity difference or marble tests. Water is fed continuously to a leveling bulb or separatory funnel partly filled with $CaCO_3$. The effluent from this device is filtered through crushed marble so that the filtrate is assumed to be in equilibrium with $CaCO_3$. The CCPP equals the change in alkalinity (or calcium) values that occurs during passage through the apparatus.

e. Calcium carbonate deposition test:[6] The calcium carbonate deposition test (CCDT) is an electrochemical method that measures the electric current produced when dissolved oxygen is

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reduced on a rotating electrode. When an oversaturated water is placed in the apparatus, $CaCO_3$ deposits on the electrode. The deposits interfere with oxygen transfer and the current diminishes. The rate of $CaCO_3$ deposition is directly proportional to the rate at which the current declines. The CCDT and the CCPP are related, but they are not the same. The CCDT is a rate, and the CCPP is a quantity.

For realistic assessments of the CCPP (or CCDT) keep test temperature the same as the temperature of the water source. Alternatively, correct test results to the temperature of the water source.

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2330 D. Diagrams and Computer Codes for $CaCO_3$ Indices

1. Description

Table 2330:III lists diagrams and computer codes that can be used to determine the SI and CCPP. It also provides a brief description of their characteristics.

Many computer codes do not calculate *SI* directly, but instead calculate the relative saturation (*RS*). When *RS* data are presented, calculate the *SI* from:[1]

$$SI = \log_{10} RS \qquad (6)$$

where:

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RS = ratio of $CaCO_3$ activity product to $CaCO_3$ solubility product constant.

The diagrams and a few of the codes define pH_s as the pH the water would exhibit if it were in equilibrium with $CaCO_3$ at the existing calcium and total alkalinity concentrations.[2] This definition of pH_s differs from the definition following Equation 1 because alkalinity is used instead of bicarbonate. Within the pH range 6 to 9, alkalinity-based pH_s and bicarbonate-based pH_s are virtually equal, because total alkalinity is due almost entirely to bicarbonate ion. Above pH 9 they differ and Equation 6 no longer applies if *SI* is calculated with alkalinity-based pH_s. However, if *SI* is determined from bicarbonate-based pH, Equation 6 continues to apply.

Furthermore, calculating *SI* with alkalinity-based pH_s reverses the sign of the *SI* above pH values of approximately pK_2, i.e., a positive, not the usual negative, *SI* connotes an undersaturated water.[3] With bicarbonate-based pH_s or RS, sign reversal does not occur, thereby eliminating the confusing sign change. For these reasons, bicarbonate-based pH_s or RS is preferred. Table 2330:III lists the definition of pH_s used for each code.

Some models calculate only the amount of $CaCO_3$ that can be precipitated but not the amount of $CaCO_3$ that can be dissolved. Others calculate both.

The diagrams and codes can be used to determine many more parameters than the $CaCO_3$ saturation indices. A fee may be charged for computer software or graphs. The information in Table 2330:III describes parameters each code uses to calculate *SI*. Contact the sources listed below the table for current information.

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2340 HARDNESS*#(31)

2340 A. Introduction

1. Definition

Originally, water hardness was understood to be a measure of the capacity of water to precipitate soap. Soap is precipitated chiefly by the calcium and magnesium ions present. Other polyvalent cations also may precipitate soap, but they often are in complex forms, frequently with organic constituents, and their role in water hardness may be minimal and difficult to define. In conformity with current practice, total hardness is defined as the sum of the calcium and magnesium concentrations, both expressed as calcium carbonate, in milligrams per liter.

When hardness numerically is greater than the sum of carbonate and bicarbonate alkalinity, that amount of hardness equivalent to the total alkalinity is called ‘‘carbonate hardness’’; the

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amount of hardness in excess of this is called ‘‘noncarbonate hardness.’’ When the hardness numerically is equal to or less than the sum of carbonate and bicarbonate alkalinity, all hardness is carbonate hardness and noncarbonate hardness is absent. The hardness may range from zero to hundreds of milligrams per liter, depending on the source and treatment to which the water has been subjected.

2. Selection of Method

Two methods are presented. Method B, hardness by calculation, is applicable to all waters and yields the higher accuracy. If a mineral analysis is performed, hardness by calculation can be reported. Method C, the EDTA titration method, measures the calcium and magnesium ions and may be applied with appropriate modification to any kind of water. The procedure described affords a means of rapid analysis.

3. Reporting Results

When reporting hardness, state the method used, for example, ‘‘hardness (calc.)’’ or ‘‘hardness (EDTA).’’

2340 B. Hardness by Calculation

1. Discussion

The preferred method for determining hardness is to compute it from the results of separate determinations of calcium and magnesium.

2. Calculation

Hardness, mg equivalent $CaCO_3$/L = 2.497 [Ca, mg/L] + 4.118 [Mg, mg/L]

2340 C. EDTA Titrimetric Method

1. General Discussion

a. Principle: Ethylenediaminetetraacetic acid and its sodium salts (abbreviated EDTA) form a chelated soluble complex when added to a solution of certain metal cations. If a small amount of a dye such as Eriochrome Black T or Calmagite is added to an aqueous solution containing calcium and magnesium ions at a pH of 10.0 ± 0.1, the solution becomes wine red. If EDTA is added as a titrant, the calcium and magnesium will be complexed, and when all of the magnesium and calcium has been complexed the solution turns from wine red to blue, marking the end point of the titration. Magnesium ion must be present to yield a satisfactory end point. To insure this, a small amount of complexometrically neutral magnesium salt of EDTA is added to the buffer; this automatically introduces sufficient magnesium and obviates the need for a blank correction.

The sharpness of the end point increases with increasing pH. However, the pH cannot be

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increased indefinitely because of the danger of precipitating calcium carbonate, $CaCO_3$, or magnesium hydroxide, $Mg(OH)_2$, and because the dye changes color at high pH values. The specified pH of 10.0 ± 0.1 is a satisfactory compromise. A limit of 5 min is set for the duration of the titration to minimize the tendency toward $CaCO_3$ precipitation.

b. Interference: Some metal ions interfere by causing fading or indistinct end points or by stoichiometric consumption of EDTA. Reduce this interference by adding certain inhibitors before titration. MgCDTA [see 2*b*3)], selectively complexes heavy metals, releases magnesium into the sample, and may be used as a substitute for toxic or malodorous inhibitors. It is useful only when the magnesium substituted for heavy metals does not contribute significantly to the total hardness. With heavy metal or polyphosphate concentrations below those indicated in Table 2340:I, use Inhibitor I or II. When higher concentrations of heavy metals are present, determine calcium and magnesium by a non-EDTA method (see Section 3500-Ca and Section 3500-Mg) and obtain hardness by calculation. The figures in Table 2340:I are intended as a rough guide only and are based on using a 25-mL sample diluted to 50 mL.

Suspended or colloidal organic matter also may interfere with the end point. Eliminate this interference by evaporating the sample to dryness on a steam bath and heating in a muffle furnace at 550°C until the organic matter is completely oxidized. Dissolve the residue in 20 mL 1*N* hydrochloric acid (HCl), neutralize to pH 7 with 1*N* sodium hydroxide (NaOH), and make up to 50 mL with distilled water; cool to room temperature and continue according to the general procedure.

c. Titration precautions: Conduct titrations at or near normal room temperature. The color change becomes impractically slow as the sample approaches freezing temperature. Indicator decomposition becomes a problem in hot water.

The specified pH may produce an environment conducive to $CaCO_3$ precipitation. Although the titrant slowly redissolves such precipitates, a drifting end point often yields low results. Completion of the titration within 5 min minimizes the tendency for $CaCO_3$ to precipitate. The following three methods also reduce precipitation loss:

1) Dilute sample with distilled water to reduce $CaCO_3$ concentration. This simple expedient has been incorporated in the procedure. If precipitation occurs at this dilution of 1 + 1 use modification 2) or 3). Using too small a sample contributes a systematic error due to the buret-reading error.

2) If the approximate hardness is known or is determined by a preliminary titration, add 90% or more of titrant to sample *before* adjusting pH with buffer.

3) Acidify sample and stir for 2 min to expel CO_2 *before* pH adjustment. Determine alkalinity to indicate amount of acid to be added.

2. Reagents

a. Buffer solution:

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1) Dissolve 16.9 g ammonium chloride (NH_4Cl) in 143 mL conc ammonium hydroxide (NH_4OH). Add 1.25 g magnesium salt of EDTA (available commercially) and dilute to 250 mL with distilled water.

2) If the magnesium salt of EDTA is unavailable, dissolve 1.179 g disodium salt of ethylenediaminetetraacetic acid dihydrate (analytical reagent grade) and 780 mg magnesium sulfate ($MgSO_4 \cdot 7H_2O$) or 644 mg magnesium chloride ($MgCl_2 \cdot 6H_2O$) in 50 mL distilled water. Add this solution to 16.9 g NH_4Cl and 143 mL conc NH_4OH with mixing and dilute to 250 mL with distilled water. To attain the highest accuracy, adjust to exact equivalence through appropriate addition of a small amount of EDTA or $MgSO_4$ or $MgCl_2$.

Store Solution 1) or 2) in a plastic or borosilicate glass container for no longer than 1 month. Stopper tightly to prevent loss of ammonia (NH_3) or pickup of carbon dioxide (CO_2). Dispense buffer solution by means of a bulb-operated pipet. Discard buffer when 1 or 2 mL added to the sample fails to produce a pH of 10.0 ± 0.1 at the titration end point.

3) Satisfactory alternate ‘‘odorless buffers’’ also are available commercially. They contain the magnesium salt of EDTA and have the advantage of being relatively odorless and more stable than the NH_4Cl-NH_4OH buffer. They usually do not provide as good an end point as NH_4Cl-NH_4OH because of slower reactions and they may be unsuitable when this method is automated. Prepare one of these buffers by mixing 55 mL conc HCl with 400 mL distilled water and then, slowly and with stirring, adding 300 mL 2-aminoethanol (free of aluminum and heavier metals). Add 5.0 g magnesium salt of EDTA and dilute to 1 L with distilled water.

b. Complexing agents: For most waters no complexing agent is needed. Occasionally water containing interfering ions requires adding an appropriate complexing agent to give a clear, sharp change in color at the end point. The following are satisfactory:

1) *Inhibitor I:* Adjust acid samples to pH 6 or higher with buffer or 0.1*N* NaOH. Add 250 mg sodium cyanide (NaCN) in powder form. Add sufficient buffer to adjust to pH 10.0 ± 0.1. (CAUTION: *NaCN is extremely poisonous. Take extra precautions in its use.* Flush solutions containing this inhibitor down the drain with large quantities of water after insuring that no acid is present to liberate volatile poisonous hydrogen cyanide.)

2) *Inhibitor II:* Dissolve 5.0 g sodium sulfide nonahydrate ($Na_2S \cdot 9H_2O$) or 3.7 g $Na_2S \cdot 5H_2O$ in 100 mL distilled water. Exclude air with a tightly fitting rubber stopper. This inhibitor deteriorates through air oxidation. It produces a sulfide precipitate that obscures the end point when appreciable concentrations of heavy metals are present. Use 1 mL in ¶ 3*b* below.

3) *MgCDTA:* Magnesium salt of 1, 2-cyclohexanediaminetetraacetic acid. Add 250 mg per 100 mL sample and dissolve completely before adding buffer solution. Use this complexing agent to avoid using toxic or odorous inhibitors when interfering substances are present in concentrations that affect the end point but will not contribute significantly to the hardness value.

Commercial preparations incorporating a buffer and a complexing agent are available. Such

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mixtures must maintain pH 10.0 ± 0.1 during titration and give a clear, sharp end point when the sample is titrated.

c. Indicators: Many types of indicator solutions have been advocated and may be used if the analyst demonstrates that they yield accurate values. The prime difficulty with indicator solutions is deterioration with aging, giving indistinct end points. For example, alkaline solutions of Eriochrome Black T are sensitive to oxidants and aqueous or alcoholic solutions are unstable. In general, use the least amount of indicator providing a sharp end point. It is the analyst's responsibility to determine individually the optimal indicator concentration.

1) *Eriochrome Black T:* Sodium salt of 1-(1-hydroxy-2-naphthylazo)-5-nitro-2-naphthol-4-sulfonic acid; No. 203 in the Color Index. Dissolve 0.5 g dye in 100 g 2,2′,2″-nitrilotriethanol (also called triethanolamine) or 2-methoxymethanol (also called ethylene glycol monomethyl ether). Add 2 drops per 50 mL solution to be titrated. Adjust volume if necessary.

2) *Calmagite:* 1-(1-hydroxy-4-methyl-2-phenylazo)-2-naphthol-4-sulfonic acid. This is stable in aqueous solution and produces the same color change as Eriochrome Black T, with a sharper end point. Dissolve 0.10 g Calmagite in 100 mL distilled water. Use 1 mL per 50 mL solution to be titrated. Adjust volume if necessary.

3) Indicators 1 and 2 can be used in dry powder form if care is taken to avoid excess indicator. Prepared dry mixtures of these indicators and an inert salt are available commercially.

If the end point color change of these indicators is not clear and sharp, it usually means that an appropriate complexing agent is required. If NaCN inhibitor does not sharpen the end point, the indicator probably is at fault.

d. Standard EDTA titrant, 0.01*M*: Weigh 3.723 g analytical reagent-grade disodium ethylenediaminetetraacetate dihydrate, also called (ethylenedinitrilo)tetraacetic acid disodium salt (EDTA), dissolve in distilled water, and dilute to 1000 mL. Standardize against standard calcium solution (¶ 2*e*) as described in ¶ 3*b* below.

Because the titrant extracts hardness-producing cations from soft-glass containers, store in polyethylene (preferable) or borosilicate glass bottles. Compensate for gradual deterioration by periodic restandardization and by using a suitable correction factor.

e. Standard calcium solution: Weigh 1.000 g anhydrous $CaCO_3$ powder (primary standard or special reagent low in heavy metals, alkalis, and magnesium) into a 500-mL erlenmeyer flask. Place a funnel in the flask neck and add, a little at a time, 1 + 1 HCl until all $CaCO_3$ has dissolved. Add 200 mL distilled water and boil for a few minutes to expel CO_2. Cool, add a few drops of methyl red indicator, and adjust to the intermediate orange color by adding 3*N* NH_4OH or 1 + 1 HCl, as required. Transfer quantitatively and dilute to 1000 mL with distilled water; 1 mL = 1.00 mg $CaCO_3$.

f. Sodium hydroxide, NaOH, 0.1*N*.

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3. Procedure

a. Pretreatment of polluted water and wastewater samples: Use nitric acid-sulfuric acid or nitric acid-perchloric acid digestion (Section 3030).

b. Titration of sample: Select a sample volume that requires less than 15 mL EDTA titrant and complete titration within 5 min, measured from time of buffer addition.

Dilute 25.0 mL sample to about 50 mL with distilled water in a porcelain casserole or other suitable vessel. Add 1 to 2 mL buffer solution. Usually 1 mL will be sufficient to give a pH of 10.0 to 10.1. The absence of a sharp end-point color change in the titration usually means that an inhibitor must be added at this point (¶ 2*b* et seq.) or that the indicator has deteriorated.

Add 1 to 2 drops indicator solution or an appropriate amount of dry-powder indicator formulation [¶ 2*c*3)]. Add standard EDTA titrant slowly, with continuous stirring, until the last reddish tinge disappears. Add the last few drops at 3- to 5-s intervals. At the end point the solution normally is blue. Daylight or a daylight fluorescent lamp is recommended highly because ordinary incandescent lights tend to produce a reddish tinge in the blue at the end point.

If sufficient sample is available and interference is absent, improve accuracy by increasing sample size, as described in ¶ 3*c* below.

c. Low-hardness sample: For ion-exchanger effluent or other softened water and for natural wat ers of low hardness (less than 5 mg/L), take a larger sample, 100 to 1000 mL, for titration and add proportionately larger amounts of buffer, inhibitor, and indicator. Add standard EDTA titrant slowly from a microburet and run a blank, using redistilled, distilled, or deionized water of the same volume as the sample, to which identical amounts of buffer, inhibitor, and indicator have been added. Subtract volume of EDTA used for blank from volume of EDTA used for sample.

4. Calculation

$$\text{Hardness (EDTA) as mg } CaCO_3\text{/L} = \frac{A \times B \times 1000}{\text{mL sample}}$$

where:

A = mL titration for sample and
B = mg $CaCO_3$ equivalent to 1.00 mL EDTA titrant.

5. Precision and Bias

A synthetic sample containing 610 mg/L total hardness as $CaCO_3$ contributed by 108 mg Ca/L and 82 mg Mg/L, and the following supplementary substances: 3.1 mg K/L, 19.9 mg Na/L, 241 mg Cl^-/L, 0.25 mg NO_2^--N/L, 1.1 mg NO_3^--N/L, 259 mg SO_4^{2-}/L, and 42.5 mg total alkalinity/L (contributed by $NaHCO_3$) in distilled water was analyzed in 56 laboratories by the

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EDTA titrimetric method with a relative standard deviation of 2.9% and a relative error of 0.8%.

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2350 OXIDANT DEMAND/REQUIREMENT*#(32)

2350 A. Introduction

1. Significance and Chemistry

Oxidants are added to water supplies and wastewater primarily for disinfection. Other beneficial uses include slime removal, oxidation of undesirable inorganic species (e.g., ferrous ion, reduced manganese, sulfide, and ammonia) and oxidation of organic constituents (e.g., taste- and odor-producing compounds). Oxidant demand refers to the difference between the added oxidant dose and the residual oxidant concentration measured after a prescribed contact time at a given pH and temperature. Oxidant requirement refers to the oxidant dose required to achieve a given oxidant residual at a prescribed contact time, pH, and temperature.

The fate of oxidants in water and wastewater is complex. For example, chlorine reacts with sample constituents by three general pathways: oxidation, addition, and substitution. First, chlorine can oxidize reduced species, such as Fe^{2+}, Mn^{2+}, and sulfide. In these reactions, chlorine is reduced to inorganic chloride (Cl^-). Second, chlorine can add to olefins and other double-bond-containing organic compounds to produce chlorinated organic compounds. Third, chlorine can substitute onto chemical substrates. The addition and substitution reactions produce

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organochlorine species (e.g., chlorination of phenol to chlorophenols) or active chlorine species (e.g., chlorination of ammonia to produce monochloramine). Chlorine reacts with naturally occurring organic compounds by a combination of these mechanisms to generate such products as trihalomethanes. See Section 4500-Cl (chlorine), 4500-ClO_2 (chlorine dioxide), and 4500-O_3 (ozone) for additional information.

Oxidant demand and oxidant requirement are significantly affected by the chemical and physical characteristics of the sample and the manner in which the oxidant consumption is measured. In particular, oxidant reactivity is influenced by temperature, pH, contact time, and oxidant dose. Oxidant demand and oxidant requirement are defined operationally by the analytical method used to determine the residual oxidant concentration. *Report sample temperature, pH, contact time, oxidant dose, and analytical method with oxidant demand or oxidant requirement.* Sample temperature strongly affects reaction kinetics and thus the demand exerted in a given contact time. Sample pH affects the form of the oxidant and the nature and extent of the demand. For example, ozone is unstable at high pH values and ozone demand is especially sensitive to sample pH. Oxidant demand increases with time and therefore the demand must be defined for a given contact time. Oxidant demand also is dependent on oxidant dose. Increasing oxidant dose usually will increase demand, but it is incorrect to assume that doubling the oxidant dose will double the oxidant demand. For these reasons, it is difficult to extrapolate oxidant demand data from one set of conditions to another. *Always study oxidant consumption under the range of conditions expected in the field.*

Oxidant consumption is used to evaluate oxidant demand and oxidant requirement. Report consumption values according to the objective of the study. For example, report chlorine *demand* as follows: ‘‘The sample dosed at 5.0 mg/L consumed 3.9 mg/L after 24 h at 20°C and pH 7.1, as measured by amperometric titration.’’ By contrast, report ozone *requirement* as follows: ‘‘The sample required a dose of 2.1 mg/L to achieve an ozone residual of 0.5 mg/L after 20 min at 15°C and pH 6.5, as measured by the indigo method.’’

2. Selection of Method

Select a method to measure oxidant residuals used in the demand calculation that is specific and has adequate sensitivity. Some oxidant residual measurement techniques are subject to interferences from oxidation-produced oxidants. Interferences affect oxidant demand measurements because the concentrations of the interferents may change as the oxidant residual changes. Thus, calculate free chlorine demand in municipal wastewater as the difference between free chlorine dose and free chlorine residual measured after a desired contact time at a given temperature, pH, and chlorine dose for a specified analytical method. Chlorination of non-nitrified municipal wastewater probably produces chloramines. If the analytical method for free chlorine is subject to interferences from chloramines, then the free chlorine residual measurement will be too large (see Section 4500-Cl.A.3), and the resulting free chlorine demand value will be incorrectly low. It is sometimes difficult to predict the manner in which oxidant-produced oxidants will affect the demand measurement. The best approach is to use the analytical method most specific to the oxidant of interest but always indicate the method with the

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result.

The addition of reagents may cause loss of oxidant residual or other changes in oxidant demand. The loss of total chlorine upon addition of acid and KI is discussed in Section 4500-Cl.A.3*a*.

2350 B. Chlorine Demand/Requirement

1. General Discussion

a. Principle: The sample is divided into subsamples and each is dosed with the standardized oxidant (chlorine) solution to yield a series of increasing doses. After the appropriate contact time, oxidant residual, pH, and temperature are measured and the demand/requirement determined by difference between initial and final concentrations.

b. Selection of method: Chlorine consumption tests may be made to examine the demand or requirement for total chlorine, free chlorine, combined chlorine, monochloramine, or dichloramine. Specify the chlorine species consumed in the chlorine demand/requirement test. The analytical method should exhibit minimal interferences for the species examined. For demand/ requirement studies with free chlorine, use only amperometric titration (Section 4500-Cl.D) or DPD methods (Section 4500-Cl.F and Section 4500-Cl.G).

c. Interference: Refer to Section 4500-Cl.D.1*b* (amperometric titration), Section 4500-Cl.F.1*d* (DPD ferrous titrimetric method), or Section 4500-Cl.G.1*b* (DPD colorimetric method). Pay special attention to interferences caused by oxidation products such as MnO_2, NH_2Cl, and $NHCl_2$. If the ammonia or organic nitrogen content of the water is significant, combined chlorine may form. See Section Section 4500-Cl for details. Under these conditions, expect interferences in the measurement of free chlorine by combined chlorine.

d. Minimum detectable concentration: Because it is calculated by difference, the minimum detectable chlorine demand/requirement is $\sqrt{2}$ times the minimum chlorine residual detectable by the analytical method. For minimum detectable chlorine residual, see Section 4500-Cl.F.1*e* (DPD ferrous titrimetric method) or Section 4500-Cl.G.1*c* (DPD colorimetric method). Minimum detectable demand also is influenced by amount of oxidant consumed relative to oxidant dose (see ¶ 6 below).

e. Sampling: Most reliable results are obtained on fresh samples that contain low amounts of suspended solids. If samples will be analyzed within 24 h of collection, refrigerate unacidified at 4°C immediately after collection. To preserve for up to 28 d, freeze unacidified samples at −20°C. Warm chilled samples to desired test condition before analysis.

2. Apparatus

See Section 4500-Cl.D (amperometric titration) or Section 4500-Cl.G (DPD colorimetric method).

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3. Reagents

a. Chlorine-demand-free water: See Section 4500-Cl.C.3*m*. Alternatively, prepare dilutions, blanks, and dosing solutions from high-quality distilled water (preferably carbon-filtered redistilled water).

b. Acetic acid, conc (glacial).

c. Potassium iodide, KI, crystals.

d. Standard sodium thiosulfate titrant, 0.025*N:* See Section 4500-Cl.B.2*d*.

e. Starch indicator solution: See Section 4500-Cl.B.2*e*.

f. Reagents for determining residual chlorine: See Section 4500-Cl.D.3 (amperometric titration), Section 4500-Cl.F.2 (DPD ferrous titrimetric method), or Section 4500-Cl.G.3 (DPD colorimetric method).

g. Standard chlorine solution: Prepare by bubbling chlorine gas through distilled water or by diluting commercially available 5–7% (50 000–70 000 mg/L) sodium hypochlorite. Store in the dark or in a brown, glass-stoppered bottle. Standardize each day of use. A suitable strength of chlorine solution usually will be between 100 and 1000 mg/L, preferably about 100 times estimated chlorine demand. Use a solution of sufficient concentration so that adding the chlorine solution will not increase the volume of the treated portions by more than 5%.

Standardization—Place 2 mL acetic acid and 10 to 15 mL chlorine-demand-free water in a flask. Add about 1 g KI. Measure into the flask a suitable volume of chlorine solution. In choosing a convenient volume, note that 1 mL 0.025*N* $Na_2S_2O_3$ titrant is equivalent to about 0.9 mg chlorine as Cl_2. Select volumes that will require no more than 20 mL titrant.

Titrate with standardized 0.025*N* $Na_2S_2O_3$ titrant until the yellow iodine color almost disappears. Add 1 to 2 mL starch indicator solution and continue titrating until the blue color disappears.

Determine the blank by adding identical quantities of acid, KI, and starch indicator to a volume of chlorine-demand-free water corresponding to the sample used for titration. Perform whichever blank titration applies, according to Section 4500-Cl.B.3*d*. Calculate the chlorine stock concentration as described in Section 4500-Cl.B.4.

4. Procedure

Measure sample temperature and pH. Keep sample and sample portions at desired temperature and protect from light throughout the procedure. If pH adjustment is desired, prepare a blank in distilled water containing the same amount of buffer as in the sample. Carry the blank throughout the procedure.

Measure 5*#(33) equal sample portions of 200 mL†#(34) each into glass-stoppered bottles or flasks of ample capacity to permit mixing. Add increasing amounts of standard chlorine solution (¶ 3*g*) to successive portions in the series. Try to bracket the estimated demand/requirement and satisfy criteria of ¶ 5*a*. Increase dosage between portions in increments of 0.1 mg/L for

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determining low demands/requirements and up to 1.0 mg/L or more for higher demands. Mix while adding. Dose sample portions according to a staggered schedule that will permit determining the residual after predetermined contact times.

Conduct test over desired contact period. Record contact time. At end of contact period, measure sample temperature, sample pH, and residual chlorine. Record residual measurement method used.

5. Calculation

a. Chlorine demand: Select sample portion with a residual at the end of the contact period that satisfies the following criteria:

1) $R_s < D_s - 1.4\ R_{min}$,
2) $R_s > R_{min}$, and
3) Dose is most similar to the dosage range expected in the field

where:

R_s= residual after contact time, mg/L,
D_s= dose, mg/L, and
R_{min}= minimum residual measurable by the method, mg/L.

The first two criteria insure that the chlorine residual and demand are greater than their respective minimum detection limits. If no sample portion satisfies all criteria, repeat the test and adjust doses accordingly. Calculate chlorine demand as follows:

$$\text{Chlorine demand, mg/L} = (D_S - R_S) - (D_B - R_B)$$

where R_s and D_s are defined as above, and:

R_B= residual of blank after contact time, mg/L, and
D_B = blank dose, mg/L.

When reporting chlorine demand, include dose, contact time, sample temperature, sample pH, and analytical method.

b. Chlorine requirement: Report the chlorine dose that produced the target residual after the desired contact time. When reporting chlorine requirement, include the target residual, contact time, sample temperature, sample pH, and analytical method. Report chlorine demand of blank if it is greater than 10% of the difference between the requirement and the target residual.

6. Precision and Bias

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For data on precision and bias of concentration measurements, see analytical method used. Because demand is calculated by difference, the uncertainty associated with the demand value will be greater than the uncertainty of the individual residual measurements. If the standard deviations of the dose measurement and residual measurements are the same, then the standard deviation and minimum detection limit of the oxidant demand will be $\sqrt{2}$ (approximately 1.4) times the standard deviation and minimum detection limit of the measurement technique, respectively.

The chlorine dose and amount consumed affect the precision and bias of demand calculation in two ways. First, the amount consumed must be sufficiently large, relative to the dose, to minimize errors associated with a value calculated from the difference of two numbers of approximately equal value. Second, the amount consumed must be small enough, relative to the dose, to prevent the residual concentration from being too small.

7. Bibliography

See Section 4500-Cl.D.7 or Section 4500-Cl.F.6, according to analytical method used.

2350 C. Chlorine Dioxide Demand/Requirement

1. General Discussion

a. Principle: See Section 2350B.1. Chlorine dioxide consumption studies are made by dosing samples from a ClO_2 stock solution.

b. Selection of method: Use the amperometric method II (Section 4500-ClO_2.E) because of its high degree of accuracy and minimal interferences.

c. Interference: See Section 4500-ClO_2.E.1*b*.

d. Minimum detectable concentration: The minimum detectable chlorine dioxide demand/requirement is $\sqrt{2}$ times the minimum chlorine dioxide residual detectable by the analytical method (see Section 2350B.1*d* and Section 2350B.6).

2. Apparatus

See Section 4500-ClO_2.E.2.

3. Reagents

See Section 4500-ClO_2.B.2 to prepare and standardize ClO_2.

See Section 4500-ClO_2.E.3 for reagents required to determine ClO_2 residual.

4. Procedure

Follow procedure of Section 2350B.4, using ClO_2 solution, rather than chlorine solution, for

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dosing sample portions.

Follow procedure of Section 4500-ClO_2.E.4 to measure ClO_2 residual.

5. Calculation

a. Chlorine dioxide demand: See Section 2350B.5*a*.

b. Chlorine dioxide requirement: See Section 2350B.5*b*.

6. Precision and Bias

See Section 2350B.6.

7. Bibliography

See Section 4500-ClO_2.E.6 and Section 4500-ClO_2.E.7.

2350 D. Ozone Demand/Requirement—Batch Method

1. General Discussion

a. Principle: See Section 2350B.1. Samples can be ozonated in batch and semi-batch modes. In batch ozone consumption studies, an ozone stock solution is used to add ozone to the samples. In semi-batch ozone consumption studies, a stream of ozone gas is added continuously to the sample.

Ozone decomposes at high pH. Thus, even pH-buffered distilled water has a non-zero ozone demand/requirement. Analyze blanks with all ozone consumption tests. Do not subtract the ozone demand of the blank from the ozone demand of the sample, but report it separately.

b. Selection of method: Ozone produces oxidants that interfere with iodometric methods. The indigo method (Section 4500-O_3.B) is recommended for measuring ozone residuals in ozone consumption studies. The indigo method measures only the demand for ozone; it does not measure the demand for ozone-produced oxidants such as the hydroxyl radical.

c. Interference: See Section 4500-O_3.B.1*b*.

d. Minimum detectable concentration: The minimum detectable ozone demand/requirement is $\sqrt{2}$ times the minimum ozone residual detectable by the analytical method (see Section 2350B.1*d* and Section 2350B.6).

For minimum detectable ozone residuals, see Section 4500-O_3.B.1*c*.

2. Apparatus

a. Ozone generator: Use a laboratory-scale ozonator, capable of providing up to about 5% ozone in the gas phase at a gas flow of up to about 1 L/min.

b. Apparatus for measuring residual ozone: See Section 4500-O_3.B.2.

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3. Reagents

a. Ozone-demand-free water: Ozonate reagent water (see Section 1080) for at least 1 h and purge with nitrogen gas for at least 1 h. CAUTION: *Conduct all laboratory ozonations under a vented hood.*

b. Standard ozone solution: Put about 800 mL of ozone-demand-free water in a 1-L flask. Bubble ozone (approximately 1 to 5% O_3 in the gas phase) through the water for about 30 min while stirring. At room temperature the ozone solution will contain about 10 to 20 mg O_3/L. If the flask is cooled in an ice bath throughout the procedure, the ozone concentration will be about 30 to 40 mg O_3/L. Standardize the ozone solution by the indigo method. Use a small sample volume (typically 1 mL) as directed in Section 4500-O_3.B.4*a*3).

4. Procedure

Follow procedure of Section 2350B.4, using standard ozone solution, rather than chlorine solution, for dosing sample portions. Carry a reagent blank through the procedure.

Follow procedure of Section 4500-O_3.B.4 to measure O_3 residual.

5. Calculation

a. Ozone demand: See Section 2350B.5*a* for selection of the proper sample portion. Calculate ozone demand in sample as follows:

$$\text{Ozone demand, mg/L} = D_S - R_S$$

where:

R_s = oxidant residual of sample after contact time, mg/L, and
D_s = sample oxidant dose, mg/L.

Calculate ozone demand in the blank separately.

$$\text{Ozone demand of blank, mg/L} = D_B - R_B$$

where:

R_B = oxidant residual of blank after contact time, mg/L, and
D_B = blank oxidant dose, mg/L.

Report the ozone demand and the ozone demand of the blank, ozone dose, contact time, sample temperature, sample pH, and analytical method.

b. Ozone requirement: See Section 2350B.5*b*.

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6. Precision and Bias

See Section 2350B.6.

7. Bibliography

See Section 4500-O_3.B.7 and Section 4500-O_3.B.8.

2350 E. Ozone Demand/Requirement—Semi-Batch Method

1. General Discussion

See Section 2350D.1.

The semi-batch method involves determination of ozone demand with the continuous addition of gaseous ozone to a batch reactor. The results obtained in this method depend on the mass-transfer characteristics of the reactor. In addition, some compounds that consume ozone may volatilize during the test.

2. Apparatus

All apparatus listed in Section 2350D.2 is required, plus:

a. Gas washing bottles, borosilicate glass, minimum volume 250 mL.

b. Tubing: Use only stainless steel or TFE tubing.

c. Glassware: Buret, 50 mL; beaker, 400 mL; graduated cylinder, 250 mL.

d. Wash bottle, 500 mL.

e. Magnetic stirrer (optional).

3. Reagents

a. Ozone-demand-free water: See Section 2350D.3*a*.

b. Sulfuric acid, H_2SO_4, 2*N*: Cautiously add 56 mL conc H_2SO_4 to 800 mL ozone-demand-free water in a 1-L volumetric flask. Mix thoroughly, cool, add up to mark with ozone-demand-free water.

c. Potassium iodide, KI: Dissolve 20 g KI in about 800 mL of ozone-demand-free water in a 1-L volumetric flask. Make up to mark with ozone-demand-free water.

d. Standard sodium thiosulfate titrant, $Na_2S_2O_3$, 0.1*N*: See Section 4500-Cl.B.2*c*.

e. Standard sodium thiosulfate titrant, $Na_2S_2O_3$, 0.005*N*: Dilute the proper volume (approximately 50 mL) of standardized 0.1*N* $Na_2S_2O_3$ to 1 L.

f. Starch indicator solution: See Section 4500-Cl.B.2*e*.

4. Procedure

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Determine the output of the ozone generator by passing the ozone gas through two serial KI traps (Traps A and B) for about 10 min. For best results, keep gas flow below approximately 1 L/min. Each trap is a gas washing bottle containing a known volume (at least 200 mL) of 2% KI. Quantitatively transfer contents of each trap into a beaker, add 10 mL of 2*N* H_2SO_4, and titrate with standardized 0.005*N* $Na_2S_2O_3$ until the yellow iodine color almost disappears. Add 1 to 2 mL starch indicator solution and continue titrating to the disappearance of blue color.

Put a known volume (at least 200 mL) of sample in a separate gas washing bottle (label gas washing bottles to avoid contaminating the reaction vessel with iodide). Direct ozone gas through this reaction vessel. For ozone demand studies, direct gas stream leaving reaction vessel through a KI trap (Trap C) prepared as above. Ozonate sample for a given contact time. For ozone demand studies, turn ozonator off at end of contact time and pour contents of Trap C into a beaker. Add 10 mL 2*N* H_2SO_4 and titrate with 0.005*N* $Na_2S_2O_3$ as described above. For ozone requirement studies, remove a portion from the reaction vessel at the end of contact time and measure residual ozone concentration by the indigo method.

5. Calculation

a. Ozone dose:

$$\text{Ozone dose, mg/min} = \frac{(A + B) \times N \times 24}{T}$$

where:

A = mL titrant for Trap A,
B = mL titrant for Trap B,
N = normality of $Na_2S_2O_3$, and
T = ozonation time, min.

b. Ozone demand:

$$\text{Ozone demand, mg/min} = \text{ozone dose, mg/min} - \frac{C \times N \times 24}{T}$$

where:

C = mL titrant for Trap C.

Report sample ozone demand and blank ozone demand, ozone dose, ozonation time, sample temperature, sample pH, sample volume, and analytical method. Because the ozone transfer rate is highly dependent on experimental conditions, also report vessel volume, vessel type, gas flow rate, and sample volume.

c. Ozone requirement: The ozone requirement in the semi-batch test is the ozone dose,

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mg/min, required to obtain the target ozone residual after the desired ozonation time. See Section 2350E.5*a* to calculate dose. When reporting ozone requirement, also include target oxidant residual as well as other experimental characteristics listed in ¶ 5*b* above.

6. Precision and Bias

See Section 2350B.6.

7. Bibliography

See Section 4500-O_3.B.7 and Section 4500-O_3.B.8.

2510 CONDUCTIVITY*#(35)

2510 A. Introduction

Conductivity, *k*, is a measure of the ability of an aqueous solution to carry an electric current. This ability depends on the presence of ions; on their total concentration, mobility, and valence; and on the temperature of measurement. Solutions of most inorganic compounds are relatively good conductors. Conversely, molecules of organic compounds that do not dissociate in aqueous solution conduct a current very poorly, if at all.

1. Definitions and Units of Expression

Conductance, *G*, is defined as the reciprocal of resistance, *R*:

$$G = \frac{1}{R}$$

where the unit of *R* is ohm and *G* is ohm^{-1} (sometimes written mho). Conductance of a solution is measured between two spatially fixed and chemically inert electrodes. To avoid polarization at the electrode surfaces the conductance measurement is made with an alternating current signal.[1] The conductance of a solution, *G*, is directly proportional to the electrode surface area, *A*, cm^2, and inversely proportional to the distance between the electrodes, *L*, cm. The constant of proportionality, *k*, such that:

$$G = k\left(\frac{A}{L}\right)$$

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is called ‘‘conductivity’’ (preferred to ‘‘specific conductance’’). It is a characteristic property of the solution between the electrodes. The units of k are 1/ohm-cm or mho per centimeter. Conductivity is customarily reported in micromhos per centimeter (μmho/cm).

In the International System of Units (SI) the reciprocal of the ohm is the siemens (S) and conductivity is reported as millisiemens per meter (mS/m); 1 mS/m = 10 μmhos/cm and 1 μS/cm = 1 μmho/cm. To report results in SI units of mS/m divide μmhos/cm by 10.

To compare conductivities, values of k are reported relative to electrodes with A = 1 cm^2 and L = 1 cm. Absolute conductances, G_s, of standard potassium chloride solutions between electrodes of precise geometry have been measured; the corresponding standard conductivities, k_s, are shown in Table 2510:I.

The equivalent conductivity, Λ, of a solution is the conductivity per unit of concentration. As the concentration is decreased toward zero, Λ approaches a constant, designated as Λ°. With k in units of micromhos per centimeter it is necessary to convert concentration to units of equivalents per cubic centimeter; therefore:

$$\Lambda = 0.001k/\text{concentration}$$

where the units of Λ, k, and concentration are mho-cm^2/equivalent, μmho/cm, and equivalent/L, respectively. Equivalent conductivity, Λ, values for several concentrations of KCl are listed in Table 2510:I. In practice, solutions of KCl more dilute than 0.001M will not maintain stable conductivities because of absorption of atmospheric CO_2. Protect these dilute solutions from the atmosphere.

2. Measurement

a. Instrumental measurements: In the laboratory, conductance, G_s, (or resistance) of a standard KCl solution is measured and from the corresponding conductivity, k_s, (Table 2510:I) a cell constant, C, cm^{-1}, is calculated:

$$C = \frac{k_s}{G_s}$$

Most conductivity meters do not display the actual solution conductance, G, or resistance, R; rather, they generally have a dial that permits the user to adjust the internal cell constant to match the conductivity, k_s, of a standard. Once the cell constant has been determined, or set, the conductivity of an unknown solution,

$$k_u = CG_u$$

will be displayed by the meter.

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Distilled water produced in a laboratory generally has a conductivity in the range 0.5 to 3 μmhos/cm. The conductivity increases shortly after exposure to both air and the water container.

The conductivity of potable waters in the United States ranges generally from 50 to 1500 μmhos/cm. The conductivity of domestic wastewaters may be near that of the local water supply, although some industrial wastes have conductivities above 10 000 μmhos/cm. Conductivity instruments are used in pipelines, channels, flowing streams, and lakes and can be incorporated in multiple-parameter monitoring stations using recorders.

Most problems in obtaining good data with conductivity monitoring equipment are related to electrode fouling and to inadequate sample circulation. Conductivities greater than 10 000 to 50 000 μmho/cm or less than about 10 μmho/cm may be difficult to measure with usual measurement electronics and cell capacitance. Consult the instrument manufacturer's manual or published references.[1,5,6]

Laboratory conductivity measurements are used to:

- Establish degree of mineralization to assess the effect of the total concentration of ions on chemical equilibria, physiological effect on plants or animals, corrosion rates, etc.
- Assess degree of mineralization of distilled and deionized water.
- Evaluate variations in dissolved mineral concentration of raw water or wastewater. Minor seasonal variations found in reservoir waters contrast sharply with the daily fluctuations in some polluted river waters. Wastewater containing significant trade wastes also may show a considerable daily variation.
- Estimate sample size to be used for common chemical determinations and to check results of a chemical analysis.
- Determine amount of ionic reagent needed in certain precipitation and neutralization reactions, the end point being denoted by a change in slope of the curve resulting from plotting conductivity against buret readings.
- Estimate total dissolved solids (mg/L) in a sample by multiplying conductivity (in micromhos per centimeter) by an empirical factor. This factor may vary from 0.55 to 0.9, depending on the soluble components of the water and on the temperature of measurement. Relatively high factors may be required for saline or boiler waters, whereas lower factors may apply where considerable hydroxide or free acid is present. Even though sample evaporation results in the change of bicarbonate to carbonate the empirical factor is derived for a comparatively constant water supply by dividing dissolved solids by conductivity.
- Approximate the milliequivalents per liter of either cations or anions in some waters by multiplying conductivity in units of micromhos per centimeter by 0.01.

b. Calculation of conductivity: For naturally occurring waters that contain mostly Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, SO_4^{2-}, and Cl^{-} and with TDS less than about 2500 mg/L, the following procedure can be used to calculate conductivity from measured ionic concentrations.[7] The abbreviated water analysis in Table 2510:II illustrates the calculation procedure.

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At infinite dilution the contribution to conductivity by different kinds of ions is additive. In general, the relative contribution of each cation and anion is calculated by multiplying equivalent conductances, λ°_+ and λ°_-, mho-cm^2/equivalent, by concentration in equivalents per liter and correcting units. Table 2510:III contains a short list of equivalent conductances for ions commonly found in natural waters.[8] Trace concentrations of ions generally make negligible contribution to the overall conductivity. A temperature coefficient of 0.02/deg is applicable to all ions, except H^+ (0.0139/deg) and OH^- (0.018/deg).

At finite concentrations, as opposed to infinite dilution, conductivity per equivalent decreases with increasing concentration (see Table 2510:I). For solutions composed of one anion type and one cation type, e.g., KCl as in Table 2510:I, the decrease in conductivity per equivalent with concentration can be calculated, ±0.1%, using an ionic-strength-based theory of Onsager.[9] When mixed salts are present, as is nearly always the case with natural and wastewaters, the theory is quite complicated.[10] The following semiempirical procedure can be used to calculate conductivity for naturally occurring waters:

First, calculate infinite dilution conductivity (Table 2510:II, Column 4):

$$k^\circ = \sum|z_i|(\lambda^\circ_{+i})(\mathrm{m}M_i) + \sum|z_i|(\lambda^\circ_{-i})(\mathrm{m}M_i)$$

where:

$|z_i|$ = absolute value of the charge of the *i*-th ion,
$\mathrm{m}M_i$ = millimolar concentration of the *i*-th ion, and
λ°_{+i}, λ°_{-i} = equivalent conductance of the *i*-th ion.

If m*M* is used to express concentration, the product, (λ°_+) $(\mathrm{m}M_i)$ or $(\lambda^\circ_-)(\mathrm{m}M_i)$, corrects the units from liters to cm^3. In this case k° is 578.2 µmho/cm (Table 2510:II, Column 4).

Next, calculate ionic strength, *IS* in molar units:

$$IS = \sum z_i^2(\mathrm{m}M_i)/2000$$

The ionic strength is 15.33/2000 = 0.00767 *M* (Table 2510:II, Column 5).

Calculate the monovalent ion activity coefficient, *y*, using the Davies equation for IS ≤ 0.5 *M* and for temperatures from 20 to 30°C.[9,11]

$$y = 10^{-0.5[IS^{1/2}/(1 + IS^{1/2}) - 0.3IS]}$$

In the present example *IS* = 0.00767 *M* and *y* = 0.91.

Finally, obtain the calculated value of conductivity, k_{calc}, from:

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$$k_{calc} = k°y^2$$

In the example being considered, $k_{calc} = 578.2 \times 0.91^2 = 478.8$ μmho/cm versus the reported value as measured by the USGS of 477 μmho/cm.

For 39 analyses of naturally occurring waters,[7,12] conductivities calculated in this manner agreed with the measured values to within 2%.

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2510 B. Laboratory Method

1. General Discussion

See Section 2510A.

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2. Apparatus

a. Self-contained conductivity instruments: Use an instrument capable of measuring conductivity with an error not exceeding 1% or 1 μmho/cm, whichever is greater.

b. Thermometer, capable of being read to the nearest 0.1°C and covering the range 23 to 27°C. Many conductivity meters are equipped to read an automatic temperature sensor.

c. Conductivity cell:

1) Platinum-electrode type—Conductivity cells containing platinized electrodes are available in either pipet or immersion form. Cell choice depends on expected range of conductivity. Experimentally check instrument by comparing instrumental results with true conductivities of the KCl solutions listed in Table 2510:I. Clean new cells, not already coated and ready for use, with chromic-sulfuric acid cleaning mixture [see Section 2580B.3*a*2)] and platinize the electrodes before use. Subsequently, clean and replatinize them whenever the readings become erratic, when a sharp end point cannot be obtained, or when inspection shows that any platinum black has flaked off. To platinize, prepare a solution of 1 g chloroplatinic acid, $H_2PtCl_6 \cdot 6H_2O$, and 12 mg lead acetate in 100 mL distilled water. A more concentrated solution reduces the time required to platinize electrodes and may be used when time is a factor, e.g., when the cell constant is 1.0/cm or more. Immerse electrodes in this solution and connect both to the negative terminal of a 1.5-V dry cell battery. Connect positive side of battery to a piece of platinum wire and dip wire into the solution. Use a current such that only a small quantity of gas is evolved. Continue electrolysis until both cell electrodes are coated with platinum black. Save platinizing solution for subsequent use. Rinse electrodes thoroughly and when not in use keep immersed in distilled water.

2) Nonplatinum-electrode type—Use conductivity cells containing electrodes constructed from durable common metals (stainless steel among others) for continuous monitoring and field studies. Calibrate such cells by comparing sample conductivity with results obtained with a laboratory instrument. Use properly designed and mated cell and instrument to minimize errors in cell constant. Very long meter leads can affect performance of a conductivity meter. Under such circumstances, consult the manufacturer's manual for appropriate correction factors if necessary.

3. Reagents

a. Conductivity water: Any of several methods can be used to prepare reagent-grade water. The methods discussed in Section 1080 are recommended. The conductivity should be small compared to the value being measured.

b. Standard potassium chloride solution, KCl, 0.0100*M:* Dissolve 745.6 mg anhydrous KCl in conductivity water and dilute to 1000 mL in a class A volumetric flask at 25°C and store in a CO_2-free atmosphere. This is the standard reference solution, which at 25°C has a conductivity of 1412 μmhos/cm. It is satisfactory for most samples when the cell has a constant between 1

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and 2 cm^{-1}. For other cell constants, use stronger or weaker KCl solutions listed in Table 2510:I. Care must be taken when using KCl solutions less than 0.001*M*, which can be unstable because of the influence of carbon dioxide on pure water. For low conductivity standards, Standard Reference Material 3190, with a certified conductivity of 25.0 µS/cm ± 0.3 µS/cm, may be obtained from NIST. Store in a glass-stoppered borosilicate glass bottle.

4. Procedure

a. Determination of cell constant: Rinse conductivity cell with at least three portions of 0.01*M* KCl solution. Adjust temperature of a fourth portion to 25.0 ± 0.1°C. If a conductivity meter displays resistance, *R*, ohms, measure resistance of this portion and note temperature. Compute cell constant, *C:*

$$C, \text{ cm}^{-1} = (0.001412)(R_{\text{KCl}})[1 + 0.0191(t - 25)]$$

where:

R_{KCl} = measured resistance, ohms, and
t = observed temperature, °C.

Conductivity meters often indicate conductivity directly. Commercial probes commonly contain a temperature sensor. With such instruments, rinse probe three times with 0.0100*M* KCl, as above. Adjust temperature compensation dial to 0.0191 C^{-1}. With probe in standard KCl solution, adjust meter to read 1412 µmho/cm. This procedure automatically adjusts cell constant internal to the meter.

b. Conductivity measurement: Thoroughly rinse cell with one or more portions of sample. Adjust temperature of a final portion to about 25°C. Measure sample resistance or conductivity and note temperature to ±0.1°C.

5. Calculation

The temperature coefficient of most waters is only approximately the same as that of standard KCl solution; the more the temperature of measurement deviates from 25.0°C, the greater the uncertainty in applying the temperature correction. Report temperature-compensated conductivities as ‘‘µmho/cm 25.0°C.’’

a. When sample resistance is measured, conductivity at 25°C is:

$$k = \frac{(1\,000\,000)(C)}{R_m[1 + 0.0191(t - 25)]}$$

where:

k = conductivity, µmhos/cm,

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C = cell constant, cm^{-1},
R_m = measured resistance of sample, ohms, and
t = temperature of measurement.

b. When sample conductivity is measured without internal temperature compensation conductivity at 25°C is:

$$k, \mu mho/cm = \frac{(k_m)}{1 + 0.0191(t - 25)}$$

where:

k_m = measured conductivity in units of μmho/cm at t°C, and other units are defined as above.

For instruments with automatic temperature compensation and readout directly in μmho/cm or similar units, the readout automatically is corrected to 25.0°C. Report displayed conductivity in designated units.

6. Precision and Bias

The precision of commercial conductivity meters is commonly between 0.1 and 1.0%. Reproducibility of 1 to 2% is expected after an instrument has been calibrated with such data as is shown in Table 2510:I.

2520 SALINITY*#(36)

2520 A. Introduction

1. General Discussion

Salinity is an important unitless property of industrial and natural waters. It was originally conceived as a measure of the mass of dissolved salts in a given mass of solution. The experimental determination of the salt content by drying and weighing presents some difficulties due to the loss of some components. The only reliable way to determine the true or absolute salinity of a natural water is to make a complete chemical analysis. However, this method is time-consuming and cannot yield the precision necessary for accurate work. Thus, to determine salinity, one normally uses indirect methods involving the measurement of a physical property such as conductivity, density, sound speed, or refractive index. From an empirical relationship of salinity and the physical property detemined for a standard solution it is possible

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to calculate salinity. The resultant salinity is no more accurate than the empirical relationship. The precision of the measurement of a physical property will determine the precision in salinity. Following are the precisions of various physical measurements and the resultant salinity presently attainable with commercial instruments:

Property	Precision of Measurement	Precision of Salinity
Conductivity	±0.0002	±0.0002
Density	$\pm 3 \times 10^{-6}$ g/cm^3	±0.004
Sound speed	±0.02 m/s	±0.01

Although conductivity has the greatest precision, it responds only to ionic solutes. Density, although less precise, responds to all dissolved solutes.

2. Selection of Method

In the past, the salinity of seawater was determined by hydrometric and argentometric methods, both of which were included in previous editions of *Standard Methods*. In recent years the conductivity (2520B) and density (2520C) methods have been used because of their high sensitivity and precision. These two methods are recommended for precise field and laboratory work.

3. Quality Assurance

Calibrate salinometer or densimeter against standards of KCl or standard seawater. Expected precision is better than ±0.01 salinity units with careful analysis and use of bracketing standards.

2520 B. Electrical Conductivity Method

1. Determination

See Conductivity, Section 2510. Because of its high sensitivity and ease of measurement, the conductivity method is most commonly used to determine salinity.[1] For seawater measurements use the Practical Salinity Scale 1978.[2-5] This scale was developed relative to a KCl solution. A seawater with a conductivity, C, at 15°C equal to that of a KCl solution containing a mass of 32.4356 g in a mass of 1 kg of solution is defined as having a practical salinity of 35. This value was determined as an average of three independent laboratory studies. The salinity dependence of the conductivity ratio, R_t, as a function of temperature (t °C, International Practical Temperature Scale 1968) of a given sample to a standard S= 35 seawater is used to determine the salinity

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$$S = a_0 + a_1 R_t^{1/2} + a_2 R_t + a_3 R_t^{3/2} + a_4 R_t^2 + a_5 R_t^{5/2} + S$$

where S is given by

$$\Delta S = \left[\frac{t - 15}{1 + 0.0162\ (t - 15)}\right](b_0 + b_1 R_t^{1/2} + b_2 R_t + b_3 R_t^{3/2} + b_4 R_t^2 + b_5 R_t^{5/2})$$

and:

$a_0 = 0.0080$	$b_0 = 0.0005$
$a_1 = -0.1692$	$b_1 = -0.0056$
$a_2 = 25.3851$	$b_2 = -0.0066$
$a_3 = 14.0941$	$b_3 = -0.0375$
$a_4 = -7.0261$	$b_4 = 0.0636$
$a_5 = 2.7081$	$b_5 = -0.0144$

valid from S = 2 to 42, where:

$$R_t = \frac{C\ (\text{sample at } t)}{C\ (\text{KCl solution at } t)}.$$

To measure the conductivity, use a conductivity bridge calibrated with standard seawater*#(37) with a known conductivity relative to KCl, following manufacturer's instructions and the procedures noted in Section 2510. If the measurements are to be made in estuarine waters, make secondary calibrations of weight-diluted seawater of known conductivity to ensure that the bridge is measuring true conductivities.

The Practical Salinity Scale recently has been extended to low salinities[6] to give an equation that is valid from 0 to 40 salinity. The equation is:

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$$S = S_{PSS} - \frac{a_0}{1 + 1.5X + X^2} - \frac{b_0 f(t)}{1 + Y^{1/2} + Y^{3/2}}$$

where:

S_{PSS} = value determined from the Practical Salinity Scale given earlier,
a_0 = 0.008,
b_0 = 0.0005,
X = $400R_t$,
Y = $100R_t$, and
f(t) = (t–15)/[1 + 0.0162 (t–15)]

The practical salinity breaks with the old salinity-chlorinity relationship, $S = 1.806\ 55\ Cl$. Although the scale can be used for estuarine waters[7-10] and brines[11-13], there are limitations.[12,14-22]

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2520 C. Density Method

1. Determination

With a precise vibrating flow densimeter, it is possible to make rapid measurements of the density of natural waters. The measurements are made bypassing the sample through a vibrating tube encased in a constant-temperature jacket. The solution density (ρ) is proportional to the square of the period of the vibration (τ).

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$$\rho = A + B\tau^2$$

where *A* and *B* are terms determined by calibration, *B* being determined by calibration with a densimeter with standard seawater. The difference between the density of the sample and that of pure water is given by:

$$\rho - \rho_0 = B(\tau^2 - \tau_0^2)$$

where τ and τ_0 are, respectively, the periods of the sample and water. The system is calibrated with two solutions of known density. Follow manufacturer's recommendations for calibration. These two solutions can be nitrogen gas and water or standard seawater and water. The salinity of the sample can be determined from the 1 atm international equation of state for seawater. This equation relates $(\rho - \rho_0)$ to the practical salinity (*S*) as a function of temperature.[1]

$$\rho\ (\text{kg/m}^3) = \rho_0 + AS + BS^{3/2} + CS^2$$

where:

$$\begin{aligned} A = {} & 8.244\,93 \times 10^{-1} - 4.0899 \times 10^{-3} t \\ & + 7.6438 \times 10^{-5} t^2 - 8.2467 \times 10^{-7} t^3 + 5.3875 \times 10^{-9} t^4, \\ B = {} & -5.724\,66 \times 10^{-3} + 1.0227 \times 10^{-4} t - 1.6546 \times 10^{-6} t^2, \\ C = {} & 4.8314 \times 10^{-4}, \end{aligned}$$

and the density of water is given by:

$$\begin{aligned} \rho_0 = {} & 999.842\,594 + 6.793\,952 \times 10^{-2} t - 9.095\,290 \times 10^{-3} t^2 \\ & + 1.001\,685 \times 10^{-4} t^3 - 1.120\,083 \times 10^{-6} t^4 + 6.536\,332 \\ & \times 10^{-9} t^5 \end{aligned}$$

Perform simple iteration by adjusting *S* until it gives the measured $\rho - \rho_0$ at a given temperature. If the measurements are made at 25°C, the salinity can be determined from the following equation:

$$S = 1.3343\,(\rho - \rho_0) + 2.155\,306 \times 10^{-4}\,(\rho - \rho_0)^2 - 1.171\,16 \times 10^{-5}\,(\rho - \rho_0)^3$$

which has a $\tau = 0.0012$ in *S*. Approximate salinities also can be determined from densities or specific gravities obtained with a hydrometer at a given temperature (Section 210B, 16th edition).

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2520 D. Algorithm of Practical Salinity

Because all practical salinity measurements are carried out in reference to the conductivity of standard seawater (corrected to $S = 35$), it is the quantity R_t that will be available for salinity calculations. R_t normally is obtained directly by laboratory salinometers, but *in situ* measurements usually produce the quantity R, the ratio of the *in situ* conductivity to the standard conductivity at $S = 35$, $t = 15°C$, $p = 0$ (where p is the pressure above one standard atmosphere and the temperature is on the 1968 International Temperature Scale). R is factored into three parts, i.e.,

$$R = R_p r_t R_t$$

where:

R_p = ratio of *in situ* conductivity to conductivity of the same sample at the same temperature, but at $p = 0$ and r_t = ratio of conductivity of reference seawater, having a practical salinity of 35, at temperature t, to its conductivity at $t = 15°C$. From R_p and r_t calculate R_t using the *in situ* results, i.e.,

$$R_t = \frac{R}{R_p r_t}$$

R_p and r_t can be expressed as functions of the numerical values of the *in situ* parameters, R, t, and p, when t is expressed in °C and p in bars (10^5 Pa), as follows:

$$R_p = 1 + \frac{p(e_1 + e_2 p + e_3 p^2)}{1 + d_1 t + d_2 t^2 + (d_3 + d_4 t)R}$$

where:

$$e_1 = 2.070 \times 10^{-4}, \qquad d_1 = 3.426 \times 10^{-2},$$

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$e_2 = -6.370 \times 10^{-8}$, $d_2 = 4.464 \times 10^{-4}$,
$e_3 = 3.989 \times 10^{-12}$, $d_3 = 4.215 \times 10^{-1}$,
and $d_4 = -3.107 \times 10^{-3}$,

and

$$r_t = c_0 + c_1 t + c_2 t^2 + c_3 t^3 + c_4 t^4$$

where:

$c_0 = 0.676\ 609\ 7$,
$c_1 = 2.005\ 64 \times 10^{-2}$,
$c_2 = 1.104\ 259 \times 10^{-4}$,
$c_3 = -6.9698 \times 10^{-7}$, and
$c_4 = 1.0031 \times 10^{-9}$.

2530 FLOATABLES#(38)*

2530 A. Introduction

One important criterion for evaluating the possible effect of waste disposal into surface waters is the amount of floatable material in the waste. Two general types of floating matter are found: particulate matter that includes ‘‘grease balls,’’ and liquid components capable of spreading as a thin, highly visible film over large areas. Floatable material in wastewaters is important because it accumulates on the surface, is often highly visible, is subject to wind-induced transport, may contain pathogenic bacteria and/or viruses associated with individual particles, and can significantly concentrate metals and chlorinated hydrocarbons such as pesticides and PCBs. Colloidally dispersed oil and grease behave like other dispersed organic matter and are included in the material measured by the COD, BOD, and TOC tests. The floatable oil test indicates the readily separable fraction. The results are useful in designing oil and grease separators, in ascertaining the efficiency of operating separators, and in monitoring raw and treated wastewater streams. Many cities and districts have specified floatable oil and grease limits for wastewater discharged to sewers.

2530 B. Particulate Floatables (GENERAL)

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1. Discussion

a. Principle: This method depends on the gravity separation of particles having densities less than that of the surrounding water. Particles that collect on the surface and can be filtered out and dried at 103 to 105°C are defined by this test as floatable particles.

b. Application: This method is applicable to raw wastewater, treated primary and secondary effluent, and industrial wastewater. Because of the limited sensitivity, it is not applicable to tertiary effluents or receiving waters, whether freshwater or seawater.

c. Precautions: Even slight differences in sampling and handling during and after collection can give large differences in the measured amount of floatable material. Additionally, uniformity of the TFE#(39)* coating of the separation funnel is critical to obtaining reliable results. For a reproducible analysis treat all samples uniformly, preferably by mixing them in a standard manner, before flotation and use consistently prepared separation funnels as much as possible. Because the procedure relies on the difference in specific gravity between the liquid and the floating particles, temperature variations may affect the results. Conduct the test at a constant temperature the same as that of the receiving water body, and report temperature with results.

d. Minimum detectable concentration: The minimum reproducible detectable concentration is approximately 1 mg/L. Although the minimum levels that can be measured are below 1 mg/ L, the results are not meaningful within the current established accuracy of the test.

2. Apparatus

a. Floatables sampler with mixer: Use a metal container of at least 5 L capacity equipped with a propeller mixer on a separate stand (Figure 2530:1), and with a 20-mm-ID bottom outlet cocked at an angle of 45° to the container wall in the direction of fluid movement. The 45° angle assures that even large particles will flow from the container into the flotation funnels where the sample is withdrawn. Fit exterior of bottom outlet with a short piece of tubing and a pinch clamp to allow unrestricted flow through the outlet. Coat inside of container with TFE as uniformly as possible, using a TFE spray to prevent oil and grease from sticking to the surface.

b. Flotation funnel: Use an Imhoff cone provided with a TFE stopcock at the bottom and extended at the top to a total volume of 3.5 L (Figure 2530:2). Coat inside of flotation funnel with TFE as uniformly as possible to prevent floatable grease particles sticking to the sides. Mount flotation funnels as shown in Figure 2530:3 with a light behind the bottom of the funnels to aid in reading levels.

c. Filter holder: Coat inside of top of a standard 500-mL membrane filter holder with TFE, again taking all possible precautions to obtain a uniform TFE coating.

d. Filters, glass fiber, fine porosity.#(40)†

e. Vacuum flask, 500 mL.

f. TFE coating: Follow instructions that accompany commercially available coating kits. Alternatively, have necessary glassware coated commercially. Uniform coatings are key to the

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reliability of the test results, but in practice are difficult to obtain.

3. Procedure

a. Preparation of glass fiber filters: See Section 2540D.3*a*.

b. Sample collection and treatment: Collect sample in the floatables sampler at a point of complete mixing, transport to the laboratory, and place 3.0 L in the flotation funnel within 2 h after sample collection to minimize changes in the floatable material. While the flotation funnel is being filled, mix sampler contents with a small propeller mixer. Adjust mixing speed to provide uniform distribution of floating particles throughout the liquid but avoid extensive air entrapment through formation of a large vortex.

c. Correction for density and for concentration effects: When a receiving water has a density and ion concentration different from that of the waste, adjust sample density and ion concentration to that of the receiving water. For example, if the receiving water is ocean water, place 1.5 L sample in flotation funnel and add 1.5 L filtered seawater from the receiving area together with mixture of 39.8 g NaCl, 8.0 g $MgCl_2 \cdot 6H_2O$, and 2.3 g $CaCl_2 \cdot 2H_2O$. The final mixture contains the amount of floatables in a 1.5-L sample in a medium of approximately the same density and ion concentration as seawater.

d. Flotation: Mix flotation funnel contents at 40 rpm for 15 min using a paddle mixer (Figure 2530:3). Let settle for 5 min, mix at 100 rpm for 1 min, and let settle for 30 min. Discharge 2.8 L through bottom stopcock at a rate of 500 mL/min. Do not disturb the sample surface in the flotation funnel during discharge. With distilled water from a wash bottle, wash down any floatable material sticking to sides of stirring paddle and funnel. Let remaining 200 mL settle for 15 min and discharge settled solids and liquid down to the 40-mL mark on the Imhoff cone. Let settle again for 10 min and discharge until only 10 mL liquid and the floating particles remain in funnel. Add 500 mL distilled water and stir by hand to separate entrapped settleable particles from the floatable particles. Let settle for 15 min, then discharge to the 40-mL mark. Let settle for 10 min, then discharge dropwise to the 10-mL mark. Filter remaining 10 mL and floating particles through a preweighed glass fiber filter. Wash sides of flotation funnel with distilled water to transfer all floatable material to filter.

e. Weighing: Dry and weigh glass fiber filter at 103 to 105° C for exactly 2 h (see Section 2540D.3*c*).

4. Calculation

$$\text{mg particulate floatables/L} = \frac{(A - B)}{C}$$

where:

A = weight of filter + floatables, mg,
B = weight of filter, mg, and

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C = sample volume, L. (Do not include volume used for density or concentration correction, if used.)

5. Precision and Bias

Precision varies with the concentration of suspended matter in the sample. There is no completely satisfactory procedure for determining the bias of the method for wastewater samples but approximate recovery can be determined by running a second test for floatables on all water discharged throughout the procedure, with the exception of the last 10 mL. Precision and bias are summarized in Table 2530:I. Experience with the method at one municipal treatment plant indicates that the practical lower limit of detection is approximately 1 mg/L.

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2530 C. Trichlorotrifluoroethane-Soluble Floatable Oil and Grease (GENERAL)

1. Discussion

The floatable oil and grease test does not measure a precise class of substances; rather, the results are determined by the conditions of the test. The fraction measured includes oil and grease, both floating and adhering to the sides of the test vessel. The adhering and the floating portions are of similar practical significance because it is assumed that most of the adhering

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portion would otherwise float under receiving water conditions. The results have been found to represent well the amount of oil removed in separators having overflow rates equivalent to test conditions.

2. Apparatus

a. Floatable oil tube (Figure 2530:4): Before use, carefully clean tube by brushing with a mild scouring power. Water must form a smooth film on inside of cleaned glass. Do not use lubricant on stopcock.

b. Conical flask, 300 mL.

3. Reagents

a. 1,1,2-trichloro-1,2,2-trifluoroethane#(41)*: See Section 5520B.3*b*.

b. Hydrochloric acid, HCl, 6*N*.

c. Filter paper.#(42)†

4. Procedure

a. Sampling: Collect samples at a place where there is a strong turbulence in the water and where floating material is not trapped at the surface. Fill floatable oil tube to mark by dipping into water. *Do not use samples taken to the laboratory in a bottle, because oil and grease cannot be redispersed to their original condition.*

b. Flotation: Support tube in a vertical position. Start flotation period at sampling site immediately after filling tube. The standard flotation time is 30 min. If a different time is used, state this variation in reporting results. At end of flotation period, discharge the first 900 mL of water carefully through bottom stopcock, stopping before any surface oil or other floating material escapes. Rotate tube slightly back and forth about its vertical axis to dislodge sludge from sides, and let settle for 5 min. Completely discharge sludge that has settled to the bottom or that comes down from the sides with the liquid. Scum on top of the liquid may mix with the water as it moves down the tube. If mixing occurs, stop drawing off water before any floatables have been lost. Let settle for 5 min before withdrawing remainder of water. After removing water, return tube to laboratory to complete test.

c. Extraction: Acidify to pH 2 or lower with a few drops of 6*N* HCl, add 50 to 100 mL trichlorotrifluoroethane, and shake vigorously. Let settle and draw off solvent into a clean dry beaker. Filter solvent through a dry filter paper into a tared 300-mL conical flask, taking care not to get any water on filter paper. Add a second 50-mL portion of trichlorotrifluoroethane and repeat extraction, settling, and filtration into the same 300-mL flask. A third extraction may be needed if the amount of floatables in sample exceeds 4 mg/L. Wash filter paper carefully with fresh solvent discharged from a wash bottle with a fine tip. Evaporate solvent from flask as described in Section 5520B.4. For each solvent batch, determine weight of residue left after evaporation from the same volume as used in the analysis.

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5. Calculations

Report results as ‘‘soluble floatable oil and grease, 30 min (or other specified) settling time, mg/L.’’

Trichlorotrifluoroethane-soluble floatable oil and grease, 30 min settling time, mg/L

$$= \frac{(A - B) \times 1000}{\text{mL sample}}$$

where:

A = total gain in weight of tared flask, mg, and
B = calculated residue from solvent blank of the same volume as that used in the test, mg.

6. Precision and Bias

There is no standard against which bias of this test can be determined. Variability of replicates is influenced by sample heterogeneity. If large grease particles are present, the element of chance in sampling may be a major factor. One municipal wastewater discharge and two meat-packing plant discharges, both containing noticeable particles of grease, were analyzed in triplicate. Averages for the three wastewaters were 48, 57, and 25 mg/L; standard deviations averaged 11%. An oil refinery made duplicate determinations of its separator effluent on 15 consecutive days, obtaining results ranging from 5.1 to 11.2 mg/L. The average difference between pairs of samples was 0.37 mg/L.

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2540 SOLIDS#(43)*

2540 A. Introduction

Solids refer to matter suspended or dissolved in water or wastewater. Solids may affect water or effluent quality adversely in a number of ways. Waters with high dissolved solids generally are of inferior palatability and may induce an unfavorable physiological reaction in the transient consumer. For these reasons, a limit of 500 mg dissolved solids/L is desirable for drinking waters. Highly mineralized waters also are unsuitable for many industrial applications. Waters high in suspended solids may be esthetically unsatisfactory for such purposes as bathing. Solids analyses are important in the control of biological and physical wastewater treatment processes and for assessing compliance with regulatory agency wastewater effluent limitations.

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1. Definitions

‘‘Total solids’’ is the term applied to the material residue left in the vessel after evaporation of a sample and its subsequent drying in an oven at a defined temperature. Total solids includes ‘‘total suspended solids,’’ the portion of total solids retained by a filter, and ‘‘total dissolved solids,’’ the portion that passes through the filter.

The type of filter holder, the pore size, porosity, area, and thickness of the filter and the physical nature, particle size, and amount of material deposited on the filter are the principal factors affecting separation of suspended from dissolved solids. ‘‘Dissolved solids’’ is the portion of solids that passes through a filter of 2.0 μm (or smaller) nominal pore size under specified conditions. ‘‘Suspended solids’’ is the portion retained on the filter.

‘‘Fixed solids’’ is the term applied to the residue of total, suspended, or dissolved solids after heating to dryness for a specified time at a specified temperature. The weight loss on ignition is called ‘‘volatile solids.’’ Determinations of fixed and volatile solids do not distinguish precisely between inorganic and organic matter because the loss on ignition is not confined to organic matter. It includes losses due to decomposition or volatilization of some mineral salts. Better characterization of organic matter can be made by such tests as total organic carbon (Section 5310), BOD (Section 5210), and COD (Section 5220).

‘‘Settleable solids’’ is the term applied to the material settling out of suspension within a defined period. It may include floating material, depending on the technique (Section 2540F.3*b*).

2. Sources of Error and Variability

Sampling, subsampling, and pipeting two-phase or three-phase samples may introduce serious errors. Make and keep such samples homogeneous during transfer. Use special handling to insure sample integrity when subsampling. Mix small samples with a magnetic stirrer. If suspended solids are present, pipet with wide-bore pipets. If part of a sample adheres to the sample container, consider this in evaluating and reporting results. Some samples dry with the formation of a crust that prevents water evaporation; special handling is required to deal with this. Avoid using a magnetic stirrer with samples containing magnetic particles.

The temperature at which the residue is dried has an important bearing on results, because weight losses due to volatilization of organic matter, mechanically occluded water, water of crystallization, and gases from heat-induced chemical decomposition, as well as weight gains due to oxidation, depend on temperature and time of heating. Each sample requires close attention to desiccation after drying. Minimize opening desiccator because moist air enters. Some samples may be stronger desiccants than those used in the desiccator and may take on water.

Residues dried at 103 to 105°C may retain not only water of crystallization but also some mechanically occluded water. Loss of CO_2 will result in conversion of bicarbonate to carbonate. Loss of organic matter by volatilization usually will be very slight. Because removal of occluded water is marginal at this temperature, attainment of constant weight may be very slow.

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Residues dried at 180 ± 2°C will lose almost all mechanically occluded water. Some water of crystallization may remain, especially if sulfates are present. Organic matter may be lost by volatilization, but not completely destroyed. Loss of CO_2 results from conversion of bicarbonates to carbonates and carbonates may be decomposed partially to oxides or basic salts. Some chloride and nitrate salts may be lost. In general, evaporating and drying water samples at 180°C yields values for dissolved solids closer to those obtained through summation of individually determined mineral species than the dissolved solids values secured through drying at the lower temperature.

To rinse filters and filtered solids and to clean labware use Type III water. Special samples may require a higher quality water; see Section 1080.

Results for residues high in oil or grease may be questionable because of the difficulty of drying to constant weight in a reasonable time.

To aid in quality assurance, analyze samples in duplicate. Dry samples to constant weight if possible. This entails multiple drying-cooling-weighing cycles for each determination.

Analyses performed for some special purposes may demand deviation from the stated procedures to include an unusual constituent with the measured solids. Whenever such variations of technique are introduced, record and present them with the results.

3. Sample Handling and Preservation

Use resistant-glass or plastic bottles, provided that the material in suspension does not adhere to container walls. Begin analysis as soon as possible because of the impracticality of preserving the sample. Refrigerate sample at 4°C up to the time of analysis to minimize microbiological decomposition of solids. Preferably do not hold samples more than 24 h. In no case hold sample more than 7 d. Bring samples to room temperature before analysis.

4. Selection of Method

Methods B through F are suitable for the determination of solids in potable, surface, and saline waters, as well as domestic and industrial wastewaters in the range up to 20 000 mg/L.

Method G is suitable for the determination of solids in sediments, as well as solid and semisolid materials produced during water and wastewater treatment.

5. Bibliography

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2540 B. Total Solids Dried at 103–105°C

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1. General Discussion

a. Principle: A well-mixed sample is evaporated in a weighed dish and dried to constant weight in an oven at 103 to 105°C. The increase in weight over that of the empty dish represents the total solids. The results may not represent the weight of actual dissolved and suspended solids in wastewater samples (see above).

b. Interferences: Highly mineralized water with a significant concentration of calcium, magnesium, chloride, and/or sulfate may be hygroscopic and require prolonged drying, proper desiccation, and rapid weighing. Exclude large, floating particles or submerged agglomerates of nonhomogeneous materials from the sample if it is determined that their inclusion is not desired in the final result. Disperse visible floating oil and grease with a blender before withdrawing a sample portion for analysis. Because excessive residue in the dish may form a water-trapping crust, limit sample to no more than 200 mg residue (see Section 2540A.2).

2. Apparatus

a. Evaporating dishes: Dishes of 100-mL capacity made of one of the following materials:

1) Porcelain, 90-mm diam.

2) Platinum—Generally satisfactory for all purposes.

3) High-silica glass.#(44)*

b. Muffle furnace for operation at 550°C.

c. Steam bath.

d. Desiccator, provided with a desiccant containing a color indicator of moisture concentration or an instrumental indicator.

e. Drying oven, for operation at 103 to 105°C.

f. Analytical balance, capable of weighing to 0.1 mg.

g. Magnetic stirrer with TFE stirring bar.

h. Wide-bore pipets.#(45)†

i. Graduated cylinder.

j. Low-form beaker.#(46)‡

3. Procedure

a. Preparation of evaporating dish: If volatile solids are to be measured ignite clean evaporating dish at 550°C for 1 h in a muffle furnace. If only total solids are to be measured, heat clean dish to 103 to 105°C for 1 h. Store and cool dish in desiccator until needed. Weigh immediately before use.

b. Sample analysis: Choose a sample volume that will yield a residue between 2.5 and 200 mg. Pipet a measured volume of well-mixed sample, during mixing, to a preweighed dish. For homogeneous samples, pipet from the approximate midpoint of the container but not in the vortex. Choose a point both middepth and midway between wall and vortex. Evaporate to

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dryness on a steam bath or in a drying oven. Stir sample with a magnetic stirrer during transfer. If necessary, add successive sample portions to the same dish after evaporation. When evaporating in a drying oven, lower temperature to approximately 2°C below boiling to prevent splattering. Dry evaporated sample for at least 1 h in an oven at 103 to 105°C, cool dish in desiccator to balance temperature, and weigh. Repeat cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained, or until weight change is less than 4% of previous weight or 0.5 mg, whichever is less. When weighing dried sample, be alert to change in weight due to air exposure and/or sample degradation. Analyze at least 10% of all samples in duplicate. Duplicate determinations should agree within 5% of their average weight.

4. Calculation

$$\text{mg total solids/L} = \frac{(A - B) \times 1000}{\text{sample volume, mL}}$$

where:

A = weight of dried residue + dish, mg, and
B = weight of dish, mg.

5. Precision

Single-laboratory duplicate analyses of 41 samples of water and wastewater were made with a standard deviation of differences of 6.0 mg/L.

6. Bibliography

SYMONS, G.E. & B. MOREY. 1941. The effect of drying time on the determination of solids in sewage and sewage sludges. *Sewage Works J.* 13:936.

2540 C. Total Dissolved Solids Dried at 180°C

1. General Discussion

a. Principle: A well-mixed sample is filtered through a standard glass fiber filter, and the filtrate is evaporated to dryness in a weighed dish and dried to constant weight at 180°C. The increase in dish weight represents the total dissolved solids. This procedure may be used for drying at other temperatures.

The results may not agree with the theoretical value for solids calculated from chemical analysis of sample (see above). Approximate methods for correlating chemical analysis with dissolved solids are available.[1] The filtrate from the total suspended solids determination (Section 2540D) may be used for determination of total dissolved solids.

b. Interferences: See Section 2540A.2 and Section 2540B.1. Highly mineralized waters

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with a considerable calcium, magnesium, chloride, and/or sulfate content may be hygroscopic and require prolonged drying, proper desiccation, and rapid weighing. Samples high in bicarbonate require careful and possibly prolonged drying at 180°C to insure complete conversion of bicarbonate to carbonate. Because excessive residue in the dish may form a water-trapping crust, limit sample to no more than 200 mg residue.

2. Apparatus

Apparatus listed in Section 2540B.2*a* - h is required, and in addition:

a. Glass-fiber filter disks#(47)* without organic binder.

b. Filtration apparatus: One of the following, suitable for the filter disk selected:

1) *Membrane filter funnel.*

2) *Gooch crucible,* 25-mL to 40-mL capacity, with Gooch crucible adapter.

3) *Filtration apparatus* with reservoir and coarse (40- to 60-µm) fritted disk as filter support.#(48)†

c. Suction flask, of sufficient capacity for sample size selected.

d. Drying oven, for operation at 180 ± 2°C.

3. Procedure

a. Preparation of glass-fiber filter disk: If pre-prepared glass fiber filter disks are used, eliminate this step. Insert disk with wrinkled side up into filtration apparatus. Apply vacuum and wash disk with three successive 20-mL volumes of reagent-grade water. Continue suction to remove all traces of water. Discard washings.

b. Preparation of evaporating dish: If volatile solids are to be measured, ignite cleaned evaporating dish at 550°C for 1 h in a muffle furnace. If only total dissolved solids are to be measured, heat clean dish to 180 ± 2°C for 1 h in an oven. Store in desiccator until needed. Weigh immediately before use.

c. Selection of filter and sample sizes: Choose sample volume to yield between 2.5 and 200 mg dried residue. If more than 10 min are required to complete filtration, increase filter size or decrease sample volume.

d. Sample analysis: Stir sample with a magnetic stirrer and pipet a measured volume onto a glass-fiber filter with applied vacuum. Wash with three successive 10-mL volumes of reagent-grade water, allowing complete drainage between washings, and continue suction for about 3 min after filtration is complete. Transfer total filtrate (with washings) to a weighed evaporating dish and evaporate to dryness on a steam bath or in a drying oven. If necessary, add successive portions to the same dish after evaporation. Dry evaporated sample for at least 1 h in an oven at 180 ± 2°C, cool in a desiccator to balance temperature, and weigh. Repeat drying cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained or until weight change is less than 4% of previous weight or 0.5 mg, whichever is less. Analyze at least 10% of all samples in duplicate. Duplicate determinations should agree within 5% of their

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average weight. If volatile solids are to be determined, follow procedure in Section 2540E.

4. Calculation

$$\text{mg total dissolved solids/L} = \frac{(A - B) \times 1000}{\text{sample volume, mL}}$$

where:

A = weight of dried residue + dish, mg, and
B = weight of dish, mg.

5. Precision

Single-laboratory analyses of 77 samples of a known of 293 mg/L were made with a standard deviation of differences of 21.20 mg/L.

6. Reference

1. SOKOLOFF, V.P. 1933. Water of crystallization in total solids of water analysis. *Ind. Eng. Chem.*, Anal. Ed. 5:336.

7. Bibliography

HOWARD, C.S. 1933. Determination of total dissolved solids in water analysis. *Ind. Eng. Chem.*, Anal. Ed. 5:4.

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2540 D. Total Suspended Solids Dried at 103–105°C

1. General Discussion

a. Principle: A well-mixed sample is filtered through a weighed standard glass-fiber filter and the residue retained on the filter is dried to a constant weight at 103 to 105°C. The increase in weight of the filter represents the total suspended solids. If the suspended material clogs the filter and prolongs filtration, it may be necessary to increase the diameter of the filter or decrease the sample volume. To obtain an estimate of total suspended solids, calculate the difference between total dissolved solids and total solids.

b. Interferences: See Section 2540A.2 and Section 2540B.1. Exclude large floating particles or submerged agglomerates of nonhomogeneous materials from the sample if it is determined that their inclusion is not representative. Because excessive residue on the filter may form a

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water-entrapping crust, limit the sample size to that yielding no more than 200 mg residue. For samples high in dissolved solids thoroughly wash the filter to ensure removal of dissolved material. Prolonged filtration times resulting from filter clogging may produce high results owing to increased colloidal materials captured on the clogged filter.

2. Apparatus

Apparatus listed in Section 2540B.2 and Section 2540C.2 is required, except for evaporating dishes, steam bath, and 180°C drying oven. In addition:

Aluminum weighing dishes.

3. Procedure

a. Preparation of glass-fiber filter disk: If pre-prepared glass fiber filter disks are used, eliminate this step. Insert disk with wrinkled side up in filtration apparatus. Apply vacuum and wash disk with three successive 20-mL portions of reagent-grade water. Continue suction to remove all traces of water, turn vacuum off, and discard washings. Remove filter from filtration apparatus and transfer to an inert aluminum weighing dish. If a Gooch crucible is used, remove crucible and filter combination. Dry in an oven at 103 to 105°C for 1 h. If volatile solids are to be measured, ignite at 550°C for 15 min in a muffle furnace. Cool in desiccator to balance temperature and weigh. Repeat cycle of drying or igniting, cooling, desiccating, and weighing until a constant weight is obtained or until weight change is less than 4% of the previous weighing or 0.5 mg, whichever is less. Store in desiccator until needed.

b. Selection of filter and sample sizes: Choose sample volume to yield between 2.5 and 200 mg dried residue. If volume filtered fails to meet minimum yield, increase sample volume up to 1 L. If complete filtration takes more than 10 min, increase filter diameter or decrease sample volume.

c. Sample analysis: Assemble filtering apparatus and filter and begin suction. Wet filter with a small volume of reagent-grade water to seat it. Stir sample with a magnetic stirrer at a speed to shear larger particles, if practical, to obtain a more uniform (preferably homogeneous) particle size. Centrifugal force may separate particles by size and density, resulting in poor precision when point of sample withdrawal is varied. While stirring, pipet a measured volume onto the seated glass-fiber filter. For homogeneous samples, pipet from the approximate midpoint of container but not in vortex. Choose a point both middepth and midway between wall and vortex. Wash filter with three successive 10-mL volumes of reagent-grade water, allowing complete drainage between washings, and continue suction for about 3 min after filtration is complete. Samples with high dissolved solids may require additional washings. Carefully remove filter from filtration apparatus and transfer to an aluminum weighing dish as a support. Alternatively, remove the crucible and filter combination from the crucible adapter if a Gooch crucible is used. Dry for at least 1 h at 103 to 105°C in an oven, cool in a desiccator to balance temperature, and weigh. Repeat the cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained or until the weight change is less than 4% of the previous weight or 0.5 mg, whichever is less. Analyze at least 10% of all samples in duplicate. Duplicate determinations should agree

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within 5% of their average weight. If volatile solids are to be determined, treat the residue according to 2540E.

4. Calculation

$$\text{mg total suspended solids/L} = \frac{(A - B) \times 1000}{\text{sample volume, mL}}$$

where:

A = weight of filter + dried residue, mg, and
B = weight of filter, mg.

5. Precision

The standard deviation was 5.2 mg/L (coefficient of variation 33%) at 15 mg/L, 24 mg/L (10%) at 242 mg/L, and 13 mg/L (0.76%) at 1707 mg/L in studies by two analysts of four sets of 10 determinations each.

Single-laboratory duplicate analyses of 50 samples of water and wastewater were made with a standard deviation of differences of 2.8 mg/L.

6. Bibliography

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determination. *J. Water Pollut. Control Fed.* 50:2370.

2540 E. Fixed and Volatile Solids Ignited at 550°C

1. General Discussion

a. Principle: The residue from Method B, C, or D is ignited to constant weight at 550°C. The remaining solids represent the fixed total, dissolved, or suspended solids while the weight lost on ignition is the volatile solids. The determination is useful in control of wastewater treatment plant operation because it offers a rough approximation of the amount of organic matter present in the solid fraction of wastewater, activated sludge, and industrial wastes.

b. Interferences: Negative errors in the volatile solids may be produced by loss of volatile matter during drying. Determination of low concentrations of volatile solids in the presence of high fixed solids concentrations may be subject to considerable error. In such cases, measure for suspect volatile components by another test, for example, total organic carbon (Section 5310). Highly alkaline residues may react with silica in sample or silica-containing crucibles.

2. Apparatus

See Section 2540B.2, Section 2540C.2, and Section 2540D.2.

3. Procedure

Ignite residue produced by Method 2540B, C, or D to constant weight in a muffle furnace at a temperature of 550°C. Ignite a blank glass fiber filter along with samples. Have furnace up to temperature before inserting sample. Usually, 15 to 20 min ignition are required for 200 mg residue. However, more than one sample and/or heavier residues may overtax the furnace and necessitate longer ignition times. Let dish or filter disk cool partially in air until most of the heat has been dissipated. Transfer to a desiccator for final cooling in a dry atmosphere. Do not overload desiccator. Weigh dish or disk as soon as it has cooled to balance temperature. Repeat cycle of igniting, cooling, desiccating, and weighing until a constant weight is obtained or until weight change is less than 4% or 0.5 mg, whichever is less. Analyze at least 10% of all samples in duplicate. Duplicate determinations should agree within 5% of their average weight. Weight loss of the blank filter is an indication of unsuitability of a particular brand or type of filter for this analysis.

4. Calculation

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$$\text{mg volatile solids/L} = \frac{(A - B) \times 1000}{\text{sample volume, mL}}$$

$$\text{mg fixed solids/L} = \frac{(B - C) \times 1000}{\text{sample volume, mL}}$$

where:

A = weight of residue + dish before ignition, mg,
B = weight of residue + dish or filter after ignition, mg, and
C = weight of dish or filter, mg.

5. Precision

The standard deviation was 11 mg/L at 170 mg/L volatile total solids in studies by three laboratories on four samples and 10 replicates. Bias data on actual samples cannot be obtained.

2540 F. Settleable Solids

1. General Discussion

Settleable solids in surface and saline waters as well as domestic and industrial wastes may be determined and reported on either a volume (mL/L) or a weight (mg/L) basis.

2. Apparatus

The volumetric test requires only an Imhoff cone. The gravimetric test requires all the apparatus listed in Section 2540D.2 and a glass vessel with a minimum diameter of 9 cm.

3. Procedure

a. Volumetric: Fill an Imhoff cone to the 1-L mark with a well-mixed sample. Settle for 45 min, gently agitate sample near the sides of the cone with a rod or by spinning, settle 15 min longer, and record volume of settleable solids in the cone as milliliters per liter. If the settled matter contains pockets of liquid between large settled particles, estimate volume of these and subtract from volume of settled solids. The practical lower limit of measurement depends on sample composition and generally is in the range of 0.1 to 1.0 mL/L. Where a separation of settleable and floating materials occurs, do not estimate the floating material as settleable matter. Replicates usually are not required.

Where biological or chemical floc is present, the gravimetric method (3*b*) is preferred.

b. Gravimetric:

1) Determine total suspended solids as in Section 2540D.

2) Pour a well-mixed sample into a glass vessel of not less than 9 cm diam using not less

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than 1 L and sufficient sample to give a depth of 20 cm. Alternatively use a glass vessel of greater diameter and a larger volume of sample. Let stand quiescent for 1 h and, without disturbing the settled or floating material, siphon 250 mL from center of container at a point halfway between the surface of the settled material and the liquid surface. Determine total suspended solids (milligrams per liter) of this supernatant liquor (Section 2540D). These are the nonsettleable solids.

4. Calculation

mg settleable solids/L = mg total suspended solids/L – mg nonsettleable solids/L

5. Precision and Bias

Precision and bias data are not now available.

6. Bibliography

FISCHER, A.J. & G.E. SYMONS. 1944. The determination of settleable sewage solids by weight. *Water Sewage Works* 91:37.

2540 G. Total, Fixed, and Volatile Solids in Solid and Semisolid Samples

1. General Discussion

a. Applicability: This method is applicable to the determination of total solids and its fixed and volatile fractions in such solid and semisolid samples as river and lake sediments, sludges separated from water and wastewater treatment processes, and sludge cakes from vacuum filtration, centrifugation, or other sludge dewatering processes.

b. Interferences: The determination of both total and volatile solids in these materials is subject to negative error due to loss of ammonium carbonate and volatile organic matter during drying. Although this is true also for wastewater, the effect tends to be more pronounced with sediments, and especially with sludges and sludge cakes. The mass of organic matter recovered from sludge and sediment requires a longer ignition time than that specified for wastewaters, effluents, or polluted waters. Carefully observe specified ignition time and temperature to control losses of volatile inorganic salts if these are a problem. Make all weighings quickly because wet samples tend to lose weight by evaporation. After drying or ignition, residues often are very hygroscopic and rapidly absorb moisture from the air. Highly alkaline residues may react with silica in the samples or silica-containing crucibles.

2. Apparatus

All the apparatus listed in Section 2540B.2 is required except that a magnetic stirrer and pipets are not used and a balance capable of weighing to 10 mg may be used.

3. Procedure

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a. Total solids:

1) Preparation of evaporating dish—If volatile solids are to be measured, ignite a clean evaporating dish at 550°C for 1 h in a muffle furnace. If only total solids are to be measured, heat dish at 103 to 105°C for 1 h in an oven. Cool in desiccator, weigh, and store in desiccator until ready for use.

2) Sample analysis

a) Fluid samples—If the sample contains enough moisture to flow more or less readily, stir to homogenize, place 25 to 50 g in a prepared evaporating dish, and weigh. Evaporate to dryness on a water bath, dry at 103 to 105°C for 1 h, cool to balance temperature in an individual desiccator containing fresh desiccant, and weigh. Repeat heating, cooling, desiccating, and weighing procedure until the weight change is less than 4% or 50 mg, whichever is less. Analyze at least 10% of all samples in duplicate. Duplicate determinations should agree within 5% of their average weight.

b) Solid samples—If the sample consists of discrete pieces of solid material (dewatered sludge, for example), take cores from each piece with a No. 7 cork borer or pulverize the entire sample coarsely on a clean surface by hand, using rubber gloves. Place 25 to 50 g in a prepared evaporating dish and weigh. Place in an oven at 103 to 105°C overnight. Cool to balance temperature in a desiccator and weigh. Repeat drying (1 h), cooling, weighing, and desiccating steps until weight change is less than 4% or 50 mg, whichever is less. Analyze at least 10% of all samples in duplicate. Duplicate determinations should agree within 5% of their average weight.

b. Fixed and volatile solids: Transfer the dried residue from 2)a) above to a cool muffle furnace, heat furnace to 550°C, and ignite for 1 h. (If the residue contains large amounts of organic matter, first ignite it over a gas burner and under an exhaust hood in the presence of adequate air to lessen losses due to reducing conditions and to avoid odors in the laboratory.) Cool in desiccator to balance temperature and weigh. Repeat igniting (30 min), cooling, desiccating and weighing steps until the weight change is less than 4% or 50 mg, whichever is less. Analyze at least 10% of all samples in duplicate. Duplicate determinations should agree within 5% of their average weight.

4. Calculation

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$$\% \text{ total solids} = \frac{(A - B) \times 100}{C - B}$$

$$\% \text{ volatile solids} = \frac{(A - D) \times 100}{A - B}$$

$$\% \text{ fixed solids} = \frac{(D - B) \times 100}{A - B}$$

where:

A = weight of dried residue + dish, mg,
B = weight of dish,
C = weight of wet sample + dish, mg, and
D = weight of residue + dish after ignition, mg.

5. Precision and Bias

Precision and bias data are not now available.

6. Bibliography

GOODMAN, B.L. 1964. Processing thickened sludge with chemical conditioners. Pages 78 et seq. *in* Sludge Concentration, Filtration and Incineration. Univ. Michigan Continued Education Ser. No. 113, Ann Arbor.

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2550 TEMPERATURE#(49)*

2550 A. Introduction

Temperature readings are used in the calculation of various forms of alkalinity, in studies of saturation and stability with respect to calcium carbonate, in the calculation of salinity, and in general laboratory operations. In limnological studies, water temperatures as a function of depth often are required. Elevated temperatures resulting from discharges of heated water may have significant ecological impact. Identification of source of water supply, such as deep wells, often is possible by temperature measurements alone. Industrial plants often require data on water temperature for process use or heat-transmission calculations.

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2550 B. Laboratory and Field Methods

1. Laboratory and Other Non-Depth Temperature Measurements

Normally, temperature measurements may be made with any good mercury-filled Celsius thermometer. As a minimum, the thermometer should have a scale marked for every 0.1°C, with markings etched on the capillary glass. The thermometer should have a minimal thermal capacity to permit rapid equilibration. Periodically check the thermometer against a precision thermometer certified by the National Institute of Standards and Technology (NIST, formerly National Bureau of Standards)#(50)* that is used with its certificate and correction chart. For field operations use a thermometer having a metal case to prevent breakage.

Thermometers are calibrated for total immersion or partial immersion. One calibrated for total immersion must be completely immersed to the depth of the etched circle around the stem just below the scale level.

2. Depth Temperature Measurements

Depth temperature required for limnological studies may be measured with a reversing thermometer, thermophone, or thermistor. The thermistor is most convenient and accurate; however, higher cost may preclude its use. Calibrate any temperature measurement devices with a NIST-certified thermometer before field use. Make readings with the thermometer or device immersed in water long enough to permit complete equilibration. Report results to the nearest 0.1 or 1.0°C, depending on need.

The thermometer commonly used for depth measurements is of the reversing type. It often is mounted on the sample collection apparatus so that a water sample may be obtained simultaneously. Correct readings of reversing thermometers for changes due to differences between temperature at reversal and temperature at time of reading. Calculate as follows:

$$\Delta T = \left[\frac{(T^1 - t)(T^1 + V_0)}{K}\right] \times \left[1 + \frac{(T^1 - t)(T^1 + V_0)}{K}\right] + L$$

where:

ΔT = correction to be added algebraically to uncorrected reading,
T^1 = uncorrected reading at reversal,
t = temperature at which thermometer is read,
V_0 = volume of small bulb end of capillary up to 0°C graduation,
K = constant depending on relative thermal expansion of mercury and glass (usual

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value of K = 6100), and

L = calibration correction of thermometer depending on T^1.

If series observations are made it is convenient to prepare graphs for a thermometer to obtain ΔT from any values of T^1 and t.

3. Bibliography

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REE, W.R. 1953. Thermistors for depth thermometry. *J. Amer. Water Works Assoc.* 45:259.

2560 PARTICLE COUNTING AND SIZE DISTRIBUTION (PROPOSED)#(51)*

2560 A. Introduction

1. General Discussion

Particles are ubiquitous in natural waters and in water and wastewater treatment streams. Particle counting and size distribution analysis can help to determine the makeup of natural waters, treatment plant influent, process water, and finished water. Similarly, it can aid in designing treatment processes, making decisions about changes in operations, and/or determining process efficiency. Methods for measuring particle size distribution included herein depend on electronic measurement devices because manual methods are likely to be too slow for routine analysis. However, when particle size analysis is to include size distribution of large (>500-μm) aggregates, use direct microscopic counting and sizing. Principles of various types of instruments capable of producing both size and number concentration information on particulate dispersions are included. Unless explicitly stated otherwise, the term ‘‘size distribution’’ means an absolute size distribution, i.e., one that includes the number concentration or count.

In most particle-counting instruments, particles pass though a sensing zone where they are measured individually; the only exception included is the static type of light-scattering instrument. Instruments create an electronic pulse (voltage, current, or resistance) that is proportional to a characteristic size of the particle. The instrument responses (pulse height, width, or area) are classified by magnitude and counted in each class to yield the particle size distribution.

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2. Selection of Method

Three instrument types are included: electrical sensing zone instruments, light-blockage instruments, and light-scattering instruments.

Select instrument consistent with expected use of the particle size analysis. Instruments vary in the particle characteristic being sensed, lower and upper size limits of detection, degree of resolution of the size distribution, particle number concentration range that can be measured accurately, amount of shear to which a sample is subjected before measurement, amount of sample preparation, operator skill required, and the ease with which data can be obtained and manipulated into the desired forms. See Section 2560B.1, Section 2560C.1, and Section 2560D.1, and manufacturers' literature for information on characteristics of each type of instrumentation.

Some instruments can be set up for either continuous-flow or batch sampling. Others can be used only for batch analysis. For instruments usable in both modes, check that no systematic differences in particle size distributions occur between continuous-flow measurements and batch samples taken at or near the intake point for continuous-flow samples.

3. Sample Collection and Handling

a. Batch samples: Use extreme care in obtaining, handling, and preparing batch samples to avoid changing total particle count and size distribution.

Choose representative times and locations for sampling. Ensure that particles are not subjected to greater physical forces during collection than in their natural setting. Collect samples from a body of water with submerged vessels to minimize turbulence and bubble entrainment. If sampling from particular depths, use standard samplers designed for that purpose. For flowing systems, make sure that the velocity into the opening of the sampling device is the same as that of the flowing stream (isokinetic sampling) and that the opening diameter is at least 50 times as large as the particles to be measured. For sampling from a tap, let water flow slowly and continuously down the side of the collection vessel.

Minimize particle contamination from the air, dilution water (or, for electrical sensing zone instruments, electrolyte solution) (see ¶ 4 below), and any vessel or glassware that comes in contact with the sample. Minimize exposure to air by keeping sample in a closed container and by minimizing time between sampling and analysis.

Preferably use glass bottles and other vessels with bottle cap liners of TFE.

Clean all glassware scrupulously by automatic dishwashing, vigorous hand brushing, and/or ultrasonication. Rinse glassware immediately before use with particle-free water. Between samples, rinse any part of the instrument that comes in contact with samples with either clean water or the upcoming sample. Alternatively, run multiple replicates and discard the first results.

To avoid breakup of aggregates of particles or flocs, sample and make dilutions very slowly using wide-bore pipets, needles, or other sampling devices; cut off pipet tips to avoid high velocities at the entrance. If sample dilution is required, add sample to dilution water, not vice

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versa, by submerging the pipet tip in the dilution water and releasing sample slowly. Use minimum intensity and duration of mixing adequate to dilute the suspension into the dilution water. Avoid mechanical stirrers inside the sample or ultrasonication. Simultaneously gently rotate and partially invert entire sample in a closed bottle. Use cylindrical dilution bottles to avoid sharp corners. Leave less than approximately 25% air space during mixing. To avoid sedimentation, make measurements immediately after mixing. Do not mix during measurement unless absolutely necessary to prevent sedimentation.

Most surface and ground waters contain relatively stable particles that aggregate slowly. Particle size distribution in biologically active waters or waters that have been treated with coagulants is more likely to change over short time periods. To minimize flocculation, minimize time between sampling and measurement. In highly flocculent systems, maximum holding time should be only a few minutes; for more stable samples, a few hours may be acceptable. Dilution slows flocculation kinetics and, in some cases, makes flocculation less likely. Make dilutions only immediately before measurement.

Samples measured at different temperature or pressure than when collected and those with biological activity may develop entrained air bubbles that interfere with measurement accuracy. If any gas bubbles are visible, let sample stand for a short time to degas naturally or use a mild vacuum to speed degassing. Use ultrasound to aid degassing, but only if floc breakup is not a problem.

Minimize time between sampling and analysis; if at all possible, make measurements immediately after sampling. If storage is unavoidable, refrigerate at 4°C but restore samples to room temperature, preferably in water bath, before measurement.

b. Continuous-flow: Using a particle counter as a continuous-flow monitor may be desirable. Many more samples can be processed by automated particle counting than by batch sample analysis. All the instruments mentioned in Methods B through D can be used in this mode, although instruments and samples not requiring dilution are easier to set up. For some instruments, this type of operation requires custom hardware; for others there is commercially available hardware.

Problems of batch samples are equally relevant to continuous analysis. Other critical considerations include selection of sampling point, velocity at entrance and throughout sample line, maintenance of stable sample flow rate, position of instrument's sensor in the sample line, and absence of flow-modifying devices upstream of the sensor.

Choose a sampling point that is representative and away from wall surfaces. Place entrance to sample line facing the flow, with the velocity at the opening nearly the same as the surrounding flow.

Sample preservation within the instrument is difficult because both deposition (or temporary holdup) of particles and floc breakup must be avoided. Deposition occurs by gravity settling of particles onto horizontal surfaces. Floc breakup occurs because of excessive shear forces. Minimize length of transmission lines, especially in horizontal components, and preferably have no horizontal lines. Avoid drastic changes in flow direction or velocity. Do not use

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flow-modifying devices such as pumps, fittings with irregular surfaces, sharp angle changes, flow controllers, etc., between the sampling point and the sensor. Locate pumps after the sensor. Preferably, provide curved sample lines (e.g., flexible tubing or bent glass tubing) rather than right-angle fittings.

For most instruments, flow rate is specified. Because calibration (see ¶ 5) can change with flow rate within the range, flow control within very narrow limits is essential. Calibrate and use the sensor at the same flow rate. For continuous particle size distribution measurements, flow control, not simply flow monitoring, is necessary. Do not make measurements at a flow rate different from that used for calibration. Provide a flow control system downstream of the sensor, maintain a constant rate, and do not introduce turbulence or pulsations before or through the sensor.

4. Dilution Water

Particle-free water is virtually impossible to obtain, but it is possible to produce water containing very few particles within the size range to be measured. Produce ‘‘particle-free’’ or ‘‘clean’’ water from distilled, deionized water or water taken from the same source as the samples. If all samples are from the same source or have similar chemical characteristics, preferably filter sample water to produce ‘‘particle-free’’ water with no change in chemical environment. Distilled, deionized water produced by ion exchange and cartridge filtration may produce acceptable ‘‘particle free’’ dilution water, but preferably use continuous closed-loop membrane filtration.

Dilution water preparation systems are available from particle-counter manufacturers. Alternatively, assemble a system similar to that shown in Figure 2560:1 (or any system that produces a water of sufficient quality). In the system shown, a pump draws the water from a bottle and puts it through the in-line filter. Use membrane filters with nominal pore sizes no more than 10% of the smallest particle size expected; alternatively use cartridge filters. Pass water through the filter several times. The system lets water be passed directly from the product-water bottle to the source-water bottle by opening of the clamps and three-way stopcock. Use glass tubing in the bottles, but use flexible tubing to allow draining product-water bottle into source-water bottle. Attach a glass wool or membrane filter to air inlets. Dilute samples by drawing water directly from the three-way stopcock into the bottle to be used in sample analysis.

A simpler system with one-pass filtration directly into the sample bottle may be adequate for many samples, depending on the particle size range to be measured. Such a system would omit the product-water bottle, the connections between the two bottles and associated stopcock and clamps of Figure 2560:1. Dilution water is produced on demand and the effluent is put directly, without additional handling, into the sample container.

Guard against biological growth within filtration systems by frequent disassembly and adequate washing or replacement of components. For many samples, do not use chemical disinfectants because they might change the particle count and size distribution by their oxidizing potential.

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5. Calibration

As a particle is detected in the sensing zone of any instrument, an electrical response is generated and sorted into a channel of the instrument based on its magnitude.

Calibrate by determining the channel number into which particles of known size are sorted by the instrument. Use spherical particles manufactured for this purpose. Calibration particles are available in suspension or as dry particles. Over time, suspensions are likely to undergo some aggregation; use ultrasound to break up flocs before calibration. Calibration particles are nearly monodisperse but do exhibit a small inherent (true) variance.

The precision (see Section 1030A.1) and resolution of the instrument influence its ability to sort particles into different channels. Resolution is a measure of the ability of an instrument to distinguish between particles of similar but different sizes. An instrument with high precision and good resolution will measure monodisperse particles in a very narrow size range; some instruments have sufficient precision and resolution so that calibration particles with extremely narrow size distributions (very small variance) are sorted into a few adjacent channels. In such cases, the true variance of the particle size and the measured variance will be nearly equal. An instrument with low precision but high resolution will yield a wide distribution on the same particles (i.e., measured variance > true variance). An instrument with high precision but low resolution (e.g., few channels) may yield a narrow measured distribution (e.g., all the particles in the same channel) even though the true distribution is broader (i.e., measured variance < true variance).

Use at least three sizes of calibration particles in reasonably similar number concentrations to calibrate a sensor. To analyze different-size particles in a mixture, ensure that the different sizes do not interfere with one another. Calibrate under conditions identical with those of sample measurements, e.g., settingson the instrument, flow rate, type of sample cell, dilution water or electrolyte solution, and mixing during measurement. Do not exceed the maximum concentration for the sensor during calibration.

The calibration curve depends on the characteristic of the particle measured by the instrument (diameter, area, or volume) and whether the pulses are sorted into channels on an arithmetic or logarithmic basis. For example, if an electrical sensing zone instrument (which responds to particle volume) is used in a logarithmic mode, the calibration curve will be the logarithm of particle volume vs. channel number.

Generally, increments between channels are equal on an arithmetic or logarithmic basis. In most light-blockage and light-scattering instruments, the lower and upper limits for each channel can be set by the user. Because most samples have broad particle size distributions, spanning at least one order of magnitude, and often two or three, preferably use larger increments for larger sizes. This is consistent with equal logarithmic spacing, although other less systematic intervals that preserve the characteristic of larger increments for larger sizes are permissible. Such intervals also are consistent with the resolution capabilities of most available instruments, which respond to a characteristic particle area or volume (proportional to square or cube of diameter, respectively), and therefore require greater resolution for larger particles than for smaller ones on

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a diameter basis.

At a given set of settings for a given sensor, each channel represents a certain average size and size increment. After measuring the channel number associated with several sizes of calibration particles, use a calibration equation to assign average sizes or, in some cases, the lower limit of size, to all other channels. Knowledge of the average size and both the arithmetic and logarithmic increment of each channel is necessary for reporting. In contrast to calibration particles, environmental particles are rarely spherical. Generally report measurements in terms of ‘‘equivalent spherical diameter,’’ i.e., size of any particle taken as that of a sphere that would give the same response in the instrument. Because most sample particles are nonspherical and different instruments respond to different characteristics of particles, different measured particle size distributions result from different instruments.

Some light-scattering instruments calculate particle size from first principles and do not require calibration per se. For those instruments, periodically adjust the system optics. Make frequent checks that the instrument response is consistent by following the calibration procedures for other instruments.

6. Data Reporting

a. Particle concentrations: Number, surface, or volume concentration over a specified size range is particularly valuable as a summary factor for particle counting and size distribution. Its variation with some changes in an independent variable in a natural or engineered system may be of interest.

When reporting the number concentration (number per milliliter) of particles, report also the size range measured (both lower and upper size limits). The lower limit is particularly important, because most samples have large number concentrations near the lower limit of detection of currently available instruments. Never state or imply a lower size limit of zero.

In some studies a surface area concentration (μm^2/mL) or volume concentration (μm^3/mL) may be more relevant; convert number concentration to these forms by multiplying by the area or volume, respectively, of a sphere with the mean diameter for each size class. (This is an approximation based on the assumption that particles are spherical.) In such cases, also report lower and upper limits of size class.

b. Tabulated size distributions: If the distribution itself (i.e., the variation of particle number, surface area, or volume concentration with particle size) is to be shown in tabular format, give for each instrument channel (or grouping of channels) the number concentration and the associated size range (lower and upper limits).

c. Graphical size distributions: For graphical reporting, preferably use the count information (on a number, surface area, or volume basis) as the ordinate and particle size as the abscissa.

For the count information, use absolute, rather than relative, scales because they indicate both concentration and size distribution. Also, preferably use differential, rather than cumulative, distributions because they show directly what size range contained the most particles. For ease of plotting, associate the number (or surface area or volume) concentration with a mean size for

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each channel, rather than with the size range (the lower and upper limit). To account for that change without losing information, normalize the data by dividing the concentration of particles in a given size class by the size interval for that class (on either an arithmetic or a logarithmic basis). Normalization prevents creation of artificial (or apparent) peaks or valleys in a distribution and ensures that the same distribution measured by different instruments with different size increments will be the same graphically. If data are not normalized, plot size distribution data (absolute and differential) as a discrete histogram (i.e., as a bar chart with the upper limit of one channel being identical to the lower limit of the next).

Preferably show particle sizes with a logarithmic scale. Most samples have broad distributions and most analyzers use larger increments of diameter with increasing size; these characteristics are consistent with a logarithmic scale, which also intrinsically avoids showing a zero size. Produce the logarithmic scale by showing the log of diameter on an arithmetic scale or the arithmetic values of diameter on a logarithmic scale.

d. Example calculations: A calculation layout (with example data) useful for preparing either tabular or graphical presentation is shown in Table 2560:I. This format may be abbreviated or modified to suit the data presentation being developed.

Columns A through G represent calibration information. Which of these values are set (or determined from calibration by the user) and which are calculated from this primary information depends on the type of instrument. In constructing such a table, preferably place primary information first. In most light-blockage and light-scattering instruments, the lower and upper size limits for each channel are known; calculate mean diameter as the arithmetic or logarithmic (geometric) mean of these limits, depending on whether instrument channels represent arithmetic or logarithmic increments. In electrical sensing zone instruments, the mean size (or log size) is determined directly from the calibration equation and increment width (arithmetic, Δd_{pi}, or logarithmic, $\Delta \log d_{pi}$) is pre-set; calculate lower and upper limits as mean size ± one half the arithmetic or logarithmic increment.

Columns H through O represent counting information for a sample. The corrected counts (Column H) are the direct counts from the particle size analyzer minus the background count for each channel. Adjust background count for dilution and differences in sample measured and dilution water measured for background count. Adjust this figure for sample dilution and volume analyzed to obtain the number concentration of particles (Column I). For example, for corrected count n, a 1:10 dilution, and 0.5 mL analyzed, number concentration is calculated as $(n \times 10)/0.5 = 20n$/mL. Volume concentration (Column J) may be approximated as the number of particles multiplied by the volume of a spherical particle with the mean diameter for the channel ($\pi d^3_p/6$). Values in the remaining columns are calculated as shown in the table. The normalized, differential, absolute distribution functions obtained in Columns K (particle size distribution function) through O give the values needed for graphic presentations as follows:

K: particle numbers (arithmetic scale) vs. diameter (arithmetic scale)

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L: particle volume (arithmetic scale) vs. diameter (arithmetic scale)
M: particle number (arithmetic scale) vs. diameter (logarithmic scale)
N: particle volume (arithmetic scale) vs. diameter (logarithmic scale)
O: log of particle number (arithmetic scale) vs. diameter (logarithmic scale).

(Alternatively, plot values from Column K directly on a logarithmic scale.)

If distribution K, L, M, or N is plotted, the area under the resulting graph between any two values of diameter represents the total number or volume concentration between those size limits. The logarithmic graph (O) shows the entire distribution better than other distributions, but can hide differences between similar distributions. It often is linear over specified size ranges.

7. Quality Control

See Section 1020 and Section 1030. Observe precautions for sampling and handling discussed in ¶ 3 above. Particle counting and size analysis requires experienced analysts capable of judgment in recognizing unusual behavior of an instrument. Ability to recognize partial blockage of an aperture or sensor or electronic noise is essential.

Electronic noise can be detected directly in some instruments by making a particle count when no flow is being put through a sensor. Ensure that the noise is not environmental, i.e., due to other nearby instruments, poor grounding, or inconsistent electrical supply. Noise also can be created by excessive cable length between the sensor and instrument or worn cables and connectors. Perform noise checks periodically.

Analyze sample blanks, handled identically to real samples, daily. Discard data from all channels that yield counts in the blanks greater than 5% of the counts for real samples. This procedure accounts for both particle contamination and electronic noise. Develop a maximum acceptable total count for blanks for each sensor (or for each set of standard settings for one sensor); if blanks give more than this maximum, discontinue particle counting until the contamination or noise is eliminated. Set maximum so that the 5% rule is met for all channels of interest (i.e., down to some minimum size limit acceptable in the laboratory for the sensor in use and the samples being measured). Recognize that the lower size limit of measurement for every sensor and every instrument is more likely to be dictated by electronic noise and particle contamination than by electronic settings.

Test cleaning and rinsing for sample bottles by partially filling the container with clean water, swirling the water to contact all sides, and performing a particle count. When the container has been shown to contribute negligible counts, check cleanliness of the cap similarly. Develop and document the standard washing and rinsing procedure, verify its validity as indicated, and follow the procedure without exception.

Also develop standard procedure for mixing samples and dilution water. Test mixing by varying the mixing intensity and/or duration to determine the minimum that gives adequate reproducibility (a sign of uniform concentration) and to determine if greater mixing increases the total particle counts (a sign of floc breakup). Follow an established mixing procedure without

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exception.

To determine precision, make replicate measurements on at least 5% of the samples. Report standard deviation (or range) of the total particle number concentration for each sensor or the total of all sensors, if more than one is used. See Section 1030.

Particle counting and size distribution analyzers are calibrated for size, not concentration. Standards for calibrating (or checking) the ability of an instrument to measure particle concentration accurately are under development. Currently, only precision, not bias, can be measured well for particle concentration. Obtain an indication of bias by preparing standards of particles of known density at a known suspended solids concentration; multiply total measured particle volume concentration by the known density to estimate the suspended solids concentration from the particle measurements. Compare this estimate with the known suspended solids concentration as an indicator of the combined instrument and laboratory bias.

Periodically calibrate with particles traceable to the National Institute of Standards and Technology (NIST).

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2560 B. Electrical Sensing Zone Method

1. General Discussion

a. Principle: In electrical sensing zone instruments, particles are suspended in an electrolyte solution and pass through a small orifice. A constant current or potential is applied between electrodes on either side of the orifice; the change in resistance caused by the particle taking up volume in the orifice causes a change in potential or current (whichever is not being held constant electronically). The pulse is proportional to the particle volume.

The voltage or current pulses are amplified and sorted into size classes or channels based on their maximum height. Some instruments have fixed channels; others permit selection of number of size classes, size width of each channel, and/or lowest size to be measured.

b. Interferences: Interferences are caused by contamination with particles, the presence of gas bubbles, and electronic noise. See Section 2560A.3*a* and *b* for sampling precautions, and Section 2560A.4 for particle-free water preparation. Minimize electronic noise as directed in Section 2560A.7. Increasing electrolyte strength is another method for minimizing electronic noise.

c. Detectable sizes and concentrations: The lower size limit of measurement depends on both electronic noise and aperture size. Manufacturers claim that the lower size limit (diameter) is approximately 2% of the aperture size, but not lower than approximately 0.4 μm, but values as low as approximately 0.7 μm have been reported. For the upper size limit, manufacturers state the maximum size is 40 to 60% of the aperture size, but a realistic upper limit for measuring flocs is 20% of the aperture size.

The minimum concentration limit depends on the ability to distinguish particles from background counts. For each channel, background count should be less than 5% of total count. In size ranges in which the count is very low (zero or nearly so), counts may be statistically unreliable. Determine if a larger sample volume provides more satisfactory (less scattered) data. Grouping data from several adjacent channels, thereby increasing the size increment, also can give a more accurate size distribution.

The maximum concentration limit depends on the rate at which the instrument can process different pulses and the need to avoid more than one particle in the sensing zone at the same time (coincidence). Follow manufacturers' instructions for upper limits on particle counts for each aperture size. Some instruments include a capability for correcting for overly concentrated samples, but do not use this feature because each particle is not measured individually and errors in absolute size distribution may result.

2. Apparatus

a. Particle counter and size-distribution analyzer.

b. Glassware: For glassware preparation, see Section 2560A.3*a* and Section 2560A.7.

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3. Reagents

a. Particle-free electrolyte solution: Prepare an electrolyte solution of NaCl, $CaCl_2$, $NaNO_3$, $Ca(NO_3)_2$, or some other simple inorganic salt at a concentration of 1 to 10% by weight. Pass solution through a continuous-flow membrane microfiltration system (see Section 2560A.4). Alternatively, use a commercially prepared electrolyte solution (filtration also may be required).

b. Calibration particles: See Section 2560A.5.

4. Procedure

a. Preparation: Let instrument warm up according to manufacturer's instructions. Select proper size aperture for particle sizes of interest; use more than one aperture if size distribution is wider than the range that can be measured with one aperture. Rinse aperture with acid solution, distilled water, and finally clean electrolyte solution. Install aperture. Choose settings on the instrument for each type of choice, including linear or logarithmic mode (spacing of sizes for each channel; logarithmic is preferable for environmental samples), desired size width of each channel, total number of channels and which channels are to be included, and method of starting and stopping counting. Counting can be started and stopped manually, by switches built into the manometer representing set sample volumes, by a set maximum count in any one channel, or stopped by time after a manual start. For reporting absolute measurements, choose a method that measures volume sampled.

b. Calibration: See Section 2560A.5. Calibrate each aperture with at least three particle sizes, determining the channel number at which the maximum count for each size is located. Handle calibration samples identically to those used for measurement. Because calibration can change, check it at each use of the instrument. Plot results as the volume of calibration particles vs. channel number (linear mode) or as the logarithm (base 10 or e) of the volume of calibration particles vs. channel number (logarithmic mode). The results should plot as a straight line. Use an equation for that line to assign an average size to each channel. Convert results from particle volume to particle diameter for reporting.

c. Blank sample: Measure at least one blank sample of the electrolyte solution. Carry a sample bottle with only electrolyte solution through procedures identical to those used for samples. Subtract counts from the blank solution (i.e., background counts), channel by channel, from the counts of the samples. See Section 2560A.7.

d. Measurement of samples: Prepare diluted sample, ensuring that the volume of sample is no greater than the volume of the electrolyte solution (dilution water); if a more concentrated suspension is necessary, prepare dilution water with a higher electrolyte concentration. Mix gently (see Section 2560A.3*a*). Insert sample container into the instrument. Start vacuum to control the mercury column and start particle counting. During counting, continuously watch the monitor provided on the instrument to check for blockage of the aperture by oversized particles. Check that the time for the specified volume (if the count is controlled by the stop and start switches on the manometer) is consistent with that found for particle-free electrolyte solution.

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When count is complete, check that the concentration did not exceed the manufacturer's recommendations. Repeat with a greater dilution if necessary. When a series of samples with various concentrations is to be measured and sample order is not critical, measure samples in order of expected increasing particle concentration, rinsing with next sample.

5. Calculation

See Section 2560A.6.

2560 C. Light-Blockage Methods

1. General Discussion

a. Principle: In light-blockage instruments, a focused beam of light shines from one side of the measurement zone toward a photovoltaic cell on the other side. The illuminated volume of liquid constitutes the sensing zone. Particles pass through the sensing zone at a known velocity. The blockage of light by the particle creates a change in the voltage at the photovoltaic cell. In different instruments, different characteristics of the resulting signal are used to determine size: light obscuration instruments use pulse height (related to the cross-sectional area of the particle) while time-of-transition instruments use the pulse width (proportional to a characteristic length of the particle). In all cases, measurements usually are reported in terms of equivalent spherical diameter.

For light-obscuration instruments, consult manufacturer's literature to determine the relationship between height of the voltage pulse and particle size (and increment of particle size).

Time-of-transition devices typically utilize a laser beam as the light source. The beam may scan a stationary sample at a fixed velocity as it sweeps out an optical sensing zone. Alternatively, a suspension can be passed through a fixed optical sensing zone. In the latter case, the measured particle size is sensitive to flow rate through the sensor.

Devices using light blockage principles vary in the number of channels (size classes) into which particles are sorted. In some cases, these are pre-set by the manufacturer; in others, they can be set by the analyst. Different (interchangeable) sensors are available to measure different size ranges and different particle concentrations.

b. Interferences: Interferences are caused by contamination with particles, the presence of gas bubbles, and electronic noise. See Section 2560A.3*a* and *b* for sampling precautions and Section 2560A.4 for particle-free dilution water preparation. Dilution water is necessary only for samples with particle number concentrations exceeding the capacity of the sensor to distinguish different particles. If dilution water is to be used, analyze it without sample and subtract particle counts in each channel from sample counts.

For devices in which sample flows through the sensor, some electronic noise can be detected by counting with clean water in the sensor and no flow (that is, with no true particle counts). If noise is present, it is likely to occur as a very large number of counts in the smallest size range (lowest channel). Eliminate this noise by re-setting the size range of the smallest channel

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(increasing the lowest size range to be measured) high enough to avoid significant counts in the lowest channel. For further measures to minimize electronic noise, see Section 2560A.7.

c. Detectable sizes and concentrations: The lower size limit of measurement depends on both electronic noise and sensor capability. Devices using the principle of light obscuration typically are limited to particles larger than approximately 1 μm. Devices using the time-of-transition principle can detect particles as small as 0.1 μm. The upper particle size limit usually is determined by the size of the orifice through which particles pass. Manufacturers state particle size limits (lower and upper) for each sensor. See Section 2560B.1*c*.

2. Apparatus

a. Particle counter and size distribution analyzer.

b. Glassware: See Section 2560A.3*a* and Section 2560A.7.

3. Reagents

a. Particle-free dilution water: See Section 2560A.4.

b. Calibration particles: See Section 2560A.5.

4. Procedure

a. Preparation: Let instrument warm up according to manufacturer's instructions. Select sensor to measure size and concentration ranges expected; use more than one sensor if size distribution is wider than the range that can be measured with one sensor. Rinse sensor with a volume of particle-free dilution water equivalent to at least three times that used in measuring samples.

Choose settings on the instrument for each type of choice available: including total number of channels and which channels are to be included, absolute or relative counts, cumulative or differential counts, etc. Also choose method of starting and stopping counting based on total count, maximum count in one channel, duration of counting, or analysis of a specified volume of sample. Usually, the known-volume method is preferable because it lends itself to determination of absolute size distribution.

b. Calibration: See Section 2560A.5. Initial calibration of each sensor on an instrument requires several particle sizes to determine the relationship between particle size and channel number. Either this relationship may be controlled by varying the range of millivolt responses that are sorted into each channel or it is pre-set by the manufacturer.

After initial calibration, use at least two sizes of calibration particles for each sensor each time the instrument is used. For instruments in which the sample flows through a stationary sensing zone, measure flow rate of sample and adjust it to that used during initial calibration.

c. Blank sample: See Section 2560B.4*c* but substitute particle-free dilution water for electrolyte solution.

d. Measurement of samples: Dilute sample, if necessary to keep within manufacturer's guidelines. Mix gently (see Section 2560A.3*a*). For flow-type instruments with pressure-based

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samplers, insert sample container into the instrument; for vacuum-based samplers, insert sampler tubing into the sample container. Start counting only after sufficient sample has passed through the tubing connecting the sample and sensor to ensure that the sensor is receiving the sample. For instruments that scan a stationary sample, gently transfer sample into the measurement device and insert.

For all instruments, when the count is complete, check that the concentration did not exceed the manufacturer's recommendations. Repeat with a greater dilution if necessary.

Between samples, rinse with dilution water or the upcoming sample. When a series of samples with various concentrations is to be measured and sample order is not critical, measure samples in order of expected increasing particle concentration; preferably, rinse with the next sample.

5. Calculation

See Section 2560A.6.

2560 D. Light-Scattering Method

1. General Discussion

a. Principle: Light-scattering instruments may be either flow or static devices. In flow instruments, the direct path of the light beam through the flow cell is blocked by a particle as it flows through the measurement zone with the fluid, and light scattered over a fixed range of angles is collected and measured. Particle size is determined from the angle and intensity of scattering based on the principles of Fraunhofer diffraction and/or Mie scattering. In static instruments, the particles remain quiescent and a laser light beam scans part of the suspension. Scattered light is collected by a photovoltaic cell and the resulting response from all particles scanned is mathematically deconvoluted to generate the size distribution.

Available particle counters vary in the angle or range of angles at which scattered light is measured and in the number of channels (size classes) into which particles are sorted. For flow-type instruments, different (interchangeable) sensors are available to measure different size ranges and different particle concentrations. The particle sizes determined by these instruments are equivalent spherical diameters, i.e., they are determined from the amount of light that would have been scattered at the angle(s) built in to the instrument by a calibration sphere of that diameter.

b. Interferences: For both types of instruments, interferences are caused by contamination of the sample with particles, the presence of gas bubbles, and electronic noise. For static-type instruments, additional sources of interference can be surface contamination (particles, markings, or scratches) on the sample container and sample color. See Section 2560A.3*a* and *b* for sampling precautions and 2560A.4 for particle-free dilution water preparation. Dilution water is necessary only for samples with particle number concentrations exceeding the capacity of the sensor to distinguish different particles. If dilution water is to be used, analyze it without sample

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and subtract particle counts in each channel from sample counts. To correct for color interference, consult the instrument manual.

In flow-type instruments, some electronic noise can be detected by counting with clean water in the sensor and no flow (that is, with no true particle counts). If noise is present, it is likely to occur as a very large number of counts in the smallest size range (lowest channel). Eliminate this noise by resetting the size range of the smallest channel (increasing the lowest size range to be measured) high enough to avoid significant counts in the lowest channel. For further measures to minimize electronic noise, see Section 2560A.7.

For static-type instruments, use a glass container that is optically clear and has no lettering or markings, at least in the light path. Minimize the effect of specific glassware by using the same sample container for all samples that will be compared and ensuring that the orientation of the sample container in the light beam is the same for every sample.

c. Detectable sizes and concentrations: The lower size limit of measurement depends on both electronic noise and sensor capability. For flow-type instruments, the upper particle size limit usually is determined by the size of the orifice through which particles pass. Manufacturers state particle size limits (lower and upper) for each sensor. See Section 2560B.1*c*.

Application of the Mie theory to the scattering data can extend the range of light-scattering instruments to as low as 0.1 μm. Alternatively, some instruments extend the lower limit of detectable diameters to 0.1 μm by augmenting Fraunhofer diffraction data with scattering intensity measurements at a fixed angle (often 90°) using two or three different wavelengths of incident light.

2. Apparatus

a. Particle counter and size distribution analyzer.

b. Glassware: See Section 2560A.3*a* and Section 2560A.7.

3. Reagents

a. Particle-free dilution water: See Section 2560A.4.

b. Calibration particles: See Section 2560A.5.

4. Procedure

a. Preparation: Let instrument warm up according to manufacturer's instructions. For flow-type instruments, select sensor to measure size and concentration ranges expected; use more than one sensor if size distribution is wider than the range that can be measured with one sensor. Preferably use a sensor designed for the concentration range of the undiluted sample rather than diluting samples into the concentration range of the sensor. For both types of instruments, place in or pass through the sensor at least three times a volume of particle-free dilution water equivalent to that used in measuring samples, before the first sample.

Choose settings on the instrument for each type of choice available, including flow rate, total number of channels and which channels are to be included, absolute or relative counts, etc.

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Also choose method of starting and stopping counting: total count, maximum count in one channel, duration of counting, or analysis of a specified volume of sample. For flow-type instruments, the known-volume method is preferable because it lends itself to determination of absolute size distribution. For static-type analyzers, the analyst does not control sample size directly, but can control duration of measurement. Take care not to exceed maximum particle number concentration limits suggested by manufacturer.

Some flow-type instruments permit choice between vacuum or pressure systems for transporting the sample through the sensor. If floc preservation is essential, preferably use a vacuum system but ensure that bubbles do not form before the sensor; otherwise, use a pressure system with a pulseless gear pump.

b. Calibration: See Section 2560A.5. For flow-type instruments, initial calibration of each sensor on an instrument requires several particle sizes to determine the relationship between particle size and channel number. Either this relationship may be controlled by varying the range of millivolt responses that are sorted into each channel, or it is pre-set by the manufacturer. Static-type instruments are pre-set by the manufacturer because sizing is done by a software conversion of the light sensed. After initial calibration, use at least two sizes of calibration particles for each sensor each time the instrument is used. Although the calculation of particle sizes is based on first principles and not on this calibration, calibrate to ensure that the instrument is functioning properly. For flow-type instruments, measure flow rate through the sensor and adjust to that used during initial calibration.

c. Blank sample: See Section 2560B.4*c*, but substitute particle-free dilution water for electrolyte solution.

d. Measurement of samples: If dilution is necessary, dilute sample to keep within manufacturer's guidelines for the maximum counting rate. Mix gently (see Section 2560A.3*a*).

For flow-type instruments, initiate the flow from the sample through the sensor. Check that flow rate is the same as that used for sensor calibration. Start counting only after sufficient sample has passed through the tubing connecting the sample and sensor to ensure that the sensor is receiving the sample. When counting is complete, check that the concentration did not exceed the manufacturer's recommendations. Repeat with a greater dilution if necessary. For subsequent samples, rinse with dilution water or the next sample. When a series of samples with varying concentrations is to be measured and sample order is not critical, measure samples in order of expected increasing particle concentration; in this case, preferably rinse with next sample.

For static-type instruments, insert sample beaker or bottle and start particle counting. When counting is complete, check that the concentration did not exceed the manufacturer's recommendations by diluting and measuring again. If the second count is related to the first according to the ratio of the dilution factors of the two measurements, consider the first measurement acceptable. Repeat with a greater dilution if necessary. For subsequent samples, see directions in preceding paragraph.

5. Calculation

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See Section 2560A.6.

2570 ASBESTOS#(52)*

2570 A. Introduction

1. Occurrence and Significance

The term ‘‘asbestos’’ describes a group of naturally occurring, inorganic, highly fibrous silicate minerals that are easily separated into long, thin, flexible fibers when crushed or processed. Included in the definition are the asbestiform (see ¶ 2 below) varieties of serpentine (chrysotile), riebeckite (crocidolite), grunerite (grunerite asbestos), anthophyllite (anthophyllite asbestos), tremolite (tremolite asbestos), and actinolite (actinolite asbestos).

Asbestos has been used widely as a thermal insulator and in filtration. The tiny, almost indestructible fibers penetrate lung tissue and linings of other body cavities, causing asbestosis and cancer in the lungs and mesothelioma in other cavity linings.

2. Definitions

Asbestiform—having a special type of fibrous habit (form) in which the fibers are separable into thinner fibers and ultimately into fibrils. This habit accounts for greater flexibility and higher tensile strength than other habits of the same mineral. More information on asbestiform mineralogy is available.[1,2]

Aspect ratio—ratio of the length of a fibrous particle to its average width.

Bundle—structure composed of three or more fibers in parallel arrangement with the fibers closer than one fiber diameter to each other.

Cluster—structure with fibers in a random arrangement such that all fibers are intermixed and no single fiber is isolated from the group; groupings of fibers must have more than two points touching.

Fiber (AHERA)—structure having a minimum length greater than or equal to 0.5 μm, an aspect ratio of 5:1 or greater, and substantially parallel sides.[3]

Fibril—single fiber that cannot be separated into smaller components without losing its fibrous properties or appearance.

Fibrous—composed of parallel, radiating, or interlaced aggregates of fibers, from which the fibers are sometimes separable. The crystalline aggregate of a mineral may be referred to as fibrous even if it is not composed of separable fibers, but has that distinct appearance. ‘‘Fibrous’’ is used in a general mineralogical way to describe aggregates of grains that crystallize in a needle-like habit and appear to be composed of fibers; it has a much more general meaning than ‘‘asbestos.’’ While all asbestos minerals are fibrous, not all minerals having fibrous habits are asbestos.

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Matrix—fiber or fibers with one end free and the other end embedded in, or hidden by, a particle. The exposed fiber must meet the fiber definition.

Structures—all the types of asbestos particles, including fibers, bundles, clusters, and matrices.

3. References

1. STEEL, E. & A. WYLIE. 1981. Mineralogical characteristics of asbestos. *In* P.H. Riordon, ed. Geology of Asbestos Deposits. Soc. Mining Engineers—American Inst. Mechanical Engineers, New York, N.Y.
2. ZUSSMAN, J. 1979. The mineralogy of asbestos. *In* Asbestos: Properties, Applications and Hazards. John Wiley & Sons, New York, N.Y.
3. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1987. Asbestos-containing materials in schools: Final rule and notice. *Federal Register*, 40 CFR Part 763, Appendix A to Sub-part E, Oct. 30, 1987.

2570 B. Transmission Electron Microscopy Method

1. General Discussion

This method is used to determine the concentration of asbestos structures, expressed as the number of such structures per liter of water. Asbestos identification by transmission electron microscopy (TEM) is based on morphology, selected area electron diffraction (SAED), and energy dispersive X-ray analysis (EDXA). Information about structure size also is generated. Only asbestos structures containing fibers greater than or equal to 0.5 μm in length are counted. The concentrations of both fibrous asbestos structures greater than 10 μm in length and total asbestos structures per liter of water are determined. The fibrous asbestos structures greater than 10 μm in length are of specific interest for meeting the Federal Maximum Contaminant Level Goal (MCLG) for drinking water, but in many cases the total asbestos concentration provides important additional information.

a. Principle: Sample portions are filtered through a membrane filter. A section of the filter is prepared and transferred to a TEM grid using the direct transfer method. The asbestiform structures are identified, sized, and counted by transmission electron microscopy (TEM), using selected area electron diffraction (SAED) and energy dispersive spectroscopy (EDS or EDXA) at a magnification of 15 000 to 20 000×.

b. Interferences: Certain minerals have properties (i.e., chemical or crystalline structure) that are very similar to those of asbestos minerals and may interfere with the analysis by causing false positives. Maintain references for the following materials in the laboratory for comparison with asbestos minerals, so that they are not misidentified as asbestos minerals: antigorite, attapulgite (palygorskite), halloysite, hornblende, pyroxenes, sepiolite, and vermiculite scrolls.

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High concentrations of iron or other minerals in the water may coat asbestos fibers and prevent their full identification.

2. Sampling

a. Containers: Use new, pre-cleaned, capped bottles of glass or low-density (conventional) polyethylene, capable of holding at least 1 L. Do not use polypropylene bottles. Rinse bottles twice by filling approximately one-third full with fiber-free water and shaking vigorously for 30 s. Discard rinse water, fill bottles with fiber-free water, treat in ultrasonic bath (60 to 100 W) for 15 min, and rinse several times with fiber-free water.

Make blank determinations on the bottles before collecting a sample. Use one bottle in each batch or a minimum of one bottle in each 24 to test for background level when using polyethylene bottles. When sampling waters probably containing very low levels of asbestos, or for additional confidence in the bottle blanks, run additional blank determinations.

b. Collection: Follow general principles for water sampling (see Section 1060). Some specific considerations apply to asbestos fibers, which range in length from 0.1 μm to 20 μm or more. In large bodies of water, because of the range of sizes there may be a vertical distribution of particle sizes that may vary with depth. If a representative sample from a water supply tank or impoundment is required, take a carefully designated set of samples representing vertical as well as horizontal distribution and composite for analysis. When sampling from a distribution system, choose a commonly used faucet, remove all hoses or fittings, and let water run to waste for 1 to 3 min. (Often, the appropriate time to obtain a main's sample can be determined by waiting for a change in water temperature.) Because sediment may build up in valving works, do not adjust faucets or valves until all samples have been collected. Similarly, do not consider samples at hydrants and at dead ends of the distribution systems to be representative of the water in the system. As an additional precaution against contamination, rinse each bottle several times with the source water being sampled. For depth sampling, omit rinsing. Obtain a sample of approximately 800 mL from each sampling site, leaving some air space in each bottle. Using a waterproof marker, label each container with date, time, place, and sampler's initials.

c. Shipment: Ship water samples in a sealed container, but separate from any bulk or air samples intended for asbestos analysis. Preferably, ship in a cooler to retard bacterial or algal growth. Do not freeze the sample. In the laboratory, prepare sample within 48 h of collection.

3. Apparatus

a. High-efficiency particulate air (HEPA) filtered negative-flow hood.

b. Filter funnel assemblies, either 25 mm or 47 mm, of either of the following types:

1) *Disposable plastic units*, or

2) *Glass filtering unit*. With this type of unit, observe the following precautions: Never let unit dry after filtering. Immediately place it in detergent solution, scrub with a test-tube brush, and rinse several times in particle-free water. Periodically treat unit in detergent solution in an ultrasonic bath. Clean unit after each sample is filtered. Run a blank on particle-free water

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filtered through the glass filtering unit at frequent intervals to ensure absence of residual asbestos contamination.

c. Side-arm filter flask, 1000 mL.

d. Either:

1) *Mixed cellulose ester (MCE) membrane filters,* 25- or 47-mm diam, ≤ 0.45-µm and 5-µm pore size, or

2) *Polycarbonate (PC) filters,* 25- or 47-mm diam, ≤ 0.4-µm pore size.

e. Ultrasonic bath, tabletop model, 60 to 100 W.

f. Graduated pipet, disposable glass, 1, 5, and 10 mL.

g. Cabinet-type dessicator or *low-temperature drying oven.*

h. Cork borer, 7 mm.

i. Glass slides.

j. Petri dishes, glass, approximately 90-mm diam.

k. Mesh screen, stainless steel or aluminum, 30 to 40 mesh.

l. Ashless filter paper filters, 90-mm diam.

m. Exhaust or fume hood.

n. Scalpel blades.

o. Low-temperature plasma asher.

p. High-vacuum carbon evaporator with rotating stage, capable of less than 0.013 Pa pressure. Do not use units that evaporate carbon filaments in a vacuum generated only by oil rotary pump. Use carbon rods sharpened with a carbon rod sharpener to necks about 4 mm long and 1 mm in diam. Install rods in the evaporator so that the points are approximately 100 to 120 mm from surface of microscope slide held in the rotating device.

q. Lens tissue.

r. Copper TEM finder grids, 200 mesh. Use pre-calibrated grids, or determine grid opening area by either of the following methods:

1) Measure at least 20 grid openings in each of 20 random 200-mesh grids (total of 400 grid openings for every 1000 grids used) by placing the 20 grids on a glass slide and examining them under an optical microscope. Use a calibrated reticule to measure average length and width of 20 openings from each of the individual grids. From the accumulated data, calculate the average grid opening area.

2) Measure grid area at the TEM (¶ s below) at a calibrated screen magnification of between 15 000 and 20 000×. Measure one grid opening for each grid examined. Measure grid openings in both the x and y directions and calculate area.

s. Transmission electron microscope (TEM), 80 to 120 kV, equipped with energy dispersive X-ray system (EDXA), capable of performing electron diffraction with a fluorescent screen

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inscribed with calibrated gradations. The TEM must have a scanning transmission electron microscopy (STEM) attachment or be capable of producing a spot size of less than 250 nm diam at crossover. Calibrate routinely for magnification, camera constant, and EDXA settings according to procedures of 5*d*.

4. Reagents and Materials

a. Acetone.

b. Dimethylformamide (DMF). CAUTION: *Toxic; use only in a fume hood.*

c. Glacial acetic acid. CAUTION: *Use in a fume hood.*

d. Chloroform.

e. 1-Methyl-2-pyrrolidinone.

f. Particle-free water: Use glass-distilled water or treat by reverse osmosis; filter through a filter with pore diam 0.45 μm or smaller.

g. Non-asbestos standards for minerals listed in ¶ 1*b* above.

h. Asbestos standards for minerals listed in Section 2570A.1.

5. Procedure

a. Sample filtration: Samples with high levels of organic contaminants may require pretreatment. A process using ultraviolet light and ozone bubbling is described elsewhere.[1] Drinking water samples prepared within 48 h of collection do not require pretreatment.

Under a HEPA hood, carefully wet-wipe exterior of sample bottle to remove any possible contamination before taking bottle into a clean preparation area separated from preparation areas for bulk or air-sample handling.

Prepare specimen in a clean HEPA filtered negative-pressure hood. Measure cleanliness of preparation area hoods by cumulative process blank concentrations (see ¶ b below).

If using a disposable plastic filter funnel unit, remove funnel assembly and discard top filter supplied with the apparatus, but be sure to retain the coarse polypropylene support pad in place. Assemble unit with the adapter and a properly sized neoprene stopper, and attach funnel to the 1000-mL side-arm vacuum flask. Moisten support pad with a few milliliters distilled water, place a 5.0-μm-pore-size MCE backing filter on support pad, and place an MCE or PC filter (≤0.45-μm-pore-size) on top of backing filter. After both filters are completely wet, apply vacuum, ensuring that filters are centered and pulled flat without air bubbles. If there are any irregularities on the filter surface, discard filters and repeat process. Replace funnel assembly. Return flask to atmospheric pressure. Alternatively, use glass filtering unit, following the same procedure to set up filters.

With flask at atmospheric pressure, add 20 mL particle-free water to funnel. Cover funnel with its plastic cover if the disposable filtering unit is used.

Briefly, by hand, shake capped bottle with sample suspension, then place it in tabletop ultrasonic bath and sonicate for 3.0 min. The water level in the bath should be approximately the

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same as that of the sample. After treatment, return sample bottle to work surface of HEPA hood. Carry out all preparation steps, until filters are ready for drying, in this hood.

Shake suspension vigorously by hand for 2 to 3 s. Estimate amount of liquid to be withdrawn to produce an adequate filter preparation. Experience has shown that a light staining of the filter surface will usually yield a suitable preparation. If the sample is relatively clean, use a volumetric cylinder to measure sample. If sample has a high particulate or asbestos content, withdraw a small volume (but at least 1 mL) with disposable glass pipet, inserting pipet halfway into sample.

NOTE: If, after examination in the TEM, the smallest volume measured (1.0 mL) yields an overloaded sample, make additional serial dilutions of the suspension. Shake suspension vigorously by hand for 2 to 3 s before taking serial dilution portion. Do not re-treat in ultrasonic bath either original solution or any dilutions. Mix 10 mL sample with 90 mL particle-free water in a clean sample bottle to obtain a 1:10 serial dilution.

Uncover filter funnel and dispense mixture into the water in the funnel. Recover funnel and agitate but do not swirl the liquid. (One acceptable means of agitation is to inject 5 to 10 mL particle-free water from a squeeze bottle into the funnel.) Apply vacuum and filter. Discard pipet, if used.

Disassemble filtering unit and carefully remove filter with clean forceps. Place filter, particle side up, in a precleaned, labeled, disposable plastic petri dish or similar container.

To obtain an optimally loaded filter, make several filtrations with different sample portions. Use new disposable plastic funnel units or carefully cleaned glass units for each filtration. When additional filters are prepared, shake suspension without additional ultrasonic treatment before removing the sample portion. Each new filtration should represent at least a five-fold loading difference.

Dry MCE filters for at least 12 h (over desiccant) in airtight, cabinet-type desiccator. Alternatively, to shorten drying time for filters prepared using the acetone collapsing method, plug damp filter and attach to a glass slide as described in ¶ c1)a) below. Place the slide with filter plug(s) (up to eight plugs can be attached to one slide) on a bed of desiccant, cover, and place in desiccator for 1 to 2 h.

Place PC filters in a dessicator for at least 30 min before preparation; lengthy drying is not required.

b. Sample blank preparation: Prepare sample blanks that include both a process blank (50 mL particle-free water) for each set of samples analyzed and one unused filter from each new box of sample filters (MCE or PC). Blanks are considered contaminated if, after analysis, they are shown to contain more than 53 asbestos structures/mm^2. This corresponds to 3 or 4 asbestos structures found in 10 grid openings. Identify source of contamination before making any further analysis. Reject samples that were processed with the contaminated blanks and prepare new samples after source of contamination is found. Take special care with polycarbonate filters, because some have been shown to contain asbestos contamination.

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c. Specimen preparation:

1) Mixed cellulose ester (MCE) filters

a) Filter fusing—Use either the acetone or the DMF-acetic acid method.

(1) Acetone fusing method—Remove a section from any quadrant of the sample and blank filters with a 7-mm cork borer. Place filter section (particle side up) on a clean microscope slide. Affix filter section to slide with a gummed page reinforcement or other suitable means. Label slide with a glass scribing tool or permanent marker.

Prepare a fusing dish as follows: Make a pad from five to six ashless paper filters and place in bottom of a glass petri dish. Place metal screen bridge on top of pad and saturate filter pads with acetone. Place slide on top of bridge and cover the petri dish. Wait approximately 5 min for sample filter to fuse and clear completely.

(2) DMF-acetic acid fusing method—Place drop of clearing solution (35% dimethylformamide [DMF], 15% glacial acetic acid, and 50% particle-free water by volume) on a clean microscope slide. CAUTION: *DMF is a toxic solvent; use only in a fume hood*. Use an amount of clearing solution that just saturates the filter. Using a clean scalpel blade, cut a wedge-shaped section of filter. A one-eighth filter section is sufficient. Carefully lay filter segment, sample surface upward, on top of solution. Bring filter and solution together at an angle of about 20 deg to help exclude air bubbles. Remove excess clearing solution with filter paper. Place slide in oven, on a slide-warmer, or on hot plate, in a fume hood, at 65 to 70°C for 5 to 10 min. The filter section should fuse and clear completely.

b) Plasma etching—Place microscope slide, with attached collapsed filter pieces, in a low-temperature plasma asher. Because plasma ashers vary greatly in their performance, both from unit to unit and between different positions in the asher barrel, it is difficult to specify operating conditions. Insufficient etching will result in a failure to expose embedded fibers; too much etching may result in the loss of particles from the filter surface. Calculate time for ashing on the basis of final sample observations in transmission electron microscope. Additional information on calibration is available.[2,3]

c) Carbon coating—Using high-vacuum carbon evaporator (¶ 3 *p*), proceed as follows: Place glass slide holding filters on the rotation device and evacuate evaporator chamber to a pressure of less than 0.013 Pa. Perform evaporation in very short bursts, separated by 3 to 4 s to let electrodes cool. An experienced analyst can judge the thickness of the carbon film. Make initial tests on unused filters. If the carbon film is too thin, large particles will be lost from the TEM specimen, and there will be few complete and undamaged grid openings. A coating that is too thick will lead to a TEM image lacking in contrast and a compromised ability to obtain electron diffraction patterns. The carbon film should be as thin as possible and still remain intact on most of the grid openings of the TEM specimen.

d) Specimen washing—Prepare a Jaffe washer according to any published design.[1,4] One such washer consists of a simple stainless steel bridge contained in a glass petri dish. Place on the stainless steel bridge several pieces of lens tissue large enough to hang completely over the

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bridge and into the solvent. In a fume hood, fill petri dish with either acetone or DMF to one quarter of the level in the dish.

Place TEM grids, shiny side up, on a piece of lens tissue or filter paper so that individual grids can be easily picked up with forceps. Prepare from each sample three grids. Using a curved scalpel blade, excise three square (3-mm × 3-mm) pieces of carbon-coated MCE filter from random areas on the filter. Place each square filter piece, carbon-side up, on top of a TEM specimen grid (¶ 3*r*).

Place all three assemblies (filter/grid) for each sample on the same piece of saturated lens tissue in Jaffe washer. Place lid on the Jaffe washer and let system stand, preferably overnight.

Alternatively, place grids on a low-level (petri dish is filled only enough to wet paper on screen bridge) DMF Jaffe washer for 60 min. Then add enough solution of equal parts DMF/acetone to fill washer up to screen level. Remove grids after 30 min if they have cleared, i.e., all filter material has been removed from the carbon film, as determined by inspecting in the TEM. Let grids dry before placing in TEM.

2) Polycarbonate (PC) filters—Cover surface of a clean microscope slide with two strips of double-sided cellophane tape. Cut a strip of filter paper slightly narrower than width of slide. Position filter paper strip on center of length of slide. Using a clean, curved scalpel blade, cut a strip of the PC filter approximately 25 × 6 mm. Use a rocking motion of the scalpel blade to avoid tearing filter. Place PC strip, particle side up, on slide perpendicular to long axis of slide, making sure that the ends of the PC strip contact the double-sided cellophane tape. Each slide can hold several PC strips. Label filter paper next to each PC strip with sample number.

Carbon-coat filter strips as directed in ¶ 1)c) above. (Etching is not required.) Take special care to avoid overheating filter sections during carbon coating.

Prepare a Jaffe washer as described in ¶ 1)d) above, but fill washer with chloroform or 1-methyl-2-pyrrolidinone to the level of the screen. Using a clean curved scalpel blade, excise three 3-mm-square filter pieces from each PC strip. Place filter squares, carbon side up, on shiny side of a TEM grid (¶ 3*r*). Pick up grid and filter section together and place them on lens tissue in the Jaffe washer. Place lid on Jaffe washer and leave grids for at least 4 h. Best results are obtained with longer wicking times, up to 12 h. Carefully remove grids from the Jaffe washer and let dry in the grid box before placing them in a clean, marked grid box.

d. Instrument calibration: Calibrate instrumentation regularly, and keep a calibration record for each TEM in the laboratory, in accordance with the laboratory's quality assurance program. Record all calibrations in a log book along with dates of calibration and attached backup documentation.

Check TEM for both alignment and systems operation. Refer to manufacturer's operational manual for detailed instructions.

Calibrate camera length of TEM in electron diffraction (ED) operating mode before observing ED patterns of unknown samples. Measure camera length by using a carbon-coated grid on which a thin film of gold has been sputtered or evaporated. A thin film of gold may be evaporated directly on to a specimen grid containing asbestos fibers. This yields zone-axis ED

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patterns from the asbestos fibers superimposed on a ring pattern from the polycrystalline gold film. Optimize thickness of gold film so that only one or two sharp rings are obtained. Thicker gold films may mask weaker diffraction spots from the fibrous particles. Because unknown d-spacings of most interest in asbestos analysis are those lying closest to the transmitted beam, multiple gold rings from thicker films are unnecessary. Alternatively, use a gold standard specimen to obtain an average camera constant calculated for that particular instrument, which can then be used for ED patterns of unknowns taken during the corresponding period.

Calibrate magnification at the fluorescent screen at magnification used for structure counting. Use a grating replica (e.g., one containing at least 2160 lines/mm). Define a field of view on the fluorescent screen; the field must be measurable or previously inscribed with a scale or concentric circles (use metric scales). Place grating replica at the same distance from the objective lens as the specimen. For instruments that incorporate a eucentric tilting specimen stage, place all specimens and the grating replica at the eucentric position. Follow the instructions provided with the grating replica to calculate magnification. Frequency of calibration depends on service history of the microscope. Check calibration after any maintenance that involves adjustment of the power supply to the lens, the high-voltage system, or the mechanical disassembly of the electron optical column (apart from filament exchange).

Check smallest spot size of the TEM. At the crossover point, photograph spot size at a magnification of 25 000× (screen magnification 20 000×). An exposure time of 1 s usually is adequate. Measured spot size must be less than or equal to 250 nm.

Verify resolution and calibration of the EDXA as follows: Collect a standard EDXA Cu peak from the Cu grid and compare X-ray energy with channel number for Cu peak to make sure readings are within ± 10 eV. Collect a standard EDXA of crocidolite asbestos; elemental analysis of the crocidolite must resolve the Na peak. Collect a standard EDXA spectrum of chrysotile asbestos; elemental analysis of chrysotile must resolve both Si and Mg on a single chrysotile fiber.

e. Sample analysis: Carefully load TEM grid with grid bars oriented parallel/perpendicular to length of specimen holder. Use a hand lens or eye loupe if necessary. This procedure will line up the grid with the x and y translation directions of the microscope. Insert specimen holder into microscope.

Scan entire grid at low magnification (250× to 1000×) to determine its acceptability for high-magnification analysis. Grids are acceptable if the following conditions are met:

- The fraction of grid openings covered by the replica section is at least 50%.
- Relative to that section of the grid covered by the carbon replica, the fraction of intact grid openings is greater than 50%.
- The fractional area of undissolved filter is less than 10%.
- The fraction of grid squares with overlapping or folded replica film is less than 50%.
- At least 20 grid squares have no overlapping or folded replica, are less than 5% covered with

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holes, and have less than 5% opaque area due to incomplete filter dissolution.

If the grid meets these criteria, chose grid squares for analysis from various areas of the grid so that the entire grid is represented. To be suitable for analysis, an individual grid square must meet the following criteria:

- It must have less than 5% holes over its area.
- It must be less than 25% covered with particulate matter.
- It must be uniformly loaded.

Observe and record orientation of grid at 80 to 150× on a grid map record sheet along with the location of the grid squares examined. If indexed grids are used, a grid map is not needed, but record identifying coordinates of the grid square.

At a screen magnification of 15 000 to 25 000×, evaluate the grids for the most concentrated sample loading. Reject sample if it is estimated to contain more than about 25 asbestos structures per grid opening. Proceed to the next most concentrated sample until a set of grids is obtained that have less than 25 asbestos structures per grid opening.

Analyze a minimum of four grid squares for each sample.

Analyze approximately one-half of the predetermined sample area on one sample grid preparation and the remainder on a second sample grid preparation.

Use structure definitions given in Section 2570A.2 to enumerate asbestos structures. Record all data on count sheet. Record asbestos structures in two size categories: ≥0.5 μm to ≥ 10.0 μm and >10.0 μm. For fibers and bundles, record size category of greatest length of the structure. For matrices and clusters, record size category of the visible portion of the longest fiber or bundle involved with the structure, not the greatest overall dimension of the structure. No minimum or maximum width restrictions are applied to the fiber definition, as long as the minimum length and aspect ratio criteria are met. Record ‘‘NSD’’ (no structures detected) when no structures are found in the grid opening.

Record a typical electron diffraction pattern for each type of asbestos observed for each group of samples (or a minimum of every five samples) analyzed. Record micrograph number on count sheet. For chrysotile, record one X-ray spectrum for each tenth structure analyzed. For each type of amphibole, record one X-ray spectrum for each fifth structure analyzed. (More information on identification is available.[1,4]) Attach the printouts to the back of the count sheet. If the X-ray spectrum is stored, record file and disk number on count sheet.

Analytical sensitivity can be improved by increasing amount of liquid filtered, increasing number of grid openings analyzed, or decreasing size of filter used. Occasionally, because of high particle loadings or high asbestos concentration, the desired analytical sensitivity cannot be achieved in practice.

Unless a specific analytical sensitivity is desired, stop analysis on the 10th grid opening or

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the grid opening that contains the 100th asbestos structure, whichever comes first. If the analysis is stopped at the grid opening that contains the 100th asbestos structure, count entire grid square containing the 100th structure.

After analysis, remove grids from TEM, replace them in grid storage holder, and store for a minimum of one year from the date of the analysis for legal purposes. Sample filters also may be stored in the plastic petri dishes, if necessary. Prolonged storage of the remaining water sample is not recommended, because microbial growth may cause loss of asbestos structures to the sides of the storage container.

Report the following information for each water sample analyzed: asbestos concentration in structures per liter, for total structures and fibrous asbestos structures greater than 10 μm in length; types of asbestos present; number of asbestos structures counted; effective filtration area; average size of TEM grid openings counted; number of grid openings examined; size category for each structure counted. Include a copy of the TEM count sheet, either hand-written or computer-generated.

6. Calculations

Calculate amount of asbestos in a sample as follows:

$$\text{Asbestos concentration, structures/L} = \frac{N \times A_f \times D}{G \times A_G \times V_s}$$

where:

N = number of asbestos structures counted,
A_f = effective filter area of final sampling filter, mm^2,
D = dilution factor (if applicable),
G = number of grid openings counted,
A_G = area of grid openings, mm^2, and
V_s = volume of sample, L.

The same formula may be used to calculate asbestos fibers greater than 10 μm in length per liter based on the total number of fibers and bundles greater than 10 μm in length whether free or associated with matrices and clusters. Express final results as million structures per liter (MSL) and million fibers per liter (MFL).

7. Quality Control/Quality Assurance

Use the laboratory's quality-control checks to verify that system is performing according to accuracy and consistency specifications. Because of the difficulties in preparing known quantitative asbestos samples, routine quality-control testing focuses on reanalysis of samples

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(duplicate recounts). Reanalyze 1 out of every 10 samples, not including laboratory blanks.

In addition, set up quality assurance programs according to the criteria developed by Federal agencies.[2,3] These documents cover sample custody, sample preparation, blank checks for contamination, calibration, sample analysis, analyst qualifications, and technical facilities.

8. Precision and Bias

Precision measurements for intralaboratory comparisons have been found to have a relative standard deviation (RSD) of 13 to 22% for standard and environmental water samples, with an RSD of 8.4 to 29% for interlaboratory comparisons.[1] An earlier study found an interlaboratory reproducibility of 25 to 50% in standard samples.[5]

Accuracy measurements from inter- and intralaboratory studies have demonstrated an RSD of 17% for standard chrysotile suspensions, and an RSD of 16% for standard crocidolite suspensions.[1]

9. References

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2580 OXIDATION-REDUCTION POTENTIAL (ORP)#(53)*

2580 A. Introduction

1. Significance

Oxidation and reduction (redox) reactions mediate the behavior of many chemical

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constituents in drinking, process, and wastewaters as well as most aquatic compartments of the environment.[1-5] The reactivities and mobilities of important elements in biological systems (e.g., Fe, S, N, and C), as well as those of a number of other metallic elements, depend strongly on redox conditions. Reactions involving both electrons and protons are pH- and Eh-dependent; therefore, chemical reactions in aqueous media often can be characterized by pH and Eh together with the activity of dissolved chemical species. Like pH, Eh represents an intensity factor. It does not characterize the capacity (i.e., poise) of the system for oxidation or reduction.

The potential difference measured in a solution between an inert indicator electrode and the standard hydrogen electrode should not be equated to Eh, a thermodynamic property, of the solution. The assumption of a reversible chemical equilibrium, fast electrode kinetics, and the lack of interfering reactions at the electrode surface are essential for such an interpretation. These conditions rarely, if ever, are met in natural water.

Thus, although measurement of Eh in water is relatively straightforward, many factors limit the interpretation of these values. These factors include irreversible reactions, electrode poisoning, the presence of multiple redox couples, very small exchange currents, and inert redox couples. Eh values measured in the field correlate poorly with Eh values calculated from the redox couples present. Nevertheless, measurement of redox potential, when properly performed and interpreted, is useful in developing a more complete understanding of water chemistry.

2. Sampling and Storage

Do not store samples; analyze on collection. Minimize both atmospheric contact and delay in analysis.

3. References

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2580 B. Oxidation-Reduction Potential Measurement in Clean Water

1. General Discussion

a. Principle: Electrometric measurements are made by potentiometric determination of electron activity (or intensity) with an inert indicator electrode and a suitable reference electrode. Ideally, the indicator electrode will serve as either an electron donor or acceptor with respect to electroactive oxidized or reduced chemical species in solution. At redox equilibrium, the potential difference between the ideal indicator electrode and the reference electrode equals the redox potential of the system. However, inert indicator electrodes that behave ideally in all aqueous systems, particularly in natural waters, do not exist. Electrodes made of platinum are most commonly used for Eh measurements. They have limitations,[1] as do alternative materials such as gold and graphite.

The standard hydrogen reference electrode is fragile and impractical for routine laboratory and field use. Therefore, silver: silver-chloride or calomel reference electrodes are used commonly. The redox potential measurement is corrected for the difference between the potential of the reference electrode and that of the standard hydrogen electrode. See Section 4500-H pH Value.

It is not possible to calibrate Eh electrodes over a range of redox potentials (as is done with pH electrodes). Instead, standard solutions that exhibit both chemical stability and known redox potentials for specific indicator electrodes are used to check electrode response at the temperature of measurement.

The potential of the platinum (Pt) Eh electrode versus the Ag/AgCl reference electrode with KCl electrolyte in ZoBell's solution ($3 \times 10^{-3}M$ potassium ferrocyanide and $3 \times 10^{-3}M$ potassium ferricyanide in $0.1M$ KCl)[2] has been measured as a function of temperature.[3] Good agreement was obtained between Eh values measured with this electrode pair in ZoBell's solution and those calculated from the stability constants at 8 to 85°C. The potential of the ZoBell's solution with this electrode configuration

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as a function of temperature can be calculated:[4]

$$Eh, \text{ V} = 0.428 - 0.0022\ (T - 25)$$

where T = solution temperature, °C. Alternatively, select the value from Table 2580:I.

To determine the Eh of a sample relative to the standard hydrogen electrode, measure Eh of both sample and standard solution at the same temperature (within ±0.1°C). Then calculate Eh value of the sample:

$$Eh_{\text{system}} = \text{E}_{\text{observed}} + \text{Eh}_{\text{ZoBell/reference}} - \text{Eh}_{\text{ZoBell observed}}$$

where:

E_{observed} = sample potential relative to reference electrode.

$Eh_{\text{ZoBell/reference}}$ = theoretical Eh of reference electrode and ZoBell's solution, relative to the standard hydrogen electrode (see Table 2580:I), and

$Eh_{\text{ZoBellobserved}}$ = observed potential of ZoBell's solution, relative to the reference electrode.

The measurements described above can be applied analogously to other indicator electrode/reference electrode pairs and standard solutions.

b. Interferences: Specific interferences may be due to operation of either indicator or reference electrode, redox capacity or poise of the sample, sample preservation and handling, and temperature equilibration.

1) Sorption and poisoning effects on electrodes—Contamination of the electrode surface, salt bridge, or internal electrolyte in the case of reference electrodes, can lead to excessive drift, poor electrode response, and artifact potentials. Organic matter, sulfide, and bromide may cause these problems, particularly in long-term electrode use.[1,5-7] If excessive drift occurs or erratic performance of paired electrodes is observed in redox standard solutions after appropriate cleaning, refilling, or regeneration procedures, discard the faulty electrode and use a new one.

2) pH variations—Redox potential is sensitive to pH if hydrogen ion or hydroxide ion is involved in the redox half-cells. Cell potentials tend to increase as proton concentration increases (i.e., pH decreases) and Eh values drop as hydroxide concentrations increase (i.e., pH increase).

3) Sample handling and preservation—The sample poise will govern the resistance of the sample to change in redox potential; this phenomenon is analogous to the resistance to pH change afforded by buffer capacity. Except in concentrated process streams, sludges, leachates, and highly reducing or treated waters, the concentrations of oxidized or reduced species may be fairly low (i.e., $<10^{-4}M$). Under these conditions, handle reduced samples very carefully to avoid exposure to atmospheric oxygen. A closed cell sampling configuration may be used.[4,8] Samples cannot be stored or preserved; analyze at sampling.

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4) Temperature equilibration—Obtain Eh standard solution reading for the electrode pair at a temperature as close as possible to that of the sample. Temperature determines the Eh reference potential for a particular solution and electrode pair. It also may affect the reversibility of the redox reaction, the magnitude of the exchange current, and the stability of the apparent redox potential reading, particularly in poorly poised solutions. Hold temperature constant for all measurements and report it with Eh results.

2. Apparatus

a. pH or millivolt meter: Use a pH meter or other type of high-impedance potentiometer capable of reading either pH or millivolts (mV). For most applications, a meter scale readable to ±1400 mV is sufficient.

b. Reference electrode consisting of a half-cell providing a constant electrode potential. See Section 4500-H^+.B.2*b*.

c. Oxidation-reduction indicator electrode: The platinum electrode is used most commonly. A noble metal or graphite electrode may be useful for specific applications.

1) Noble metal electrode—Noble metal (i.e., gold or platinum) foil, wire, or billet types of electrode are inert and resistant to chemical reaction. Clean and polish electrode surface to insure reliable performance. Platinum electrodes may be cleaned by strong acid soaking,[9,10] hydrogen peroxide and detergent washing,[11] and anodic activation.[10] Abrasive polishing with crocus cloth, jeweler's rouge, or 400 to 600 grit wet/dry carborundum paper may be best.[5]

2) Graphite electrode—A wax-impregnated graphite (WIG) electrode may be used, especially in aqueous suspensions or soils.[12,13] The WIG electrode is more resistant to electrode poisoning than electrodes made of platinum wire.

d. Beakers: Preferably use polyethylene, TFE, or glass beakers.

e. Stirrer: Use a magnetic TFE-coated stirring-bar-type mixer.

f. Flow cell: Use for continuous flow measurements and for poorly buffered solutions.

3. Reagents

a. Standard redox solutions: Standardize the electrode system against redox solutions that provide stable known Eh values over a range of temperatures. Although standard solutions are available, they do not cover the anticipated range of Eh values. Commercially prepared solutions may be used, particularly in field testing. The composition and Eh values of standard solutions are shown in Table 2580:II. With reasonable care, these solutions are stable for several months.

b. Eh electrode cleaners: Use either:

1) Aqua regia—Mix 1 volume conc nitric acid with 3 volumes conc hydrochloric acid. Prepare fresh and dilute by at least 50% with water. Neutralize prior to discarding.

2) Chromic acid—Dissolve 5 g potassium dichromate, $K_2Cr_2O_7$, in 500 mL conc sulfuric acid. Conduct cleaning procedure in a fume hood.

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4. Procedure

a. Instrument calibration: Follow manufacturer's instructions for using pH/millivolt meter and in preparing electrodes for use. Use a shorting lead to verify the zero point on the meter's millivolt scale. Equilibrate the standard solution to the temperature of the sample. Immerse electrodes in the gently stirred, standard solution in a beaker (or flow cell). Turn on meter, placing the function switch in the millivolt mode.

After several minutes for electrode equilibration, record reading to nearest millivolt. If the reading is more than ±10 mV from the theoretical redox standard value at that temperature, replace reference electrode fluid and repeat the measurement. If that procedure fails to bring the reading to within ±10 mV of the theoretical value, polish the sensing element of the indicator electrode with carborundum paper, crocus cloth, or jeweler's rouge. Rinse electrode thoroughly and recheck reading with a fresh portion of the standard solution. If the reading is within ±10 mV of the theoretical value, record it and the temperature. If the reading is not within ±10 mV, repeat the cleaning procedure or try another electrode. Then rinse the electrode with distilled water and proceed with the sample measurement. Recalibrate daily and more frequently if turbid, organic-rich, or high-dissolved-solids solutions are being measured.

b. Electrode cleaning procedure: Useful treatments for noble metal electrodes in restoring performance after long periods of use include immersion in warm (70°C) aqua regia for 1 to 2 min or 5 min in 6*N* HNO_3 after bringing to a boil. Alternatively treat with chromic acid solution followed by 6*N* HCl and rinse with water.

c. Sample analysis: Check system for performance with the standard solution, rinse electrodes thoroughly with sample water, then immerse them in the gently stirred sample. Let equilibrate, record Eh value to the nearest millivolt, and temperature to ±0.1°C. Repeat with a second sample portion to confirm successive readings within ±10 mV. Equilibration times vary and may take many minutes in poorly poised solutions. Successive readings that vary less than ±10 mV over 10 min are adequate for most purposes. Make continuous flow or pumped sample measurements, particularly of poorly poised solutions, in a closed flow cell after external calibration of the electrode system.

See Table 2580:III for recommended combinations of electrodes, standards, and sample handling.

5. Trouble Shooting

a. Meter: Use a shorting lead to establish meter reading at zero millivolts whenever possible. If the meter cannot be zeroed, follow the manufacturer's instructions for service.

b. Electrodes: If the potentiometer is in good working order, the fault may be in the electrodes. Frequently, renewal of the filling solution for the salt bridge for the reference electrode is sufficient to restore electrode performance. Another useful check is to oppose the emf of a questionable reference electrode with that of the same type known to be in good order. Using an adapter, plug the good reference electrode into the indicator electrode jack of the

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potentiometer. Then plug the questionable electrode into the reference electrode jack. With the meter in the millivolt position, immerse electrodes in an electrolyte (e.g., KCl) solution and then into a redox standard solution. The two millivolt readings should be 0 ± 5 mV for both solutions. If different electrodes are used (e.g., silver:silver chloride versus calomel or vice versa), the reading should be 44 ± 5 mV for a good reference electrode.

Unless an indicator electrode has been poisoned, physically damaged, or shorted out, it usually is possible to restore function by proper cleaning.

6. Calculation

$$Eh_{system} = E_{observed} + E_{reference\ standard} - E_{reference\ observed}$$

Report temperature at which readings were made.

7. Precision and Bias

Standard solution measurements made at stable temperatures with a properly functioning electrode system should be accurate to within ±10 mV. Calibration precision as reflected by the agreement of dual platinum electrodes versus an Ag:AgCl reference electrode for over a 2-year period has been estimated at ±15 mV (i.e., one standard deviation) in ZoBell's solution (N = 78) at approximately 12°C. Precision on groundwater samples (N = 234) over the same period has been estimated at ±22 mV (i.e., ± one standard deviation) in a closed flow cell.[15]

8. References

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2710 TESTS ON SLUDGES#(54)*

2710 A. Introduction

This section presents a series of tests uniquely applicable to sludges or slurries. The test data are useful in designing facilities for solids separation and concentration and for assessing operational behavior, especially of the activated sludge process.

2710 B. Oxygen-Consumption Rate

1. General Discussion

This test is used to determine the oxygen consumption rate of a sample of a biological suspension such as activated sludge. It is useful in laboratory and pilot-plant studies as well as in the operation of full-scale treatment plants. When used as a routine plant operation test, it often will indicate changes in operating conditions at an early stage. However, because test conditions are not necessarily identical to conditions at the sampling site, the observed measurement may

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not be identical with actual oxygen consumption rate.

2. Apparatus

a. Oxygen-consumption rate device: Either:

1) *Probe with an oxygen-sensitive electrode* (polarographic or galvanic), or

2) *Manometric or respirometric device* with appropriate readout and sample capacity of at least 300 mL. The device should have an oxygen supply capacity greater than the oxygen consumption rate of the biological suspension, or at least 150 mg/L·h.

b. Stopwatch or other suitable timing device.

c. Thermometer to read to ± 0.5°C.

3. Procedure

a. Calibration of oxygen-consumption rate device: Either:

1) Calibrate the oxygen probe and meter according to the method given in Section 4500-O.G, or

2) Calibrate the manometric or respirometric device according to manufacturer's instructions.

b. Volatile suspended solids determination: See Section 2540.

c. Preparation of sample: Adjust temperature of a suitable sample portion to that of the basin from which it was collected or to required evaluation temperature, and maintain constant during analysis. Record temperature. Increase DO concentration of sample by shaking it in a partially filled bottle or by bubbling air or oxygen through it.

d. Measurement of oxygen consumption rate:

1) Fill sample container to overflowing with an appropriate volume of a representative sample of the biological suspension to be tested.

2) If an oxygen-sensing probe is used, immediately insert it into a BOD bottle containing a magnetic stirring bar and the biological suspension. Displace enough suspension with probe to fill flared top of bottle and isolate its contents from the atmosphere. Activate probe stirring mechanism and magnetic stirrer. (NOTE: Adequate mixing is essential. For suspensions with high concentrations of suspended solids, i.e., >5000 mg/L, more vigorous mixing than that provided by the probe stirring mechanism and magnetic stirrer may be required.) If a manometric or respirometric device is used, follow manufacturer's instructions for startup.

3) After meter reading has stabilized, record initial DO and manometric or respirometric reading, and start timing device. Record appropriate DO, manometric, or respirometric data at time intervals of less than 1 min, depending on rate of consumption. Record data over a 15-min period or until DO becomes limiting, whichever occurs first. The oxygen probe may not be accurate below 1 mg DO/L. If a manometric or respirometric device is used, refer to manufacturer's instructions for lower limiting DO value. Low DO (≤2 mg/L at the start of the test) may limit oxygen uptake by the biological suspension and will be indicated by a decreasing

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rate of oxygen consumption as the test progresses. Reject such data as being unrepresentative of suspension oxygen consumption rate and repeat test beginning with higher initial DO levels.

The results of this determination are quite sensitive to temperature variations and poor precision is obtained unless replicate determinations are made at the same temperature. When oxygen consumption is used as a plant control test, run periodic (at least monthly) replicate determinations to establish the precision of the technique. This determination also is sensitive to the time lag between sample collection and test initiation.

4. Calculations

If an oxygen probe is used, plot observed readings (DO, milligrams per liter) versus time (minutes) on arithmetic graph paper and determine the slope of the line of best fit. The slope is the oxygen consumption rate in milligrams per liter per minute.

If a manometric or respirometric device is used, refer to manufacturer's instructions for calculating the oxygen consumption rate.

Calculate specific oxygen consumption rate in milligrams per gram per hour as follows:

Specific oxygen consumption rate, (mg/g)/h

$$= \frac{\text{oxygen consumption rate, (mg/L)/min}}{\text{volatile suspended solids, g/L}} \times \frac{60 \text{ min}}{\text{h}}$$

5. Precision and Bias

Bias is not applicable. The precision for this test has not been determined.

6. Bibliography

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2710 C. Settled Sludge Volume

1. General Discussion

The settled sludge volume of a biological suspension is useful in routine monitoring of biological processes. For activated sludge plant control, a 30-min settled sludge volume or the ratio of the 15-min to the 30-min settled sludge volume has been used to determine the returned-sludge flow rate and when to waste sludge. The 30-min settled sludge volume also is used to determine sludge volume index[1] (Section 2710D).

This method is inappropriate for dilute sludges because of the small volume of settled material. In such cases, use the volumetric test for settleable solids using an Imhoff cone

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(2540F). Results from 2540F are not comparable with those obtained with the procedure herein.

2. Apparatus

a. Settling column: Use 1-L graduated cylinder equipped with a stirring mechanism consisting of one or more thin rods extending the length of the column and positioned within two rod diameters of the cylinder wall. Provide a stirrer able to rotate the stirring rods at no greater than 4 rpm (peripheral tip speed of approximately 1.3 cm/s). See Figure 2710:1.

b. Stopwatch.

c. Thermometer.

3. Procedure

Place 1.0 L sample in settling column and distribute solids by covering the top and inverting cylinder three times. Insert stirring rods, activate stirring mechanism, start the stop watch, and let suspension settle. Continue stirring throughout test. Maintain suspension temperature during test at that in the basin from which the sample was taken.

Determine volume occupied by suspension at measured time intervals, e.g., 5, 10, 15, 20, 30, 45, and 60 min.

Report settled sludge volume of the suspension in milliliters for an indicated time interval.

Variations in suspension temperature, sampling and agitation methods, dimensions of settling column, and time between sampling and start of the determination significantly affect results.

4. Precision and Bias

Bias is not applicable. The precision for this test has not been determined.

5. Reference

1. DICK, R.I. & P.A. VESILIND. 1969. The SVI—What is It? *J. Water Pollut. Control Fed.* 41:1285.

2710 D. Sludge Volume Index

1. General Discussion

The sludge volume index (SVI) is the volume in milliliters occupied by 1 g of a suspension after 30 min settling. SVI typically is used to monitor settling characteristics of activated sludge and other biological suspensions.[1] Although SVI is not supported theoretically,[2] experience has shown it to be useful in routine process control.

2. Procedure

Determine the suspended solids concentration of a well-mixed sample of the suspension (See Section 2540D).

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Determine the 30 min settled sludge volume (See Section 2710C).

3. Calculations

$$\text{SVI} = \frac{\text{settled sludge volume (mL/L)} \times 1000}{\text{suspended solids (mg/L)}}$$

4. Precision and Bias

Precision is determined by the precision achieved in the suspended solids measurement, the settling characteristics of the suspension, and variables associated with the measurement of the settled sludge volume. Bias is not applicable.

5. References

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2710 E. Zone Settling Rate

1. General Discussion

At high concentrations of suspended solids, suspensions settle in the zone-settling regime. This type of settling takes place under quiescent conditions and is characterized by a distinct interface between the supernatant liquor and the sludge zone. The height of this distinct sludge interface is measured with time. Zone settling data for suspensions that undergo zone settling, e.g., activated sludge and metal hydroxide suspensions, can be used in the design, operation, and evaluation of settling basins.[1-3]

2. Apparatus

a. Settling vessel: Use a transparent cylinder at least 1 m high and 10 cm in diameter. To reduce the discrepancy between laboratory and full-scale thickener results, use larger diameters

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and taller cylinders.[1,3] Attach a calibrated millimeter tape to outside of cylinder. Equip cylinder with a stirring mechanism, e.g., one or more thin rods positioned within two rod diameters of the internal wall of settling vessel. Stir suspension near vessel wall over the entire depth of suspension at a peripheral speed no greater than 1 cm/s. Greater speeds may interfere with the thickening process and yield inaccurate results.[4] Provide the settling vessel with a port in the bottom plate for filling and draining. See Figure 2710:2.

b. Stopwatch.

c. Thermometer.

3. Procedure

Maintain suspension in a reservoir in a uniformly mixed condition. Adjust temperature of suspension to that of the basin from which it was collected or to required evaluation temperature. Record temperature. Remove a well-mixed sample from reservoir and measure suspended solids concentration (Section 2540D).

Activate stirring mechanism. Fill settling vessel to a fixed height by pumping suspension from reservoir or by gravity flow. Fill at a rate sufficient to maintain a uniform suspended solids concentration throughout settling vessel at end of filling. The suspension should agglomerate, i.e., form a coarse structure with visible fluid channels, within a few minutes. If suspension does not agglomerate, test is invalid and should be repeated.

Record height of solids-liquid interface at intervals of about 1 min. Collect data for sufficient time to assure that suspension is exhibiting a constant zone-settling velocity and that any initial reflocculation period, characterized by an accelerating interfacial settling velocity, has been passed.

Zone settling rate is a function of suspended solids concentration, suspension characteristics, vessel dimensions, and laboratory artifacts. With the filling method described above and a sufficiently large cylinder, these artifacts should be minimized. However, even with careful testing suspensions often may behave erratically. Unpredictable behavior increases for sludges with high solids concentrations and poor settling characteristics, and in small cylinders.

4. Calculations

Plot interface height in centimeters vs. time in minutes.[1,3] Draw straight line through data points, ignoring initial shoulder or reflocculation period and compression shoulder. Calculate interfacial settling rate as slope of line in centimeters per minute.

5. Precision and Bias

Bias is not applicable. The precision for this test has not been determined.

6. References

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2710 F. Specific Gravity

1. General Discussion

The specific gravity of a sludge is the ratio of the masses of equal volumes of a sludge and distilled water. It is determined by comparing the mass of a known volume of a homogeneous sludge sample at a specific temperature to the mass of the same volume of distilled water at 4°C.

2. Apparatus

Container: A marked flask or bottle to hold a known sludge volume during weighing.

3. Procedure

Follow either *a* or *b*.

a. Record sample temperature, *T*. Weigh empty container and record weight, *W*. Fill empty container to mark with sample, weigh, and record weight, *S*. Fill empty container to mark with water, weigh, and record weight, *R*. Measure all masses to the nearest 10 mg.

b. If sample does not flow readily, add as much of it to container as possible without exerting pressure, record volume, weigh, and record mass, *P*. Fill container to mark with distilled water, taking care that air bubbles are not trapped in the sludge or container. Weigh and record mass, *Q*. Measure all masses to nearest 10 mg.

4. Calculation

Use *a* or *b*, matching choice of procedure above.

a. Calculate specific gravity, *SG*, from the formula

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$$SG_{T/4°C} = \frac{\text{weight of sample}}{\text{weight of equal volume of water at 4°C}} = \frac{S - W}{R - W} \times F$$

The values of the temperature correction factor *F* are given in Table 2710:I.

b. Calculate specific gravity, *SG*, from the formula

$$SG_{T/4°C} = \frac{\text{weight of sample}}{\text{weight of equal volume of water at 4°C}} = \frac{(P - W)}{(R - W) - (Q - P)} \times F$$

For values of *F*, see Table 2710:I.

2710 G. Capillary Suction Time

1. General Discussion

The capillary suction time (CST) test determines rate of water release from sludge. It provides a quantitative measure, reported in seconds, of how readily a sludge releases its water. The results can be used to assist in sludge dewatering processes; to evaluate sludge conditioning aids and dosages; or, when used with a jar test and the settleable solids procedure, to evaluate coagulation effects on the rate of water release from sludges.

The test consists of placing a sludge sample in a small cylinder on a sheet of chromatography paper. The paper extracts liquid from the sludge by capillary action. The time required for the liquid to travel a specified distance is recorded automatically by monitoring the conductivity change occurring at two contact points appropriately spaced and in contact with the chromatography paper. The elapsed time is indicative of the water drainage rate. The CST test has been used as a relative indicator to characterize the performance of most sludge dewatering processes.

2. Apparatus

a. Test materials and apparatus may be fabricated (see Figure 2710:3) or are commercially available.#(55)* The unit includes a paper support block, stainless steel reservoir with 18-mm ID and 25-mm height, and a digital timer.

b. CST paper.#(56)†

c. Thermometer to read ± 0.5C.

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d. Pipet, 10-mL, plastic with tip trimmed to allow free passage of sludge flocs.

3. Procedure

Turn on and reset CST meter. Dry CST test block and reservoir. Place a new CST paper on lower test block with rough side up and grain parallel to the 9-cm side. Add upper test block, insert sludge reservoir into test block, and seat it using light pressure and a quarter turn to prevent surface leaks. Measure and record temperature of sludge. Pipet 6.4 mL sludge into test cell reservoir; if pipetting is difficult because of sludge consistency, pour a representative sludge sample into the test cell until it is full. The CST device will begin time measurement as liquid being drawn into the paper reaches the inner pair of electrical contacts. Timing ends when the outer contact is reached. Record CST shown on digital display. Empty remaining sludge from reservoir and remove and discard used CST paper. Rinse and dry test block and reservoir. Repeat for a minimum of five determinations per sample to account for measurement variation and to allow identification of any faulty readings due to leaks or spills.

Variations in sludge temperature and sample volume can affect CST results. Ensure that all analyses are run under similar conditions. Sludge suspended solids concentration has a significant effect on test results. In evaluating sludge conditioners or monitoring operation of a dewatering process, avoid this effect by ensuring homogeneity among sludge samples. Comparison of CST data from different sludge samples from the same source (especially if taken on different days) cannot be made with confidence unless suspended solids concentrations are comparable. Make a rough correction for different solids contents by dividing the sludge's CST value by its corresponding solids concentration.

Characteristics of CST paper may vary between lots. If comparison of CST values for distilled water indicates such variations, subtract times for distilled water blanks from sample times to improve comparisons.

Record CST model used, paper type, sludge type, sludge temperature, and capillary suction time. Measure solids concentration and CST of distilled water using the same paper to provide useful information.

4. Precision and Bias

Ten tests conducted on an anaerobically digested pulp mill sludge resulted in a mean CST of 363.2 s with a standard deviation of 36.2 s. Twenty tests using an anaerobically digested municipal wastewater sludge gave a mean of 85.2 s with a standard deviation of 14.12 s. Triplicate analyses of 30 sample sets of conditioned and unconditioned alum sludge resulted in an average standard deviation of 1.0 s with means between 5 and 80 s. Method bias cannot be determined.

5. Bibliography

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2710 H. Time-to-Filter

1. General Discussion

The time to filter (TTF) correlates with capillary suction time (CST) and is similar to the specific resistance to filtration if sludge solids content and filtrate viscosity do not vary among compared samples. The test requires approximately 200 mL sludge and can be used to assist in the daily operation of sludge dewatering processes or to evaluate sludge-conditioning polymers and dosages.

Testing with a smaller volume is possible in applications to evaluate water drainage rate subsequent to jar tests and settleable solids determination (see Section 2540F). In this case, drain collected sludge from one or more Imhoff cones after decanting as much supernatant as possible; use a small-volume TTF apparatus.

The test consists of placing a sludge sample in a Buchner funnel with a paper support filter, applying vacuum, and measuring the time required for 100 mL filtrate (or, for reduced sample volumes, 50% of original sample) to collect. While similar to the specific resistance to filtration test, the time-to-filter test is superior because of its ease of use and simplicity.

2. Apparatus

a. Time-to-filter large-volume or small-volume (Figure 2710:4) *assembly.*

*b. Filter paper#(57)**

c. Stopwatch.

3. Procedure

Place paper filter in funnel and make a firm seal by pre-wetting with a small volume of water with vacuum on. If using large-volume apparatus, take a 200-mL sample of sludge. With vacuum pump providing a constant vacuum of 51 kPa, pour sample into funnel. Start stopwatch or timer and determine time required for 100 mL of sample to collect in graduated cylinder. This is the time to filter. Make a minimum of three replicate determinations.

For the small-volume test, use 7 to 10 mL sludge. Record time required for 50% of sample to collect in graduated cylinder. Compare this time to filter only to other results using the same sample volume.

Sludge suspended solids concentration has a significant effect on test results. In evaluating sludge-conditioning products, compare results for which initial suspended solids concentrations

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are comparable. Make a rough correction for different solids contents by dividing the time-to-filter value by its corresponding solids concentration. However, variations in solids concentration occur in full-scale applications, and the time-to-filter results may be interpreted as indicating the overall rate of water release from sludges, including the effect of differing solids concentrations.

4. Precision and Bias

Variations in vacuum pressure, support filter type, sludge temperature, and sample volume can affect test results. Triplicate analyses of 18 sample sets of conditioned and unconditioned alum sludge resulted in an average method precision of 19 s (approximately 4% of the average value) for the large-volume TTF test. Triplicate analyses of 9 sample sets of conditioned and unconditioned alum sludge resulted in a method precision of 9 s (approximately 6% of the average value) for the small-volume TTF test. Method bias, which refers to the agreement between the value determined by the test method and the real value, cannot be determined.

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2720 ANAEROBIC SLUDGE DIGESTER GAS ANALYSIS*#(58)

2720 A. Introduction

Gas produced during the anaerobic decomposition of wastes contains methane (CH_4) and carbon dioxide (CO_2) as the major components with minor quantities of hydrogen (H_2), hydrogen sulfide (H_2S), nitrogen (N_2), and oxygen (O_2). It is saturated with water vapor. Common practice is to analyze the gases produced to estimate their fuel value and to check on the treatment process. The relative proportions of CO_2, CH_4, and N_2 are normally of most concern and the easiest to determine because of the relatively high percentages of these gases.

1. Selection of Method

Two procedures are described for gas analysis, the volumetric method (B), and the gas chromatographic method (C). The volumetric analysis is suitable for the determination of CO_2, H_2, CH_2, and O_2. Nitrogen is estimated indirectly by difference. Although the method is time-consuming, the equipment is relatively simple. Because no calibration is needed before use, the procedure is particularly appropriate when analyses are conducted infrequently.

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The principal advantage of gas chromatography is speed. Commercial equipment is designed specifically for isothermal or temperature-programmed gas analysis and permits the routine separation and measurement of CO_2, N_2, O_2, and CH_4 in less than 15 to 20 min. The requirements for a recorder, pressure-regulated bottles of carrier gas, and certified standard gas mixtures for calibration raise costs to the point where infrequent analyses by this method may be uneconomical. The advantages of this system are freedom from the cumulative errors found in sequential volumetric measurements, adaptability to other gas component analyses, adaptability to intermittent on-line sampling and analysis, and the use of samples of 1 mL or less.[1]

2. Sample Collection

When the source of gas is some distance from the apparatus used for analysis, collect samples in sealed containers and bring to the instrument. Displacement collectors are the most suitable containers. Glass sampling bulbs (or tubes) with three-way glass or TFE stopcocks at each end, as indicated in Figure 2720:1, are particularly useful. These also are available with centrally located ports provided with septa for syringe transfer of samples. Replace septa periodically to prevent contamination by atmospheric gases. Connect one end of collector to gas source and vent three-way stopcock to the atmosphere. Clear line of air by passing 10 to 15 volumes of gas through vent and open stopcock to admit sample. If large quantities of gas are available, sweep air away by passing 10 to 15 volumes of gas through tube. If the gas supply is limited, fill the gas sampling bulb (tube) with an acidic salt solution.[2] Then completely displace the acidic salt solution in the gas sampling bulb (tube) with the sample gas. Because the acidic salt solution absorbs gases to some extent, fill the gas sampling bulb completely with the gas and seal off from any contact with displacement fluid during temporary storage. When transferring gas to the gas-analyzing apparatus, do not transfer any fluid.

3. References

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2720 B. Volumetric Method

1. General Discussion

a. Principle: This method may be used for the analysis either of digester gas or of methane in water (see Section 6211, Methane). A measured volume of gas is passed first through a solution of potassium hydroxide (KOH) to remove CO_2, next through a solution of alkaline pyrogallol to remove O_2, and then over heated cupric oxide, which removes H_2 by oxidation to water. After

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each of the above steps, the volume of gas remaining is measured; the decrease that results is a measure of the relative percentage of volume of each component in the mixture. Finally, CH_4 is determined by conversion to CO_2 and H_2O in a slow-combustion pipet or a catalytic oxidation assembly. The volume of CO_2 formed during combustion is measured to determine the fraction of methane originally present. Nitrogen is estimated by assuming that it represents the only gas remaining and equals the difference between 100% and the sum of the measured percentages of the other components.

When only CO_2 is measured, report only CO_2. No valid assumptions may be made about the remaining gases present without making a complete analysis.

Follow the equipment manufacturers' recommendations with respect to oxidation procedures.

CAUTION: *Do not attempt any slow-combustion procedure on digester gas because of the high probability of exceeding the explosive 5% by volume concentration of* CH_4.

2. Apparatus

Orsat-type gas-analysis apparatus, consisting of at least: (1) a water-jacketed gas buret with leveling bulb; (2) a CO_2-absorption pipet; (3) an O_2-absorption pipet; (4) a cupric oxide-hydrogen oxidation assembly; (5) a shielded catalytic CH_4-oxidation assembly or slow-combustion pipet assembly; and (6) a leveling bulb. With the slow-combustion pipet use a controlled source of current to heat the platinum filament electrically. Preferably use mercury as the displacement fluid; alternatively use aqueous Na_2SO_4-H_2SO_4 solution for sample collection. Use any commercially available gas analyzer having these units.

3. Reagents

a. Potassium hydroxide solution: Dissolve 500 g KOH in distilled water and dilute to 1 L.

b. Alkaline pyrogallol reagent: Dissolve 30 g pyrogallol (also called pyrogallic acid) in distilled water and make up to 100 mL. Add 500 mL KOH solution.

c. Oxygen gas: Use approximately 100 mL for each gas sample analyzed.

d. Displacement liquid (acidic salt solution): Dissolve 200 g Na_2SO_4 in 800 mL distilled water; add 30 mL conc H_2SO_4. Add a few drops of methyl orange indicator. When color fades, replace solution.

4. Procedure

a. Sample introduction: Transfer 5 to 10 mL gas sample into gas buret through a capillary-tube connection to the collector. Expel this sample to the atmosphere to purge the system. Transfer up to 100 mL gas sample to buret. Bring sample in buret to atmospheric or reference pressure by adjusting leveling bulb. Measure volume accurately and record as V_1.

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b. Carbon dioxide absorption: Remove CO_2 from sample by passing it through the CO_2-absorption pipet charged with the KOH solution. Pass gas back and forth until sample volume remains constant. Before opening stopcocks between buret and any absorption pipet, make sure that the gas in the buret is under a slight positive pressure to prevent reagent in the pipet from contaminating stopcock or manifold. After absorption of CO_2, transfer sample to buret and measure volume. Record as V_2.

c. Oxygen absorption: Remove O_2 by passing sample through O_2-absorption pipet charged with alkaline pyrogallol reagent until sample volume remains constant. Measure volume and record as V_3 . For digester gas samples, continue as directed in ¶ 4*d*. For CH_4 in water, store gas in CO_2 pipet and proceed ¶ 4*e* below.

d. Hydrogen oxidation: Remove H_2 by passing sample through CuO assembly maintained at a temperature in the range 290 to 300°C. When a constant volume has been obtained, transfer sample back to buret, cool, and measure volume. Record as V_4.

Waste to the atmosphere all but 20 to 25 mL of remaining gas. Measure volume and record as V_5. Store temporarily in CO_2-absorption pipet.

e. Methane oxidation: Purge inlet connections to buret with O_2 by drawing 5 to 10 mL into buret and expelling to the atmosphere. Oxidize CH_4 either by the catalytic oxidation process for digester gas and gas phase of water samples or by the slow-combustion process for gas phase of water samples.

1) Catalytic oxidation process—For catalytic oxidation of digester gas and gas phase of water samples, transfer 65 to 70 mL O_2 to buret and record this volume as V_6 . Pass O_2 into CO_2-absorption pipet so that it will mix with sample stored there. Return this mixture to buret and measure volume. Record as V_7. This volume should closely approximate V_5 plus V_6 . Pass O_2-sample mixture through catalytic oxidation assembly, which should be heated in accordance with the manufacturer's directions. Keep rate of gas passage less than 30 mL/min. After first pass, transfer mixture back and forth through the assembly between buret and reservoir at a rate not faster than 60 mL/min until a constant volume is obtained. Record as V_8.

2) Slow-combustion process—For slow combustion of the gas phase of water samples, transfer 35 to 40 mL O_2 to buret and record volume as V_6 . Transfer O_2 to slow-combustion pipet and then transfer sample from CO_2-absorption pipet to buret. Heat platinum coil in combustion pipet to yellow heat while controlling temperature by adjusting current. Reduce pressure of O_2 in pipet to somewhat less than atmospheric pressure by means of the leveling bulb attached to the pipet. Pass sample into slow-combustion pipet at rate of approximately 10 mL/min. After the first pass, transfer sample and O_2 mixture back and forth between pipet and buret several times at a faster rate, allowing mercury in pipet to rise to a point just below heated

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coil. Collect sample in combustion pipet, turn off coil, and cool pipet and sample to room temperature with a jet of compressed air. Transfer sample to buret and measure volume. Record as V_8.

f. Measurement of carbon dioxide produced: Determine amount of CO_2 formed in the reaction by passing sample through CO_2-absorption pipet until volume remains constant. Record volume as V_9 . Check accuracy of determination by absorbing residual O_2 from sample. After this absorption, record final volume as V_{10}.

5. Calculation

a. CH_4 and H_2 usually are the only combustible gases present in sludge digester gas. When this is the case, determine percentage by volume of each gas as follows:

$$\% \ CO_2 = \frac{(V_1 - V_2) \times 100}{V_1}$$

$$\% \ O_2 = \frac{(V_2 - V_3) \times 100}{V_1}$$

$$\%H_2 = \frac{(V_3 - V_4) \times 100}{V_1}$$

$$\% \ CH_4 = \frac{V_4 \times (V_8 - V_9) \times 100}{V_1 \times V_5}$$

$$\% \ N_2 = 100 - (\% \ CO_2 + \%O_2 + \%H_2 + \%CH_4)$$

b. Alternatively, calculate CH_4 by either of the two following equations:

$$\%CH_4 = \frac{V_4 \times (V_6 + V_{10} - V_9) \times 100}{2 \times V_1 \times V_5}$$

$$\%CH_4 = \frac{V_4 \ (V_7 - V_8) \times 100}{2 \times V_1 \times V_5}$$

Results from the calculations for CH_4 by the three equations should be in reasonable agreement.

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If not, repeat analysis after checking apparatus for sources of error, such as leaking stopcocks or connections. Other combustible gases, such as ethane, butane, or pentane, will cause a lack of agreement among the calculations; however, the possibility that digester gas contains a significant amount of any of these is remote.

6. Precision and Bias

A gas buret measures gas volume with a precision of 0.05 mL and a probable accuracy of 0.1 mL. With the large fractions of CO_2 and CH_4 normally present in digester gas, the overall error for their determination can be made less than 1%. The error in the determination of O_2 and H_2, however, can be considerable because of the small concentrations normally present. For a concentration as low as 1%, an error as large as 20% can be expected. When N_2 is present in a similar low-volume percentage, the error in its determination would be even greater, because errors in each of the other determinations would be reflected in the calculation for N_2.

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2720 C. Gas Chromatographic Method

1. General Discussion

See Section 6010C for discussions of gas chromatography.

2. Apparatus

a. Gas chromatograph: Use any instrument system equipped with a thermal conductivity detector (TCD), carrier-gas flow controllers, injector and column temperature setting dials, TCD current controller, attenuator, carrier-gas pressure gauge, injection port, signal output, and power switch. Some columns require temperature programming while others are isothermal. Preferably use a unit with a gas sampling loop and valve that allow automatic injection of a constant sample volume.

b. Sample introduction apparatus: An instrument equipped with gas-sampling valves is designed to permit automatic injection of a specific sample volume into the chromatograph. If such an instrument is not available, introduce samples with a 2-mL syringe fitted with a 27-gauge hypodermic needle. Reduce escape of gas by greasing plunger lightly with mineral oil or preferably by using a special gas-tight syringe. One-step separation of oxygen, nitrogen, methane, and carbon dioxide may be accomplished in concentric columns (column within a column) under isothermal conditions at room temperature instead of performing two column

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analyses. These concentric columns permit the simultaneous use of two different packings for the analysis of gas samples.

*c. Chromatographic column:#(59)** Select column on the basis of manufacturer's recommendations.#(60)† Report column and packing specifications and conditions of analyses with results.

A two-column system usually is required. A molecular sieve column separates H_2, O_2, N_2, CO, and CH_4 isothermally, but because CO_2 is adsorbed by the molecular sieve, a second column is needed to complete the analysis. A commonly used two-column system utilizes a Chromosorb 102 column and a Molecular Sieve 5A or 13X column to separate H_2, O_2, N_2, CH_4, and CO_2 isothermally.[1,2]

A single-column procedure can be used; however, it requires temperature programming. Columns packed with special porous spherical or granular packing materials effect separation with sharp, well-resolved peaks.[3] With temperature programming, columns packed with Chromosorb 102,[2] Carbosphere,[4] and Carbosieve[3] separate the gases listed.†#(61) Commercial equipment specifically designed for such operations is available.[2,4-6]

d. Integrator/recorder: Use a 10–mV full-span strip chart recorder with the gas chromatograph. When minor components such as H_2 and H_2S are to be detected, a 1-mV full-span recorder is preferable.

Integrators that can easily detect very minute quantities of gases are available. Computerized data-processing systems, to record and manipulate the chromatographic signal, chromatographic base line, etc., also are available.

3. Reagents

a. Carrier gases: Preferably use helium for separating digester gases. It is impossible to detect less than 1% hydrogen when helium is used as the carrier gas.[1] Obtain linear TCD responses for molar concentrations of hydrogen between 0 and 60% by using an 8.5% hydrogen–91.5% helium carrier gas mixture.[7] To detect trace quantities of hydrogen use argon or nitrogen as carrier gas.[1]

b. Calibration gases: Use samples of CH_4, CO_2, and N_2 of known purity, or gas mixtures of certified composition, for calibration. Also use samples of O_2, H_2, and H_2S of known purity if these gases are to be measured. Preferably use custom-made gas mixtures to closely approximate digester gas composition.

c. Displacement liquids: See Section 2720B.3*d*.

4. Procedure

a. Preparation of gas chromatograph: Open main valve of carrier-gas cylinder and adjust carrier-gas flow rate to recommended values. To obtain accurate flow measurements, connect a soap-film flow meter to the TCD vent. Turn power on. Turn on oven heaters, if used, and

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detector current and adjust to desired values.

Set injection port and column temperatures as specified for the column being used. Set TCD current. Turn on recorder or data processor. Check that the injector/detector temperature has risen to the appropriate level and confirm that column temperature is stabilized. Set range and attenuation at appropriate positions.

The instrument is ready for use when the recorder yields a stable base line. Silica gel and molecular sieve columns gradually lose activity because of adsorbed moisture or materials permanently adsorbed at room temperature. If insufficient separations occur, reactivate by heating or repacking.

b. Calibration: For accurate results, prepare a calibration curve for each gas to be measured because different gas components do not give equivalent detector responses on either a weight or a molar basis. Calibrate with synthetic mixtures or with pure gases.

1) Synthetic mixtures—Use purchased gas mixtures of certified composition or prepare in the laboratory. Inject a standard volume of each mixture into the gas chromatograph and note response for each gas. Compute detector response, either as area under a peak or as height of peak, after correcting for attenuation. Read peak heights accurately and correlate with concentration of component in sample. Reproduce operating parameters exactly from one analysis to the next. If sufficient reproducibility cannot be obtained by this procedure, use peak areas for calibration. Preferably use peak areas when peaks are not symmetrical. Prepare calibration curve by plotting either peak area or peak height against volume or mole percent for each component.

Modern integrators and data-processing systems are able to generate calibration tables for certified gas mixtures.

2) Pure gases—Introduce pure gases into chromatograph individually with a syringe. Inject sample volumes of 0.25, 0.5, 1.0 mL, etc., and plot detector response, corrected for attenuation, against gas volume.

When the analysis system yields a linear detector response with increasing gas component concentration from zero to the range of interest, run standard mixtures along with samples. If the same sample size is used, calculate gas concentration by direct proportions.

c. Sample analysis: If samples are to be injected with a syringe, equip sample collection container with a port closed by a rubber or silicone septum. To take a sample for analysis, expel air from barrel of syringe by depressing plunger and force needle through the septum. Withdraw plunger to take gas volume desired, pull needle from collection container, and inject sample rapidly into chromatograph.

When samples are to be injected through a gas-sampling valve, connect sample collection container to inlet tube. Let gas flow from collection tube through the valve to purge dead air space and fill sample tube. About 15 mL normally are sufficient to clear the lines and to provide a sample of 1 to 2 mL. Transfer sample from loop into carrier gas stream by following manufacturer’s instructions. Bring samples to atmospheric pressure before injection.

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When calibration curves have been prepared with a synthetic gas mixture of certified composition, use the same sample volume as that used during calibration. When calibration curves are prepared by the procedure using varying volumes of pure gases, inject any convenient gas sample volume up to about 2 mL.

Inject sample and standard gases in sequence to permit calculation of unknown gas concentration in volume (or mole) percent by direct comparison of sample and standard gas peak heights or areas. For more accurate analysis, make duplicate or triplicate injections of sample and standard gases.

5. Calculation

a. When calibration curves have been prepared with synthetic mixtures and the volume of the sample analyzed is the same as that used in calibration, read volume percent of each component directly from calibration curve after detector response for that component is computed.

b. When calibration curves are prepared with varying volumes of pure gases, calculate the percentage of each gas in the mixture as follows:

$$\text{Volume \%} = \frac{A}{B} \times 100$$

where:

A = partial volume of component (read from calibration curve) and
B = volume sample injected.

c. Where standard mixtures are run with samples and instrument response is linear from zero to the concentration range ofinterest:

$$\text{Volume \%} = \text{volume \% (std)} \frac{C}{D}$$

where:

C = recorder value of sample and
D = recorder value of standard.

d. Digester gases usually are saturated with water vapor that is not a digestion product. Therefore, apply corrections to calculate the dry volume percent of each digester gas component as follows:

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$$\text{Dry volume \%} = \frac{\text{volume \% as above}}{1 - P_v}$$

where:

P_v = saturated water vapor pressure at room temperature and pressure, decimal %.

The saturation water vapor pressure can be found in common handbooks. The correction factor $\frac{1}{1 - P_v}$ is usually small and is often neglected by analysts.

6. Precision and Bias

Precision and bias depend on the instrument, the column, operating conditions, gas concentrations, and techniques of operation. The upper control limits for replicate analyses of a high-methane-content standard gas mixture (65.01% methane, 29.95% carbon dioxide, 0.99% oxygen, and 4.05% nitrogen) by a single operator were as follows: 65.21% for methane, 30.36% for carbon dioxide, 1.03% for oxygen, and 4.15% for nitrogen. The lower control limits for this same standard gas mixture were: 64.67% for methane, 29.88% for carbon dioxide, 0.85% for oxygen, and 3.85% for nitrogen. The observed relative standard deviations (RSD) were: 0.14% for methane, 0.26% for carbon dioxide, 3.2% for oxygen, and 1.25% for nitrogen.

In a similar analysis of another standard gas mixture (55% methane, 35% carbon dioxide, 10% diatomic gases—2% hydrogen, 6% nitrogen, 2% oxygen), typical upper control limits for precision of duplicate determinations were: 55.21% for methane, 35.39% for carbon dioxide, and 10.26% for the diatomic gases. The lower control limits for this standard gas mixture were: 54.78% for methane, 34.62% for carbon dioxide, and 9.73% for the diatomic gases. The observed RSDs for this analysis were: 0.13% for methane, 0.36% for carbon dioxide, and 0.88% for the diatomic gases.

A low-methane-content standard gas mixture (35.70% methane, 47.70% carbon dioxide, 3.07% oxygen, 8.16% nitrogen, and 5.37% hydrogen) was analyzed as above yielding upper control limits as follows: 34.4% for methane, 49.46% for carbon dioxide, 3.07% for oxygen, and 8.2% for nitrogen. The lower control limits were: 34.18% for methane, 49.11% for carbon dioxide, 2.83% for oxygen, and 7.98% for nitrogen. The observed RSDs were: 0.11% for methane, 0.16% for carbon dioxide, 1.37% for oxygen, and 0.46% for nitrogen.

With digester gas the sum of the percent CH_4, CO_2, and N_2 should approximate 100%. If it does not, suspect errors in collection, handling, storage, and injection of gas, or in instrumental operation or calibration.

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2810 DISSOLVED GAS SUPERSATURATION#(62)*

2810 A. Introduction

Water can become supersaturated with atmospheric gases by various means, heating and air entrainment in spilled or pumped water being the most common. The primary sign of gas supersaturation is the formation of bubbles on submerged surfaces or within the vascular systems and tissues of aquatic organisms.

Gas supersaturation can limit aquatic life and interfere with water treatment processes. Levels of supersaturation lethal to aquatic organisms have been found in springs, rivers, wells, lakes, estuaries, and seawater. Gas supersaturation can be produced in pumped or processed water intended for drinking, fish hatchery supply, and laboratory bioassays. Seasonal and other temporal variations in supersaturation may occur in surface waters as a result of solar heating and photosynthesis. Because the rate of equilibration may be slow, supersaturation may persist in flowing water for days and excessive dissolved gas levels thus may persist far from the source of

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supersaturation.

Gas bubbles form only when the total dissolved gas pressure is greater than the sum of compensating pressures. Compensating pressures include water, barometric and, for organisms, tissue or blood pressure. The total dissolved gas pressure is equal to the sum of the partial pressures of all the dissolved gases, including water vapor. Typically, only nitrogen, oxygen, argon, carbon dioxide, and water vapor pressures need to be considered in most natural waters. Gas bubble disease, of fish or other aquatic organisms, is a result of excessive uncompensated gas pressure. A single supersaturated gas such as oxygen or nitrogen may not necessarily result in gas bubble disease because bubble formation depends largely on total dissolved gas pressure. The degree of gas saturation should be described in terms of pressures rather than concentration or volume units.

2810 B. Direct-Sensing Membrane-Diffusion Method

1. General Discussion

a. Principle: This method requires an instrument with a variable length of ‘‘gas permeable’’ tubing, connected to a pressure-measuring device. Dimethyl silicone rubber tubing often is used because it is highly permeable to dissolved gases, including water vapor. At steady state, the gauge pressure inside the tubing is equal to the difference in gas pressure (ΔP) between the total dissolved gas pressure and the ambient barometric pressure. When the water is in equilibrium with the atmosphere, ΔP equals zero.

If ΔP is greater than zero, the water is supersaturated. Conversely, if ΔP is negative the water is undersaturated.

b. Working range: The working range of this method depends on the pressure-sensing device used, but typically will range from –150 to +600 mm Hg. Dissolved solids in wastewater will not interfere with this method. The practical depth range for these instruments is 1 to 10 m.

2. Apparatus

Several types of membrane-diffusion instruments are available commercially.#(63)* Alternatively, construct a unit from commercially available parts. Several units have been described, including a direct-reading instrument using pressure transducers and a digital readout,[1] an on-line unit that can activate an alarm system,[2] and an early model of the Weiss saturometer.[3] Each of these units has specific advantages and limitations; the instrument of choice will depend on the specific application. All these instruments are portable so that data collection is completed in the field.

Test the instrument for leaks according to the manufacturer’s recommendation. Even a very small leak, difficult to detect and locate, will result in useless data. Calibrate the pressure-measuring device with a mercury manometer or certified pressure gauge. If a manometer is used, include fresh mercury that flows freely in the tubing. An alternative method

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for directly testing membrane-diffusion instruments in a small, closed chamber where induced ΔP levels can be compared against observed ΔP levels is available.[2]

Van Slyke-Neill[4] or gas chromatography methods[1] are inappropriate for calibration but they may be used to verify results. These methods measure individual gas concentrations and require further conversion to ΔP or partial pressure and suffer from sampling and sample handling problems.[5-7]

3. Procedure

At the start of each day, test the instrument for leaks and recalibrate. At a monitoring site, completely submerge the sensing element in the water, preferably below the hydrostatic compensation depth. This is the depth where the hydrostatic and total gas pressures are equal and as a result, bubbles will not form on the tubing. Bubble formation on the silicone rubber tubing seriously reduces accuracy. Compute hydrostatic compensation depth[5] as follows:

$$Z = \frac{\Delta P}{73.42}$$

where:

Z = hydrostatic compensation depth, m, and
ΔP = pressure difference between total dissolved gas pressure and the ambient barometric pressure, mm Hg.

The factor 73.42 is the hydrostatic pressure of fresh water at 20°C expressed in terms of mm Hg/m water depth. Because the variation of hydrostatic pressure with temperature and salinity is small, this equation can be used for all natural waters.

Dislodge formed bubbles on the tubing by gently striking the instrument or moving the instrument rapidly in the water. Movement of water across the silicone rubber tubing also facilitates establishing the equilibrium between gas pressure in the water and in the tubing.

Operate the instrument ‘‘bubble free’’ until a stable ΔP is observed. This may take from 5 to 30 min, depending on the ΔP, water temperature, water flow, and geometry of the system. The time response of the membrane-diffusion method is shown in Figure 2810:1 for ‘‘bubble-free’’ and ‘‘bubble’’ conditions.

If the instrument is used in heavily contaminated water containing oil or other organic compounds, clean the silicone tubing with a mild detergent according to the manufacturer’s instructions. Silicone rubber tubing has been used in uncontaminated natural water for at least eight years without being adversely affected by attached algal growth.[2] The tubing can be damaged by abrasive grit, diatoms, biting aquatic organisms, certain organic compounds, and strong acids.[2]

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Obtain the barometric pressure with each measurement by using a laboratory mercury barometer, a calibrated portable barometer, or pressure transducer. Barometric pressures reported by weather agencies (or airports) are corrected to sea level and are unusable.

4. Calculation

a. Total gas pressure: Preferably report total gas pressure as ΔP.[2,6,8] Express pressure as millimeters of mercury.

Total gas pressure also has been reported as a percentage of local barometric pressure:

$$\text{TGP } \% = \left[\frac{P_b + \Delta P}{P_b}\right] \times 100$$

where:

P_b = true local barometric pressure, mm Hg.

The reporting of total gas pressure as a percentage is not encouraged.[8]

b. Component gas pressures: When information on component gas supersaturation is needed, express data as partial pressures, differential pressures, or percent saturation.[5,8] This requires additional measurements of dissolved oxygen, temperature, and salinity#(64)† at the monitoring site. In a mixture of gases in a given volume, the partial pressure of a gas is the pressure that this gas would exert if it were the only gas present.

1) Oxygen partial pressure—Calculate partial pressure of oxygen as follows:

$$P_{O_2} = \frac{DO}{\beta_{O_2}} \times 0.5318$$

where:

P_{O_2} = partial pressure of dissolved oxygen, mm Hg,

β_{O_2} = Bunsen coefficient for oxygen (Table 2810:I), L/(L·atm), and

DO = measured concentration of oxygen, mg/L.

Bunsen coefficients for marine waters are available.[5] The factor 0.5318 equals 760/(1000 K), where K is the ratio of molecular weight to molecular volume for oxygen gas.[5]

2) Nitrogen partial pressure—Estimate the partial pressure of nitrogen by subtracting the partial pressures of oxygen and water vapor from the total gas pressure.

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$$P_{N_2} = P_b + \Delta P - P_{O_2} - P_{H_2O}$$

where:

P_{H_2O} = vapor pressure of water in mm Hg from Table 2810:II.

This term includes a small contribution from argon and any other gases present, including carbon dioxide and methane. The partial pressure of carbon dioxide is negligible in natural waters of pH > 7.0.

3) Nitrogen:oxygen partial pressure ratio—The ratio of the partial pressure of nitrogen to the partial pressure of oxygen (N_2:O_2) characterizes the relative contribution of the two gases to the total dissolved gas pressure. In water in equilibrium with air, this ratio is 3.77.

c. Differential pressures: The differential pressure of a gas is the difference between the partial pressures of that gas in water and air. The oxygen differential pressure may be calculated as

$$\Delta P_{O_2} = P_{O_2} - 0.209\,46(P_b - P_{H_2O})$$

and the nitrogen differential pressure as

$$\Delta P_{N_2} = \Delta P - \Delta P_{O_2}$$

d. Percent of saturation: In older literature, supersaturation values have been reported as percent saturation. This method of reporting component gases is discouraged but can be calculated as follows:

$$N_2(\%) = \left[\frac{P_{N_2}}{0.7902\ (P_b - P_{H_2O})}\right] \times 100$$

$$O_2(\%) = \left[\frac{P_{O_2}}{0.20946(P_b - P_{H_2O})}\right] \times 100$$

The following relationships are useful conversions:

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$$TGP(\%) = 0.209\ 46\ O_2(\%) + 0.7902\ N_2(\%)$$

$$\Delta P = 0.20946\left[\frac{O_2(\%)}{100} - 1\right][P_b - P_{H_2O}] + 0.7902\left[\frac{N_2(\%)}{100} - 1\right][P_b - P_{H_2O}]$$

$$\Delta P = \frac{DO}{\beta_{O_2}}(0.5318)(1 + N_2{:}O_2) - (P_b - P_{H_2O})$$

Use care with these relationships with older data because both TGP(%) and N_2(%) have been differently defined.[5]

5. Quality Control

The precision of the membrane-diffusion method depends primarily on the pressure-sensing instrument. For an experienced operator it is approximately ±1 to 2 mm Hg with an accuracy of ±3 to 5 mm Hg.[3,6] Air leaks, bubble formation, biofilm development, incomplete equilibration, or condensation produce negative errors while direct water leaks can result in positive errors in submersible units.

For accurate work, measure water temperature to the nearest ±0.1°C.

6. Reporting of Results

In reporting results, include the following data:

Sensor depth, m,

Barometric pressure, mm Hg,

Water temperature, °C,

Dissolved oxygen, mm Hg or mg/L,

Salinity, g/kg, and

ΔP, mm Hg.

If component gas information is needed add:

Partial pressure of oxygen, mm Hg,

Partial pressure of nitrogen, mm Hg, and

Nitrogen:oxygen partial pressure ratio

or

ΔP_{O_2}, mm Hg, and

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ΔP_{N_2}, mm Hg.

7. Interpretation of Results

The biological effects of dissolved gas supersaturation depend on the species, age, depth in water column, length of exposure, temperature, and nitrogen:oxygen partial pressure ratio.[12] Safe limits generally are segregated into wild/natural circumstances, where behavior and hydrostatic pressure can modify the exposure by horizontal and vertical movements away from dangers, and captive environments such as aquaria, hatcheries, or laboratories, where conditions not only preclude escape but also include other significant stresses. Of these two realms, captive circumstances are more likely to cause illness or mortality from gas bubble disease and will do so sooner and at the lower ΔP levels.

In wild/natural circumstances, the limit of safe levels of gas supersaturation depends on the depth available to the species and/ or species behavior, but this limit usually occurs at a ΔP between 50 and 150 mm Hg. Under captive conditions, the ΔP should be as close to zero as possible. For sensitive species and life stages, sublethal and lethal effects have been observed at ΔP of 10 to 50 mm Hg.[13]

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Figures

Figure 2120:1. Filtration system for color determinations.

Figure 2120:2. Chromaticity diagrams.

Figure 2150:1. Odor-free-water generator.

Figure 2530:1. Floatables sampler with mixer.

Figure 2530:2. Floatables flotation funnel and filter holder.

Figure 2530:3. Flotation funnels and mixing unit.

Figure 2530:4. Floatable oil tube, 1-L capacity.

Figure 2560:1. Schematic of filtration apparatus for preparation of particle-free dilution water or electrolyte solution.

Figure 2710:1. Schematic diagram of settling vessel for settled sludge volume test.

Figure 2710:2. Schematic diagram of settling vessel for zone settling rate test.

Figure 2710:3. Capillary suction time apparatus.

Figure 2710:4. TTF equipment. Large-volume equipment requires a 9-cm- diam Buchner funnel and a 250-mL graduated cylinder. Small-volume equipment requires a 2.5-cm-diam funnel and a 10-mL cylinder.

Figure 2720:1. Gas collection apparatus.

Figure 2810:1. Time response for the membrane-diffusion method.

Tables

TABLE 2120:I. SELECTED ORDINATES FOR SPECTROPHOTOMETRIC COLOR DETERMINATIONS*

	X	*Y*	*Z*
Ordinate No.	**Wavelength *nm***		

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Ordinate No.	*X*	*Y*	*Z*
	Wavelength *nm*		
1	424.4	465.9	414.1
2*	435.5*	489.5*	422.2*
3	443.9	500.4	426.3
4	452.1	508.7	429.4
5*	461.2*	515.2*	432.0*
6	474.0	520.6	434.3
7	531.2	525.4	436.5
8*	544.3*	529.8*	438.6*
9	552.4	533.9	440.6
10	558.7	537.7	442.5
11*	564.1*	541.4*	444.4*
12	568.9	544.9	446.3
13	573.2	548.4	448.2
14*	577.4*	551.8*	450.1*
15	581.3	555.1	452.1
16	585.0	558.5	454.0
17*	588.7*	561.9*	455.9*
18	592.4	565.3	457.9
19	596.0	568.9	459.9
20*	599.6*	572.5*	462.0*
21	603.3	576.4	464.1
22	607.0	580.4	466.3
23*	610.9*	584.8*	468.7*
24	615.0	589.6	471.4
25	619.4	594.8	474.3
26*	624.2*	600.8*	477.7*
27	629.8	607.7	481.8
28	636.6	616.1	487.2
29*	645.9*	627.3*	495.2*
30	663.0	647.4	511.2

Factors When 30 Ordinates Used

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Ordinate No.	*X*	*Y*	*Z*
	Wavelength *nm*		
38	0.032 69	0.033 33	0.039
Factors When 10 Ordinates Used			
14	0.098 06	0.100 00	0.118

* Insert in each column the transmittance value (%) corresponding to the wavelengthshown. Where limited accuracy is sufficient, use only the ordinates marked with anasterisk.

TABLE 2120:II. COLOR HUES FOR DOMINANT WAVELENGTH RANGES

Wavelength Range *nm*	Hue
400–465	Violet
465–482	Blue
482–497	Blue-green
497–530	Green
530–575	Greenish yellow
575–580	Yellow
580–587	Yellowish orange
587–598	Orange
598–620	Orange-red
620–700	Red
400–530c*	Blue-purple
530c–700*	Red-purple

* See Figure 2120:2 for significance of ‘‘c’’.

TABLE 2150:I. THRESHOLD ODOR NUMBERS CORRESPONDING TO VARIOUS DILUTIONS

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* See Figure 2120:2 for significance of ''c''.

TABLE 2150:I. THRESHOLD ODOR NUMBERS CORRESPONDING TO VARIOUS DILUTIONS

Sample Volume Diluted to 200 mL *mL*	Threshold Odor No.	Sample Volume Diluted to 200 mL *mL*	Threshold Odor No.
200	1	12.0	17
140	1.4	8.3	24
100	2	5.7	35
70	3	4.0	50
50	4	2.8	70
35	6	2.0	100
25	8	1.4	140
17	12	1.0	200

TABLE 2150:II. DILUTIONS FOR VARIOUS ODOR INTENSITIES

Sample Volume in Which Odor Is First Noted *mL*	Volumes to Be Diluted to 200 mL *mL*
200	200, 140, 100, 70, 50
50	50, 35, 25, 17, 12
12	12, 8.3, 5.7, 4.0, 2.8
2.8	Intermediate dilution

TABLE 2160:I. FLAVOR THRESHOLD NUMBERS CORRESPONDING TO VARIOUS DILUTIONS

Sample Volume *mL*	Diluent Volume *mL*	Flavor Threshold No. *FTN*
200	0	1
100	100	2
70	130	3

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Sample Volume *mL*	Diluent Volume *mL*	Flavor Threshold No. *FTN*
50	150	4
35	165	6
25	175	8
17	183	12
12	188	17
8	192	25
6	194	33
4	196	50
3	197	67
2	198	100
1	199	200

TABLE 2160:II. DILUTIONS FOR DETERMINING THE FTN

Sample Volume in Which Taste Is First Noted *mL*	Volumes to be Diluted to 200 mL *mL*
200	200, 100, 70, 50, 35, 25, 17
50	50, 35, 25, 17, 12, 8, 6
12	12, 8, 6, 4, 3, 2, 1
4	Intermediate dilution

TABLE 2170:I. QUANTITATIVE ODOR REFERENCES*

Compound	Odor Characteristics	Stock Solution Concentration *mg/L*	Amount Placed Ir 200 mL Pure Wate 25°C for Presentat
Geosmin	Earthy, red beets	0.2†	300 μL for 300 ng
2-Methylisoborneol	Earthy, peat-like, Brazil nut, soil	0.2†	200 μL for 200 ng
Free chlorine	Chlorinous	1.0	0.1 mL for 0.5 mg

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Compound	Odor Characteristics	Stock Solution Concentration *mg/L*	Amount Placed Ir 200 mL Pure Wate 25°C for Presentat
		pH = 7	
Dichloramine	Swimming pool chlorine	pH = 7	
Monochloramine	Chlorinous	pH = 7	
trans,2-*cis*,6-Nonadienal	Cucumber, green vegetation	1000	1 μL for 5 μg/L
Styrene	Model airplane glue	1000	100 μL for 500 μg
Toluene	Glue, sweet solventy	1000	100 μL for 500 μg
cis-3-Hexenyl-1-acetate	Grassy	1000	100 μL for 500 μg
cis-3-Hexene-1-ol	Grassy, green apple	1000	100 μL for 500 μg
Cumene	Paste shoe polish, solventy	1000	20 μL for 100 μg/l
m-Xylene	Sweet solventy	1000	40 μL for 200 μg/l
Methylisobutyl ketone	Paint solventy	1000	200 μL for 1.0 mg
1,2,4-Trimethylbenzene	Shoe polish, coal tar	1000	50 μL for 250 μg/l
Indene	Glue, moth balls	1000	1 μL for 5 μg/L
Indan	Varnish, coal tar	1000	5 μL for 25 μg/L
Naphthalene	Sweet solventy	1000	1 μL for 5 μg/L
Benzofuran	Shoe polish, moth balls	1000	2 μL for 10 μg/L
2-Methyl-benzofuran	Moth balls, sweet solventy	1000	50 μL for 250 μg/l

NOTE: These compounds have actually been identified as causes of odors in raw and finished drinking water.
* Adapted from AMERICAN WATER WORKS ASSOCIATION. 1993. Flavor Profile Analysis: Screening and Training of Panelists. AWWA Manual, American Water Works Assoc.,Denver, Colo.
† Compounds available only in solid form and must be dissolved in methanol.

TABLE 2170:II. REPRESENTATIVE ODOR REFERENCE STANDARDS*

Compound	Odor Characteristics	Stock Solution Concentration *mg/L*	Amou mL Pu
2,3,6-Trichloroanisole	Leather, earthy	1000	4 μL
2,3-Diethylpyrazine	Mildew, damp basement	1000	2 μL
2-Isopropyl-3-methoxypyrazine	Potato bin, musty	1000	40 μ
Nonanal	Hay, sweet	1000	40 μ
Dimethyl sulfide	Decaying vegetation, canned corn	1000	1 μL

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Compound	Odor Characteristics	Stock Solution Concentration *mg/L*	Amou mL Pu
Dimethyl disulfide	Septic	1000	2 µL
Dimethyltrisulfide	Garlicky, oniony, septic	0.2	50 µ
Butyric acid	Putrid, sickening	1000	200
trans,2-Nonenal	Cucumber with skin	1000	40 µ
Diphenyl ether	Geranium	1000†	20 µ
D-Limonene	Citrusy	1000	400
Hexanal	Lettuce heart, pumpkin, green pistachio	1000	40 µ
Benzaldehyde	Sweet almond	1000	200
Ethyl-2-methyl-butyrate	Fruity, pineapple	1000	100
2-Heptanone	Banana-like, sweet solventy	1000	100
Hexachloro-1,3-butadiene	Sweet, minty, Vapo Rub	1000	800
2-Isobutyl-3-methoxypyrazine	Green/bell pepper, musty	1000	40 µ
trans,2-*trans*,4-Decadienal	Rancid oily	1000	100
Butanol	Alcohol, solventy	1000	200
Eucalyptol (cincole)	Topical ointment for chest colds	1000	40 µ
Pyridine	Sweet, alcohol, organic	1000	400

NOTE: Possible causes of odors or chemical substitutes for causes of odors.
* Adapted from AMERICAN WATER WORKS ASSOCIATION. 1993. FLAVOR PROFILE ANALYSIS: SCREENING AND TRAINING OF PANELISTS. AWWA Manual, American Water Works Assoc., Denver, Colo.
* Compounds available only in solid form and must be dissolved in methanol.

TABLE 2170:III. SUBSTITUTE ODOR REFERENCE STANDARDS*

Compound	Odor Characteristic	Preparation
Cloves	Spicy like cloves	Use supermarket brand of dried clove buds (spice). Add 3 clove buds to 200 mL pure water and swirl 1–2 min. Allow to stand overnight at room temperature, then discard the buds.

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Compound	Odor Characteristic	Preparation
Dried grass	Hay	Place dried cut grass in erlenmeyer flask until half full.
Grass	Decaying vegetation	Weigh 2 g of fresh grass and mix into 200 mL pure water and let stand at room temperature. In 1–3 d, the odor will appear.
Grass	Septic	Allow the solution above for decaying vegetation to stand for an additional 1–2 weeks.
Rubber hose	Rubber hose	Boil a short section of rubber hose in 200 mL pure water for 5 min. Allow to cool and remove the hose.
Soap	Soapy	Place 5 g of chipped nonscented bar soap in 200 mL pure water.
Pencil shavings	Woody	Instruct panel member to sharpen a wood pencil and sniff the freshly exposed wood.

NOTE: Standards made from materials rather than chemicals.* Adapted from AMERICAN WATER WORKS ASSOCIATION. 1993. Flavor Profile Analysis: Screening and Training of Panelists. AWWA Manual. American Water WorksAssoc., Denver, Colo.

TABLE 2170:IV. BASIC TASTE STANDARDS

Chemical for Basic Tastes	Food or Beverage Corresponding to Intensity	Concentration %	Intensity Scale (1 to 12)*
Sweet: sugar	Canned fruit or vegetables	5.00	4 W
	Carbonated soda	10.00	8 M
	Syrup, jelly	15.00	12 S
Sour: citric acid	Fresh fruit jelly	0.05	4 W
	Some carbonated sodas	0.10	8 M
	Lemon juice	0.20	12 S

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Chemical for Basic Tastes	Food or Beverage Corresponding to Intensity	Concentration %	Intensity Scale (1 to 12)*
Salt: sodium chloride	Level in bread	0.40	4 W
	Dehydrated soup mix	0.70	8 M
	Soy sauce	1.00	12 S
Bitter: caffeine	Strong coffee	0.05	4 W
		0.10	8 M
		0.20	12 S
	or quinine hydrochloride dihydrate	0.001	4 W
		0.002	8 M
		0.004	12 S

* W = weak; M = moderate; S = strong.

TABLE 2320:I. END-POINT pH VALUES

Test Condition	End Point pH	
	Total Alkalinity	Phenolphthalein Alkalinity
Alkalinity, mg $CaCO_3$/L:		
30	4.9	8.3
150	4.6	8.3
500	4.3	8.3
Silicates, phosphates known or suspected	4.5	8.3
Routine or automated analyses	4.5	8.3
Industrial waste or complex system	4.5	8.3

TABLE 2320:II. ALKALINITY RELATIONSHIPS*

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TABLE 2320:II. ALKALINITY RELATIONSHIPS*

Result of Titration	Hydroxide Alkalinity as $CaCO_3$	Carbonate Alkalinity as $CaCO_3$	Bicarbonate Concentration as $CaCO_3$
P = 0	0	0	T
P < *tfrac*12T	0	2P	T – 2P
P = *tfrac*12T	0	2P	0
P > *tfrac*12T	2P – T	2(T – P)	0
P = T	T	0	0

*Key: P–phenolphthalein alkalinity; T–total alkalinity.

Table 2330:I. Estimating Equilibrium Constants and Activity Coefficients

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TABLE 2330:I. ESTIMATING EQUILIBRIUM CONSTANTS AND ACTIVITY COEFFICIENTS

Equation	Temperature Range	References
When complete mineral analysis is available:		
$I = {}^1/_2 \sum_{i=1}^{i} [X_i]\, Z_i^2$	—	3
When only conductivity is available:		
$I = 1.6 \times 10^{-5} C$	—	4
When only TDS is available:		
$I = TDS/40\,000$	—	5
$pf_m = A\left[\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I\right]$ (valid to $I < 0.5$)	—	3
$A = 1.82 \times 10^6\,(ET)^{-1.5}$	—	3
$E = \frac{60\,954}{T + 116} - 68.937$	—	6
$pK_2 = 107.8871 + 0.032\,528\,49T - 5151.79/T - 38.925\,61 \log_{10}T + 563\,713.9/T^2$	273–373	7
$pK_w = 4471/T + 0.017\,06T - 6.0875$	280–338	8
$pK_{sc} = 171.9065 + 0.077\,993T - 2839.319/T - 71.595 \log_{10}T$	273–363	7
$pK_{sa} = 171.9773 + 0.077\,993T - 2903.293/T - 71.595 \log_{10}T$	273–363	7
$pK_{sv} = 172.1295 + 0.077\,993T - 3074.688/T - 71.595 \log_{10}T$	273–363	7

*I = ionic strength
$[X_i]$ = concentration of component i, g-moles/L
Z_i = charge of species i
C = conductivity, µmhos/cm
TDS = total dissolved solids, mg/L
pY = $-\log_{10}$ of the value of any factor Y
f_m = activity coefficient for monovalent species
E = dielectric constant
T = temperature, °K (°C + 273.2)
K_2 = second dissociation constant for carbonic acid
K_w = dissociation constant for water
K_{sc} = solubility product constant for calcite
K_{sa} = solubility product constant for aragonite
K_{sv} = solubility product constant for vaterite

TABLE 2330:II. PRECALCULATED VALUES FOR *pK* AND *A* AT SELECTED TEMPERATURES

Temperature °C	pK_2	pK_S Calcite	pK_S Aragonite	pK_S Vaterite	pK_W	A

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Temperature °C	pK_2	pK_s Calcite	Aragonite	Vaterite	pK_w	A
5	10.55	8.39	8.24	7.77	14.73	0.494
10	10.49	8.41	8.26	7.80	14.53	0.498
15	10.43	8.43	8.28	7.84	14.34	0.502
20	10.38	8.45	8.31	7.87	14.16	0.506
25*	10.33	8.48	8.34	7.91	13.99	0.511
30	10.29	8.51	8.37	7.96	13.83	0.515
35	10.25	8.54	8.41	8.00	13.68	0.520
40	10.22	8.58	8.45	8.05	13.53	0.526
45	10.20	8.62	8.49	8.10	13.39	0.531
50	10.17	8.66	8.54	8.16	13.26	0.537
60	10.14	8.76	8.64	8.28	13.02	0.549
70	10.13	8.87	8.75	8.40	—	0.562
80	10.13	8.99	8.88	8.55	—	0.576
90	10.14	9.12	9.02	8.70	—	0.591

NOTE: All values determined from the equations of Table 2330:I.
A is used to calculate pf_m (see Table 2330:I).

* pf_m estimated from TDS values at 25°C care as follows:

TDS	pf_m
100	0.024
200	0.033
400	0.044
800	0.060
1000	0.066

TABLE 2330:III. GRAPHS AND COMPUTER SOFTWARE THAT CAN BE USED TO CALCULATE $CaCO_3$ SATURATION INDICES*

Item†	$CaCO_3$ Indices: Basis for Calculation of SI	CCPP	Approximate Temperature Range °C	Approximate Limit of Ionic Strength	Ion Pairs Considered?	C
1. Caldwell Lawrence diagrams[4]	pH_{sa}	P, D	2–25	0.030	No	

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Item†	$CaCO_3$ Indices: Basis for Calculation of SI	$CaCO_3$ Indices: CCPP	Approximate Temperature Range °C	Approximate Limit of Ionic Strength	Ion Pairs Considered?	C
2. ACAPP	RS	P, D	−10–110	6+	Yes	
3. DRIVER	RS	P	7–65	2.5	Yes	
4. INDEX C	pH_{sa} pH_{sb}	P, D	0–50	0.5	No	
5. LEQUIL	RS	No	5–90	0.5	Yes	
6. MINTEQA1	RS	P, D	0–100	0.5	Yes	

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Item†	$CaCO_3$ Indices: Basis for Calculation of SI	$CaCO_3$ Indices: CCPP	Approximate Temperature Range °C	Approximate Limit of Ionic Strength	Ion Pairs Considered?	C
7. PHREEQE Standard	RS	P, D	0–100	0.5	Yes	
For high-salinity waters	RS	P, D	0–80	7–8	Yes	
8. SEQUIL	RS	P, D	7–65	2.5	Yes	
9. SOLMINEQ.88	RS	P, D	0–350	6	Yes	
10. WTRCHEM	pH_{sa}	P, D	0–100	0.5	No	

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Item†	$CaCO_3$ Indices: Basis for Calculation of SI	$CaCO_3$ Indices: CCPP	Approximate Temperature Range °C	Approximate Limit of Ionic Strength	Ion Pairs Considered?	C
11. WATEQ4F	RS	No	0–100	0.5	Yes	

*SI = saturation index
CCPP = $CaCO_3$ precipitation potential
pH_{sa} = alkalinity-based pH
pH_{sb} = bicarbonate-based pH
P = calculates amount of $CaCO_3$ theoretically precipitated
D = calculates amount of $CaCO_3$ theoretically dissolved
RS = relative saturation
PC = personal computer
RAM = random access memory

†1. Loewenthal and Marais[3] provide 10.2- by 11.4-cm diagrams, with documentation; Merrill[5] provides 10.2- by 16.5-cm diagrams, with documentation.
2. Radian Corp., 8501 MoPac Blvd., P.O. Box 201088, Austin, TX 78720-1088 Attn: J.G. Noblett (software and documentation).
3. Power Computing Co., 1930 Hi Line Dr., Dallas, TX, 74207 (software and documentation[6]).
4. Brown and Caldwell, P.O. Box 8045, Walnut Creek, CA 94596-1220 Attn: D.T. Merrill (software and documentation).
5. Illinois State Water Survey, Aquatic Chemistry Section, 2204 Griffith Dr., Champaign, IL 61820-7495 Attn: T.R. Holm (software and documentation).
6. Center for Exposure Assessment Modeling, Environmental Research Laboratory, Office of Research and Development. U.S. Environmental Protection Agency,Athens, GA 30613 (software and documentation[7]).
7. U.S. Geological Survey, National Center, MS 437, Reston, VA 22902, Chief of WATSTORE Program (provides software for mainframe version of standard code);U.S. Geological Survey, Water Resources Division, MS 420, 345 Middlefield Rd., Menlo Park, CA 94025 Attn: K. Nordstrom (provides software for personalcomputer version of standard code); National Water Research Institute, Canada Centre for Inland Waters, 867 Lakeshore Rd., Burlington, Ont., Canada L7R 4A6Attn: A.S. Crowe (provides software and documentation [8,9] for personal computer versions of both standard and high-salinity codes); U.S. Geological Survey, Booksand Open File Report Section, Box 25425, Federal Center, Denver, CO 80225 (provides documentation[8,10] for mainframe and personal computer versions ofstandard code).
8. Power Computing Company, 1930 Hi Line Dr., Dallas, TX 74207 (software and documentation[11]).
9. U.S. Geological Survey, Water Resources Division, MS 427, 345 Middlefield Rd., Menlo Park, CA 94025 Attn: Y.K. Kharaka (software and documentation[12]).
10. D.T. Merrill, Brown and Caldwell, P.O. Box 8045, Walnut Creek, CA 94596-1220 (code listing and documentation).
11. U.S. Geological Survey, Water Resources Division, MS 420, 345 Middlefield Rd., Menlo Park, CA 94025 Attn: K. Nordstrom (software), Books and Open FileReport Section, Box 25425, Federal Center, Denver, CO 80225 (documentation[13]).
‡Codes differ in the species included in Alk_0.

TABLE 2340:I. MAXIMUM CONCENTRATIONS OF INTERFERENCES PERMISSIBLEWITH VARIOUS INHIBITORS*

	Max. Interference Concentration *mg/L*

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TABLE 2340:I. MAXIMUM CONCENTRATIONS OF INTERFERENCES PERMISSIBLEWITH VARIOUS INHIBITORS*

Interfering Substance	Max. Interference Concentration *mg/L*	
	Inhibitor I	**Inhibitor II**
Aluminum	20	20
Barium	†	†
Cadmium	†	20
Cobalt	over 20	0.3
Copper	over 30	20
Iron	over 30	5
Lead	†	20
Manganese (Mn^{2+})	†	1
Nickel	over 20	0.3
Strontium	†	†
Zinc	†	200
Polyphosphate		10

* Based on 25-mL sample diluted to 50 mL.
† Titrates as hardness.

TABLE 2510:I. EQUIVALENT CONDUCTIVITY, Λ, AND CONDUCTIVITY, *k*, OF POTASSIUM CHLORIDE AT 25.0°C.*[2–4]

KCl Concentration *M or equivalent/L*	Equivalent Conductivity, Λ *mho-cm²/equivalent*	Conductivity, k_S *μmho/cm*
0	149.9	
0.0001	148.9	14.9
0.0005	147.7	73.9
0.001	146.9	146.9
0.005	143.6	717.5
0.01	141.2	1 412
0.02	138.2	2 765

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KCl Concentration *M or equivalent/L*	Equivalent Conductivity, Λ *mho-cm²/equivalent*	Conductivity, k_S *μmho/cm*
0.05	133.3	6 667
0.1	128.9	12 890
0.2	124.0	24 800
0.5	117.3	58 670
1	111.9	111 900

* Based on the absolute ohm, the 1968 temperature standard, and the dm^3 volumestandard.[2] Values are accurate to ±0.1% or 0.1 μmho/cm, whichever is greater.

TABLE 2510:II. SAMPLE ANALYSIS ILLUSTRATING CALCULATION OF CONDUCTIVITY, k_{calc}, FOR NATURAL WATERS.[7]

Ions	mg/L	m*M*	|*z*| λ°±m*M*	z^2m*M*
Ca	55	1.38	164.2	5.52
Mg	12	0.49	52.0	1.96
Na	28	1.22	61.1	1.22
K	3.2	0.08	5.9	0.08
HCO_3	170	2.79	124.2	2.79
SO_4	77	0.80	128.0	3.20
Cl	20	0.56	42.8	0.56
			578.2	15.33

TABLE 2510:III. EQUIVALENT CONDUCTANCES, λ°+ AND λ°–, (MHO-CM^2/EQUIVALENT) FOR IONS IN WATER AT 25.0 C.[8]

Cation	λ°+	Anion	λ°–
H^+	350	OH^-	198.6
$1/2Ca^{2+}$	59.5	HCO_3^-	44.5
$1/2Mg^{2+}$	53.1	$1/2CO_3^{2-}$	72
Na^+	50.1	$1/2SO_4^{2-}$	80.0

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Cation	λ°+	Anion	λ°–
K^+	73.5	Cl^-	76.4
NH_4^+	73.5	Ac^-	40.9
$1/2Fe^{2+}$	54	F^-	54.4
$1/3Fe^{3+}$	68	NO_3^-	71.4
		$H_2PO_4^-$	33
		$1/2HPO_4^{2-}$	57

TABLE 2530:I. COEFFICIENT OF VARIATION AND RECOVERY FOR PARTICULATE FLOATABLES TEST

Type of Wastewater	Average Floatables Concentration *mg/L*	No. of Samples	Coefficient of Variation *%*	Recovery *%*
Raw*	49	5	5.7	96
Raw	1.0	5	20	92
Primary effluent	2.7	5	15	91

* Additional floatable material added from skimmings of a primarysedimentation basin.

TABLE 2560:I. EXAMPLE CALCULATIONS FOR PARTICLE SIZE DISTRIBUTION ANALYSIS

Channel No. (A)	Lower Limit d_p μm (B)	Upper Limit d_p μm (C)	Mean Diam. d_{pi} μm (D)	Δd_{pi} μm (E)	log d_{pi} d_p in μm (F)	Δ log d_{pi} (G)	Corrected Count (H)	Number Conc. ΔN_i *No./mL* (I)
6	2.95	3.39	3.16	0.44	0.50	0.06	5125	102 500
7	3.39	3.89	3.63	0.50	0.56	0.06	4568	91 360
8	3.89	4.47	4.17	0.58	0.62	0.06	3888	77 760
9	4.47	5.13	4.79	0.66	0.68	0.06	3088	61 760
10	5.13	5.89	5.50	0.76	0.74	0.06	2289	45 780
11	5.89	6.76	6.31	0.87	0.80	0.06	1584	31 680
12	6.76	7.76	7.24	1.00	0.86	0.06	1023	20 460

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Channel No. (A)	Lower Limit d_p μm (B)	Upper Limit d_p μm (C)	Mean Diam. d_{pi} μm (D)	Δd_{pi} μm (E)	log d_{pi} d_p in μm (F)	Δ log d_{pi} (G)	Corrected Count (H)	Number Conc. ΔN_i No./mL (I)
13	7.76	8.91	8.32	1.15	0.92	0.06	631	12 620
14	8.91	10.23	9.55	1.32	0.98	0.06	363	7 260
15	10.23	11.75	10.96	1.52	1.04	0.06	199	3 980

TABLE 2580:I. POTENTIAL OF ZOBELL'S SOLUTION AS FUNCTION OF TEMPERATURE

T °C	E V	T °C	E V
1	0.481	16	0.448
2	0.479	17	0.446
3	0.476	18	0.443
4	0.474	19	0.441
5	0.472	20	0.439
6	0.470	21	0.437
7	0.468	22	0.435
8	0.465	23	0.432
9	0.463	24	0.430
10	0.461	25	0.428
11	0.459	26	0.426
12	0.457	27	0.424
13	0.454	28	0.421
14	0.452	29	0.419
15	0.450	30	0.417

TABLE 2580:II. PREPARATION OF REDOX STANDARD SOLUTIONS

Standard Solution	Potentials of Pt Electrode vs. Selected Reference Electrodes at 25°C in Standard Solution			Weight of Aqu
	Calomel	Silver:Silver Chloride Ag/AgCl	Standard Hydrogen	

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TABLE 2580:II. PREPARATION OF REDOX STANDARD SOLUTIONS

Standard Solution	Potentials of Pt Electrode vs. Selected Reference Electrodes at 25°C in Standard Solution					Weight of Aqu
	Calomel	Silver:Silver Chloride Ag/AgCl			Standard Hydrogen	
	Hg/Hg_2Cl_2 saturated KCl	KCl 1.00*M*	KCl 4.00*M*	KCl saturated		
Light's solution[14]	+430	+439	+475	+476	+675	39.21 g ferr $Fe(NH_4)$ 48.22 g fe Fe(NH 56.2 mL s 1.84
ZoBell's solution*[2]	+183	+192	+228	+229	+428	1.4080 g po $K_4Fe(C$ 1.0975 g $K_3Fe(C$ 7.4555 g

* Store in dark plastic bottle in a refrigerator.

TABLE 2580:III. RECOMMENDED COMBINATIONS FOR SELECTED SAMPLE TYPES

Sample Type	Indicator Electrode(s)	Reference Electrode	Type of Sample Cell
Process stream			
(low Br^-) (S^{2-})	Pt or Au	Calomel or silver: silver chloride	Closed continuous flow (dual indicator electrode)
(high Br^-)	Pt or Au	Calomel or silver: silver chloride with salt bridge (double junction reference electrode)	
Natural waters			
Surface waters	Pt or Au	Calomel or silver: silver chloride	Closed continuous flow (dual indicator electrode) or beaker
Groundwater	Pt or Au	Calomel or silver: silver chloride	Closed continuous flow (dual indicator electrode)

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Sample Type	Indicator Electrode(s)	Reference Electrode	Type of Sample Cell
Soils, sludges	WIG, Pt wire	Calomel or silver: silver chloride	Beaker or soil core

TABLE 2710:I. TEMPERATURE CORRECTION FACTOR

Temperature °C	Temperature Correction Factor
15	0.9991
20	0.9982
25	0.9975
30	0.9957
35	0.9941
40	0.9922
45	0.9903

TABLE 2810:I. BUNSEN COEFFICIENT FOR OXYGEN IN FRESH WATER

	Bunsen Coefficient at Given Temperature (to nearest 0.1°C) *L real gas at STP/(L · atmosphere)*							
Temperature °C	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7
0	0.04914	0.04901	0.04887	0.04873	0.04860	0.04847	0.04833	0.0482(
1	0.04780	0.04767	0.04754	0.04741	0.04728	0.04716	0.04703	0.0468(
2	0.04653	0.04640	0.04628	0.04615	0.04603	0.04591	0.04579	0.0456(
3	0.04531	0.04519	0.04507	0.04495	0.04484	0.04472	0.04460	0.0444(
4	0.04414	0.04403	0.04392	0.04381	0.04369	0.04358	0.04347	0.0433(
5	0.04303	0.04292	0.04282	0.04271	0.04260	0.04250	0.04239	0.0422(
6	0.04197	0.04187	0.04177	0.04166	0.04156	0.04146	0.04136	0.0412(
7	0.04096	0.04086	0.04076	0.04066	0.04056	0.04047	0.04037	0.0402(
8	0.03999	0.03989	0.03980	0.03971	0.03961	0.03952	0.03943	0.0393(
9	0.03906	0.03897	0.03888	0.03879	0.03870	0.03861	0.03852	0.0384(
10	0.03817	0.03809	0.03800	0.03791	0.03783	0.03774	0.03766	0.0375(
11	0.03732	0.03724	0.03716	0.03707	0.03699	0.03691	0.03683	0.0367(
12	0.03651	0.03643	0.03635	0.03627	0.03619	0.03611	0.03604	0.0359(

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Temperature °C	Bunsen Coefficient at Given Temperature (to nearest 0.1°C) *L real gas at STP/(L · atmosphere)*							
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7
13	0.03573	0.03565	0.03558	0.03550	0.03543	0.03535	0.03528	0.0352(
14	0.03498	0.03491	0.03448	0.03476	0.03469	0.03462	0.03455	0.0344{
15	0.03426	0.03419	0.03412	0.03406	0.03399	0.03392	0.03385	0.0337{
16	0.03358	0.03351	0.03344	0.03338	0.03331	0.03324	0.03318	0.0331(
17	0.03292	0.03285	0.03279	0.03272	0.03266	0.03260	0.03253	0.0324{
18	0.03228	0.03222	0.03216	0.03210	0.03204	0.03198	0.03192	0.0318(
19	0.03168	0.03162	0.03156	0.03150	0.03144	0.03138	0.03132	0.0312(
20	0.03109	0.03103	0.03098	0.03092	0.03086	0.03081	0.03075	0.0307(
21	0.03053	0.03048	0.03042	0.03037	0.03031	0.03026	0.03020	0.0301{
22	0.02999	0.02994	0.02989	0.02983	0.02978	0.02973	0.02968	0.0296(
23	0.02947	0.02942	0.02937	0.02932	0.02927	0.02922	0.02917	0.0291(
24	0.02897	0.02893	0.02888	0.02883	0.02878	0.02873	0.02868	0.0286{
25	0.02850	0.02845	0.02840	0.02835	0.02831	0.02826	0.02822	0.0281(
26	0.02803	0.02799	0.02794	0.02790	0.02785	0.02781	0.02777	0.0277(
27	0.02759	0.02755	0.02750	0.02746	0.02742	0.02737	0.02733	0.0272{
28	0.02716	0.02712	0.02708	0.02704	0.02700	0.02695	0.02691	0.0268(
29	0.02675	0.02671	0.02667	0.02663	0.02659	0.02655	0.02651	0.0264(
30	0.02635	0.02632	0.02628	0.02624	0.02620	0.02616	0.02612	0.0260{
31	0.02597	0.02594	0.02590	0.02586	0.02582	0.02579	0.02575	0.0257(
32	0.02561	0.02557	0.02553	0.02550	0.02546	0.02543	0.02539	0.0253(
33	0.02525	0.02522	0.02518	0.02515	0.02511	0.02508	0.02504	0.0250(
34	0.02491	0.02488	0.02484	0.02481	0.02478	0.02474	0.02471	0.0246{
35	0.02458	0.02455	0.02452	0.02448	0.02445	0.02442	0.02439	0.0243(
36	0.02426	0.02423	0.02420	0.02417	0.02414	0.02411	0.02408	0.0240{
37	0.02396	0.02393	0.02390	0.02387	0.02384	0.02381	0.02378	0.0237{
38	0.02366	0.02363	0.02360	0.02358	0.02355	0.02352	0.02349	0.0234(
39	0.02338	0.02335	0.02332	0.02329	0.02327	0.02324	0.02321	0.0231{
40	0.02310	0.02308	0.02305	0.02302	0.02300	0.02297	0.02294	0.0229(

Based on Benson and Krause.[9,10] $\beta = 9.9902 \times 10^{-4} \exp(9.7265 - 5.26895 \times 10^{3}/T + 1.00417 \times 10^{6}/T^{2})$, where $T = 273.15 + °C$.

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TABLE 2810:II. VAPOR PRESSURE OF FRESH WATER

Temperature °C	Vapor Pressure at Given Temperature (to nearest 0.1°C) *mm Hg*									
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	4.58	4.61	4.64	4.68	4.71	4.75	4.78	4.82	4.85	4.89
1	4.92	4.96	4.99	5.03	5.07	5.10	5.14	5.18	5.21	5.25
2	5.29	5.33	5.36	5.40	5.44	5.48	5.52	5.56	5.60	5.64
3	5.68	5.72	5.76	5.80	5.84	5.88	5.92	5.97	6.01	6.05
4	6.09	6.14	6.18	6.22	6.27	6.31	6.36	6.40	6.44	6.49
5	6.54	6.58	6.63	6.67	6.72	6.77	6.81	6.86	6.91	6.96
6	7.01	7.05	7.10	7.15	7.20	7.25	7.30	7.35	7.40	7.45
7	7.51	7.56	7.61	7.66	7.71	7.77	7.82	7.87	7.93	7.98
8	8.04	8.09	8.15	8.20	8.26	8.31	8.37	8.43	8.48	8.54
9	8.60	8.66	8.72	8.87	8.84	8.89	8.95	9.02	9.08	9.14
10	9.20	9.26	9.32	9.39	9.45	9.51	9.58	9.64	9.70	9.77
11	9.83	9.90	9.97	10.03	10.10	10.17	10.23	10.30	10.37	10.44
12	10.51	10.58	10.65	10.72	10.76	10.86	10.93	11.00	11.07	11.15
13	11.22	11.29	11.37	11.44	11.52	11.59	11.67	11.74	11.82	11.90
14	11.98	12.05	12.13	12.21	12.29	12.37	12.45	12.53	12.61	12.69
15	12.78	12.86	12.94	13.05	13.11	13.19	13.28	13.36	13.45	13.54
16	13.62	13.71	13.80	13.89	13.97	14.06	14.15	14.24	14.33	14.43
17	14.52	14.61	14.70	14.80	14.89	14.98	15.08	15.17	15.27	15.37
18	15.46	15.56	15.66	15.76	15.86	15.96	16.06	16.16	16.26	16.36
19	16.46	16.57	16.67	16.77	16.88	16.98	17.09	17.20	17.30	17.41
20	17.52	17.63	17.74	17.85	17.96	18.07	18.18	18.29	18.41	18.52
21	18.64	18.75	18.87	18.98	19.10	19.22	19.33	19.45	19.57	19.69
22	19.81	19.93	20.05	20.48	20.60	20.42	20.55	20.67	20.80	20.93
23	21.05	21.18	21.31	21.44	21.57	21.70	21.83	21.96	22.09	22.23
24	22.36	22.50	22.63	22.77	22.90	23.04	23.18	23.32	23.46	23.60
25	23.74	23.88	24.03	24.17	24.31	24.46	24.60	24.75	24.90	25.04
26	25.19	25.34	25.49	25.64	25.80	25.95	26.10	26.26	26.41	26.57
27	26.72	26.88	27.04	27.20	27.36	27.52	27.68	27.84	28.00	28.17
28	28.33	28.50	28.66	28.83	29.00	29.17	29.34	29.51	29.68	29.85

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Temperature °C	Vapor Pressure at Given Temperature (to nearest 0.1°C) *mm Hg*									
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
29	30.03	30.80	30.37	30.55	30.73	30.91	31.08	31.26	31.44	31.62
30	31.81	31.99	32.17	32.36	32.54	32.73	32.92	33.11	33.30	33.49
31	33.68	33.87	34.06	34.26	34.45	34.65	34.85	35.05	35.24	35.44
32	35.65	35.85	36.05	36.25	36.46	36.67	36.87	37.08	37.29	37.50
33	37.71	37.92	38.14	38.35	38.57	38.78	39.00	39.22	39.44	39.66
34	39.88	40.10	40.33	40.55	40.78	41.01	41.23	41.46	41.69	41.92
35	42.16	42.39	42.63	42.86	43.10	43.34	43.58	43.82	44.06	44.30
36	44.55	44.79	45.04	45.28	45.53	45.78	46.03	46.29	46.54	46.79
37	47.05	47.31	47.56	47.82	48.08	48.35	48.61	48.87	49.14	49.41
38	49.67	49.94	50.21	50.49	50.76	51.03	51.31	51.59	51.87	52.14
39	52.43	52.71	52.99	53.28	53.56	53.85	54.14	54.43	54.72	55.01
40	55.31	55.60	55.90	56.20	56.50	56.80	57.10	57.41	57.71	58.02

Based on an equation presented by Green and Carritt.[11] This equation is cumbersome to use. The following equation[9] is adequate for most applications:

$P_{H_2O} = 760\{\exp(11.8571 - 3{,}840.70/T - 216{,}961/T^2)\}$, where $T = 273.15 + °C$.[5]

Part 3000 METALS

3010 INTRODUCTION

3010 A. General Discussion

1. Significance

The effects of metals in water and wastewater range from beneficial through troublesome to dangerously toxic. Some metals are essential to plant and animal growth while others may adversely affect water consumers, wastewater treatment systems, and receiving waters. The benefits versus toxicity of some metals depend on their concentrations in waters.

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2. Types of Methods

Preliminary treatment is often required to present the metals to the analytical methodology in an appropriate form. Alternative methods for pretreatment of samples are presented in Section 3030.

Metals may be determined satisfactorily by a variety of methods, with the choice often depending on the precision and sensitivity required. Part 3000 describes colorimetric methods as well as instrumental methods, i.e., atomic absorption spectrometry, including flame, electrothermal (furnace), hydride, and cold vapor techniques; flame photometry; inductively coupled plasma emission spectrometry; inductively coupled plasma mass spectrometry, and anodic stripping voltammetry. Flame atomic absorption methods generally are applicable at moderate (0.1- to 10-mg/L) concentrations in clean and complex-matrix samples. Electrothermal methods generally can increase sensitivity if matrix problems do not interfere. Inductively coupled plasma emission techniques are applicable over a broad linear range and are especially sensitive for refractory elements. Inductively coupled plasma mass spectrometry offers significantly increased sensitivity for some elements (as low as 0.01 μg/L) in a variety of environmental matrices. Flame photometry gives good results at higher concentrations for several Group I and II elements. Anodic stripping offers high sensitivity for several elements in relatively clean matrices. Colorimetric methods are applicable to specific metal determinations where interferences are known not to compromise method accuracy; these methods may provide speciation information for some metals. Table 3010:I lists the methods available in Part 3000 for each metal.

3. Definition of Terms

a. Dissolved metals: Those metals in an unacidified sample that pass through a 0.45-μm membrane filter.

b. Suspended metals: Those metals in an unacidified sample that are retained by a 0.45-μm membrane filter.

c. Total metals: The concentration of metals determined in an unfiltered sample after vigorous digestion, or the sum of the concentrations of metals in the dissolved and suspended fractions. Note that total metals are defined operationally by the digestion procedure.

d. Acid-extractable metals: The concentration of metals in solution after treatment of an unfiltered sample with hot dilute mineral acid. To determine either dissolved or suspended metals, filter sample immediately after collection. Do not preserve with acid until after filtration.

3010 B. Sampling and Sample Preservation

Before collecting a sample, decide what fraction is to be analyzed (dissolved, suspended, total, or acid-extractable). This decision will determine in part whether the sample is acidified with or without filtration and the type of digestion required.

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Serious errors may be introduced during sampling and storage because of contamination from sampling device, failure to remove residues of previous samples from sample container, and loss of metals by adsorption on and/or precipitation in sample container caused by failure to acidify the sample properly.

1. Sample Containers

The best sample containers are made of quartz or TFE. Because these containers are expensive, the preferred sample container is made of polypropylene or linear polyethylene with a polyethylene cap. Borosilicate glass containers also may be used, but avoid soft glass containers for samples containing metals in the microgram-per-liter range. Store samples for determination of silver in light-absorbing containers. Use only containers and filters that have been acid rinsed.

2. Preservation

Preserve samples immediately after sampling by acidifying with concentrated nitric acid (HNO_3) to pH <2. Filter samples for dissolved metals before preserving (see Section 3030). Usually 1.5 mL conc HNO_3/L sample (or 3 mL 1 + 1 HNO_3/L sample) is sufficient for short-term preservation. For samples with high buffer capacity, increase amount of acid (5 mL may be required for some alkaline or highly buffered samples). Use commercially available high-purity acid#(65)* or prepare high-purity acid by sub-boiling distillation of acid.

After acidifying sample, preferably store it in a refrigerator at approximately 4°C to prevent change in volume due to evaporation. Under these conditions, samples with metal concentrations of several milligrams per liter are stable for up to 6 months (except mercury, for which the limit is 5 weeks). For microgram-per-liter metal levels, analyze samples as soon as possible after sample collection.

Alternatively, preserve samples for mercury analysis by adding 2 mL/L 20% (w/v) $K_2Cr_2O_7$ solution (prepared in 1 + 1 HNO_3). Store in a refrigerator not contaminated with mercury. (CAUTION: Mercury concentrations may increase in samples stored in plastic bottles in mercury-contaminated laboratories.)

3. Bibliography

STRUEMPLER, A.W. 1973. Adsorption characteristics of silver, lead, calcium, zinc and nickel on borosilicate glass, polyethylene and polypropylene container surfaces. *Anal. Chem.* 45:2251.

FELDMAN, C. 1974. Preservation of dilute mercury solutions. *Anal. Chem.* 46:99.

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BATLEY, G.E. & D. GARDNER. 1977. Sampling and storage of natural waters for trace metal analysis. *Water Res.* 11:745.

SUBRAMANIAN, K.S., C.L. CHAKRABARTI, J.E. SUETIAS & I.S. MAINES. 1978. Preservation of some trace metals in samples of natural waters. *Anal. Chem.* 50:444.

BERMAN, S. & P. YEATS. 1985. Sampling of seawater for trace metals. *Crit. Rev. Anal. Chem.*

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16:1.

WENDLANDT, E. 1986. Sample containers and analytical accessories made of modern plastics for trace analysis. *Gewaess. Wass. Abwass.* 86:79.

3010 C. General Precautions

1. Sources of Contamination

Avoid introducing contaminating metals from containers, distilled water, or membrane filters. Some plastic caps or cap liners may introduce metal contamination; for example, zinc has been found in black bakelite-type screw caps as well as in many rubber and plastic products, and cadmium has been found in plastic pipet tips. Lead is a ubiquitous contaminant in urban air and dust.

2. Contaminant Removal

Thoroughly clean sample containers with a metal-free nonionic detergent solution, rinse with tap water, soak in acid, and then rinse with metal-free water. For quartz, TFE, or glass materials, use 1 + 1 HNO_3, 1 + 1 HCl, or aqua regia (3 parts conc HCl + 1 part conc HNO_3) for soaking. For plastic material, use 1 + 1 HNO_3 or 1 + 1 HCl. Reliable soaking conditions are 24 h at 70°C. Chromic acid or chromium-free substitutes#(66)* may be used to remove organic deposits from containers, but rinse containers thoroughly with water to remove traces of chromium. Do not use chromic acid for plastic containers or if chromium is to be determined. Always use metal-free water in analysis and reagent preparation (see Section 3111B.3*c*). In these methods, the word ‘‘water’’ means metal-free water.

3. Airborne Contaminants

For analysis of microgram-per-liter concentrations of metals, airborne contaminants in the form of volatile compounds, dust, soot, and aerosols present in laboratory air may become significant. To avoid contamination use ‘‘clean laboratory’’ facilities such as commercially available laminar-flow clean-air benches or custom-designed work stations and analyze blanks that reflect the complete procedure.

4. Bibliography

MITCHELL, J.W. 1973. Ultrapurity in trace analysis. *Anal. Chem.* 45:492A.

GARDNER, M., D. HUNT & G. TOPPING. 1986. Analytical quality control (AQC) for monitoring trace metals in the coastal and marine environment. *Water Sci. Technol.* 18:35.

3020 QUALITY ASSURANCE/QUALITY CONTROL

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3020 A. Introduction

General information and recommendations for quality assurance (QA) and quality control (QC) are provided in Section 1020 Quality Assurance, 1030 Data Quality, and 1040 Method Development and Evaluation. This section discusses QA/QC requirements that are common to the analytical methods presented in Part 3000. The requirements are recommended minimum QA/QC activities; refer to individual methods and regulatory program requirements for method-specific QA/QC requirements. Always consider the overall purpose of analyses. QA/QC measures and substantiation for operational-control determinations may differ significantly from those for determinations of trace metals at water quality criteria levels. Levels of trace metals in environmental samples may be orders of magnitude lower than in potential sources of contamination.

Use replicates of measurable concentration to establish precision and known-additions recovery to determine bias. Use blanks, calibrations, control charts, known additions, standards, and other ancillary measurement tools as appropriate. Provide adequate documentation and record keeping to satisfy client requirements and performance criteria established by the laboratory.

3020 B. Quality Control Practices

1. Initial Quality Control

a. Initial demonstration of capability: Verify analyst capability before analyzing any samples and repeat periodically to demonstrate proficiency with the analytical method. Verify that the method being used provides sufficient sensitivity for the purpose of the measurement. Test analyst capability by analyzing at least four reagent water portions containing known additions of the analyte of interest. Confirm proficiency by generating analytical results that demonstrate precision and bias within acceptable limits representative of the analytical method.

b. Method detection limit (MDL): Before samples are analyzed, determine the MDL for each analyte by the procedures of Section 1030, or other applicable procedure.[1] Determine MDL at least annually for each method and major matrix category. Verify MDL for a new analyst or whenever instrument hardware or method operating conditions are modified. Analyze samples for MDL determinations over a 3- to 5-d period to generate a realistic value. Preferably use pooled data from several analysts rather than data from a single analyst.

c. Dynamic range (DR): Before using a new method, determine the dynamic range, i.e., the concentration range over which a method has an increasing response (linear or second-order), for each analyte by analyzing several standard solutions that bracket the range of interest. Each standard measurement should be within 10% of the true value for acceptance into the DR determination. Take measurements at both the low and high end of the calibration range to

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determine method suitability. Analytical instrumentation with curve-fitting features may allow utilization of nonlinear instrument response.

2. Calibration

a. Initial calibration: Calibrate initially with a minimum of a blank and three calibration standards of the analyte(s) of interest. Select calibration standards that bracket the expected concentration of the sample and that are within the method's dynamic range. The number of calibration points depends on the width of the dynamic range and the shape of the calibration curve. One calibration standard should be below the reporting limit for the method. As a general rule, differences between calibration standard concentrations should not be greater than one order of magnitude (i.e., 1, 10, 100, 1000). Apply linear or polynomial curve-fitting statistics, as appropriate, for analysis of the concentration-instrument response relationship. The appropriate linear or nonlinear correlation coefficient for standard concentration to instrument response should be ≥ 0.995. Use initial calibration for quantitation of analyte concentration in samples. Use calibration verification, ¶ b below, only for checks on the initial calibration and not for sample quantitation. Repeat initial calibration daily and whenever calibration verification acceptance criteria are not satisfied.

b. Calibration verification: Calibration verification is the periodic confirmation that instrument response has not changed significantly from the initial calibration. Verify calibration by analyzing a midpoint calibration standard (check standard) and calibration blank at the beginning and end of a sample run, periodically during a run (normally after each set of ten samples). A check standard determination outside 90 to 110% of the expected concentration indicates a potential problem. If a check standard determination is outside 80 to 120% of the expected concentration, immediately cease sample analyses and initiate corrective action. Repeat initial calibration and sample determinations since the last acceptable calibration verification. Use calculated control limits (Section 1020B) to provide better indications of system performance and to provide tighter control limits.

c. Quality control sample: Analyze an externally generated quality control sample of known concentration at least quarterly and whenever new calibration stock solutions are prepared. Obtain this sample from a source external to the laboratory or prepare it from a source different from those used to prepare working standards. Use to validate the laboratory's working standards both qualitatively and quantitatively.

3. Batch Quality Control

a. Method blank (MB): A method blank (also known as reagent blank) is a portion of reagent water treated exactly as a sample, including exposure to all equipment, glassware, procedures, and reagents. The MB is used to assess whether analytes or interference are present within the analytical process or system. No analyte of interest should be present in the MB at a warning level based on the end user's requirements. Undertake immediate corrective action for MB measurements above the MDL. Include a minimum of one MB with each set of 20 or fewer samples.

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b. Laboratory-fortified blank (LFB): The laboratory-fortified blank (also known as blank spike) is a method blank that has been fortified with a known concentration of analyte. It is used to evaluate ongoing laboratory performance and analyte recovery in a clean matrix. Prepare fortified concentrations approximating the midpoint of the calibration curve or lower with stock solutions prepared from a source different from those used to develop working standards. Calculate percent recovery, plot control charts, and determine control limits (Section 1020B) for these measurements. Ensure that the LFB meets performance criteria for the method. Establish corrective actions to be taken in the event that LFB does not satisfy acceptance criteria. Include a minimum of one LFB with each set of 20 or fewer samples.

c. Duplicates: Use duplicate samples of measurable concentration to measure precision of the analytical process. Randomly select routine samples to be analyzed twice. Process duplicate sample independently through entire sample preparation and analytical process. Include a minimum of one duplicate for each matrix type with each set of 20 or fewer samples.

d. Laboratory-fortified matrix (LFM)/laboratory-fortified matrix duplicate: Use LFM (also known as matrix spike) and LFM duplicate to evaluate the bias and precision, respectively, of the method as influenced by a specific matrix. Prepare by adding a known concentration of analytes to a randomly selected routing sample. Prepare addition concentrations to approximately double the concentration present in the original sample. If necessary, dilute sample to bring the measurement within the established calibration curve. Limit addition volume to 5% or less of sample volume. Calculate percent recovery and relative percent difference, plot control charts, and determine control limits (Section 1020B). Ensure that performance criteria for the method are satisfied. Process fortified samples independently through entire sample preparation and analytical process. Include a minimum of one LFM/LFM duplicate with each set of 20 or fewer samples.

e. Method of known additions: To analyze a new or unfamiliar matrix, use the method of known additions (Section 1020B) to demonstrate freedom from interference before reporting concentration data for the analyte. Verify absence of interferences by analyzing such samples undiluted and in a 1:10 dilution; results should be within 10% of each other. Limit known-addition volume to 10% or less of the sample volume.

4. Reference

1. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1995. Definition and procedure for the determination of the method detection limit, revision 1.11. 40 CFR Part 136, Appendix B. *Federal Register* 5:23703.

3030 PRELIMINARY TREATMENT OF SAMPLES*#(67)

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3030 A. Introduction

Samples containing particulates or organic material generally require pretreatment before spectroscopic analysis. ‘‘Total metals’’ includes all metals, inorganically and organically bound, both dissolved and particulate. Colorless, transparent samples (primarily drinking water) having a turbidity of <1 NTU, no odor, and single phase may be analyzed directly by atomic absorption spectroscopy (flame or electrothermal vaporization) or inductively coupled plasma spectroscopy (atomic emission or mass spectrometry) for total metals without digestion. For further verification or if changes in existing matrices are encountered, compare digested and undigested samples to ensure comparable results. On collection, acidify such samples to pH <2 with conc nitric acid (1.5 mL HNO_3/L is usually adequate for drinking water) and analyze directly. Digest all other samples before determining total metals. To analyze for dissolved metals, filter sample, acidify filtrate, and store until analyses can be performed. To determine suspended metals, filter sample, digest filter and the material on it, and analyze. To determine acid-extractable metals, extract metals as indicated in Section 3030E through K and analyze extract.

This section describes general pretreatment for samples in which metals are to be determined according to Section 3110 through 3500-Zn with several exceptions. The special digestion techniques for mercury are given in Section 3112B.4*b* and *c*, and those for arsenic and selenium in Section 3114 and Section 3500-Se.

Take care not to introduce metals into samples during preliminary treatment. During pretreatment avoid contact with rubber, metal-based paints, cigarette smoke, paper tissues, and all metal products including those made of stainless steel, galvanized metal, and brass. Conventional fume hoods can contribute significantly to sample contamination, particularly during acid digestion in open containers. Keep vessels covered with watch glasses and turn spouts away from incoming air to reduce airborne contamination. Plastic pipet tips often are contaminated with copper, iron, zinc, and cadmium; before use soak in 2*N* HCl or HNO_3 for several days and rinse with deionized water. Avoid using colored plastics, which can contain metals. Use certified metal-free plastic containers and pipet tips when possible. Avoid using glass if analyzing for aluminum or silica.

Use metal-free water (see Section 3111B.3*c*) for all operations. Check reagent-grade acids used for preservation, extraction, and digestion for purity. If excessive metal concentrations are found, purify the acids by distillation or use ultra-pure acids. Inductively coupled plasma mass spectrometry (ICP-MS) may require use of ultra-pure acids and reagents to avoid measurable contamination. Process blanks through all digestion and filtration steps and evaluate blank results relative to corresponding sample results. Either apply corrections to sample results or take other corrective actions as necessary or appropriate.

3030 B. Filtration for Dissolved and Suspended Metals

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1. Filtration Procedures

If dissolved or suspended metals (see Section 3010A) are to be determined, filter sample at time of collection using a preconditioned plastic filtering device with either vacuum or pressure, containing a filter support of plastic or fluorocarbon, through a prewashed ungridded 0.4- to 0.45-μm-pore-diam membrane filter (polycarbonate or cellulose esters). Before use filter a blank consisting of metal-free (deionized) water to insure freedom from contamination. Precondition filter and filter device by rinsing with 50 mL deionized water. If the filter blank contains significant metals concentrations, soak membrane filters in approximately 0.5*N* HCl or 1*N* HNO_3 (recommended for electrothermal and ICP-MS analyses) and rinse with deionized water before use.

Before filtering, centrifuge highly turbid samples in acid-washed fluorocarbon or high-density plastic tubes to reduce loading on filters. Stirred, pressure filter units foul less readily than vacuum filters; filter at a pressure of 70 to 130 kPa. After filtration acidify filtrate to pH 2 with conc HNO_3 and store until analyses can be performed. If a precipitate forms on acidification, digest acidified filtrate before analysis as directed (see Section 3030E). Retain filter and digest it for direct determination of suspended metals.

If it is not possible to field-filter the sample without contaminating it, obtain sample in an ‘‘unpreserved’’ bottle as above and promptly cool to 4°C. Do not acid-preserve the sample. Then, without delay, filter sample under cleaner conditions in the laboratory.

Test pH of a portion of aqueous sample upon receipt in the laboratory to ensure that the sample has been properly filtered and acid-preserved.[1]

NOTE: Different filters display different sorption and filtration characteristics[2]; for trace analysis, test filter and filtration sytem to verify complete recovery of metals.

If suspended metals (see Section 3010A) are to be determined, filter sample as above for dissolved metals, but do not centrifuge before filtration. Retain filter and digest it for direct determination of suspended metals. Record sample volume filtered and include a filter in determination of the blank.

CAUTION: *Do not use perchloric acid to digest membrane filters*. (See Section 3030H for more information on handling $HClO_4$).

2. References

1. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1994. Sample Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements, Method 200.2. Environmental Monitoring Systems Lab., Cincinnati, Ohio.
2. HOROWITZ, A.J., K.R. LUM, J.R. GARBARINO, G.E.M. HALL, C. LEMIEUX & C.R. DEMAS. 1996. Problems with using filtration to define dissolved trace element concentrations in natural water samples. *Environ. Sci. Technol.* 30, 954.

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3030 C. Treatment for Acid-Extractable Metals

Extractable metals (see Section 3010A) are lightly adsorbed on particulate material. Because some sample digestion may be unavoidable use rigidly controlled conditions to obtain meaningful and reproducible results. Maintain constant sample volume, acid volume, and contact time. Express results as extractable metals and specify extraction conditions.

At collection, acidify entire sample with 5 mL conc HNO_3/L sample. To prepare sample, mix well, transfer 100 mL to a beaker or flask, and add 5 mL 1 + 1 high-purity HCl. Heat 15 min on a steam bath. Filter through a membrane filter (preconditioned as in Section 3030B) and carefully transfer filtrate to a tared volumetric flask. Adjust volume to 100 mL with metal-free water, mix, and analyze. If volume is greater than 100 mL, determine volume to nearest 0.1 mL by weight, analyze, and correct final concentration measurement by multiplying by the dilution factor (final volume ÷ 100).

3030 D. Digestion for Metals

To reduce interference by organic matter and to convert metals associated with particulates to a form (usually the free metal) that can be determined by atomic absorption spectrometry or inductively-coupled plasma spectroscopy, use one of the digestion techniques presented below. Use the least rigorous digestion method required to provide acceptable and consistent recovery compatible with the analytical method and the metal being analyzed.[1-3]

1. Selection of Acid

Nitric acid will digest most samples adequately (Section 3030E). Nitrate is an acceptable matrix for both flame and electrothermal atomic absorption and the preferred matrix for ICP-MS.[4] Some samples may require addition of perchloric, hydrochloric, hydrofluoric, or sulfuric acid for complete digestion. These acids may interfere in the analysis of some metals and all provide a poorer matrix for both electrothermal and ICP-MS analysis. Confirm metal recovery for each digestion and analytical procedure used. Use Table 3030:I as a guide in determining which acids (in addition to HNO_3) to use for complete digestion. As a general rule, HNO_3 alone is adequate for clean samples or easily oxidized materials; HNO_3-H_2SO_4 or HNO_3-HCl digestion is adequate for readily oxidizable organic matter; HNO_3-$HClO_4$ or HNO_3-$HClO_4$-HF digestion is necessary for difficult-to-oxidize organic matter or minerals containing silicates. Although dry ashing is not generally recommended because of the loss of many volatile elements, it may be helpful if large amounts of organic matter are present.

2. Digestion Procedures

Dilute samples with Ag concentrations greater than 1 mg/L to contain less than 1 mg Ag/L for flame atomic absorption methods and 25 µg/L or less for electrothermal analysis.[2,5,6] To

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address problems with silver halide solubility in HNO_3, digest using method 3030F.3*b*.

Report digestion technique used.

Acid digestion techniques (Section 3030E through I) generally yield comparable precision and bias for most sample types that are totally digested by the technique. Because acids used in digestion will add metals to the samples and blanks, minimize the volume of acids used.

Because the acid digestion techniques (Section 3030E and F) normally are not total digestions, the microwave digestion procedure (Section 3030K) may be used as an alternative. The microwave method is a closed-vessel procedure and thus is expected to provide improved precision when compared with hot-plate techniques. Microwave digestion is recommended for samples being analyzed by ICP-MS. The microwave digestion method is recommended for the analysis of Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Tl, V, and Zn. Microwave digestion may be acceptable for additional analytes provided its performance for those elements is validated.

Suggested sample volumes are indicated below for flame atomic absorption spectrometry. Lesser volumes, to a minimum of 5 mL, are appropriate for graphite furnace, ICP, and ICP-MS. Do not subsample volumes less than 5 mL, especially when particulates are present. Instead dilute samples with elevated analyte concentrations after digestion. If the recommended volume exceeds digestion vessel capacity, add sample as evaporation proceeds. For samples containing particulates, wide-bore pipets maybe useful for volume measurement and transfer.

When samples are concentrated during digestion (e.g., >100mL sample used) determine metal recovery for each matrix digested, to verify method validity. Using larger samples will require additional acid, which also would increase the concentration of impurities.

Estimated Metal Concentration ***mg/L***	**Sample Volume*** ***mL***
<0.1	1000
0.1–10	100
10–100+	10

*For flame atomic absorption spectrometry.

Report results as follows:

$$\text{Metal concentration, mg/L} = A \times \frac{B}{C}$$

where:

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A = concentration of metal in digested solution, mg/L,
B = final volume of digested solution, mL, and
C = sample size, mL.

Prepare solid samples or liquid sludges with high solids contents on a weight basis. Mix sample and transfer a suitable amount (typically 1 g of a sludge with 15% total solids) directly into a preweighed digestion vessel. Reweigh and calculate weight of sample. Proceed with one of the digestion techniques presented below. However, as these digestion methods are predominantly for dissolved and extractable metals in aqueous samples, other approaches may be more appropriate for solid samples. For complete mineralization of solid samples, consult methods available elsewhere.[1,4,6,7] Report results on wet- or dry-weight basis as follows:

$$\text{Metal concentration, mg/kg (wet-weight basis)} = \frac{A \times B}{\text{g sample}}$$

$$\text{Metal concentration, mg/kg (dry-weight basis)} = \frac{A \times B}{\text{g sample}} \times \frac{100}{D}$$

where:
A = concentration of metal in digested solution, mg/L,
B = final volume of digested solution, mL, and
D = total solids, % (see Section 2540G).

Always prepare acid blanks for each type of digestion performed. Although it is always best to eliminate all relevant sources of contamination, a reagent blank prepared with the same acids and subjected to the same digestion procedure as the sample can correct for impurities present in acids and reagent water. However, blank correction is not recommended for any other sources of contamination such as impurities adsorbed on glassware.

3. References

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3. HOENIG, M. & A.M. DE KERSABIEC. 1996. Sample preparation steps for analysis by atomic spectroscopy methods: Present status. *Spectrochim. Acta.* B51:1297.
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6. KINGSTON, H.M. & S. HASWELL, eds. 1997. Microwave Enhanced Chemistry: Fundamentals, Sample Preparation and Applications. American Chemical Soc., Washington, D.C.
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3030 E. Nitric Acid Digestion

Because of the wide variation in concentration levels detected by various instrumental techniques and the need to deal adequately with sources of contamination at trace levels, this method presents one approach for high-level analytes (>0.1 mg/L) and another for trace levels (≤0.1 mg/L).

1. Digestion for Flame Atomic Absorption and High-Level Concentrations

a. Apparatus:

1) *Hot plate.*

2) *Conical (erlenmeyer) flasks,* 125-mL, or *Griffin beakers,* 150-mL, acid-washed and rinsed with water.

3) *Volumetric flasks,* 100-mL.

4) *Watch glasses,* ribbed and unribbed.

b. Reagent:

Nitric acid, HNO_3, conc, analytical or trace-metals grade.

c. Procedure: Transfer a measured volume (100 mL recommended) of well-mixed, acid-preserved sample appropriate for the expected metals concentrations to a flask or beaker (see Section 3030D for sample volume). In a hood, add 5 mL conc HNO_3. If a beaker is used, cover with a ribbed watch glass to minimize contamination. Boiling chips, glass beads, or Hengar granules may be added to aid boiling and minimize spatter when high concentration levels (>10 mg/L) are being determined. Bring to a slow boil and evaporate on a hot plate to the lowest volume possible (about 10 to 20 mL) before precipitation occurs. Continue heating and adding conc HNO_3 as necessary until digestion is complete as shown by a light-colored, clear solution. Do not let sample dry during digestion.

Wash down flask or beaker walls and watch glass cover (if used) with metal-free water and

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then filter if necessary (see Section 3030B). Transfer filtrate to a 100-mL volumetric flask with two 5-mL portions of water, adding these rinsings to the volumetric flask. Cool, dilute to mark, and mix thoroughly. Take portions of this solution for required metal determinations.

2. Digestion for Trace-Level (≤0.1 mg/L) Concentrations for ICP and ICP-MS[1]

a. Apparatus:

1) *Block heater*, dry, with temperature control.

2) *Polypropylene tubes**#(68), graduated, round-bottom tubes with caps, 17 × 100 mm, acid-washed and rinsed with metal-free water. Preferably use tubes that simultaneously match the analysis instrument autosampler and the block digester. A fit with the centrifuge is secondary but also desirable.

3) *Pipetters*, assorted sizes or adjustable.

4) *Pipet tips*.

5) *Centrifuge*.

b. Reagent:

Nitric acid, HNO_3, conc, double distilled.†#(69)

c. Procedure: Soak new polypropylene tubes and caps overnight or for several days in 2*N* HNO_3. Triple rinse with metal-free water, and preferably dry in poly rackets or baskets in a low-temperature oven overnight. Store cleaned tubes in plastic bags before use. Pipet tips also may need to be cleaned; evaluate before use.

Pipet 10 mL well-mixed, acid-preserved sample into a precleaned, labeled tube with a macropipet. With a minimum volume change (<0.5 mL), add appropriate amount of analyte for matrix fortified samples. With a pipet, add 0.5 mL conc HNO_3 (or 1.0 mL 1 + 1 HNO_3) to all samples, blanks, standards, and quality control samples.

Place tubes in block heater in a hood and adjust temperature to 105°C. Drape caps over each tube to allow escape of acid vapors while preventing contamination. NOTE: Do not screw on caps at this time. Digest samples for a minimum of 2 h. Do not let samples boil. Add more conc nitric acid as necessary until digestion is complete by observation of a clear solution.

Remove tubes from heat and cool. Dilute back to original 10 mL volume with metal-free water. Adjust over-volume samples to next convenient gradation for calculations and note volume. (Apply concentration correction from Section 3030D.) If tubes contain particulates, centrifuge and decant clear portion into another precleaned tube. Tighten screw caps and store at 4°C until ready for analysis.

3. Reference

1. JARVIS, K.E., A.L. GRAY & R.S. HOUK, eds. 1992. Sample preparation for ICP-MS. Chapter 7 *in* Handbook of Inductively Coupled Plasma Mass Spectrometry. Blackie & Son, Ltd., Glasgow & London, U.K.

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3030 F. Nitric Acid-Hydrochloric Acid Digestion

1. Apparatus

See Section 3030E.1*a*. The following also may be needed:

Steam bath.

2. Reagents

a. Nitric acid, HNO_3, conc, analytical grade or better (see Section 3030E).

b. Hydrochloric acid, HCl, 1 + 1.

c. Nitric acid, HNO_3, 1 + 1.

3. Procedure

a. Total HNO_3/HCl: Transfer a measured volume of well-mixed, acid-preserved sample appropriate for the expected metals concentrations to a flask or beaker (see Section 3030D for sample volume). In a hood add 3 mL conc HNO_3 and cover with a ribbed watch glass. Place flask or beaker on a hot plate and cautiously evaporate to less than 5 mL, making certain that sample does not boil and that no area of the bottom of the container is allowed to go dry. Cool. Rinse down walls of beaker and watch glass with a minimum of metal-free water and add 5 mL conc HNO_3. Cover container with a nonribbed watch glass and return to hot plate. Increase temperature of hot plate so that a gentle reflux action occurs. Continue heating, adding additional acid as necessary, until digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Cool. Add 10 mL 1 + 1 HCl and 15 mL water per 100 mL anticipated final volume. Heat for an additional 15 min to dissolve any precipitate or residue. Cool, wash down beaker walls and watch glass with water, filter to remove insoluble material that could clog the nebulizer (see Section 3030B), and transfer filtrate to a 100-mL volumetric flask with rinsings. Alternatively centrifuge or let settle overnight. Adjust to volume and mix thoroughly.

b. Recoverable HNO_3/HCl: For this less rigorous digestion procedure, transfer a measured volume of well-mixed, acid-preserved sample to a flask or beaker. Add 2 mL 1 + 1 HNO_3 and 10 mL 1 + 1 HCl and cover with a ribbed watch glass. Heat on a steam bath or hot plate until volume has been reduced to near 25 mL, making certain sample does not boil. Cool and filter to remove insoluble material or alternatively centrifuge or let settle overnight. Quantitatively transfer sample to volumetric flask, adjust volume to 100 mL, and mix.

For trace-level digestion, use precautionary measures similar to those detailed in Section 3030E.

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3030 G. Nitric Acid-Sulfuric Acid Digestion

1. Apparatus

See Section 3030E.1*a*.

2. Reagents

a. Nitric acid, HNO_3, conc. (See Section 3030E for acid grades.)

b. Sulfuric acid, H_2SO_4, conc.

3. Procedure

Transfer a measured volume of well-mixed, acid-preserved sample appropriate for the expected metals concentrations to a flask or beaker (see Section 3030D for sample volume). Add 5 mL conc HNO_3 and cover with a ribbed watch glass. Bring to slow boil on hot plate and evaporate to 15 to 20 mL. Add 5 mL conc HNO_3 and 10 mL conc H_2SO_4, cooling flask or beaker between additions. Evaporate on a hot plate until dense white fumes of SO_3 just appear. If solution does not clear, add 10 mL conc HNO_3 and repeat evaporation to fumes of SO_3. Heat to remove all HNO_3 before continuing treatment. All HNO_3 will be removed when the solution is clear and no brownish fumes are evident. Do not let sample dry during digestion.

Cool and dilute to about 50 mL with water. Heat to almost boiling to dissolve slowly soluble salts. Filter if necessary, then complete procedure as directed in Section 3030E.1*c* beginning with, ‘‘Transfer filtrate . . .’’

3030 H. Nitric Acid-Perchloric Acid Digestion

1. Apparatus

See Section 3030E.1*a*. The following also are needed:

a. Safety shield.

b. Safety goggles.

c. Watch glasses.

2. Reagents

a. Nitric acid, HNO_3, conc.

b. Perchloric acid, $HClO_4$.

c. Ammonium acetate solution: Dissolve 500 g $NH_4C_2H_3O_2$ in 600 mL water.

3. Procedure

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CAUTION: *Heated mixtures of $HClO_4$* and organic matter may explode violently. Avoid this hazard by taking the following precautions: (a) do not add $HClO_4$ to a hot solution containing organic matter; (b) always pretreat samples containing organic matter with HNO_3 before adding $HClO_4$; (c) avoid repeated fuming with $HClO_4$ in ordinary hoods (For routine operations, use a water pump attached to a glass fume eradicator. Stainless steel fume hoods with adequate water washdown facilities are available commercially and are acceptable for use with $HClO_4$); and (d) never let samples being digested with $HClO_4$ evaporate to dryness.

Transfer a measured volume of well-mixed, acid-preserved sample appropriate for the expected metals concentrations to a flask or beaker (see Section 3030D for sample volume). In a hood add 5 mL conc HNO_3 and cover with a ribbed watch glass. Evaporate sample to 15 to 20 mL on a hot plate. Add 10 mL each of conc HNO_3 and $HClO_4$, cooling flask or beaker between additions. Evaporate gently on a hot plate until dense white fumes of $HClO_4$ just appear. If solution is not clear, keep solution just boiling until it clears. If necessary, add 10 mL conc HNO_3 to complete digestion. Cool, dilute to about 50 mL with water, and boil to expel any chlorine or oxides of nitrogen. Filter, then complete procedure as directed in 3030E.1*c* beginning with, ‘‘Transfer filtrate . . .’’

If lead is to be determined in the presence of high amounts of sulfate (e.g., determination of Pb in power plant fly ash samples), dissolve $PbSO_4$ precipitate as follows: Add 50 mL ammonium acetate solution to flask or beaker in which digestion was carried out and heat to incipient boiling. Rotate container occasionally to wet all interior surfaces and dissolve any deposited residue. Reconnect filter and slowly draw solution through it. Transfer filtrate to a 100-mL volumetric flask, cool, dilute to mark, mix thoroughly, and set aside for determination of lead.

3030 I. Nitric Acid-Perchloric Acid-Hydrofluoric Acid Digestion

1. Apparatus

a. Hot plate.

b. TFE beakers, 250-mL, acid-washed and rinsed with water.

c. Volumetric flasks, 100-mL, polypropylene or other suitable plastic.

2. Reagents

a. Nitric acid, HNO_3, conc and 1 + 1.

b. Perchloric acid, $HClO_4$.

c. Hydrofluoric acid, HF, 48 to 51%.

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3. Procedure

CAUTION: *See precautions for using $HClO_4$* in 3030H; handle HF with extreme care and provide adequate ventilation, especially for the heated solution. Avoid all contact with exposed skin. Provide medical attention for HF burns.

Transfer a measured volume of well-mixed, acid-preserved sample appropriate for the expected metals concentrations into a 250-mL TFE beaker (see Section 3030D for sample volume). Evaporate on a hot plate to 15 to 20 mL. Add 12 mL conc HNO_3 and evaporate to near dryness. Repeat HNO_3 addition and evaporation. Let solution cool, add 20 mL $HClO_4$ and 1 mL HF, and boil until solution is clear and white fumes of $HClO_4$ have appeared. Cool, add about 50 mL water, filter, and proceed as directed in Section 3030E.1*c* beginning with, ‘‘Transfer filtrate . . .’’

3030 J. Dry Ashing

The procedure appears in the Eighteenth Edition of *Standard Methods*. It has been deleted from subsequent editions.

3030 K. Microwave-Assisted Digestion

1. Apparatus

a. Microwave unit with programmable power (minimum 545 W) to within ± 10 W of required power, having a corrosion-resistant, well-ventilated cavity and having all electronics protected against corrosion for safe operation. Use a unit having a rotating turntable with a minimum speed of 3 rpm to insure homogeneous distribution of microwave radiation. Use only laboratory-grade microwave equipment and closed digestion containers with pressure relief that are specifically designed for hot acid.[1]

b. Vessels: Construction requires an inner liner of perfluoroalkoxy (PFA) Teflon™,*#(70) other TFE, or composite fluorinated polymers,†#(71) capable of withstanding pressures of at least 760 ± 70 kPa (110 ± 10 psi), and capable of controlled pressure relief at the manufacturer’s maximum pressure rating.

Acid wash all digestion vessels and rinse with water (¶ 2*a*). For new vessels or when changing between high- and low-concentration samples, clean by leaching with hot‡#(72) hydrochloric acid (1:1) for a minimum of 2 h and then with hot nitric acid (1:1) for a minimum of 2 h; rinse with water and dry in a clean environment. Use this procedure whenever the previous use of digestion vessels is unknown or cross-contamination from vessels is suspected.

c. Temperature feedback control system, using shielded thermocouple, fiber-optic probe, or infrared detector.

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d. Bottles, polyethylene, 125-mL, with caps.

e. Thermometer, accurate to ± 0.1°C.

f. Balance, large-capacity (1500 g), accurate to 0.1 g.

g. Filtration or centrifuge equipment (optional).

h. Plastic container with cover, 1-L, preferably made of PFA Teflon™§.#(73)

2. Reagents

a. Metal-free water: See Section 3111B.3*c*.

b. Nitric acid, HNO_3, conc, sub-boiling distilled. Non-sub-boiling acids can be used if they are shown not to contribute blanks.

3. Calibration of Microwave Unit

NOTE: For microwave units equipped with temperature feedback electronic controls, calibration of the microwave unit is not required provided performance specifications can be duplicated.

For cavity-type microwave equipment, evaluate absolute power (watts) by measuring the temperature rise in 1 kg water exposed to microwave radiation for a fixed time. With this measurement, the relationship between available power (W) and the partial power setting (%) of the unit can be estimated, and any absolute power in watts may be transferred from one unit to another. The calibration format required depends on type of electronic system used by manufacturer to provide partial microwave power. Few units have an accurate and precise linear relationship between percent power settings and absorbed power. Where linear circuits have been used, determine calibration curve by a three-point calibration method; otherwise, use the multiple-point calibration method.

a. Three-point calibration method: Measure power at 100% and 50% power using the procedure described in ¶ 3*c* and calculate power setting corresponding to required power in watts as specified in the procedure from the two-point line. Measure absorbed power at the calculated partial power setting. If the measured absorbed power does not correspond to the calculated power within ± 10 W, use the multiple-point calibration method, ¶ 3*b*. Use this point periodically to verify integrity of calibration.

b. Multiple-point calibration method: For each microwave unit, measure the following power settings: 100, 99, 98, 97, 95, 90, 80, 70, 60, 50, and 40% using the procedure described in ¶ 3*c*. These data are clustered about the customary working power ranges. Nonlinearity commonly is encountered at the upper end of the calibration curve. If the unit's electronics are known to have nonlinear deviations in any region of proportional power control, make a set of measurements that bracket the power to be used. The final calibration point should be at the partial power setting that will be used in the test. Check this setting periodically to evaluate the integrity of the calibration. If a significant change (± 10 W) is detected, re-evaluate entire calibration.

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c. Equilibrate a large volume of water to room temperature (23 ± 2°C). Weigh 1 kg water (1000 g ± 1 g) or measure (1000 mL ± 1 mL) into a plastic, not glass, container, and measure the temperature to ± 0.1°C. Condition microwave unit by heating a glass beaker with 500 to 1000 mL tap water at full power for 5 min with the exhaust fan on. Loosely cover plastic container to reduce heat loss and place in normal sample path (at outer edge of rotating turntable); circulate continuously through the microwave field for 120 s at desired power setting with exhaust fan on as it will be during normal operation. Remove plastic container and stir water vigorously. Use a magnetic stirring bar inserted immediately after microwave irradiation; record maximum temperature within the first 30 s to ± 0.1°C. Use a new sample for each additional measurement. If the water is reused, return both water and beaker to 23 ± 2°C. Make three measurements at each power setting. When any part of the high-voltage circuit, power source, or control components in the unit have been serviced or replaced, recheck calibration power. If power output has changed by more than ± 10 W, re-evaluate entire calibration.

Compute absorbed power by the following relationship:

$$P = \frac{(K)\ (Cp)\ (m)\ (\Delta T)}{t}$$

where:

P = apparent power absorbed by sample, W,
K = conversion factor for thermochemical calories sec^{-1} to watts (4.184),
Cp = heat capacity, thermal capacity, or specific heat (cal g^{-1} $°C^{-1}$) of water,
m = mass of water sample, g,
ΔT = final temperature minus initial temperature, °C, and
t = time, s.

For the experimental conditions of 120 s and 1 kg water (Cp at 25°C = 0.9997), the calibration equation simplifies to:

$$P = (\Delta T)\ (34.85)$$

Stable line voltage within the manufacturer's specification is necessary for accurate and reproducible calibration and operation. During measurement and operation it must not vary by more than ± 2 V. A constant power supply may be necessary if line voltage is unstable.

4. Procedure

CAUTION: *This method is designed for microwave digestion of waters only. It is not intended for the digestion of solids, for which high concentrations of organic compounds may result in high pressures and possibly unsafe conditions.*

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CAUTION: *As a safety measure, never mix different manufacturers' vessels in the same procedure. Vessels constructed differently will retain heat at different rates; control of heating conditions assumes that all vessels have the same heat-transfer characteristics. Inspect casements for cracks and chemical corrosion. Failure to maintain the vessels' integrity may result in catastrophic failure.*

Both prescription controls and performance controls are provided for this procedure. Performance controls are the most general and most accurate. When equipment capability permits, use the performance criterion.

a. Performance criterion: The following procedure is based on heating acidified samples in two stages where the first stage is to reach 160 ± 4° in 10 min and the second stage is to permit a slow rise to 165 to 170°C during the second 10 min. This performance criterion is based on temperature feedback control system capability that is implemented in various ways by different manufacturers. Because the temperature of the acid controls the reaction, this is the essential condition that will reproduce results in this preparation method. Verification of temperature conditions inside the vessel at these specific times is sufficient to verify the critical procedural requirements.

b. Prescription criterion: For all PFA vessels without liners, a verified program that meets the performance-based temperature-time profile is 545 W for 10 min followed by 344 W for 10 min using five single-wall PFA Teflon^{TM}‖#(74) digestion vessels.[2] Any verified program for a given microwave unit depends on unit power and operational power settings, heating times, number, type, and placement of digestion vessels within the unit, and sample and acid volumes. The change in power, time, and temperature profile is not directly proportional to the change in the number of sample vessels. Any deviations from the verified program conditions will require verification of the time-temperature profile to conform to the given two-stage profile. This may be done by laboratory personnel if suitable test equipment is available, or by the manufacturer of the microwave equipment.

c. General conditions: Weigh entire digestion vessel assembly to 0.1 g before use and record (*A*). Accurately transfer 45 mL of well-shaken sample into the digestion vessel. Pipet 5 mL conc HNO_3 into each vessel. Attach all safety equipment required for appropriate and safe vessel operation following manufacturer's specifications. Tighten cap to manufacturer's specifications. Weigh each capped vessel to the nearest 0.1 g (*B*).

Place appropriate number of vessels evenly distributed in the carousel. Treat sample blanks, known additions, and duplicates in the same manner as samples. For prescription control only, when fewer samples than the appropriate number are digested, fill remaining vessels with 45 mL water and 5 mL conc HNO_3 to obtain full complement of vessels for the particular program being used.

Place carousel in unit and seat it carefully on turntable. Program microwave unit to heat samples to 160 ± 4°C in 10 min and then, for the second stage, to permit a slow rise to 165 to 170°C for 10 min. Start microwave generator, making sure that turntable is turning and that

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exhaust fan is on.

At completion of the microwave program, let vessels cool for at least 5 min in the unit before removal. Cool samples further outside the unit by removing the carousel and letting them cool on a bench or in a water bath. When cooled to room temperature, weigh each vessel (to 0.1 g) and record weight (*C*).

If the net weight of sample plus acid decreased by more than 10%, discard sample.

Complete sample preparation by carefully uncapping and venting each vessel in a fume hood. Follow individual manufacturer's specifications for relieving pressure in individual vessel types. Transfer to acid-cleaned noncontaminating plastic bottles. If the digested sample contains particulates, filter, centrifuge, or settle overnight and decant.

5. Calculations

a. Dilution correction: Multiply results by 50/45 or 1.11 to account for the dilution caused by the addition of 5 mL acid to 45 mL sample.

b. Discarding of sample: To determine if the net weight of sample plus acid decreased by more than 10% during the digestion process, use the following calculation

$$\frac{[(B - A) - (C - A)]}{(B - A)} \times 100 > 10\% \text{ (1\% for multilayer vessels)}$$

6. Quality Control

NOTE: When nitric acid digestion is used, recoveries of silver and antimony in some matrices may be unacceptably low. Verify recoveries using appropriate known additions.

Preferably include a quality-control sample in each loaded carousel. Prepare samples in batches including preparation blanks, sample duplicates, and pre-digestion known additions. Determine size of batch and frequency of quality-control samples by method of analysis and laboratory practice. The power of the microwave unit and batch size may prevent including one or more of the quality-control samples in each carousel. Do not group quality-control samples together but distribute them throughout the various carousels to give the best monitoring of digestion.

7. References

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3110 METALS BY ATOMIC ABSORPTION SPECTROMETRY

Because requirements for determining metals by atomic absorption spectrometry vary with metal and/or concentration to be determined, the method is presented as follows:

Section 3111, Metals by Flame Atomic Absorption Spectrometry, encompasses:

- Determination of antimony, bismuth, cadmium, calcium, cesium, chromium, cobalt, copper, gold, iridium, iron, lead, lithium, magnesium, manganese, nickel, palladium, platinum, potassium, rhodium, ruthenium, silver, sodium, strontium, thallium, tin, and zinc by direct aspiration into an air-acetylene flame (Section 3111B),
- Determination of low concentrations of cadmium, chromium, cobalt, copper, iron, lead, manganese, nickel, silver, and zinc by chelation with ammonium pyrrolidine dithiocarbamate (APDC), extraction into methyl isobutyl ketone (MIBK), and aspiration into an air-acetylene flame (Section 3111C),
- Determination of aluminum, barium, beryllium, calcium, molybdenum, osmium, rhenium, silicon, thorium, titanium, and vanadium by direct aspiration into a nitrous oxide-acetylene flame (Section 3111D), and
- Determination of low concentrations of aluminum and beryllium by chelation with 8-hydroxyquinoline, extraction into MIBK, and aspiration into a nitrous oxide-acetylene flame (Section 3111E).

Section 3112 covers determination of mercury by the cold vapor technique.

Section 3113 concerns determination of micro quantities of aluminum, antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, iron, lead, manganese, molybdenum, nickel, selenium, silver, and tin by electrothermal atomic absorption spectrometry.

Section 3114 covers determination of arsenic and selenium by conversion to their hydrides and aspiration into an argon-hydrogen or nitrogen-hydrogen flame.

3111 METALS BY FLAME ATOMIC ABSORPTION SPECTROMETRY*#(75)

3111 A. Introduction

1. Principle

In flame atomic absorption spectrometry, a sample is aspirated into a flame and atomized. A light beam is directed through the flame, into a monochromator, and onto a detector that

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measures the amount of light absorbed by the atomized element in the flame. For some metals, atomic absorption exhibits superior sensitivity over flame emission. Because each metal has its own characteristic absorption wavelength, a source lamp composed of that element is used; this makes the method relatively free from spectral or radiation interferences. The amount of energy at the characteristic wavelength absorbed in the flame is proportional to the concentration of the element in the sample over a limited concentration range. Most atomic absorption instruments also are equipped for operation in an emission mode, which may provide better linearity for some elements.

2. Selection of Method

See Section 3110.

3. Interferences

a. Chemical interference: Many metals can be determined by direct aspiration of sample into an air-acetylene flame. The most troublesome type of interference is termed ‘‘chemical’’ and results from the lack of absorption by atoms bound in molecular combination in the flame. This can occur when the flame is not hot enough to dissociate the molecules or when the dissociated atom is oxidized immediately to a compound that will not dissociate further at the flame temperature. Such interferences may be reduced or eliminated by adding specific elements or compounds to the sample solution. For example, the interference of phosphate in the magnesium determination can be overcome by adding lanthanum. Similarly, introduction of calcium eliminates silica interference in the determination of manganese. However, silicon and metals such as aluminum, barium, beryllium, and vanadium require the higher-temperature, nitrous oxide-acetylene flame to dissociate their molecules. The nitrous oxide-acetylene flame also can be useful in minimizing certain types of chemical interferences encountered in the air-acetylene flame. For example, the interference caused by high concentrations of phosphate in the determination of calcium in the air-acetylene flame is reduced in the nitrous oxide-acetylene flame.

MIBK extractions with APDC (see Section 3111C) are particularly useful where a salt matrix interferes, for example, in seawater. This procedure also concentrates the sample so that the detection limits are extended.

Brines and seawater can be analyzed by direct aspiration but sample dilution is recommended. Aspiration of solutions containing high concentrations of dissolved solids often results in solids buildup on the burner head. This requires frequent shutdown of the flame and cleaning of the burner head. Preferably use background correction when analyzing waters that contain in excess of 1% solids, especially when the primary resonance line of the element of interest is below 240 nm. Make more frequent recovery checks when analyzing brines and seawaters to insure accurate results in these concentrated and complex matrices.

Barium and other metals ionize in the flame, thereby reducing the ground state (potentially absorbing) population. The addition of an excess of a cation (sodium, potassium, or lithium) having a similar or lower ionization potential will overcome this problem. The wavelength of

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maximum absorption for arsenic is 193.7 nm and for selenium 196.0 nm—wavelengths at which the air-acetylene flame absorbs intensely. The sensitivity for arsenic and selenium can be improved by conversion to their gaseous hydrides and analyzing them in either a nitrogen-hydrogen or an argon-hydrogen flame with a quartz tube (see Section 3114).

b. Background correction: Molecular absorption and light scattering caused by solid particles in the flame can cause erroneously high absorption values resulting in positive errors. When such phenomena occur, use background correction to obtain accurate values. Use any one of three types of background correction: continuum-source, Zeeman, or Smith-Hieftje correction.

1) Continuum-source background correction—A continuum-source background corrector utilizes either a hydrogen-filled hollow cathode lamp with a metal cathode or a deuterium arc lamp. When both the line source hollow-cathode lamp and the continuum source are placed in the same optical path and are time-shared, the broadband background from the elemental signal is subtracted electronically, and the resultant signal will be background-compensated.

Both the hydrogen-filled hollow-cathode lamp and deuterium arc lamp have lower intensities than either the line source hollow-cathode lamp or electrodeless discharge lamps. To obtain a valid correction, match the intensities of the continuum source with the line source hollow-cathode or electrodeless discharge lamp. The matching may result in lowering the intensity of the line source or increasing the slit width; these measures have the disadvantage of raising the detection limit and possibly causing nonlinearity of the calibration curve. Background correction using a continuum source corrector is susceptible to interference from other absorbing lines in the spectral bandwidth. Miscorrection occurs from significant atomic absorption of the continuum source radiation by elements other than that being determined. When a line source hollow-cathode lamp is used without background correction, the presence of an absorbing line from another element in the spectral bandwidth will not cause an interference unless it overlaps the line of interest.

Continuum-source background correction will not remove direct absorption spectral overlap, where an element other than that being determined is capable of absorbing the line radiation of the element under study.

2) Zeeman background correction—This correction is based on the principle that a magnetic field splits the spectral line into two linearly polarized light beams parallel and perpendicular to the magnetic field. One is called the pi (π) component and the other the sigma (σ) component. These two light beams have exactly the same wavelength and differ only in the plane of polarization. The π line will be absorbed by both the atoms of the element of interest and by the background caused by broadband absorption and light scattering of the sample matrix. The σ line will be absorbed only by the background.

Zeeman background correction provides accurate background correction at much higher absorption levels than is possible with continuum source background correction systems. It also virtually eliminates the possibility of error from structured background. Because no additional light sources are required, the alignment and intensity limitations encountered using continuum sources are eliminated.

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Disadvantages of the Zeeman method include reduced sensitivity for some elements, reduced linear range, and a ‘‘rollover’’ effect whereby the absorbance of some elements begins to decrease at high concentrations, resulting in a two-sided calibration curve.

3) Smith-Hieftje background correction—This correction is based on the principle that absorbance measured for a specific element is reduced as the current to the hollow cathode lamp is increased while absorption of nonspecific absorbing substances remains identical at all current levels. When this method is applied, the absorbance at a high-current mode is subtracted from the absorbance at a low-current mode. Under these conditions, any absorbance due to nonspecific background is subtracted out and corrected for.

Smith-Hieftje background correction provides a number of advantages over continuum-source correction. Accurate correction at higher absorbance levels is possible and error from structured background is virtually eliminated. In some cases, spectral interferences also can be eliminated. The usefulness of Smith-Hieftje background correction with electrodeless discharge lamps has not yet been established.

4. Sensitivity, Detection Limits, and Optimum Concentration Ranges

The sensitivity of flame atomic absorption spectrometry is defined as the metal concentration that produces an absorption of 1% (an absorbance of approximately 0.0044). The instrument detection limit is defined here as the concentration that produces absorption equivalent to twice the magnitude of the background fluctuation. Sensitivity and detection limits vary with the instrument, the element determined, the complexity of the matrix, and the technique selected. The optimum concentration range usually starts from the concentration of several times the detection limit and extends to the concentration at which the calibration curve starts to flatten. To achieve best results, use concentrations of samples and standards within the optimum concentration range of the spectrometer. See Table 3111:I for indication of concentration ranges measurable with conventional atomization. In many instances the concentration range shown in Table 3111:I may be extended downward either by scale expansion or by integrating the absorption signal over a long time. The range may be extended upward by dilution, using a less sensitive wavelength, rotating the burner head, or utilizing a microprocessor to linearize the calibration curve at high concentrations.

5. Preparation of Standards

Prepare standard solutions of known metal concentrations in water with a matrix similar to the sample. Use standards that bracket expected sample concentration and are within the method’s working range. Very dilute standards should be prepared daily from stock solutions in concentrations greater than 500 mg/L. Stock standard solutions can be obtained from several commercial sources. They also can be prepared from National Institute of Standards and Technology (NIST) reference materials or by procedures outlined in the following sections.

For samples containing high and variable concentrations of matrix materials, make the major ions in the sample and the dilute standard similar. If the sample matrix is complex and components cannot be matched accurately with standards, use the method of standard additions,

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Section 3113B.4*d*2), to correct for matrix effects. If digestion is used, carry standards through the same digestion procedure used for samples.

6. Apparatus

a. Atomic absorption spectrometer, consisting of a light source emitting the line spectrum of an element (hollow-cathode lamp or electrodeless discharge lamp), a device for vaporizing the sample (usually a flame), a means of isolating an absorption line (monochromator or filter and adjustable slit), and a photoelectric detector with its associated electronic amplifying and measuring equipment.

b. Burner: The most common type of burner is a premix, which introduces the spray into a condensing chamber for removal of large droplets. The burner may be fitted with a conventional head containing a single slot; a three-slot Boling head, which may be preferred for direct aspiration with an air-acetylene flame; or a special head for use with nitrous oxide and acetylene.

c. Readout: Most instruments are equipped with either a digital or null meter readout mechanism. Most modern instruments are equipped with microprocessors or stand-alone control computers capable of integrating absorption signals over time and linearizing the calibration curve at high concentrations.

d. Lamps: Use either a hollow-cathode lamp or an electrodeless discharge lamp (EDL). Use one lamp for each element being measured. Multi-element hollow-cathode lamps generally provide lower sensitivity than single-element lamps. EDLs take a longer time to warm up and stabilize.

e. Pressure-reducing valves: Maintain supplies of fuel and oxidant at pressures somewhat higher than the controlled operating pressure of the instrument by using suitable reducing valves. Use a separate reducing valve for each gas.

f. Vent: Place a vent about 15 to 30 cm above the burner to remove fumes and vapors from the flame. This precaution protects laboratory personnel from toxic vapors, protects the instrument from corrosive vapors, and prevents flame stability from being affected by room drafts. A damper or variable-speed blower is desirable for modulating air flow and preventing flame disturbance. Select blower size to provide the air flow recommended by the instrument manufacturer. In laboratory locations with heavy particulate air pollution, use clean laboratory facilities (Section 3010C).

7. Quality Assurance/Quality Control

Some data typical of the precision and bias obtainable with the methods discussed are presented in Table 3111:II and Table 3111:III.

Analyze a blank between sample or standard readings to verify baseline stability. Rezero when necessary.

To one sample out of every ten (or one sample from each group of samples if less than ten are being analyzed) add a known amount of the metal of interest and reanalyze to confirm recovery. The amount of metal added should be approximately equal to the amount found. If

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little metal is present add an amount close to the middle of the linear range of the test. Recovery of added metal should be between 85 and 115%.

Analyze an additional standard solution after every ten samples or with each batch of samples, whichever is less, to confirm that the test is in control. Recommended concentrations of standards to be run, limits of acceptability, and reported single-operator precision data are listed in Table 3111:III.

See Section 3020 for additional recommended quality control procedures.

8. References

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3111 B. Direct Air-Acetylene Flame Method

1. General Discussion

This method is applicable to the determination of antimony, bismuth, cadmium, calcium,

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cesium, chromium, cobalt, copper, gold, iridium, iron, lead, lithium, magnesium, manganese, nickel, palladium, platinum, potassium, rhodium, ruthenium, silver, sodium, strontium, thallium, tin, and zinc.

2. Apparatus

Atomic absorption spectrometer and associated equipment: See Section 3111A.6. Use burner head recommended by the manufacturer.

3. Reagents

a. Air, cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or commercially bottled gas.

b. Acetylene, standard commercial grade. Acetone, which always is present in acetylene cylinders, can be prevented from entering and damaging the burner head by replacing a cylinder when its pressure has fallen to 689 kPa (100 psi) acetylene.

CAUTION: *Acetylene gas represents an explosive hazard in the laboratory. Follow instrument manufacturer's directions in plumbing and using this gas. Do not allow gas contact with copper, brass with >65% copper, silver, or liquid mercury; do not use copper or brass tubing, regulators, or fittings.*

c. Metal-free water: Use metal-free water for preparing all reagents and calibration standards and as dilution water. Prepare metal-free water by deionizing tap water and/or by using one of the following processes, depending on the metal concentration in the sample: single distillation, redistillation, or sub-boiling. Always check deionized or distilled water to determine whether the element of interest is present in trace amounts. (NOTE: *If the source water contains Hg or other volatile metals, single- or redistilled water may not be suitable for trace analysis because these metals distill over with the distilled water. In such cases, use sub-boiling to prepare metal-free water).*

d. Calcium solution: Dissolve 630 mg calcium carbonate, $CaCO_3$, in 50 mL of 1 + 5 HCl. If necessary, boil gently to obtain complete solution. Cool and dilute to 1000 mL with water.

e. Hydrochloric acid, HCl, 1%, 10%, 20% (all v/v), 1 + 5, 1 + 1, and conc.

f. Lanthanum solution: Dissolve 58.65 g lanthanum oxide, La_2O_3, in 250 mL conc HCl. Add acid slowly until the material is dissolved and dilute to 1000 mL with water.

g. Hydrogen peroxide, 30%.

h. Nitric acid, HNO_3, 2% (v/v), 1 + 1, and conc.

i. Aqua regia: Add 3 volumes conc HCl to 1 volume conc HNO_3.

j. Standard metal solutions: Prepare a series of standard metal solutions in the optimum concentration range by appropriate dilution of the following stock metal solutions with water containing 1.5 mL conc HNO_3/L. Stock standard solutions are available from a number of commercial suppliers. Alternatively, prepare as described below. Thoroughly dry reagents before

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use. In general, use reagents of the highest purity. For hydrates, use fresh reagents.

1) *Antimony:* Dissolve 0.2669 g $K(SbO)C_4H_4O_6$ in water, add 10 mL 1 + 1 HCl and dilute to 1000 mL with water; 1.00 mL = 100 μg Sb.

2) *Bismuth:* Dissolve 0.100 g bismuth metal in a minimum volume of 1 + 1 HNO_3. Dilute to 1000 mL with 2% (v/v) HNO_3; 1.00 mL = 100 μg Bi.

3) *Cadmium:* Dissolve 0.100 g cadmium metal in 4 mL conc HNO_3. Add 8.0 mL conc HNO_3 and dilute to 1000 mL with water; 1.00 mL = 100 μg Cd.

4) *Calcium:* Suspend 0.2497 g $CaCO_3$ (dried at 180° for 1 h before weighing) in water and dissolve cautiously with a minimum amount of 1 + 1 HNO_3. Add 10.0 mL conc HNO_3 and dilute to 1000 mL with water; 1.00 mL = 100 μg Ca.

5) *Cesium:* Dissolve 0.1267 g cesium chloride, CsCl, in 1000 mL water; 1.00 mL = 100 μg Cs.

6) *Chromium:* Dissolve 0.1923 g CrO_3 in water. When solution is complete, acidify with 10 mL conc HNO_3 and dilute to 1000 mL with water; 1.00 mL = 100 μg Cr.

7) *Cobalt:* Dissolve 0.1000 g cobalt metal in a minimum amount of 1 + 1 HNO_3. Add 10.0 mL 1 + 1 HCl and dilute to 1000 mL with water; 1.00 mL = 100 μg Co.

8) *Copper:* Dissolve 0.100 g copper metal in 2 mL conc HNO_3, add 10.0 mL conc HNO_3 and dilute to 1000 mL with water; 1.00 mL = 100 μg Cu.

9) *Gold:* Dissolve 0.100 g gold metal in a minimum volume of aqua regia. Evaporate to dryness, dissolve residue in 5 mL conc HCl, cool, and dilute to 1000 mL with water; 1.00 mL = 100 μg Au.

10) *Iridium:* Dissolve 0.1147 g ammonium chloroiridate, $(NH_4)_2IrCl_6$, in a minimum volume of 1% (v/v) HCl and dilute to 100 mL with 1% (v/v) HCl; 1.00 mL = 500 μg Ir.

11) *Iron:* Dissolve 0.100 g iron wire in a mixture of 10 mL 1 + 1 HCl and 3 mL conc HNO_3. Add 5 mL conc HNO_3 and dilute to 1000 mL with water; 1.00 mL = 100 μg Fe.

12) *Lead:* Dissolve 0.1598 g lead nitrate, $Pb(NO_3)_2$, in a minimum amount of 1 + 1 HNO_3, add 10 mL conc HNO_3, and dilute to 1000 mL with water; 1.00 mL = 100 μg Pb.

13) *Lithium:* Dissolve 0.5323 g lithium carbonate, Li_2CO_3, in a minimum volume of 1 + 1 HNO_3. Add 10.0 mL conc HNO_3 and dilute to 1000 mL with water; 1.00 mL = 100 μg Li.

14) *Magnesium:* Dissolve 0.1658 g MgO in a minimum amount of 1 + 1 HNO_3. Add 10.0 mL conc HNO_3 and dilute to 1000 mL with water; 1.00 mL = 100 μg Mg.

15) *Manganese:* Dissolve 0.1000 g manganese metal in 10 mL conc HCl mixed with 1 mL

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conc HNO_3. Dilute to 1000 mL with water; 1.00 mL = 100 μg Mn.

16) *Nickel:* Dissolve 0.1000 g nickel metal in 10 mL hot conc HNO_3, cool, and dilute to 1000 mL with water; 1.00 mL = 100 μg Ni.

17) *Palladium:* Dissolve 0.100 g palladium wire in a minimum volume of aqua regia and evaporate just to dryness. Add 5 mL conc HCl and 25 mL water and warm until dissolution is complete. Dilute to 1000 mL with water; 1.00 mL = 100 μg Pd.

18) *Platinum:* Dissolve 0.100 g platinum metal in a minimum volume of aqua regia and evaporate just to dryness. Add 5 mL conc HCl and 0.1 g NaCl and again evaporate just to dryness. Dissolve residue in 20 mL of 1 + 1 HCl and dilute to 1000 mL with water; 1.00 mL = 100 μg Pt.

19) *Potassium:* Dissolve 0.1907 g potassium chloride, KCl, (dried at 110°C) in water and make up to 1000 mL; 1.00 mL = 100 μg K.

20) *Rhodium:* Dissolve 0.386 g ammonium hexachlororhodate, $(NH_4)_3RhCl_6 \cdot 1.5H_2O$, in a minimum volume of 10% (v/v) HCl and dilute to 1000 mL with 10% (v/v) HCl; 1.00 mL = 100 μg Rh.

21) *Ruthenium:* Dissolve 0.205 g ruthenium chloride, $RuCl_3$, in a minimum volume of 20% (v/v) HCl and dilute to 1000 mL with 20% (v/v) HCl; 1.00 mL = 100 μg Ru.

22) *Silver:* Dissolve 0.1575 g silver nitrate, $AgNO_3$, in 100 mL water, add 10 mL conc HNO_3, and make up to 1000 mL; 1.00 mL = 100 μg Ag.

23) *Sodium:* Dissolve 0.2542 g sodium chloride, NaCl, dried at 140°C, in water, add 10 mL conc HNO_3 and make up to 1000 mL; 1.00 mL = 100 μg Na.

24) *Strontium:* Suspend 0.1685 g $SrCO_3$ in water and dissolve cautiously with a minimum amount of 1 + 1 HNO_3. Add 10.0 mL conc HNO_3 and dilute to 1000 mL with water: 1 mL = 100 μg Sr.

25) *Thallium:* Dissolve 0.1303 g thallium nitrate, $TlNO_3$, in water. Add 10 mL conc HNO_3 and dilute to 1000 mL with water; 1.00 mL = 100 μg Tl.

27) *Zinc:* Dissolve 0.100 g zinc metal in 20 mL 1 + 1 HCl and dilute to 1000 mL with water; 1.00 mL = 100 μg Zn.

4. Procedure

a. Sample preparation: Required sample preparation depends on the metal form being measured.

If dissolved metals are to be determined, see Section 3030B for sample preparation. If total or acid-extractable metals are to be determined, see Section 3030C through K. For all samples, make certain that the concentrations of acid and matrix modifiers are the same in both samples and standards.

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When determining Ca or Mg, dilute and mix 100 mL sample or standard with 10 mL lanthanum solution (¶ 3 *f*) before aspirating. When determining Fe or Mn, mix 100 mL with 25 mL of Ca solution (¶ 3*d*) before aspirating. When determining Cr, mix 1 mL 30% H_2O_2 with each 100 mL before aspirating. Alternatively use proportionally smaller volumes.

b. Instrument operation: Because of differences between makes and models of atomic absorption spectrometers, it is not possible to formulate instructions applicable to every instrument. See manufacturer's operating manual. In general, proceed according to the following: Install a hollow-cathode lamp for the desired metal in the instrument and roughly set the wavelength dial according to Table 3111:I. Set slit width according to manufacturer's suggested setting for the element being measured. Turn on instrument, apply to the hollow-cathode lamp the current suggested by the manufacturer, and let instrument warm up until energy source stabilizes, generally about 10 to 20 min. Readjust current as necessary after warmup. Optimize wavelength by adjusting wavelength dial until optimum energy gain is obtained. Align lamp in accordance with manufacturer's instructions.

Install suitable burner head and adjust burner head position. Turn on air and adjust flow rate to that specified by manufacturer to give maximum sensitivity for the metal being measured. Turn on acetylene, adjust flow rate to value specified, and ignite flame. Let flame stabilize for a few minutes. Aspirate a blank consisting of deionized water containing the same concentration of acid in standards and samples. Zero the instrument. Aspirate a standard solution and adjust aspiration rate of the nebulizer to obtain maximum sensitivity. Adjust burner both vertically and horizontally to obtain maximum response. Aspirate blank again and rezero the instrument. Aspirate a standard near the middle of the linear range. Record absorbance of this standard when freshly prepared and with a new hollow-cathode lamp. Refer to these data on subsequent determinations of the same element to check consistency of instrument setup and aging of hollow-cathode lamp and standard.

The instrument now is ready to operate. When analyses are finished, extinguish flame by turning off first acetylene and then air.

c. Standardization: Select at least three concentrations of each standard metal solution (prepared as in ¶ 3 *j* above) to bracket the expected metal concentration of a sample. Aspirate blank and zero the instrument. Then aspirate each standard in turn into flame and record absorbance.

Prepare a calibration curve by plotting on linear graph paper absorbance of standards versus their concentrations. For instruments equipped with direct concentration readout, this step is unnecessary. With some instruments it may be necessary to convert percent absorption to absorbance by using a table generally provided by the manufacturer. Plot calibration curves for Ca and Mg based on original concentration of standards before dilution with lanthanum solution. Plot calibration curves for Fe and Mn based on original concentration of standards before dilution with Ca solution. Plot calibration curve for Cr based on original concentration of standard before addition of H_2O_2.

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d. Analysis of samples: Rinse nebulizer by aspirating water containing 1.5 mL conc HNO_3/L. Aspirate blank and zero instrument. Aspirate sample and determine its absorbance.

5. Calculations

Calculate concentration of each metal ion, in micrograms per liter for trace elements, and in milligrams per liter for more common metals, by referring to the appropriate calibration curve prepared according to ¶ 4*c*. Alternatively, read concentration directly from the instrument readout if the instrument is so equipped. If the sample has been diluted, multiply by the appropriate dilution factor.

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Also see Section 3111A.8 and Section 3111A.9.

3111 C. Extraction/Air-Acetylene Flame Method

1. General Discussion

This method is suitable for the determination of low concentrations of cadmium, chromium, cobalt, copper, iron, lead, manganese, nickel, silver, and zinc. The method consists of chelation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction into methyl isobutyl ketone (MIBK), followed by aspiration into an air-acetylene flame.

2. Apparatus

a. Atomic absorption spectrometer and associated equipment: See Section 3111A.6.

b. Burner head, conventional. Consult manufacturer's operating manual for suggested burner head.

3. Reagents

a. Air: See Section 3111B.3*a*.

b. Acetylene: See Section 3111B.3*b*.

c. Metal-free water: See Section 3111B.3*c*.

d. Methyl isobutyl ketone (MIBK), reagent grade. For trace analysis, purify MIBK by redistillation or by sub-boiling distillation.

e. Ammonium pyrrolidine dithiocarbamate (APDC) solution: Dissolve 4 g APDC in 100 mL water. If necessary, purify APDC with an equal volume of MIBK. Shake 30 s in a separatory funnel, let separate, and withdraw lower portion. Discard MIBK layer.

f. Nitric acid, HNO_3, conc, ultrapure.

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g. Standard metal solutions: See Section 3111B.3 *j*.

h. Potassium permanganate solution, $KMnO_4$, 5% (w/v) aqueous.

i. Sodium sulfate, Na_2SO_4, anhydrous.

j. Water-saturated MIBK: Mix one part purified MIBK with one part water in a separatory funnel. Shake 30 s and let separate. Discard aqueous layer. Save MIBK layer.

k. Hydroxylamine hydrochloride solution, 10% (w/v). This solution can be purchased commercially.

4. Procedure

a. Instrument operation: See Section 3111B.4*b*. After final adjusting of burner position, aspirate water-saturated MIBK into flame and gradually reduce fuel flow until flame is similar to that before aspiration of solvent.

b. Standardization: Select at least three concentrations of standard metal solutions (prepared as in Section 3111B.3 *j*) to bracket expected sample metal concentration and to be, after extraction, in the optimum concentration range of the instrument. Adjust 100mL of each standard and 100 mL of a metal-free water blank to pH 3 by adding 1*N* HNO_3 or 1*N* NaOH. For individual el-ement extraction, use the following pH ranges to obtain optimum extraction efficiency:

Element	pH Range for Optimum Extraction
Ag	2–5 (complex unstable)
Cd	1–6
Co	2–10
Cr	3–9
Cu	0.1–8
Fe	2–5
Mn	2–4 (complex unstable)
Ni	2–4
Pb	0.1–6
Zn	2–6

NOTE: For Ag and Pb extraction the optimum pH value is 2.3 ± 0.2. The Mn complex deteriorates rapidly at room temperature, resulting in decreased instrument response. Chilling the extract to 0°C may preserve the complex for a few hours. If this is not possible and Mn cannot be analyzed immediately after extraction, use another analytical procedure.

Transfer each standard solution and blank to individual 200-mL volumetric flasks, add 1 mL

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APDC solution, and shake to mix. Add 10 mL MIBK and shake vigorously for 30 s. (The maximum volume ratio of sample to MIBK is 40.) Let contents of each flask separate into aqueous and organic layers, then carefully add water (adjusted to the same pH at which the extraction was carried out) down the side of each flask to bring the organic layer into the neck and accessible to the aspirating tube.

Aspirate organic extracts directly into the flame (zeroing instrument on a water-saturated MIBK blank) and record absorbance.

Prepare a calibration curve by plotting on linear graph paper absorbances of extracted standards against their concentrations before extraction.

c. Analysis of samples: Prepare samples in the same manner as the standards. Rinse atomizer by aspirating water-saturated MIBK. Aspirate organic extracts treated as above directly into the flame and record absorbances.

With the above extraction procedure only hexavalent chromium is measured. To determine total chromium, oxidize trivalent chromium to hexavalent chromium by bringing sample to a boil and adding sufficient $KMnO_4$ solution dropwise to give a persistent pink color while the solution is boiled for 10 min. Destroy excess $KMnO_4$ by adding 1 to 2 drops hydroxylamine hydrochloride solution to the boiling solution, allowing 2 min for the reaction to proceed. If pink color persists, add 1 to 2 more drops hydroxylamine hydrochloride solution and wait 2 min. Heat an additional 5 min. Cool, extract with MIBK, and aspirate.

During extraction, if an emulsion forms at the water-MIBK interface, add anhydrous Na_2SO_4 to obtain a homogeneous organic phase. In that case, also add Na_2SO_4 to all standards and blanks.

To avoid problems associated with instability of extracted metal complexes, determine metals immediately after extraction.

5. Calculations

Calculate the concentration of each metal ion in micrograms per liter by referring to the appropriate calibration curve.

6. Bibliography

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3111 D. Direct Nitrous Oxide-Acetylene Flame Method

1. General Discussion

This method is applicable to the determination of aluminum, barium, beryllium, calcium,

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molybdenum, osmium, rhenium, silicon, thorium, titanium, and vanadium.

2. Apparatus

a. Atomic absorption spectrometer and associated equipment: See Section 3111A.6.

b. Nitrous oxide burner head: Use special burner head as suggested in manufacturer's manual. At roughly 20-min intervals of operation it may be necessary to dislodge the carbon crust that forms along the slit surface with a carbon rod or appropriate alternative.

c. T-junction valve or other switching valve for rapidly changing from nitrous oxide to air, so that flame can be turned on or off with air as oxidant to prevent flashbacks.

3. Reagents

a. Air: See Section 3111B.3*a*.

b. Acetylene: See Section 3111B.3*b*.

c. Metal-free water: See Section 3111B.3*c*.

d. Hydrochloric acid, HCl, 1*N*, 1+1, and conc.

e. Nitric acid, HNO_3, conc.

f. Sulfuric acid, H_2SO_4, 1% (v/v).

g. Hydrofluoric acid, HF, 1*N*.

h. Nitrous oxide, commercially available cylinders. Fit nitrous oxide cylinder with a special nonfreezable regulator or wrap a heating coil around an ordinary regulator to prevent flashback at the burner caused by reduction in nitrous oxide flow through a frozen regulator. (Most modern atomic absorption instruments have automatic gas control systems that will shut down a nitrous oxide-acetylene flame safely in the event of a reduction in nitrous oxide flow rate.)

CAUTION: *Use nitrous oxide with strict adherence to manufacturer's directions. Improper sequencing of gas flows at startup and shutdown of instrument can produce explosions from flashback.*

i. Potassium chloride solution: Dissolve 250 g KCl in water and dilute to 1000 mL.

j. Aluminum nitrate solution: Dissolve 139 g $Al(NO_3)_3 \cdot 9H_2O$ in 150 mL water. Acidify slightly with conc HNO_3 to preclude possible hydrolysis and precipitation. Warm to dissolve completely. Cool and dilute to 200 mL.

k. Standard metal solutions: Prepare a series of standard metal solutions in the optimum concentration ranges by appropriate dilution of stock metal solutions with water containing 1.5 mL conc HNO_3/L. Stock standard solutions are available from a number of commercial suppliers. Alternatively, prepare as described below.

1) *Aluminum:* Dissolve 0.100 g aluminum metal in an acid mixture of 4 mL 1 + 1 HCl and 1 mL conc HNO_3 in a beaker. Warm gently to effect solution. Transfer to a 1-L flask, add 10 mL 1 + 1 HCl, and dilute to 1000 mL with water; 1.00 mL = 100 µg Al.

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2) *Barium:* Dissolve 0.1516 g $BaCl_2$ (dried at 250° for 2 h), in about 10 mL water with 1 mL 1+ 1 HCl. Add 10.0 mL 1 + 1 HCl and dilute to 1000 mL with water; 1.00 mL = 100 µg Ba.

3) *Beryllium*: *Do not dry.* Dissolve 1.966 g $BeSO_4 \cdot 4H_2O$ in water, add 10.0 mL conc HNO_3, and dilute to 1000 mL with water; 1.00 mL = 100 µg Be.

4) *Calcium:* See Section 3111B.3 *j*4).

5) *Molybdenum:* Dissolve 0.2043 g $(NH_4)_2\ MoO_4$ in water and dilute to 1000 mL; 1.00 mL = 100 µg Mo.

6) *Osmium:* Obtain standard 0.1*M* osmium tetroxide solution*#(76) and store in glass bottle; 1.00 mL = 19.02 mg Os. Make dilutions daily as needed using 1% (v/v) H_2SO_4. CAUTION: *OsO_4 is extremely toxic and highly volatile.*

7) *Rhenium:* Dissolve 0.1554 g potassium perrhenate, $KReO_4$, in 200 mL water. Dilute to 1000 mL with 1% (v/v) H_2SO_4; 1.00 mL = 100 µg Re.

8) *Silica: Do not dry.* Dissolve 0.4730 g $Na_2SiO_3 \cdot 9H_2O$ in water. Add 10.0 mL conc HNO_3 and dilute to 1000 mL with water. 1.00 mL = 100 µg SiO_2. Store in polyethylene.

9) *Thorium:* Dissolve 0.238 g thorium nitrate, $Th(NO_3)_4 \cdot 4H_2O$ in 1000 mL water; 1.00 mL = 100 µg Th.

10) *Titanium:* Dissolve 0.3960 g pure (99.8 or 99.9%) titanium chloride, $TiCl_4$,†#(77) in a mixture of equal volumes of 1*N* HCl and 1*N* HF. Make up to 1000 mL with this acid mixture; 1.00 mL = 100 µg Ti.

11) *Vanadium:* Dissolve 0.2297 g ammonium metavanadate, NH_4VO_3, in a minimum amount of conc HNO_3. Heat to dissolve. Add 10 mL conc HNO_3, and dilute to 1000 mL with water; 1.00 mL = 100 µg V.

4. Procedure

a. Sample preparation: See Section 3111B.4*a*.

When determining Al, Ba, or Ti, mix 2 mL KCl solution into 100 mL sample or standard before aspiration. When determining Mo and V, mix 2 mL $Al(NO_3)_3 \cdot 9H_2O$ into 100 mL sample or standard before aspiration.

b. Instrument operation: See Section 3111B.4*b*. After adjusting wavelength, install a nitrous oxide burner head. Turn on acetylene (without igniting flame) and adjust flow rate to value specified by manufacturer for a nitrous oxide-acetylene flame. Turn off acetylene. With both air and nitrous oxide supplies turned on, set T-junction valve to nitrous oxide and adjust flow rate according to manufacturer's specifications. Turn switching valve to the air position and verify that flow rate is the same. Turn acetylene on and ignite to a bright yellow flame. With a rapid motion, turn switching valve to nitrous oxide. The flame should have a red cone above the

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burner. If it does not, adjust fuel flow to obtain red cone. After nitrous oxide flame has been ignited, let burner come to thermal equilibrium before beginning analysis.

Aspirate a blank consisting of deionized water containing 1.5 mL conc HNO_3/L and check aspiration rate. Adjust if necessary to a rate between 3 and 5 mL/ min. Zero the instrument. Aspirate a standard of the desired metal with a concentration near the midpoint of the optimum concentration range and adjust burner (both horizontally and vertically) in the light path to obtain maximum response. Aspirate blank again and re-zero the instrument. The instrument now is ready to run standards and samples.

To extinguish flame, turn switching valve from nitrous oxide to air and turn off acetylene. This procedure eliminates the danger of flashback that may occur on direct ignition or shutdown of nitrous oxide and acetylene. (See also discussion in Section 3111B.4*b*.)

c. Standardization: Select at least three concentrations of standard metal solutions (prepared as in ¶ 3*k*) to bracket the expected metal concentration of a sample. Aspirate each in turn into the flame and record absorbances.

Most modern instruments are equipped with microprocessors and digital readout which permit calibration in direct concentration terms. If instrument is not so equipped, prepare a calibration curve by plotting on linear graph paper absorbance of standards versus concentration. Plot calibration curves for Al, Ba, and Ti based on original concentration of standard before adding KCl solution. Plot calibration curves for Mo and V based on original concentration of standard before adding $Al(NO_3)_3$ solution.

d. Analysis of samples: Rinse atomizer by aspirating water containing 1.5 mL conc HNO_3/L and zero instrument. Aspirate a sample and determine its absorbance.

5. Calculations

Calculate concentration of each metal ion in micrograms per liter by referring to the appropriate calibration curve prepared according to ¶ 4*c*.

Alternatively, read the concentration directly from the instrument readout if the instrument is so equipped. If sample has been diluted, multiply by the appropriate dilution factor.

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WILLIS, J.B. 1965. Nitrous oxide-acetylene flame in atomic absorption spectroscopy. *Nature* 207:715.

Also see Section 3111A.8 and Section 3111A.9.

3111 E. Extraction/Nitrous Oxide-Acetylene Flame Method

1. General Discussion

a. Application: This method is suitable for the determination of aluminum at concentrations

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less than 900 µg/L and beryllium at concentrations less than 30 µg/L. The method consists of chelation with 8-hydroxyquinoline, extraction with methyl isobutyl ketone (MIBK), and aspiration into a nitrous oxide-acetylene flame.

b. Interferences: Concentrations of Fe greater than 10 mg/L interfere by suppressing Al absorption. Iron interference can be masked by addition of hydroxylamine hydrochloride/1,10-phenanthroline. Mn concentrations up to 80 mg/L do not interfere if turbidity in the extract is allowed to settle. Mg forms an insoluble chelate with 8-hydroxyquinoline at pH 8.0 and tends to remove Al complex as a coprecipitate. However, the Mg complex forms slowly over 4 to 6 min; its interference can be avoided if the solution is extracted immediately after adding buffer.

2. Apparatus

Atomic absorption spectrometer and associated equipment: See Section 3111A.6.

3. Reagents

a. Air: See Section 3111B.3*a*.

b. Acetylene: See Section 3111B.3*b*.

c. Ammonium hydroxide, NH_4OH, conc.

d. Buffer: Dissolve 300 g ammonium acetate, $NH_4C_2H_3O_2$, in water, add 105 mL conc NH_4OH, and dilute to 1 L.

e. Metal-free water: See Section 3111B.3*c*.

f. Hydrochloric acid, HCl, conc.

g. 8-Hydroxyquinoline solution: Dissolve 20 g 8-hydroxyquinoline in about 200 mL water, add 60 mL glacial acetic acid, and dilute to 1 L with water.

h. Methyl isobutyl ketone: See Section 3111C.3*d*.

i. Nitric acid, HNO_3, conc.

j. Nitrous oxide: See Section 3111D.3*h*.

k. Standard metal solutions: Prepare a series of standard metal solutions containing 5 to 1000 µg/L by appropriate dilution of the stock metal solutions prepared according to Section 3111D.3*k*.

l. Iron masking solution: Dissolve 1.3 g hydroxylamine hydrochloride and 6.58 g 1,10-phenanthroline monohydrate in about 500 mL water and dilute to 1 L with water.

4. Procedure

a. Instrument operation: See Section 3111B.4*b*, Section 3111C.4*a*, and Section 3111D.4*b*. After final adjusting of burner position, aspirate MIBK into flame and gradually reduce fuel flow until flame is similar to that before aspiration of solvent. Adjust wavelength setting according to Table 3111:I.

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b. Standardization: Select at least three concentrations of standard metal solutions (prepared as in ¶ 3*k*) to bracket the expected metal concentration of a sample and transfer 100 mL of each (and 100 mL water blank) to four different 200-mL volumetric flasks. Add 2 mL 8-hydroxyquinoline solution, 2 mL masking solution (if required), and 10 mL buffer to one flask, immediately add 10 mL MIBK, and shake vigorously. The duration of shaking affects the forms of aluminum complexed. A fast, 10-s shaking time favors monomeric Al, whereas 5 to 10 min of shaking also will complex polymeric species. Adjustment of the 8-hydroxyquinoline to sample ratio can improve recoveries of extremely high or low concentrations of aluminum. Treat each blank, standard, and sample in similar fashion. Continue as in Section 3111C.4*b*.

c. Analysis of samples: Rinse atomizer by aspirating water-saturated MIBK. Aspirate extracts of samples treated as above, and record absorbances.

5. Calculations

Calculate concentration of each metal in micrograms per liter by referring to the appropriate calibration curve prepared according to ¶ 4*b*.

3112 METALS BY COLD-VAPOR ATOMIC ABSORPTION SPECTROMETRY*#(78)

3112 A. Introduction

For general introductory material on atomic absorption spectrometric methods, see Section 3111A.

3112 B. Cold-Vapor Atomic Absorption Spectrometric Method

1. General Discussion

This method is applicable to the determination of mercury.

2. Apparatus

When possible, dedicate glassware for use in Hg analysis. Avoid using glassware previously exposed to high levels of Hg, such as those used in COD, TKN, or Cl^- analysis.

a. Atomic absorption spectrometer and associated equipment: See Section 3111A.6. Instruments and accessories specifically designed for measurement of mercury by the cold vapor technique are available commercially and may be substituted.

b. Absorption cell, a glass or plastic tube approximately 2.5 cm in diameter. An 11.4-cm-long tube has been found satisfactory but a 15-cm-long tube is preferred. Grind tube ends perpendicular to the longitudinal axis and cement quartz windows in place. Attach gas inlet and

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outlet ports (6.4 mm diam) 1.3 cm from each end.

c. Cell support: Strap cell to the flat nitrous-oxide burner head or other suitable support and align in light beam to give maximum transmittance.

d. Air pumps: Use any peristaltic pump with electronic speed control capable of delivering 2 L air/min. Any other regulated compressed air system or air cylinder also is satisfactory.

e. Flowmeter, capable of measuring an air flow of 2 L/min.

f. Aeration tubing, a straight glass frit having a coarse porosity for use in reaction flask.

g. Reaction flask, 250-mL erlenmeyer flask or a BOD bottle, fitted with a rubber stopper to hold aeration tube.

h. Drying tube, 150-mm × 18-mm-diam, containing 20 g Mg $(ClO_4)_2$. A 60-W light bulb with a suitable shade may be substituted to prevent condensation of moisture inside the absorption cell. Position bulb to maintain cell temperature at 10°C above ambient.

i. Connecting tubing, glass tubing to pass mercury vapor from reaction flask to absorption cell and to interconnect all other components. Clear vinyl plastic*#(79) tubing may be substituted for glass.

3. Reagents†#(80)

a. Metal-free water: See Section 3111B.3*c*.

b. Stock mercury solution: Dissolve 0.1354 g mercuric chloride, $HgCl_2$, in about 70 mL water, add 1 mL conc HNO_3, and dilute to 100 mL with water; 1.00 mL = 1.00 mg Hg.

c. Standard mercury solutions: Prepare a series of standard mercury solutions containing 0 to 5 µg/L by appropriate dilution of stock mercury solution with water containing 10 mL conc HNO_3/L. Prepare standards daily.

d. Nitric acid, HNO_3, conc.

e. Potassium permanganate solution: Dissolve 50 g $KMnO_4$ in water and dilute to 1 L.

f. Potassium persulfate solution: Dissolve 50 g $K_2S_2O_8$ in water and dilute to 1 L.

g. Sodium chloride-hydroxylamine sulfate solution: Dissolve 120 g NaCl and 120 g $(NH_2OH)_2 \cdot H_2SO_4$ in water and dilute to 1 L. A 10% hydroxylamine hydrochloride solution may be substituted for the hydroxylamine sulfate.

h. Stannous ion (Sn^{2+}) solution: Use either stannous chloride, ¶ 1), or stannous sulfate, ¶ 2), to prepare this solution containing about 7.0 g Sn^{2+}/100 mL.

1) Dissolve 10 g $SnCl_2$ in water containing 20 mL conc HCl and dilute to 100 mL.

2) Dissolve 11 g $SnSO_4$ in water containing 7 mL conc H_2SO_4 and dilute to 100 mL.

Both solutions decompose with aging. If a suspension forms, stir reagent continuously during use. Reagent volume is sufficient to process about 20 samples; adjust volumes prepared to

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accommodate number of samples processed.

i. Sulfuric acid, H_2SO_4, conc.

4. Procedure

a. Instrument operation: See Section 3111B.4*b*. Set wavelength to 253.7 nm. Install absorption cell and align in light path to give maximum transmission. Connect associated equipment to absorption cell with glass or vinyl plastic tubing as indicated in Figure 3112:1. Turn on air and adjust flow rate to 2 L/min. Allow air to flow continuously. Alternatively, follow manufacturer's directions for operation. NOTE: Fluorescent lighting may increase baseline noise.

b. Standardization: Transfer 100 mL of each of the 1.0, 2.0, and 5.0 µg/L Hg standard solutions and a blank of 100 mL water to 250-mL erlenmeyer reaction flasks. Add 5 mL conc H_2SO_4 and 2.5 mL conc HNO_3 to each flask. Add 15 mL $KMnO_4$ solution to each flask and let stand at least 15 min. Add 8 mL $K_2S_2O_8$ solution to each flask and heat for 2 h in a water bath at 95°C. Cool to room temperature.

Treating each flask individually, add enough NaCl-hydroxylamine solution to reduce excess $KMnO_4$, then add 5 mL $SnCl_2$ or $SnSO_4$ solution and immediately attach flask to aeration apparatus. As Hg is volatilized and carried into the absorption cell, absorbance will increase to a maximum within a few seconds. As soon as recorder returns approximately to the base line, remove stopper holding the frit from reaction flask, and replace with a flask containing water. Flush system for a few seconds and run the next standard in the same manner. Construct a standard curve by plotting peak height versus micrograms Hg.

c. Analysis of samples: Transfer 100 mL sample or portion diluted to 100 mL containing not more than 5.0 µg Hg/L to a reaction flask. Treat as in ¶ 4*b*. Seawaters, brines, and effluents high in chlorides require as much as an additional 25 mL $KMnO_4$ solution. During oxidation step, chlorides are converted to free chlorine, which absorbs at 253 nm. Remove all free chlorine before the Hg is reduced and swept into the cell by using an excess (25 mL) of hydroxylamine reagent.

Remove free chlorine by sparging sample gently with air or nitrogen after adding hydroxylamine reducing solution. Use a separate tube and frit to avoid carryover of residual stannous chloride, which could cause reduction and loss of mercury.

5. Calculation

Determine peak height of sample from recorder chart and read mercury value from standard curve prepared according to ¶ 4*b*.

6. Precision and Bias

Data on interlaboratory precision and bias for this method are given in Table 3112:I.

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3113 METALS BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY*#(81)

3113 A. Introduction

1. Applications

Electrothermal atomic absorption permits determination of most metallic elements with sensitivities and detection limits from 20 to 1000 times better than those of conventional flame techniques without extraction or sample concentration. This increase in sensitivity results from an increase in atom density within the furnace as compared to flame atomic absorption. Many

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elements can be determined at concentrations as low as 1.0 µg/L. An additional advantage of electrothermal atomic absorption is that only a very small volume of sample is required.

The electrothermal technique is used only at concentration levels below the optimum range of direct flame atomic absorption because it is subject to more interferences than the flame procedure and requires increased analysis time. The method of standard additions may be required to insure validity of data. Because of the high sensitivity of this technique, it is extremely susceptible to contamination; extra care in sample handling and analysis may be required.

2. Principle

Electrothermal atomic absorption spectroscopy is based on the same principle as direct flame atomization but an electrically heated atomizer or graphite furnace replaces the standard burner head. A discrete sample volume is dispensed into the graphite sample tube (or cup). Typically, determinations are made by heating the sample in three or more stages. First, a low current heats the tube to dry the sample. The second, or charring, stage destroys organic matter and volatilizes other matrix components at an intermediate temperature. Finally, a high current heats the tube to incandescence and, in an inert atmosphere, atomizes the element being determined. Additional stages frequently are added to aid in drying and charring, and to clean and cool the tube between samples. The resultant ground-state atomic vapor absorbs monochromatic radiation from the source. A photoelectric detector measures the intensity of transmitted radiation. The inverse of the transmittance is related logarithmically to the absorbance, which is directly proportional to the number density of vaporized ground-state atoms (the Beer-Lambert law) over a limited concentration range.

3. Interferences

Electrothermal atomization determinations may be subject to significant interferences from molecular absorption as well as chemical and matrix effects. Molecular absorption may occur when components of the sample matrix volatilize during atomization, resulting in broadband absorption. Several background correction techniques are available commercially to compensate for this interference. A continuum source such as a deuterium arc can correct for background up to absorbance levels of about 0.8. Continuum lamp intensity diminishes at long wavelengths and use of continuum background correction is limited to analytical wavelengths below 350 nm. Zeeman effect background correctors can handle background absorbance up to 1.5 to 2.0. The Smith-Hieftje correction technique can accommodate background absorbance levels as large as 2.5 to 3.0 (see Section 3111A.3). Both Zeeman and Smith-Hieftje background corrections are susceptible to rollover (development of a negative absorbance-concentration relationship) at high absorbances. The rollover absorbance for each element should be available in the manufacturer's literature. Curvature due to rollover should become apparent during calibration; dilution produces a more linear calibration plot. Use background correction when analyzing samples containing high concentrations of acid or dissolved solids and in determining elements for which an absorption line below 350 nm is used.

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Matrix modification can be useful in minimizing interference and increasing analytical sensitivity. Determine need for a modifier by evaluating recovery of a sample with a known addition. Recovery near 100% indicates that sample matrix does not affect analysis. Chemical modifiers generally modify relative volatilities of matrix and metal. Some modifiers enhance matrix removal, isolating the metal, while other modifiers inhibit metal volatilization, allowing use of higher ashing/charring temperatures and increasing efficiency of matrix removal. Chemical modifiers are added at high concentration (percent level) and can lead to sample contamination from impurities in the modifier solution. Heavy use of chemical modifiers may reduce the useful life (normally 50 to 100 firings) of the graphite tube. Some specific chemical modifiers and approximate concentrations are listed in Table 3113:I.

Addition of a chemical modifier directly to the sample before analysis is restricted to inexpensive additives (e.g. phosphoric acid). Use of palladium salts for matrix modification normally requires methods of co-addition, in which sample and modifier are added consecutively to the furnace either manually or, preferably, with an automatic sampler. Palladium salts (nitrate is preferred, chloride is acceptable) are listed in Table 3113:I as a modifier for many metals. The palladium solution (50 to 2000 mg/L) generally includes citric or ascorbic acid, which aids reduction of palladium in the furnace. Citric acid levels of 1 to 2% are typical. Use of hydrogen (5%) in the coolant gas (available commercially as a mixture) also reduces palladium, eliminating need for organic reducing acids. CAUTION: *Do not mix hydrogen and other gases in the laboratory; hydrogen gas is very flammable—handle with caution*. Use low levels of palladium (50 to 250 mg/L) for normal samples and higher levels for complex samples. Addition of excess palladium modifier may widen atomization peaks; in such cases peak area measurements may provide higher quality results. The recommended mode of modifier use is through co-addition to the furnace of about 10 µL of the palladium (or other) modifier solution. Palladium may not be the best modifier in all cases and cannot be recommended unconditionally. Test samples requiring a modifier first with palladium; test other modifiers only if palladium is unsuccessful or to minimize modifier cost. See Section 3113B.3 for preparation of modifier solution.

Temperature ramping, i.e., gradual heating, can be used to decrease background interferences and permits analysis of samples with complex matrices. Ramping permits a controlled, continuous increase of furnace temperature in any of the various steps of the temperature sequence. Ramp drying is used for samples containing mixtures of solvents or for samples with a high salt content (to avoid spattering). If spattering is suspected, develop drying ramp by visual inspection of the drying stage, using a mirror. Samples that contain a complex mixture of matrix components sometimes require ramp charring to effect controlled, complete thermal decomposition. Ramp atomization may minimize background absorption by permitting volatilization of the element being determined before the matrix. This is especially applicable in the determination of such volatile elements as cadmium and lead. Use of time-resolved absorbance profiles (available on most modern instruments) greatly aids method development. Changes in atomization, notably the element peak appearance time and magnitude of background

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and metal absorbances, can be monitored directly.

Improve analysis by using a graphite platform, inserted into the graphite tube, as the atomization site. The platform is not heated as directly by the current flowing through the graphite tube; thus the metal atomizes later and under more uniform conditions.

Use standard additions to compensate for matrix interferences. When making standard additions, determine whether the added metal and that in the sample behave similarly under the specified conditions. [See Section 3113B.4*d*2)]. In the extreme, test every sample for recovery (85 to 115% recovery desired) to determine if standard addition is needed. Test every sample type for recovery. Recovery of only 40 to 85% generally indicates that standard addition is required. Often, as long as the samples are from sources of consistent properties, a representative recovery can be used to characterize the analysis and determine the necessity of standard addition. Test samples of unknown origin or of complex composition (digestates, for example) individually for metal recovery. Ideally, chemical modifiers and graphite platforms render the sample fit to be analyzed using a standard analytical calibration curve. Always verify this assumption; however, a properly developed method with judicious use of chemical modifiers should eliminate the necessity for standard addition in all but the most extreme samples.

Chemical interaction of the graphite tube with various elements to form refractory carbides occurs at high charring and atomization temperatures. Elements that form carbides are barium, molybdenum, nickel, titanium, vanadium, and silicon. Carbide formation is characterized by broad, tailing atomization peaks and reduced sensitivity. Using pyrolytically coated tubes for these metals minimizes the problem.

4. Sensitivity, Detection Limits, and Optimum Concentration Range

Estimated detection limits and optimum concentration ranges are listed in Table 3113:II. These values may vary with the chemical form of the element being determined, sample composition, or instrumental conditions.

For a given sample, increased sensitivity may be achieved by using a larger sample volume or by reducing flow rate of the purge gas or by using gas interrupt during atomization. Note, however, that these techniques also will increase the effects of any interferences present. Sensitivity can be decreased by diluting the sample, reducing sample volume, increasing purge-gas flow, or using a less sensitive wavelength. Use of argon, rather than nitrogen, as the purge gas generally improves sensitivity and reproducibility. Hydrogen mixed with the inert gas may suppress chemical interference and increase sensitivity by acting as a reducing agent, thereby aiding in producing more ground-state atoms. Pyrolytically coated graphite tubes can increase sensitivity for the more refractory elements and are recommended. The optical pyrometer/maximum power accessory available on some instruments also offers increased sensitivity with lower atomization temperatures for many elements.

Using the Stabilized Temperature Platform Furnace (STPF) technique, which is a combination of individual techniques, also offers significant interference reduction with improved sensitivity. Sensitivity changes with sample tube age. Discard graphite tubes when

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significant variations in sensitivity or poor reproducibility are observed. The use of high acid concentrations, brine samples, and matrix modifiers often drastically reduces tube life. Preferably use the graphite platform in such situations.

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3113 B. Electrothermal Atomic Absorption Spectrometric Method

1. General Discussion

This method is suitable for determination of micro quantities of aluminum, antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, iron, lead, manganese, molybdenum, nickel, selenium, silver, and tin. It is also applicable to analysis of bismuth, gallium, germanium, gold, indium, mercury, tellurium, thallium, and vanadium, but precision and accuracy data are not yet available.

2. Apparatus

a. Atomic absorption spectrometer: See Section 3111A.6*a*. The instrument must have background correction capability.

b. Source lamps: See Section 3111A.6*d*.

c. Graphite furnace: Use an electrically heated device with electronic control circuitry designed to carry a graphite tube or cup through a heating program that provides sufficient thermal energy to atomize the elements of interest. Furnace heat controllers with only three heating steps are adequate only for fresh waters with low dissolved solids content. For salt waters, brines, and other complex matrices, use a furnace controller with up to seven individually programmed heating steps. Fit the furnace into the sample compartment of the spectrometer in place of the conventional burner assembly. Use argon as a purge gas to minimize oxidation of the furnace tube and to prevent the formation of metallic oxides. Use graphite tubes with platforms to minimize interferences and to improve sensitivity.

d. Readout: See Section 3111A.6*c*.

e. Sample dispensers: Use microliter pipets (5 to 100 µL) or an automatic sampling device designed for the specific instrument.

f. Vent: See Section 3111A.6 *f*.

g. Cooling water supply: Cool with tap water flowing at 1 to 4 L/min or use a recirculating cooling device.

h. Membrane filter apparatus: Use an all-glass filtering device and 0.45-µm or smaller-pore-diameter membrane filters. For trace analysis of aluminum, use polypropylene or TFE devices.

3. Reagents

a. Metal-free water: See Section 3111B.3*c*.

b. Hydrochloric acid, HCl, 1 + 1 and conc.

c. Nitric acid, HNO_3, 1 + 1 and conc.

d. Matrix modifier stock solutions:

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1) *Magnesium nitrate,* 10 000 mg Mg/L: Dissolve 10.5 g $Mg(NO_3)_2 \cdot 6H_2O$ in water. Dilute to 100 mL.

2) *Nickel nitrate,* 10 000 mg Ni/L: Dissolve 4.96 g $Ni(NO_3)_2 \cdot 6H_2O$ in water. Dilute to 100 mL.

3) *Phosphoric acid,* 10% (v/v): Add 10 mL conc H_3PO_4 to water. Dilute to 100 mL.

4) *Palladium nitrate,* 4000 mg Pd/L: Dissolve 8.89 g $Pd(NO_3)_2 \cdot H_2O$ in water. Dilute to 1 L.

5) *Citric acid,* 4%: Dissolve 40 g citric acid in water. Dilute to 1 L.

NOTE: All of the modifier solutions recommended in Table 3113:I can be prepared with volumetric combination of the above solutions and water. For preparation of other matrix modifiers, see references or follow manufacturers' instructions.

e. Stock metal solutions: Refer to Section 3111B and Section 3114.

f. Chelating resin: 100 to 200 mesh#(82)* purified by heating at 60°C in 10*N* NaOH for 24 h. Cool resin and rinse 10 times each with alternating portions of 1*N* HCl, metal-free water, 1*N* NaOH, and metal-free water.

g. Metal-free seawater (or brine): Fill a 1.4-cm-ID × 20-cm-long borosilicate glass column to within 2 cm of the top with purified chelating resin. Elute resin with successive 50-mL portions of 1*N* HCl, metal-free water, 1*N* NaOH, and metal-free water at the rate of 5 mL/min just before use. Pass salt water or brine through the column at a rate of 5 mL/min to extract trace metals present. Discard the first 10 bed volumes (300 mL) of eluate.

4. Procedures

a. Sample pretreatment: Before analysis, pretreat all samples as indicated below. Rinse all glassware with 1 + 1 HNO_3 and water. Carry out digestion procedures in a clean, dust-free laboratory area to avoid sample contamination. For digestion of trace aluminum, use polypropylene or TFE utensils to avoid leachable aluminum from glassware.

1) Dissolved metals—See Section 3030B. For samples requiring arsenic and/or selenium analysis add 3 mL 30% hydrogen peroxide/100 mL sample and an appropriate volume of nickel nitrate solution (see Table 3113:I) before analysis. For all other metals no further pretreatment is required except for adding an optional matrix modifier.

2) Total recoverable metals (Al, Sb, Ba, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Ag, and Sn)—NOTE: Sb and Sn are not recovered unless HCl is used in the digestion. See Section 3030D. Quantitatively transfer digested sample to a 100-mL volumetric flask, add an appropriate amount of matrix modifier (see Table 3113:I), and dilute to volume with water.

3) Total recoverable metals (As, Se)—Transfer 100 mL of shaken sample, 1 mL conc HNO_3, and 2 mL 30% H_2O_2 to a clean, acid-washed 250-mL beaker. Heat on a hot plate without allowing solution to boil until volume has been reduced to about 50 mL. Remove from hot plate and let cool to room temperature. Add an appropriate concentration of nickel (see Table 3113:I),

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and dilute to volume in a 100-mL volumetric flask with water. Substitution of palladium is uneconomical. Nickel may be deleted if palladium is co-added during analysis. Simultaneously prepare a digested blank by substituting water for sample and proceed with digestion as described above.

b. Instrument operation: Mount and align furnace device according to manufacturer's instructions. Turn on instrument and data collection system. Select appropriate light source and adjust to recommended electrical setting. Select proper wavelength and set all conditions according to manufacturer's instructions, including background correction. Background correction is important when elements are determined at short wavelengths or when sample has a high level of dissolved solids. Background correction normally is not necessary at wavelengths longer than 350 nm. If background correction above 350 nm is needed deuterium arc background correction is not useful and other types must be used.

Select proper inert- or sheath-gas flow. In some cases, it is desirable to interrupt the inert-gas flow during atomization. Such interruption results in increased sensitivity by increasing residence time of the atomic vapor in the optical path. Gas interruption also increases background absorption and intensifies interference effects, but modern background correction methods usually eliminate these problems. Consider advantages and disadvantages of this option for each matrix when optimizing analytical conditions.

To optimize graphite furnace conditions, carefully adjust furnace temperature settings to maximize sensitivity and precision and to minimize interferences. Follow manufacturer's instructions.

Use drying temperatures slightly above the solvent boiling point and provide enough time and temperature for complete evaporation without boiling or spattering.

Select atomization temperature by determining the lowest temperature providing maximum sensitivity without significantly eroding precision. Optimize by a series of successive determinations at various atomization temperatures using a standard solution giving an absorbance of 0.2 to 0.5.

The charring temperature must be high enough to maximize volatilization of interfering matrix components yet too low to volatilize the element of interest. With the drying and atomization temperatures set to their optimum values, analyze a standard solution at a series of charring temperatures in increasing increments of 50 to 100°C. When the optimum charring temperature is exceeded, there will be a significant drop in sensitivity. Plot charring temperature versus sample absorbance: the optimum charring temperature is the highest temperature without reduced sensitivity. Verify optimization with major changes in sample matrix.

c. Instrument calibration: Prepare standard solutions for instrument calibration by diluting metal stock solutions. Prepare standard solutions fresh daily.

Prepare a blank and at least three calibration standards in the appropriate concentration range (see Table 3113:II) for correlating element concentration and instrument response. Match the matrix of the standard solutions to those of the samples as closely as possible. In most cases, this simply requires matching the acid background of the samples. For seawaters or brines,

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however, use the metal-free matrix (¶ 3*g*) as the standard solution diluent. In addition, add the same concentration of matrix modifier (if required for sample analysis) to the standard solutions.

Inject a suitable portion of each standard solution, in order of increasing concentration. Analyze each standard solution in triplicate to verify method precision.

Construct an analytical curve by plotting the average peak absorbances or peak areas of the standard solution versus concentration on linear graph paper. Alternatively, use electronic instrument calibration if the instrument has this capability.

d. Sample analysis: Analyze all samples except those demonstrated to be free of matrix interferences (based on recoveries of 85% to 115% for known additions) using the method of standard additions. Analyze all samples at least in duplicate or until reproducible results are obtained. A variation of ≤ 10% is considered acceptable reproducibility. Average replicate values.

1) Direct determination—Inject a measured portion of pretreated sample into the graphite furnace. Use the same volume as was used to prepare the calibration curve. Usually add modifier immediately after the sample, preferably using an automatic sampler or a micropipet. Some methods require modifier to be injected before the sample. Use the same volume and concentration of modifier for all standards and samples. Dry, char, and atomize according to the preset program. Repeat until reproducible results are obtained.

Compare the average absorbance value or peak area to the calibration curve to determine concentration of the element of interest. Alternatively, read results directly if the instrument is equipped with this capability. If absorbance (or concentration) or peak area of the sample is greater than absorbance (concentration) or peak area of the most concentrated standard solution, dilute sample and reanalyze. If very large dilutions are required, another technique (e.g., flame AA or ICP) may be more suitable for this sample. Large dilution factors magnify small errors on final calculation. Keep acid background and concentration of matrix modifier (if present in the solutions) constant. Dilute the sample in a blank solution of acid and matrix modifiers.

Proceed to ¶ 5*a* below.

2) Method of standard additions—Refer to ¶ 4*c* above. The method of standard additions is valid only when it falls in the linear portion of the calibration curve. Once instrument sensitivity has been optimized for the element of interest and the linear range for the element has been established, proceed with sample analyses.

Inject a measured volume of sample into furnace device. Dry, char or ash, and atomize samples according to preset program. Repeat until reproducible results are obtained. Record instrument response in absorbance or concentration as appropriate. Add a known concentration of the element of interest to a separate portion of sample so as not to change significantly the sample volume. Repeat the determination.

Add a known concentration (preferably twice that used in the first addition) to a separate sample portion. Mix well and repeat the determination.

Using linear graph paper, plot average absorbance or instrument response for the sample and

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the additions on the vertical axis against the concentrations of the added element on the horizontal axis, using zero as the concentration for the sample. Draw a straight line connecting the three points and extrapolate to zero absorbance. The intercept at the horizontal axis is the negative of the element concentration in the sample. The concentration axis to the left of the origin should be a mirror image of the axis to the right.

5. Calculations

a. Direct determination:

$$\mu g \text{ metal/L} = C \times F$$

where:

C = metal concentration as read directly from the instrument or from the calibration curve, µg/L, and

F = dilution factor.

b. Method of additions:

$$\mu g \text{ metal/L} = C \times F$$

where:

C = metal concentration as read from the method of additions plot, µg/L, and

F = dilution factor.

6. Precision and Bias

Data typical of the precision and bias obtainable are presented in Table 3113:III, Table 3113:IV, and Table 3113:V.

7. Quality Control

See Section 3020 for specific quality control procedures to be followed during analysis. Although previous indications were that very low optimum concentration ranges were attainable for most metals (see Table 3113:II), data in Table 3113:III using variations of these protocols show that this may not be so. Exercise extreme care when applying this method to the lower concentration ranges. Verify analyst precision at the beginning of each analytical run by making triplicate analyses. Verify autosampler precision by checking volumes (by weight) delivered by the autosampler at routinely used injection volume settings.

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3114 ARSENIC AND SELENIUM BY HYDRIDE GENERATION/ATOMIC ABSORPTION SPECTROMETRY*#(83)

3114 A. Introduction

For general introductory material on atomic absorption spectrometric methods, see Section 3111A.

Two methods are presented in this section: A manual method and a continuous-flow method

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especially recommended for selenium. Continuous-flow automated systems are preferable to manual hydride generators because the effect of sudden hydrogen generation on light-path transparency is removed and any blank response from contamination of the HCl reagent by the elements being determined is incorporated into the background base line.

3114 B. Manual Hydride Generation/Atomic Absorption Spectrometric Method

1. General Discussion

a. Principle: This method is applicable to the determination of arsenic and selenium by conversion to their hydrides by sodium borohydride reagent and transport into an atomic absorption atomizer.

Arsenous acid and selenous acid, the As(III) and Se(IV) oxidation states of arsenic and selenium, respectively, are instantaneously converted by sodium borohydride reagent in acid solution to their volatile hydrides. The hydrides are purged continuously by argon or nitrogen into a quartz cell heated electrically or by the flame of an atomic absorption spectrometer and converted to the gas-phase atoms. The sodium borohydride reducing agent, by rapid generation of the elemental hydrides in an appropriate reaction cell, minimizes dilution of the hydrides by the carrier gas and provides rapid, sensitive determinations of arsenic and selenium.

CAUTION: *Arsenic and selenium and their hydrides are toxic. Handle with care.*

At room temperature and solution pH values of 1 or less, arsenic acid, the As(V) oxidation state of arsenic, is reduced relatively slowly by sodium borohydride to As(III), which is then instantaneously converted to arsine. The arsine atomic absorption peaks commonly are decreased by one-fourth to one-third for As(V) when compared to As(III). Determination of total arsenic requires that all inorganic arsenic compounds be in the As(III) state. Organic and inorganic forms of arsenic are first oxidized to As(V) by acid digestion. The As(V) then is quantitatively reduced to As(III) with sodium or potassium iodide before reaction with sodium borohydride.

Selenic acid, the Se(VI) oxidation state of selenium, is not measurably reduced by sodium borohydride. To determine total selenium by atomic absorption and sodium borohydride, first reduce Se(VI) formed during the acid digestion procedure to Se(IV), being careful to prevent reoxidation by chlorine. Efficiency of reduction depends on temperature, reduction time, and HCl concentration. For 4*N* HCl, heat 1 h at 100°C. For 6*N* HCl, boiling for 10 min is sufficient.[1-3] Alternatively, autoclave samples in sealed containers at 121°C for 1 h. NOTE: Autoclaving in sealed containers may result in incomplete reduction, apparently due to the buildup of chlorine gas. To obtain equal instrument responses for reduced Se(VI) and Se (IV) solutions of equal concentrations, manipulate HCl concentration and heating time. For further details, see Section 3500-Se.

b. Equipment selection:

Certain atomic absorption atomizers and hydride reaction cells are available commercially

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for use with the sodium borohydride reagent. A functional manual system that can be constructed in the laboratory is presented in Figure 3114:1. Irrespective of the hydride reaction cell-atomizer system selected, it must meet the following quality-control considerations: (*a*) it must provide a precise and reproducible standard curve between 0 and 20 µg As or Se/L and an instrumental detection limit between 0.1 and 0.5 µg As or Se/L; (*b*) when carried through the entire procedure, oxidation state couples [As (III) - As (V) or Se (IV) - Se (VI)] must cause equal instrument response; and (*c*) sample digestion must yield 80% or greater recovery of added cacodylic acid (dimethyl arsinic acid) and 90% or greater recovery of added As(III), As(V), Se(VI), or Se(IV).

Quartz atomization cells provide for the most sensitive arsenic and selenium hydride determinations. The quartz cell can be heated electrically or by an air-acetylene flame in an atomic absorption unit.

c. Digestion techniques: Waters and wastewaters may contain varying amounts of organic arsenic compounds and inorganic compounds of As(III), As(V), Se(IV), and Se(VI). To measure total arsenic and selenium in these samples requires sample digestion to solubilize particulate forms and oxidize reduced forms of arsenic and selenium and to convert any organic compounds to inorganic ones. Organic selenium compounds rarely have been demonstrated in water. It is left to the experienced analyst's judgment whether sample digestion is required.

Various alternative digestion procedures are provided in ¶s 4*c* and 4*d* below. Consider sulfuric-nitric-perchloric acid digestion (¶ 4*c*) or sulfuric-nitric acid digestion (Section 3030F) as providing a measure of total recoverable arsenic rather than total arsenic because they do not completely convert certain organic arsenic compounds to As(V). The sulfuric-nitric-perchloric acid digestion effectively destroys organics and most particulates in untreated wastewaters or solid samples, but does not convert all organic arsenicals to As(V). The potassium persulfate digestion (¶ 4*d*) is effective for converting organic arsenic and selenium compounds to As(V) and Se(VI) in potable and surface waters and in most wastewaters.[4]

The HCl-autoclave reduction of Se(VI) described above and in ¶ 4 *f* is an effective digestion procedure for total inorganic selenium; however, it has not been found effective for converting benzene substituted selenium compounds to inorganic selenium. In all cases, verify the effectiveness of digestion methods by carrying samples with known additions of organic As or Se(IV) through the entire procedure.

d. Interferences: Interferences are minimized because the As and Se hydrides are removed from the solution containing most potential interfering substances. Slight response variations occur when acid matrices are varied. Control these variations by treating standards and samples in the same manner. Low concentrations of noble metals (approximately 100 µg/L of Ag, Au, Pt, Pd, etc.), concentrations of copper, lead, and nickel at or greater than 1 mg/L, and concentrations between 0.1 and 1 mg/L of hydride-forming elements (Bi, Sb, Sn, and Te) may suppress the response of As and Se hydrides. Interference by transition metals depends strongly on HCl concentration. Interferences are less pronounced at 4 to 6*N* HCl than at lower concentrations.[5] The presence of As or Se in each other's matrices can cause similar suppression. Reduced

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nitrogen oxides resulting from HNO_3 digestion and nitrite also can suppress instrumental response for both elements. Large concentrations of iodide interfere with the Se determination by reducing Se to its elemental form. Do not use any glassware for determining Se that has been used for iodide reduction of As(V).

To prevent chlorine gas produced in the reduction of Se(VI) to Se(IV) from reoxidizing the Se(IV), generate the hydride within a few hours of the reduction steps or purge the chlorine from the samples by sparging.[6]

Interferences depend on system design and defy quantitative description because of their synergistic effects. Certain waters and wastewaters can contain interferences in sufficient concentration to suppress absorption responses of As and Se. For representative samples in a given laboratory and for initial analyses of unknown wastewaters, add appropriate inorganic forms of As or Se to digested sample portions and measure recovery. If average recoveries are less than 90%, consider using alternative analytical procedures.

e. Detection limit and optimum concentration range: For both arsenic and selenium, analyzed by aspiration into a nitrogen-hydrogen flame after reduction, the method detection limit is 2 μg/L or lower and the optimum concentration range 2 to 20 μg/L.

2. Apparatus

a. Atomic absorption spectrometer equipped with air-acetylene flame and quartz cell with mounting bracket or an electrically heated quartz cell, As and Se electrodeless discharge lamps with power supply, background correction at measurement wavelengths, and appropriate strip-chart recorder. A good-quality 10-mV recorder with high sensitivity and a fast response time is needed.

b. Atomizer: Use one of the following:

1) *Cylindrical quartz cell,* 10 to 20 cm long, bracket-mountable above air-acetylene burner.

2) *Cylindrical quartz cell,* 10 to 20 cm long, electrically heated by external nichrome wire to 800 to 900°C.[7]

3) *Cylindrical quartz cell* with internal fuel rich hydrogen-oxygen (air) flame.[8]

The sensitivity of quartz cells deteriorates over several months of use. Sensitivity sometimes may be restored by treatment with 40% HF. CAUTION: *HF is extremely corrosive. Avoid all contact with exposed skin. Handle with care.*

c. Reaction cell for producing As or Se hydrides: See Figure 3114:1 for an example of a manual, laboratory-made system. A commercially available system is acceptable if it utilizes liquid sodium borohydride reagents; accepts samples digested in accordance with ¶s 4*c*, *d*, and *e*; accepts 4 to 6*N* HCl; and is efficiently and precisely stirred by the purging gas and/or a magnetic stirrer.

d. Eye dropper or syringe capable of delivering 0.5 to 3.0 mL sodium borohydride reagent. Exact and reproducible addition is required so that production of hydrogen gas does not vary

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significantly between determinations.

e. Vent: See Section 3111A.6 *f*.

3. Reagents

a. Sodium borohydride reagent: Dissolve 8 g $NaBH_4$ in 200 mL 0.1*N* NaOH. Prepare fresh daily.

b. Sodium iodide prereductant solution: Dissolve 50 g NaI in 500 mL water. Prepare fresh daily. Alternatively use an equivalent KI solution.

c. Sulfuric acid, 18*N*.

d. Sulfuric acid, 2.5*N*: Cautiously add 35 mL conc H_2SO_4 to about 400 mL water, let cool, and adjust volume to 500 mL.

e. Potassium persulfate, 5% solution: Dissolve 25 g $K_2S_2O_8$ in water and dilute to 500 mL. Store in glass and refrigerate. Prepare weekly.

f. Nitric acid, HNO_3, conc.

g. Perchloric acid, $HClO_4$, conc.

h. Hydrochloric acid, HCl, conc.

i. Argon (or nitrogen), commercial grade.

j. Arsenic(III) solutions:

1) *Stock As(III) solution:* Dissolve 1.320 g arsenic trioxide, As_2O_3, in water containing 4 g NaOH. Dilute to 1 L; 1.00 mL = 1.00 mg As(III).

2) *Intermediate As(III) solution:* Dilute 10 mL stock As solution to 1000 mL with water containing 5 mL conc HCl; 1.00 mL = 10.0 μg As(III).

3) *Standard As(III) solution:* Dilute 10 mL intermediate As(III) solution to 1000 mL with water containing the same concentration of acid used for sample preservation (2 to 5 mL conc HNO_3); 1.00 mL = 0.100 μg As(III). Prepare diluted solutions daily.

k. Arsenic(V) solutions:

1) *Stock As(V) solution:* Dissolve 1.534 g arsenic pentoxide, As_2O_5, in distilled water containing 4 g NaOH. Dilute to 1 L; 1.00 mL = 1.00 mg As(V).

2) *Intermediate As(V) solution:* Prepare as for As(III) above; 1.00 mL = 10.0 μg As(V).

3) *Standard As(V) solution:* Prepare as for As(III) above; 1.00 mL = 0.100 μg As(V).

l. Organic arsenic solutions:

1) *Stock organic arsenic solution:* Dissolve 1.842 g dimethylarsinic acid (cacodylic acid), $(CH_3)_2AsOOH$, in water containing 4 g NaOH. Dilute to 1 L; 1.00 mL = 1.00 mg As. [NOTE: Check purity of cacodylic acid reagent against an intermediate arsenic standard (50 to 100 mg As/L) using flame atomic absorption.]

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2) *Intermediate organic arsenic solution:* Prepare as for As(III) above; 1.00 mL = 10.0 μg As.

3) *Standard organic arsenic solution:* Prepare as for As(III) above; 1.00 mL = 0.100 μg As.

m. Selenium(IV) solutions:

1) *Stock Se(IV) solution:* Dissolve 2.190 g sodium selenite, Na_2SeO_3, in water containing 10 mL HCl and dilute to 1 L; 1.00 mL = 1.00 mg Se(IV).

2) *Intermediate Se(IV) solution:* Dilute 10 mL stock Se(IV) to 1000 mL with water containing 10 mL conc HCl; 1.00 mL = 10.0 μg Se(IV).

3) *Standard Se(IV) solution:* Dilute 10 mL intermediate Se(IV) solution to 1000 mL with water containing the same concentration of acid used for sample preservation (2 to 5 mL conc HNO_3). Prepare solution daily when checking the equivalency of instrument response for Se(IV) and Se(VI); 1.00 mL = 0.100 μg Se(IV).

n. Selenium(VI) solutions:

1) *Stock Se(VI) solution*: Dissolve 2.393 g sodium selenate, Na_2SeO_4, in water containing 10 mL conc HNO_3. Dilute to 1 L; 1.00 mL = 1.00 mg Se(VI).

2) *Intermediate Se(VI) solution:* Prepare as for Se(IV) above; 1.00 mL = 10.0 μg Se (VI).

3) *Standard Se(VI) solution:* Prepare as for Se(IV) above; 1.00 mL = 0.100 μg Se(VI).

4. Procedure

a. Apparatus setup: Either see Figure 3114:1 or follow manufacturer's instructions. Connect inlet of reaction cell with auxiliary purging gas controlled by flow meter. If a drying cell between the reaction cell and atomizer is necessary, use only anhydrous $CaCl_2$ but not $CaSO_4$ because it may retain SeH_2. Before using the hydride generation/analysis system, optimize operating parameters. Align quartz atomizers for maximum absorbance. Aspirate a blank until memory effects are removed. Establish purging gas flow, concentration and rate of addition of sodium borohydride reagent, solution volume, and stirring rate for optimum instrument response for the chemical species to be analyzed. Optimize quartz cell temperature. If sodium borohydride reagent is added too quickly, rapid evolution of hydrogen will unbalance the system. If the volume of solution being purged is too large, the absorption signal will be decreased. Recommended wavelengths are 193.7 and 196.0 nm for As and Se, respectively.

b. Instrument calibration standards: Transfer 0.00, 1.00, 2.00, 5.00, 10.00, 15.00, and 20.00 mL standard solutions of As(III) or Se(IV) to 100-mL volumetric flasks and bring to volume with water containing the same acid concentration used for sample preservation (commonly 2 to 5 mL conc HNO_3/L). This yields blank and standard solutions of 0, 1, 2, 5, 10, 15, and 20 μg As or Se/L. Prepare fresh daily. In all cases, standards must be carried through the same digestion protocol as the samples to monitor digestion effectiveness.

c. Preparation of samples and standards for total recoverable arsenic and selenium: Use

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digestion procedure described in 3030F for samples and standards. Alternatively, add 50 mL sample, As(III), or Se(IV) standard to 200-mL Berzelius beaker or 100-mL micro-kjeldahl flask. Add 7 mL 18*N* H_2SO_4 and 5 mL conc HNO_3. Add a small boiling chip or glass beads if necessary. Evaporate to SO_3 fumes. Maintain oxidizing conditions at all times by adding small amounts of HNO_3 to prevent solution from darkening. Maintain an excess of HNO_3 until all organic matter is destroyed. Complete digestion usually is indicated by a light-colored solution. Cool slightly, add 25 mL water and 1 mL conc $HClO_4$ and again evaporate to SO_3 fumes to expel oxides of nitrogen. CAUTION: *See Section 3030H for cautions on use of $HClO_4$*. Monitor effectiveness of either digestion procedure used by adding 5 mL of standard organic arsenic solution or 5 mL of a standard selenium solution to a 50-mL sample and measuring recovery, carrying standards and the sample with known addition through entire procedure. To report total recoverable arsenic as total arsenic, average recoveries of cacodylic acid must exceed 80%. After final evaporation of SO_3 fumes, dilute to 50 mL for arsenic measurements or to 30 mL for selenium measurements. For analysis of both elements in a single sample, increase sample volume to 100 mL and double the volumes of acids used in the digestion. Adjust final digestate volume to 100 mL. Use 50 mL for As and 30 mL for Se determinations, making appropriate volume corrections in calculating results.

d. Preparation of samples and standards for total arsenic and selenium: Add 50 mL undigested sample or standard to a 200-mL Berzelius beaker or 100-mL micro-kjeldahl flask. Add 1 mL 2.5*N* H_2SO_4 and 5 mL 5% $K_2S_2O_8$. Boil gently on a pre-heated hot plate for approximately 30 to 40 min or until a final volume of 10 mL is reached. Do not let sample go to dryness. Alternatively heat in an autoclave at 121°C for 1 h in capped containers. After manual digestion, dilute to 50 mL for subsequent arsenic measurements and to 30 mL for selenium measurements. Monitor effectiveness of digestion by measuring recovery of As or Se as above. If poor recovery of arsenic added as cacodylic acid is obtained, reanalyze using double the amount of $K_2S_2O_8$. For analysis of both elements in a single sample, increase sample volume to 100 mL and double the volumes of acids used in the digestion. Adjust final digestate volume to 100 mL. Use 50 mL for As and 30 mL for Se determinations, making appropriate volume corrections in calculating results.

e. Determination of arsenic with sodium borohydride: To 50 mL digested standard or sample in a 200-mL Berzelius beaker (see Figure 3114:1) add 5 mL conc HCl and mix. Add 5 mL NaI prereductant solution, mix, and wait at least 30 min. (NOTE: The NaI reagent has not been found necessary for certain hydride reaction cell designs if a 20 to 30% loss in instrument sensitivity is not important and variables of solution acid conditions, temperatures, and volumes for production of As(V) and arsine can be controlled strictly. Such control requires an automated delivery system; see Section 3114C.)

Attach one Berzelius beaker at a time to the rubber stopper containing the gas dispersion tube for the purging gas, the sodium borohydride reagent inlet, and the outlet to the quartz cell. Turn on strip-chart recorder and wait until the base line is established by the purging gas and all

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air is expelled from the reaction cell. Add 0.5 mL sodium borohydride reagent. After the instrument absorbance has reached a maximum and returned to the base line, remove beaker, rinse dispersion tube with water, and proceed to the next sample or standard. Periodically compare standard As(III) and As(V) curves for response consistency. Check for presence of chemical interferences that suppress instrument response for arsine by treating a digested sample with 10 µg/L As(III) or As(V) as appropriate. Average recoveries should be not less than 90%.

f. Determination of selenium with sodium borohydride: To 30 mL digested standard or sample in a 200-mL Berzelius beaker or 100-mL micro-kjeldahl flask, add 15 mL conc HCl and mix. Heat for a predetermined period at 90 to 100°C. Alternatively autoclave at 121°C in capped containers for 60 min, or heat for a predetermined time in open test tubes using a 90 to 100°C hot water bath or an aluminum block digester. Check effectiveness of the selected heating time by demonstrating equal instrument responses for calibration curves prepared either from standard Se(IV) or from Se(VI) solutions. Effective heat exposure for converting Se(VI) to Se(IV), with no loss of Se(IV), ranges between 5 and 60 min when open beakers or test tubes are used. Establish a heating time for effective conversion and apply this time to all samples and standards. Do not digest standard Se(IV) and Se(VI) solutions used for this check of equivalency. After prereduction of Se(VI) to Se(IV), attach Berzelius beakers, one at a time, to the purge apparatus. For each, turn on the strip-chart recorder and wait until the base line is established. Add 0.50 mL sodium borohydride reagent. After the instrument absorbance has reached a maximum and returned to the base line, remove beaker, rinse dispersion tube with water, and proceed to the next sample or standard. Check for presence of chemical interferences that suppress selenium hydride instrument response by treating a digested sample with 10 µg Se (IV)/L. Average recoveries should be not less than 90%.

5. Calculation

Construct a standard curve by plotting peak heights or areas of standards versus concentration of standards. Measure peak heights or areas of samples and read concentrations from curve. If sample was diluted (or concentrated) before sample digestion, apply an appropriate factor. On instruments so equipped, read concentrations directly after standard calibration.

6. Precision and Bias

Single-laboratory, single-operator data were collected forAs(III) and organic arsenic by both manual and automated methods, and for the manual determination of selenium. Recovery values (%) from seven replicates are given below:

Method	As(III)	Org As	Se(IV)	Se(VI)
Manual with digestion	91.8	87.3	—	—
Manual without digestion	109.4	19.4	100.6	110.8
Automated with digestion	99.8	98.4	—	—

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Method	As(III)	Org As	Se(IV)	Se(VI)
Automated without digestion	92.5	10.4	—	—

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3114 C. Continuous Hydride Generation/Atomic Absorption Spectrometric Method

1. General Discussion

The continuous hydride generator offers the advantages of simplicity in operation, excellent reproducibility, low detection limits, and high sample volume throughput for selenium analysis following preparations as described in Section 3500-Se.B or Section 3114B.4*c* and *d*.

a. Principle: See Section 3114B.

b. Interferences: Free chlorine in hydrochloric acid is a common but difficult-to-diagnose interference. (The amount of chlorine varies with manufacturer and with each lot from the same manufacturer). Chlorine oxidizes the hydride and can contaminate the hydride generator to prevent recoveries under any conditions. When interference is encountered, or preferably before using each new bottle of HCl, eliminate chlorine from a 2.3-L bottle of conc HCl by bubbling with helium (commercial grade, 100 mL/min) for 3 h.

Excess oxidant (peroxide, persulfate, or permanganate) from the total selenium digestion can oxidize the hydride. Follow procedures in 3500-Se.B.2, 3, or 4 to ensure removal of all oxidizing agents before hydride generation.

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Nitrite is a common trace constituent in natural and waste waters, and at levels as low as 10 µg/L nitrite can reduce the recovery of hydrogen selenide from Se(IV) by over 50%. Moreover, during the reduction of Se(VI) to Se(IV) by digestion with HCl (3500-Se.B.5), some nitrate is converted to nitrite, which subsequently interferes. When this interference is suspected, add sulfanilamide after sample acidification (or HCl digestion). The diazotization reaction between nitrite and sulfanilamide completely removes the interferent effect (i.e., the standard addition slope is normal).

2. Apparatus

a. Continuous hydride generator: The basic unit is composed of two parts: a precision peristaltic pump, which is used to meter and mix reagents and sample solutions, and the gas-liquid separator. At the gas-liquid separator a constant flow of argon strips out the hydrogen and metal hydride gases formed in the reaction and carries them to the heated quartz absorption cell (Section 3114B.1*b* and Section 3114B.2*b*), which is supported by a metal bracket mounted on top of the regular air acetylene burner head. The spent liquid flows out of the separator via a constant level side drain to a waste bucket. Schematics and operating parameters are shown in Figure 3114:2.

Check flow rates frequently to ensure a steady flow; an uneven flow in any tubing will cause an erratic signal. Remove tubings from pump rollers when not in use. Typical flow rates are: sample, 7 mL/min; acid, 1 mL/min; borohydride reagent, 1 mL/min. Argon flow usually is pre-fixed, typically at 90 mL/min.

b. Atomic absorption spectrometric equipment: See Section 3111A.6.

3. Reagents

a. Hydrochloric acid, HCl, 5 + 1: Handle conc HCl under a fume hood. If necessary, remove free Cl_2 by stripping conc HCl with helium as described above.

b. Borohydride reagent: Dissolve 0.6 g $NaBH_4$ and 0.5 g NaOH in 100 mL water.

CAUTION: *Sodium borohydride is toxic, flammable, and corrosive.*

c. Selenium reference standard solution, 1000 mg/L: Use commercially available standard; verify that selenium is Se(IV).

d. Intermediate standard solution, 1 mg/L: Dilute 1 mL reference standard solution to 1 L in a volumetric flask with distilled water.

e. Working standard solutions, 5, 10, 20, 30, and 40 µg/L: Dilute 0.5, 1.0, 2.0, 3.0, and 4.0 mL intermediate standard solution to 100 mL in a volumetric flask.

f. Sulfanilamide solution: Prepare a 2.5% (w/v) solution daily; add several drops conc HCl per 50 mL solution to facilitate dissolution.

4. Procedure

a. Sample preparation: See Section 3500-Se or Section 3114B.4*c* and *d* for preparation

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steps for various Se fractions or total Se.

b. Preconditioning hydride generator: For newly installed tubing, turn on pump for at least 10 to 15 min before instrument calibration. Sample the highest standard for a few minutes to let volatile hydride react with the reactive sites in the transfer lines and on the quartz absorption cell surfaces.

c. Instrument calibration: Depending on total void volume in sample tubing, sampling time of 15 to 20 s generally is sufficient to obtain a steady signal. Between samples, submerge uptake tube in rinse water. Calibrate instrument daily after a 45-min lamp warmup time. Use either the hollow cathode or the electrodeless discharge lamp.

d. Antifoaming agents: Certain samples, particularly wastewater samples containing a high concentration of proteinaceous substances, can cause excessive foaming that could carry the liquid directly into the heated quartz absorption cell and cause splattering of salty deposits onto the windows of the spectrometer. Add a drop of antifoaming agent*#(84) to eliminate this problem.

e. Nitrite removal: After samples have been acidified, or after acid digestion, add 0.1 mL sulfanilamide solution per 10 mL sample and let react for 2 min.

f. Analysis: Follow manufacturer's instructions for operation of analytical equipment.

5. Calculation

Construct a calibration curve based on absorbance vs. standard concentration. Apply dilution factors on diluted samples.

6. Precision and Bias

Working standards were analyzed together with batches of

water samples on a routine production basis. The standards werecompounded using chemically pure sodium selenite and sodiumselenate. The values of Se(IV) + Se(VI) were determined byconverting Se(VI) to Se(IV) by digestion with HCl. Results aretabulated below.

No. Analyses	Mean Se(IV) µg/L	Rel. Dev. %	Se(IV) + Se(VI) µg/L	Rel. Del. %
21	4.3	12	10.3	7
26	8.5	12	19.7	6
22	17.2	7	39.2	8
20	52.8	5	106.0	6

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3120 METALS BY PLASMA EMISSION SPECTROSCOPY*#(85)

3120 A. Introduction

1. General Discussion

Emission spectroscopy using inductively coupled plasma (ICP) was developed in the mid-1960's[1,2] as a rapid, sensitive, and convenient method for the determination of metals in water and wastewater samples.[3-6] Dissolved metals are determined in filtered and acidified samples. Total metals are determined after appropriate digestion. Care must be taken to ensure that potential interferences are dealt with, especially when dissolved solids exceed 1500 mg/L.

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3120 B. Inductively Coupled Plasma (ICP) Method

1. General Discussion

a. Principle: An ICP source consists of a flowing stream of argon gas ionized by an applied radio frequency field typically oscillating at 27.1 MHz. This field is inductively coupled to the ionized gas by a water-cooled coil surrounding a quartz ‘‘torch’’ that supports and confines the plasma. A sample aerosol is generated in an appropriate nebulizer and spray chamber and is carried into the plasma through an injector tube located within the torch. The sample aerosol is injected directly into the ICP, subjecting the constituent atoms to temperatures of about 6000 to 8000°K.[1] Because this results in almost complete dissociation of molecules, significant reduction in chemical interferences is achieved. The high temperature of the plasma excites atomic emission efficiently. Ionization of a high percentage of atoms produces ionic emission spectra. The ICP provides an optically ‘‘thin’’ source that is not subject to self-absorption except at very high concentrations. Thus linear dynamic ranges of four to six orders of magnitude are observed for many elements.[2]

The efficient excitation provided by the ICP results in low detection limits for many elements. This, coupled with the extended dynamic range, permits effective multielement determination of metals.[3] The light emitted from the ICP is focused onto the entrance slit of either a monochromator or a polychromator that effects dispersion. A precisely aligned exit slit is used to isolate a portion of the emission spectrum for intensity measurement using a photomultiplier tube. The monochromator uses a single exit slit/photomultiplier and may use a computer-controlled scanning mechanism to examine emission wavelengths sequentially. The polychromator uses multiple fixed exit slits and corresponding photomultiplier tubes; it simultaneously monitors all configured wavelengths using a computer-controlled readout system. The sequential approach provides greater wavelength selection while the simultaneous

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approach can provide greater sample throughput.

b. Applicable metals and analytical limits: Table 3120:I lists elements for which this method applies, recommended analytical wavelengths, and typical estimated instrument detection limits using conventional pneumatic nebulization. Actual working detection limits are sample-dependent. Typical upper limits for linear calibration also are included in Table 3120:I.

c. Interferences: Interferences may be categorized as follows:

1) Spectral interferences—Light emission from spectral sources other than the element of interest may contribute to apparent net signal intensity. Sources of spectral interference include direct spectral line overlaps, broadened wings of intense spectral lines, ion-atom recombination continuum emission, molecular band emission, and stray (scattered) light from the emission of elements at high concentrations.[4] Avoid line overlaps by selecting alternate analytical wavelengths. Avoid or minimize other spectral interference by judicious choice of background correction positions. A wavelength scan of the element line region is useful for detecting potential spectral interferences and for selecting positions for background correction. Make corrections for residual spectral interference using empirically determined correction factors in conjunction with the computer software supplied by the spectrometer manufacturer or with the calculation detailed below. The empirical correction method cannot be used with scanning spectrometer systems if the analytical and interfering lines cannot be precisely and reproducibly located. In addition, if using a polychromator, verify absence of spectral interference from an element that could occur in a sample but for which there is no channel in the detector array. Do this by analyzing single-element solutions of 100 mg/L concentration and noting for each element channel the apparent concentration from the interfering substance that is greater than the element's instrument detection limit.

2) Nonspectral interferences

a) Physical interferences are effects associated with sample nebulization and transport processes. Changes in the physical properties of samples, such as viscosity and surface tension, can cause significant error. This usually occurs when samples containing more than 10% (by volume) acid or more than 1500 mg dissolved solids/L are analyzed using calibration standards containing ≤ 5% acid. Whenever a new or unusual sample matrix is encountered, use the test described in ¶ 4*g*. If physical interference is present, compensate for it by sample dilution, by using matrix-matched calibration standards, or by applying the method of standard addition (see ¶ 5*d* below).

High dissolved solids content also can contribute to instrumental drift by causing salt buildup at the tip of the nebulizer gas orifice. Using prehumidified argon for sample nebulization lessens this problem. Better control of the argon flow rate to the nebulizer using a mass flow controller improves instrument performance.

b) Chemical interferences are caused by molecular compound formation, ionization effects, and thermochemical effects associated with sample vaporization and atomization in the plasma. Normally these effects are not pronounced and can be minimized by careful selection of

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operating conditions (incident power, plasma observation position, etc.). Chemical interferences are highly dependent on sample matrix and element of interest. As with physical interferences, compensate for them by using matrix matched standards or by standard addition (¶ 5*d*). To determine the presence of chemical interference, follow instructions in ¶ 4*g*.

2. Apparatus

a. ICP source: The ICP source consists of a radio frequency (RF) generator capable of generating at least 1.1 KW of power, torch, tesla coil, load coil, impedance matching network, nebulizer, spray chamber, and drain. High-quality flow regulators are required for both the nebulizer argon and the plasma support gas flow. A peristaltic pump is recommended to regulate sample flow to the nebulizer. The type of nebulizer and spray chamber used may depend on the samples to be analyzed as well as on the equipment manufacturer. In general, pneumatic nebulizers of the concentric or cross-flow design are used. Viscous samples and samples containing particulates or high dissolved solids content (>5000 mg/L) may require nebulizers of the Babington type.[5]

b. Spectrometer: The spectrometer may be of the simultaneous (polychromator) or sequential (monochromator) type with air-path, inert gas purged, or vacuum optics. A spectral bandpass of 0.05 nm or less is required. The instrument should permit examination of the spectral background surrounding the emission lines used for metals determination. It is necessary to be able to measure and correct for spectral background at one or more positions on either side of the analytical lines.

3. Reagents and Standards

Use reagents that are of ultra-high-purity grade or equivalent. Redistilled acids are acceptable. Except as noted, dry all salts at 105°C for 1 h and store in a desiccator before weighing. Use deionized water prepared by passing water through at least two stages of deionization with mixed bed cation/anion exchange resins.[6] Use deionized water for preparing all calibration standards, reagents, and for dilution.

a. Hydrochloric acid, HCl, conc and 1+1.

b. Nitric acid, HNO_3, conc.

c. Nitric acid, HNO_3, 1+1: Add 500 mL conc HNO_3 to 400 mL water and dilute to 1 L.

d. Standard stock solutions: See Section 3111B, Section 3111D, and Section 3114B.

CAUTION: *Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling.*

1) *Aluminum:* See Section 3111D.3*k*1).

2) *Antimony:* See Section 3111B.3 *j*1).

3) *Arsenic:* See Section 3114B.3*k*1).

4) *Barium:* See Section 3111D.3*k*2).

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5) *Beryllium:* See Section 3111D.3*k*3).

6) *Boron: Do not dry* but keep bottle tightly stoppered and store in a desiccator. Dissolve 0.5716 g anhydrous H_3BO_3 in water and dilute to 1000 mL; 1 mL = 100 μg B.

7) *Cadmium:* See Section 3111B.3 *j*3).

8) *Calcium:* See Section 3111B.3 *j*4).

9) *Chromium:* See Section 3111B.3 *j*6).

10) *Cobalt:* See Section 3111B.3 *j*7).

11) *Copper*: See Section 3111B.3 *j*8).

12) *Iron:* See Section 3111B.3 *j*11).

13) *Lead:* See Section 3111B.3 *j*12).

14) *Lithium:* See Section 3111B.3 *j*13).

15) *Magnesium:* See Section 3111B.3 *j*14).

16) *Manganese:* See Section 3111B.3 *j*15).

17) *Molybdenum:* See Section 3111D.3*k*4).

18) *Nickel:* See Section 3111B.3 *j*16).

19) *Potassium:* See Section 3111B.3 *j*19).

20) *Selenium:* See Section 3114B.3*n*1).

21) *Silica:* See Section 3111D.3*k*7).

22) *Silver:* See Section 3111B.3 *j*22).

23) *Sodium:* See Section 3111B.3 *j*23).

24) *Strontium:* See Section 3111B.3 *j*24).

25) *Thallium:* See Section 3111B.3 *j*25).

26) *Vanadium:* See Section 3111D.3*k*10).

27) *Zinc:* See Section 3111B.3 *j*27).

e. Calibration standards: Prepare mixed calibration standards containing the concentrations shown in Table 3120:I by combining appropriate volumes of the stock solutions in 100-mL volumetric flasks. Add 2 mL 1+1 HNO_3 and 10 mL 1+1 HCl and dilute to 100 mL with water. Before preparing mixed standards, analyze each stock solution separately to determine possible spectral interference or the presence of impurities. When preparing mixed standards take care that the elements are compatible and stable. Store mixed standard solutions in an FEP fluorocarbon or unused polyethylene bottle. Verify calibration standards initially using the quality control standard; monitor weekly for stability. The following are recommended combinations using the suggested analytical lines in Table 3120:I. Alternative combinations are acceptable.

1) *Mixed standard solution I:* Manganese, beryllium, cadmium, lead, selenium, and zinc.

2) *Mixed standard solution II:* Barium, copper, iron, vanadium, and cobalt.

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3) *Mixed standard solution III:* Molybdenum, silica, arsenic, strontium, and lithium.

4) *Mixed standard solution IV:* Calcium, sodium, potassium, aluminum, chromium, and nickel.

5) *Mixed standard solution V:* Antimony, boron, magnesium, silver, and thallium. If addition of silver results in an initial precipitation, add 15 mL water and warm flask until solution clears. Cool and dilute to 100 mL with water. For this acid combination limit the silver concentration to 2 mg/L. Silver under these conditions is stable in a tap water matrix for 30 d. Higher concentrations of silver require additional HCl.

f. Calibration blank: Dilute 2 mL 1+1 HNO_3 and 10 mL 1+1 HCl to 100 mL with water. Prepare a sufficient quantity to be used to flush the system between standards and samples.

g. Method blank: Carry a reagent blank through entire sample preparation procedure. Prepare method blank to contain the same acid types and concentrations as the sample solutions.

h. Instrument check standard: Prepare instrument check standards by combining compatible elements at a concentration of 2 mg/L.

i. Instrument quality control sample: Obtain a certified aqueous reference standard from an outside source and prepare according to instructions provided by the supplier. Use the same acid matrix as the calibration standards.

j. Method quality control sample: Carry the instrument quality control sample (¶ 3*i*) through the entire sample preparation procedure.

k. Argon: Use technical or welder's grade. If gas appears to be a source of problems, use prepurified grade.

4. Procedure

a. Sample preparation: See Section 3030F.

b. Operating conditions: Because of differences among makes and models of satisfactory instruments, no detailed operating instructions can be provided. Follow manufacturer's instructions. Establish instrumental detection limit, precision, optimum background correction positions, linear dynamic range, and interferences for each analytical line. Verify that the instrument configuration and operating conditions satisfy the analytical requirements and that they can be reproduced on a day-to-day basis. An atom-to-ion emission intensity ratio [Cu(I) 324.75 nm/ Mn(II) 257.61 nm] can be used to reproduce optimum conditions for multielement analysis precisely. The Cu/Mn intensity ratio may be incorporated into the calibration procedure, including specifications for sensitivity and for precision.[7] Keep daily or weekly records of the Cu and Mn intensities and/or the intensities of critical element lines. Also record settings for optical alignment of the polychromator, sample uptake rate, power readings (incident, reflected), photomultiplier tube attenuation, mass flow controller settings, and system maintenance.

c. Instrument calibration: Set up instrument as directed (¶ b). Warm up for 30 min. For polychromators, perform an optical alignment using the profile lamp or solution. Check

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alignment of plasma torch and spectrometer entrance slit, particularly if maintenance of the sample introduction system was performed. Make Cu/Mn or similar intensity ratio adjustment.

Calibrate instrument according to manufacturer's recommended procedure using calibration standards and blank. Aspirate each standard or blank for a minimum of 15 s after reaching the plasma before beginning signal integration. Rinse with calibration blank or similar solution for at least 60 s between each standard to eliminate any carryover from the previous standard. Use average intensity of multiple integrations of standards or samples to reduce random error.

Before analyzing samples, analyze instrument check standard. Concentration values obtained should not deviate from the actual values by more than ±5% (or the established control limits, whichever is lower).

d. Analysis of samples: Begin each sample run with an analysis of the calibration blank, then analyze the method blank. This permits a check of the sample preparation reagents and procedures for contamination. Analyze samples, alternating them with analyses of calibration blank. Rinse for at least 60 s with dilute acid between samples and blanks. After introducing each sample or blank let system equilibrate before starting signal integration. Examine each analysis of the calibration blank to verify that no carry-over memory effect has occurred. If carry-over is observed, repeat rinsing until proper blank values are obtained. Make appropriate dilutions and acidifications of the sample to determine concentrations beyond the linear calibration range.

e. Instrumental quality control: Analyze instrument check standard once per 10 samples to determine if significant instrument drift has occurred. If agreement is not within ± 5% of the expected values (or within the established control limits, whichever is lower), terminate analysis of samples, correct problem, and recalibrate instrument. If the intensity ratio reference is used, resetting this ratio may restore calibration without the need for reanalyzing calibration standards. Analyze instrument check standard to confirm proper recalibration. Reanalyze one or more samples analyzed just before termination of the analytical run. Results should agree to within ± 5%, otherwise all samples analyzed after the last acceptable instrument check standard analysis must be reanalyzed.

Analyze instrument quality control sample within every run. Use this analysis to verify accuracy and stability of the calibration standards. If any result is not within ± 5% of the certified value, prepare a new calibration standard and recalibrate the instrument. If this does not correct the problem, prepare a new stock solution and a new calibration standard and repeat calibration.

f. Method quality control: Analyze the method quality control sample within every run. Results should agree to within ± 5% of the certified values. Greater discrepancies may reflect losses or contamination during sample preparation.

g. Test for matrix interference: When analyzing a new or unusual sample matrix verify that neither a positive nor negative nonlinear interference effect is operative. If the element is present at a concentration above 1 mg/L, use serial dilution with calibration blank. Results from the analyses of a dilution should be within ± 5% of the original result. Alternately, or if the concentration is either below 1 mg/L or not detected, use a post-digestion addition equal to 1

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mg/L. Recovery of the addition should be either between 95% and 105% or within established control limits of ± 2 standard deviations around the mean. If a matrix effect causes test results to fall outside the critical limits, complete the analysis after either diluting the sample to eliminate the matrix effect while maintaining a detectable concentration of at least twice the detection limit or applying the method of standard additions.

5. Calculations and Corrections

a. Blank correction: Subtract result of an adjacent calibration blank from each sample result to make a baseline drift correction. (Concentrations printed out should include negative and positive values to compensate for positive and negative baseline drift. Make certain that the calibration blank used for blank correction has not been contaminated by carry-over.) Use the result of the method blank analysis to correct for reagent contamination. Alternatively, intersperse method blanks with appropriate samples. Reagent blank and baseline drift correction are accomplished in one subtraction.

b. Dilution correction: If the sample was diluted or concentrated in preparation, multiply results by a dilution factor (*DF*) calculated as follows:

$$DF = \frac{\text{Final weight or volume}}{\text{Initial weight or volume}}$$

c. Correction for spectral interference: Correct for spectral interference by using computer software supplied by the instrument manufacturer or by using the manual method based on interference correction factors. Determine interference correction factors by analyzing single-element stock solutions of appropriate concentrations under conditions matching as closely as possible those used for sample analysis. Unless analysis conditions can be reproduced accurately from day to day, or for longer periods, redetermine interference correction factors found to affect the results significantly each time samples are analyzed.[7,8] Calculate interference correction factors (K_{ij}) from apparent concentrations observed in the analysis of the high-purity stock solutions:

$$K_{ij} = \frac{\text{Apparent concentration of element } i}{\text{Actual concentration of interfering element } j}$$

where the apparent concentration of element *i* is the difference between the observed concentration in the stock solution and the observed concentration in the blank. Correct sample concentrations observed for element *i* (already corrected for baseline drift), for spectral interferences from elements *j*, *k*, and *l*; for example:

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Concentration of element i corrected for spectral interference

$$= \text{Observed concentration of } i - (K_{ij})\,\text{Observed concentration of interfering element } j - (K_{ik})\,\text{Observed concentration of interfering element } k - (K_{il})\,\text{Observed concentration of interfering element } l$$

Interference correction factors may be negative if background correction is used for element *i*. A negative K_{ij} can result where an interfering line is encountered at the background correction wavelength rather than at the peak wavelength. Determine concentrations of interfering elements *j*, *k*, and *l* within their respective linear ranges. Mutual interferences (*i* interferes with *j* and *j* interferes with *i*) require iterative or matrix methods for calculation.

d. Correction for nonspectral interference: If nonspectral interference correction is necessary, use the method of standard additions. It is applicable when the chemical and physical form of the element in the standard addition is the same as in the sample, *or* the ICP converts the metal in both sample and addition to the same form; the interference effect is independent of metal concentration over the concentration range of standard additions; and the analytical calibration curve is linear over the concentration range of standard additions.

Use an addition not less than 50% nor more than 100% of the element concentration in the sample so that measurement precision will not be degraded and interferences that depend on element/interferent ratios will not cause erroneous results. Apply the method to all elements in the sample set using background correction at carefully chosen off-line positions. Multielement standard addition can be used if it has been determined that added elements are not interferents.

e. Reporting data: Report analytical data in concentration units of milligrams per liter using up to three significant figures. Report results below the determined detection limit as not detected less than the stated detection limit corrected for sample dilution.

6. Precision and Bias

As a guide to the generally expected precision and bias, see the linear regression equations in Table 3120:II.[9] Additional interlaboratory information is available.[10]

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3125 METALS BY INDUCTIVELY COUPLED PLASMA/MASS SPECTROMETRY*#(86)

3125 A. Introduction

1. General Discussion

This method is used for the determination of trace metals and metalloids in surface, ground, and drinking waters by inductively coupled plasma/mass spectrometry (ICP/MS). It may also be suitable for wastewater, soils, sediments, sludge, and biological samples after suitable digestion followed by dilution and/or cleanup.[1,2] Additional sources of information on quality assurance and other aspects of ICP/MS analysis of metals are available.[3-5]

The method is intended to be performance-based, allowing extension of the elemental analyte

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list, implementation of ‘‘clean’’ preparation techniques as they become available, and other appropriate modifications of the base method as technology evolves. Preferably validate modifications to the base method by use of the quality control standards specified in the method.

Instrument detection limits for many analytes are between 1 and 100 ng/L. The method is best suited for the determination of metals in ambient or pristine fresh-water matrices. More complex matrices may require some type of cleanup to reduce matrix effects to a manageable level. Various cleanup techniques are available to reduce matrix interferences and/or concentrate analytes of interest.[6-10]

This method is ideally used by analysts experienced in the use of ICP/MS, the interpretation of spectral and matrix interference, and procedures for their correction. Preferably demonstrate analyst proficiency through analysis of a performance evaluation sample before the generation of data.

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3125 B. Inductively Coupled Plasma/Mass Spectrometry (ICP/MS) Method

1. General Discussion

a. Principle: Sample material is introduced into an argon-based, high-temperature radio-frequency plasma, usually by pneumatic nebulization. Energy transfer from the plasma to the sample stream causes desolvation, atomization, and ionization of target elements. Ions generated by these energy-transfer processes are extracted from the plasma through a differential vacuum interface, and separated on the basis of their mass-to-charge ratio by a mass spectrometer. The mass spectrometer usually is of the quadrupole or magnetic sector type. The ions passing through the mass spectrometer are counted, usually by an electron multiplier detector, and the resulting information processed by a computer-based data-handling system.

b. Applicable elements and analytical limits: This method is suitable for aluminum, antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, molybdenum, nickel, selenium, silver, strontium, thallium, uranium, vanadium, and zinc. The method is also acceptable for other elemental analytes as long as the same quality assurance practices are followed. The basic element suite and recommended analytical masses are given in Table 3125:I.

Typical instrument detection limits (IDL)[1,2] for method analytes are presented in Table 3125:I. Determine the IDL and method detection level (or limit) (MDL) for all analytes before method implementation. Section 1030 contains additional information and approaches for the evaluation of detection capabilities.

The MDL is defined in Section 1010C and elsewhere.[2] Determination of the MDL for each element is critical for complex matrices such as seawater, brines, and industrial effluents. The MDL will typically be higher than the IDL, because of background analyte in metals preparation and analysis laboratories and matrix-based interferences. Determine both IDL and MDL upon initial implementation of this method, and then yearly or whenever the instrument configuration changes or major maintenance occurs, whichever comes first.

Determine linear dynamic ranges (LDR) for all method analytes. LDR is defined as the maximum concentration of analyte above the highest calibration point where analyte response is within ±10% of the theoretical response. When determining linear dynamic ranges, avoid using unduly high concentrations of analyte that might damage the detector. Determine LDR on multielement mixtures, to account for possible interelement effects. Determine LDR on initial implementation of this method, and then yearly.

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c. Interferences: ICP/MS is subject to several types of interferences.

1) Isotopes of different elements that form ions of the same nominal mass-to-charge ratio are not resolved by the quadrupole mass spectrometer, and cause isobaric elemental interferences. Typically, ICP/MS instrument operating software will have all known isobaric interferences entered, and will perform necessary calculations automatically. Table 3125:II shows many of the commonly used corrections. Monitor the following additional masses: ^{83}Kr, ^{99}Ru, ^{118}Sn, and ^{125}Te. It is necessary to monitor these masses to correct for isobaric interference caused by ^{82}Kr on ^{82}Se, by ^{98}Ru on ^{98}Mo, by ^{114}Sn on ^{114}Cd, and by ^{123}Te on ^{123}Sb. Monitor ArCl at mass 77, to estimate chloride interferences. Verify that all elemental and molecular correction equations used in this method are correct and appropriate for the mass spectrometer used and sample matrix.

2) Abundance sensitivity is an analytical condition in which the tails of an abundant mass peak contribute to or obscure adjacent masses. Adjust spectrometer resolution to minimize these interferences.

3) Polyatomic (molecular) ion interferences are caused by ions consisting of more than one atom and having the same nominal mass-to-charge ratio as the isotope of interest. Most of the common molecular ion interferences have been identified and are listed in Table 3125:III. Because of the severity of chloride ion interference on important analytes, particularly arsenic and selenium, hydrochloric acid is not recommended for use in preparation of any samples to be analyzed by ICP/MS. The mathematical corrections for chloride interferences only correct chloride to a concentration of 0.4%. Because chloride ion is present in most environmental samples, it is critical to use chloride correction equations for affected masses. A high-resolution ICP/MS may be used to resolve interferences caused by polyatomic ions. Polyatomic interferences are strongly influenced by instrument design and plasma operating conditions, and can be reduced in some cases by careful adjustment of nebulizer gas flow and other instrument operating parameters.

4) Physical interferences include differences in viscosity, surface tension, and dissolved solids between samples and calibration standards. To minimize these effects, dissolved solid levels in analytical samples should not exceed 0.5%. Dilute water and wastewater samples containing dissolved solids at or above 0.5% before analysis. Use internal standards for correction of physical interferences. Any internal standards used should demonstrate comparable analytical behavior to the elements being determined.

5) Memory interferences occur when analytes from a previous sample or standard are measured in the current sample. Use a sufficiently long rinse or flush between samples to minimize this type of interference. If memory interferences persist, they may be indications of problems in the sample introduction system. Severe memory interferences may require disassembly and cleaning of the entire sample introduction system, including the plasma torch, and the sampler and skimmer cones.

6) Ionization interferences result when moderate (0.1 to 1%) amounts of a matrix ion change

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the analyte signal. This effect, which usually reduces the analyte signal, also is known as ‘‘suppression.’’ Correct for suppression by use of internal standardization techniques.

2. Apparatus

a. Inductively coupled plasma/mass spectrometer: Instrumentation, available from several manufacturers, includes a mass spectrometer detector, inductively coupled plasma source, mass flow controllers for regulation of ICP gas flows, peristaltic pump for sample introduction, and a computerized data acquisition and instrument control system. An x-y autosampler also may be used with appropriate control software.

b. Laboratory ware: Use precleaned plastic laboratory ware for standard and sample preparation. Teflon,*#(87) either tetrafluoroethylene hexafluoropropylene-copolymer (FEP), polytetrafluoroethylene (PTFE), or perfluoroalkoxy PTFE (PFA) is preferred for standard preparation and sample digestion, while high-density polyethylene (HDPE) and other dense, metal-free plastics may be acceptable for internal standards, known-addition solutions, etc. Check each new lot of autosampler tubes for suitability, and preclean autosampler tubes and pipettor tips (see Section 3010C.2).

c. Air displacement pipets, 10 to 100 µL, 100 to 1000 µL, and 1 to 10 mL size.

d. Analytical balance, accurate to 0.1 mg.

e. Sample preparation apparatus, such as hot plates, microwave digestors, and heated sand baths. Any sample preparation device has the potential to introduce trace levels of target analytes to the sample.

f. Clean hood (optional), Class 100 (certified to contain less than 100 particles/m^3), for sample preparation and manipulation. Preferably perform all sample manipulations, digestions, dilutions, etc. in a certified Class 100 environment. Alternatively, handle samples in glove boxes, plastic fume hoods, or other environments where random contamination by trace metals can be minimized.

3. Reagents

a. Acids: Use ultra-high-purity grade (or equivalent) acids to prepare standards and to process sample. Redistilled acids are acceptable if each batch is demonstrated to be free from contamination by target analytes. Use extreme care in the handling of acids in the laboratory to avoid contamination of the acids with trace levels of metals.

1) *Nitric acid,* HNO_3, conc (specific gravity 1.41).

2) *Nitric acid,* 1 + 1: Add 500 mL conc HNO_3 to 500 mL reagent water.

3) *Nitric acid,* 2%: Add 20 mL conc HNO_3 to 100 mL reagent water; dilute to 1000 mL.

4) *Nitric acid,* 1%: Add 10 mL conc HNO_3 to 100 mL reagent water; dilute to 1000 mL.

b. Reagent water: Use water of the highest possible purity for blank, standard, and sample preparation (see Section 1080). Alternatively, use the procedure described below to produce

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water of acceptable quality. Other water preparation regimes may be used, provided that the water produced is metal-free. Reagent water containing trace amounts of analyte elements will cause erroneous results.

Produce reagent water using a softener/reverse osmosis unit with subsequent UV sterilization. After the general deionization system use a dual-column strong acid/strong base ion exchange system to polish laboratory reagent water before production of metal-free water. Use a multi-stage reagent water system, with two strong acid/strong base ion exchange columns and an activated carbon filter for organics removal for final polishing of laboratory reagent water. Use only high-purity water for preparation of samples and standards.

c. Stock, standard, and other required solutions: See Section 3120B.3*d* for preparation of standard stock solutions from elemental materials (pure metals, salts). Preferably, purchase high-purity commercially prepared stock solutions and dilute to required concentrations. Single- or multi-element stock solutions (1000 mg/L) of the following elements are required: aluminum, antimony, arsenic, barium, beryllium, cerium, cadmium, chromium, cobalt, copper, germanium, indium, lead, magnesium, manganese, molybdenum, nickel, rhodium, scandium, selenium, silver, strontium, terbium, thallium, thorium, uranium, vanadium, and zinc. Prepare internal standard stock separately from target element stock solution. The potential for incompatibility between target elements and/or internal standards exists, and could cause precipitation or other solution instability.

1) *Internal standard stock solution:* Lithium, scandium, germanium, indium, and thorium are suggested as internal standards. The following masses are monitored: ^{6}Li, ^{45}Sc, ^{72}Ge, ^{115}In, and ^{232}Th. Add to all samples, standards, and quality control (QC) samples a level of internal standard that will give a suitable counts/second (cps) signal (for most internal standards, 200 000 to 500 000 cps; for lithium, 20 000 to 70 000 cps). Minimize error introduced by dilution during this addition by using an appropriately high concentration of internal standard mix solution. Maintain volume ratio for all internal standard additions.

Prepare internal standard mix as follows: Prepare a nominal 50-mg/L solution of ^{6}Li by dissolving 0.15 g $^{6}Li_2CO_3$ (isotopically pure, i.e., 95% or greater purity†#(88)) in a minimal amount of 1:1 HNO_3. Pipet 5.0 mL 1000-mg/L scandium, germanium, indium, and thorium standards into the lithium solution, dilute resulting solution to 500.0 mL, and mix thoroughly. The resultant concentration of Sc, Ge, In, and Th will be 10 mg/L. Older instruments may require higher levels of internal standard to achieve acceptable levels of precision.

Other internal standards, such as rhodium, yttrium, terbium, holmium, and bismuth may also be used in this method. Ensure that internal standard mix used is stable and that there are no undesired interactions between elements.

Screen all samples for internal standard elements before analysis. The analysis of a few representative samples for internal standards should be sufficient. Analyze samples ‘‘as received’’ or ‘‘as digested’’ (before addition of internal standard), then add internal standard mix and reanalyze. Monitor counts at the internal standard masses. If the ‘‘as received’’ or ‘‘as

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digested'' samples show appreciable detector counts (10% or higher of samples with added internal standard), dilute sample or use an alternate internal standard. If the internal standard response of the sample with the addition is not within 70 to 125% of the response for a calibration blank with the internal standard added, either dilute the sample before analysis, or use an alternate internal standard. During actual analysis, monitor internal standard masses and note all internal standard recoveries over 125% of internal standard response in calibration blank. Interpret results for these samples with caution.

The internal standard mix may be added to blanks, standards, and samples by pumping the solution so it is mixed with the sample stream in the sample introduction process.

2) *Instrument optimization/tuning solution,* containing the following elements: barium, beryllium, cadmium, cerium, cobalt, copper, germanium, indium, magnesium, rhodium, scandium, terbium, thallium, and lead. Prepare this solution in 2% HNO_3. This mix includes all common elements used in optimization and tuning of the various ICP/MS operational parameters. It may be possible to use fewer elements in this solution, depending on the instrument manufacturer's recommendations.

3) *Calibration standards,* 0, 5, 10, 20, 50, and 100 µg/L.‡#(89) Other calibration regimes are acceptable, provided the full suite of quality assurance samples and standards is run to validate these method changes. Fewer standards may be used, and a two-point blank/mid-range calibration technique commonly used in ICP optical methods should also produce acceptable results. Calibrate all analytes using the selected concentrations. Prepare all calibration standards and blanks in a matrix of 2% nitric acid. Add internal standard mix to all calibration standards to provide appropriate count rates for interference correction. NOTE: All standards and blanks used in this method have the internal standard mix added at the same ratio.

4) *Method blank,* consisting of reagent water (¶ 3*b*) taken through entire sample preparation process. For dissolved samples, take reagent water through same filtration and preservation processes used for samples. For samples requiring digestion, process reagent water with the same digestion techniques as samples. Add internal standard mix to method blank.

5) *Calibration verification standard:* Prepare a mid-range standard, from a source different from the source of the calibration standards, in 2% HNO_3, with equivalent addition of internal standard.

6) *Calibration verification blank:* Use 2% HNO_3.

7) *Laboratory fortified blank* (optional)*:* Prepare solution with 2% nitric acid and method analytes added at about 50 µg/L. This standard, sometimes called a laboratory control sample (LCS), is used to validate digestion techniques and known-addition levels.

8) *Reference materials:* Externally prepared reference material, preferably from National Institute of Standards and Technology (NIST) 1643 series or equivalent.

9) *Known-addition solution for samples:* Add stock standard to sample in such a way that volume change is less than 5%. In the absence of information on analyte levels in the sample,

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prepare known additions at around 50 μg/L. If analyte concentration levels are known, add at 50 to 200% of the sample levels. For samples undergoing digestion, make additions before digestion. For the determination of dissolved metals, make additions after filtration, preferably immediately before analysis.

10) *Low-level standards:* Use both a 0.3- and a 1.0-μg/L standard when expected analyte concentration is below 5 μg/L. Prepare both these standards in 2% nitric acid.

Prepare volumetrically a mixed standard containing the method analytes at desired concentration(s) (0.30 μg/L, 1.0 μg/L, or both). Prepare weekly in 100-mL quantities.

d. Argon: Use a prepurified grade of argon unless it can be demonstrated that other grades can be used successfully. The use of prepurified argon is usually necessary because of the presence of krypton as an impurity in technical argon. ^{82}Kr interferes with the determination of ^{82}Se. Monitor ^{83}Kr at all times.

4. Procedures

a. Sample preparation: See Section 3010 and Section 3020 for general guidance regarding sampling and quality control. See Section 3030E for recommended sample digestion technique for all analytes except silver and antimony. If silver and antimony are target analytes, use method given in 3030F, paying special attention to interferences caused by chloride ion, and using all applicable elemental corrections. Alternative digestion techniques and additional guidance on sample preparation are available.[3,4]

Ideally use a ‘‘clean’’ environment for any sample handling, manipulation, or preparation. Preferably perform all sample manipulations in a Class 100 clean hood or room to minimize potential contamination artifacts in digested or filtered samples.

b. Instrument operating conditions: Follow manufacturer’s standard operating procedures for initialization, mass calibration, gas flow optimization, and other instrument operating conditions. Maintain complete and detailed information on the operational status of the instrument whenever it is used.

c. Analytical run sequence: A suggested analytical run sequence, including instrument tuning/optimization, checking of reagent blanks, instrument calibration and calibration verification, analysis of samples, and analysis of quality control samples and blanks, is given in Table 3125:IV.

d. Instrument tuning and optimization: Follow manufacturer’s instructions for optimizing instrument performance. The most important optimization criteria include nebulizer gas flows, detector and lens voltages, radio-frequency forward power, and mass calibration. Periodically check mass calibration and instrument resolution. Ideally, optimize the instrument to minimize oxide formation and doubly-charged species formation. Measure the CeO/Ce ratio to monitor oxide formation, and measure doubly-charged species by determination of the Ba^{2+}/Ba^{+} ratio. Both these ratios should meet the manufacturer’s criteria before instrument calibration. Monitor background counts at mass 220 after optimization and compare with manufacturer’s criteria. A

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summary of performance criteria related to optimization and tuning, calibration, and analytical performance for this method is given in Table 3125:V.

e. Instrument calibration: After optimization and tuning, calibrate instrument using an appropriate range of calibration standards. Use appropriate regression techniques to determine calibration lines or curves for each analyte. For acceptable calibrations, correlation coefficients for regression curves are ideally 0.995 or greater.

Immediately after calibration, run initial calibration verification standard, ¶ 3*c*5); acceptance criteria are ±10% of known analyte concentration. Next run initial calibration verification blank, ¶ 3*c*6); acceptance criteria are ideally ± the absolute value of the instrument detection limit for each analyte, but in practice, ± the absolute value of the laboratory reporting limit or the laboratory method detection limit for each analyte is acceptable. Verify low-level calibration by running 0.3- and/or 1.0-µg/L standards, if analyte concentrations are less than 5 µg/L.

f. Sample analysis: Ensure that all vessels and reagents are free from contamination. During analytical run (see Table 3125:IV), include quality control analyses according to schedule of Table 3125:VI, or follow project-specific QA/QC protocols.

Internal standard recoveries must be between 70% and 125% of internal standard response in the laboratory-fortified blank; otherwise, dilute sample, add internal standard mix, and reanalyze.

Make known-addition analyses for each separate matrix in a digestion or filtration batch.

5. Calculations and Corrections

Configure instrument software to report internal standard corrected results. For water samples, preferably report results in micrograms per liter. Report appropriate number of significant figures.

a. Correction for dilutions and solids: Correct all results for dilutions, and raise reporting limit for all analytes reported from the diluted sample by a corresponding amount. Similarly, if results for solid samples are to be determined, use Method 2540B to determine total solids. Report results for solid samples as micrograms per kilogram, dry weight. Correct all results for solids content of solid samples. Use the following equation to correct solid or sediment sample results for dilution during digestion and moisture content:

$$R_{corr} = \frac{R_{uncorr} \times V}{W \times \%\ TS/100}$$

where:

R_{corr} = corrected result, µg/kg,
R_{uncorr} = uncorrected elemental result, µg/L,
V = volume of digestate (after digestion), L,

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W = mass of the wet sample, kg, and
% TS = percent total solids determined in the solid sample.

b. Compensation for interferences: Use instrument software to correct for interferences listed previously for this method. See Table 3125:III for a listing of the most common molecular ion interferences.

c. Data reporting: Establish appropriate reporting limits for method analytes based on instrument detection limits and the laboratory blank. For regulatory programs, ensure that reporting limits for method analytes are a factor of three below relevant regulatory criteria.

If method blank contamination is typically random, sporadic, or otherwise not in statistical control, do not correct results for the method blank. Consider the correction of results for laboratory method blanks only if it can be demonstrated that the concentration of analytes in the method blank is within statistical control over a period of months. Report all method blank data explicitly in a manner identical to sample reporting procedures.

d. Documentation: Maintain documentation for the following (where applicable): instrument tuning, mass calibration, calibration verification, analyses of blanks (method, field, calibration, and equipment blanks), IDL and MDL studies, analyses of samples and duplicates with known additions, laboratory and field duplicate information, serial dilutions, internal standard recoveries, and any relevant quality control charts.

Also maintain, and keep available for review, all raw data generated in support of the method.[5]

6. Method Performance

Table 3125:I presents instrument detection limit (IDL) data generated by this method; this represents optimal state-of-the-art instrument detection capabilities, not recommended method detection or reporting limits. Table 3125:VII through IX contain single-laboratory, single-operator, single-instrument performance data generated by this method for calibration verification standards, low-level standards, and known-addition recoveries for fresh-water matrices. Performance data for this method for some analytes are not currently available. However, performance data for similar ICP/MS methods are available in the literature.[1,4]

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3130 METALS BY ANODIC STRIPPING VOLTAMMETRY*#(90)

3130 A. Introduction

Anodic stripping voltammetry (ASV) is one of the most sensitive metal analysis techniques; it is as much as 10 to 100 times more sensitive than electrothermal atomic absorption spectroscopy for some metals. This corresponds to detection limits in the nanogram-per-liter range. The technique requires no sample extraction or preconcentration, it is nondestructive, and it allows simultaneous determination of four to six trace metals, utilizing inexpensive instrumentation. The disadvantages of ASV are that it is restricted to amalgam-forming metals, analysis time is longer than for spectroscopic methods, and interferences and high sensitivity can present severe limitations. The analysis should be performed only by analysts skilled in ASV methodology because of the interferences and potential for trace background contamination.

3130 B. Determination of Lead, Cadmium, and Zinc

1. General Discussion

a. Principle: Anodic stripping voltammetry is a two-step electroanalytical technique. In the preconcentration step, metal ions in the sample solution are reduced at negative potential and concentrated into a mercury electrode. The concentration of the metal in the mercury is 100 to 1000 times greater than that of the metal ion in the sample solution. The preconcentration step is followed by a stripping step applying a positive potential scan. The amalgamated metal is oxidized rapidly and the accompanying current is proportional to metal concentration.

b. Detection limits and working range: The limit of detection for metal determination using ASV depends on the metal determined, deposition time, stirring rate, solution pH, sample matrix, working electrode (hanging mercury drop electrode, HMDE, or thin mercury film electrode, TMFE), and mode of the stripping potential scan (square wave or differential pulse). Cadmium, lead, and zinc are concentrated efficiently during pre-electrolysis because of their high solubility

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in mercury and thus have low detection limits (<1 μg/L). Long deposition times and high stirring rates increase the concentration of metal preconcentrated in the mercury phase and reduce detection limits. The effects of solution pH and matrix are more complicated. In general, add a high concentration of inert electrolyte to samples to maintain a high, constant ionic strength. Acidify sample to a low pH or add a pH buffer. If the pH buffer or other component of the sample matrix complexes the metal (3130B.1*c*), detection limits often are increased.

The choice of working electrode is determined largely by the working range of concentration required. The HMDE is best suited for analysis from approximately 1 μg/L to 10 mg/L, while the TMFE is superior for detection below 1 μg/L.

c. Interferences: Major interferences include intermetallic compound formation, overlapping stripping peaks, adsorption of organics, and complexation. Intermetallic compounds can form in the mercury phase when high concentrations of certain metals are present simultaneously. Zinc forms intermetallic compounds with cobalt and nickel, and both zinc and cadmium form intermetallic compounds with copper, silver, and gold. As a result, the stripping peak for the constituent metals may be severely depressed or shifted and additional peaks due to intermetallic compound stripping may be observed. Minimize or avoid intermetallic compound formation by use of a hanging mercury drop electrode instead of a thin film mercury electrode when metal concentrations are above 1 μg/L, application of a preconcentration potential sufficiently negative to reduce the desired but not the interfering metal, and use of a relatively short preconcentration period followed by a relatively large pulse modulation (50 mV) during the stripping stage. In general, suspect formation of intermetallic compounds if metals are present in concentrations above 1 mg/L. If metals are present at concentrations above 10 mg/L, do not use anodic stripping voltammetry. Concentrations above 10 mg/L usually can be quantitated by methods such as those given in Section 3111 and Section 3120.

Separate overlapping stripping peaks by various methods, including appropriate choice of buffer and electrolyte.[1-3] If only one of the metal peaks is of interest, eliminate interfering peaks by selective complexation with a suitable ligand, such as EDTA. Judicious choice of preconcentration potential can result in the deposition of the selected metal but not the interfering metal in the mercury electrode. Selection of buffer/ligand also may help to distinguish metals during the preconcentration step. Alternatively, use ‘‘medium exchange,’’ in which preconcentration is performed with the electrodes in the sample and stripping is performed in a different electrolyte solution. In this procedure, metals are deposited from the sample into the amalgam as usual, but they may be stripped into a medium that provides different stripping peak potentials for the overlapping metals.

Minimize interferences from adsorption of organic compounds and complexation by removal of the organic matter. Digest samples with high-purity acids as described in Section 3030. Make standard additions to determine if complexation or adsorption remains a problem. Analyze a metal-free solution with a matrix similar to that of the sample both before and after addition of known quantities of standard. Repeat procedure for sample. If the slope of the stripping current versus added metal is significantly different in the sample relative to the metal-free solution,

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digest sample further. The choice of stripping waveform also is important. While both square-wave and differential-pulse stripping attempt to minimize the contribution of adsorption currents to the total measured stripping current, square-wave stripping does this more effectively. Thus, use square-wave stripping instead of differential-pulse stripping when adsorption occurs.

2. Apparatus

a. Electrochemical analyzer: The basic electrochemical analyzer for ASV applications contains a three-electrode potentiostat, which very precisely controls potential applied to the working electrode relative to the reference electrode, and a sensitive current measuring device. It is capable of delivering potential pulses of various amplitudes and frequencies, and provides several scan rates and current ranges. More advanced ASV instruments offer automated timing, gas purge and stirring, and data processing routines including curve smoothing, baseline correction, and background subtraction.

Two variations of stripping waveforms are commonly used: differential pulse (DPASV) and square wave (SWASV) waveforms. The differential-pulse waveform consists of a series of pulses superimposed on a linear voltage ramp, while the square-wave waveform consists of a series of pulses superimposed on a staircase potential waveform. Square-wave stripping is significantly faster than differential-pulse stripping and is typically ten times more sensitive. Most commercially available ASV instruments perform both differential-pulse and square-wave stripping.

b. Electrodes and cell: Provide working, reference, and auxiliary electrodes. Working electrodes are either hanging mercury drop or thin mercury film electrodes. Hanging mercury drop electrodes must be capable of dispensing mercury in very precisely controlled drop sizes. Three types of electrodes meet this requirement: static mercury drop electrodes, controlled growth mercury drop electrodes, or Kemula-type electrodes. In any case, use a drop knocker to remove an old drop before dispensing a fresh mercury drop.

When the lowest detection limits are required, a thin mercury film electrode is preferred. This electrode consists of a rotating glassy carbon disk plated with mercury in situ during preconcentration of the analyte. A high-precision, constant-speed rotator controls the rotation rate of the electrode and provides reproducible mass transport.

Reference electrodes may be either saturated calomel or silver/ silver chloride electrodes. Use a platinum wire for the auxiliary electrode.

Use cells constructed of glass, or preferably fused silica or TFE, because they are more resistant to solution adsorption or leaching. Cover cell with a lid that provides reproducible placement of the electrodes and gas purging tubes. Provide an additional hole in the cell lid for addition of standards. Most commercially available mercury drop electrodes include electrolytic cells, reference and auxiliary electrodes, and gas purging tubes.

Use a constant-speed stirring mechanism to provide reproducible mass transport in samples and standards.

Locate the cell in an area where temperature is relatively constant. Alternatively, use a

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constant-temperature water bath and cell jacket.

c. Oxygen-removal apparatus: Oxygen interferes in electrochemical analyses; remove it from solution before preconcentration by purging with nitrogen or argon. Provide two gas inlet tubes through the cell lid: one extends into the solution and the second purges the space above the solution. A gas outlet hole in the lid provides for removal of oxygen and excess purging gas.

d. Recording device: If the electrochemical analyzer is not equipped with a digital data acquisition system, use an XY plotter to record stripping voltammograms.

e. Timer: If preconcentration and equilibration periods are not controlled by the instrument, use an accurate timing device.

f. Polishing wheel: To obtain the high polish required for a glassy carbon disk electrode, use a motorized polishing wheel.

3. Reagents

CAUTION: *Follow proper practices for disposal of any solutions containing mercury.*

a. Metal-free water: Use deionized water to prepare buffers, electrolytes, standards, etc. Use water with at least 18 megohm-cm resistivity (see Section 1080).

b. Nitric acid, HNO_3, conc, high-purity.*#(91)

c. Nitric acid, HNO_3, 6*N*, 1.6*N* (10%), and 0.01*N*.

d. Purging gas (nitrogen or argon), high-purity. Remove traces of oxygen in nitrogen or argon gas before purging the solution. Pass gas through sequential scrubbing columns containing vanadous chloride in the first, deionized water in the second, and buffer (or electrolyte) solution in the third column.

e. Metal standards: Prepare stock solutions containing 1 mg metal/mL in polyethylene bottles. Purchase these solutions commercially or prepare as in Section 3111. Daily prepare dilutions of stock standards in a matrix similar to that of the samples to cover the concentration range desired.

f. Electrolyte/buffer: Use one of the following:

1) *Acetate buffer,* pH 4.5: Dissolve 16.4 g anhydrous sodium acetate, $NaC_2H_3O_2$, in 800 mL water. Adjust to pH 4.5 with high-purity glacial acetic acid.*#(92) Dilute to 1 L with water.

2) *Citrate buffer,* pH 3: Dissolve 42.5 g citric acid (monohydrate) in 700 mL water. Adjust to pH 3 with high-purity NH_4OH.*#(93) Dilute to 1 L with water.

3) *Phosphate buffer,* pH 6.8: Dissolve 24 g NaH_2PO_4 in 500 mL water. Adjust to pH 6.8 with 1*N* NaOH. Dilute to 1 L with water.

g. Mercury: Use commercially available triply distilled metallic mercury for hanging mercury drop electrodes. CAUTION: *Mercury vapors are highly toxic. Use only in well-ventilated area.*

h. Mercuric nitrate solution, $Hg(NO_3)_2$: For thin mercury film electrodes, dissolve 0.325 g

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$Hg(NO_3)_2$ in 100 mL 0.01*N* HNO_3.

i. Reference electrode filling solution: Available from electrode manufacturer.

j. Amalgamated zinc: Dissolve 2 g $Hg(NO_3)_2$ in 25 mL conc HNO_3; dilute to 250 mL with water. In a separate beaker, clean approximately 50 g mossy zinc by gently oxidizing the surface with 10% HNO_3 and rinse with water. Add $Hg(NO_3)_2$ solution to cleaned zinc and stir with a glass rod. If barely visible bubbles do not appear, add a small amount of 6*N* HNO_3. Zinc should rapidly acquire a shiny, metallic appearance. Decant solution and store for amalgamating future batches of zinc. Rinse amalgamated zinc copiously with water and transfer to a gas scrubbing column.

k. Hydrochloric acid, HCl, conc.

l. Vanadous chloride: Add 2 g ammonium metavanadate, NH_4VO_3, to 25 mL conc HCl and heat to boiling. Solution should turn blue-green. Dilute to 250 mL with water. Pour solution into gas scrubbing column packed with amalgamated zinc and bubble purging gas through it until the solution turns a clear violet color. When the violet color is replaced by a blue, green, or brown color, regenerate vanadous chloride by adding HCl.

m. Siliconizing solution: Preferably use commercially available solutions in sealed ampules for siliconizing capillaries used for hanging mercury drops. CAUTION: *Most commercial siliconizing reagents contain* CCl_4, a toxic and cancer-suspect agent. Handle with gloves and avoid breathing vapors.

n. Alumina suspensions, 1, 0.3, and 0.05 μm. Use commercially available alumina suspensions in water, or make a suspension by adding a small amount of water to the alumina.

o. Hydrofluoric acid, HF, 5%: Dilute 5 mL conc HF to 100 mL with water.

p. Methanol.

q. Sodium hydroxide, NaOH, 1*N*.

4. Procedure

a. Sample preparation and storage: Collect samples in pre-cleaned, acid-soaked polyethylene or TFE bottles. Add 2 mL conc HNO_3/L sample and mix well. Cap tightly and store in refrigerator or freezer until ready for analysis.

b. Cell preparation: Soak clean cell in 6*N* HNO_3 overnight and rinse well with water before use.

c. Electrode preparation:

1) HMDE—Follow manufacturer's guidance for capillary cleaning. If not available, use the following procedure. Remove all mercury from the capillary. Aspirate the following through the capillary in the order listed: 6*N* HNO_3, water, 5% HF, water, methanol, and air. Dry capillary at 100°C for 1 h. Siliconize cooled capillary using a siliconizing solution. Between uses, fill

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capillary with clean mercury and immerse tip in clean mercury. If the capillary fails to suspend a drop of mercury, repeat cleaning.

2) TMFE—Polish glassy carbon disks used for thin mercury film electrodes to a high metallic sheen with alumina suspensions, progressively decreasing particle size from 1 μm to 0.05 μm. Use a motorized polishing wheel for best results. Completely rinse off all traces of alumina with water. Check disk frequently for etching or pitting; repolish as necessary to maintain reproducible mercury film deposition.

d. Instrumental conditions: Use the following conditions:

Variable	Value
Initial potential	−1.00 V (Pb, Cd); −1.20 V (Zn)
Final potential	0.00 V
Equilibration potential	−1.00 V (Pb, Cd); −1.20 V (Zn)
HMDE drop size	medium
TMFE rotation rate	2000 rpm
DPASV:	
Pulse amplitude	25 mV
Pulse period	0.5 s
Pulse width	50 ms
Sample width	17 ms
Scan rate	5 mV/s
SWASV:	
SW amplitude	25 mV
Step potential	4 mV
Frequency	100 Hz

e. Deoxygenation: Pipet 2 mL sample and 3 mL electrolyte/ buffer into cell. If using a TMFE, add 10 μL $Hg(NO_3)_2$ solution. Place electrodes in cell and secure cell lid. Deoxygenate solution with purified purging gas for 10 min while stirring. When solution purge is completed, purge the space above the solution with purified purging gas. Continue head-space purge throughout analysis.

f. Preconcentration: If using a HMDE, dispense a new mercury drop. Start preconcentration, stirring and timing simultaneously. Precisely control and keep constant preconcentration times and stirring rates for solutions and standards. Generally use 120 s and a rotation rate of 2000 rpm for the TMFE.

After the metal is sufficiently concentrated in the amalgam, stop stirring or TMFE rotation

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for an equilibration period of precisely 30 s.

g. Anodic stripping: After equilibration period, begin anodic stripping without stirring and make potential at the working electrode progressively more positive as a function of time. Monitor stripping current and plot as a function of applied potential in stripping voltammograms. Use peak current to quantify metal concentration and peak potential to identify the metal.

h. Add 5 to 50 µL standard solution and repeat analysis, beginning with deoxygenation of sample. Adjust volume of added standard solution to obtain 30 to 70% increase of the stripping peak. If 50 µL addition is not sufficient, use standard solution with a higher concentration of metal. Shorten deoxygenation step to 1 min after initial gas purge.

5. Calculations

Calculate the concentration of metal in the original sample using the following equation:

$$C_o = \frac{C_s \times V_s}{V_o} \times \frac{i_o}{(i_s - i_o)}$$

where:

C_o = concentration of metal in sample, mg/ L,
C_s = concentration of metal in standard solution, mg/L,
i_o = stripping peak height in original sample,
i_s = stripping peak height in sample with standard addition,
V_o = volume of sample, mL, and
V_s = volume of standard solution added, mL.

6. Quality Control

Follow quality control guidelines outlined in Section 3020 with respect to use of additions, duplicates, and blanks for best results. Blanks are critical because of the high sensitivity of the method.

7. Precision and Bias

Table 3130:I gives precision data for analyses of samples with various matrices.

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3500-Al ALUMINUM*#(94)

3500-Al A. Introduction

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1. Occurrence and Significance

Aluminum (Al) is the second element in Group IIIA of the periodic table; it has an atomic number of 13, an atomic weight of 26.98, and a valence of 3. The average abundance in the earth's crust is 8.1%; in soils it is 0.9 to 6.5%; in streams it is 400 µg/L; in U.S. drinking waters it is 54 µg/L, and in groundwater it is <0.1 µg/L. Aluminum occurs in the earth's crust in combination with silicon and oxygen to form feldspars, micas, and clay minerals. The most important minerals are bauxite and corundum, which is used as an abrasive. Aluminum and its alloys are used for heat exchangers, aircraft parts, building materials, containers, etc. Aluminum potassium sulfate (alum) is used in water-treatment processes to flocculate suspended particles, but it may leave a residue of aluminum in the finished water.

Aluminum's occurrence in natural waters is controlled by pH and by very finely suspended mineral particles. The cation Al^{3+} predominates at pH less than 4. Above neutral pH, the predominant dissolved form is $Al(OH)_4^-$. Aluminum is nonessential for plants and animals. Concentrations exceeding 1.5 mg/L constitute a toxicity hazard in the marine environment, and levels below 200 µg/L present a minimal risk. The United Nations Food and Agriculture Organization's recommended maximum level for irrigation waters is 5 mg/L. The possibility of a link between elevated aluminum levels in brain tissues and Alzheimer's disease has been raised. The proposed U.S. EPA secondary drinking water standard MCL is 0.05 mg/L.

2. Selection of Method

The atomic absorption spectrometric methods (Section 3111D and Section 3111E, and Section 3113B) and the inductively coupled plasma methods (Section 3120 and Section 3125) are free from such common interferences as fluoride and phosphate, and are preferred. The Eriochrome cyanine R colorimetric method (B) provides a means for estimating aluminum with simpler instrumentation.

3500-Al B. Eriochrome Cyanine R Method

1. General Discussion

a. Principle: With Eriochrome cyanine R dye, dilute aluminum solutions buffered to a pH of 6.0 produce a red to pink complex that exhibits maximum absorption at 535 nm. The intensity of the developed color is influenced by the aluminum concentration, reaction time, temperature, pH, alkalinity, and concentration of other ions in the sample. To compensate for color and turbidity, the aluminum in one portion of sample is complexed with EDTA to provide a blank. The interference of iron and manganese, two elements commonly found in water when aluminum is present, is eliminated by adding ascorbic acid. The optimum aluminum range lies between 20 and 300 µg/L but can be extended upward by sample dilution.

b. Interference: Negative errors are caused by both fluoride and polyphosphates. When the fluoride concentration is constant, the percentage error decreases with increasing amounts of

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aluminum. Because the fluoride concentration often is known or can be determined readily, fairly accurate results can be obtained by adding the known amount of fluoride to a set of standards. A simpler correction can be determined from the family of curves in Figure 3500-Al:1. A procedure is given for the removal of complex phosphate interference. Orthophosphate in concentrations under 10 mg/L does not interfere. The interference caused by even small amounts of alkalinity is removed by acidifying the sample just beyond the neutralization point of methyl orange. Sulfate does not interfere up to a concentration of 2000 mg/L.

c. Minimum detectable concentration: The minimum aluminum concentration detectable by this method in the absence of fluorides and complex phosphates is approximately 6 µg/L.

d. Sample handling: Collect samples in clean, acid-rinsed bottles, preferably plastic, and examine them as soon as possible after collection. If only soluble aluminum is to be determined, filter a portion of sample through a 0.45-µm membrane filter; discard first 50 mL of filtrate and use succeeding filtrate for the determination. Do not use filter paper, absorbent cotton, or glass wool for filtering any solution that is to be tested for aluminum, because they will remove most of the soluble aluminum.

2. Apparatus

a. Colorimetric equipment: One of the following is required:

1) *Spectrophotometer,* for use at 535 nm, with a light path of 1 cm or longer.

2) *Filter photometer,* providing a light path of 1 cm or longer and equipped with a green filter with maximum transmittance between 525 and 535 nm.

3) *Nessler tubes,* 50-mL, tall form, matched.

b. Glassware: Treat all glassware with warm 1 + 1 HCl and rinse with aluminum-free distilled water to avoid errors due to materials absorbed on the glass. Rinse sufficiently to remove all acid.

3. Reagents

Use reagents low in aluminum, and aluminum-free distilled water.

a. Stock aluminum solution: Use either the metal (1) or the salt (2) for preparing stock solution; 1.00 mL = 500 µg Al:

1) Dissolve 500.0 mg aluminum metal in 10 mL conc HCl by heating gently. Dilute to 1000 mL with water, or

2) Dissolve 8.791 g aluminum potassium sulfate (also called potassium alum), $AlK(SO_4)_2 \cdot 12H_2O$, in water and dilute to 1000 mL. Correct this weight by dividing by the decimal fraction of assayed $AlK(SO_4)_2 \cdot 12H_2O$ in the reagent used.

b. Standard aluminum solution: Dilute 10.00 mL stock aluminum solution to 1000 mL with water; 1.00 mL = 5.00 µg Al. Prepare daily.

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c. Sulfuric acid, H_2SO_4, 0.02*N* and 6*N*.

d. Ascorbic acid solution: Dissolve 0.1 g ascorbic acid in water and make up to 100 mL in a volumetric flask. Prepare fresh daily.

e. Buffer reagent: Dissolve 136 g sodium acetate, $NaC_2H_3O_2 \cdot 3H_2O$, in water, add 40 mL 1*N* acetic acid, and dilute to 1 L.

f. Stock dye solution: Use any of the following products:

1) *Solochrome cyanine R-200*#(95) or Eriochrome cyanine:*†#(96) Dissolve 100 mg in water and dilute to 100 mL in a volumetric flask. This solution should have a pH of about 2.9.

2) *Eriochrome cyanine R:*‡#(97) Dissolve 300 mg dye in about 50 mL water. Adjust pH from about 9 to about 2.9 with 1 + 1 acetic acid (approximately 3 mL will be required). Dilute with water to 100 mL.

3) *Eriochrome cyanine R:*§#(98) Dissolve 150 mg in about 50 mL water. Adjust pH from about 9 to about 2.9 with 1 + 1 acetic acid (approximately 2 mL will be required). Dilute with water to 100 mL.

Stock solutions have excellent stability and can be kept for at least a year.

g. Working dye solution: Dilute 10.0 mL of selected stock dye solution to 100 mL in a volumetric flask with water. Working solutions are stable for at least 6 months.

h. Methyl orange indicator solution, or bromcresol green indicator solution specified in the total alkalinity determination (Section 2320B.3*d*).

i. EDTA (sodium salt of ethylenediamine-tetraacetic acid dihydrate), 0.01*M*: Dissolve 3.7 g in water, and dilute to 1 L.

j. Sodium hydroxide, NaOH, 1*N* and 0.1*N*.

4. Procedure

a. Preparation of calibration curve:

1) Prepare a series of aluminum standards from 0 to 7 µg (0 to 280 µg/L based on a 25-mL sample) by accurately measuring the calculated volumes of standard aluminum solution into 50-mL volumetric flasks or nessler tubes. Add water to a total volume of approximately 25 mL.

2) Add 1 mL 0.02*N* H_2SO_4 to each standard and mix. Add 1 mL ascorbic acid solution and mix. Add 10 mL buffer solution and mix. With a volumetric pipet, add 5.00 mL working dye reagent and mix. Immediately make up to 50 mL with distilled water. Mix and let stand for 5 to 10 min. The color begins to fade after 15 min.

3) Read transmittance or absorbance on a spectrophotometer, using a wavelength of 535 nm or a green filter providing maximum transmittance between 525 and 535 nm. Adjust instrument to zero absorbance with the standard containing no aluminum.

Plot concentration of Al (micrograms Al in 50 mL final volume) against absorbance.

b. Sample treatment in absence of fluoride and complex phosphates: Place 25.0 mL sample,

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or a portion diluted to 25 mL, in a porcelain dish or flask, add a few drops of methyl orange indicator, and titrate with 0.02*N* H_2SO_4 to a faint pink color. Record reading and discard sample. To two similar samples at room temperature add the same amount of 0.02*N* H_2SO_4 used in the titration and 1 mL in excess.

To one sample add 1 mL EDTA solution. This will serve as a blank by complexing any aluminum present and compensating for color and turbidity. To both samples add 1 mL ascorbic acid, 10 mL buffer reagent, and 5.00 mL working dye reagent as prescribed in ¶ a2) above.

Set instrument to zero absorbance or 100% transmittance using the EDTA blank. After 5 to 10 min contact time, read transmittance or absorbance and determine aluminum concentration from the calibration curve previously prepared.

c. Visual comparison: If photometric equipment is not available, prepare and treat standards and a sample, as described above, in 50-mL nessler tubes. Make up to mark with water and compare sample color with the standards after 5 to 10 min contact time. A sample treated with EDTA is not needed when nessler tubes are used. If the sample contains turbidity or color, the use of nessler tubes may result in considerable error.

d. Removal of phosphate interference: Add 1.7 mL 6*N* H_2SO_4 to 100 mL sample in a 200-mL erlenmeyer flask. Heat on a hot plate for at least 90 min, keeping solution temperature just below the boiling point. At the end of the heating period solution volume should be about 25 mL. Add water if necessary to keep it at or above that volume.

After cooling, neutralize to a pH of 4.3 to 4.5 with NaOH, using 1*N* NaOH at the start and 0.1*N* for the final fine adjustment. Monitor with a pH meter. Make up to 100 mL with water, mix, and use a 25-mL portion for the aluminum test.

Run a blank in the same manner, using 100 mL distilled water and 1.7 mL 6*N* H_2SO_4. Subtract blank reading from sample reading or use it to set instrument to zero absorbance before reading the sample.

e. Correction for samples containing fluoride: Measure sample fluoride concentration by the SPADNS or electrode method. Either:

1) Add the same amount of fluoride as in the sample to each aluminum standard, or
2) Determine fluoride correction from the set of curves in Figure 3500-Al:1.

5. Calculation

$$\text{mg Al/L} = \frac{\mu\text{g Al (in 50 mL final volume)}}{\text{mL sample}}$$

6. Precision and Bias

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A synthetic sample containing 520 µg Al/L and no interference in distilled water was analyzed by the Eriochrome cyanine R method in 27 laboratories. Relative standard deviation was 34.4% and relative error 1.7%.

A second synthetic sample containing 50 µg Al/L, 500 µg Ba/L, and 5 µg Be/L in distilled water was analyzed in 35 laboratories. Relative standard deviation was 38.5% and relative error 22.0%.

A third synthetic sample containing 500 µg Al/L, 50 µg Cd/L, 110 µg Cr/L, 1000 µg Cu/L, 300 µg Fe/L, 70 µg Pb/L, 50 µg Mn/L, 150 µg Ag/L, and 650 µg Zn/L in distilled water was analyzed in 26 laboratories. Relative standard deviation was 28.8% and relative error 6.2%.

A fourth synthetic sample containing 540 µg Al/L and 2.5 mg polyphosphate/L in distilled water was analyzed in 16 laboratories that hydrolyzed the sample in the prescribed manner. Relative standard deviation was 44.3% and relative error 1.3%. In 12 laboratories that applied no corrective measures, the relative standard deviation was 49.2% and the relative error 8.9%.

A fifth synthetic sample containing 480 µg Al/L and 750 µg F/L in distilled water was analyzed in 16 laboratories that relied on the curve to correct for the fluoride content. Relative standard deviation was 25.5% and relative error 2.3%. The 17 laboratories that added fluoride to the aluminum standards showed a relative standard deviation of 22.5% and a relative error of 7.1%.

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3500-Sb ANTIMONY

Antimony (Sb) is the fourth element in Group VA in the periodic table; it has an atomic number of 51, an atomic weight of 121.75, and valences of 3 and 5. The average abundance of Sb in the earth's crust is 0.2 ppm; in soils it is 1 ppm; in streams it is 1 µg/L, and in groundwaters it is <0.1 mg/L. Antimony is sometimes found native, but more commonly in stibnite (Sb_2S_3). It is used in alloys of lead and in batteries, bullets, solder, pyrotechnics, and semiconductors.

The common aqueous species are SbO_2^-, $HSbO_2$, and complexes with carbonate and sulfate. Soluble salts of antimony are toxic. The U.S. EPA primary drinking water standard MCL is 6 µg/L.

The electrothermal atomic absorption spectrometric method (Section 3113B) or the inductively coupled plasma/mass spectrometric method (Section 3125) are the methods of choice because of their sensitivity. Alternatively use the flame atomic absorption spectrometric method (Section 3111B) or the inductively coupled plasma method (Section 3120) when high sensitivity is not required.

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3500-As ARSENIC*#(99)

3500-As A. Introduction

1. Occurrence and Significance

Arsenic (As) is the third element in Group VA of the periodic table; it has an atomic number of 33, an atomic weight of 74.92, and valences of 3 and 5. The average abundance of As in the earth's crust is 1.8 ppm; in soils it is 5.5 to 13 ppm; in streams it is less than 2 µg/L, and in groundwater it is generally less than 100 µg/L. It occurs naturally in sulfide minerals such as pyrite. Arsenic is used in alloys with lead, in storage batteries, and in ammunition. Arsenic compounds are widely used in pesticides and in wood preservatives.

Arsenic is nonessential for plants but is an essential trace element in several animal species. The predominant form between pH 3 and pH 7 is $H_2AsO_4^-$, between pH 7 and pH 11 it is $HAsO_4^{2-}$, and under reducing conditions it is $HAsO_2$(aq) (or H_3AsO_3). Aqueous arsenic in the form of arsenite, arsenate, and organic arsenicals may result from mineral dissolution, industrial discharges, or the application of pesticides. The chemical form of arsenic depends on its source (inorganic arsenic from minerals, industrial discharges, and pesticides; organic arsenic from industrial discharges, pesticides, and biological action on inorganic arsenic).

Severe poisoning can arise from the ingestion of as little as 100 mg arsenic trioxide; chronic effects may result from the accumulation of arsenic compounds in the body at low intake levels. Carcinogenic properties also have been imputed to arsenic compounds. The toxicity of arsenic depends on its chemical form. Arsenite is many times more toxic than arsenate. For the protection of aquatic life, the average concentration of As^{3+} in water should not exceed 72 µg/L and the maximum should not exceed 140 µg/L. The United Nations Food and Agriculture Organization's recommended maximum level for irrigation waters is 100 µg/L. The U.S. EPA primary drinking water standard MCL is 0.05 mg/L.

2. Selection of Method

Methods are available to identify and determine total arsenic, arsenite, and arsenate. Unpolluted fresh water normally does not contain organic arsenic compounds, but may contain inorganic arsenic compounds in the form of arsenate and arsenite. The electrothermal atomic absorption spectrometric method (Section 3113B) is the method of choice in the absence of overwhelming interferences. The hydride generation-atomic absorption method (Section 3114B) is preferred when interferences are present that cannot be overcome by standard electrothermal techniques (e.g., matrix modifiers, background correction). The silver diethyldithiocarbamate method (B), in which arsine is generated by reaction with sodium borohydride in acidic solution, is applicable to the determination of total inorganic arsenic when interferences are absent and

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when the sample contains no methylarsenic compounds. This method also provides the advantage of being able to identify and quantify arsenate and arsenite separately by generating arsine at different pHs. The inductively coupled plasma (ICP) emission spectroscopy method (Section 3120) is useful at higher concentrations (greater than 50 µg/L) while the ICP-mass spectrometric method (Section 3125) is applicable at lower concentrations if chloride does not interfere. When measuring arsenic species, document that speciation does not change over time. No universal preservative for speciation measurements has been identified.

3500-As B. Silver Diethyldithiocarbamate Method

1. General Discussion

a. Principle: Arsenite, containing trivalent arsenic, is reduced selectively by aqueous sodium borohydride solution to arsine, AsH_3, in an aqueous medium of pH 6. Arsenate, methylarsonic acid, and dimethylarsenic acid are not reduced under these conditions. The generated arsine is swept by a stream of oxygen-free nitrogen from the reduction vessel through a scrubber containing glass wool or cotton impregnated with lead acetate solution into an absorber tube containing silver diethyldithiocarbamate and morpholine dissolved in chloroform. The intensity of the red color that develops is measured at 520 nm. To determine total inorganic arsenic in the absence of methylarsenic compounds, a sample portion is reduced at a pH of about l. Alternatively, arsenate is measured in a sample from which arsenite has been removed by reduction to arsine gas at pH 6 as above. The sample is then acidified with hydrochloric acid and another portion of sodium borohydride solution is added. The arsine formed from arsenate is collected in fresh absorber solution.

b. Interferences: Although certain metals—chromium, cobalt, copper, mercury, molybdenum, nickel, platinum, silver, and selenium—influence the generation of arsine, their concentrations in water are seldom high enough to interfere, except in the instance of acid rock drainage. H_2S interferes, but the interference is removed with lead acetate. Antimony is reduced to stibine, which forms a colored complex with an absorption maximum at 510 nm and interferes with the arsenic determination. Methylarsenic compounds are reduced at pH l to methylarsines, which form colored complexes with the absorber solution. If methylarsenic compounds are present, measurements of total arsenic and arsenate are unreliable. The results for arsenite are not influenced by methylarsenic compounds.

c. Minimum detectable quantity: 1 µg arsenic.

2. Apparatus

a. Arsine generator, scrubber, and absorption tube: See Figure 3500-As:1. Use a 200-mL three-necked flask with a sidearm (19/ 22 or similar size female ground-glass joint) through which the inert gas delivery tube reaching almost to the bottom of the flask is inserted; a 24/40 female ground-glass joint to carry the scrubber; and a second side arm closed with a rubber

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septum, or preferably by a screw cap with a hole in its top for insertion of a TFE-faced silicone septum. Place a small magnetic stirring bar in the flask. Fit absorber tube (20 mL capacity) to the scrubber and fill with silver diethyldithiocarbamate solution. Do not use rubber or cork stoppers because they may absorb arsine. Clean glass equipment with concentrated nitric acid.

b. Fume hood: Use apparatus in a well-ventilated hood with flask secured on top of a magnetic stirrer.

c. Photometric equipment:

1) *Spectrophotometer,* for use at 520 nm.

2) *Filter photometer,* with green filter having a maximum transmittance in the 500- to 540-nm range.

3) *Cells,* for spectrophotometer or filter photometer, 1-cm, clean, dry, and each equipped with a tightly fitting cover (TFE stopper) to prevent chloroform evaporation.

3. Reagents

a. Reagent water: See Section 1080A.

b. Acetate buffer, pH 5.5: Mix 428 mL 0.2*M* sodium acetate, $NaC_2H_3O_2$, and 72 mL 0.2*M* acetic acid, CH_3COOH.

c. Sodium acetate, 0.2*M*: Dissolve 16.46 g anhydrous sodium acetate or 27.36 g sodium acetate trihydrate, $NaC_2H_3O_2 \cdot 3H_2O$, in water. Dilute to 1000 mL with water.

d. Acetic acid, 0.2*M*: Dissolve 11.5 mL glacial acetic acid in water. Dilute to 1000 mL.

e. Sodium borohydride solution, 1%: Dissolve 0.4 g sodium hydroxide, NaOH (4 pellets), in 400 mL water. Add 4.0 g sodium borohydride, $NaBH_4$ (check for absence of arsenic). Shake to dissolve and to mix. Prepare fresh every few days.

f. Hydrochloric acid, HCl, 2*M*: Dilute 165 mL conc HCl to 1000 mL with water.

g. Lead acetate solution: Dissolve 10.0 g $Pb(CH_3COO)_2 \cdot 3H_2O$ in 100 mL water.

h. Silver diethyldithiocarbamate solution: Dissolve 1.0 mL morpholine (CAUTION: *Corrosive—avoid contact with skin*) in 70 mL chloroform, $CHCl_3$. Add 0.30 g silver diethyldithiocarbamate, $AgSCSN(C_2H_5)_2$; shake in a stoppered flask until most is dissolved. Dilute to 100 mL with chloroform. Filter and store in a tightly closed brown bottle in a refrigerator.

i. Standard arsenite solution: Dissolve 0.1734 g $NaAsO_2$ in water and dilute to 1000 mL with water. CAUTION: *Toxic—avoid contact with skin and do not ingest.* Dilute 10.0 mL to 100 mL with water; dilute 10.0 mL of this intermediate solution to 100 mL with water; 1.00 mL = 1.00 μg As.

j. Standard arsenate solution: Dissolve 0.416 g $Na_2HAsO_4 \cdot 7H_2O$ in water and dilute to 1000 mL. Dilute 10.0 mL to 100 mL with water; dilute 10 mL of this intermediate solution to

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100 mL; 1.00 mL = 1.00 μg As.

4. Procedure

a. Arsenite:

1) Preparation of scrubber and absorber—Dip glass wool into lead acetate solution; remove excess by squeezing glass wool. Press glass wool between pieces of filter paper, then fluff it. Alternatively, if cotton is used treat it similarly but dry in a desiccator and fluff thoroughly when dry. Place a plug of loose glass wool or cotton in scrubber tube. Add 4.00 mL silver diethyldithiocarbamate solution to absorber tube (5.00 mL may be used to provide enough volume to rinse spectrophotometer cell).

2) Loading of arsine generator—Pipet not more than 70 mL sample containing not more than 20.0 μg As (arsenite) into the generator flask. Add 10 mL acetate buffer. If necessary, adjust total volume of liquid to 80 mL. Flush flask with nitrogen at the rate of 60 mL/min.

3) Arsine generation and measurement—While nitrogen is passing through the system, use a 30-mL syringe to inject through the septum 15 mL 1% sodium borohydride solution within 2 min. Stir vigorously with magnetic stirrer. Pass nitrogen through system for an additional 15 min to flush arsine into absorber solution. Pour absorber solution into a clean and dry spectrophotometric cell and measure absorbance at 520 nm against chloroform. Determine concentration from a calibration curve obtained with arsenite standards. If arsenate also is to be determined for this sample by using the same sample portion, save the liquid in the generator flask.

4) Preparation of standard curves—Treat standard arsenite solution containing 0.0, 1.0, 2.0, 5.0, 10.0, and 20.0 μg As described in ¶s 1) through 3) above. Plot absorbance versus micrograms arsenic in the standard.

b. Arsenate: After removal of arsenite as arsine, treat sample to convert arsenate to arsine:

If the lead acetate-impregnated glass wool has become ineffective in removing hydrogen sulfide (if it has become gray to black) replace glass wool [see ¶ a1)]. Pass nitrogen through system at the rate of 60 mL/min. Cautiously add 10 mL 2.0*N* HCl. Generate arsine as directed in ¶ 4*a*3) and prepare standard curves with standard solutions of arsenate according to procedure of ¶ 4*a*4).

c. Total inorganic arsenic: Prepare scrubber and absorber as directed in ¶ 4*a*1) and load arsine generator as directed in ¶ 4*a*2) using 10 mL 2.0*N* HCl instead of acetate buffer. Generate arsine and measure as directed in ¶ 4*a*3). Prepare standard curves according to ¶ 4*a*4). Curves obtained with standard arsenite solution are almost identical to those obtained with arsenate standard solutions. Therefore, use either arsenite or arsenate standards.

5. Calculation

Calculate arsenite, arsenate, and total inorganic arsenic from readings and calibration curves obtained in 4*a*, *b*, and *c*, respectively, as follows:

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$$\text{mg As/L} = \frac{\mu\text{g As (from calibration curve)}}{\text{mL sample in generator flask}}$$

6. Precision and Bias

Interlaboratory comparisons are not available. The relative standard deviation of results obtained with arsenite/arsenate mixtures containing approximately 10 µg arsenic was less than 10%.

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3500-Ba BARIUM

Barium (Ba) is the fifth element in Group IIA in the periodic table; it has an atomic number of 56, an atomic weight of 137.33, and a valence of 2. The average abundance of Ba in the earth's crust is 390 ppm; in soils it is 63 to 810 ppm; in streams it is 10 mg/L; in U.S. drinking waters it is 49 µg/L; and in groundwaters it is 0.05 to 1 mg/L. It is found chiefly in barite ($BaSO_4$) or in witherite ($BaCO_3$). Barium's main use is in mud slurries used in drilling oil and exploration wells, but it is also used in pigments, rat poisons, pyrotechnics, and in medicine.

The solubility of barium in natural waters is controlled by the solubility of $BaSO_4$, and somewhat by its adsorption on hydroxides. High concentrations of barium occur in some brines. Concentrations exceeding 1 mg/L constitute a toxicity hazard in the marine environment. The U.S. EPA primary drinking water standard MCL is 1 mg/L.

Perform analyses by the atomic absorption spectrometric methods (Section 3111D or Section 3111E), the electrothermal atomic absorption method (Section 3113B), or the inductively

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coupled plasma methods (Section 3120 or Section 3125).

3500-Be BERYLLIUM

Beryllium (Be) is the first element in Group IIA of the periodic table; it has an atomic number of 4, an atomic weight of 9.01, and a valence of 2. The average abundance of Be in the earth's crust is 2 ppm; in soils it is 0.8 to 1.3 ppm; in streams it is 0.2 μg/L, in U.S. drinking waters and in groundwaters it is typically <0.1 μg/L. Beryllium occurs in nature in deposits of beryls in granitic rocks. Beryllium is used in high-strength alloys of copper and nickel, windows in X-ray tubes, and as a moderator in nuclear reactors.

Beryllium solubility is controlled in natural waters by the solubility of beryllium hydroxides. The solubility at pH 6.0 is approximately 0.1 μg/L. It is nonessential for plants and animals. Acute toxicity occurs at 130 μg/L, and chronic toxicity at 5 μg/L in freshwater species. The United Nations Food and Agriculture Organization recommended maximum level for irrigation waters is 100 μg/L. The U.S. EPA primary drinking water standard MCL for beryllium is 4 μg/L.

The atomic absorption spectrometric methods (Section 3111D and Section 3111E, and Section 3113B) and the inductively coupled plasma (ICP) methods (Section 3120 and Section 3125) are the methods of choice. If atomic absorption or ICP instrumentation is not available, the aluminon colorimetric method detailed in the 19th Edition of *Standard Methods* may be used. This method has poorer precision and bias than the methods of choice.

3500-Bi BISMUTH

Bismuth (Bi) is the fifth element in Group VA in the periodic table; it has an atomic number of 83, an atomic weight of 208.98, and valences of 3 and 5. The average abundance of Bi in the earth's crust in 0.08 ppm; in streams it is <0.02 mg/L, and in groundwaters it is <0.1 mg/L. Bismuth occurs in association with lead and silver ores, and occasionally as the native element. ^{210}Bi, ^{212}Bi, and ^{214}Bi are naturally occuring radioisotopes produced in the decay of uranium and thorium. The metal is used in alloys of lead, tin, and cadmium, and in some pharmaceuticals.

In natural water, Bi^{3+} ion will occur, and complex ions with nitrate and chloride also might be expected. The iodide and telluride compounds are toxic by ingestion or inhalation.

Perform analyses by the atomic absorption spectrometric method (Section 3111B) or by the electrothermal atomic absorption method (Section 3113B). The inductively coupled plasma mass spectrometric method (Section 3125) also may be applied successfully in most cases (with lower detection limits), even though bismuth is not specifically listed as an analyte in the method.

3500-B BORON

See Section 4500-B.

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3500-Cd CADMIUM

Cadmium (Cd) is the second element in Group IIB of the periodic table; it has an atomic number of 48, an atomic weight of 112.41, and a valence of 2. The average abundance of Cd in the earth's crust is 0.16 ppm; in soils it is 0.1 to 0.5 ppm; in streams it is 1 μg/L, and in groundwaters it is from 1 to 10 μg/L. Cadmium occurs in sulfide minerals that also contain zinc, lead, or copper. The metal is used in electroplating, batteries, paint pigments, and in alloys with various other metals. Cadmium is usually associated with zinc at a ratio of about 1 part cadmium to 500 parts zinc in most rocks and soils.

The solubility of cadmium is controlled in natural waters by carbonate equilibria. Guidelines for maximum cadmium concentrations in natural water are linked to the hardness or alkalinity of the water (i.e., the softer the water, the lower the permitted level of cadmium). It is nonessential for plants and animals. Cadmium is extremely toxic and accumulates in the kidneys and liver, with prolonged intake at low levels sometimes leading to dysfunction of the kidneys. The United Nations Food and Agriculture Organization recommended maximum level for cadmium in irrigation waters is 10 μg/L. The U.S. EPA primary drinking water standard MCL is 10 μg/L.

The electrothermal atomic absorption spectrometric method (Section 3113B) is preferred. The flame atomic absorption methods (Section 3111B and Section 3111C) and inductively coupled plasma methods (Section 3120 and Section 3125) provide acceptable precision and bias, with higher detection limits. Anodic stripping voltammetry (Section 3130B) can achieve superior detection limits, but is susceptible to interferences from copper, silver, gold, and organic compounds. When atomic absorption spectrometric or inductively coupled plasma apparatus is unavailable and the desired precision is not as great, the dithizone method detailed in the 19th Edition of *Standard Methods* is suitable.

3500-Ca CALCIUM*#(100)

3500-Ca A. Introduction

1. Occurrence and Significance

Calcium (Ca) is the third element in Group IIA of the periodic table; it has an atomic number of 20, an atomic weight of 40.08, and a valence of 2. The average abundance of Ca in the earth's crust is 4.9%; in soils it is 0.07 to 1.7%; in streams it is about 15 mg/L; and in groundwaters it is from 1 to >500 mg/L. The most common forms of calcium are calcium carbonate (calcite) and calcium-magnesium carbonate (dolomite). Calcium compounds are widely used in pharmaceuticals, photography, lime, de-icing salts, pigments, fertilizers, and plasters. Calcium carbonate solubility is controlled by pH and dissolved CO_2. The CO_2 , HCO_3^-,

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and CO_3^{2-} equilibrium is the major buffering mechanism in fresh waters. Hardness is based on the concentration of calcium and magnesium salts, and often is used as a measure of potable water quality.

NOTE: Calcium is necessary in plant and animal nutrition and is an essential component of bones, shells, and plant structures. The presence of calcium in water supplies results from passage over deposits of limestone, dolomite, gypsum, and gypsiferous shale. Small concentrations of calcium carbonate combat corrosion of metal pipes by laying down a protective coating. Because precipitation of calcite in pipes and in heat-exchangers can cause damage, the amount of calcium in domestic and industrial waters is often controlled by water softening (e.g., ion exchange, reverse osmosis). Calcium carbonate saturation and water hardness are discussed in Section 2330 and Section 2340, respectively.

Calcium contributes to the total hardness of water. Chemical softening treatment, reverse osmosis, electrodialysis, or ion exchange is used to reduce calcium and the associated hardness.

2. Selection of Method

The atomic absorption methods (Section 3111B, Section 3111D, and Section 3111E) and inductively coupled plasma method (Section 3120) are accurate means of determining calcium. The EDTA titration method gives good results for control and routine applications, but for samples containing high P levels (>50 mg/L) only the atomic absorption or atomic emission methods are recommended because of interferences often encountered with EDTA indicators.

3. Storage of Samples

The customary precautions are sufficient if care is taken to redissolve any calcium carbonate that may precipitate on standing.

3500-Ca B. EDTA Titrimetric Method

1. General Discussion

a. Principle: When EDTA (ethylenediaminetetraacetic acid or its salts) is added to water containing both calcium and magnesium, it combines first with the calcium. Calcium can be determined directly, with EDTA, when the pH is made sufficiently high that the magnesium is largely precipitated as the hydroxide and an indicator is used that combines with calcium only. Several indicators give a color change when all of the calcium has been complexed by the EDTA at a pH of 12 to 13.

b. Interference: Under conditions of this test, the following concentrations of ions cause no interference with the calcium hardness determination: Cu^{2+}, 2 mg/L; Fe^{2+}, 20 mg/L; Fe^{3+}, 20 mg/L; Mn^{2+}, 10 mg/L; Zn^{2+}, 5 mg/L; Pb^{2+}, 5 mg/L; Al^{3+}, 5 mg/L; and Sn^{4+}, 5 mg/L. Orthophosphate precipitates calcium at the pH of the test. Strontium and barium give a positive interference and alkalinity in excess of 300 mg/L may cause an indistinct end point in hard

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waters.

2. Reagents

a. Sodium hydroxide, NaOH, 1*N*.

b. Indicators: Many indicators are available for the calcium titration. Some are described in the literature (see Bibliography ¶ 6); others are commercial preparations and also may be used. Murexide (ammonium purpurate) was the first indicator available for detecting the calcium end point; directions for its use are presented in this procedure. Individuals who have difficulty recognizing the murexide end point may find the indicator Eriochrome Blue Black R (color index number 202) or Solochrome Dark Blue an improvement because of the color change from red to pure blue. Eriochrome Blue Black R is sodium-1-(2-hydroxy-1-naphthylazo)-2-naphthol-4-sulfonic acid. Other indicators specifically designed for use as end-point detectors in EDTA titration of calcium may be used.

1) *Murexide (ammonium purpurate) indicator:* This indicator changes from pink to purple at the end point. Prepare by dissolving 150 mg dye in 100 g absolute ethylene glycol. Water solutions of the dye are not stable for longer than 1 d. A ground mixture of dye powder and sodium chloride (NaCl) provides a stable form of the indicator. Prepare by mixing 200 mg murexide with 100 g solid NaCl and grinding the mixture to 40 to 50 mesh. Titrate immediately after adding indicator because it is unstable under alkaline conditions. Facilitate end-point recognition by preparing a color comparison blank containing 2.0 mL NaOH solution, 0.2 g solid indicator mixture (or 1 to 2 drops if a solution is used), and sufficient standard EDTA titrant (0.05 to 0.10 mL) to produce an unchanging color.

2) *Eriochrome Blue Black R indicator:* Prepare a stable form of the indicator by grinding together in a mortar 200 mg powdered dye and 100 g solid NaCl to 40 to 50 mesh. Store in a tightly stoppered bottle. Use 0.2 g of ground mixture for the titration in the same manner as murexide indicator. During titration the color changes from red through purple to bluish purple to a pure blue with no trace of reddish or purple tint. The pH of some (not all) waters must be raised to 14 (rather than 12 to 13) by the use of 8*N* NaOH to get a good color change.

c. Standard EDTA titrant, 0.01*M:* Prepare standard EDTA titrant and standardize against standard calcium solution as described in Section 2340C to obtain EDTA/$CaCO_3$ equivalence. Standard EDTA titrant, 0.0100*M*, is equivalent to 1000 mg $CaCO_3$/1.00 mL; use titrated equivalent for *B* in the calculations in 4.

3. Procedure

a. Pretreatment of water and wastewater samples: Follow the procedure described in Section 3030E or I if samples require preliminary digestion.

b. Sample preparation: Because of the high pH used in this procedure, titrate immediately after adding alkali and indicator. Use 50.0 mL sample, or a smaller portion diluted to 50 mL so that the calcium content is about 5 to 10 mg. Analyze hard waters with alkalinity higher than 300

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mg $CaCO_3$/L by taking a smaller portion and diluting to 50 mL. Alternatively, adjust sample pH into the acid range (pH <6), boil for 1 min to dispel CO_2, and cool before beginning titration.

c. Titration: Add 2.0 mL NaOH solution or a volume sufficient to produce a pH of 12 to 13. Stir. Add 0.1 to 0.2 g indicator mixture selected (or 1 to 2 drops if a solution is used). Add EDTA titrant slowly, with continuous stirring to the proper end point. When using murexide, check end point by adding 1 to 2 drops of titrant in excess to make certain that no further color change occurs.

4. Calculation

$$\text{mg Ca/L} = \frac{A \times B \times 400.8}{\text{mL sample}}$$

$$\text{Calcium hardness as mg } CaCO_3\text{/L} = \frac{A \times B \times 1000}{\text{mL sample}}$$

where:

A = mL titrant for sample and
B = mg $CaCO_3$ equivalent to 1.00 mL EDTA titrant at the calcium indicator end point.

5. Precision and Bias

A synthetic sample containing 108 mg Ca/L, 82 mg Mg/L, 3.1 mg K/L, 19.9 mg Na/L, 241 mg Cl^-/L, 1.1 mg NO_3^--N/L, 0.25 mg NO_2^--N/L, 259 mg SO_4^{2-}/L, and 42.5 mg total alkalinity/L (contributed by $NaHCO_3$) in distilled water was analyzed in 44 laboratories by the EDTA titrimetric method, with a relative standard deviation of 9.2% and a relative error of 1.9%.

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3500-Cs CESIUM

Cesium (Cs) is the sixth element in Group IA of the periodic table; it has an atomic number of 55, an atomic weight of 132.90, and a valence of 1. The average abundance of Cs in the earth's crust is 2.6 ppm; in soils it is 1 to 5 ppm; in streams it is 0.02 mg/L; and in groundwaters it is generally <0.1 mg/L. Cesium is found in lepidolite and in the water of certain mineral springs. ^{137}Cs, with a 33-year half-life, is widely dispersed on the earth's surface as a result of the radioactive fallout from the atmospheric testing of nuclear weapons. Cesium compounds are used in photoelectric cells, as a catalyst, and in brewing. Some cesium compounds are fire hazards.

Perform analyses by the flame atomic absorption spectrometric method (Section 3111B). The inductively coupled plasma/mass spectrometric method (Section 3125) also may be applied successfully in most cases (with lower detection limits), even though cesium is not specifically listed as an analyte in the method.

3500-Cr CHROMIUM*#(101)

3500-Cr A. Introduction

1. Occurrence and Significance

Chromium (Cr) is the first element in Group VIB in the periodic table; it has an atomic number of 24, an atomic weight of 51.99, and valences of 1 through 6. The average abundance of Cr in the earth's crust is 122 ppm; in soils Cr ranges from 11 to 22 ppm; in streams it averages about 1 µg/L, and in groundwaters it is generally 100 µg/L. Chromium is found chiefly in chrome-iron ore ($FeO{\cdot}Cr_2O_3$). Chromium is used in alloys, in electroplating, and in pigments. Chromate compounds frequently are added to cooling water for corrosion control.

In natural waters trivalent chromium exists as Cr^{3+}, $Cr(OH)^{2+}$, $Cr(OH)_2^{+}$, and $Cr(OH)_4^{-}$; in the hexavalent form chromium exists as CrO_4^{2-} and as $Cr_2O_7^{2-}$. Cr^{3+} would be expected to form strong complexes with amines, and would be adsorbed by clay minerals. Chromium may exist in water supplies in both the hexavalent and the trivalent state although the trivalent form rarely occurs in potable water.

Chromium is considered nonessential for plants, but an essential trace element for animals. Hexavalent compounds have been shown to be carcinogenic by inhalation and are corrosive to tissue. The chromium guidelines for natural water are linked to the hardness or alkalinity of the water (i.e., the softer the water, the lower the permitted level for chromium). The United Nations

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Food and Agriculture Organization recommended maximum level for irrigation waters is 100 µg/L. The U.S. EPA primary drinking water standard MCL is 0.1 mg/L for total chromium.

2. Selection of Method

The colorimetric method (B) is useful for the determination of hexavalent chromium in a natural or treated water in the range from 100 to 1000 µg/L. This range can be extended by appropriate sample dilution or concentration and/or use of longer cell paths. The ion chromatographic method with photometric detection (C) is suitable for determining dissolved hexavalent chromium in drinking water, groundwater, and industrial wastewater effluents. The electrothermal atomic absorption spectrometric method (Section 3113B) is suitable for determining low levels of total chromium (< 50 µg/L) in water and wastewater, and the flame atomic absorption spectrometric methods (Section 3111B and Section 3111C) and the inductively coupled plasma methods (Section 3120 and Section 3125) are appropriate for measuring concentrations up to milligram-per-liter levels.

3. Sample Handling

If only the dissolved metal content is desired, filter sample through a 0.45-µm membrane filter at time of collection, and after filtration acidify filtrate with conc nitric acid (HNO_3) to pH <2. If only dissolved hexavalent chromium is desired, adjust pH of filtrate to 8 or above with 1*N* sodium hydroxide solution and refrigerate. If the total chromium content is desired, acidify unfiltered sample at time of collection with conc HNO_3 to pH <2. If total hexavalent chromium is desired, adjust the pH of unfiltered sample to 8 or above with 1*N* sodium hydroxide and refrigerate.

3500-Cr B. Colorimetric Method

1. General Discussion

a. Principle: This procedure measures only hexavalent chromium (Cr^{6+}). Therefore, to determine total chromium convert all the chromium to the hexavalent state by oxidation with potassium permanganate. NOTE: The oxidation process may not provide total conversion of all chromium species to Cr^{6+}.[1-3] For total chromium determination, acid-digest the sample (see Section 3030) and follow with a suitable instrumental analysis technique. The hexavalent chromium is determined colorimetrically by reaction with diphenylcarbazide in acid solution. A red-violet colored complex of unknown composition is produced. The reaction is very sensitive, the molar absorptivity based on chromium being about 40 000 L g^{-1} cm^{-1} at 540 nm. To determine total chromium, digest the sample with a sulfuric-nitric acid mixture and then oxidize with potassium permanganate before reacting with the diphenylcarbazide.

b. Interferences: The reaction with diphenylcarbazide is nearly specific for chromium. Hexavalent molybdenum and mercury salts will react to form color with the reagent but the

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intensities are much lower than that for chromium at the specified pH. Concentrations as high as 200 mg Mo or Hg/L can be tolerated. Vanadium interferes strongly but concentrations up to 10 times that of chromium will not cause trouble. Potential interference from permanganate is eliminated by prior reduction with azide. Iron in concentrations greater than 1 mg/L may produce a yellow color but the ferric ion (Fe^{3+}) color is not strong and no difficulty is encountered normally if the absorbance is measured photometrically at the appropriate wavelength. Interfering amounts of molybdenum, vanadium, iron, and copper can be removed by extraction of the cupferrates of these metals into chloroform ($CHCl_3$). A procedure for this extraction is provided but do not use it unless necessary, because residual cupferron and $CHCl_3$ in the aqueous solution complicate the later oxidation. Therefore, follow the extraction by additional treatment with acid fuming to decompose these compounds.

2. Apparatus

a. Colorimetric equipment: One of the following is required:

1) *Spectrophotometer,* for use at 540 nm, with a light path of 1 cm or longer.

2) *Filter photometer,* providing a light path of 1 cm or longer and equipped with a greenish yellow filter having maximum transmittance near 540 nm.

b. Separatory funnels, 125-mL, Squibb form, with glass or TFE stopcock and stopper.

c. Acid-washed glassware: New and unscratched glassware will minimize chromium adsorption on glass surfaces during the oxidation procedure. Do not use glassware previously treated with chromic acid. Thoroughly clean other used glassware and new glassware with nitric or hydrochloric acid to remove chromium traces.

3. Reagents

Use reagent water (see Section 1080) for reagent preparation and analytical procedure.

a. Stock chromium solution: Dissolve 141.4 mg $K_2Cr_2O_7$ in water and dilute to 100 mL; 1.00 mL = 500 μg Cr.

b. Standard chromium solution: Dilute 1.00 mL stock chromium solution to 100 mL; 1.00 mL = 5.00 μg Cr.

c. Nitric acid, HNO_3, conc.

d. Sulfuric acid, H_2SO_4, conc, 18*N*, and 6*N*.

e. Sulfuric acid, H_2SO_4, 0.2*N*: Dilute 17 mL 6*N* H_2SO_4 to 500 mL with water.

f. Phosphoric acid, H_3PO_4, conc.

g. Methyl orange indicator solution.

h. Hydrogen peroxide, H_2O_2, 30%.

i. Ammonium hydroxide, NH_4OH, conc.

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j. Potassium permanganate solution: Dissolve 4 g $KMnO_4$ in 100 mL water.

k. Sodium azide solution: Dissolve 0.5 g NaN_3 in 100 mL water.

l. Diphenylcarbazide solution: Dissolve 250 mg 1,5-diphenylcarbazide (1,5-diphenylcarbohydrazide) in 50 mL acetone. Store in a brown bottle. Discard when solution becomes discolored.

m. Chloroform, $CHCl_3$: Avoid or redistill material that comes in containers with metal or metal-lined caps.

n. Cupferron solution: Dissolve 5 g cupferron, $C_6H_5N(NO)ONH_4$, in 95 mL water.

o. Sodium hydroxide,1N: Dissolve 40 g NaOH in 1 L water. Store in plastic bottle.

4. Procedure

a. Preparation of calibration curve: To compensate for possible slight losses of chromium during digestion or other analytical operations, treat standards by the same procedure as the sample. Accordingly, pipet measured volumes of standard chromium solution (5 µg/mL) ranging from 2.00 to 20.0 mL, to give standards for 10 to 100 µg Cr, into 250-mL beakers or conical flasks. Depending on pretreatment used in ¶ b below, proceed with subsequent treatment of standards as if they were samples, also carrying out cupferron treatment of standards if this is required for samples.

Develop color as for samples, transfer a suitable portion of each colored solution to a 1-cm absorption cell, and measure absorbance at 540 nm, using reagent water as reference. Correct absorbance readings of standards by subtracting absorbance of a reagent blank carried through the method.

Construct a calibration curve by plotting corrected absorbance values against micrograms chromium in 102 mL final volume.

b. Treatment of sample: If sample has been filtered and/or only hexavalent chromium is desired, start analysis within 24 h of collection and proceed to ¶ 4*e*. NOTE: Recent evidence[4] suggests that preserved samples can be held for 30 d without substantial changes to Cr^{6+} concentrations. If total dissolved chromium is desired and there are interfering amounts of molybdenum, vanadium, copper, or iron present, proceed to ¶ 4*c*. If interferences are not present, proceed to ¶ 4*d*.

If sample is unfiltered and total chromium is desired, digest with HNO_3 and H_2SO_4 as in Section 3030G. If interferences are present, proceed to ¶ 4*c*, ¶ 4*d*, and ¶ 4*e*. If there are no interferences, proceed to ¶ 4*d* and ¶ 4*e*.

c. Removal of molybdenum, vanadium, iron, and copper with cupferron: Pipet a portion of sample containing 10 to 100 µg Cr into a 125-mL separatory funnel. Dilute to about 40 mL with water and chill in an ice bath. Add 5 mL ice-cold cupferron solution, shake well, and let stand in ice bath for 1 min. Extract in separatory funnel with three successive 5-mL portions of $CHCl_3$;

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shake each portion thoroughly with aqueous solution, let layers separate, and withdraw and discard $CHCl_3$ extract. Transfer extracted aqueous solution to a 125-mL conical flask. Wash separatory funnel with a small amount of water and add wash water to flask. Boil for about 5 min to volatilize $CHCl_3$ and cool. Add 5 mL HNO_3 and 3 mL H_2SO_4. Boil samples to the appearance of SO_3 fumes. Cool slightly, carefully add 5 mL HNO_3, and again boil to fumes to complete decomposition of organic matter. Cool, wash sides of flask, and boil once more to SO_3 fumes, assuming elimination of all HNO_3. Cool and add 25 mL water.

d. Oxidation of trivalent chromium: Pipet a portion of digested sample with or without interferences removed, and containing 10 to 100 µg Cr, into a 125-mL conical flask. Add several drops of methyl orange indicator, then add conc NH_4OH until solution just begins to turn yellow. Add 1 + 1 H_2SO_4 dropwise until it is acidic, plus 1 mL (20 drops) in excess. Adjust volume to about 40 mL, add two or more acid-washed glass beads, and heat to boiling. Add 2 drops $KMnO_4$ solution to give a dark red color. If fading occurs, add $KMnO_4$ dropwise to maintain an excess of about 2 drops. Boil for 2 min longer. Add 1 mL NaN_3 solution and continue boiling gently. If red color does not fade completely after boiling for approximately 30 s, add another 1 mL NaN_3 solution. Continue boiling for 1 min after color has faded completely, then cool.

e. Color development and measurement: Add 0.25 mL (5 drops) H_3PO_4. Use 0.2*N* H_2SO_4 and a pH meter to adjust solution to pH 1.0 ± 0.3. NOTE: Recent work[5] identifies the optimum pH range for color development to be 1.6 to 2.2; the matter of optimum pH range is currently being considered by *Standard Methods*. Transfer solution to a 100-mL volumetric flask, dilute to 100 mL, and mix. Add 2.0 mL diphenylcarbazide solution, mix, and let stand 5 to 10 min for full color development. Transfer an appropriate portion to a 1-cm absorption cell and measure its absorbance at 540 nm, using reagent water as reference. Correct absorbance reading of sample by subtracting absorbance of a blank carried through the method (see also note below). From the corrected absorbance, determine micrograms chromium present by reference to the calibration curve.

NOTE: If the solution is turbid after dilution to 100 mL in ¶ e above, take an absorbance reading before adding carbazide reagent and correct absorbance reading of final colored solution by subtracting the absorbance measured previously.

5. Calculation

For digested samples:

$$\text{mg Cr/L} = \frac{\mu\text{g Cr (in 102 mL final volume)}}{A \times B} \times 100$$

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where:

A = mL original sample, and
B = mL portion from 100 mL digested sample.

For undigested samples:

$$\text{mg Cr/L} = \frac{\mu\text{g Cr (in 102 mL final volume)}}{A}$$

6. Precision and Bias

Collaborative test data from 16 laboratories were obtained on reagent water, tap water, 10% NaCl solution, treated water from synthetic organic industrial waste, EPA extraction leachate, process water, lake water, and effluent from a steel pickle liquor treatment plant.[6] The test data yielded the following relationships:

Reagent water:

$$S_t = 0.037x + 0.006$$

$$S_o = 0.022x + 0.004$$

Drinking or wastewater:

$$S_t = 0.067x + 0.004$$

$$S_o = 0.037x + 0.002$$

Leachate:

$$S_t = 0.032x + 0.007$$

$$S_o = 0.017x + 0.004$$

where:

S_t = overall precision,
S_o = single-operator precision, and
x = chromium concentration, mg/L.

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3500-Cr C. Ion Chromatographic Method

1. General Discussion

a. Principle: This method is applicable to determination of dissolved hexavalent chromium in drinking water, groundwater, and industrial wastewater effluents. An aqueous sample is filtered and its pH adjusted to 9 to 9.5 with a concentrated buffer. This pH adjustment reduces the solubility of trivalent chromium and preserves the hexavalent chromium oxidation state. The sample is introduced into the instrument's eluent stream of ammonium sulfate and ammonium

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hydroxide. Trivalent chromium in solution is separated from the hexavalent chromium by the column. After separation, hexavalent chromium reacts with an azide dye to produce a chromogen that is measured at 530 nm. Hexavalent chromium is identified on the basis of retention time.

Although this method was developed using specific commercial equipment, use of another manufacturer's equipment should be acceptable if appropriate adjustments are made.

b. Interferences: Interferences may come from several sources. Use a good grade of salts for the buffer because trace amounts of chromium may be included.

Several soluble species of trivalent chromium in the sample may be oxidized to the hexavalent form in an alkaline medium in the presence of such oxidants as hydrogen peroxide, ozone, and manganese dioxide. The hexavalent form can be reduced to the trivalent in the presence of reducing species in an acid medium.

High ionic concentration may cause column overload. Samples high in chloride and/or sulfate might show this phenomenon, which is characterized by a change in peak geometry.

Interfering organic compounds are removed by the guard column.

c. Minimum detectable concentrations: The method detection limits obtained in a single laboratory with a 250-µL loop were as follows:

Reagent water	0.4 µg/L
Drinking water	0.3 µg/L
Groundwater	0.3 µg/L
Primary wastewater effluent	0.3 µg/L
Electroplating waste	0.3 µg/L

d. Sample preservation and holding time: Filter sample through a 0.45-µm filter. Use a portion of sample to rinse syringe filter unit and filter, then collect the required volume of filtrate. Adjust pH to 9 to 9.5 by adding buffer solution dropwise while checking pH with a pH meter.

Ship and store sample at 4°C. Bring to room temperature before analysis. Analyze samples within 24 h of collection.

2. Apparatus

a. Ion chromatograph equipped with a pump capable of precisely delivering a flow of 1 to 5 mL/min. The metallic parts of the pump must not contact sample, eluent, or reagent. Sample loops should be available or the instrument should be capable of delivering from 50 to 250-µL injections of sample. The visible absorption cell should not contain metallic parts that contact the eluent-sample flow. The cell must be usable at 530 nm. Use plastic pressurized containers to deliver eluent and post-column reagent. Use high-purity helium (99.995%) to pressurize the eluent and post-column reagent vessel.

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b. Guard column, to be placed before the separator column, containing an adsorbent capable of adsorbing organic compounds and particulates that would damage or interfere with the analysis or equipment.*#(102)

c. Separator column, packed with a high-capacity anion-exchange resin capable of resolving chromate from other sample constituents.†#(103)

d. Recorder, integrator, or computer for receiving signals from the detector as a function of time.

e. Labware: Soak all reusable labware (glass, plastic, etc.) including sample containers, overnight in laboratory-grade detergent, rinse, and soak for 4 h in a mixture of nitric acid (1 part), hydrochloric acid (2 parts), and reagent water (9 parts). Rinse with tap water and reagent water. NOTE: Never use chromic acid cleaning solution.

f. Syringe, equipped with male luer-type fitting and a capacity of at least 3 mL.

3. Reagents

a. Reagent water: Deionized or distilled water free from interferences at the minimum detection limit of each constituent, filtered through a 0.2-µm membrane filter and having a conductance of less than 0.1 µS/cm. Use for preparing all reagents.

b. Cr(VI) stock solution, 100 mg Cr^{6+}/L: Prepare from primary standard grade potassium dichromate. Dissolve 0.1414 g $K_2Cr_2O_7$ in water and dilute to 500 mL in a volumetric flask. pH adjustment is not required. Store in plastic. CAUTION: *Hexavalent chromium is toxic and a suspected carcinogen; handle with care.*

c. Eluent: Dissolve 33 g ammonium sulfate $(NH_4)_2SO_4$, in 500 mL water and add 6.5 mL conc ammonium hydroxide, NH_4OH. Dilute to 1 L with water.

d. Post-column reagent: Dissolve 0.5 g 1,5-diphenylcarbazide in 100 mL HPLC-grade methanol. Add with stirring to 500 mL water containing 28 mL conc H_2SO_4. Dilute to 1 L with water. Reagent is stable for 4 or 5 d; prepare only as needed.

e. Buffer solution: Dissolve 33 g ammonium sulfate, $(NH_4)_2SO_4$, in 75 mL water and add 6.5 mL conc ammonium hydroxide, NH_4OH. Dilute to 100 mL with water.

4. Procedure

a. Instrument setup: Establish ion chromatograph operating conditions as indicated in Table 3500-Cr:I. Set flow rate of the eluent pump at 1.5 mL/min and adjust pressure of reagent delivery module so that the system flow rate, measured after the detector, is 2.0 mL/min. Measure system flow rate using a graduated cylinder and stopwatch. Allow approximately 30 min after adjustment before measuring flow.

Use an injection loop size based on required sensitivity. A 50-µL loop is sufficient, although a 250-µL loop was used to determine the method detection limit.

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b. Calibration: Before sample analysis, construct a calibration curve using a minimum of a blank and three standards that bracket the expected sample concentration range. Prepare calibration standards from the stock standard (3*b*) by appropriate dilution with water in volumetric flasks. Adjust to pH 9 to 9.5 with buffer solution (3*e*) before final dilution. Injection volumes of standards should be about 10 times the injection loop volume to insure complete loop flushing.

c. Sample analysis: Bring chilled, pH-adjusted sample to ambient temperature. Fill a clean syringe with sample, attach a 0.45-µm syringe filter, and inject 10 times the sample loop volume into the instrument. Dilute any sample that has a concentration greater than the highest calibration standard.

5. Calculation

Determine area or height of the Cr(VI) peak in the calibration standard chromatograms. Calculate a calibration line by regressing peak area (or height) against standard concentration in mg/L. A correlation coefficient less than 0.995 may indicate a problem with the analysis.

For samples, measure area (or height) of Cr(VI) peak in sample chromatogram, as determined by retention time. Calculate Cr(VI) concentration by interpolating from the calibration line. Correct data for any dilutions made.

Currently available instrumentation automates the entire measurement process (peak measurement, calibration, and sample measurements and calculations). Ensure that enough quality control samples are analyzed to monitor the instrumental processes.

6. Quality Control

a. Initial demonstration of performance: Before sample analysis, set up instrument and analyze enough known samples to determine estimates for the method detection limit and linear calibration range. Use the initial demonstration of performance to characterize instrument performance, i.e., method detection levels (MDLs) and linear calibration range.

b. Initial and continuing calibration performance: Initially, after every 10 samples, and after the final sample, analyze an independent check sample and a calibration blank. The concentration of the calibration check sample should be near the mid-calibration range; prepare from a source independent of the calibration standards. Use acceptance criteria for check standard recovery and calibration standard concentration based on project goals for precision and accuracy. Typical values for recovery of the check standard range from 90 to 110%. The acceptance criteria for the calibration blank are typically set at ± the nominal MDL.

c. Reagent blank analysis: Analyze one laboratory reagent blank with each batch of samples. Significant Cr(VI) detected in the reagent blank is a sign of contamination. Identify source and eliminate contamination.

d. Laboratory-fortified matrix (also known as matrix spike) analysis: To a portion of a sample, add a known quantity of Cr(VI). After analysis, calculate percent recovery of the known addition. If the recovery falls outside the control limits (typically 75 to 125%), the matrix may be

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interfering with the results. Perform additional testing to determine whether analysis by the method of standard additions will overcome the interference. Analyze fortified matrix samples as frequently as dictated by project goals and anticipated similarity of matrices in the sample set.

e. Laboratory control sample: Analyze a laboratory control sample (LCS) from an external source with every sample batch. Process LCS and samples identically, including filtering and pH adjustment. Base acceptance criteria for LCS recovery on project goals for precision and bias. Typical values for acceptable recovery range from 90 to 110%.

7. Precision and Bias

The instrument operating conditions and data from a single- laboratory test of the method are shown in Table 3500-Cr:I and Table 3500-Cr:II, respectively.

Multilaboratory test data are shown in Table 3500-Cr:III.‡#(104) Fifteen laboratories analyzed samples ranging from 1.2 to 960 μg Cr/L.

For reagent water matrix:

$$S_o = 0.033x + 0.106$$

$$S_t = 0.050x + 0.559$$

$$\text{Mean recovery} = 1.04x + 0.183$$

where:

S_o = single-operator precision,
S_t = overall precision, and
x = added amount.

For wastewater matrix:

$$S_o = 0.041x + 0.039$$

$$S_t = 0.059x + 1.05$$

$$\text{Mean recovery} = 0.989x - 0.41$$

The eleven water samples consisted of a reagent water blank and five Youden pairs. The nine wastewater samples consisted of a wastewater blank and four Youden pairs.

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3500-Co COBALT

Cobalt (Co) is the second element in Group VIII in the periodic table; it has an atomic number of 27, an atomic weight of 58.93, and valences of 1, 2, and 3. The average abundance of Co in the earth's crust is 29 ppm; in soils it is 1.0 to 14 ppm; in streams it is 0.2 μg/L; and in groundwaters it is 1 to 10 μg/L. Cobalt occurs only sparingly in ores, usually as the sulfide or the arsenide. It is widely used in alloys of various steels, in electroplating, in fertilizers, and in porcelain and glass.

The solubility of cobalt is controlled by coprecipitation or adsorption by oxides or manganese and iron, by carbonate precipitation, and by the formation of complex ions. Cobalt dust is flammable and is toxic by inhalation. Cobalt is considered essential for algae and some bacteria, nonessential for higher plants, and an essential trace element for animals. The United Nations Food and Agriculture Organization recommended maximum level for irrigation waters is 100 μg/L.

Perform analyses by the flame atomic absorption spectrometric methods (Section 3111B and Section 3111C), by the electrothermal atomic absorption method (Section 3113B), or by the inductively coupled plasma methods (Section 3120 and Section 3125).

3500-Cu COPPER*#(105)

3500-Cu A. Introduction

1. Occurrence and Significance

Copper (Cu) is the first element in Group IB in the periodic table; it has an atomic number of 29, an atomic weight of 63.54, and valences of 1 and 2. The average abundance of Cu in the earth's crust is 68 ppm; in soils it is 9 to 33 ppm; in streams it is 4 to 12 μg/L; and in groundwater it is <0.1 mg/L. Copper occurs in its native state, but is also found in many minerals, the most important of which are those containing sulfide compounds (e.g., chalcopyrite), but also those with oxides and carbonates. Copper is widely used in electrical wiring, roofing, various alloys, pigments, cooking utensils, piping, and in the chemical industry.

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Copper salts are used in water supply systems to control biological growths in reservoirs and distribution pipes and to catalyze the oxidation of manganese. Copper forms a number of complexes in natural waters with inorganic and organic ligands. Among the common aqueous species are Cu^{2+}, $Cu(OH)_2$, and $CuHCO_3^+$. Corrosion of copper-containing alloys in pipe fittings may introduce measurable amounts of copper into the water in a pipe system.

Copper is considered an essential trace element for plants and animals. Some compounds are toxic by ingestion or inhalation. The United Nations Food and Agriculture Organization recommended maximum level for irrigation waters is 200 µg/L. Under the lead-copper rule, the U.S. EPA drinking water 90th percentile action level is 1.3 mg/L.

2. Selection of Method

The atomic absorption spectrometric methods (Section 3111B and Section 3111C), the inductively coupled plasma methods (Section 3120 and Section 3125), and the neocuproine method (B) are recommended because of their freedom from interferences. The electrothermal atomic absorption method (Section 3113B) also may be used with success with an appropriate matrix modifier. The bathocuproine method (C) may be used for potable waters.

3. Sampling and Storage

Copper ion tends to be adsorbed on the surface of sample containers. Therefore, analyze samples as soon as possible after collection. If storage is necessary, use 0.5 mL 1 + 1 HCl/100 mL sample, or acidify to pH <2 with HNO_3, to prevent this adsorption.

3500-Cu B. Neocuproine Method

1. General Discussion

a. Principle: Cuprous ion (Cu^+) in neutral or slightly acidic solution reacts with 2,9-dimethyl-1,10-phenanthroline (neocuproine) to form a complex in which 2 moles of neocuproine are bound by 1 mole of Cu^+ ion. The complex can be extracted by a number of organic solvents, including a chloroform-methanol ($CHCl_3$-CH_3OH) mixture, to give a yellow solution with a molar absorptivity of about 8000 at 457 nm. The reaction is virtually specific for copper; the color follows Beer's law up to a concentration of 0.2 mg Cu/25 mL solvent; full color development is obtained when the pH of the aqueous solution is between 3 and 9; the color is stable in $CHCl_3$-CH_3OH for several days.

The sample is treated with hydroxylamine-hydrochloride to reduce cupric ions to cuprous ions. Sodium citrate is used to complex metallic ions that might precipitate when the pH is raised. The pH is adjusted to 4 to 6 with NH_4OH, a solution of neocuproine in methanol is added, and the resultant complex is extracted into $CHCl_3$. After dilution of the $CHCl_3$ to an exact volume with CH_3OH, the absorbance of the solution is measured at 4571 nm.

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b. Interference: Large amounts of chromium and tin may interfere. Avoid interference from chromium by adding sulfurous acid to reduce chromate and complex chromic ion. In the presence of much tin or excessive amounts of other oxidizing ions, use up to 20 mL additional hydroxylamine-hydrochloride solution.

Cyanide, sulfide, and organic matter interfere but can be removed by a digestion procedure.

c. Minimum detectable concentration: The minimum detectable concentration, corresponding to 0.01 absorbance or 98% transmittance, is 3 µg Cu when a 1-cm cell is used and 0.6 µg Cu when a 5-cm cell is used.

2. Apparatus

a. Colorimetric equipment: One of the following is required:

1) *Spectrophotometer,* for use at 4571 nm, providing a light path of 1 cm or longer.

2) *Filter photometer,* providing a light path of 1 cm or longer and equipped with a narrow-band violet filter having maximum transmittance in the range 450 to 460 nm.

b. Separatory funnels, 125-mL, Squibb form, with glass or TFE stopcock and stopper.

3. Reagents

a. Redistilled water, copper-free: Because most ordinary distilled water contains detectable amounts of copper, use redistilled water, prepared by distilling singly distilled water in a resistant-glass still, or distilled water passed through an ion-exchange unit, to prepare all reagents and dilutions.

b. Stock copper solution: To 200.0 mg polished electrolytic copper wire or foil in a 250-mL conical flask, add 10 mL water and 5 mL conc HNO_3. After the reaction has slowed, warm gently to complete dissolution of the copper and boil to expel oxides of nitrogen, using precautions to avoid loss of copper. Cool, add about 50 mL water, transfer quantitatively to a 1-L volumetric flask, and dilute to the mark with water; 1 mL = 200 µg Cu.

c. Standard copper solution: Dilute 50.00 mL stock copper solution to 500 mL with water; 1.00 mL = 20.0 µg Cu.

d. Sulfuric acid, H_2SO_4, conc.

e. Hydroxylamine-hydrochloride solution: Dissolve 50 g $NH_2OH{\cdot}HCl$ in 450 mL water.

f. Sodium citrate solution: Dissolve 150 g $Na_3C_6H_5O_7{\cdot}2H_2O$ in 400 mL water. Add 5 mL $NH_2OH{\cdot}HCl$ solution and 10 mL neocuproine reagent. Extract with 50 mL $CHCl_3$ to remove copper impurities and discard $CHCl_3$ layer.

g. Ammonium hydroxide, NH_4OH, 5*N*: Dilute 330 mL conc NH_4OH (28-29%) to 1000 mL with water. Store in a polyethylene bottle.

h. Congo red paper, or other pH test paper showing a color change in the pH range of 4 to 6.

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i. Neocuproine reagent: Dissolve 100 mg 2,9-dimethyl-1,10-phenanthroline hemihydrate*#(106) in 100 mL methanol. This solution is stable under ordinary storage conditions for a month or more.

j. Chloroform, $CHCl_3$: Avoid or redistill material that comes in containers with metal-lined caps.

k. Methanol, CH_3OH, reagent grade.

l. Nitric acid, HNO_3, conc.

m. Hydrochloric acid, HCl, conc.

4. Procedure

a. Preparation of calibration curve: Pipet 50 mL water into a 125-mL separatory funnel for use as a reagent blank. Prepare standards by pipetting 1.00 to 10.00 mL (20.0 to 200 µg Cu) standard copper solution into a series of 125-mL separatory funnels, and dilute to 50 mL with water. Add 1 mL conc H_2SO_4 and use the extraction procedure given in ¶ 4*b* below.

Construct a calibration curve by plotting absorbance versus micrograms of copper.

To prepare a calibration curve for smaller amounts of copper, dilute 10.0 mL standard copper solution to 100 mL. Carry 1.00-to 10.00-mL volumes of this diluted standard through the previously described procedure, but use 5-cm cells to measure absorbance.

b. Treatment of sample: Transfer 100 mL sample to a 250-mL beaker, add 1 mL conc H_2SO_4 and 5 mL conc HNO_3. Add a few boiling chips and cautiously evaporate to dense white SO_3 fumes on a hot plate. If solution remains colored, cool, add another 5 mL conc HNO_3, and again evaporate to dense white fumes. Repeat, if necessary, until solution becomes colorless.

Cool, add about 80 mL water, and bring to a boil. Cool and filter into a 100-mL volumetric flask. Make up to 100 mL with water using mostly beaker and filter washings.

Pipet 50.0 mL or other suitable portion containing 4 to 200 µg Cu, from the solution obtained from preliminary treatment, into a 125-mL separatory funnel. Dilute, if necessary, to 50 mL with water. Add 5 mL $NH_2OH{\cdot}HCl$ solution and 10 mL sodium citrate solution, and mix thoroughly. Adjust pH to approximately 4 by adding 1-mL increments of NH_4OH until Congo red paper is just definitely red (or other suitable pH test paper indicates a value between 4 and 6).

Add 10 mL neocuproine reagent and 10 mL $CHCl_3$. Stopper and shake vigorously for 30 s or more to extract the copper-neocuproine complex into the $CHCl_3$. Let mixture separate into two layers and withdraw lower $CHCl_3$ layer into a 25-mL volumetric flask, taking care not to transfer any of the aqueous layer. Repeat extraction of the water layer with an additional 10 mL $CHCl_3$ and combine extracts. Dilute combined extracts to 25 mL with CH_3OH, stopper, and mix thoroughly.

Transfer an appropriate portion of extract to a suitable absorption cell (1 cm for 40 to 200 µg

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Cu; 5 cm for lesser amounts) and measure absorbance at 4571 nm or with a 450- to 460-nm filter. Use a sample blank prepared by carrying 50 mL water through the complete digestion and analytical procedure.

Determine micrograms copper in final solution by reference to the appropriate calibration curve.

5. Calculation

$$\text{mg Cu/L} = \frac{\mu\text{g Cu (in 25 mL final volume)}}{\text{mL portion taken for extraction}}$$

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3500-Cu C. Bathocuproine Method

1. General Discussion

a. Principle: Cuprous ion forms a water-soluble orange-colored chelate with bathocuproine disulfonate (2,9-dimethyl-4,7-diphenyl-1,10-phenanthrolinedisulfonic acid, disodium salt). While the color forms over the pH range 3.5 to 11.0, the recommended pH range is between 4 and 5. The sample is buffered at a pH of about 4.3 and reduced with hydroxylamine hydrochloride. The absorbance is measured at 4841 nm. The method can be applied to copper concentrations up to at least 5 mg/L with a sensitivity of 20 µg/L.

b. Interference: The following substances can be tolerated with an error of less than ±2%:

Substance	Concentration *mg/L*
Cations	

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Substance	Concentration *mg/L*
Aluminum	100
Beryllium	10
Cadmium	100
Calcium	1000
Chromium (III)	10
Cobalt (II)	5
Iron (II)	100
Iron (III)	100
Lithium	500
Magnesium	100
Manganese (II)	500
Nickel (II)	500
Sodium	1000
Strontium	200
Thorium (IV)	100
Zinc	200
Anions	
Chlorate	1000
Chloride	1000
Fluoride	500
Nitrate	200
Nitrite	200
Orthophosphate	1000
Perchlorate	1000
Sulfate	1000
Compounds	
Residual chlorine	1
Linear alkylate sulfonate (LAS)	40

Cyanide, thiocyanate, persulfate, and EDTA also can interfere.

c. Minimum detectable concentration: 20 µg/L with a 5-cm cell.

2. Apparatus

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a. Colorimetric equipment: One of the following, with a light path of 1 to 5 cm (unless nessler tubes are used):

1) *Spectrophotometer,* for use at 4841 nm.

2) *Filter photometer,* equipped with a blue-green filter exhibiting maximum light transmission near 4841 nm.

3) *Nessler tubes,* matched, 100-mL, tall form.

b. Acid-washed glassware: Rinse all glassware with conc HCl and then with copper-free water.

3. Reagents

a. Copper-free water: See Method B, ¶ 3*a*.

b. Stock copper solution: Prepare as directed in Method B, ¶ 3*b*, but use 20.00 mg copper wire or foil; 1.00 mL = 20.00 µg Cu.

c. Standard copper solution: Dilute 250 mL stock copper solution to 1000 mL with water; 1.00 mL = 5.00 µg Cu. Prepare daily.

d. Hydrochloric acid, HCl, 1 + 1.

e. Hydroxylamine hydrochloride solution: See Method B, ¶ 3*e*.

f. Sodium citrate solution: Dissolve 300 g $Na_3C_6H_5O_7 \cdot 2H_2O$ in water and make up to 1000 mL.

g. Disodium bathocuproine disulfonate solution: Dissolve 1.000 g $C_{12}H_4N_2(CH_3)_2(C_6H_4)_2(SO_3Na)_2$ in water and make up to 1000 mL.

4. Procedure

Pipet 50.0 mL sample, or a suitable portion diluted to 50.0 mL, into a 250-mL erlenmeyer flask. In separate 250-mL erlenmeyer flasks, prepare a 50.0-mL water blank and a series of 50.0-mL copper standards containing 5.0, 10.0, 15.0, 20.0, and 25.0 µg Cu. To sample, blank, and standards add, mixing after each addition, 1.00 mL 1 + 1 HCl, 5.00 mL $NH_2OH \cdot HCl$ solution, 5.00 mL sodium citrate solution, and 5.00 mL disodium bathocuproine disulfonate solution. Transfer to cells and read sample absorbance against the blank at 4841 nm. Plot absorbance against micrograms Cu in standards for the calibration curve. Estimate concentration from the calibration curve.

5. Calculation

$$\text{mg Cu/L} = \frac{\text{µg Cu (in 66 mL final volume)}}{\text{mL sample}}$$

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6. Precision and Bias

A synthetic sample containing 1000 µg Cu/L, 500 µg Al/L, 50 µg Cd/L, 110 µg Cr/L, 300 µg Fe/L, 70 µg Pb/L, 50 µg Mn/ L, 150 µg Ag/L, and 650 µg Zn/L was analyzed in 33 laboratories by the bathocuproine method, with a relative standard deviation of 4.1% and a relative error of 0.3%.

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3500-Ga GALLIUM

Gallium (Ga) is the third element in Group IIIA in the periodic table; it has an atomic number of 31, an atomic weight of 67.72, and valences of 1, 2, and 3. The average abundance of Ga in the earth's crust is 19 ppm; in soils it is 1.9 to 29 ppm; in streams it is 0.09 µg/L; and in groundwaters it is <0.1 mg/L. Gallium occurs in many zinc ores, and nearly always in bauxite. Gallium compounds are used in semiconducting devices.

The element exists as Ga^{3+} in natural water, and its solubility is controlled by formation of the hydroxide. It is considered nonessential for plants and animals.

Perform analyses by the electrothermal atomic absorption method (Section 3113B). The inductively coupled plasma/mass spectrometric method (Section 3125) also may be applied successfully in most cases (with lower detection limits), even though gallium is not specifically listed as an analyte in the method.

3500-Ge GERMANIUM

Germanium (Ge) is the third element in Group IVA in the periodic table; it has an atomic number of 32, an atomic weight bnof 72.59, and valences of 2 and 4. The average abundance of Ge in the earth's crust is 1.5 ppm; in streams it is 0.03 to 0.1 µg/ L; and in groundwaters it is <0.1 mg/L. Germanium is found in germanite, in certain zinc ores, and in elevated levels in certain

hot spring waters. Germanium alloys are used in transistors, gold alloys, phosphors, and semiconducting devices.

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Germanium is present in natural waters in the tetravalent state, and its distribution in natural waters probably is controlled by adsorption on clay mineral surfaces. It is nonessential for plants and animals.

Perform analyses by the electrothermal atomic absorption method (Section 3113B). The inductively coupled plasma/mass spectrometric method (Section 3125) also may be applied successfully in most cases (with lower detection limits), even though germanium is not specifically listed as an analyte in the method.

3500-Au GOLD

Gold (Au) is the third element in Group IB in the periodic table; it has an atomic number of 79, an atomic weight of 196.97, and valences of 1 and 3. The average abundance of Au in the earth's crust is 0.004 ppm; in streams it is 2 μg/L; and in groundwater it is <0.1 mg/L. Gold occurs in the native form, and is associated with quartz or pyrite. The main uses of gold are in jewelry, dentistry, electronics, and the aerospace industry.

Gold solubility is restricted to acidic waters in the presence of oxidizing agents and chloride, or in alkaline solutions in the presence of hydrogen sulfide. Its solubility may be influenced by natural organic acids. Compounds of gold containing thiosulfate and cyanide have some human toxicity.

Perform analyses by the atomic absorption spectrometric method (Section 3111B) or by the electrothermal atomic absorption method (Section 3113B). The inductively coupled plasma mass spectrometric method (Section 3125) also may be applied successfully in most cases (with lower detection limits), even though gold is not specifically listed as an analyte in the method.

3500-In INDIUM

Indium (In) is the fourth element in Group IIIA in the periodic table; it has an atomic number of 49, an atomic weight of 114.82, and valences of 1, 2, and 3. The average abundance of indium in the earth's crust is 0.19 ppm; in streams it is <0.01 μg/L; and in groundwaters it is <0.1 mg/L. Indium often occurs in combination with zinc ores, and sometimes with pyrites and siderite. Indium is used in alloys for bearings, brazing, solder, and in electrical devices.

Indium exists as In^{3+} and as a number of complex ions. Its solubility is controlled by the formation of the insoluble hydroxide. The metal and its compounds are toxic by inhalation.

Perform analyses by the electrothermal atomic absorption method (Section 3113B). The inductively coupled plasma mass spectrometric method (Section 3125) also may be applied successfully in most cases (with lower detection limits), even though indium is not specifically listed as an analyte in the method.

3500-Ir IRIDIUM

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Iridium (Ir) is the eighth element in Group VIII of the periodic table; it has an atomic number of 77, an atomic weight of 192.2, and valences of 1, 3, and 4. The average abundance of Ir in the earth's crust is probably <0.001 ppm, and in groundwaters it is <0.1 mg/L. Iridium occurs uncombined with platinum and other metals. It is used in alloys with platinum in catalysts, thermocouples, electrodes, and wires.

The aqueous chemistry is controlled by complex compounds, although the solubility in natural waters is relatively unknown.

Perform analyses by the flame atomic absorption spectrometric method (Section 3111B). The inductively coupled plasma/mass spectrometric method (Section 3125) also may be applied successfully in most cases (with lower detection limits), even though iridium is not specifically listed as an analyte in the method.

3500-Fe IRON*#(107)

3500-Fe A. Introduction

1. Occurrence and Significance

Iron (Fe) is the first element in Group VIII of the periodic table; it has an atomic number of 26, an atomic weight of 55.85, and common valences of 2 and 3 (and occasionally valences of 1, 4, and 6). The average abundance of Fe in the earth's crust is 6.22%; in soils Fe ranges from 0.5 to 4.3%; in streams it averages about 0.7 mg/L; and in groundwater it is 0.1 to 10 mg/L. Iron occurs in the minerals hematite, magnetite, taconite, and pyrite. It is widely used in steel and in other alloys.

The solubility of ferrous ion (Fe^{2+}) is controlled by the carbonate concentration. Because groundwater is often anoxic, any soluble iron in groundwater is usually in the ferrous state. On exposure to air or addition of oxidants, ferrous iron is oxidized to the ferric state (Fe^{3+}) and may hydrolyze to form red, insoluble hydrated ferric oxide. In the absence of complex-forming ions, ferric iron is not significantly soluble unless the pH is very low.

Elevated iron levels in water can cause stains in plumbing, laundry, and cooking utensils, and can impart objectionable tastes and colors to foods. The United Nations Food and Agriculture Organization recommended level for irrigation waters is 5 mg/L. The U.S. EPA secondary drinking water standard MCL is 0.3 mg/L.

2. Selection of Method

Sensitivity and detection limits for the atomic absorption spectrometric methods (Section 3111B and Section 3111C), the inductively coupled plasma method (Section 3120), and the phenanthroline colorimetric procedure described here (B) are similar and generally adequate for analysis of natural or treated waters. Lower detection limits can be achieved with electrothermal

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atomic absorption spectrometry (Section 3113B) when an appropriate matrix modifier is used. The complexing reagents used in the colorimetric procedures are specific for ferrous iron but the atomic absorption procedures are not. However, because of the instability of ferrous iron, which is changed easily to the ferric form in solutions in contact with air, determination of ferrous iron requires special precautions and may need to be done in the field at the time of sample collection.

The procedure for determining ferrous iron using 1,10-phenanthroline (Section 3500-Fe.B.4*c*) has a somewhat limited applicability; avoid long storage time or exposure of samples to light. A rigorous quantitative distinction between ferrous and ferric iron can be obtained with a special procedure using bathophenanthroline. Spectrophotometric methods using bathophenanthroline[1-6] and other organic complexing reagents such as ferrozine[7] or TPTZ[8] are capable of determining iron concentrations as low as 1 µg/L. A chemiluminescence procedure[9] is stated to have a detection limit of 5 ng/L. Additional procedures are described elsewhere.[10-13]

3. Sampling and Storage

Plan in advance the methods of collecting, storing, and pretreating samples. Clean sample container with acid and rinse with reagent water. Equipment for membrane filtration of samples in the field may be required to determine iron in solution (dissolved iron). Dissolved iron, considered to be that passing through a 0.45-µm membrane filter, may include colloidal iron. The value of the determination depends greatly on the care taken to obtain a representative sample. Iron in well or tap water samples may vary in concentration and form with duration and degree of flushing before and during sampling. When taking a sample portion for determining iron in suspension, shake the sample bottle often and vigorously to obtain a uniform suspension of precipitated iron. Use particular care when colloidal iron adheres to the sample bottle. This problem can be acute with plastic bottles.

For a precise determination of total iron, use a separate container for sample collection. Treat with acid at the time of collection to place the iron in solution and prevent adsorption or deposition on the walls of the sample container. Take account of the added acid in measuring portions for analysis. The addition of acid to the sample may eliminate the need for adding acid before digestion (Section 3500-Fe.B.4*a*).

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3500-Fe B. Phenanthroline Method

1. General Discussion

a. Principle: Iron is brought into solution, reduced to the ferrous state by boiling with acid and hydroxylamine, and treated with 1,10-phenanthroline at pH 3.2 to 3.3. Three molecules of phenanthroline chelate each atom of ferrous iron to form an orange-red complex. The colored solution obeys Beer's law; its intensity is independent of pH from 3 to 9. A pH between 2.9 and 3.5 insures rapid color development in the presence of an excess of phenanthroline. Color standards are stable for at least 6 months.

b. Interference: Among the interfering substances are strong oxidizing agents, cyanide, nitrite, and phosphates (polyphosphates more so than orthophosphate), chromium, zinc in concentrations exceeding 10 times that of iron, cobalt and copper in excess of 5 mg/L, and nickel in excess of 2 mg/L. Bismuth, cadmium, mercury, molybdate, and silver precipitate phenanthroline. The initial boiling with acid converts polyphosphates to orthophosphate and removes cyanide and nitrite that otherwise would interfere. Adding excess hydroxylamine eliminates errors caused by excessive concentrations of strong oxidizing reagents. In the presence of interfering metal ions, use a larger excess of phenanthroline to replace that complexed by the interfering metals. Where excessive concentrations of interfering metal ions

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are present, the extraction method may be used.

If noticeable amounts of color or organic matter are present, it may be necessary to evaporate the sample, gently ash the residue, and redissolve in acid. The ashing may be carried out in silica, porcelain, or platinum crucibles that have been boiled for several hours in 6*N* HCl. The presence of excessive amounts of organic matter may necessitate digestion before use of the extraction procedure.

c. Minimum detectable concentration: Dissolved or total concentrations of iron as low as 10 µg/L can be determined with a spectrophotometer using cells with a 5 cm or longer light path.

Carry a blank through the entire procedure to allow for correction.

2. Apparatus

a. Colorimetric equipment: One of the following is required:

1) *Spectrophotometer,* for use at 510 nm, providing a light path of 1 cm or longer.

2) *Filter photometer,* providing a light path of 1 cm or longer and equipped with a green filter having maximum transmittance near 510 nm.

3) *Nessler tubes,* matched, 100-mL, tall form.

b. Acid-washed glassware: Wash all glassware with conc hydrochloric acid (HCl) and rinse with reagent water before use to remove deposits of iron oxide.

c. Separatory funnels: 125-mL, Squibb form, with ground-glass or TFE stopcocks and stoppers.

3. Reagents

Use reagents low in iron. Use reagent water (see Section 1080 and Section 3111B.3*c*) in preparing standards and reagent solutions and in procedure. Store reagents in glass-stoppered bottles. The HCl and ammonium acetate solutions are stable indefinitely if tightly stoppered. The hydroxylamine, phenanthroline, and stock iron solutions are stable for several months. The standard iron solutions are not stable; prepare daily as needed by diluting the stock solution. Visual standards in nessler tubes are stable for several months if sealed and protected from light.

a. Hydrochloric acid, HCl, conc, containing less than 0.5 ppm iron.

b. Hydroxylamine solution: Dissolve 10 g $NH_2OH{\cdot}HCl$ in 100 mL water.

c. Ammonium acetate buffer solution: Dissolve 250 g $NH_4C_2H_3O_2$ in 150 mL water. Add 700 mL conc (glacial) acetic acid. Because even a good grade of $NH_4C_2H_3O_2$ contains a significant amount of iron, prepare new reference standards with each buffer preparation.

d. Sodium acetate solution: Dissolve 200 g $NaC_2H_3O_2{\cdot}3H_2O$ in 800 mL water.

e. Phenanthroline solution: Dissolve 100 mg 1,10-phenanthroline monohydrate, $C_{12}H_8N_2{\cdot}H_2O$, in 100 mL water by stirring and heating to 80°C. Do not boil. Discard the solution if it darkens. Heating is unnecessary if 2 drops conc HCl are added to the water. (NOTE:

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One milliliter of this reagent is sufficient for no more than 100 µg Fe.)

f. Potassium permanganate, 0.1*M:* Dissolve 0.316 $KMnO_4$ in reagent water and dilute to 100 mL.

g. Stock iron solution: Use metal (1) or salt (2) for preparing the stock solution.

1) Use electrolytic iron wire, or ''iron wire for standardizing,'' to prepare the solution. If necessary, clean wire with fine sandpaper to remove any oxide coating and to produce a bright surface. Weigh 200.0 mg wire and place in a 1000-mL volumetric flask. Dissolve in 20 mL 6*N* sulfuric acid (H_2SO_4) and dilute to mark with water; 1.00 mL = 200 µg Fe.

2) If ferrous ammonium sulfate is preferred, slowly add 20 mL conc H_2SO_4 to 50 mL water and dissolve 1.404 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$. Add 0.1*M* potassium permanganate ($KMnO_4$) dropwise until a faint pink color persists. Dilute to 1000 mL with water and mix; 1.00 mL = 200 µg Fe.

h. Standard iron solutions: Prepare daily for use.

1) Pipet 50.00 mL stock solution into a 1000-mL volumetric flask and dilute to mark with water; 1.00 mL = 10.0 µg Fe.

2) Pipet 5.00 mL stock solution into a 1000-mL volumetric flask and dilute to mark with water; 1.00 mL = 1.00 µg Fe.

i. Diisopropyl or isopropyl ether. CAUTION: *Ethers may form explosive peroxides; test before using.*

4. Procedure

a. Total iron: Mix sample thoroughly and measure 50.0 mL into a 125-mL erlenmeyer flask. If this sample volume contains more than 200 µg iron use a smaller accurately measured portion and dilute to 50.0 mL. Add 2 mL conc HCl and 1 mL $NH_2OH \cdot HCl$ solution. Add a few glass beads and heat to boiling. To insure dissolution of all the iron, continue boiling until volume is reduced to 15 to 20 mL. (If the sample is ashed, take up residue in 2 mL conc HCl and 5 mL water.) Cool to room temperature and transfer to a 50- or 100-mL volumetric flask or nessler tube. Add 10 mL $NH_4C_2H_3O_2$ buffer solution and 4 mL phenanthroline solution, and dilute to mark with water. Mix thoroughly and allow a minimum of 10 min for maximum color development.

b. Dissolved iron: Immediately after collection filter sample through a 0.45-µm membrane filter into a vacuum flask containing 1 mL conc HCl/100 mL sample. Analyze filtrate for total dissolved iron (¶ 4*a*) and/or dissolved ferrous iron (¶ 4*c*). (This procedure also can be used in the laboratory if it is understood that normal sample exposure to air during shipment may result in precipitation of iron.)

Calculate suspended iron by subtracting dissolved from total iron.

c. Ferrous iron: Determine ferrous iron at sampling site because of the possibility of change

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in the ferrous-ferric ratio with time in acid solutions. To determine ferrous iron only, acidify a separate sample with 2 mL conc HCl/100 mL sample at time of collection. Fill bottle directly from sampling source and stopper. Immediately withdraw a 50-mL portion of acidified sample and add 20 mL phenanthroline solution and 10 mL $NH_4C_2H_3O_2$ solution with vigorous stirring. Dilute to 100 mL and measure color intensity within 5 to 10 min. Do not expose to sunlight. (Color development is rapid in the presence of excess phenanthroline. The phenanthroline volume given is suitable for less than 50 μg total iron; if larger amounts are present, use a correspondingly larger volume of phenanthroline or a more concentrated reagent.)

Calculate ferric iron by subtracting ferrous from total iron.

d. Color measurement: Prepare a series of standards by accurately pipetting calculated volumes of standard iron solutions [use solution described in ¶ 3*h*2) to measure 1- to 10-μg portions] into 125-mL erlenmeyer flasks, diluting to 50 mL by adding measured volumes of water, and carrying out the steps in ¶ 4*a* beginning with transfer to a 100-mL volumetric flask or nessler tube.

For visual comparison, prepare a set of at least 10 standards, ranging from 1 to 100 μg Fe in the final 100-mL volume. Compare colors in 100-mL tall-form nessler tubes.

For photometric measurement, use Table 3500-Fe:I as a rough guide for selecting proper light path at 510 nm. Read standards against water set at zero absorbance and plot a calibration curve, including a blank (see ¶ 3*c* and General Introduction).

If samples are colored or turbid, carry a second set of samples through all steps of the procedure without adding phenanthroline. Instead of water, use the prepared blanks to set photometer to zero absorbance and read each sample developed with phenanthroline against the corresponding blank without phenanthroline. Translate observed photometer readings into iron values by means of the calibration curve. This procedure does *not* compensate for interfering ions.

e. Samples containing organic interferences: Digest samples containing substantial amounts of organic substances according to the directions given in Section 3030G or Section 3030H.

1) If a digested sample has been prepared according to the directions given in Section 3030G or Section 3030H, pipet 10.0 mL or other suitable portion containing 20 to 500 μg Fe into a 125-mL separatory funnel. If the volume taken is less than 10 mL, add water to make up to 10 mL. To the separatory funnel add 15 mL conc HCl for a 10-mL aqueous volume; or, if the portion taken was greater than 10.0 mL, add 1.5 mL conc HCl/mL sample. Mix, cool, and proceed with ¶ 4*e*3) below.

2) To prepare a sample solely for determining iron, measure a suitable volume containing 20 to 500 μg Fe and carry it through the digestion procedure described in either Section 3030G or Section 3030H. However, use only 5 mL H_2SO_4 or $HClO_4$ and omit H_2O_2. When digestion is complete, cool, dilute with 10 mL water, heat almost to boiling to dissolve slowly soluble salts, and, if the sample is still cloudy, filter through a glass-fiber, sintered-glass, or porcelain filter, washing with 2 to 3 mL water. Quantitatively transfer filtrate or clear solution to a 25-mL

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volumetric flask and make up to 25 mL with water. Empty flask into a 125-mL separatory funnel, rinse flask with 5 mL conc HCl and add to the funnel. Add 25 mL conc HCl measured with the same flask. Mix and cool to room temperature.

3) Extract the iron from the HCl solution in the separatory funnel by shaking for 30 s with 25 mL isopropyl ether (CAUTION). Draw off lower acid layer into a second separatory funnel. Extract acid solution again with 25 mL isopropyl ether, drain acid layer into a suitable clean vessel, and add ether layer to the ether in the first funnel. Pour acid layer back into second separatory funnel and re-extract with 25 mL isopropyl ether. Withdraw and discard acid layer and add ether layer to first funnel. Persistence of a yellow color in the HCl solution after three extractions does not signify incomplete separation of iron because copper, which is not extracted, gives a similar yellow color.

Shake combined ether extracts with 25 mL water to return iron to aqueous phase and transfer lower aqueous layer to a 100-mL volumetric flask. Repeat extraction with a second 25-mL portion of water, adding this to the first aqueous extract. Discard ether layer.

4) Add 1 mL $NH_2OH{\cdot}HCl$ solution, 10 mL phenanthroline solution, and 10 mL $NaC_2H_3O_2$ solution. Dilute to 100 mL with water, mix thoroughly, and let stand for a minimum of 10 min. Measure absorbance at 510 nm using a 5-cm absorption cell for amounts of iron less than 100 µg or 1-cm cell for quantities from 100 to 500 µg. As reference, use either water or a sample blank prepared by carrying the specified quantities of acids through the entire analytical procedure. If water is used as reference, correct sample absorbance by subtracting absorbance of a sample blank.

Determine micrograms of iron in the sample from the absorbance (corrected, if necessary) by reference to the calibration curve prepared by using a suitable range of iron standards containing the same amounts of phenanthroline, hydroxylamine, and sodium acetate as the sample.

5. Calculation

When the sample has been treated according to ¶ 4*a*, ¶ 4*b*, ¶ 4*c*, or ¶ 4*e*2):

$$\text{mg Fe/L} = \frac{\text{µg Fe (in 100 mL final volume)}}{\text{mL sample}}$$

When the sample has been treated according to ¶ 4*e*1):

$$\text{mg Fe/L} = \frac{\text{µg Fe (in 100 mL final volume)}}{\text{mL sample}} \times \frac{100}{\text{mL portion}}$$

Report details of sample collection, storage, and pretreatment if they are pertinent to interpretation of results.

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6. Precision and Bias

Precision and bias depend on the method of sample collection and storage, the method of color measurement, the iron concentration, and the presence of interfering color, turbidity, and foreign ions. In general, optimum reliability of visual comparison in nessler tubes is not better than 5% and often only 10%, whereas, under optimum conditions, photometric measurement may be reliable to 3% or 3 µg, whichever is greater. The sensitivity limit for visual observation in nessler tubes is approximately 1 µg Fe. Sample variability and instability may affect precision and bias of this determination more than will the errors of analysis. Serious divergences have been found in reports of different laboratories because of variations in methods of collecting and treating samples.

A synthetic sample containing 300 µg Fe/L, 500 µg Al/L, 50 µg Cd/L, 110 µg Cr/L, 470 µg Cu/L, 70 µg Pb/L, 120 µg Mn/L, 150 µg Ag/L, and 650 µg Zn/L in distilled water was analyzed in 44 laboratories by the phenanthroline method, with a relative standard deviation of 25.5% and a relative error of 13.3%.

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3500-Pb A. Introduction

1. Occurrence and Significance

Lead (Pb) is the fifth element in Group IVA in the periodic table; it has an atomic number of 82, an atomic weight of 207.19, and valences of 2 and 4. The average abundance of Pb in the earth's crust is 13 ppm; in soils it ranges from 2.6 to 25 ppm; in streams it is 3 μg/L, and in groundwaters it is generally <0.1 mg/L. Lead is obtained chiefly from galena (PbS). It is used in batteries, ammunition, solder, piping, pigments, insecticides, and alloys. Lead also was used in gasoline for many years as an anti-knock agent in the form of tetraethyl lead.

The common aqueous species are Pb^{2+} and hydroxide and carbonate complexes. Lead in a water supply may come from industrial, mine, and smelter discharges or from the dissolution of plumbing and plumbing fixtures. Tap waters that are inherently noncorrosive or not suitably treated may contain lead resulting from an attack on lead service pipes, lead interior plumbing, brass fixtures and fittings, or solder pipe joints.

Lead is nonessential for plants and animals. It is toxic by ingestion and is a cumulative poison. The Food and Drug Administration regulates lead content in food and in house paints. Under the lead-copper rule, the U.S. EPA drinking water 90th percentile action level is 15 μg/L.

2. Selection of Method

The atomic absorption spectrometric method (Section 3111B) has a relatively high detection limit in the flame mode and requires an extraction procedure (Section 3111C) for the low concentrations common in potable water. The electrothermal atomic absorption (AA) method (Section 3113B) is more sensitive for low concentrations and does not require extraction. The inductively coupled plasma/mass spectrometric method (Section 3125) is even more sensitive than the electrothermal AA method. The inductively coupled plasma method (Section 3120) has a sensitivity similar to that of the flame atomic absorption method. Anodic stripping voltammetry (Section 3130B) can achieve superior detection limits, but is susceptible to interferences from copper, silver, gold, and organic compounds. The dithizone method (B) is sensitive and specific as a colorimetric procedure.

3500-Pb B. Dithizone Method

1. General Discussion

a. Principle: An acidified sample containing microgram quantities of lead is mixed with ammoniacal citrate-cyanide reducing solution and extracted with dithizone in chloroform ($CHCl_3$) to form a cherry-red lead dithizonate. The color of the mixed color solution is measured photometrically.[1,2] Sample volume taken for analysis may be 2 L when digestion is used.

b. Interference: In a weakly ammoniacal cyanide solution (pH 8.5 to 9.5) dithizone forms

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colored complexes with bismuth, stannous tin, and monovalent thallium. In strongly ammoniacal citrate-cyanide solution (pH 10 to 11.5) the dithizonates of these ions are unstable and are extracted only partially.[3] This method uses a high pH, mixed color, single dithizone extraction. Interference from stannous tin and monovalent thallium is reduced further when these ions are oxidized during preliminary digestion. A modification of the method allows detection and elimination of bismuth interference. Excessive quantities of bismuth, thallium, and tin may be removed.[4]

Dithizone in $CHCl_3$ absorbs at 510 nm; control its interference by using nearly equal concentrations of excess dithizone in samples, standards, and blank.

The method is without interference for the determination of 0.0 to 30.0 μg Pb in the presence of 20 μg Tl^+, 100 μg Sn^{2+}, 200 μg In^{3+}, and 1000 μg each of Ba^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Mg^{2+}, Mn^{2+}, Hg^{2+}, Sr^{2+}, Zn^{2+}, Al^{3+}, Sb^{3+}, As^{3+}, Cr^{3+}, Fe^{3+}, V^{3+}, PO_4^{3-}, and SO_4^{2-}. Gram quantities of alkali metals do not interfere. A modification is provided to avoid interference from excessive quantities of bismuth or tin.

c. Preliminary sample treatment: At time of collection acidify with conc HNO_3 to pH <2 but avoid excess HNO_3. Add 5 mL 0.1*N* iodine solution to avoid losses of volatile organo-lead compounds during handling and digesting of samples. Prepare a blank of lead-free water and carry through the procedure.

d. Digestion of samples: Unless digestion is shown to be unnecessary, digest all samples for dissolved or total lead as described in 3030H or K.

e. Minimum detectable concentration: 1.0 μg Pb/10 mL dithizone solution.

2. Apparatus

a. Spectrophotometer for use at 510 nm, providing a light path of 1 cm or longer.

b. pH meter.

c. Separatory funnels: 250-mL Squibb type. Clean all glassware, including sample bottles, with 1 + 1 HNO_3. Rinse thoroughly with reagent water.

d. Automatic dispensing burets: Use for all reagents to minimize indeterminate contamination errors.

3. Reagents

Prepare all reagents in lead-free water.

a. Stock lead solution: Dissolve 0.1599 g lead nitrate, $Pb(NO_3)_2$ (minimum purity 99.5%), in approximately 200 mL water. Add 10 mL conc HNO_3 and dilute to 1000 mL with water. Alternatively, dissolve 0.1000 g pure Pb metal in 20 mL 1 + 1 HNO_3 and dilute to 1000 mL with water; 1.00 mL = 100 μg Pb.

b. Working lead solution: Dilute 2.0 mL stock solution to 100 mL with water; 1 mL = 2.00

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μg Pb.

c. Nitric acid, HNO_3, 1 + 4: Dilute 200 mL conc HNO_3 to 1 L with water.

d. Ammonium hydroxide, NH_4OH, 1 + 9: Dilute 10 mL conc NH_4OH to 100 mL with water.

e. Citrate-cyanide reducing solution: Dissolve 400 g dibasic ammonium citrate, $(NH_4)_2HC_6H_5O_7$, 20 g anhydrous sodium sulfite, Na_2SO_3, 10 g hydroxylamine hydrochloride, $NH_2OH{\cdot}HCl$, and 40 g potassium cyanide, KCN (CAUTION: *Poison*) in water and dilute to 1 L. Mix this solution with 2 L conc NH_4OH. *Do not pipet by mouth. Prepare solution in a fume hood.*

f. Stock dithizone solution: The dithizone concentration in the stock dithizone solutions is based on having a 100% pure dithizone reagent. Some commercial grades of dithizone are contaminated with the oxidation product diphenylthiocarbodiazone or with metals. Purify dithizone as directed below. For dithizone solutions not stronger than 0.001% (w/v), calculate the exact concentration by dividing the absorbance of the solution in a 1.00-cm cell at 606 nm by 40.6×10^3, the molar absorptivity.

In a fume hood, dissolve 100 mg dithizone in 50 mL $CHCl_3$ in a 150-mL beaker and filter through a 7-cm-diam paper.*#(109) Receive filtrate in a 500-mL separatory funnel or in a 125-mL erlenmeyer flask under slight vacuum; use a filtering device designed to handle the $CHCl_3$ vapor. Wash beaker with two 5-mL portions $CHCl_3$, and filter. Wash the paper with three 5-mL portions $CHCl_3$, adding final portion dropwise to edge of paper. If filtrate is in flask, transfer with $CHCl_3$ to a 500-mL separatory funnel.

Add 100 mL 1 + 99 NH_4OH to separatory funnel and shake moderately for 1 min; excessive agitation produces slowly breaking emulsions. Let layers separate, swirling funnel gently to submerge $CHCl_3$ droplets held on surface of aqueous layer. Transfer $CHCl_3$ layer to 250-mL separatory funnel, retaining the orange-red aqueous layer in the 500-mL funnel. Repeat extraction, receiving $CHCl_3$ layer in another 250-mL separatory funnel and transferring aqueous layer, using 1 + 99 NH_4OH, to the 500-mL funnel holding the first extract. Repeat extraction, transferring the aqueous layer to 500-mL funnel. Discard $CHCl_3$ layer.

To combined extracts in the 500-mL separatory funnel add 1 + 1 HCl in 2-mL portions, mixing after each addition, until dithizone precipitates and solution is no longer orange-red. Extract precipitated dithizone with three 25-mL portions $CHCl_3$. Dilute combined extracts to 1000 mL with $CHCl_3$; 1.00 mL = 100 μg dithizone.

g. Dithizone working solution: Dilute 100 mL stock dithizone solution to 250 mL with $CHCl_3$; 1 mL = 40 μg dithizone.

h. Special dithizone solution: Dissolve 250 mg dithizone in 250 mL $CHCl_3$. This solution may be prepared without purification because all extracts using it are discarded.

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i. Sodium sulfite solution: Dissolve 5 g anhydrous Na_2SO_3 in 100 mL water.

j. Iodine solution: Dissolve 40 g KI in 25 mL water, add 12.7 g resublimed iodine, and dilute to 1000 mL.

4. Procedure

a. With sample digestion: CAUTION: *Perform the following procedure (excluding use of spectrophotometer) in a fume hood.* To a digested sample containing not more than 1 mL conc acid add 20 mL 1 + 4 HNO_3 and filter through lead-free filter paper†#(110) and filter funnel directly into a 250-mL separatory funnel. Rinse digestion beaker with 50 mL water and add to filter. Add 50 mL ammoniacal citrate-cyanide solution, mix, and cool to room temperature. Add 10 mL dithizone working solution, shake stoppered funnel vigorously for 30 s, and let layers separate. Insert lead-free cotton in stem of separatory funnel and draw off lower layer. Discard 1 to 2 mL $CHCl_3$ layer, then fill absorption cell. Measure absorbance of extract at 510 nm, using dithizone working solution, ¶ 3*g*, to zero spectrophotometer.

b. Without sample digestion: To 100 mL acidified sample (pH 2) in a 250-mL separatory funnel add 20 mL 1 + 4 HNO_3 and 50 mL citrate-cyanide reducing solution; mix. Add 10 mL dithizone working solution and proceed as in ¶ 4*a*.

c. Calibration curve: Plot concentration of at least five standards and a blank against absorbance. Determine concentration of lead in extract from curve. All concentrations are µg Pb/10 mL final extract.

d. Removal of excess interferences: The dithizonates of bismuth, tin, and thallium differ from lead dithizonate in maximum absorbance. Detect their presence by measuring sample absorbance at 510 nm and at 465 nm. Calculate corrected absorbance of sample at each wavelength by subtracting absorbance of blank at same wavelength. Calculate ratio of corrected absorbance at 510 nm to corrected absorbance at 465 nm. The ratio of corrected absorbances for lead dithizonate is 2.08 and for bismuth dithizonate is 1.07. If the ratio for the sample indicates interference, i.e., is markedly less than 2.08, proceed as follows with a new 100-mL sample: If the sample has not been digested, add 5 mL Na_2SO_3 solution to reduce iodine preservative. Adjust sample to pH 2.5 using a pH meter and 1 + 4 HNO_3 or 1 + 9 NH_4OH as required. Transfer sample to 250-mL separatory funnel, extract with a minimum of three 10-mL portions special dithizone solution, or until the $CHCl_3$ layer is distinctly green. Extract with 20-mL portions $CHCl_3$ to remove dithizone (absence of green). Add 20 mL 1 + 4 HNO_3, 50 mL citrate-cyanide reducing solution, and 10 mL dithizone working solution. Extract as in ¶ 4*a* and measure absorbance.

5. Calculation

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$$\text{mg Pb/L} = \frac{\mu\text{g Pb (in 10 mL, from calibration curve)}}{\text{mL sample}}$$

6. Precision and Bias

Single-operator precision in recovering 0.0104 mg Pb/L from Mississippi River water was 6.8% relative standard deviation and −1.4% relative error. At the level of 0.026 mg Pb/L, recovery was made with 4.8% relative standard deviation and 15% relative error.

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3500-Li LITHIUM*#(111)

3500-Li A. Introduction

1. Occurrence and Significance

Lithium (Li) is the second element in Group IA of the periodic table; it has an atomic number of 3, an atomic weight of 6.94, and a valence of 1. The average abundance of Li in the earth's crust is 18 ppm; in soils it is 14 to 32 ppm; in streams it is 3 μg/ L, and in groundwaters it is <0.1 mg/L. The more important minerals containing lithium are lepidolite, spodumene, petalite, and amblygonite. Lithium compounds are used in pharmaceuticals, soaps, batteries, welding flux, ceramics, reducing agents (e.g., lithium aluminum hydride), and cosmetics.

Many lithium salts are only slightly soluble, and the metal's concentration in water is controlled by incorporation in clay minerals of soils. Lithium is considered nonessential for plants and animals, but it is essential for some microorganisms. Some lithium salts are toxic by ingestion. The United Nations Food and Agriculture Organization recommended maximum level for lithium in irrigation waters is 2.5 mg/L.

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2. Selection of Method

The atomic absorption spectrometric method (Section 3111B) and the inductively coupled plasma method (Section 3120) are preferred. The flame emission photometric method (B) also is available for laboratories not equipped to use preferred methods. The inductively coupled plasma/mass spectrometric method (Section 3125) may be applied successfully in most cases (with lower detection limits), even though lithium is not specifically listed as an analyte in the method.

3500-Li B. Flame Emission Photometric Method

1. General Discussion

a. Principle: Lithium can be determined in trace amounts by flame photometric methods at a wavelength of 670.8 nm.

b. Interference: A molecular band of strontium hydroxide with an absorption maximum at 671.0 nm interferes in the flame photometric determination of lithium. Ionization of lithium can be significant in both the air-acetylene and nitrous oxide-acetylene flames and can be suppressed by adding potassium. See Section 3500-NaB.1*a* for additional information on minimizing interferences in flame photometry.

c. Minimum detectable concentration: The minimum lithium concentration detectable is approximately 0.1 µg/L for reagent water analyzed on an atomic absorption spectrophotometer in the emission mode with an air-acetylene flame, or 0.03 µg/L with a nitrous oxide-acetylene flame.

d. Sampling and storage: Preferably collect sample in a polyethylene bottle, although borosilicate glass containers also may be used. At time of collection adjust sample to pH <2 with nitric acid (HNO_3).

2. Apparatus

Flame photometer: A flame photometer or an atomic absorption spectrometer operating in the emission mode using a lean air-acetylene flame is recommended.

3. Reagents

Use reagent water (see Section 3111B.3*c*) in reagent preparation and analysis.

a. Potassium ionization suppressant: Dissolve 95.35 g KCl dried at 110°C and dilute to 1000 mL with water; 1.00 mL = 50 mg K.

b. Stock lithium solution: Dissolve 152.7 mg anhydrous lithium chloride, LiCl, in water and dilute to 250 mL; 1.00 mL = 100 µg Li. Dry salt overnight in an oven at 105°C. Cool in a desiccator and weigh immediately after removal from desiccator. Alternatively, purchase prepared stock from a reputable supplier.

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c. Standard lithium solution: Dilute 10.00 mL stock LiCl solution to 500 mL with water; 1.00 mL = 2.0 µg Li.

4. Procedure

a. Pretreatment of polluted water and wastewater samples: Choose digestion method appropriate to matrix (see Section 3030).

b. Suppressing ionization: If necessary, filter sample through medium-porosity paper, add 1.0 mL potassium ionization suppressant to 50 mL volumetric flask, and dilute with sample for flame photometric determination. Sample solution will be in a 0.1% K matrix.

c. Treatment of standard solutions: Prepare dilutions of the Li standard solution to bracket sample concentration or to establish at least three points on a calibration curve of emission intensity against Li concentration. Prepare standards by adding appropriate volumes of standard lithium solution to 25 mL water + 1.0 mL potassium ionization suppressant reagent in a 50-mL volumetric flask. Dilute to 50.0 mL and mix. Both samples and standards will be in a 0.1% K matrix to suppress ionization of lithium.

d. Flame photometric measurement: Determine lithium concentration by direct intensity measurements at a wavelength of 670.8 nm. The bracketing method (Section 3500-NaB.4*d*) can be used with some photometric instruments, while the construction of a calibration curve is necessary with others. Run sample, water, and lithium standard as nearly simultaneously as possible. For best results, average several readings on each solution.

Follow the manufacturer's instructions for instrument operation.

5. Calculation

$$\mu g\ Li/L = (\mu g\ Li/L \text{ in portion analyzed}) \times D$$

where:

$$D = \text{dilution ratio} = \frac{\text{mL sample} + \text{mL water}}{\text{mL sample}}$$

6. Quality Control

Process a QC standard through entire analytical protocol as a way of determining systematic bias. The control limits for precision of duplicate determinations at concentrations (in water) of 4.0 µg/L and 10.0 µg/L were 4.09 ± 0.056 µg/L and 9.96 ± 0.094 µg/L, respectively. The single-operator RSD was 1.38% for a lithium solution containing 10 µg/L.

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3500-Mg MAGNESIUM*#(112)

3500-Mg A. Introduction

1. Occurrence and Significance

Magnesium (Mg) is the second element in Group IIA of the periodic table; it has an atomic number of 12, an atomic weight of 24.30, and a valence of 2. The average abundance of Mg in the earth's crust is 2.1%; in soils it is 0.03 to 0.84%; in streams it is 4 mg/L, and in groundwaters it is >5 mg/L. Magnesium occurs commonly in the minerals magnesite and dolomite. Magnesium is used in alloys, pyrotechnics, flash photography, drying agents, refractories, fertilizers, pharmaceuticals, and foods.

The common aqueous species is Mg^{2+}. The carbonate equilibrium reactions for magnesium are more complicated than for calcium, and conditions for direct precipitation of dolomite in natural waters are not common. Important contributors to the hardness of a water, magnesium salts break down when heated, forming scale in boilers. Chemical softening, reverse osmosis, or ion exchange reduces magnesium and associated hardness to acceptable levels.

Magnesium is an essential element in chlorophyll and in red blood cells. Some salts of magnesium are toxic by ingestion or inhalation. Concentrations greater than 125 mg/L also can have a cathartic and diuretic effect.

2. Selection of Method

The methods presented are applicable to waters and wastewaters. Direct determinations can

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be made with the atomic absorption spectrometric method (Section 3111B) and inductively coupled plasma method (Section 3120). The inductively coupled plasma mass spectrometric method (Section 3125) also may be applied successfully in most cases (with lower detection limits), even though magnesium is not specifically listed as an analyte in the method. These methods can be applied to most concentrations encountered, although sample dilution may be required. Choice of method is largely a matter of personal preference and analyst experience. A calculation method (B) also is available.

3500-Mg B. Calculation Method

Magnesium may be estimated as the difference between hardness and calcium as $CaCO_3$ if interfering metals are present in noninterfering concentrations in the calcium titration (Section 3500-Ca.B) and suitable inhibitors are used in the hardness titration (Section 2340C).

$$\text{mg Mg/L} = [\text{total hardness (as mg } CaCO_3\text{/L)} - \text{calcium hardness (as mg } CaCO_3\text{/L)}] \times 0.243$$

3500-Mn MANGANESE*#(113)

3500-Mn A. Introduction

1. Occurrence and Significance

Manganese (Mn) is the first element in Group VIIB in the periodic table; it has an atomic number of 25, an atomic weight of 54.94, and common valences of 2, 4, and 7 (and more rarely, valences of 1, 3, 5, and 6). The average abundance of Mn in the earth's crust is 1060 ppm; in soils it is 61 to 1010 ppm; in streams it is 7 µg/L, and in groundwaters it is <0.1 mg/L. Manganese is associated with iron minerals, and occurs in nodules in ocean, fresh waters, and soils. The common ores are pyrolusite (MnO_2) and psilomelane. Manganese is used in steel alloys, batteries, and food additives.

The common aqueous species are the reduced Mn^{2+} and the oxidized Mn^{4+}. The aqueous chemistry of manganese is similar to that of iron. Since groundwater is often anoxic, any soluble manganese in groundwater is usually in the reduced state (Mn^{2+}). Upon exposure to air or other oxidants, groundwater containing manganese usually will precipitate black MnO_2. Elevated manganese levels therefore can cause stains in plumbing/laundry, and cooking utensils. It is considered an essential trace element for plants and animals. The United Nations Food and Agriculture Organization recommended maximum level for manganese in irrigation waters is 0.2 mg/L. The U.S. EPA secondary drinking water standard MCL is 50 µg/L.

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2. Selection of Method

The atomic absorption spectrometric methods (Section 3111B and Section 3111C), the electrothermal atomic absorption method (Section 3113B), and the inductively coupled plasma methods (Section 3120 and Section 3125) permit direct determination with acceptable sensitivity and are the methods of choice. Of the various colorimetric methods, the persulfate method (B) is preferred because the use of mercuric ion can control interference from a limited chloride ion concentration.

3. Sampling and Storage

Manganese may exist in a soluble form in a neutral water when first collected, but it oxidizes to a higher oxidation state and precipitates or becomes adsorbed on the container walls. Determine manganese very soon after sample collection. When delay is unavoidable, total manganese can be determined if the sample is acidified at the time of collection with HNO_3 to pH <2. See Section 3010B.

3500-Mn B. Persulfate Method

1. General Discussion

a. Principle: Persulfate oxidation of soluble manganous compounds to form permanganate is carried out in the presence of silver nitrate. The resulting color is stable for at least 24 h if excess persulfate is present and organic matter is absent.

b. Interference: As much as 0.1 g chloride (Cl^-) in a 50-mL sample can be prevented from interfering by adding 1 g mercuric sulfate ($HgSO_4$) to form slightly dissociated complexes. Bromide and iodide still will interfere and only trace amounts may be present. The persulfate procedure can be used for potable water with trace to small amounts of organic matter if the period of heating is increased after more persulfate has been added.

For wastewaters containing organic matter, use preliminary digestion with nitric and sulfuric acids (HNO_3 and H_2SO_4) (see Section 3030G). If large amounts of Cl^- also are present, boiling with HNO_3 helps remove it. Interfering traces of Cl^- are eliminated by $HgSO_4$ in the special reagent.

Colored solutions from other inorganic ions are compensated for in the final colorimetric step.

Samples that have been exposed to air may give low results due to precipitation of manganese dioxide (MnO_2). Add 1 drop 30% hydrogen peroxide (H_2O_2) to the sample, after adding the special reagent, to redissolve precipitated manganese.

c. Minimum detectable concentration: The molar absorptivity of permanganate ion is about 2300 L g^{-1} cm^{-1}. This corresponds to a minimum detectable concentration (98% transmittance)

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of 210 µg Mn/L when a 1-cm cell is used or 42 µg Mn/L when a 5-cm cell is used.

2. Apparatus

Colorimetric equipment: One of the following is required:

a. Spectrophotometer, for use at 525 nm, providing a light path of 1 cm or longer.

b. Filter photometer, providing a light path of 1 cm or longer and equipped with a green filter having maximum transmittance near 525 nm.

c. Nessler tubes, matched, 100-mL, tall form.

3. Reagents

a. Special reagent: Dissolve 75 g $HgSO_4$ in 400 mL conc HNO_3 and 200 mL distilled water. Add 200 mL 85% phosphoric acid (H_3PO_4), and 35 mg silver nitrate ($AgNO_3$). Dilute the cooled solution to 1 L.

b. Ammonium persulfate, $(NH_4)_2S_2O_8$, solid.

c. Standard manganese solution: Prepare a 0.1*N* potassium permanganate ($KMnO_4$) solution by dissolving 3.2 g $KMnO_4$ in distilled water and making up to 1 L. Age for several weeks in sunlight or heat for several hours near the boiling point, then filter through a fine fritted-glass filter crucible and standardize against sodium oxalate as follows:

Weigh several 100- to 200-mg samples of $Na_2C_2O_4$ to 0.1 mg and transfer to 400-mL beakers. To each beaker, add 100 mL distilled water and stir to dissolve. Add 10 mL 1 + 1 H_2SO_4 and heat rapidly to 90 to 95°C. Titrate rapidly with the $KMnO_4$ solution to be standardized, while stirring, to a slight pink end-point color that persists for at least 1 min. Do not let temperature fall below 85°C. If necessary, warm beaker contents during titration; 100 mg $Na_2C_2O_4$ will consume about 15 mL permanganate solution. Run a blank on distilled water and H_2SO_4.

$$\text{Normality of } KMnO_4 = \frac{\text{g } Na_2C_2O_4}{(A - B) \times 0.067\ 01}$$

where:

A = mL titrant for sample and
B = mL titrant for blank.

Average results of several titrations. Calculate volume of this solution necessary to prepare 1 L of solution so that 1.00 mL = 50.0 µg Mn, as follows:

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$$\text{mL } KMnO_4 = \frac{4.55}{\text{normality } KMnO_4}$$

To this volume add 2 to 3 mL conc H_2SO_4 and $NaHSO_3$ solution dropwise, with stirring, until the permanganate color disappears. Boil to remove excess SO_2, cool, and dilute to 1000 mL with distilled water. Dilute this solution further to measure small amounts of manganese.

d. Standard manganese solution (alternate): Dissolve 1.000 g manganese metal (99.8% min.) in 10 mL redistilled HNO_3. Dilute to 1000 mL with 1% (v/v) HCl; 1 mL = 1.000 mg Mn. Dilute 10 mL to 200 mL with distilled water; 1 mL = 0.05 mg Mn. Prepare dilute solution daily.

e. Hydrogen peroxide, H_2O_2, 30%.

f. Nitric acid, HNO_3, conc.

g. Sulfuric acid, H_2SO_4, conc.

h. Sodium nitrite solution: Dissolve 5.0 g $NaNO_2$ in 95 mL distilled water.

i. Sodium oxalate, $Na_2C_2O_4$, primary standard.

j. Sodium bisulfite: Dissolve 10 g $NaHSO_3$ in 100 mL distilled water.

4. Procedure

a. Treatment of sample: If a digested sample has been prepared according to directions for reducing organic matter and/or excessive chlorides in Section 3030G, pipet a portion containing 0.05 to 2.0 mg Mn into a 250-mL conical flask. Add distilled water, if necessary, to 90 mL and proceed as in ¶ b.

b. To a suitable sample portion add 5 mL special reagent and 1 drop H_2O_2. Concentrate to 90 mL by boiling or dilute to 90 mL. Add 1 g $(NH_4)_2S_2O_8$, bring to a boil, and boil for 1 min. Do not heat on a water bath. Remove from heat source, let stand 1 min, then cool under the tap. (Boiling too long results in decomposition of excess persulfate and subsequent loss of permanganate color; cooling too slowly has the same effect.) Dilute to 100 mL with distilled water free from reducing substances and mix. Prepare standards containing 0, 5.00, . . . 1500 µg Mn by treating various amounts of standard Mn solution in the same way.

c. Nessler tube comparison: Use standards prepared as in ¶ 4*b* and containing 5 to 100 µg Mn/100 mL final volume. Compare samples and standards visually.

d. Photometric determination: Use a series of standards from 0 to 1500µg Mn/100mL final volume. Make photometric measurements against a distilled water blank. The following table shows light path length appropriate for various amounts of manganese in 100mL final volume:

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shows light path length appropriate for various amounts of manganese in 100mL final volume:

Mn Range *µg*	Light Path *cm*
5–200	15
20–400	5
50–1000	2
100–1500	1

Prepare a calibration curve of manganese concentration vs. absorbance from the standards and determine Mn in the samples from the curve. If turbidity or interfering color is present, make corrections as in 4e.

e. Correction for turbidity or interfering color: Avoid filtration because of possible retention of some permanganate on the filter paper. If visual comparison is used, the effect of turbidity only can be estimated and no correction can be made for interfering colored ions. When photometric measurements are made, use the following ‘‘bleaching’’ method, which also corrects for interfering color: As soon as the photometer reading has been made, add 0.05 mL H_2O_2 solution directly to the sample in the optical cell. Mix and, as soon as the permanganate color has faded completely and no bubbles remain, read again. Deduct absorbance of bleached solution from initial absorbance to obtain absorbance due to Mn.

5. Calculation

a. When all of the original sample is taken for analysis:

$$\text{mg Mn/L} = \frac{\mu\text{g Mn/100 mL}}{\text{mL sample}} \times \frac{100}{\text{mL portion}}$$

b. When a portion of the digested sample (100 mL final volume) is taken for analysis:

$$\text{mg Mn/L} = \frac{\mu\text{g Mn (in 100 mL final volume)}}{\text{mL sample}}$$

6. Precision and Bias

A synthetic sample containing 120 µg Mn/L, 500 µg Al/L, 50 µg Cd/L, 110 µg Cr/L, 470 µg Cu/L, 300 µg Fe/L, 70 µg Pb/L, 150 µg Ag/L, and 650 µg Zn/L in distilled water was analyzed in 33 laboratories by the persulfate method, with a relative standard deviation of 26.3% and a

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relative error of 0%.

A second synthetic sample, similar in all respects except for 50 µg Mn/L and 1000 µg Cu/L, was analyzed in 17 laboratories by the persulfate method, with a relative standard deviation of 50.3% and a relative error of 7.2%.

7. Bibliography

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MILLS, S.M. 1950. Elusive manganese. *Water Sewage Works* 97:92.

SANDELL, E.B. 1959. Colorimetric Determination of Traces of Metals, 3rd ed. Interscience Publishers, New York, N.Y., Chapter 26.

3500-Hg MERCURY

Mercury (Hg) is the third element in Group IIB in the periodic table; it has an atomic number of 80, an atomic weight of 200.59, and valences of 1 and 2. The average abundance of Hg in the earth's crust is 0.09 ppm; in soils it is 30 to 160 ppb; in streams it is 0.07 µg/L, and in groundwaters it is 0.5 to 1 µg/L. Mercury occurs free in nature, but the chief source is cinnibar (HgS). Mercury is used in amalgams, mirror coatings, vapor lamps, paints, measuring devices (thermometers, barometers, manometers), pharmaceuticals, pesticides, and fungicides. It is often used in paper mills as a mold retardant for paper.

The common aqueous species are Hg^{2+}, $Hg(OH)_2^0$, Hg^0, and stable complexes with organic ligands. Inorganic mercury can be methylated in sediments when sulfides are present to form dimethyl mercury, $(CH_3)_2Hg$, which is very toxic and can concentrate in the aquatic food chain. Mercury poisoning occurred in Japan in the 1950s as the result of consumption of shellfish that had accumulated mercury. In times past, mercury was used in the haberdashery industry to block hats (the cause of the ''mad hatter'' syndrome).

Mercury is considered nonessential for plants and animals. The U.S. EPA primary drinking water standard MCL is 2 µg/L.

The cold-vapor atomic absorption method (Section 3112B) is the method of choice for all samples. The inductively coupled plasma mass spectrometric method (Section 3125) also may be applied successfully in some cases, even though mercury is not specifically listed as an analyte in the method. The dithizone method detailed in the 19th edition of *Standard Methods* can be used for determining high levels of mercury (>2 µg/L) in potable waters.

Because mercury can be lost readily from samples, preserve them by treating with HNO_3 to reduce the pH to <2 (see Section 1060). Glass storage containers are preferred to plastic, because they can extend the holding time to 30 d, rather than only the 14 d allowed in plastic containers.

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3500-Mo MOLYBDENUM

Molybdenum (Mo) is the second element in Group VIB in the periodic table; it has an atomic number of 42, and atomic weight of 95.95, and valences of 2, 3, 4, 5, and 6. The average abundance of Mo in the earth's crust is 1.2 ppm; in soils it is 2.5 ppm; in streams it is 1 μg/L, and in groundwaters it is <0.1 mg/L. Molybdenum occurs naturally as molybdenite (MoS_2) and wulfenite

($PbMoO_4$). It is used in alloys, ink pigments, catalysts, and lubricants.

The common aqueous species are $HMoO_4^-$, MoO_4^{2-}, and organic complexes. It is considered an essential trace element for plants and animals. The United Nations Food and Agriculture Organization recommended maximum level for irrigation waters is 0.01 mg/L.

Use one of the flame atomic absorption spectrometric methods (Section 3111D or Section 3111E), the electrothermal atomic absorption spectrometric method (Section 3113B), or one of the inductively coupled plasma methods (Section 3120 or Section 3125).

3500-Ni NICKEL

Nickel (Ni) is the third element in Group VIII in the periodic table; it has an atomic number of 28, an atomic weight of 58.69, and a common valence of 2 and less commonly 1, 3, or 4. The average abundance of Ni in the earth's crust is 1.2 ppm; in soils it is 2.5 ppm; in streams it is 1 μg/L, and in groundwaters it is <0.1 mg/L. Nickel is obtained chiefly from pyrrhotite and garnierite. Nickel is used in alloys, magnets, protective coatings, catalysts, and batteries.

The common aqueous species is Ni^{2+}. In reducing conditions insoluble sulfides can form, while in aerobic conditions nickel complexes with hydroxide, carbonates, and organic ligands can form. It is suspected to be an essential trace element for some plants and animals. The United Nations Food and Agriculture Organization recommended maximum level for irrigation waters is 200 μg/L. The U.S. EPA primary drinking water standard MCL is 0.1 mg/L.

The atomic absorption spectrometric methods (Section 3111B and Section 3111C), the inductively coupled plasma methods (Section 3120 and Section 3125), and the electrothermal atomic absorption spectrometric method (Section 3113B) are the methods of choice for all samples.

3500-Os OSMIUM

Osmium (Os) is the seventh element in Group VIII in the periodic table; it has an atomic number of 76, an atomic weight of 190.2, and valences of 3, 4, and 6, and less commonly 1, 2, 5, 7, and 8. The average abundance of Os in the earth's crust is probably <0.005 ppm, and in groundwaters it is <0.01 mg/L. Osmium occurs in iridosime and in platinum-bearing river sands.

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Osmium is used as a hardener with iridium and as a catalyst with platinum.

The aqueous chemistry is controlled by complex compounds, although the solubility in natural waters is relatively unknown.

Analyze by flame atomic absorption methods (Section 3111D and Section 3111E).

3500-Pd PALLADIUM

Palladium (Pd) is the sixth element in Group VIII of the periodic table; it has an atomic number of 46, an atomic weight of 106.42, and valences of 2 and 4. Palladium occurs with platinum in nature. It is used in alloys to make electrical relays, catalysts, in the making of ‘‘white gold,’’ and in protective coatings.

Palladium has no known toxic effects. The United Nations Food and Agriculture Organization recommended maximum level for irrigation waters is 5 mg/L.

Preferably analyze by flame atomic absorption method (Section 3111B). The inductively coupled plasma mass spectrometric method (Section 3125) also may be applied successfully in most cases (with lower detection limits), even though palladium is not specifically listed as an analyte in the method.

3500-Pt PLATINUM

Platinum (Pt) is the ninth element in Group VIII of the periodic table; it has an atomic number of 78, an atomic weight of 195.1, and valences of 2 and 4. The average abundance of Pt in the earth’s crust is probably <0.01 ppm, and in groundwaters it is <0.1 mg/L. Platinum is usually found in its native state, but also may be found as sperrylite ($PtAs_2$). Platinum is used as a catalyst and in laboratoryware, jewelry, and surgical wire.

The aqueous chemistry in natural waters is relatively unknown, although its solubility is probably controlled by complex compounds. In powder form, platinum can be flammable, and its soluble salts are toxic by inhalation.

Preferably analyze by flame atomic absorption method (Section 3111B). The inductively coupled plasma mass spectrometric method (Section 3125) also may be applied successfully in most cases (with lower detection limits), even though platinum is not specifically listed as an analyte in the method.

3500-K POTASSIUM*#(114)

3500-K A. Introduction

1. Occurrence and Significance

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Potassium (K) is the fourth element in Group IA of the periodic table; it has an atomic number of 19, an atomic weight of 39.10, and a valence of 1. The average abundance of K in the earth's crust is 1.84%; in soils it has a range of 0.1 to 2.6%; in streams it is 2.3 mg/L, and in groundwaters it has a range of 0.5 to 10 mg/L. Potassium is commonly associated with aluminosilicate minerals such as feldspars. ^{40}K is a naturally occurring radioactive isotope with a half-life of 1.3×10^9 years. Potassium compounds are used in glass, fertilizers, baking powder, soft drinks, explosives, electroplating, and pigments. Potassium is an essential element in both plant and human nutrition, and occurs in groundwaters as a result of mineral dissolution, from decomposing plant material, and from agricultural runoff.

The common aqueous species is K^+. Unlike sodium, it does not remain in solution, but is assimilated by plants and is incorporated into a number of clay-mineral structures.

2. Selection of Method

Methods for the determination of potassium include flame atomic absorption (Section 3111B), inductively coupled plasma (Section 3120), flame photometry (B), and selective ion electrode (C). The inductively coupled plasma/mass spectrometric method (Section 3125) usually may be applied successfully (with lower detection limits), even though potassium is not specifically listed as an analyte in the method. The preferred methods are rapid, sensitive, and accurate; selection depends on instrument availability and analyst choice.

3. Storage of Samples

Do not store samples in soft-glass bottles because of the possibility of contamination from leaching of the glass. Use acid-washed polyethylene or borosilicate glass bottles. Adjust sample to pH < 2 with nitric acid. This will dissolve potassium salts and reduce adsorption on vessel walls.

3500-K B. Flame Photometric Method

1. General Discussion

a. Principle: Trace amounts of potassium can be determined in either a direct-reading or internal-standard type of flame photometer at a wavelength of 766.5 nm. Because much of the information pertaining to sodium applies equally to the potassium determination, carefully study the entire discussion dealing with the flame photometric determination of sodium (Section 3500-Na.B) before making a potassium determination.

b. Interference: Interference in the internal-standard method may occur at sodium-to-potassium ratios of 5:1 or greater. Calcium may interfere if the calcium-to-potassium ratio is 10:1 or more. Magnesium begins to interfere when the magnesium-to-potassium ratio exceeds 100:1.

c. Minimum detectable concentration: Potassium levels of approximately 0.1 mg/L can be

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determined.

2. Apparatus

See Section 3500-Na.B.2.

3. Reagents

To minimize potassium pickup, store all solutions in plastic bottles. Shake each container thoroughly to dissolve accumulated salts from walls before pouring.

a. Reagent water: See Section 1080. Use this water for preparing all reagents and calibration standards, and as dilution water.

b. Stock potassium solution: Dissolve 1.907 g KCl dried at 110°C and dilute to 1000 mL with water; 1 mL = 1.00 mg K.

c. Intermediate potassium solution: Dilute 10.0 mL stock potassium solution with water to 100 mL; 1.00 mL = 0.100 mg K.

Use this solution to prepare calibration curve in potassium range of 1 to 10 mg/L.

d. Standard potassium solution: Dilute 10.0 mL intermediate potassium solution with water to 100 mL; 1.00 mL = 0.010 mg K. Use this solution to prepare calibration curve in potassium range of 0.1 to 1.0 mg/L.

4. Procedure

Make determination as described in Section 3500-Na.B.4, but measure emission intensity at 766.5 nm.

5. Calculation

See Section 3500-Na.B.5.

6. Precision and Bias

A synthetic sample containing 3.1 mg K^+/L, 108 mg Ca^{2+}/L, 82 mg Mg^{2+}/L, 19.9 mg Na^+/L, 241 mg Cl^-/L, 0.25 mg NO_2^--N/L, 1.1 mg NO_3^--N/L, 259 mg SO_4^{2-}/L, and 42.5 mg total alkalinity/L (contributed by $NaHCO_3$) was analyzed in 33 laboratories by the flame photometric method, with a relative standard deviation of 15.5% and a relative error of 2.3%.

7. Bibliography

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Also see Section 3500-Na.B.7.

3500-K C. Potassium-Selective Electrode Method

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1. General Discussion

a. Principle: Potassium ion is measured potentiometrically by using a potassium ion-selective electrode and a double-junction, sleeve-type reference electrode. The analysis is performed with either a pH meter having an expanded millivolt scale capable of being read to the nearest 0.1 mV or a specific ion meter having a direct concentration scale for potassium.

Before measurement, an ionic strength adjustor reagent is added to both standards and samples to maintain a constant ionic strength. The electrode response is measured in standard solutions with potassium concentrations spanning the range of interest using a calibration line derived either by the instrument meter or manually. The electrode response in sample solutions is measured following the same procedure and potassium concentration determined from the calibration line or instrument direct readout.

b. Interferences: Although most sensitive to potassium, the potassium electrode will respond to other cations at high concentrations; this can result in a positive bias. Table 3500-K:I lists the concentration of common cations causing a 10% error at various concentrations of potassium chloride with a background ionic strength of 0.12*N* sodium chloride. Of the cations listed, ammonium ion is most often present in samples at concentrations high enough to result in a significant bias. It can be converted to gaseous ammonia by adjusting to pH > 10.

An electrode exposed to interfering cations tends to drift and respond sluggishly. To restore normal performance soak electrode for 1 h in distilled water and then for several hours in a standard potassium solution.

c. Detection limits: Samples containing from 0.1 to 1000 mg K^+/L may be analyzed. To measure higher concentrations dilute the sample.

2. Apparatus

a. Expanded-scale or digital pH meter or ion-selective meter.

b. Potassium ion-selective electrode.

c. Sleeve-type double-junction reference electrode: Fill outer sleeve with reference electrode filling solution (see ¶ 3*b*). Fill inner sleeve with inner filling solution provided with the electrode.

d. pH electrode.

e. Mixer, magnetic, with a TFE-coated stirring bar.

3. Reagents

a. Ionic strength adjustor (ISA): Dissolve 29.22 g NaCl in reagent water and dilute to 100 mL.

b. Reference electrode outer sleeve filling solution: Dilute 2 mL ISA solution to 100 mL with reagent water.

c. Stock potassium solution: See Section 3500-K.B.3*b*.

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d. Sodium hydroxide, NaOH, 6*N*.

e. Reagent water: See Section 1080.

4. Procedure

a. Preparation of standards: Prepare a series of standards containing 100.0, 10.0, 1.0, and 0.1 mg K^+/L by making serial dilutions of the stock potassium solution as in Section 3500-K.B.3*c* and Section 3500-K.B.3*d*.

b. Instrument calibration: Fill reference electrode according to the manufacturer's instructions using reference electrode filling solution. Transfer 100 mL 0.1 mg K^+/L standard into a 150-mL beaker and add 2 mL ISA. Raise pH to about 11. Stir gently with magnetic mixer. Immerse electrodes, wait approximately 2 min for potential stabilization and record meter reading. Thoroughly rinse electrodes and blot dry. Repeat for each standard solution in order of increasing concentration. Prepare calibration curve on semilogarithmic graph paper by plotting observed potential in millivolts (linear scale) against concentration (log scale). Alternatively, calculate calibration line by regression analysis.

c. Analysis of samples: Transfer 100 mL sample into a 150-mL beaker and follow procedure applied to standards in ¶ 4*b* above. From the measured response, calculate K^+ concentration from calibration curve.

5. Precision

Reproducibility of potential measured, over the method's range, can be expected to be ± 0.4 mV, corresponding to about ± 2.5% in concentration.

6. Quality Assurance

The slope of the calibration line should be –56 mV/10-fold concentration change. If the slope is outside the range of –56 ±3 mV, the electrode may require maintenance (replace filling solutions). If the proper electrode response cannot be obtained, replace electrode.

Analyze an independent check standard with a mid-range potassium concentration throughout analysis of a series, initially, every ten samples, and after final sample. If the value has changed by more than 5%, recalibrate electrode. Analyze a reagent blank at the same frequency. Readings must represent a lower concentration than the lowest concentration standard (0.1 mg/L).

7. Bibliography

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3500-Re RHENIUM

Rhenium (Re) is the third element in Group VIIB in the periodic table; it has an atomic number of 75, an atomic weight of 186.21, and valences of 1 through 7, with 7 being the most stable. The average abundance of Re in the earth's crust is 7 ppm, and in groundwaters it is <0.1 mg/L. Rhenium is found in columbite, tantalite, and wolframite, as well as in molybdenum ore concentrates. It is used in tungsten-molybdenum-based alloys, thermocouples, filaments, and flash bulbs. Rhenium in the powderform can be flammable.

For analysis methods, see flame atomic absorption methods (Section 3111D and Section 3111E). The inductively coupled plasma mass spectrometric method (Section 3125) also may be applied successfully in most cases (with lower detection limits), even though rhenium is not specifically listed as an analyte in the method.

3500-Rh RHODIUM

Rhodium (Rh) is the fifth element in Group VIII in the periodic table; it has an atomic number of 45, an atomic weight of 102.91, and valences of 1 through 6, the most common being 1 and 3. Rhodium is found in its native state in platinum-bearing sands. It is used in platinum alloys for thermocouples, electrical contacts, and jewelry.

The aqueous chemistry in natural waters is relatively unknown. The metal is flammable in the powder form, and its salts are toxic by inhalation.

For analysis see flame atomic absorption method (Section 3111B). The inductively coupled plasma/mass spectrometric method (Section 3125) also may be applied successfully in most cases (with lower detection limits), even though rhodium is not specifically listed as an analyte in the method.

3500-Ru RUTHENIUM

Ruthenium (Ru) is the fourth element in Group VIII in the periodic table; it has an atomic number of 44, an atomic weight of 101.07, and valences of 1 through 7, the most common being 2, 3, and 4. The average abundance of Ru in the earth's crust is probably <0.01 ppm, and in groundwaters it is <0.1 mg/L. It occurs in its native state in platinum-bearing river sands. It is used in jewelry with platinum, in electrical contacts, and as a catalyst.

The aqueous chemistry in natural waters is relatively unknown. Ruthenium has no known toxic effects.

For analysis see flame atomic absorption method (Section 3111B). The inductively coupled plasma mass spectrometric method (Section 3125) also may be applied successfully in most cases (with lower detection limits), even though ruthenium is not specifically listed as an analyte in the method.

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3500-Se SELENIUM*#(115)

3500-Se A. Introduction

1. Occurrence and Significance

Selenium (Se) is the third element in Group VIA in the periodic table; it has an atomic number of 34, an atomic weight of 78.96, and valences of 2, 4, or 6. The average abundance of Se in the earth's crust is 0.2 ppm; in soils it is 0.27 to 0.74 ppm; in streams it is 0.2 μg/L, and in groundwaters it is <0.1 mg/L. Selenium is used in electronics, ceramics, and shampoos.

The inorganic fraction of dissolved selenium consists predominantly of selenium as the selenate ion (SeO_4^{2-}), designated here as Se(VI), and selenium as the selenite ion (SeO_3^{2-}), Se(IV). Other common aqueous species include Se^{2-}, HSe^-, and Se^0. Selenium is considered a nonessential trace element for most plants, but is an essential trace nutrient for most animals, and selenium deficiency diseases are well known in veterinary medicine. Above trace levels, ingested selenium is toxic to animals and may be toxic to humans. While the selenium concentration of most natural waters is low, the pore water in seleniferous soils in semiarid areas may contain up to hundreds or thousands of micrograms dissolved selenium per liter. Certain plants that grow in such areas accumulate large concentrations of selenium and may poison livestock that graze on them. Water drained from such soil may cause severe environmental pollution and wildlife toxicity. Selenopolysulfide ions (SSe^{2-}) may occur in the presence of hydrogen sulfide in waterlogged, anoxic soils. Selenium derived from microbial degradation of seleniferous organic matter includes selenite, selenate, and the volatile organic compounds dimethylselenide and dimethyldiselenide. Nonvolatile organic selenium compounds may be released to water by microbial processes. Soluble selenium may be leached from coal ash and fly ash at electric power plants that burn seleniferous coal.

The United Nations Food and Agriculture Organization recommended maximum level for selenium in irrigation waters is 20 μg/L. The U.S. EPA primary drinking water standard MCL is 50 μg/L.

2. Selection of Method

The selenium methods using hydride generation atomic absorption (Section 3114B and Section 3114C), electrothermal atomic absorption (Section 3113B), and derivatization colorimetry (C) are the most sensitive currently available. For determination of selenium at higher concentrations, the inductively coupled plasma methods (Section 3120 and Section 3125) may be used.

By using suitable preparatory steps to convert other chemical species to Se(IV), it is possible to distinguish the chemical species in the sample. In drinking water and most surface and ground

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waters, Se(IV), Se(VI), and particulate selenium frequently are the only significant species. However, when speciation is important, for example, when a new matrix is being analyzed, the general analytical scheme shown in Figure 3500-Se:1 may be carried out as follows: Determine volatile selenium by stripping sample with nitrogen or air and collecting selenium in alkaline hydrogen peroxide (see Method D). To obtain an estimate of selenium in suspended particles, determine total selenium, filter sample, and make a second determination of total selenium. In any case, filter sample. Occasionally, a filtered sample may have the odor of hydrogen sulfide and a yellow color; such a sample may contain selenopolysulfides, which may be estimated by comparing results of total selenium analyses before and after acidification, stripping with nitrogen, settling for 10 min, and refiltration. Determine selenite, Se(IV), by analyzing filtered water sample directly by Methods 3114B or C, or by Section 3500-Se.C or Section 3500-Se.E. In principle, sample digestion with HCl will convert Se(VI) to Se(IV), and the value determined will equal the sum of the two species. In practice, samples frequently contain an unknown masking agent that produces an unduly low result. Test for this effect by analyzing samples with known additions of both species. If recovery is good, the HCl digestion followed by analyses will yield reliable results. If recovery is poor and organic selenium is to be determined subsequently, attempt to remove the interference by sample pretreatment with resin (B.1). Interference also can be eliminated by digestion with an oxidizing agent (B.2, 3, and 4), but these procedures prevent distinguishing of Se(VI) and organic selenium and also oxidize many organic selenium compounds. To measure nonvolatile organic selenium compounds, use Method E.

The choice of digestion method for oxidizing interferences and organic selenium depends on sample matrix. The methods described in B.2, 3, and 4, in order of increasing complexity and digestive ability, use ammonium (or potassium) persulfate, hydrogen peroxide, and potassium permanganate. Ammonium persulfate digestion is adequate for most filtered ground, drinking, and surface water. Hydrogen peroxide digestion may be required if organic selenium compounds are present, and potassium permanganate digestion may be needed with unfiltered samples or those containing refractory organic selenium compounds. Confirm results obtained with one digestion method by using a more rigorous method when characterizing a new matrix.

3. Interferences

Interferences are found in certain reagents, as well as in samples. Recognition of the presence of an interferant is critical, especially when unknown sample matrices are being analyzed. Routinely add Se(IV) and Se(VI) to test for interference. If present, characterize the interference and correct by the method of standard additions. A slope less than one indicates interference. In cases of mild interference (recoveries reduced by 25% or less), the standard additions method will largely correct determined values.

Because the hydride atomic absorption method is extremely sensitive, samples frequently need to be diluted to bring them within the linear range of the instrument. Diluting a filtered water sample frequently will eliminate sample-related interferences. Include full reagent blanks in each run to ensure absence of contamination from reagents. Hydride generator atomic absorption is susceptible to common interference problems related to nitrite in the sample or free

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chlorine in the reagent HCl (see Methods Section 3114B and Section 3114C).

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3500-Se B. Sample Preparation

1. Removal of Organic and Iron Interference by Resin Pretreatment

Interferences are common in selenium analysis, particularly when chemical speciation is attempted. Routine pretreatment of water samples as described here is not necessary. The methods in this section should be tried when poor recovery of standard additions indicates a problem.

Many waters contain iron and/or dissolved organic matter (humic acid) in quantities sufficient to interfere. Reduction of Se(VI) to Se(IV) usually is nonquantitative. When Se(VI) standard additions show poor recovery, treat the sample before analysis. To remove dissolved organic compounds, pass an acidified sample through a resin. Because dissolved organic selenium compounds also may be removed by this treatment, also determine total selenium in the untreated water sample (see 2, 3, or 4 below). To remove iron use a strong base ion exchange resin.*#(116) Iron is removed as the anionic chloro complex. In this treatment the acidity and ion exchanger do not alter speciation; complete speciation of selenium is possible.

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a. Apparatus:

1) *Chromatography column* for organics removal, glass, about 0.8 cm ID ×30 cm long, with fluorocarbon metering valve.

2) *Chromatography column* for ion exchange, disposable polyethylene.†#(117)

3) *pH meter.*

b. Reagents:

1) *Organics-removal resin:* Thoroughly rinse 16 to 50 mesh resin‡#(118) with deionized water and remove resin fines by decanting. Rinse three times with pH 12 solution. Store resin in pH 12 solution and refrigerate to prevent bacterial growth.

2) *Anion exchange resin:* Add 100 to 200 mesh anion exchange resin*#(119) to a beaker and thoroughly rinse with deionized water. Cover resin with 4*N* HCl, stir, and let settle. Decant and repeat acid rinse twice more. Store resin in 4*N* HCl.

3) *Hydrochloric acid,* conc: Before use, bubble helium through the acid for 3 h at rate of 100 mL/min. (CAUTION*: Use a fume hood.*)

4) *pH 1.6 solution:* Adjust pH of deionized water to 1.6 with HCl.

5) *pH 12 solution:* Adjust pH of deionized water to 12 with KOH.

c. Procedure:

1) Organic removal—Place 5 cm washed resin in a 0.8-cm-ID column. Precondition column, at 1 mL/min, with 30 mL pH 12 solution and 20 mL pH 1.6 solution. Using HCl and a pH meter adjust sample to pH 1.6 to 1.8. Pass sample through preconditioned column at rate of 1 mL/min. Discard first 10 mL and use next 11 to 50 mL collected for Se(IV) determinations by Methods 3114B or C, or 3500-Se.C preceded, if Se(VI) also is to be determined, by preparatory step B.5. If more than 50 mL sample are needed, use another column or use a column with twice as much resin.

2) Iron removal—Place 4 cm prepared resin in a small chromatographic column (add resin to column filled with 4*N* HCl to avoid air bubbles). Rinse column with 10 mL 4*N* HCl at flow rate < 6 mL/min. Let solution drain to top of resin, but do not let the column run dry. Adjust sample to 4*N* HCl and pour into column. Discard first 10 mL and collect the next 11 to 100 mL for Se(IV) analysis by Methods 3114B or C, or 3500-Se.C preceded, if necessary, by preparatory step B.2 and if Se(VI) also is to be determined, by preparatory step B.5 below.

2. Removal of Interference by Persulfate Digestion

The combination of this procedure with step B.5 below and Methods Section 3114B or Section 3114C, or Section 3500-Se.C is, in most cases, the preferred method for determining total selenium in filtered water. A small amount of ammonium or potassium persulfate is added to the mixture of sample and HCl to remove interference from reducing agents and to oxidize relatively labile organic selenium compounds such as selenoamino acids and methaneseleninic acid.

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If the sample contains hydrogen sulfide or a large concentration of organic matter or is otherwise suspect or to confirm method accuracy, reanalyze sample using digestion procedure 3 or 4 below.

Prepare 2% potassium or ammonium persulfate solution by dissolving 2.0 g in 100 mL deionized water (prepare weekly). Add 0.2 mL persulfate solution to the mixed sample and HCl of ¶ B.5*c* before heating and proceeding with pretreatment and analysis.

After completing analysis multiply concentration of selenium determined in the acidified sample by 2.04 to obtain total selenium in original sample.

3. Removal of Interference by Alkaline Hydrogen Peroxide Digestion

Occasionally, digestion with persulfate gives incomplete recovery of total selenium. In this case, digestion with hydrogen peroxide is used to remove all reducing agents that might interfere and to fully oxidize organic selenium to Se(VI). The resulting solution can be analyzed for total selenium after pretreatment according to step B.5 below.

This method is suitable for determining total selenium in unfiltered water samples, where particulate selenium is present. When working with a new matrix, confirm results obtained by reanalyzing the sample using digestion procedure 4, below.

a. Apparatus:

1) *Beakers*, 150-mL.

2) *Watch glasses*.

3) *Hot plate*.

4) *Pipetter*, 1-mL, and tips.

5) *Graduated cylinder*, 25-mL.

b. Reagents:

1) *Hydrogen peroxide*, H_2O_2, 30%. Keep refrigerated.

2) *Sodium hydroxide*, NaOH, 1*N*.

3) *Hydrochloric acid*, HCl, 1.5*N*: Dilute 125 mL conc HCl to 1 L with deionized water.

c. Procedure: Add 2 mL 30% H_2O_2 and 1 mL 1 *N* NaOH to 25 mL sample in a beaker. Cover beaker to control spattering and simmer on hot plate until fine bubbles characteristic of H_2O_2 decomposition subside and are replaced by ordinary boiling. Add 1 mL 1.5*N* HCl to redissolve any precipitate that may have formed, let cool, and pour into graduated cylinder. Rinse beaker with deionized water into graduated cylinder and make volume up to 25 mL. Proceed to B.5 and chosen analytical method.

4. Removal of Interference by Permanganate Digestion

This digestion method utilizes potassium permanganate to oxidize selenium and remove interfering organic compounds. Excess $KMnO_4$ and MnO_2 are removed by reaction with hydroxylamine. HCl digestion is included here, because it is conveniently performed in the same

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reaction vial. Selenite may then be determined directly by Methods Section 3114B or Section 3114C, or Section 3500-Se.C.

Verify recovery for the given matrix. This method gives good recovery even with heavily contaminated water samples that contain organic selenium compounds, dissolved organic matter, and visible suspended material.

Permanganate may oxidize chloride ion to free chlorine. Part of the chlorine (which interferes with hydride analysis) is removed by reaction with hydroxylamine, but the best way to eliminate free chlorine is by prolonged heating in an open vial during the digestion step. Excess hydroxylamine may reduce recovery by reducing selenium to Se(0).

a. Apparatus:

1) *Oven with thermostat,* for continuous operation at 110 ± 5°C.

2) *Digestion vials,* 40-mL, with fluorocarbon-lined screw caps.

3) *Metal support rack* to hold 40 digestion vials.

b. Reagents:

1) *Hydrochloric acid,* HCl, conc. [See ¶ B.1*b*3)].

2) *Hydrochloric acid,* HCl, 10*N:* Dilute 1000 mL conc HCl to 1200 mL with deionized water.

3) *Sulfuric acid,* H_2SO_4, conc and 25%. NOTE: Many brands of H_2SO_4 are contaminated with selenium. Run reagent blanks when starting a new bottle. Make 25% v/v solution by adding 250 mL conc H_2SO_4 to 500 mL deionized water, and diluting to 1 L.

4) *Potassium permanganate solution,* $KMnO_4$, 5% (w/v): Dissolve 50 g $KMnO_4$ in 1000 mL deionized water.

5) *Hydroxylamine hydrochloride solution:* Dissolve 100 g $NH_2OH{\cdot}HCl$ in 1000 mL deionized water.

c. Procedure: Pipe 5 mL sample into digestion vial, add 5 mL 25% H_2SO_4 and 1 mL $KMnO_4$ solution. Screw cap on and place in preheated oven at 110°C for 1 h. Remove tray with vials from the oven and cool to room temperature. Open vial, carefully add a few drops hydroxylamine hydrochloride solution, mix, and wait until sample is decolorized and residual manganese dioxide is dissolved. Avoid excess hydroxylamine solution, which can cause a low reading. Add 10 mL conc HCl to the sample and heat vial 60 min at 95°C without cap. Let cool to room temperature. Transfer sample to a 25-mL volumetric flask or graduated cylinder, rinse vial into flask, dilute to mark, and mix well. Proceed to analyze by Methods Section 3114B or Section 3114C, or Section 3500-Se.C. If Method Section 3114B or Section 3114C is used, multiply spectrometer readings by the dilution factor as follows:

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$$\text{Concentration, } \mu g/L = \frac{\text{final volume}}{\text{volume of sample}} \times \text{reading}$$

5. Reduction of Se(VI) to Se(IV) by Hydrochloric Acid Digestion

Se(VI) is reduced to Se(IV) by digestion with HCl. Determine Se(IV) + Se(VI) by either hydride generation atomic absorption spectrometer (Method Section 3114B or Section 3114C) or as an organic derivative (Method C).

Test any given sample matrix to ensure recovery of added Se(VI). If recovery is poor, try to remove interference by the procedure of ¶ B.1, above, or if at least 75% recovery is achieved, use the method of standard additions. The method described here is of limited utility for direct analysis of water samples, but is useful as a step in determining total selenium in a sample where selenium has been oxidized to Se(VI).

a. Apparatus:

1) *Dispenser,* bottle type, 5-mL, suitable for dispensing concentrated HCl.

2) *Pipetters,* 0.2- and 5-mL.

3) *Screw-cap culture tubes,* borosilicate glass, 25- × 150-mm.

4) *Boiling water bath,* suitable for heating culture tubes; a 1-L beaker on a hot plate is suitable.

b. Reagents:

1) *Sodium selenate additions solution:* Dilute 1000 mg/L stock selenate solution with deionized water to prepare a solution of 1 to 10 mg/L, such that the concentration of the additions solution will be approximately 50 times greater than anticipated total selenium in the sample to be analyzed.

2) *Hydrochloric acid,* HCl, conc: See ¶ B.1*b*3).

c. Procedure: Calibrate acid dispenser using water. Preheat water bath. Pipet 5 mL filtered sample into a culture tube. Add 5 mL conc HCl. Loosely cap tube (do not tighten) and place in boiling water bath for 20 min. Let tube cool and tighten cap. Determine total Se(IV) by Methods Section 3114B or C, or Section 3500-Se.C.

Add 0.200 mL additions solution with a microliter pipet to sample and proceed as above. Analyze a deionized water blank and a blank with the addition to ensure absence of contamination and to determine the true value of the addition.

Multiply the concentration of selenium determined in the acidified sample by 2.00 to obtain total concentration of Se(IV) + Se(VI). Multiply reading obtained for sample with addition by 2.04.

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3500-Se C. Colorimetric Method

1. General Discussion

a. Principle: This method is specific to determining selenite ion in aqueous solution. Selenite ion reacts with 2,3-diaminonaphthalene to produce a brightly colored and strongly fluorescent piazselenol compound, which is extracted in cyclohexane and measured colorimetrically.

The optimum pH for formation of the piazselenol complex is approximately 1.5 but should not be above 2.5 because above pH 2, the rate of formation of the colored compound is critically dependent on pH. When indicators are used to adjust pH, results frequently are erratic; results can be improved when pH is monitored electrochemically.

b. Interference: No inorganic compounds are known to give a positive interference. Colored organic compounds extractable by cyclohexane may be encountered, but usually they are absent or can be removed by oxidizing the sample (see B.2, 3, or 4) or by treating it to remove dissolved organics (see B.1). Negative interference results from compounds that reduce the concentration of diaminonaphthalene by oxidizing it. Addition of EDTA eliminates negative interference from at least 2.5 mg Fe^{2+}.

c. Minimum detectable quantity: 10 μg Se/L.

2. Apparatus

a. Colorimetric equipment: A spectrophotometer, for use at 480 nm, providing a light path of 1 cm or longer.

b. Separatory funnel, 250-mL, preferably with a fluorocarbon stopcock.

c. Thermostatically controlled water bath (50°C) with cover.

d. pH meter.

e. Centrifuge, with rotor for 50-mL tubes (optional).

f. Centrifuge bottles, 60-mL, screw-capped, fluorocarbon.

g. Shaker, suitable for separatory funnel (optional).

3. Reagents

Use reagent water (see Section 1080) in preparing reagents.

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a. Selenium standard reference solution: Dissolve 2.190 g sodium selenite, Na_2SeO_3, in water containing 10 mL HCl and dilute to 1 L. 1.00 mL = 1.00 mg Se(IV).

b. Working standard selenium solutions: Dilute selenium reference standard solution with water or suitable background solution to produce a series of working standards spanning the concentration range of interest.

c. Hydrochloric acid: HCl, conc and 0.1*N*.

d. Ammonium hydroxide, NH_4OH, 50% v/v.

e. Cyclohexane, C_6H_{12}.

f. 2,3-Diaminonaphthalene (DAN) solution: Dissolve 200 mg DAN in 200 mL 0.1*N* HCl. Shake 5 min. Extract three times with 25-mL portions of cyclohexane, retaining aqueous phase and discarding organic portions. Filter into opaque container*#(120) and store in cool, dark place for no longer than 8 h. CAUTION*: Toxic, handle with extreme care.*

g. Hydroxylamine-EDTA solution (HA-EDTA): Dissolve 4.5 g Na_2EDTA in approximately 450 mL water. Add 12.5 g hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) and adjust volume to 500 mL.

4. Procedure

a. Formation of piazselenol: Add 2 mL HA-EDTA solution to 10 mL sample in 60-mL centrifuge bottle (filtered if Se(IV) is to be determined; oxidized using Method B.2, 3, or 4, then reduced using Method B.5 for total Se). Adjust to pH 1.5 ± 0.3 with 0.1*N* HCl and 50% NH_4OH, using a pH meter. Add 5 mL DAN solution and heat in a covered water bath at 50°C for 30 min.

b. Extraction of piazselenol: Cool and add 2.0 mL cyclohexane. Cap container securely and shake vigorously for 5 min. Let solution stand for 5 min or until cyclohexane layer becomes well separated. If separation is slow, centrifuge for 5 min at 2000 rpm. Place bottle in a clamp on a ringstand at a 45° angle to the vertical. Remove aqueous phase using a disposable pipet attached to a vacuum line. Transfer organic phase to a small capped container using a clean disposable pipet, or to the spectrophotometer cuvette if absorbance is to be read immediately.

c. Determination of absorbance: Read absorbance at 480 nm using a zero standard. The piazselenol color is very stable but evaporation of the cyclohexane concentrates the color unless the container is capped. CAUTION*: Avoid inhaling cyclohexane vapors*. Beer's Law is obeyed up to 2 mg/L.

5. Calculation

Construct calibration curve using at least a three-point standard curve to bracket the expected sample concentration. Plot absorbance vs. concentration. Correct for digestion blank and any reagent blank.

6. Precision and Bias

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Three standard reference materials (wheat flour, water, and a commercial standard) were used to evaluate Se recovery.[1] The wheat flour sample was digested using HNO_3 and $HClO_4$ to convert total selenium to Se(VI), digested with HCl to convert Se(VI) to Se(IV) and finally, the colorimetric method was used. Results were as follows:

	Selenium Concentration *µg Se/L*	
Standard	**Expected**	**Recovered***
NBS, SRM 1567, wheat flour†	1097 ± 197	1113 ± 8
NBS, SRM 1543ib, water	9.7 ± 0.5	8.7 ± 0
Fisher Certified AAS Standard	1002 ± 8	1002 ± 0

* Analyses in triplicate.
† Dry weight basis.

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3500-Se D. Determination of Volatile Selenium

1. General Discussion

Dimethylselenide and dimethyldiselenide are low boiling, extremely malodorous organic compounds sparingly soluble in water. They are produced by microbial processes in seleniferous soil and decaying seleniferous organic matter, and occasionally are present in natural waters. They are readily air stripped from a water sample and can be collected with high efficiency in an

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alkaline solution of hydrogen peroxide, which oxidizes them quantitatively to Se(VI). Total selenium is determined by digestion with HCl and analysis by the hydride atomic absorption (Section 3114B or Section 3114C) or colorimetric (Section 3500-Se.C) methods.

Either nitrogen or air may be used to strip the sample. Preferably use nitrogen if air-sensitive compounds (e.g., selenopolysulfides) are suspected.

Because volatile selenium can be lost in the course of sample collection and handling, preferably air-strip the sample in the field immediately after it is collected. After boiling to decompose H_2O_2, return the alkaline peroxide solution to the laboratory for analysis.

2. Apparatus

All apparatus required for selenate reduction (¶ B.5) and Methods Section 3114B or Section 3114C, or Section 3500-Se.C, plus:

a. Gas washing bottles, borosilicate glass, 250-mL, with coarse porous glass gas dispersion frit. Mark 100-mL level on side of bottle.

b. Rotameter, to measure 3 L/min air flow.

c. Gas flow regulator

d. Hot plate.

e. Graduated cylinder, 100-mL.

f. Beakers, 250-mL.

g. Rubber tubing, to interconnect gas washing bottles and other gas equipment.

h. Rubber gloves.

3. Reagents

All reagents required for selenate reduction (¶ B.5) and Methods Section 3114B or Section 3114C, or Section 3500-Se.C, plus:

a. Hydrogen peroxide, 30%. Refrigerate.

b. Sodium hydroxide solution, NaOH, 1*N*.

c. Compressed air or nitrogen.

4. Procedure

Set up air-flow train in this order: Regulated air supply→rotameter→gas washing bottle 1→gas washing bottle 2.

Prepare alkaline peroxide solution immediately before use by pouring 20 mL 30% H_2O_2 into a 100-mL graduated cylinder, adding 50 to 60 mL deionized water and 5 mL 1*N* NaOH, and making up to 100 mL. CAUTION: *Alkaline* H_2O_2 is unstable. Do not keep in glass bottle; hold at about 0 °C in oversized plastic bottle. Solution is corrosive; protect eyes and skin. Pour into gas washing bottle 2. Pour approximately 100 mL freshly collected sample into gas washing bottle 1. Do not attempt to measure sample volume accurately before volatile selenium determination, as

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unnecessary handling may cause volatile selenium to be lost.

Connect and check all air lines, turn on air and adjust flow to 3 L/min. Strip for 30 min or more. After 30 min, turn off air, disconnect gas washing bottle 2, and place it on the hot plate. Adjust heat to produce a gentle simmering of oxygen bubbles from decomposition of H_2O_2. Continue heating until the characteristic effervescence of oxygen subsides and is replaced by ordinary boiling. Remove from hot plate and let cool. Pour solution into beaker. (Volume will be very near to 100 mL, and correction will usually be unnecessary.) Analyze for total selenium using HCl digestion (B.5) and Methods Section 3114B or Section 3114C, or Section 3500-Se.C. Once boiled, this solution may be safely stored and transported in plastic bottles. Measure volume of sample in gas washing bottle 1.

5. Calculation

The concentration of volatile selenium compounds in the original water sample can be calculated as:

$$C = \frac{100}{\text{volume of original sample}} \times \text{conc of Se in solution}$$

6. Precision and Bias

Approximately 90% of dimethylselenide in samples will be recovered with 30 min air stripping. The recovery of dimethyldiselenide is not known. Loss of gases to the atmosphere during sampling and handling that precede analysis may cause a significant negative error.

3500-Se E. Determination of Nonvolatile Organic Selenium Compounds

1. General Discussion

In principle, the total amount of dissolved organic selenium plus polysulfidic selenium may be estimated by comparing ‘‘total Se,’’ determined by oxidation and HCl digestion (¶ B.2 or ¶ B.3 and ¶ B.5, or ¶ B.4), followed by Methods Section 3114B or Section 3114C, or Section 3500-Se.C, with Se(IV) + Se(VI) determined by HCl digestion (¶ B.5) and Method Section 3114C, or Section 3500-Se.C. In practice, this will give a meaningful estimate only if a known addition of Se(VI) is fully recovered. Even if recovery is good, this estimate may be unreliable, because it is the difference of two (frequently larger) numbers determined by slightly different methods. Comparing total Se before and after treatment with resin [¶ B.1*c*1)] gives a similarly unreliable estimate of nonvolatile organic Se.

It is preferable to separate and directly determine nonvolatile organic selenium. One method involves adsorption of dissolved organic matter onto a C-18 reverse phase HPLC resin, elution

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with an organic solvent, and determination of selenium in this fraction. While this technique is relatively simple, it is affected by pH and small organic molecules (e.g., individual selenium containing amino acids) are not retained by the resins. Adjust sample pH to 1.5 to 2.0 before using the column, but because the latter problem cannot be solved easily, the use of organic adsorbents provides only an estimate of organic selenium concentration.

Alternatively, isolate specific compounds and determine their selenium content. In some natural waters selenium may be associated with dissolved polypeptides or small proteins, and even small amounts of free selenoamino acids may be present. Because selenoamino acids are the most toxic form of the element, a direct determination is sometimes desirable.

To determine selenium in dissolved peptides, hydrolyze with acid and isolate the free amino acids via ligand exchange chromatography. Elute the selenoamino acids from the column and determine selenium. Selenoamino acids are unstable during acid hydrolysis and even using nonoxidizing methyl sulfonic acid and nitrogen-purged glass ampules, selenoamino acid recoveries are only 50 to 80%. This method is good only for estimating protein-bound selenium. A somewhat more reliable estimate of free selenoamino acids and selenium associated with small oligopeptides is obtained by performing a similar procedure without the hydrolysis step.

While these methods are too intricate for routine use, semiquantitative, and sensitive only to certain classes of organic compounds, at present they are the only ones available with any practical experience.

Imperfect separation of organic selenium compounds from inorganic forms of selenium may cause interference. In parallel with the actual determination, always perform the procedure using a solution compounded to resemble the actual matrix and containing a similar amount of selenium, but in the form of Se(IV) and Se(VI) to determine degree of interference.

2. Apparatus

a. Rotary evaporator, with temperature-control bath and 30-mL pear-shaped flasks.

b. Glass ampule sealing apparatus, or oxygen-gas torch.

c. Heating block, 100°C, or pressure cooker.

d. Glass chromatography columns, 15 cm long, 0.7 cm ID.*#(121)

e. Glass syringe, 50-mL.

f. Glass ampules, 10- or 20- mL. Clean by heating in a muffle furnace at 400°C for 24 h.

g. pH meter.

3. Reagents

a. Hydrochloric acid, HCl, 1*N*.

b. Methyl sulfonic acid, conc.

c. Ammonium hydroxide, NH_4OH, 1.5*N:* Dilute 100 mL conc NH_4OH to 1 L with deionized water.

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d. Sodium hydroxide, NaOH pellets and 1*N* solution.

e. pH 1.6 solution: Adjust pH of deionized water to 1.6 using HCl.

f. pH 9.0 solution: Adjust pH of deionized water to 9.0 using NaOH.

g. Copper sulfate solution, $CuSO_4$, 1*M:* Dissolve 25 g $CuSO_4 \cdot 5H_2O$ in deionized water and dilute to 100 mL.

h. Methanol, purified.

i. C-18 cartridges†#(122) Using a glass syringe, pass the following sequence of reagents through the cartridge to clean the resin (6 mL/min or less): 10 mL deionized water; 20 mL 1*N* HCl; 10 mL deionized water; 20 mL methanol; 10 mL deionized water; and 20 mL pH 1.6 solution. Refrigerate but do not freeze cleaned cartridges.

j. Ligand-exchange chromatographic resin, 100/200 mesh: Rinse resin‡#(123) with deionized water to remove fines. Then rinse resin three times in the following sequence: 1*N* HCl; 1.5*N* NH_4OH; and deionized water. Store resin wet.

k. Copper-treated ligand-exchange chromatographic resin, 100/200 mesh: Rinse resin‡ with deionized water to remove fines. Then rinse three times with 1*N* HCl, followed by deionized water. Using NaOH adjust pH of supernatant above the resin to about 7. Add $CuSO_4$ solution to the resin and stir. After settling, decant supernatant and add more $CuSO_4$ solution. Decant $CuSO_4$ solution and rinse with deionized water until no copper is noticeable in the supernatant. Rinse resin three times with 1.5*N* NH_4OH and three times with deionized water. Store resin wet.

4. Procedures

a. Extractable organic selenium: Adjust sample (5 to 50 mL) to pH 1.5 to 2.0 using HCl and place in a clean glass syringe with an attached cleaned C-18 cartridge. Push sample through the cartridge at a rate of 6 mL/min. After removing the cartridge, draw 2 mL pH 1.6 solution into syringe as a rinse, reattach cartridge, and push the rinse through the cartridge. Repeat two additional times. The cartridge can be refrigerated for storage. To elute organic selenium, push 10 mL methanol through the cartridge at rate of 2 mL/min and collect eluate in a 30 mL pear-shaped flask. Remove methanol by rotary evaporation, with the water bath temperature less than 40°C. Use deionized water to solubilize and transfer the residue into the vessel used for total selenium digestions. Determine total dissolved selenium by digestion with persulfate (pG; B.2) or peroxide (pG; B.3), reduction of Se(VI) (pG; B.5), and analysis by Methods Section 3114B or Section 3114C, or Section 3500-Se.C.

b. Hydrolysis of protein-bound selenium: Place filtered sample in a 10- or 20-mL glass ampule (depending on desired volume), and add conc methyl sulfonic acid to adjust concentration to 4*M*. Purge acidified sample with nitrogen for 10 min and seal top with a torch. Heat sealed vial at 100°C for 24 h in a heating block or pressure cooker. Transfer cooled hydrolysis solution with deionized water rinses to a 50-mL beaker and place in an ice bath. Using NaOH pellets and 1*N* NaOH, adjust to pH 9.0, taking care not to allow solution to heat to

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boiling.

c. Determination of selenoamino acids: If sample is not hydrolyzed as in ¶ 4*b*, filter, and adjust pH to 9.0 using 1*N* NaOH.

Fill an empty chromatographic column with deionized water and add ammonium-form resin to a depth of 2 cm. Add copper-treated resin to form a 12-cm length of resin. (The ammonium-form resin removes any copper that bleeds from the copper-treated resin above it). Rinse with deionized water until the pH of the effluent is 9.0; maintain flow through the column by gravity. Pass sample through column, rinse sample beaker with 5 mL pH 9 solution, and place the rinse on column (after the last of the sample reaches the top of the resin). Rinse beaker twice more. Discard flow through column.

Place clean beaker under column and add 20 mL 1.5*N* NH_4OH to the column. Neutralize NH_4OH eluate with 2.5 mL conc HCl. Determine total dissolved selenium by digestion with persulfate (¶ B.2) or peroxide (¶ B.3), reduction of Se(VI) (¶ B.5) and analysis by Methods Section 3114B or Section 3114C, or Section 3500-Se.C.

5. Precision and Bias

These procedures are only semiquantitative. Typical relative standard deviation is 12% for the C-18 isolation of dissolved organic selenium, and 15% for protein-bound selenium.

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3500-Ag SILVER

Silver (Ag) is the second element in Group IB of the periodic table; it has an atomic number of 47, an atomic weight of 107.87, and valences of 1 and 2. The average abundance of Ag in the earth's crust is 0.08 ppm; in soils it is <0.01 to 0.5 ppm; in streams it is 0.3 µg/L; in U.S. drinking waters it is 0.23 µg/L, and in groundwater it is <0.1 µg/L. Silver occurs in its native state and in combination with many nonmetallic elements such as argentite (Ag_2S) and horn silver (AgCl). Lead and copper ores also may yield considerable silver. Silver is widely used in photography, silverware, jewelry, mirrors, and batteries. Silver iodide has been used in the seeding of clouds, and silver oxide to a limited extent is used as a disinfectant for water.

In acidic water Ag^+ would predominate, and in high-chloride water a series of complexes would be expected. Silver is nonessential for plants and animals. Silver can cause argyria, a permanent, blue-gray discoloration of the skin and eyes that imparts a ghostly appearance. Concentrations in the range of 0.4 to 1 mg/ L have caused pathological changes in the kidneys, liver, and spleen of rats. Toxic effects on fish in fresh water have been observed at concentrations as low as 0.17 µg/L. For freshwater aquatic life, total recoverable silver should

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not exceed 1.2 mg/L.

The atomic absorption spectrometric methods (Section 3111B and Section 3111C) and the inductively coupled plasma methods (Section 3120 and Section 3125) are preferred. The electrothermal atomization method (Section 3113B) is the most sensitive for determining silver in natural waters. The dithizone method detailed in the 19th edition of *Standard Methods* can be used when an atomic absorption spectrometer is unavailable. A method suitable for analysis of silver in industrial or other wastewaters at levels above 1 mg/L is available.[1]

If total silver is to be determined, acidify sample with conc nitric acid (HNO_3) to pH <2 at time of collection. If sample contains particulate matter and only the ‘‘dissolved’’ metal content is to be determined, filter through a 0.45-µm membrane filter at time of collection. After filtration, acidify filtrate with HNO_3 to pH <2. Complete analysis as soon after collection as possible. Some samples may require special storage and digestion; see Section 3030D.

Reference

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3500-Na SODIUM*#(124)

3500-Na A. Introduction

1. Occurrence and Significance

Sodium (Na) is the third element in Group IA of the periodic table; it has an atomic number of 11, an atomic weight of 22.99, and a valence of 1. The average abundance of Na in the earth’s crust is 2.5%; in soils it is 0.02 to 0.62%; in streams it is 6.3 mg/L, and in groundwaters it is generally >5 mg/L. Sodium occurs with silicates and with salt deposits. Sodium compounds are used in many applications, including caustic soda, salt, fertilizers, and water treatment chemicals.

Sodium is very soluble, and its monovalent ion Na^+ can reach concentrations as high as 15 000 mg/L in equilibrium with sodium bicarbonate. The ratio of sodium to total cations is important in agriculture and human physiology. Soil permeability can be harmed by a high sodium ratio. In large concentrations it may affect persons with cardiac difficulties. A limiting concentration of 2 to 3 mg/L is recommended in feedwaters destined for high-pressure boilers. When necessary, sodium can be removed by the hydrogen-exchange process or by distillation. The U.S. EPA advisory limit for sodium in drinking water is 20 mg/L.

2. Selection of Method

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Method Section 3111B uses an atomic absorption spectrometer in the flame absorption mode. Method Section 3120B uses inductively coupled plasma; this method is not as sensitive as the other methods, but usually this is not important. Method Section 3500-Na.B uses either a flame photometer or an atomic absorption spectrometer in the flame emission mode. The inductively coupled plasma/mass spectrometric method (Section 3125) also may be applied successfully in most cases (with lower detection limits), even though sodium is not specifically listed as an analyte in the method. When all of these instruments are available, the choice will depend on factors including relative quality of the instruments, precision and sensitivity required, number of samples and analytes per sample, matrix effects, and relative ease of instrument operation. If an atomic absorption spectrometer is used, operation in the emission mode is preferred.

3. Storage of Sample

Store alkaline samples or samples containing low sodium concentrations in polyethylene bottles to eliminate the possibility of sample contamination due to leaching of the glass container.

3500-Na B. Flame Emission Photometric Method

1. General Discussion

a. Principle: Trace amounts of sodium can be determined by flame emission photometry at 589 nm. Sample is nebulized into a gas flame under carefully controlled, reproducible excitation conditions. The sodium resonant spectral line at 589 nm is isolated by interference filters or by light-dispersing devices such as prisms or gratings. Emission light intensity is measured by a phototube, photomultiplier, or photodiode. The light intensity at 589 nm is approximately proportional to the sodium concentration. Alignment of the wavelength dispersing device and wavelength readout may not be precise. The appropriate wavelength setting, which may be slightly more or less than 589 nm, can be determined from the maximum emission intensity when aspirating a sodium standard solution, and then used for emission measurements. The calibration curve may be linear but has a tendency to level off or even reverse at higher concentrations. Work in the linear to near-linear range.

b. Interferences: Minimize interference by incorporation of one or more of the following:

1) Operate at the lowest practical concentration range.

2) Add releasing agents, such as strontium or lanthanum at 1000 mg/L, to suppress ionization and anion interference. Among common anions capable of causing interference are Cl^-, SO_4^{2-} and HCO_3^- in relatively large amounts.

3) Matrix-match standards and samples by adding identical amounts of interfering substances present in the sample to calibration standards.

4) Apply an experimentally determined correction in those instances where the sample

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contains a single important interference.

5) Remove interfering ions.

6) Remove burner-clogging particulate matter from the sample by filtration through a filter paper of medium retentiveness.

7) Use the standard addition technique as described in the flame photometric method for strontium (Section 3500-Sr.B). The method involves preparing a calibration curve using the sample matrix as a diluent, and determining the sample concentration either mathematically or graphically.

8) Use the internal standard technique. Potassium and calcium interfere with sodium determination by the internal-standard method if the potassium-to-sodium ratio is ≥5:1 and the calcium-to-sodium ratio is ≥10:1. When these ratios are exceeded, determine calcium and potassium concentrations and matrix-match sodium calibration standards by addition of approximately equivalent concentrations of interfering ions. Interference from magnesium is not significant until the magnesium-to-sodium ratio exceeds 100, a rare occurrence.

b. Minimum detectable concentration: Better flame photometers or atomic absorption spectrometers operating in the emission mode can be used to determine sodium levels approximating 5 µg/L.

2. Apparatus

a. Flame photometer (either direct-reading or internal-standard type) or atomic absorption spectrometer operating in the flame emission mode.

b. Glassware: Rinse all glassware with 1 + 15 HNO_3 followed by several portions of reagent water (¶ 3*a*).

3. Reagents

To minimize sodium contamination, store all solutions in plastic bottles. Use small containers to reduce the amount of dry element that may be picked up from the bottle walls when the solution is poured. Shake each container vigorously to wash accumulated salts from walls before pouring solution.

a. Reagent water: See Section 1080. Use reagent water to prepare all reagents and calibration standards, and as dilution water.

b. Stock sodium solution: Dissolve 2.542 g NaCl dried at 140°C to constant weight and dilute to 1000 mL with water; 1.00 mL = 1.00 mg Na.

c. Intermediate sodium solution: Dilute 10.00 mL stock sodium solution with water to 100.0 mL; 1.00 mL = 0.10 mg Na (1.00 mL = 100 µg Na). Use this intermediate solution to prepare calibration curve in sodium range of 1 to 10 mg/L.

d. Standard sodium solution: Dilute 10.00 mL intermediate sodium solution with water to 100 mL; 1.00 mL = 10.0 µg Na. Use this solution to prepare calibration curve in sodium range of

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0.1 to 1.0 mg/L.

4. Procedure

a. Pretreatment of polluted water and wastewater samples: Follow the procedures described in Section 3030.

b. Instrument operation: Because of differences between makes and models of instruments, it is impossible to formulate detailed operating instructions. Follow manufacturer's recommendation for selecting proper photocell and wavelength, adjusting slit width and sensitivity, appropriate fuel and oxidant gas pressures, and the steps for warm-up, correcting for interferences and flame background, rinsing of burner, igniting flame, and measuring emission intensity.

c. Direct-intensity measurement: Prepare a blank and sodium calibration standards in stepped amounts in any of the following applicable ranges: 0 to 1.0, 0 to 10, or 0 to 100 mg/L. Determine emission intensity at 589 nm. Aspirate calibration standards and samples enough times to secure a reliable average reading for each. Construct a calibration curve from the sodium standards. Determine sodium concentration of sample from the calibration curve. Where a large number of samples must be run routinely, the calibration curve provides sufficient accuracy. If greater precision and less bias are desired and time is available, use the bracketing approach described in ¶ 4*d* below.

d. Bracketing approach: From the calibration curve, select and prepare sodium standards that immediately bracket the emission intensity of the sample. Determine emission intensities of the bracketing standards (one sodium standard slightly less and the other slightly greater than the sample) and the sample as nearly simultaneously as possible. Repeat the determination on bracketing standards and sample. Calculate the sodium concentration by the equation in ¶ 5*b* and average the findings.

5. Calculation

a. For direct reference to the calibration curve:

$$\text{mg Na/L} = (\text{mg Na/L in portion}) \times D$$

b. For the bracketing approach:

$$\text{mg Na/L} = \left[\frac{(B - A)(s - a)}{(b - a)} + A\right] D$$

where:

B = mg Na/L in upper bracketing standard,
A = mg Na/L in lower bracketing standard,
b = emission intensity of upper bracketing standard,

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a = emission intensity of lower bracketing standard,
s = emission intensity of sample, and
D = dilution ratio,

$$= \frac{\text{mL sample + mL water}}{\text{mL sample}}$$

6. Precision and Bias

A synthetic sample containing 19.9 mg Na^+/L, 108 mg Ca^{2+}/L, 82 mg Mg^{2+}/L, 3.1 mg K^+/L, 241 mg Cl^-/L, 0.25 mg NO_2^--N/L, 1.1 mg NO_3^--N/L, 259 mg SO_4^{2-}/L, and 42.5 mg total alkalinity/L (as $CaCO_3$) was analyzed in 35 laboratories by the flame photometric method, with a relative standard deviation of 17.3% and a relative error of 4.0%.

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3500-Sr STRONTIUM*#(125)

3500-Sr A. Introduction

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1. Occurrence and Significance

Strontium (Sr) is the fourth element in Group IIA of the periodic table; it has an atomic number of 38, an atomic weight of 87.62, and a valence of 2. The average abundance of Sr in the earth's crust is 384 ppm; in soils Sr ranges from 3.6 to 160 ppm; in streams it averages 50 μg/L, and in groundwaters it ranges from 0.01 to 10 mg/L. Strontium is found chiefly in celestite ($SrSO_4$) and in strontianite ($SrCO_3$). Strontium compounds are used in pigments, pyrotechnics, ceramics, and flares. ^{90}Sr is a fission product of nuclear reactor fuels, and was widely distributed on the earth's surface as a result of fallout from nuclear weapons testing.

The common aqueous species is Sr^{2+}. The solubility of strontium is controlled by carbonate and sulfate. Some compounds are toxic by ingestion and inhalation. Although there is no U.S. EPA drinking water standard MCL for concentration of strontium, strontium-90 measurements are required when the gross beta activity of a water sample is greater than 50 pCi/L. The U.S. EPA primary drinking water standard MCL for ^{90}Sr is 8 pCi/L.

A method for determination of ^{90}Sr is found in Section 7500-Sr.

2. Selection of Method

The atomic absorption spectrometric method (Section 3111B) and inductively coupled plasma methods (Section 3120 and Section 3125) are preferred. The flame emission photometric method (B) also is available for those laboratories that do not have the equipment needed for one of the preferred methods.

3. Sampling and Storage

Polyethylene bottles are preferable for sample storage, although borosilicate glass containers also may be used. At time of collection adjust sample to pH <2 with nitric acid (HNO_3).

3500-Sr B. Flame Emission Photometric Method

1. General Discussion

a. Principle: The flame photometric method can be used for the determination of strontium in the concentration range prevalent in natural waters. The strontium emission is measured at a wavelength of 460.7 nm, while the background intensity is measured at a wavelength of 466 nm. The difference in readings obtained at these two wavelengths measures the light intensity emitted by strontium.

b. Interference: Emission intensity is a linear function of strontium concentration and concentration of other constituents. The standard addition technique distributes the same ions throughout the standards and the sample, thereby equalizing the radiation effect of possible interfering substances. A very low pH (<1) could produce an interference, but sample dilution should eliminate this interference.

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c. Minimum detectable concentration: Strontium levels of about 0.2 mg/L can be detected by the flame photometric method without prior sample concentration.

2. Apparatus

Spectrophotometer, equipped with photomultiplier tube and flame accessories; or an atomic absorption spectrophotometer capable of operation in flame emission mode.

3. Reagents

a. Stock strontium solution: Dissolve 2.415 g strontium nitrate, $Sr(NO_3)_2$, dried to constant weight at 140°C, in 1000 mL 1% (v/v) HNO_3; 1.00 mL = 1.00 mg Sr.

b. Standard strontium solution: Dilute 25.00 mL stock strontium solution to 1000 mL with water; 1.00 mL = 25.0 µg Sr. Use this solution for preparing Sr standards in the 0.2- to 25-mg/L range.

c. Nitric acid, HNO_3, conc.

4. Procedure

a. Pretreatment of polluted water and wastewater samples: Select an appropriate procedure from Section 3030.

b. Preparation of strontium standards: Dilute samples, if necessary, to contain less than 400 mg Ca or Ba/L and less than 40 mg Sr/L. Add 25.0 mL sample (or a lesser but consistent volume to keep all standards in the linear range of the instrument) to 25.0 mL of each of a series of four or more strontium standards containing from 0 mg/L to a concentration exceeding that of the sample. For most natural waters 0, 2.0, 5.0, and 10.0 mg Sr/L standards are sufficient. A broader range curve might be preferable for brines. Dilute the brine sufficiently to eliminate burner splatter and clogging.

c. Concentration of low-level strontium samples: Concentrate samples containing less than 2 mg Sr/L. Polluted water or wastewater samples can be concentrated during digestion by starting with a larger volume (see Section 3030D). For other samples, add 3 to 5 drops conc HNO_3 to 250 mL sample and evaporate to about 25 mL. Cool and make up to 50.0 mL with distilled water. Proceed as in ¶ b. The HNO_3 concentration in the sample prepared for atomization can approach 0.4 mL/50 mL without producing interference.

d. Flame photometric measurement: Measure emission intensity of prepared samples (standards plus sample) at wavelengths of 460.7 and 466 nm. Follow manufacturer's instructions for correct instrument operation. Use a fuel-rich nitrous oxide-acetylene flame, if possible.

5. Calculation

a. Using a calculator or computer with linear regression capability, enter the net intensity (reading at 460.7 nm minus reading at 466 nm) versus concentration added to the sample and solve the equation for zero emissions. The negative of this number multiplied by any dilution

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factor is the sample concentration.

b. Plot net intensity (reading at 460.7 nm minus reading at 466 nm) against strontium concentration added to the sample. Because the plot forms a straight calibration line that intersects the ordinate, strontium concentration can be calculated from the equation:

$$\text{mg Sr/L} = \frac{A - B}{C} \times \frac{D}{E}$$

where:

A = sample emission-intensity reading of sample plus 0 mg/L at 460.7 nm,
B = background radiation reading at 466 nm, and
C = slope of calibration line.

Use the ratio D/E only when E mL of sample are concentrated to a final volume D mL (typically 50 mL).

c. Graphical method: Strontium concentration also can be evaluated by the graphical method illustrated in Figure 3500-Sr:1. Plot net intensity against strontium concentration added to sample. If the line intersects the ordinate at Y emissions, the strontium concentration is where the abscissa value of the point on the calibration line has an ordinate value of $2Y$ emissions due to the two-fold dilution with standards (if sample and standards are mixed in equal volumes). The calibration line in the example intersects the ordinate at 12. Thus, $Y = 12$ and $2Y = 24$. The strontium concentration of the sample is the abscissa value of the point on the calibration line having an ordinate value of 24. In the example, the strontium concentration is 9.0 mg/L.

d. Report strontium concentrations below 10 mg/L to the nearest 0.1 mg/L and above 10 mg/L to the nearest whole number.

6. Quality Control

See Part 1000 and Section 3020 for specific quality control procedures to be followed during sample preparation and analysis.

7. Precision and Bias

Strontium concentrations in the range 12.0 to 16.0 mg/L can be determined with an accuracy within ±1 to 2 mg/L.

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3500-Te TELLURIUM

Tellurium (Te) is the fourth element in Group VIA in the periodic table; it has an atomic number of 52, an atomic weight of 127.60, and valences of 2, 4, and 6. The average abundance of Te in the earth's crust is 0.002 ppm; in soils it is 0.001 to 0.01 ppm; and in groundwaters it is <0.1 mg/L. Tellurium is found in its native state and as the telluride of gold and other metals. It is used in alloys, catalysts, batteries, and as a coloring agent in glass and ceramics.

The common aqueous species is TeO_3^{2-}. The metal and its compounds are toxic by inhalation.

Perform analyses by the electrothermal atomic absorption method (Section 3113B). The inductively coupled plasma mass spectrometric method (Section 3125) also may be applied successfully in most cases (with lower detection limits), even though tellurium is not specifically listed as an analyte in the method.

3500-Tl THALLIUM

Thallium (Tl) is the fifth element in Group IIIA in the periodic table; it has an atomic number of 81, an atomic weight of 204.38, and valences of 1 and 3. The average abundance in the earth's crust is 0.07 ppm, and in groundwaters it is <0.1 mg/L. The metal occurs chiefly in pyrites. Thallium is used in the production of glasses and rodenticides, in photoelectric applications, and in electrodes for dissolved oxygen meters.

The common aqueous species is Tl^+. It is nonessential for plants and animals. Compounds of thallium are toxic on contact with moisture, and by inhalation. The U.S. EPA primary drinking water standard MCL is 2 μg/L.

For analysis, use one of the atomic absorption spectrometric methods (Section 3111B or Section 3113B), or one of the inductively coupled plasma methods (Section 3120 or Section 3125), depending upon sensitivity requirements.

3500-Th THORIUM

Thorium (Th) is the first element in the actinium series of the periodic table; it has an atomic number of 90, an atomic weight of 232.04, and a valence of 4. The average abundance in the earth's crust is 8.1 ppm; in soils it is 13 ppm; in streams it is 0.1 μg/L, and in groundwaters it is <0.1 mg/L. Thorium is a radioactive element, with ^{232}Th having a half-life of 1.4×10^{10} years. It is widely distributed in the earth, with the principal mineral being monazite. Thorium is used in sun lamps, photoelectric cells, incandescent lighting, and gas mantles.

The aqueous chemistry of thorium is controlled by the Th^{4+} ion, which forms a set of

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complex species with hydroxides. Thorium's radioactive decay isotopes are dangerous when inhaled or ingested as thorium dust particles.

Either of the flame atomic absorption spectrometric methods (Section 3111D or Section 3111E) may be used for analysis. The inductively coupled plasma mass spectrometric method (Section 3125) also may be applied successfully in most cases (with lower detection limits), even though thorium is not specifically listed as an analyte in the method.

3500-Sn TIN

Tin (Sn) is the fourth element in Group IVA in the periodic table; it has an atomic number of 50, an atomic weight of 118.69, and valences of 2 and 4. The average abundance in the earth's crust is 2.1 ppm; in soils it is 10 ppm; in streams it is 0.1 μg/L, and in groundwaters it is <0.1 mg/L. Tin is found mostly in the mineral cassiterite (SnO_2), in association with granitic rocks. Tin is used in reducing agents, solder, bronze, pewter, and coatings for various metals.

The common aqueous species are Sn^{4+}, $Sn(OH)_4$, $SnO(OH)_2$, and $SnO(OH)_3^-$. Tin is adsorbed to suspended solids, sulfides, and hydroxides. Tin can be methylated in sediments. Tributyl tin undergoes biodegradation quickly. Organo-tin compounds are toxic. Tin is considered nonessential for plants and animals.

Either the flame atomic absorption method (Section 3111B) or the electrothermal atomic absorption method (Section 3113B) may be used successfully for analyses, depending upon the sensitivity desired. The inductively coupled plasma/mass spectrometric method (Section 3125) also may be applied successfully in most cases (with lower detection limits), even though tin is not specifically listed as an analyte in the method.

3500-Ti TITANIUM

Titanium (Ti) is the first element in Group IVB in the periodic table; it has an atomic number of 22, an atomic weight of 47.88, and valences of 2, 3, and 4. The average abundance of Ti in the earth's crust is 0.6%; in soils it is 1700 to 6600 ppm; in streams it is 3 μg/L, and in groundwaters it is <0.1 mg/L. The element is commonly associated with iron minerals. Titanium is used in alloys for aircraft, marine, and food-handling equipment. Compounds of the metal are used in pigments and as a reducing agent.

Titanium species are usually insoluble in natural waters, with the Ti^{4+} species being the most common ion when found. Some compounds are toxic by ingestion and the pure metal is flammable.

Either of the flame atomic absorption spectrometric methods (Section 3111D or Section 3111E) may be used. The inductively coupled plasma mass spectrometric method (Section 3125) also may be applied successfully in most cases (with lower detection limits), even though titanium is not specifically listed as an analyte in the method.

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3500-U URANIUM

Uranium (U) is the third element in the actinide series of the periodic table; it has an atomic number of 92, an atomic weight of 238.04, and valences of 3, 4, and 6. The average abundance of U in the earth's crust is 2.3 ppm, and in soils it is 1.8 ppm. Concentrations of uranium in drinking waters usually are expressed in terms of picocuries per liter, but that is now being replaced by Becquerel per liter (Bq/L). The approximate conversion factor, assuming equilibrium between ^{234}U and ^{238}U, is 1 μg uranium equals 0.67 pCi. The mean concentration of uranium in drinking water is 1.8 pCi/L. The chief ore is uraninite, or pitchblende, uranous uranate [$U(UO_4)_2$]. Uranium is known mainly for its use in the nuclear industry, but has also been used in glass, ceramics, and photography.

Uranium compounds are radioactive and are thereby toxic by inhalation and ingestion. There are three natural radioisotopes of uranium. Uranium-238 has a half-life of 4.5×10^9 years, represents 99% of uranium's natural abundance, and is not fissionable, but can be used to form plutonium-239, which is fissionable. Uranium-235 has a half-life of 7.1×10^8 years, represents 0.75% of uranium's natural abundance, is readily fissionable, and was the energy source in the original atomic bombs. Uranium-234 has a half-life of 2.5×10^5 years and represents only 0.006% of uranium's natural abundance.

The common forms in natural water are U^{4+} and UO_2^{2+}. In natural waters below pH 5, UO_2^{2+} would dominate; in the pH range of 5 to 10, soluble carbonate complexes predominate. Although there is no U.S. EPA drinking water standard MCL for uranium, an analysis for uranium is required if the gross alpha activity of a water sample is greater than 15 pCi/L.

Perform analyses by the inductively coupled plasma/mass spectrometry method (Section 3125) or by one of the methods in Section 7500-U (for regulatory compliance purposes).

3500-V VANADIUM*#(126)

3500-V A. Introduction

1. Occurrence and Significance

Vanadium (V) is the first element in Group VB in the periodic table; it has an atomic number of 23, an atomic weight of 50.94, and valences of 2, 3, 4, and 5. The average abundance of V in the earth's crust is 136 ppm; in soils it ranges from 15 to 110 ppm; in streams it averages about 0.9 μg/L, and in groundwaters it is generally <0.1 mg/L. Though relatively rare, vanadium is found in a variety of minerals; most important among these are vanadinite [$Pb_5(VO_4)_3Cl$], and patronite (possibly VS_4), occurring chiefly in Peru. Vanadium complexes have been noted in

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coal and petroleum deposits. Vanadium is used in steel alloys and as a catalyst in the production of sulfuric acid and synthetic rubber.

The dominant form in natural waters is V^{5+}. It is associated with organic complexes and is insoluble in reducing environments. It is considered nonessential for most higher plants and animals, although it may be an essential trace element for some algae and microorganisms. Laboratory and epidemiological evidence suggests that vanadium may play a beneficial role in the prevention of heart disease. In water supplies in New Mexico, which has a low incidence of heart disease, vanadium has been found in concentrations of 20 to 150 µg/L. In a state where incidence of heart disease is high, vanadium was not found in water supplies. However, vanadium pentoxide dust causes gastrointestinal and respiratory disturbances. The United Nations Food and Agriculture Organization recommended maximum level for irrigation waters is 0.1 mg/L.

2. Selection of Method

The atomic absorption spectrometric methods (Section 3111D and Section 3111E), the electrothermal atomic absorption method (Section 3113B), the inductively coupled plasma methods (Section 3120 and Section 3125), and gallic acid method (Section 3500-V.B) are suitable for potable water samples. The atomic absorption spectrometric and inductively coupled plasma methods are preferred for polluted samples. The electrothermal atomic absorption method also may be used successfully with an appropriate matrix modifier.

3500-V B. Gallic Acid Method

1. General Discussion

a. Principle: The concentration of trace amounts of vanadium in water is determined by measuring the catalytic effect it exerts on the rate of oxidation of gallic acid by persulfate in acid solution. Under the given conditions of concentrations of reactants, temperature, and reaction time, the extent of oxidation of gallic acid is proportional to the concentration of vanadium. Vanadium is determined by measuring the absorbance of the sample at 415 nm and comparing it with that of standard solutions treated identically.

b. Interference: The substances listed in Table 3500-V:I will interfere in the determination of vanadium if the specified concentrations are exceeded. This is not a serious problem for Cr^{6+}, Co^{2+}, Mo^{6+}, Ni^{2+}, Ag^{+}, and U^{6+} because the tolerable concentration is greater than that commonly encountered in fresh water. However, in some samples the tolerable concentration of Cu^{2+}, Fe^{2+}, and Fe^{3+} may be exceeded. Because of the high sensitivity of the method, interfering substances in concentrations only slightly above tolerance limits can be rendered harmless by dilution.

Traces of Br^{-} and I^{-} interfere seriously and dilution alone will not always reduce the concentration below tolerance limits. Mercuric ion may be added to complex these halides and

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minimize their interference; however, mercuric ion itself interferes if in excess. Adding 350 µg mercuric nitrate, $Hg(NO_3)_2$, per sample permits determination of vanadium in the presence of up to 100 mg Cl^-/L, 250 µg Br^-/L, and 250 µg I^-/L. Dilute samples containing high concentrations of these ions to concentrations below the values given above and add $Hg(NO_3)_2$.

c. Minimum detectable concentration: 0.025 µg V in approximately 13 mL final volume or approximately 2 µg V/L.

2. Apparatus

a. Water bath, capable of being operated at 25 ± 0.5°C.

b. Colorimetric equipment: One of the following is required:

1) *Spectrophotometer,* for measurements at 415 nm, with a light path of 1 to 5 cm.

2) *Filter photometer,* providing a light path of 1 to 5 cm and equipped with a violet filter with maximum transmittance near 415 nm.

3. Reagents

Use reagent water (see Section 1080) in preparation of reagents, for dilutions, and as blanks.

a. Stock vanadium solution: Dissolve 229.6 mg ammonium metavanadate, NH_4VO_3, in a volumetric flask containing approximately 800 mL water and 15 mL 1 + 1 nitric acid (HNO_3). Dilute to 1000 mL; 1.00 mL = 100 µg V.

b. Intermediate vanadium solution: Dilute 1.00 mL stock vanadium solution with water to 100 mL; 1.00 mL = 1.00 µg V.

c. Standard vanadium solution: Dilute 1.00 mL intermediate vanadium solution with water to 100 mL; 1.00 mL = 0.010 µg V.

d. Mercuric nitrate solution: Dissolve 350 mg $Hg(NO_3)_2 \cdot H_2O$ in 1000 mL water.

e. Ammonium persulfate-phosphoric acid reagent: Dissolve 2.5 g $(NH_4)_2S_2O_8$ in 25 mL water. Bring just to a boil, remove from heat, and add 25 mL conc H_3PO_4. Let stand approximately 24 h before use. Discard after 48 h.

f. Gallic acid solution: Dissolve 2 g $H_6C_7O_5$ in 100 mL warm water, heat to a temperature just below boiling, and filter through filter paper.*#(127) Prepare a fresh solution for each set of samples.

4. Procedure

a. Preparation of standards and sample: Prepare both blank and sufficient standards by diluting 0- to 8.0-mL portions (0 to 0.08 µg V) of standard vanadium solution to 10 mL with water. Pipet sample (10.00 mL maximum) containing less than 0.08 µg V into a suitable container and adjust volume to 10.0 mL with water. Filter colored or turbid samples. Add 1.0 mL $Hg(NO_3)_2$ solution to each blank, standard, and sample. Place containers in a water bath

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regulated to 25 ± 0.5°C and allow 30 to 45 min for samples to come to the bath temperature.

b. Color development and measurement: Add 1.0 mL ammonium persulfate-phosphoric acid reagent (temperature equilibrated), swirl to mix thoroughly, and return to water bath. Add 1.0 mL gallic acid solution (temperature equilibrated), swirl to mix thoroughly, and return to water bath. Add gallic acid to successive samples at intervals of 30 s or longer to permit accurate control of reaction time. Exactly 60 min after adding gallic acid, remove sample from water bath and measure its absorbance at 415 nm, using water as a reference. Subtract absorbance of blank from absorbance of each standard and sample. Construct a calibration curve by plotting absorbance values of standards versus micrograms vanadium. Determine amount of vanadium in a sample by referring to the corresponding absorbance on the calibration curve. Prepare a calibration curve with each set of samples.

5. Calculation

$$\text{mg V/L} = \frac{\mu\text{g V (in 13 mL final volume)}}{\text{original sample volume, mL}}$$

6. Precision and Bias

In a synthetic sample containing 6 µg V/L, 40 µg As/L, 250 µg Be/L, 240 µg B/L, and 20 µg Se/L in distilled water, vanadium was measured in 22 laboratories with a relative standard deviation of 20% and no relative error.

7. Bibliography

FISHMAN, M.J. & M.V. SKOUGSTAD. 1964. Catalytic determination of vanadium in water. *Anal. Chem.* 36:1643.

3500-Zn ZINC*#(128)

3500-Zn A. Introduction

1. Occurrence and Significance

Zinc (Zn) is the first element in Group IIB in the periodic table; it has an atomic number of 30, an atomic weight of 65.38, and a valence of 2. The average abundance of Zn in the earth's crust is 76 ppm; in soils it is 25 to 68 ppm; in streams it is 20 µg/L, and in groundwaters it is <0.1 mg/L. The solubility of zinc is controlled in natural waters by adsorption on mineral surfaces, carbonate equilibrium, and organic complexes. Zinc is used in a number of alloys such as brass and bronze, and in batteries, fungicides, and pigments. Zinc is an essential growth element for plants and animals but at elevated levels it is toxic to some species of aquatic life.

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The United Nations Food and Agriculture Organization recommended level for zinc in irrigation waters is 2 mg/L. The U.S. EPA secondary drinking water standard MCL is 5 mg/L. Concentrations above 5 mg/L can cause a bitter astringent taste and an opalescence in alkaline waters. Zinc most commonly enters the domestic water supply from deterioration of galvanized iron and dezincification of brass. In such cases lead and cadmium also may be present because they are impurities of the zinc used in galvanizing. Zinc in water also may result from industrial waste pollution.

2. Selection of Method

The atomic absorption spectrometric methods (Section 3111B and Section 3111C) and inductively coupled plasma methods (Section 3120 and Section 3125) are preferred. The zincon method (B), suitable for analysis of both potable and polluted waters, may be used if instrumentation for the preferred methods is not available..

3. Sampling and Storage

See Section 3010B.2 for sample handling and storage.

3500-Zn B. Zincon Method

1. General Discussion

a. Principle: Zinc forms a blue complex with 2-carboxy-2′-hydroxy-5′-sulfoformazyl benzene (zincon) in a solution buffered to pH 9.0. Other heavy metals likewise form colored complexes with zincon. Cyanide is added to complex zinc and heavy metals. Cyclohexanone is added to free zinc selectively from its cyanide complex so that it can be complexed with zincon to form a blue color. Sodium ascorbate reduces manganese interference. The developed color is stable except in the presence of copper (see table below).

b. Interferences: The following ions interfere at concentrations exceeding those listed:

Ion	*mg/L*	Ion	*mg/L*
Cd^{2+}	1	Cr^{3+}	10
Al^{3+}	5	Ni^{2+}	20
Mn^{2+}	5	Cu^{2+}	30
Fe^{3+}	7	Co^{2+}	30
Fe^{2+}	9	CrO_4^{2-}	50

c. Minimum detectable concentration: 0.02 mg Zn/L.

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2. Apparatus

a. Colorimetric equipment: One of the following is required:

1) *Spectrophotometer,* for measurements at 620 nm, providing a light path of 1 cm or longer.

2) *Filter photometer,* providing a light path of 1 cm or longer and equipped with a red filter having maximum transmittance near 620 nm. Deviation from Beer's Law occurs when the filter band pass exceeds 20 nm.

b. Graduated cylinders, 50-mL, with ground-glass stoppers, Class B or better.

c. Erlenmeyer flasks, 50-mL.

d. Filtration apparatus: 0.45-μm filters and filter holders.

3. Reagents

a. Metal-free water: See Section 3111B.3*c*. Use water for rinsing apparatus and preparing solutions and dilutions.

b. Stock zinc solution: Dissolve 1000 mg (1.000 g) zinc metal in 10 mL 1 + 1 HNO_3. Dilute and boil to expel oxides of nitrogen. Dilute to 1000 mL; 1.00 mL = 1.00 mg Zn.

c. Standard zinc solution: Dilute 10.00 mL stock zinc solution to 1000 mL; 1.00 mL = 10.00 μg Zn.

d. Sodium ascorbate, fine granular powder, USP.

e. Potassium cyanide solution: Dissolve 1.00 g KCN in approximately 50 mL water and dilute to 100 mL. CAUTION: *Potassium cyanide is a deadly poison. Avoid skin contact or inhalation of vapors. Do not pipet by mouth or bring in contact with acids.*

f. Buffer solution, pH 9.0: Dissolve 8.4 g NaOH pellets in about 500 mL water. Add 31.0 g H_3BO_3 and swirl or stir to dissolve. Dilute to 1000 mL with water and mix thoroughly.

g. Zincon reagent: Dissolve 100 mg zincon (2-carboxy-2′-hydroxy-5′-sulfoformazyl benzene) in 100 mL methanol. Because zincon dissolves slowly, stir and/or let stand overnight.

h. Cyclohexanone, purified.

i. Hydrochloric acid, HCl, conc and 1*N*.

j. Sodium hydroxide, NaOH, 6*N* and 1*N*.

4. Procedure

a. Preparation of colorimetric standards: Accurately deliver 0, 0.5, 1.0, 3.0, 5.0, 10.0, and 14.0 mL standard zinc solution to a series of 50-mL graduated mixing cylinders. Dilute each to 20.0 mL to yield solutions containing 0, 0.25, 0.5, 1.5, 2.5, 5.0, and 7.0 mg Zn/L, respectively. (Lower-range standards may be prepared to extend the quantitation range. Longer optical path cells can be used. Verify linearity of response in this lower concentration range.) Add the following to each solution in sequence, mixing thoroughly after each addition: 0.5 g sodium ascorbate, 5.0 mL buffer solution, 2.0 mL KCN solution, and 3.0 mL zincon solution. Pipet 20.0

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mL of the solution into a clean 50-mL erlenmeyer flask. Reserve remaining solution to zero the instrument. Add 1.0 mL cyclohexanone to the erlenmeyer flask. Swirl for 10 s and note time. Transfer portions of both solutions to clean sample cells. Use solution without cyclohexanone to zero colorimeter. Read and record absorbance for solution with cyclohexanone after 1 min. The calibration curve does not pass through zero because of the color enhancement effect of cyclohexanone on zincon.

b. Treatment of samples: To determine readily acid-extractable total zinc, add 1 mL conc HCl to 50 mL sample and mix thoroughly. Filter and adjust to pH 7. To determine dissolved zinc, filter sample through a 0.45-µm membrane filter. Adjust to pH 7 with 1*N* NaOH or 1*N* HCl if necessary after filtering.

c. Sample analysis: Cool samples to less than 30°C if necessary. Analyze 20.0 mL of prepared sample as described in ¶ 4*a* above, beginning with ‘‘Add the following to each solution . . .’’ If the zinc concentration exceeds 7 mg Zn/L prepare a sample dilution and analyze a 20.0-mL portion.

5. Calculation

Read zinc concentration (in milligrams per liter) directly from the calibration curve.

6. Precision and Bias

A synthetic sample containing 650 µg Zn/L, 500 µg Al/L, 50 µg Cd/L, 110 µg Cr/L, 470 µg Cu/L, 300 µg Fe/L, 70 µg Pb/L, 120 µg Mn/L, and 150 µg Ag/L in doubly demineralized water was analyzed in a single laboratory. A series of 10 replicates gave a relative standard deviation of 0.96% and a relative error of 0.15%. A wastewater sample from an industry in Standard Industrial Classification (SIC) No. 3333, primary smelting and refining of zinc, was analyzed by 10 different persons. The mean zinc concentration was 3.36 mg Zn/L and the relative standard deviation was 1.7%. The relative error compared to results from an atomic absorption analysis of the same sample was −1.0%.

7. Bibliography

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Figures

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Figure 3112:1. Schematic arrangement of equipment for measurement of mercury by cold-vapor atomic absorption technique.

Figure 3114:1. Manual reaction cell for producing As and Se hydrides.

Figure 3114:2. Schematic of a continuous hydride generator.

Figure 3500-Al:1. Correction curves for estimation of aluminum in the presence of fluoride. Above the mg F^-/L present, locate the point corresponding to the apparent mg Al/L measured. From this point interpolate between the curves shown, if the point does not fall directly on one of the curves, to read the true mg Al/L on the ordinate, which corresponds to 0.00 mg F^-/L. For example, an apparent 0.20 mg Al/L in a sample containing 1.00 mg F^-/L would actually be 0.30 mg Al/L if no fluoride were present to interfere.

Figure 3500-As:1. Arsine generator and absorber assembly.

Figure 3500-Se:1. General scheme for speciation of selenium in water.

Figure 3500-Sr:1. Graphical method of computing strontium concentration.

Tables

TABLE 3010:I. APPLICABLE METHODS FOR ELEMENTAL ANALYSIS

Element	Flame Atomic Absorption (Direct)	Flame Atomic Absorption (Extracted)	Flame Photometry	Electrothermal Atomic Absorption	Hydride/Cold Vapor Atomic Absorption	Inductively Coupled Plasma (ICP)	ICP/ Spect (ICF
Aluminum	3111D	3111E		3113B		3120A	3
Antimony	3111B			3113B		3120A	31
Arsenic				3113B	3114B	3120A	31
Barium	3111D	3111E		3113B		3120A	31
Beryllium	3111D	3111E		3113B		3120A	31
Bismuth	3111B			3113B			31
Boron						3120A	31
Cadmium	3111B	3111C		3113B		3120A	31
Calcium	3111B,D	3111E				3120A	31
Cesium	3111B						31
Chromium	3111B	3111C		3113B		3120A	31
Cobalt	3111B	3111C		3113B		3120A	31
Copper	3111B	3111C		3113B		3120A	31
Gallium				3113B			31
Germanium				3113B			31
Gold	3111B			3113B			31
Indium				3113B			31

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Element	Flame Atomic Absorption (Direct)	Flame Atomic Absorption (Extracted)	Flame Photometry	Electrothermal Atomic Absorption	Hydride/Cold Vapor Atomic Absorption	Inductively Coupled Plasma (ICP)	ICP/ Spect (ICF
Iridium	3111B						31
Iron	3111B	3111C		3113B		3120A	31
Lead	3111B	3111C		3113B		3120A	31
Lithium	3111B		3500-Li.B			3120A	31
Magnesium	3111B					3120A	31
Manganese	3111B	3111C		3113B		3120A	31
Mercury					3112B		31
Molybdenum	3111D	3111E		3113B		3120A	31
Nickel	3111B	3111C		3113B		3120A	31
Osmium	3111D	3111E					31
Palladium	3111B						31
Platinum	3111B						31
Potassium	3111B		3500-K.B			3120A	31
Rhenium	3111D	3111E					31
Rhodium	3111B						31
Ruthenium	3111B						31
Selenium				3113B	3114B,C	3120A	31
Silicon	3111D	3111E				3120A	31
Silver	3111B	3111C		3113B		3120A	31
Sodium	3111B		3500-Na.B			3120A	31
Strontium	3111B		3500-Sr.B			3120A	31
Tellurium				3113B			31
Thallium	3111B			3113B		3120A	31
Thorium	3111D	3111E					31
Tin	3111B			3113B			31
Titanium	3111D	3111E					31
Uranium							31
Vanadium	3111D	3111E		3113B		3120A	31
Zinc	3111B	3111C		3113B		3120A	31

* Metal is not specifically mentioned in the method, but 3125 may be used successfully in most cases.
† Additional alternative methods for aluminum, beryllium, cadmium, mercury, selenium, silver, and zinc may be found in the 19th Edition of *Standard Methods*.

TABLE 3030:I. ACIDS USED IN CONJUNCTION WITH HNO_3 for SAMPLE PREPARATION

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TABLE 3030:I. ACIDS USED IN CONJUNCTION WITH HNO_3 FOR SAMPLE PREPARATION

Acid	Recommended for	May Be Helpful for	Not Recommended for
HCl	Ag	Sb, Ru, Sn	Th, Pb
H_2SO_4	Ti	—	Ag, Pb, Ba
$HClO_4$	—	Organic materials	—
HF	—	Siliceous materials	—

TABLE 3111:I. ATOMIC ABSORPTION CONCENTRATION RANGES WITH DIRECT ASPIRATION ATOMIC ABSORPTION

Element	Wave-length *nm*	Flame Gases*	Instrument Detection Limit *mg/L*	Sensitivity *mg/L*	Optimum Concentration Range *mg/L*
Ag	328.1	A–Ac	0.01	0.06	0.1–4
Al	309.3	N–Ac	0.1	1	5–100
Au	242.8	A–Ac	0.01	0.25	0.5–20
Ba	553.6	N–Ac	0.03	0.4	1–20
Be	234.9	N–Ac	0.005	0.03	0.05–2
Bi	223.1	A–Ac	0.06	0.4	1–50
Ca	422.7	A–Ac	0.003	0.08	0.2–20
Cd	228.8	A–Ac	0.002	0.025	0.05–2
Co	240.7	A–Ac	0.03	0.2	0.5–10
Cr	357.9	A–Ac	0.02	0.1	0.2–10
Cs	852.1	A–Ac	0.02	0.3	0.5–15
Cu	324.7	A–Ac	0.01	0.1	0.2–10
Fe	248.3	A–Ac	0.02	0.12	0.3–10
Ir	264.0	A–Ac	0.6	8	—
K	766.5	A–Ac	0.005	0.04	0.1–2
Li	670.8	A–Ac	0.002	0.04	0.1–2
Mg	285.2	A–Ac	0.0005	0.007	0.02–2
Mn	279.5	A–Ac	0.01	0.05	0.1–10
Mo	313.3	N–Ac	0.1	0.5	1–20
Na	589.0	A–Ac	0.002	0.015	0.03–1
Ni	232.0	A–Ac	0.02	0.15	0.3–10

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Element	Wave-length *nm*	Flame Gases*	Instrument Detection Limit *mg/L*	Sensitivity *mg/L*	Optimum Concentration Range *mg/L*
Os	290.9	N–Ac	0.08	1	—
Pb†	283.3	A–Ac	0.05	0.5	1–20
Pt	265.9	A–Ac	0.1	2	5–75
Rh	343.5	A–Ac	0.5	0.3	—
Ru	349.9	A–Ac	0.07	0.5	—
Sb	217.6	A–Ac	0.07	0.5	1–40
Si	251.6	N–Ac	0.3	2	5–150
Sn	224.6	A–Ac	0.8	4	10–200
Sr	460.7	A–Ac	0.03	0.15	0.3–5f
Ti	365.3	N–Ac	0.3	2	5–100
V	318.4	N–Ac	0.2	1.5	2–100
Zn	213.9	A–Ac	0.005	0.02	0.05–2

* A–Ac = air-acetylene; N–Ac = nitrous oxide-acetylene.

† The more sensitive 217.0 nm wavelength is recommended for instruments with background correction capabilities.Copyright ASTM. Reprinted with permission.

TABLE 3111:II. INTERLABORATORY PRECISION AND BIAS DATA FOR ATOMIC ABSORPTION METHODS—DIRECT ASPIRATION AND EXTRACTED METALS

Metal	Conc.*	SD*	Relative SD *%*	Relative Error *%*	No. of Participants
Direct determination:					
Aluminum[1]	4.50	0.19	4.2	8.4	5
Barium[2]	1.00	0.089	8.9	2.7	11
Beryllium[1]	0.46	0.0213	4.6	23.0	11
Cadmium[3]	0.05	0.0108	21.6	8.2	26
Cadmium[1]	1.60	0.11	6.9	5.1	16
Calcium[1]	5.00	0.21	4.2	0.4	8
Chromium[1]	3.00	0.301	10.0	3.7	9

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Metal	Conc.*	SD*	Relative SD %	Relative Error %	No. of Participants
Cobalt[1]	4.00	0.243	6.1	0.5	14
Copper[3]	1.00	0.112	11.2	3.4	53
Copper[1]	4.00	0.331	8.3	2.8	15
Iron[1]	4.40	0.260	5.8	2.3	16
Iron[3]	0.30	0.0495	16.5	0.6	43
Lead[1]	6.00	0.28	4.7	0.2	14
Magnesium[3]	0.20	0.021	10.5	6.3	42
Magnesium[1]	1.10	0.116	10.5	10.0	8
Manganese[1]	4.05	0.317	7.8	1.3	16
Manganese[3]	0.05	0.0068	13.5	6.0	14
Nickel[1]	3.93	0.383	9.8	2.0	14
Silver[3]	0.05	0.0088	17.5	10.6	7
Silver[1]	2.00	0.07	3.5	1.0	10
Sodium[1]	2.70	0.122	4.5	4.1	12
Strontium[1]	1.00	0.05	5.0	0.2	12
Zinc[3]	0.50	0.041	8.2	0.4	48
Extracted determination:					
Aluminum[2]	300	32	10.7	0.7	15
Beryllium[2]	5	1.7	34.0	20.0	9
Cadmium[3]	50	21.9	43.8	13.3	12
Cobalt[1]	300	28.5	9.5	1.0	6
Copper[1]	100	71.7	71.7	12.0	8
Iron[1]	250	19.0	7.6	3.6	4
Manganese[1]	21.5	2.4	11.2	7.4	8
Molybdenum[1]	9.5	1.1	11.6	1.3	5
Nickel[1]	56.8	15.2	26.8	13.6	14
Lead[3]	50	11.8	23.5	19.0	8

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Metal	Conc.*	SD*	Relative SD %	Relative Error %	No. of Participants
Silver[1]	5.2	1.4	26.9	3.0	7

* For direct determinations, mg/L; for extracted determinations, µg/L.

Superscripts refer to reference numbers.

Source: AMERICAN SOCIETY FOR TESTING AND MATERIALS. 1986. Annual Book of ASTM Standards. Volume 11.01, Water and Environmental Technology. American Soc. Testing Materials, Philadelphia, Pa. Copyright ASTM. Reprinted with permission.

TABLE 3111:III. SINGLE-OPERATOR PRECISION AND RECOMMENDED CONTROL RANGES FOR ATOMIC ABSORPTION METHODS—DIRECT ASPIRATIONAND EXTRACTED METALS

Metal	Conc.*	SD*	Relative SD %	No. of Participants	QC Std.*	Acceptable Range*
Direct determination:						
Aluminum[1]	4.50	0.23	5.1	15	5.00	4.3–5.7
Beryllium[1]	0.46	0.012	2.6	10	0.50	0.46–0.54
Calcium[1]	5.00	0.05	1.0	8	5.00	4.8–5.2
Chromium[1]	7.00	0.69	9.9	9	5.00	3.3–6.7
Cobalt[1]	4.00	0.21	5.3	14	4.00	3.4–4.6
Copper[1]	4.00	0.115	2.9	15	4.00	3.7–4.3
Iron[1]	5.00	0.19	3.8	16	5.00	4.4–5.6
Magnesium[1]	1.00	0.009	0.9	8	1.00	0.97–1.03
Nickel[4]	5.00	0.04	0.8	—	5.00	4.9–5.1
Silver[1]	2.00	0.25	12.5	10	2.00	1.2–2.8
Sodium[4]	8.2	0.1	1.2	—	5.00	4.8–5.2
Strontium[1]	1.00	0.04	4.0	12	1.00	0.87–1.13
Potassium[4]	1.6	0.2	12.5	—	1.6	1.0–2.2
Molybdenum[4]	7.5	0.07	0.9	—	10.0	9.7–10.3
Tin[4]	20.0	0.5	2.5	—	20	.018.5–21.5
Titanium[4]	50.0	0.4	0.8	—	50.0	48.8–51.2
Vanadium	50.0	0.2	0.4	—	50.0	49.4–50.6

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Metal	Conc.*	SD*	Relative SD %	No. of Participants	QC Std.*	Acceptable Range*
Extracted determination:						
Aluminum[1]	300	12	4.0	15	300	264–336
Cobalt[1]	300	20	6.7	6	300	220–380
Copper[1]	100	21	21	8	100	22–178
Iron[1]	250	12	4.8	4	250	180–320
Manganese[1]	21.5	202	10.2	8	25	17–23
Molybdenum[1]	9.5	1.0	10.5	5	10	5.5–14.5
Nickel[1]	56.8	9.2	16.2	14	50	22–78
Silver[1]	5.2	1.2	23.1	7	5.0	0.5–9.5

* For direct determinations, mg/L; for extracted determinations, µg/L.

Superscripts refer to reference numbers.

Source: AMERICAN SOCIETY FOR TESTING AND MATERIALS. 1986. Annual Book of ASTM Standards. Volume 11.01, Water and Environmental Technology. American Soc. Testing Materials, Philadelphia, Pa. Copyright ASTM. Reprinted with permission.

TABLE 3112:I. INTERLABORATORY PRECISION AND BIAS OF COLD-VAPOR ATOMIC ABSORPTION SPECTROMETRIC METHOD FOR MERCURY[1]

Form	Conc. µg/L	SD µg/L	Relative SD %	Relative Error %	No. of Participants
Inorganic	0.34	0.077	22.6	21.0	23
Inorganic	4.2	0.56	13.3	14.4	21
Organic	4.2	0.36	8.6	8.4	21

TABLE 3113:I. POTENTIAL MATRIX MODIFIERS FOR ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY*

Modifier	Analyses for Which Modifier May Be Useful

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Modifier	Analyses for Which Modifier May Be Useful
1500 mg Pd/L + 1000 mg $Mg(NO_3)_2$/L[1]	Ag, As, Au, Bi, Cu, Ge, Mn, Hg, In, Sb, Se, Sn, Te, Tl
500–2000 mg Pd/L + reducing agent[2]†	Ag, As, Bi, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb
5000 mg $Mg(NO_3)_2$/L[1]	Be, Co, Cr, Fe, Mn, V
100–500 mg Pd/L[2]	As, Ga, Ge, Sn
50 mg Ni/L[2]	As, Se, Sb
2% PO_4^{3-} + 1000 mg Mg $(NO_3)_2$/L[1]	Cd, Pb

*Assumes 10 μL modifier/10 μL sample.†Citric acid (1–2%) preferred; ascorbic acid or H_2 acceptable.

TABLE 3113:II. DETECTION LEVELS AND CONCENTRATION RANGES FOR ELECTROTHERMAL ATOMIZATION ATOMIC ABSORPTION SPECTROMETRY

Element	Wavelength *nm*	Estimated Detection Limit *μg/L*	Optimum Concentration Range *μg/L*
Al	309.3	3	20–200
Sb	217.6	3	20–300
As	193.7	1	5–100
Ba	553.6	2	10–200
Be	234.9	0.2	1–30
Cd	228.8	0.1	0.5–10
Cr	357.9	2	5–100
Co	240.7	1	5–100
Cu	324.7	1	5–100
Fe	248.3	1	5–100
Pb*	283.3	1	5–100
Mn	279.5	0.2	1–30
Mo	313.3	1	3–60
Ni	232.0	1	5–100

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Element	Wavelength *nm*	Estimated Detection Limit *µg/L*	Optimum Concentration Range *µg/L*
Se	196.0	2	5–100
Ag	328.1	0.2	1–25
Sn	224.6	5	20–300

*The more sensitive 217.0-nm wavelength is recommended for instruments with background correction capabilities.

TABLE 3113:III. INTERLABORATORY SINGLE-ANALYST PRECISION DATA FOR ELECTROTHERMAL ATOMIZATION METHODS[1]

		Single-Analyst Precision *% RSD*					
Element	Concentration *µg/L*	Lab Pure Water	Drinking Water	Surface Water	Effluent 1	Effluent 2	Effluent 3
Al	28	66	108	70	—	—	66
	125	27	35	24	—	—	34
	11 000	11	—	—	22	—	—
	58 300	27	—	—	19	—	—
	460	9	—	—	—	30	—
	2 180	28	—	—	—	4	—
	10.5	20	13	13	13	56	18
	230	10	18	13	21	94	14
As	9.78	40	25	15	74	23	11
	227	10	6	8	11	15	6
Ba	56.5	36	21	29	59	23	27
	418	14	12	20	24	24	18
Be	0.45	18	27	15	30	2	11
	10.9	14	4	9	7	12	12
Cd	0.43	72	49	1	121	35	27
	12	11	17	22	14	11	15
Cr	9.87	24	33	10	23	15	10
	236	16	7	11	13	16	7

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Element	Concentration μg/L	Single-Analyst Precision % RSD: Lab Pure Water	Drinking Water	Surface Water	Effluent 1	Effluent 2	Effluent 3
Co	29.7	10	17	10	19	24	12
	420	8	11	13	14	9	5
Cu	10.1	49	47	17	17	—	30
	234	8	15	6	21	—	11
	300	6	—	—	—	11	—
	1 670	11	—	—	—	6	—
Fe	26.1	144	52	153	—	—	124
	455	48	37	45	—	—	31
	1 030	17	—	—	30	—	—
	5 590	6	—	—	32	—	—
	370	14	—	—	—	19	—
	2 610	9	—	—	—	18	—
Pb	10.4	6	19	17	21	19	33
	243	17	7	17	18	12	16
Mn	0.44	187	180	—	—	—	275
	14.8	32	19	—	—	—	18
	91.0	15	—	—	48	—	—
	484.0	4	—	—	12	—	—
	111.0	12	—	—	—	21	—
	666.0	6	—	—	—	20	—
Ni	26.2	20	26	25	24	18	9
	461.0	15	11	9	8	11	4
Se	10.0	12	27	16	35	41	13
	235.0	6	6	15	6	13	14
Ag	8.48	10	—	—	15	27	16
	56.5	14	—	—	7	16	23
	0.45	27	166	48	—	—	—
	13.6	15	4	10	—	—	—

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TABLE 3113:IV. INTERLABORATORY OVERALL PRECISION DATA FOR ELECTROTHERMAL ATOMIZATION METHODS[1]

		Overall Precision% *RSD*					
Element	**Concentration *µg/L***	**Lab Pure Water**	**Drinking Water**	**Surface Water**	**Effluent 1**	**Effluent 2**	**Effluent 3**
Al	28	99	114	124	—	—	131
	125	45	47	49	—	—	40
	11 000	19	—	—	43	—	—
	58 300	31	—	—	32	—	—
	460	20	—	—	—	47	—
	2 180	30	—	—	—	15	—
	10.5	37	19	22	50	103	39
	230	26	16	16	17	180	21
As	9.78	43	26	37	72	50	39
	227	18	12	13	20	15	14
Ba	56.5	68	38	43	116	43	65
	418	35	35	28	38	48	16
Be	0.45	28	31	15	67	50	35
	10.9	33	15	26	20	9	19
Cd	0.43	73	60	5	88	43	65
	12	19	25	41	26	20	27
Cr	9.87	30	53	24	60	41	23
	236	18	14	24	20	14	20
Co	29.7	13	26	17	18	21	17
	420	21	21	17	18	13	13
Cu	10.1	58	82	31	32	—	74
	234	12	33	19	21	—	26
	300	13	—	—	—	14	—
	1 670	12	—	—	—	13	—
Fe	26.1	115	93	306	—	—	204
	455	53	46	53	—	—	44
	1 030	32	—	—	25	—	—

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		Overall Precision% *RSD*					
Element	Concentration μg/L	Lab Pure Water	Drinking Water	Surface Water	Effluent 1	Effluent 2	Effluent 3
	5 590	10	—	—	43	—	—
	370	28	—	—	—	22	—
	2 610	13	—	—	—	22	—
Pb	10.4	27	42	31	23	28	47
	243	18	19	17	19	19	25
Mn	0.44	299	272	—	—	—	248
	14.8	52	41	—	—	—	29
	91.0	16	—	—	45	—	—
	484.0	5	—	—	17	—	—
	111.0	15	—	—	—	17	—
	666.0	8	—	—	—	24	—
Ni	26.2	35	30	49	35	37	43
	461.0	23	22	15	12	21	17
Se	10.0	17	48	32	30	44	51
	235.0	16	18	18	17	22	34
Ag	8.48	23	—	—	16	35	34
	56.5	15	—	—	24	32	28
	0.45	57	90	368	—	—	—
	13.6	19	19	59	—	—	—

TABLE 3113:V. INTERLABORATORY RELATIVE ERROR DATA FOR ELECTROTHERMAL ATOMIZATION METHODS[1]

		Relative Error %					
Element	Concentration μg/L	Lab Pure Water	Drinking Water	Surface Water	Effluent 1	Effluent 2	Effluent 3
Al	28.0	86	150	54	—	—	126
	125.0	4	41	39	—	—	30
	11 000.0	2	—	—	14	—	—

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		Relative Error %					
Element	Concentration µg/L	Lab Pure Water	Drinking Water	Surface Water	Effluent 1	Effluent 2	Effluent 3
	58 300.0	12	—	—	7	—	—
	460.0	2	—	—	—	11	—
	2 180.0	11	—	—	—	9	—
Sb	10.5	30	32	28	24	28	36
	230.0	35	14	19	13	73	39
As	9.78	36	1	22	106	13	16
	227.0	3	7	10	19	6	13
Ba	56.5	132	54	44	116	59	40
	418.0	4	0	0	13	6	60
Be	0.45	40	16	11	16	10	15
	10.9	13	2	9	7	8	8
Cd	0.43	58	45	37	66	16	19
	12.0	4	6	5	22	18	3
Cr	9.87	10	9	4	2	5	15
	236.0	11	0	9	13	5	8
Co	29.7	7	7	1	6	3	13
	420.0	12	8	8	11	5	18
Cu	10.1	16	48	2	5	—	15
	234.0	8	7	0	4	—	19
	300.0	4	—	—	—	21	—
	1 670.0	6	—	—	—	2	—
Fe	26.1	85	60	379	—	—	158
	455.0	43	22	31	—	—	18
	1 030.0	8	—	—	8	—	—
	5 590.0	2	—	—	12	—	—
	370.0	4	—	—	—	11	—
	2 610.0	35	—	—	—	2	—
Pb	10.4	16	10	17	1	34	14
	243.0	5	15	8	18	15	29
Mn	0.44	332	304	—	—	—	556

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		Relative Error %					
Element	Concentration μg/L	Lab Pure Water	Drinking Water	Surface Water	Effluent 1	Effluent 2	Effluent 3
	14.8	10	1	—	—	—	36
	91.0	31	—	—	10	—	—
	484.0	42	—	—	4	—	—
	111.0	1	—	—	—	29	—
	666.0	6	—	—	—	23	—
Ni	26.2	9	16	10	7	33	54
	461.0	15	19	18	31	16	18
Se	10.0	12	9	6	36	17	37
	235.0	7	7	0	13	10	17
Ag	8.48	12	—	—	1	51	20
	56.5	16	—	—	8	51	22
	0.45	34	162	534	—	—	—
	13.6	3	12	5	—	—	—

TABLE 3120:I. SUGGESTED WAVELENGTHS, ESTIMATED DETECTION LIMITS, ALTERNATE WAVELENGTHS, CALIBRATION CONCENTRATIONS, AND UPPER LIMITS

Element	Suggested Wavelength nm	Estimated Detection Limit μg/L	Alternate Wavelength* nm	Calibration Concentration mg/L	Upper Limit Concentration† mg/L
Aluminum	308.22	40	237.32	10.0	100
Antimony	206.83	30	217.58	10.0	100
Arsenic	193.70	50	189.04‡	10.0	100
Barium	455.40	2	493.41	1.0	50
Beryllium	313.04	0.3	234.86	1.0	10
Boron	249.77	5	249.68	1.0	50
Cadmium	226.50	4	214.44	2.0	50
Calcium	317.93	10	315.89	10.0	100
Chromium	267.72	7	206.15	5.0	50
Cobalt	228.62	7	230.79	2.0	50

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Element	Suggested Wavelength *nm*	Estimated Detection Limit *µg/L*	Alternate Wavelength* *nm*	Calibration Concentration *mg/L*	Upper Limit Concentration† *mg/L*
Copper	324.75	6	219.96	1.0	50
Iron	259.94	7	238.20	10.0	100
Lead	220.35	40	217.00	10.0	100
Lithium	670.78	4§	—	5.0	100
Magnesium	279.08	30	279.55	10.0	100
Manganese	257.61	2	294.92	2.0	50
Molybdenum	202.03	8	203.84	10.0	100
Nickel	231.60	15	221.65	2.0	50
Potassium	766.49	100§	769.90	10.0	100
Selenium	196.03	75	203.99	5.0	100
Silica (SiO_2)	212.41	20	251.61	21.4	100
Silver	328.07	7	338.29	2.0	50
Sodium	589.00	30§	589.59	10.0	100
Strontium	407.77	0.5	421.55	1.0	50
Thallium	190.86‡	40	377.57	10.0	100
Vanadium	292.40	8	—	1.0	50
Zinc	213.86	2	206.20	5.0	100

* Other wavelengths may be substituted if they provide the needed sensitivity and are corrected for spectral interference.† Defines the top end of the effective calibration range. Do not extrapolate to concentrations beyond highest standard.‡ Available with vacuum or inert gas purged optical path.§ Sensitive to operating conditions.

TABLE 3120:II. ICP PRECISION AND BIAS DATA

Element	Concentration Range *µg/L*	Total Digestion* *µg/L*	Recoverable Digestion* *µg/L*
Aluminum	4792 69–	$X = 0.9273C + 3.6$	$X = 0.9380C + 22.1$
		$S = 0.0559X + 18.6$	$S = 0.0873X + 31.7$
		$SR = 0.0507X + 3.5$	$SR = 0.0481X + 18.8$
Antimony	1406 77–	$X = 0.7940C - 17.0$	$X = 0.8908C + 0.9$

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Element	Concentration Range µg/L	Total Digestion* µg/L	Recoverable Digestion* µg/L
		$S = 0.1556X - 0.6$	$S = 0.0982X + 8.3$
		$SR = 0.1081X + 3.9$	$SR = 0.0682X + 2.5$
Arsenic	69–1887	$X = 1.0437C - 12.2$	$X = 1.0175C + 3.9$
		$S = 0.1239X + 2.4$	$S = 0.1288X + 6.1$
		$SR = 0.0874X + 6.4$	$SR = 0.0643X + 10.3$
Barium	9–377	$X = 0.7683C + 0.47$	$X = 0.8380C + 1.68$
		$S = 0.1819X + 2.78$	$S = 0.2540X + 0.30$
		$SR = 0.1285X + 2.55$	$SR = 0.0826X + 3.54$
Beryllium	3–1906	$X = 0.9629C + 0.05$	$X = 1.0177C - 0.55$
		$S = 0.0136X + 0.95$	$S = 0.0359X + 0.90$
		$SR = 0.0203X - 0.07$	$SR = 0.0445X - 0.10$
Boron	19–5189	$X = 0.8807C + 9.0$	$X = 0.9676C + 18.7$
		$S = 0.1150X + 14.1$	$S = 0.1320X + 16.0$
		$SR = 0.0742X + 23.2$	$SR = 0.0743X + 21.1$
Cadmium	9–1943	$X = 0.9874C - 0.18$	$X = 1.0137C - 0.65$
		$S = 0.0557X + 2.02$	$S = 0.0585X + 1.15$
		$SR = 0.0300X + 0.94$	$SR = 0.0332X + 0.90$
Calcium	17–47 170	$X = 0.9182C - 2.6$	$X = 0.9658C + 0.8$
		$S = 0.1228X + 10.1$	$S = 0.0917X + 6.9$
		$SR = 0.0189X + 3.7$	$SR = 0.0327X + 10.1$
Chromium	13–1406	$X = 0.9544C + 3.1$	$X = 1.0049C - 1.2$
		$S = 0.0499X + 4.4$	$S = 0.0698X + 2.8$
		$SR = 0.0009X + 7.9$	$SR = 0.0571X + 1.0$
Cobalt	17–2340	$X = 0.9209C - 4.5$	$X = 0.9278C - 1.5$
		$S = 0.0436X + 3.8$	$S = 0.0498X + 2.6$

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Element	Concentration Range µg/L	Total Digestion* µg/L	Recoverable Digestion* µg/L
		$SR = 0.0428X + 0.5$	$SR = 0.0407X + 0.4$
Copper	8–1887	$X = 0.9297C - 0.30$	$X = 0.9647C - 3.64$
		$S = 0.0442X + 2.85$	$S = 0.0497X + 2.28$
		$SR = 0.0128X + 2.53$	$SR = 0.0406X + 0.96$
Iron	13–9359	$X = 0.8829C + 7.0$	$X = 0.9830C + 5.7$
		$S = 0.0683X + 11.5$	$S = 0.1024X + 13.0$
		$SR = -0.0046X + 10.0$	$SR = 0.0790X + 11.5$
Lead	42–4717	$X = 0.9699C - 2.2$	$X = 1.0056C + 4.1$
		$S = 0.0558X + 7.0$	$S = 0.0799X + 4.6$
		$SR = 0.0353X + 3.6$	$SR = 0.0448X + 3.5$
Magnesium	34–13 868	$X = 0.9881C - 1.1$	$X = 0.9879C + 2.2$
		$S = 0.0607X + 11.6$	$S = 0.0564X + 13.2$
		$SR = 0.0298X + 0.6$	$SR = 0.0268X + 8.1$
Manganese	4–1887	$X = 0.9417C + 0.13$	$X = 0.9725C + 0.07$
		$S = 0.0324X + 0.88$	$S = 0.0557X + 0.76$
		$SR = 0.0153X + 0.91$	$SR = 0.0400X + 0.82$
Molybdenum	17–1830	$X = 0.9682C + 0.1$	$X = 0.9707C - 2.3$
		$S = 0.0618X + 1.6$	$S = 0.0811X + 3.8$
		$SR = 0.0371X + 2.2$	$SR = 0.0529X + 2.1$
Nickel	17–47 170	$X = 0.9508C + 0.4$	$X = 0.9869C + 1.5$
		$S = 0.0604X + 4.4$	$S = 0.0526X + 5.5$
		$SR = 0.0425X + 3.6$	$SR = 0.0393X + 2.2$
Potassium	347–14 151	$X = 0.8669C - 36.4$	$X = 0.9355C - 183.1$
		$S = 0.0934X + 77.8$	$S = 0.0481X + 177.2$
		$SR = -0.0099X + 144.2$	$SR = 0.0329X + 60.9$

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Element	Concentration Range µg/L	Total Digestion* µg/L	Recoverable Digestion* µg/L
Selenium	14–15	$X = 0.9363C - 2.5$	$X = 0.9737C - 1.0$
	69–1	$S = 0.0855X + 17.8$	$S = 0.1523X + 7.8$
		$SR = 0.0284X + 9.3$	$SR = 0.0443X + 6.6$
Silicon	189–9434	$X = 0.5742C - 35.6$	$X = 0.9737C - 60.8$
		$S = 0.4160X + 37.8$	$S = 0.3288X + 46.0$
		$SR = 0.1987X + 8.4$	$SR = 0.2133X + 22.6$
Silver	1–189	$X = 0.4466C + 5.07$	$X = 0.3987C + 8.25$
	8–1	$S = 0.5055X - 3.05$	$S = 0.5478X - 3.93$
		$SR = 0.2086X - 1.74$	$SR = 0.1836X - 0.27$
Sodium	47–170	$X = 0.9581C + 39.6$	$X = 1.0526C + 26.7$
	35–1	$S = 0.2097X + 33.0$	$S = 0.1473X + 27.4$
		$SR = 0.0280X + 105.8$	$SR = 0.0884X + 50.5$
Thallium	14–34	$X = 0.9020C - 7.3$	$X = 0.9238C + 5.5$
	79–1	$S = 0.1004X + 18.3$	$S = 0.2156X + 5.7$
		$SR = 0.0364X + 11.5$	$SR = -0.0106X + 48.0$
Vanadium	46–98	$X = 0.9615C - 2.0$	$X = 0.9551C + 0.4$
	13–1	$S = 0.0618X + 1.7$	$S = 0.0927X + 1.5$
		$SR = 0.0220X + 0.7$	$SR = 0.0472X + 0.5$
Zinc	70–76	$X = 0.9356C - 0.30$	$X = 0.9500C + 1.22$
	7–1	$S = 0.0914X + 3.75$	$S = 0.0597X + 6.50$
		$SR = -0.0130X + 10.07$	$SR = 0.0153X + 7.78$

*X=mean recovery, µg/L,C=true value, µg/L,S=multi-laboratory standard deviation, µg/L,SR=single-an

TABLE 3125:I. RECOMMENDED ANALYTE MASSES, INSTRUMENTAL DETECTION LIMITS (IDL), and INTERNAL STANDARDS

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TABLE 3125:I. RECOMMENDED ANALYTE MASSES, INSTRUMENTAL DETECTION LIMITS (IDL), and INTERNAL STANDARDS

Element	Analytical Mass	IDL µg/L	Recommended Internal Standard
Be	9	0.025	Li
Al	27	0.03	Sc
V	51	0.02	Sc
Cr	52	0.04	Sc
Cr	53	0.03	Sc
Mn	55	0.002	Sc
Co	59	0.002	Sc
Ni	60	0.004	Sc
Ni	62	0.025	Sc
Cu	63	0.003	Sc
Cu	65	0.004	Sc
Zn	66	0.017	Ge
Zn	68	0.020	Ge
As	75	0.025	Ge
Se	77	0.093	Ge
Se	82	0.064	Ge
Ag	107	0.003	In
Ag	109	0.002	In
Cd	111	0.006	In
Cd	114	0.003	In
Sb	121	0.07	In
Sb	123	0.07	In
Tl	203	0.03	Th
Tl	205	0.03	Th
Pb	208	0.005	Th
U	235	0.032	Th
U	238	0.001	Th
Mo	98	0.003†	In
Ba	135	0.008†	In
Sr	88	0.001‡	In

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* IDLs were determined on a Perkin Elmer Elan 6000 ICP/MS using seven replicate analyses of a 1% nitric acid solution, at Manchester Environmental Laboratory, July 1996.† From EPA Method 200.8 for the Analysis of Drinking Waters-Application Note, Order No. ENVA-300A, The Perkin Elmer Corporation, 1996.‡ From Perkin Elmer Technical Summary TSMS-12.

TABLE 3125:II. ELEMENTAL ABUNDANCE EQUATIONS AND COMMON MOLECULAR ION CORRECTION EQUATIONS

Elemental and Molecular Equations*†
Li 6 = *C* 6
Be 9 = *C* 9
Al 27 = *C* 27
Sc 45 = *C* 45
V 51 = *C* 51 – (3.127)[(*C* 53) – (0.113 × *C* 52)]
Cr 52 = *C* 52
Cr 53 = *C* 53
Mn 55 = *C* 55
Co 59 = *C* 59
Ni 60 = *C* 60
Ni 62 = *C* 62
Cu 63 = *C* 63
Cu 65 = *C* 65
Zn 66 = *C* 66
Zn 68 = *C* 68
As 75 = *C* 75 – (3.127)[(*C* 77) – (0.815 × *C* 82)]
Se 77 = *C* 77
Se 82 = *C* 82 – (1.008696 × *C* 83)
Sr 88 = *C* 88
Mo 98 = *C* 98 – (0.110588 × *C* 101)
Rh 103 = *C* 103
Ag 107 = *C* 107
Ag 109 = *C* 109
Cd 111 = *C* 111 – (1.073)[(*C* 108) – (0.712 × *C* 106)]
Cd 114 = *C* 114 – (0.02686 × *C* 118)
Sb 121 = *C* 121
Sb 123 = *C* 123 – (0.127189 × *C* 125)

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Elemental and Molecular Equations*†
Ba 135 = *C* 135
Ho 165 = *C* 165
Tl 203 = *C* 203
Tl 205 = *C* 205
Pb 208 = *C* 208 + (1 × *C* 206) + (1 × *C* 207)
Th 232 = *C* 232
U 238 = *C* 238

* *C* = calibration blank corrected counts at indicated mass.† From EPA Method 200.8 for the Analysis of Drinking Waters – Application Note, Order No. ENVA-300A, The Perkin Elmer Corporation, 1996.

TABLE 3125:III. COMMON MOLECULAR ION INTERFERENCES IN ICP/MS[1]

Molecular Ion	Mass	Element Measurement Affected by Interference
Background molecular ions:		
NH^+	15	—
OH^+	17	—
OH_2^+	18	—
C_2^+	24	Mg
CN^+	26	Mg
CO^+	28	Si
N_2^+	28	Si
N_2H^+	29	Si
NO^+	30	—
NOH^+	31	P
O_2^+	32	S
O_2H^+	33	—
$^{36}ArH^+$	37	Cl
$^{38}ArH^+$	39	K
$^{40}ArH^+$	41	—
CO_2^+	44	Ca

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Molecular Ion	Mass	Element Measurement Affected by Interference
CO_2^+H	45	Sc
ArC^+, ArO^+	52	Cr
ArN^+	54	Cr
$ArNH^+$	55	Mn
ArO^+	56	Fe
ArH^+	57	Fe
$^{40}Ar^{36}Ar^+$	76	Se
$^{40}Ar^{38}Ar$	78	Se
$^{40}Ar_2^+$	80	Se
Matrix molecular ions:		
Bromide:		
$^{81}BrH^+$	82	Se
$^{79}BrO^+$	95	Mo
$^{81}BrO^+$	97	Mo
$^{81}BrOH^+$	09	Mo
$Ar^{81}Br^+$	121	Sb
Chloride:		
$^{35}ClO^+$	51	V
$^{35}ClOH^+$	52	Cr
$^{37}ClO^+$	53	Cr
$^{37}ClOH^+$	54	Cr
$Ar^{35}Cl^+$	75	As
$Ar^{37}Cl^+$	77	Se
Sulfate:		
$^{32}SO^+$	48	Ti
$^{32}SOH^+$	49	—
$^{34}SO^+$	50	V, Cr
$^{34}SOH^+$	51	V
SO_2^+, S_2^+	64	Zn

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Molecular Ion	Mass	Element Measurement Affected by Interference
$Ar^{32}S^+$	72	Ge
$Ar^{34}S^+$	74	Ge
Phosphate:		
PO^+	47	Ti
POH^+	48	Ti
PO_2^+	63	Cu
ArP^+	71	Ga
Group I II metals:		
$pArNa^+$	63	Cu
ArK^+	79	Br
$ArCa^+$	80	Se
Matrix oxides*		
TiO	62–66	Ni, Cu, Zn
ZrO	106–112	Ag, Cd
MoO	108–116	Cd
NbO	109	Ag

* Oxide interferences normally will be very small and will affect the method elements only when oxide-producing elements are present at relatively high concentrations, or when the instrument is improperly tuned or maintained. Preferably monitor Ti and Zr isotopes for soil, sediment, or solid waste samples, because these samples potentially contain high levels of these interfering elements.

TABLE 3125:IV. SUGGESTED ANALYTICAL RUN SEQUENCE

Sample Type	Comments
Tuning/optimization standard	Check mass calibration and resolution
Tuning/optimization standard	Optimize instrument for maximum rhodium counts while keeping oxides, double charged ions, and background within instrument specifications
Rinse	—
Reagent blank	Check for contamination

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Sample Type	Comments
Reagent blank	Calibration standard blank
5-μg/L standard	—
10-μg/L standard	—
20-μg/L standard	—
50-μg/L standard	—
100-μg/L standard	—
Rinse	—
Initial calibration verification, 50 μg/L	—
Initial calibration blank	—
0.30-μg/L standard	Low-level calibration verification
1.0-μg/L standard	Low-level calibration verification
External reference material	NIST 1643c or equivalent
Continuing calibration verification	—
Continuing blank calibration	—
Project sample method blank	—
Project sample laboratory-fortified blank	—
Project sample 1–4	—
Project sample 5	—
Project sample 5 with known addition	—
Project sample 5 duplicate with known addition	—
Continuing calibration verification	—
Continuing calibration blank	—

TABLE 3125:V. SUMMARY OF PERFORMANCE CRITERIA

Performance Characteristic	Criteria
Mass resolution	Manufacturer's specification
Mass calibration	Manufacturer's specification
Ba^{2+}/Ba^{+}	Manufacturer's specification
CeO/Ce	Manufacturer's specification
Background counts at mass 220	Manufacturer's specification
Correlation coefficient	$\geq$0.995

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Performance Characteristic	Criteria
Calibration blanks	< Reporting limit
Calibration verification standards	±10% of true value
Laboratory fortified blank (control sample)	±30% of true value
Precision	±20% relative percent difference for lab duplicates
Known-addition recovery	75–125%
0.3 and 1.0 μg/L standards	Dependent on data quality objectives
Reference materials	Dependent on data quality objectives
Internal standard response	70–125% of response in calibration blank with known addition

TABLE 3125:VI. QUALITY CONTROL ANALYSES FOR ICP/MS METHOD

Analysis	Frequency	Acceptance Criteria
Reference material [¶3*c*9)]	Greater of: once per sample batch, or 5%	Dependent on data quality objectives
Preparatory/method blank [¶ 3*c*4)]	Greater of: once per sample batch, or 5%	± Absolute value of instrument detection limit; ± absolute value of laboratory reporting limit or MDL is acceptable
Laboratory fortified blank [¶ 3*c*7)]	Greater of: once per sample batch, or 5%	± 30% of true value
Duplicate known-addition samples	Greater of: once per sample batch, or 5%	± 20% relative percent difference
Continuing calibration verification standards [¶ 3*c*5)]	10%	± 10% of known concentration

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Analysis	Frequency	Acceptance Criteria
Continuing calibration verification blank [¶ 3*c*6)]	10%	± Absolute value of instrument detection limit; ± absolute value of laboratory reporting limit or MDL is acceptable

TABLE 3125:VII. METHOD PERFORMANCE WITH CALIBRATION VERIFICATION STANDARDS*

		Continuing Calibration Verification Standard (*N* = 44)				Initial Calibration Verifi (*N* = 12)		
Element	Mass	Mean Recovery %	Mean	Standard Deviation	Relative Standard Deviation %	Mean Recovery %	Mean	Stan Devi
Be	9	98.71	49.35	3.43	6.94	100.06	50.03	1.
Al	27	99.62	49.81	2.99	6.01	98.42	49.21	1.
V	51	100.97	50.48	1.36	2.68	99.91	49.96	1.
Cr	52	101.39	50.70	1.86	3.66	99.94	49.97	1.
Cr	53	100.68	50.34	1.91	3.79	99.13	49.56	1.
Mn	55	101.20	50.60	1.98	3.91	99.48	49.74	1.
Co	59	101.67	50.83	2.44	4.79	99.44	49.72	1.
Ni	60	99.97	49.99	2.14	4.28	97.98	48.99	1.
Ni	62	99.79	49.89	2.09	4.18	97.57	48.79	1.
Cu	63	100.51	50.25	2.19	4.36	97.87	48.93	1.
Cu	65	100.39	50.19	2.26	4.51	98.34	49.17	1.
Zn	66	101.07	50.53	1.93	3.82	98.75	49.38	0.
Zn	68	100.42	50.21	1.89	3.77	97.75	48.87	0.
As	75	100.76	50.38	1.15	2.28	98.83	49.41	0.
Se	77	101.71	50.85	1.43	2.81	99.54	49.77	1.
Se	82	101.97	50.98	1.50	2.95	99.76	49.88	0.
Ag	107	101.50	50.75	1.68	3.30	99.27	49.63	1.
Ag	109	101.65	50.83	1.68	3.31	99.66	49.83	1.
Cd	111	100.92	50.46	1.94	3.84	98.61	49.30	1.
Cd	114	100.90	50.45	2.07	4.10	99.20	49.60	1.

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Element	Mass	Continuing Calibration Verification Standard (*N* = 44) Mean Recovery %	Mean	Standard Deviation	Relative Standard Deviation %	Initial Calibration Verifi (*N* = 12) Mean Recovery %	Mean	Stan Devi
Sb	121	100.14	50.07	2.39	4.77	99.38	49.69	1.
Sb	123	99.98	49.99	2.48	4.97	99.09	49.54	1.
Tl	203	101.36	50.68	1.64	3.23	100.05	50.02	1.
Tl	205	102.40	51.20	1.93	3.78	101.23	50.62	1.
Pb	208	101.21	50.61	1.65	3.25	99.33	49.67	0.
U	238	101.54	50.77	1.93	3.80	99.80	49.90	1.

* Single-laboratory, single-operator, single-instrument data, determined using a 50-μg/L standard prepared from sources independent of calibration standard source. Data acquired January-November 1996 during actual sample determinations. Performance of continuing calibration verification standards at different levels may vary. Perkin-Elmer Elan 6000 ICP/MS used for determination.

TABLE 3125:VIII. METHOD PERFORMANCE FOR RECOVERY OF KNOWN ADDITION IN NATURAL WATERS*

Element	Mass	Total Recoverable Metals† Mean Recovery %	Relative Standard Deviation %	Dissolved Metals‡ Mean Recovery %	Relative Standard Deviation %
Be	9	89.09	5.77	—	—
V	51	87.00	8.82	—	—
Cr	52	87.33	8.42	88.38	6.43
Cr	53	86.93	7.90	88.52	5.95
Mn	55	91.81	10.12	—	—
Co	59	87.67	8.92	—	—
Ni	60	85.07	8.42	89.31	5.70
Ni	62	84.67	8.21	89.00	5.82
Cu	63	84.13	8.46	88.55	8.33
Cu	65	84.37	8.05	88.26	7.80
Zn	66	86.14	23.01	95.59	13.81
Zn	68	81.95	20.31	91.94	13.27
As	75	90.43	4.46	97.30	8.84

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		Total Recoverable Metals†		Dissolved Metals‡	
Element	Mass	Mean Recovery %	Relative Standard Deviation %	Mean Recovery %	Relative Standard Deviation %
Se	77	83.09	4.76	105.36	10.80
Se	82	83.42	4.73	105.36	10.75
Ag	107	—	—	91.98	5.06
Ag	109	—	—	92.25	4.96
Cd	111	91.37	5.47	96.91	6.03
Cd	114	91.47	6.04	97.03	5.42
Sb	121	94.40	5.24	—	—
Sb	123	94.56	5.36	—	—
Tl	203	97.24	5.42	—	—
Tl	205	98.14	6.21	—	—
Pb	208	96.09	7.08	100.69	7.28

* Single-laboratory, single-operator, single-instrument data. Samples were Washington State surface waters from various locations. Data acquired January-November 1996 during actual sample determinations. Performance of known additions at different levels may vary. Perkin-Elmer Elan 6000 ICP/MS used for determination.
† Known-addition level 20 μg/L. Additions made before preparation according to Section 3030E (modified by cleanhood digestion in TFE beakers). *N* = 20.
‡ Known-addition level for Cd and Pb 1 μg/L; for other analytes 10 μg/L. Additions made after filtration through 1;NO1 HNO_3 precleaned 0.45-μm filters. *N* = 28.

TABLE 3125:IX. METHOD PERFORMANCE WITH LOW-LEVEL CHECK STANDARDS*

		1.0-μg/L Standard				0.3-μg/L Stan		
Element	Mass	Mean Recovery %	Mean	Standard Deviation	Relative Standard Deviation %	Mean Recovery %	Mean	Stan Devi
Be	9	97	0.97	0.06	6.24	95	0.284	0.
Al	27	121	1.21	0.32	26.49	196	0.588	0.
V	51	104	1.04	0.06	5.83	111	0.332	0.
Cr	52	119	1.19	0.34	28.62	163	0.490	0.
Cr	53	102	1.02	0.36	35.54	113	0.338	0.
Mn	55	103	1.03	0.07	6.55	110	0.329	0.
Co	59	103	1.03	0.07	6.42	102	0.307	0.

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		1.0-μg/L Standard				0.3-μg/L Stan		
Element	Mass	Mean Recovery %	Mean	Standard Deviation	Relative Standard Deviation %	Mean Recovery %	Mean	Stan Devi
Ni	60	101	1.01	0.05	5.24	107	0.321	0.
Ni	62	102	1.02	0.06	5.42	109	0.326	0.
Cu	63	107	1.07	0.09	8.78	118	0.355	0.
Cu	65	107	1.07	0.10	9.05	117	0.352	0.
Zn	66	117	1.17	0.51	43.52	182	0.547	0.
Zn	68	116	1.16	0.50	42.90	179	0.537	0.
As	75	97	0.97	0.05	5.23	101	0.302	0.
Se	77	89	0.89	0.08	8.72	88	0.265	0.
Se	82	92	0.92	0.14	15.50	106	0.317	0.
Ag	107	101	1.01	0.05	4.53	94	0.282	0.
Ag	109	103	1.03	0.07	6.57	92	0.277	0.
Cd	111	98	0.98	0.04	3.80	96	0.288	0.
Cd	114	100	1.00	0.03	3.39	98	0.293	0.
Sb	121	94	0.94	0.05	5.28	93	0.280	0.
Sb	123	94	0.94	0.05	5.36	93	0.278	0.
T1	203	101	1.01	0.04	3.57	98	0.294	0.
Tl	205	104	1.04	0.05	5.15	100	0.300	0.
Pb	208	104	1.04	0.04	3.65	104	0.312	0.
U	238	106	1.06	0.05	4.64	102	0.307	0.

* Single-laboratory, single-operator, single-instrument data. *N* = 24 for both standards.

TABLE 3130:I. PRECISION OF Cd, Pb, AND Zn ANALYSIS BY ASV

			Metal Concentration μg/L			RSD %		
Sample	Electrode	ASV Mode	Cd	Pb	Zn	Cd	Pb	Zn
Tap water #1[4]	HMDE	SW	0.068	0.57	—	4.2	4.8	—
Tap water #2[4]	HMDE	SW	—	2.50	—	—	5.1	—
Seawater #1[5]	TFME	DP	0.0121	0.0086	—	10.7	8.1	—

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Sample	Electrode	ASV Mode	Metal Concentration µg/L			RSD %		
			Cd	Pb	Zn	Cd	Pb	Zn
Seawater #2[5]	TFME	DP	0.032	0.032	—	6.3	6.3	—
Soil extract #1[6]	HMDE	SW	189	11.8	—	2.5	5.6	—
Soil extract #1[6]	HMDE	DP	186	11.9	—	2.5	4.0	—
Deionized water[4]	HMDE	SW	0.13	0.79	—	5.5	2.2	—
Wastewater #1[7]	HMDE	DP	—	74	26	—	4.3	4.5
Wastewater #2[7]	HMDE	DP	—	47	86	—	5.2	6.3
Wastewater #3[7]	HMDE	DP	—	46	65	—	4.6	6.2
Wastewater #4[8]	TFME	SW	5.2	60	12	5.2	6.1	7.4

TABLE 3500-Cr:I. ION CHROMATOGRAPHIC CONDITIONS

Variable	Value
Guard column	Dionex IonPac NG1
Separator column	Dionex IonPac AS7
Eluent	250 m*M* $(NH_4)_2SO_4$ 100 m*M* NH_4OH
Eluent flow rate	1.5 mL/min
Post-column reagent	2 m*M* diphenylcarbohydrazide 10% v/v CH_3OH 1*N* H_2SO_4
Post-column reagent flow rate	0.5 mL/min
Detector	Visible 530 nm
Retention time	3.8 min

TABLE 3500-Cr:II. SINGLE-LABORATORY PRECISION AND BIAS

Simple Type	Conc.* µg/L	Mean Recovery %	RPD†

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Simple Type	Conc.* µg/L	Mean Recovery %	RPD†
Reagent water	100	100	0.8
	1000	100	0.0
Drinking water	100	105	6.7
	1000	98	1.5
Groundwater	100	98	0.0
	1000	96	0.8
Primary wastewater effluent	100	100	0.7
	1000	104	2.7
Electroplating effluent	100	99	0.4
	1000	101	0.4

*Sample fortified at this concentration level.
†RPD - relative percent difference between fortified duplicates.

TABLE 3500-Cr:III. MULTILABORATORY DETERMINATION OF BIAS FOR HEXAVALENT CHROMIUM*

Water	Amount Added µg/L	Amount Found µg/L	S_t	S_o	Bias %
Reagent	6.00	6.68	1.03	0.53	+11.3
	8.00	8.64	1.10		+8.0
	16.0	17.4	2.25	0.77	+8.8
	20.0	21.4	2.31		+7.0
	100	101	1.91	3.76	+1.0
	140	143	5.52		+2.1
	800	819	24.3	12.7	+2.4
	960	966	18.5		+7.3
Waste	6.0	5.63	1.17	0.55	–6.2
	8.0	7.31	1.91		–8.6
	16.0	15.1	2.70	1.85	–5.6
	20.0	19.8	1.01		–1.0
	100	98.9	4.36	3.31	–1.1
	140	138	8.39		–1.4

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Water	Amount Added µg/L	Amount Found µg/L	S_t	S_o	Bias %
	800	796	60.6	27.1	–0.5
	960	944	72.1		–1.7

*Each Youden pair was used to calculate one laboratory data point (S_o).

TABLE 3500-FE:I. SELECTION OF LIGHT PATH LENGTH FOR VARIOUS IRON CONCENTRATIONS

Fe µg		
50-mL Final Volume	100-mL Final Volume	Light Path *cm*
50–200	100–400	1
25–100	50–200	2
10–40	20–80	5
5–20	10–40	10

TABLE 3500-K:I. CONCENTRATION OF CATIONS INTERFERING AT VARIOUS CONCENTRATIONS OF POTASSIUM

	Concentration Causing 10% Error *mg/L*		
Cation	K conc = 1 mg/L	K conc = 10 mg/L	K conc = 100 mg/L
Cs^+	1.0	10	100
NH_4^+	2.7	27	270
Tl^+	31.4	314	3 140
Ag^+	2 765	27 650	276 500
$Tris^+$	3 105	31 050	310 500
Li^+	356	3 560	35 600
Na^+	1 179	11 790	117 900

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	Concentration Causing 10% Error *mg/L*		
Cation	**K conc = 1 mg/L**	**K conc = 10 mg/L**	**K conc = 100 mg/L**
H^+	3.6*	2.6*	1.6*

* pH.

TABLE 3500-V:I. CONCENTRATION AT WHICH VARIOUS IONS INTERFERE IN THE DETERMINATION OF VANADIUM

Ion	**Concentration *mg/L***
Cr^{6+}	1.0
Co^{2+}	1.0
Cu^{2+}	0.05
Fe^{2+}	0.3
Fe^{3+}	0.5
Mo^{6+}	0.1
Ni^{2+}	3.0
Ag^{+}	2.0
U^{6+}	3.0
Br^{-}	0.1
Cl^{-}	100.0
I^{-}	0.001

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Endnotes

1 (Popup - Footnote)
* Note that these definitions are not the same as false-positive or false-negative instrument readings, where similar terms commonly are used by laboratory or field personnel to describe a fault in a single result; false-positive and false-negative decision errors are defined in the context of hypothesis testing, where the terms are defined with respect to the null hypothesis.

2 (Popup - Footnote)
* As $CaCO_3$.

3 (Popup - Footnote)
* Pyrex or equivalent.

4 (Popup - Footnote)
† DQO-PRO, available (free) by downloading from American Chemical Society Division of Environmental Chemistry home page at http:// acs.environmental.duq.edu/acsenv/envchem.htm, and also as part of the tutorial, Reliable Environmental Sampling and Analysis, Instant Reference Sources, Inc., http://instantref.com/inst.ref.htm.

5 (Popup - Footnote)
* Ascarite II, Fisher Scientific Co., or equivalent.

6 (Popup - Footnote)
*APPROVED BY STANDARD METHODS COMMITTEE, 1993.

7 (Popup - Footnote)
*APPROVED BY STANDARD METHODS COMMITTEE, 1993.

8 (Popup - Footnote)
* Celite No. 505, Manville Corp., or equivalent.

9 (Popup - Footnote)
* Fisher Electrophotometer or equivalent.

10 (Popup - Footnote)
† General Electric lamp No. 1719 (at 6 V) or equivalent.

11 (Popup - Footnote)
‡ General Electric photovoltaic cell, Type PV-1, or equivalent.

12 (Popup - Footnote)
§ Corning CS-3-107 (No. 1), CS-4-98 (No. 2), and CS-5-70 (No. 3), or equivalent.

13 (Popup - Footnote)
* Fisher Electrocolorimeter, Model 181, or equivalent.

14 (Popup - Footnote)
† Instrumental Colour Systems, Ltd., 7 Bucklebury Place, Upper Woolhampton, Berkshire RG7 5UD, England.

15 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1994.

16 (Popup - Footnote)
† Nephelometers that instrument manufacturers claim meet the design specifications of this method may not give the same reading for a given suspension, even when each instrument has

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been calibrated using the manufacturer's manual. This differential performance is especially important when measurements are made for regulatory purposes. Consult regulatory authorities when selecting a nephelometer to be used for making measurements that will be reported for regulatory purposes.

17 (Popup - Footnote)
* Nuclepore Corp., 7035 Commerce Circle, Pleasanton, CA, or equivalent.

18 (Popup - Footnote)
† AMCO-AEPA-1 Standard, Advanced Polymer Systems, 3696 Haven Ave., Redwood City, CA, or equivalent.

19 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.

20 (Popup - Footnote)
* For approximate metric dimensions in centimeters multiply dimensions in inches by 2.54.

21 (Popup - Footnote)
† Nuchar WV-G, Westvaco, Covington, VA; Filtrasorb 200, Calgon Carbon Corporation, Pittsburgh, PA; or equivalent.

22 (Popup - Footnote)
‡ There are numerous methods of arranging and presenting samples for odor determinations. The methods offered here are practical and economical of time and personnel. If extensive tests are planned and statistical analysis of data is required, become familiar with the more accurate methods that have been used extensively by flavor and allied industries.[5]

23 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1993.

24 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.

25 (Popup - Footnote)
* Nochromix, Godax Laboratories, Inc., New York, NY, or equivalent.

26 (Popup - Footnote)
† Plastic cup, 7- or 8-ounce, Solo or equivalent, any color except clear.

27 (Popup - Footnote)
‡ Keebler Sea Toast or equivalent.

28 (Popup - Footnote)
*APPROVED BY STANDARD METHODS COMMITTEE, 1997.

29 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.

30 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1993.

31 (Popup - Footnote)
*APPROVED BY STANDARD METHODS COMMITTEE, 1997.

32 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.

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33 (Popup - Footnote)
* The number of sample portions can be increased when working with samples of unknown demand and may be decreased when working with samples of familiar origin.
34 (Popup - Footnote)
† Size of sample portions is not critical, but must be large enough to ensure reproducible results as well as provide volume sufficient to measure chlorine residual, pH, and temperature.
35 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.
36 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1993.
37 (Popup - Footnote)
* Available from Standard Seawater Services, Institute of Oceanographic Services, Warmley, Godalming, Surrey, England.
38 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1993.
39 (Popup - Footnote)
* Teflon or equivalent.
40 (Popup - Footnote)
† Whatman GF/C or equivalent.
41 (Popup - Footnote)
* Freon or equivalent.
42 (Popup - Footnote)
† Whatman No. 40 or equivalent.
43 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.
44 (Popup - Footnote)
* Vycor, product of Corning Glass Works, Corning, N.Y., or equivalent.
45 (Popup - Footnote)
† Kimble Nos. 37005 or 37034B, or equivalent.
46 (Popup - Footnote)
‡ Class B or better.
47 (Popup - Footnote)
* Whatman grade 934AH; Gelman type A/E; Millipore type AP40; E-D Scientific Specialties grade 161; Environmental Express Pro Weigh; or other products that give demonstrably equivalent results. Practical filter diameters are 2.2 to 12.5 cm.
48 (Popup - Footnote)
† Gelman No. 4201 or equivalent.
49 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1993.
50 (Popup - Footnote)
* Some commercial thermometers may be as much as 3°C in error.

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51 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1993.
52 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1993.
53 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.
54 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.
55 (Popup - Footnote)
* Venture Innovations, P.O. Box 53631, Lafayette, LA 70505; or Triton Electronics Ltd., Bigods Hall, Dunmow, Essex, England, CM63BE; or equivalent.
56 (Popup - Footnote)
† Available from CST apparatus supplier or use Whatman No. 17 chromatography grade paper cut into 7- × 9-cm sections with grain parallel to long side.
57 (Popup - Footnote)
* Whatman No. 1 or 2 or equivalent.
58 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.
59 (Popup - Footnote)
* Gas chromatographic methods are extremely sensitive to the materials used. Use of trade names in *Standard Methods* does not preclude the use of other existing or as-yet-undeveloped products that give *demonstrably* equivalent results.
60 (Popup - Footnote)
† Commercially available columns and gases they will separate include: Silica gel and activated alumina: Silica gel: H_2, air (O_2 + N_2), CO, CH_4, C_2H_6.

Activated alumina: air (O_2 + N_2), CH_4, C_2H_6, C_3H_8. Molecular sieves (zeolites):

Molecular sieve 5A: H_2, O_2 – Ar, N_2, CH_4, CO.

Molecular sieve 13X: O_2, N_2, CH_4, CO. Porous polymers:

Chromosorb 102: air (H_2, O_2, N_2, CO), CH_4, CO_2. Porapak Q: air - CO, CO_2.

HayeSep Q: H_2, air (O_2 + N_2), CH_4, CO_2, C_2H_6, H_2S. Carbon molecular sieves:

Carbosphere: O_2, N_2, CO, CH_4, CO_2, C_2H_6 (these gases can be eluted isothermally at various temperatures or by temperature programming).

Carbosieve S-II: H_2, air (O_2 + N_2), CO, CH_4, CO_2, C_2H_6 (temperature programming required).

61 (Popup - Footnote)
† Commercially available columns and gases they will separate include: Silica gel and activated alumina: Silica gel: H_2, air (O_2 + N_2), CO, CH_4, C_2H_6.

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Activated alumina: air (O_2 + N_2), CH_4, C_2H_6, C_3H_8. Molecular sieves (zeolites):

Molecular sieve 5A: H_2, O_2 – Ar, N_2, CH_4, CO.

Molecular sieve 13X: O_2, N_2, CH_4, CO. Porous polymers:

Chromosorb 102: air (H_2, O_2, N_2, CO), CH_4, CO_2. Porapak Q: air - CO, CO_2.

HayeSep Q: H_2, air (O_2 + N_2), CH_4, CO_2, C_2H_6, H_2S. Carbon molecular sieves:

Carbosphere: O_2, N_2, CO, CH_4, CO_2, C_2H_6 (these gases can be eluted isothermally at various temperatures or by temperature programming).

Carbosieve S-II: H_2, air (O_2 + N_2), CO, CH_4, CO_2, C_2H_6 (temperature programming required).

62 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1996.
63 (Popup - Footnote)
* Common Sensing, Clark Fork, ID; Eco Enterprises, Seattle, WA; Novatech, Vancouver, B.C., Canada; and Sweeney Aquametrics, Stony Creek, CT
64 (Popup - Footnote)
† Methods for these variables may be found in Section 4500-O, 2550, and Section 2520, respectively.
65 (Popup - Footnote)
* Ultrex, J.T. Baker, or equivalent.
66 (Popup - Footnote)
* Nochromix, Godax Laboratories, or equivalent.
67 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.
68 (Popup - Footnote)
* Falcon tubes or equivalent.
69 (Popup - Footnote)
† Ultrex, Optima grade or equivalent.
70 (Popup - Footnote)
* Or equivalent.
71 (Popup - Footnote)
† Such as TFM™ or equivalent.
72 (Popup - Footnote)
‡ At temperatures greater than 80°C, but not boiling.
73 (Popup - Footnote)
§ Or equivalent.
74 (Popup - Footnote)
‖ Or equivalent.

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75 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1993
76 (Popup - Footnote)
* GFS Chemicals, Inc., Columbus, OH, Cat. No. 64, or equivalent.
77 (Popup - Footnote)
† Alpha Ventron, P.O. Box 299, 152 Andover St., Danvers, MA 01923, or equivalent.
78 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITEE, 1993.
79 (Popup - Footnote)
* Tygon or equivalent.
80 (Popup - Footnote)
† Use specially prepared reagents low in mercury.
81 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1993.
82 (Popup - Footnote)
* Chelex 100, or equivalent, available from Bio-Rad Laboratories, Richmond, CA.
83 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.
84 (Popup - Footnote)
* Dow Corning or equivalent.
85 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1993.
86 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.
87 (Popup - Footnote)
* Or equivalent.
88 (Popup - Footnote)
† Cambridge Isotope Laboratories or equivalent.
89 (Popup - Footnote)
‡ Performance data for the method were obtained with these concentrations.
90 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.
91 (Popup - Footnote)
* Ultrex, Suprapur, Aristar, or equivalent.
92 (Popup - Footnote)
* Ultrex, Suprapur, Aristar, or equivalent.
93 (Popup - Footnote)
* Ultrex, Suprapur, Aristar, or equivalent.
94 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1993.
95 (Popup - Footnote)

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* Arnold Hoffman & Co., Providence, RI.
96 (Popup - Footnote)
† K & K Laboratories, K & K Lab. Div., Life Sciences Group, Plainview, NY.
97 (Popup - Footnote)
‡ Pfaltz & Bauer, Inc., Stamford, CT.
98 (Popup - Footnote)
§ EM Science, Gibbstown, NJ.
99 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.
100 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.
101 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.
102 (Popup - Footnote)
* IonPac NGl, Dionex, 4700 Lakeside Drive, Sunnyvale, CA 94086, or equivalent.
103 (Popup - Footnote)
† IonPac AS7, Dionex, or equivalent.
104 (Popup - Footnote)
‡ The multilaboratory precision and bias data cited in this method were the result of a collaborative study carried out jointly between U.S. EPA Environmental Monitoring Systems Laboratory (Cincinnati) and Committee D-19 of ASTM.
105 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1993.
106 (Popup - Footnote)
* GFS Chemicals, Inc., Columbus, OH, or equivalent.
107 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.
108 (Popup - Footnote)
*APPROVED BY STANDARD METHODS COMMITTEE, 1997.
109 (Popup - Footnote)
* Whatman No. 42 or equivalent.
110 (Popup - Footnote)
† Whatman No. 541 or equivalent.
111 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.
112 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.
113 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1993.
114 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.

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115 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1993.
116 (Popup - Footnote)
* Bio-Rad AG1-X8 or equivalent.
117 (Popup - Footnote)
† Bio-Rad Econo-Columns or equivalent.
118 (Popup - Footnote)
‡ Amberlite XAD-8, Supelco, or equivalent.
119 (Popup - Footnote)
* Bio-Rad AG1-X8 or equivalent.
120 (Popup - Footnote)
* Use Whatman No. 42 filter paper, or equivalent.
121 (Popup - Footnote)
* Bio-Rad glass Econo-Columns or equivalent.
122 (Popup - Footnote)
† Sep-Pak, Waters Associates, or equivalent.
123 (Popup - Footnote)
‡ Chelex 100 (ammonium form) Bio Rad, or equivalent.
124 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.
125 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.
126 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.
127 (Popup - Footnote)
* Whatman No. 42 or equivalent.
128 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.

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Designation: D6517 – 00 (Reapproved 2005)

Standard Guide for Field Preservation of Groundwater Samples[1]

This standard is issued under the fixed designation D6517; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This guide covers methods for field preservation of groundwater samples. Laboratory preservation methods are not described in this guide.

1.2 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

1.3 *This guide offers an organized collection of information or a series of options and does not recommend a specific course of action. This document cannot replace education or experience and should be used in conjunction with professional judgment. Not all aspects of this guide may be applicable in all circumstances. This ASTM standard is not intended to represent or replace the standard of care by which the adequacy of a given professional service must be judged, nor should this document be applied without consideration of a project's many unique aspects. The word" Standard" in the title of this document means only that the document has been approved through the ASTM consensus process.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D3694 Practices for Preparation of Sample Containers and for Preservation of Organic Constituents

D5903 Guide for Planning and Preparing for a Groundwater Sampling Event

D6089 Guide for Documenting a Ground-Water Sampling Event

2.2 *Other Documents:*

Standard Methods for the Examination of Water and Wastewater, 20th ed., 1999[3]

International Air Transport Association Dangerous Goods Regulations[4]

U.S. EPA, Office of Solid Waste, SW-846, 3rd ed.

U.S. EPA, Title 40, Code of Federal Regulations, Part 136

U.S. EPA, Title 49, Code of Federal Regulations, Part 172

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *chemical preservation*—the addition of acidic, alkaline or biologically toxic compounds, or combination thereof, to a groundwater sample to prevent changes in chemical properties of the sample that may occur after collection.

3.1.2 *holding time*—the maximum amount of time that may transpire from the moment a sample container is filled to the time the sample is extracted or analyzed. Holding times are parameter-specific, variable in length, and defined by laboratory analytical methods.

3.1.3 *physical preservation*—methods that are implemented to protect the physical integrity of a groundwater sample from the time the sample is collected until the sample is analyzed.

3.1.4 *temperature blank*—a quality control sample that is transported with samples and is used by the laboratory performing sample analyses to verify that temperature-sensitive samples have been adequately cooled to 4°C for shipment to and arrival at the laboratory (see Note 1).

NOTE 1—Forms of temperature blank include: (*1*) using a commercially prepared, fluid-filled bottle containing a permanently fixed National Institute of Standards and Technology(NIST)-certified (or NIST-traceable) thermometer, the temperature of which is read directly by the laboratory; (*2*) submission of a designated sample container filled with water (for example, groundwater, distilled water, or deionized water) that is opened by the laboratory and immediately measured for temperature of the water using a National Institute of Standards and Technology-certified (or NIST-traceable) thermometer; or (*3*) submission of a designated container filled with water (for example, groundwater, distilled water, or deionized water) on which the laboratory uses a remote infrared temperature sensor to measure the temperature. Regardless of the method used, all measured

[1] This guide is under the jurisdiction of ASTM Committee D18 on Soil and Rock and is the direct responsibility of Subcommittee D18.21 on Groundwater and Vadose Zone Investigations

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036.

[4] Available from the Superintendent of Documents, US Government Printing Office, Washington, DC 20402.

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temperatures are compared against the required temperature for each sample (for example, 4°C) in conjunction with a previously defined window of acceptable variance from this required temperature as documented in the sampling and analysis plan.

4. Significance and Use

4.1 Groundwater samples are subject to chemical, physical, and biological change relative to in- situ conditions at the ground surfaces as a result of exposure to ambient conditions during sample collection (for example, pressure, temperature, ultraviolet radiation, atmospheric oxygen, and contaminants) **(1)** **(2)**.[5] Physical and chemical preservation of samples minimize further changes in sample chemistry that can occur from the moment the groundwater sample is retrieved, to the time it is removed from the sample container for extraction or analysis, or both. Measures also must be taken to preserve the physical integrity of the sample container.

4.2 The need for sample preservation for specific analytes should be defined prior to the sampling event and documented in the site-specific sampling and analysis plan in accordance with Guide D5903. The decision to preserve a sample should be made on a parameter-specific basis as defined by individual analytical methods.

5. Timing and Purpose of Groundwater Sample Preservation

5.1 Groundwater samples should be preserved in the field at the time of sample collection using physical means to prevent sample container breakage or temperature increases, and chemical means to minimize changes in groundwater sample chemistry prior to laboratory analysis.

6. Groundwater Sample Preservation Procedures

6.1 Groundwater sample preservation procedures are grouped into two general categories: (*1*) physical preservation and (*2*) chemical preservation. Preservation procedures should address the following details on a parameter-specific basis: sample container design and construction, protection from ultraviolet light, temperature control, chemical addition, and pH control measures **(2)**.

6.1.1 *Physical Preservation of Groundwater Samples*—Physical groundwater sample preservation methods include: (*1*) use of appropriate sample collection containers for each parameter being analyzed, (*2*) use of appropriate packing of sample containers for shipment to prevent sample container breakage and potential cross-contamination of samples during shipment, and (*3*) temperature control.

6.1.1.1 *Sample Container Selection* —Proper selection of containers for groundwater sample collection is an important means of protecting the integrity of the sample. Specifications on container design, including shape, volume, gas tightness, materials of construction, and use of cap liners, are defined for specific parameters or suites of parameters (for example, amber glass containers protect photosensitive analytes such as (PCBs) from chemical alteration). Specifications for sample container selection are documented in parameter-specific analytical methods (for example, ASTM, U.S. EPA SW846, AWWA Standard Methods) as well as in Federal (40 CFR Part 136), state, and local regulatory guidelines on groundwater sample collection and preservation. The type of sample containers to be used in a sampling event should be determined during sampling event planning in accordance with Guide D5903 and documented in the sampling and analysis plan as described in 8.1 of this guide and Guide D6089.

6.1.1.2 *Sample Container Packing and Shipping*—Field personnel should package and ship samples in compliance with all applicable regulations including the Department of Transportation (for example, Title 49 Code of Federal Regulations, Part 172) and the International Air Transportation Association (IATA). Sample containers should be shipped in a manner that will ensure the samples are received intact by the laboratory, at the appropriate temperature, and as soon as possible to allow sufficient time for the laboratory to perform the requested analyses within the holding time defined by the applicable laboratory analytical method for each parameter.

6.1.1.3 *Temperature Control*—Samples analyzed for some parameters (for example, nitrite) require temperature control. The temperature of these samples should be lowered to 4°C immediately after performing any field analyses required (for example, temperature or pH) and chemical preservation **(3)**. When necessary, temperature should be lowered as soon as possible and maintained at 4°C until the sample is analyzed. Sample temperatures can be lowered most efficiently using on-site refrigeration or wet ice. Wet ice may need to be replenished prior to shipping to maintain sample temperatures at 4°C. If required by regulation, dry ice may be used to cool samples, however, care should be taken to prevent sample freezing. Reuseable ice packs may be used to lower sample temperature, however, they often do not have the capacity to adequately lower or maintain temperatures, or both; consequently, their use is not recommended **(4)**. A temperature blank should be used with each shipping container of samples to determine actual sample temperatures at the time the sample shipment is received by the laboratory.

6.1.2 *Chemical Preservation of Groundwater Samples:*

6.1.2.1 Chemical preservation of groundwater samples involves the addition of one or more chemicals (reagent-grade or better) on a parameter-specific basis to protect sample integrity. Appendix X1 provides examples of common analyte-specific chemical preservation methods.

6.1.2.2 Chemical preservation is specified in numerous analytical methods as well as in various regulatory guidance documents. Chemicals can be used to adjust sample pH or inhibit microbial activity to prevent chemical alteration of samples. Initial pH of samples should be determined prior to chemical preservation so appropriate chemical adjustment can be made.

6.1.2.3 Groundwater samples can be chemically preserved in one of several ways: (*1*) titration of pH-adjusting compounds (for example, nitric acid) while monitoring pH change with a pH meter or narrow-range litmus paper; (*2*) addition of a premeasured volume of liquid preservative (for example, sulfuric acid) contained in glass vials or ampules to the sample

[5] The boldface numbers in parentheses refer to the list of references at the end of this standard.

container (Note 2); (*3*) addition of pelletized preservative (for example, sodium hydroxide) to the sample container; and (*4*) addition of preservative to empty sample containers prior to shipment of the empty containers to the field (that is, prepreserved sample containers) Note 3. After the sample container is filled and preserved, it should be securely capped and gently inverted to ensure uniform distribution of the preservative throughout the sample (seeNote 4).

NOTE 2—Care should be taken not to add too large a volume of chemical preservative to prevent sample dilution. A generally accepted limit is 0.5 % maximum dilution.

NOTE 3—The use of prepreserved containers should be evaluated on a parameter-specific basis.

NOTE 4—Pelletized preservatives may take longer to dissolve and mix with the sample.

6.1.2.4 The end point of chemical preservation, designed to adjust pH to specific final pH levels, (for example, <2.0 or >12.0) should be verified in the field using narrow-range litmus paper (pH paper) or a properly calibrated pH meter. A small amount of sample can either be decanted into a separate container or a parallel sample can be collected for pH verification(for example, for samples containing light non-aqueous phases), rather than introducing foreign materials into the sample container being submitted for analysis. When collecting samples in prepreserved containers, care must be taken not to prerinse the container with the sample and to avoid overfilling the container to prevent loss of chemical preservative.

6.1.2.5 When using premeasured volume preservatives such as vials, ampules, or prepreserved containers, additional preservative should be provided by the laboratory and be available in the field to add to a sample if necessary to reach the required final pH. The additional preservative should be the same type, grade, and concentration as that used initially to preserve the sample (see Note 5, Note 6, and Note 7).

7. Timing of Groundwater Sample Preservation

7.1 Groundwater samples should be preserved immediately upon collection to minimize the time for chemical alteration of sample chemistry to occur (**3**). An exception is those samples requiring field filtration, which should be field-filtered first, then chemically preserved.

NOTE 5—When using ampules, care should be taken to avoid introducing glass shards or painted ampule surfaces into the sample container which could impact sample integrity (**5**).

NOTE 6—Even when following recommended chemical preservation methods, chemical reactions may occur (**2**). For example, water containing high concentrations of calcium carbonate may effervesce when acidified. In these cases, modifications of sample preservation methods may be necessary, such as collecting an unpreserved sample or using alternate chemical preservatives. Any modifications must be pre-approved by regulatory agencies and laboratories involved, and allowed by the sampling and analysis plan.

NOTE 7—It may be necessary to establish site-specific protocol to address acceptable periods for storage and storage conditions for prepreserved sample containers due to the potential for chemical reactions to occur between the chemical preservative and the empty sample container.

8. Report

8.1 Records should be kept for all forms of sample preservation used for groundwater samples. Report the following in accordance with Guide D6089:

8.1.1 Type of sample container(s) used for each parameter being analyzed (volume, materials of construction, type of cap, and so forth);

8.1.2 Number of each type of sample container actually filled;

8.1.3 Packaging method(s) used to prevent sample bottle breakage during sample storage and shipment;

8.1.4 Temperature and pH of groundwater samples at the time of sample collection;

8.1.5 How groundwater samples were cooled to 4°C, if required for physical preservation;

8.1.6 Sample temperature at the time of sample shipment;

8.1.7 Chemical preservative(s) used on a parameter-specific basis:

8.1.7.1 What chemicals were added, by whom, time, and date,

8.1.7.2 Specifications (if known) on actual preservative(s) used (that is, source, manufacturer, grade, lot number, and so forth),

8.1.7.3 How the chemical preservative was added,

8.1.7.4 Volume of chemical preservative added (if known), and

8.1.7.5 Results of field preservation verification tests when pH is adjusted (initial and after preservation).

8.1.8 Elapsed time between sample collection and preservation;

8.1.9 Description of appearance of unpreserved and preserved samples, specifically noting any chemical reactions which may occur upon addition of chemical preservative (for example, effervescence, formation of precipitates, change in color);

8.1.10 Description of the source of sample containers used; and

8.1.11 Description of temperature blank(s) submitted along with the samples: how prepared, how many submitted, and how blank was identified.

9. Keywords

9.1 chemical preservation; groundwater sampling; holding time; physical preservation; preservative; sample preservation; temperature blank

APPENDIX

(Nonmandatory Information)

X1. EXAMPLES OF CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES FOR AQUEOUS MATRICES[A]

See Table X1.1.

	[A] Name	Container[B]	Preservation	Minimum Holding Time
Inorganic Tests:				
	Chloride	P, G	None required	28 days
	Cyanide, total and amenable to chlorination	P, G	Cool to 4°C; if oxidizing agents present add 5 mL 0.1 N $N_aA_sO_2$ per L or 0.06 g of ascorbic acid per L; adjust pH >12 with 50 % NaOH. See Method 9010 for other interferences.	14 days
	Nitrate	P, G	Cool to 4°C	48 hours
	Sulfate	P, G	Cool to 4°C	28 days
	Sulfide	P, G	Cool to 4°C, add zinc acetate	7 days
Metals:				
	Chromium VI	P, G	Cool to 4°C	24 hours
	Mercury	P, G	HNO_3 to pH <2	28 days
	Metals, except chromium VI and mercury	P, G	HNO_3 to pH <2	6 months
Organic Tests:				
	Acrolein and acrylonitrile	G, PTFE-lined septum	Cool to 4°C, 0.008 % $Na_2S_2O_3$[C], Adjust pH to 4-5	14 days
	Benzidines	G, PTFE-lined cap	Cool to 4°C, 0.008 % $Na_2S_2O_3$[C]	7 days until extraction, 40 days after extraction
	Chlorinated hydrocarbons	G, PTFE-lined cap	Cool to 4°C, 0.008 % $Na_2S_2O_3$[C]	7 days until extraction, 40 days after extraction
	Dioxins and furans	G, PTFE-lined cap	Cool to 4°C, 0.008 % $Na_2S_2O_3$[C]	30 days until extraction, 45 days after extraction
	Haloethers	G, PTFE-lined cap	Cool to 4°C, 0.008 % $Na_2S_2O_3$[C]	7 days until extraction, 40 days after extraction
	Nitroaromatics and cyclic ketones	G, PTFE-lined cap	Cool to 4°C, 0.008 % $Na_2S_2O_3$[C], store in dark	7 days until extraction, 40 days after extraction
	Nitrosamines	G, PTFE-lined cap	Cool to 4°C, 0.008 % $Na_2S_2O_3$[C], store in dark	7 days until extraction, 40 days after extraction
	Oil and grease	G	Cool to 4°C, add 5 mL diluted HCl	28 days
	Organic carbon, total (TOC)	P, G	Cool to 4°C, store in dark[D]	28 days
	Organochlorine pesticides	G, PTFE-lined cap	Cool to 4°C	7 days until extraction, 40 days after extraction
	Organophosphorus pesticides	G, PTFE-lined cap	Cool to 4°C[E]	7 days until extraction, 40 days after extraction
	PCBs	G, PTFE-lined cap	Cool to 4°C	7 days until extraction, 40 days after extraction
	Phenols	G, PTFE-lined cap	Cool to 4°C, 0.008 % $Na_2S_2O_3$[C]	7 days until extraction, 40 days after extraction
	Phthalate esters	G, PTFE-lined cap	Cool to 4°C	7 days until extraction, 40 days after extraction
	Polynuclear aromatic hydrocarbons	G, PTFE-lined cap	Cool to 4°C, 0.008 % $Na_2S_2O_3$[C], store in dark	7 days until extraction, 40 days after extraction
	Purgeable aromatic hydrocarbons	G, PTFE-lined septum	Cool to 4° C, 0.008 % $Na_2S_2O_3$[C,D]	14 days
	Purgeable halocarbons	G, PTFE-lined septum	Cool to 4°C, 0.008 % $Na_2S_2O_3$[C]	14 days
	Total organic halides (TOX)	G, PTFE-lined cap	Cool to 4°C, adjust to pH<2 with H_2SO_4	28 days
Radiological Tests:				
	Alpha, beta, and radium	P, G	HNO_3 to pH<2	6 months

[A] Table originally excerpted, in part, from Table II, 49 FR 28, Oct. 26, 1984, and revised as appropriate for SW-846. See Chapter Three, Chapter Four, or Section 6.0 of the individual methods for more information.

[B] Polyethylene (P) or Glass (G)

[C] Free chlorine must be removed by the appropriate addition of $Na_2S_2O_3$.

[D] Adjust to pH<2 with H_2SO_4, HCl, or solid $NaHSO_4$. Free chlorine must be removed prior to adjustment.

[E] Adjust samples to pH 5-8 using NaOH or H_2SO_4.

[F] Other sources of preservation methods are available (for example, Practice D3694,Standard Methods, USGS OFR 95-352) and may include methods for additional parameters.

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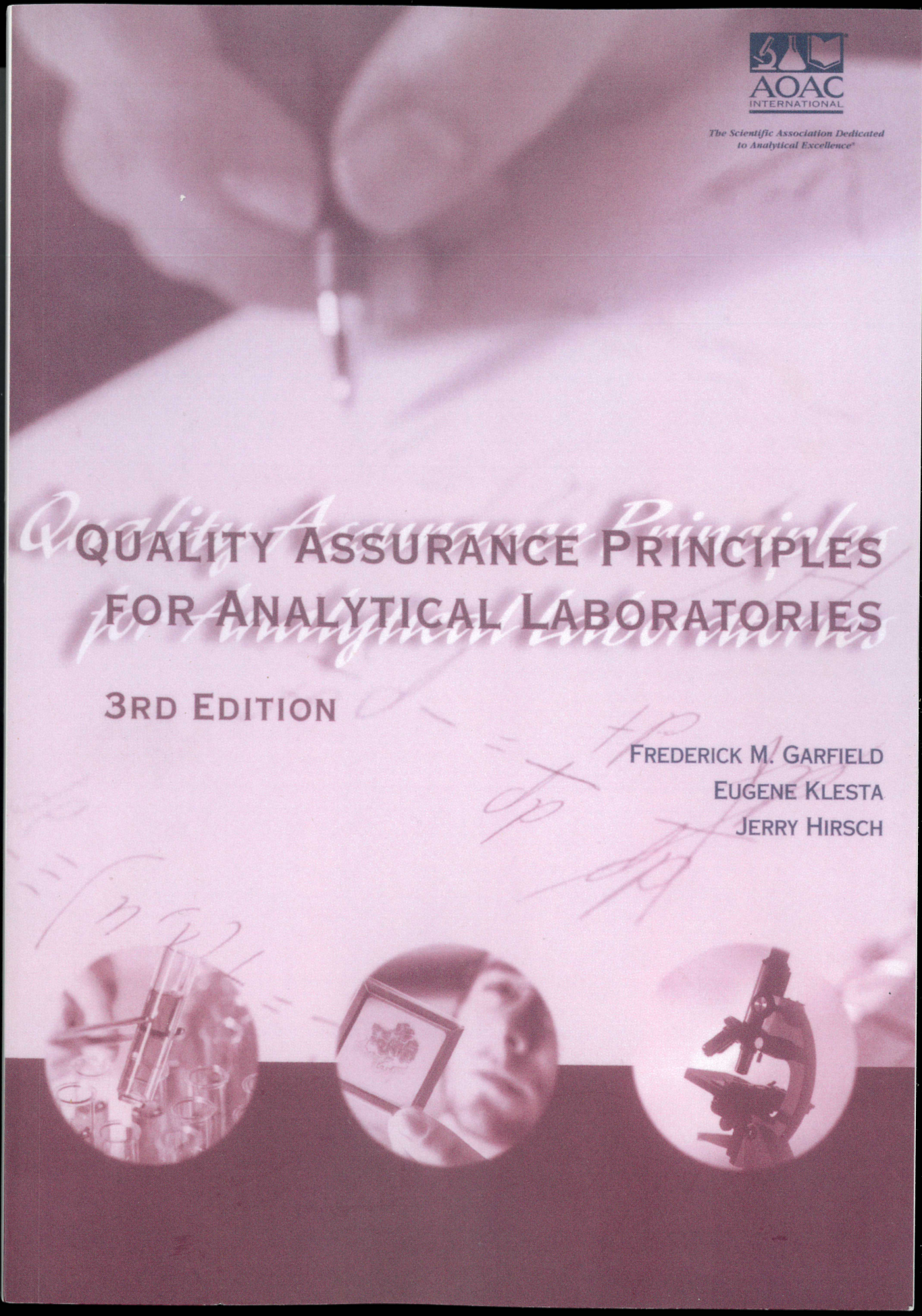
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3RD EDITION

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Quality Assurance Principles for Analytical Laboratories

THIRD EDITION

FREDERICK M. GARFIELD
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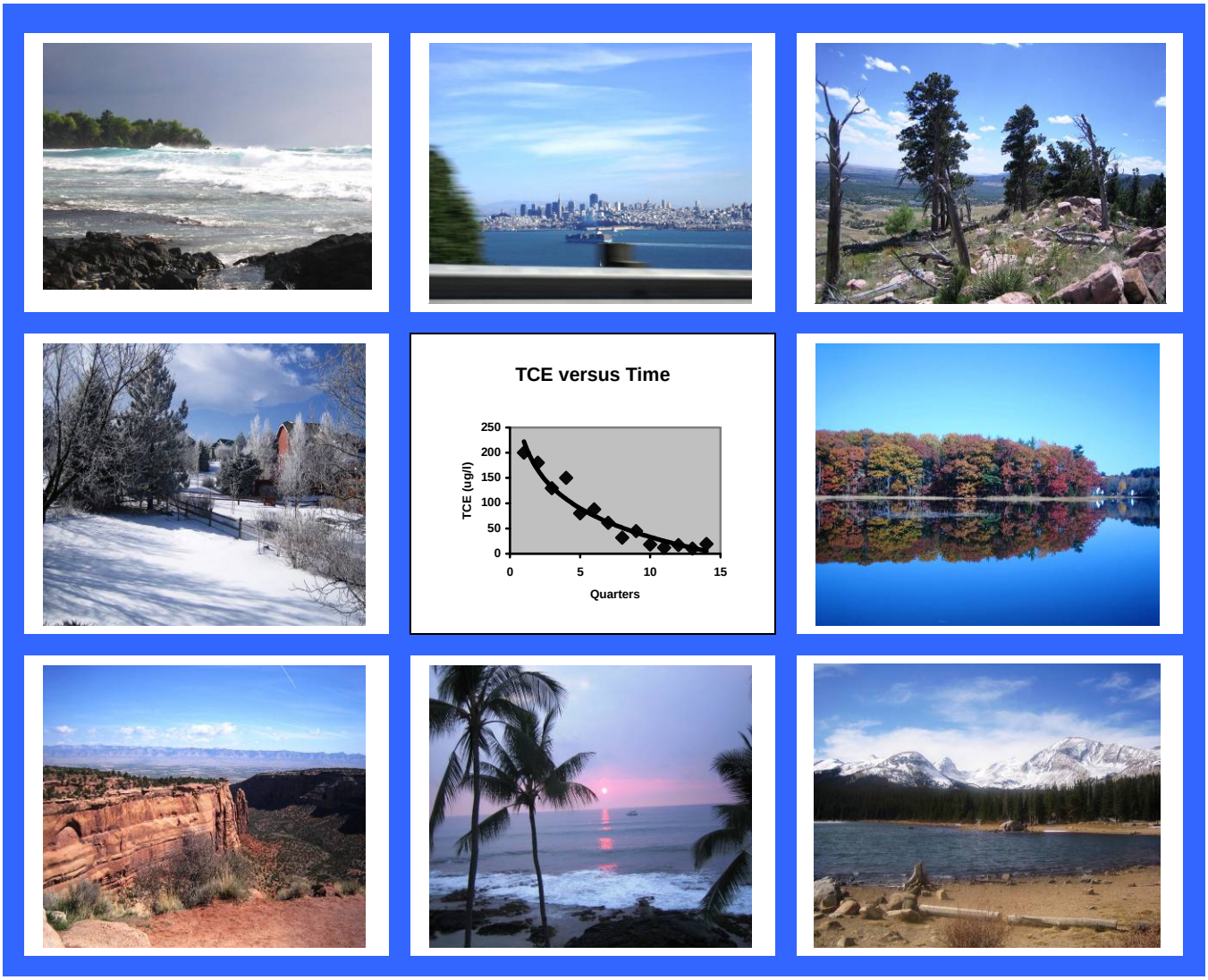
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STATISTICAL ANALYSIS OF GROUNDWATER MONITORING DATA AT RCRA FACILITIES

UNIFIED GUIDANCE MARCH 2009

EPA 530/R-09-007



ENVIRONMENTAL PROTECTION AGENCY

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UNIFIED GUIDANCE

OFFICE OF RESOURCE CONSERVATION AND RECOVERY

PROGRAM IMPLEMENTATION AND INFORMATION DIVISION

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DISCLAIMER

This Unified Guidance has been prepared to assist EPA's Regions, the States and the regulated community in testing and evaluating groundwater monitoring data under 40 CFR Parts 264 and 265 and 40 CFR Part 258. This guidance is not a rule, is not legally enforceable, and does not confer legal rights or impose legal obligations on any member of the public, EPA, the States or any other agency. While EPA has made every effort to ensure the accuracy of the discussion in this guidance, the obligations of the regulated community are determined by the relevant statutes, regulations, or other legally binding requirements. The use of the term "should" when used in this guidance does not connote a requirement. This guidance may not apply in a particular situation based on the circumstances. Regional and State personnel retain the discretion to adopt approaches on a case-by-case basis that differ from this guidance where appropriate.

It should be stressed that this guidance is a work in progress. Given the complicated nature of groundwater and geochemical behavior, statistical applications describing and evaluating data patterns have evolved over time. While many new approaches and a conceptual framework have been provided here based on our understanding at the time of publication, outstanding issues remain. The Unified Guidance sets out mostly classical statistical methods using reasonable interpretations of existing regulatory objectives and constraints. But even these highly developed mathematical models deal primarily with sorting out chance effects from potentially real differences or trends. They do not exhaust the possibilities of groundwater definition using other technical or scientific techniques (*e.g.*, contaminant modeling or geostatistical evaluations). While providing a workable decision framework, the models and approaches offered within the Unified Guidance are only approximations of a complex underlying reality.

While providing a basic understanding of underlying statistical principles, the guidance doesn't attempt to provide the reader with more thorough explanations and derivations found in standard texts and papers. It also doesn't comprehensively cover all potential statistical approaches, and confines itself to reasonable and current methods, which will work in the present RCRA groundwater context. While it is highly likely that methods promoted in this guidance will be applied using commercial or proprietary statistical software, a detailed discussion of software applications is beyond the scope of this document.

This document has been reviewed by the Office of Resource Conservation and Recovery (former Office of Solid Waste), U.S. Environmental Protection Agency, Washington, D.C., and approved for publication. Mention of trade names, commercial products, or publications does not constitute endorsement or recommendation for use.

"It is far better to have an approximate answer to the right question than a precise answer to the wrong question…" — John Hauser

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EXECUTIVE SUMMARY

The Unified Guidance provides a suggested framework and recommendations for the statistical analysis of groundwater monitoring data at RCRA facility units subject to 40 CFR Parts 264 and 265 and 40 CFR Part 258, to determine whether groundwater has been impacted by a hazardous constituent release. Specific statistical methods are identified in the RCRA regulations, but their application is not described in any detail. The Unified Guidance provides examples and background information that will aid in successfully conducting the required statistical analyses. The Unified Guidance draws upon the experience gained in the last decade in implementing the RCRA Subtitle C and D groundwater monitoring programs and new research that has emerged since earlier Agency guidance.

The guidance is primarily oriented towards the groundwater monitoring statistical analysis provisions of 40 CFR Parts 264.90 to .100. Similar requirements for groundwater monitoring at solid waste landfill facilities under 40 CFR Part 258 are also addressed. These regulations govern the detection, characterization and response to releases from regulated units into the uppermost aquifer. Some of the methods and strategies set out in this guidance may also be appropriate for analysis of groundwater monitoring data from solid waste management units subject to 40 CFR 264.101. Although the focus of this guidance is to address the RCRA regulations, it can be used by the CERCLA program and for improving remedial actions at other groundwater monitoring programs.

Part I of the Unified Guidance introduces the context for statistical testing at RCRA facilities. It provides an ***overview of the regulatory requirements***, summarizing the current RCRA Subtitle C and D regulations and outlining the statistical methods in the final rules, as well as key regulatory sections affecting statistical decisions. It explains the basic groundwater monitoring framework, philosophy and intent of each stage of monitoring — detection, compliance (or assessment), and corrective action — and certain features common to the groundwater monitoring environment. Underlying statistical ideas common to all statistical test procedures are identified, particularly issues involving false positives arising from multiple statistical comparisons and statistical power to detect contamination.

A new component of the Unified Guidance addresses issues of ***statistical design***: what factors are important in constructing a reasonable and effective statistical monitoring program. These include the establishment and updating of background data, designing an acceptable detection monitoring plan, and statistical strategies for compliance/assessment monitoring and corrective action. This part also includes a short summary of statistical methods recommended in the Unified Guidance, detailing conditions for their appropriate use.

Part II of the Unified Guidance covers diagnostic evaluations of historical facility data for the purpose of ***checking key assumptions*** implicit in the recommended statistical tests and ***for making appropriate adjustments to the data*** (*e.g.*, consideration of outliers, seasonal autocorrelation, or non-detects). Also included is a discussion of groundwater sampling and how hydrologic factors such as flow and gradient can impact the sampling program. Concepts of statistical and physical independence are compared, with caveats provided regarding the impact of dependent data on statistical test results. Statistical methods are suggested for identifying special kinds of dependence known as spatial and temporal variation, including reasonable approaches when these dependencies are observed. Tests for trends are also included in this part.

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Part III of the Unified Guidance presents a range of ***detection monitoring*** statistical procedures. First, there is a discussion of the Student's *t*-test and its non-parametric counterpart, the Wilcoxon rank-sum test, when comparing two groups of data (*e.g.*, background versus one downgradient well). This part defines both parametric and non-parametric prediction limits, and their application to groundwater analysis when multiple comparisons are involved. A variety of prediction limit possibilities are presented to cover likely interpretations of sampling and testing requirements under the RCRA regulations.

Substantial detailed guidance is offered for using prediction limits with retesting procedures, and how various retesting algorithms might be constructed. The final chapter of this Part considers another statistical method especially useful for ***intrawell*** comparisons, namely the Shewhart-CUSUM control chart. A brief discussion of analysis of variance [ANOVA] and tolerance limit tests identified in the RCRA regulations is also provided.

Part IV of the Unified Guidance is devoted to statistical methods recommended for ***compliance*** or ***assessment monitoring*** and ***corrective action***. Compliance monitoring typically involves a comparison of downgradient well data to a groundwater protection standard [GWPS], which may be a limit derived from background or a fixed concentration limit (such as in 40 CFR 264.94 Table 1, an MCL, a risk-based limit, an alternate concentration limit, or a defined clean-up standard under corrective action). The key statistical procedure is the confidence interval, and several confidence interval tests (mean, median, or upper percentile) may be appropriate for compliance evaluation depending on the circumstances. The choice depends on the distribution of the data, frequency of non-detects, the type of standard being compared, and whether or not the data exhibit a significant trend. Discussions in this part consider fixed compliance standards used in a variety of EPA programs and what they might represent in statistical terms. Strategies for corrective action differ from those appropriate for compliance monitoring primarily because statistical hypotheses are changed, although the same basic statistical methods may be employed.

Since some programs will also utilize background as standards for compliance and corrective action monitoring, those tests and discussions under **Part III** detection monitoring (including statistical design in **Part I**) may pertain in identifying the appropriate standards and tests.

A ***glossary*** of important statistical terms, ***references*** and a subject ***index*** are provided at the end of the main text. The ***Appendices*** contain additional notes on a number of topics including previous guidance, a special study for the guidance, more detailed statistical power discussions, and an extensive set of ***statistical tables*** for implementing the methods outlined in the Unified Guidance. Some tables, especially those for prediction limit retesting procedures, have been extended within the Unified Guidance beyond published sources in order to cover a wider variety of plausible scenarios.

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D STATISTICAL TABLES

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PART I. STATISTICAL DESIGN AND PHILOSOPHY

Chapter 1 provides introductory information, including the purposes and goals of the guidance, as well as its potential applicability to other environmental programs. **Chapter 2** presents a brief discussion of the existing regulations and identifies key portions of these rules which need to be addressed from a statistical standpoint, as well as some recommendations. In **Chapter 3**, fundamental statistical principles are highlighted which play a prominent role in the Unified Guidance including the notions of individual test false positive and negative decision errors and the accumulation of such errors across multiple tests or comparisons. **Chapter 4** sets the groundwater monitoring program context, the nature of formal statistical tests for groundwater and some caveats in identifying statistically significant increases. Typical groundwater monitoring scenarios also are described in this chapter. **Chapter 5** describes how to establish background and how to periodically update it. **Chapters 6** and **7** outline various factors to be considered when designing a reasonable statistical strategy for use in detection monitoring, compliance/assessment monitoring, or corrective action. Finally, **Chapter 8** summarizes the recommended statistical tests and methods, along with a concise review of assumptions, conditions of use, and limitations.

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CHAPTER 1. OBJECTIVES AND POTENTIAL USE OF THIS GUIDANCE

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1.1 OBJECTIVES

The fundamental goals of the RCRA groundwater monitoring regulations are fairly straightforward. Regulated parties are to accurately characterize existing groundwater quality at their facility, assess whether a hazardous constituent release has occurred and, if so, determine whether measured levels meet the compliance standards. Using accepted statistical testing, evaluation of groundwater quality should have a high probability of leading to correct decisions about a facility's regulatory status.

To implement these goals, EPA first promulgated regulations in 1980 (for interim status facilities) and 1982 (permitted facilities) for detecting contamination of groundwater at hazardous waste Subtitle C land disposal facilities. In 1988, EPA revised portions of those regulations found at 40 CFR Part 264, Subpart F. A similar set of regulations applying to Subtitle D municipal and industrial waste facilities was adopted in 1991 under 40 CFR Part 258. In April 2006, certain modifications were made to the 40 CFR Part 264 groundwater monitoring regulations affecting statistical testing and decision-making.

EPA released the ***Interim Final Guidance*** [IFG] in 1989 for implementing the statistical methods and sampling procedures identified in the 1988 rule. A second guidance document followed in July 1992 called ***Addendum to Interim Final Guidance*** [Addendum], which expanded certain techniques and also served as guidance for the newer Subpart D regulations.

As the RCRA groundwater monitoring program has matured, it became apparent that the existing guidance needed to be updated to adequately cover statistical methods and issues important to detecting changes in groundwater.[1] Research conducted in the area of groundwater statistics since 1992 has provided a number of improved statistical techniques. At the same time, experience gained in applying the regulatory statistical tests in groundwater monitoring contexts has identified certain constraints. Both needed to be factored into the guidance. This Unified Guidance document addresses these concerns and supercedes both the earlier IFG and Addendum.

The Unified Guidance offers guidance to owners and operators, EPA Regional and State personnel, and other interested parties in selecting, using, and interpreting appropriate statistical methods for evaluating data under the RCRA groundwater monitoring regulations. The guidance

[1] Some recommendations in EPA's **Statistical Training Course on Groundwater Monitoring** were developed to better reflect the reality of groundwater conditions at many sites, but were not generally available in published form. See RCRA Docket # EPA\530-R-93-003, 1993

identifies recent approaches and recommends a consistent framework for applying these methods. One key aspect of the Unified Guidance is providing a systematic application of the basic statistical principle of balancing false positives and negative errors in designing good testing procedures (*i.e.*, minimizing both the risk of falsely declaring a site to be out-of-compliance and of missing real evidence of an adverse change in the groundwater). Topics addressed in the guidance include basic statistical concepts, sampling design and sample sizes, selection of appropriate statistical approaches, how to check data and run statistical tests, and the interpretation of results. References for the suggested procedures and to more general statistical texts are provided. The guidance notes when expert statistical consultation may be advisable. Such guidance may also have applicability to other remedial activities as well.

Enough commonality exists in sampling, analysis, and evaluation under the RCRA regulatory requirements that the Unified Guidance often suggests relatively general strategies. At the same time, there may be situations where site-specific considerations for sampling and statistical analysis are appropriate or needed. EPA policy has been to promulgate regulations that are specific enough to implement, yet flexible in accommodating a wide variety of site-specific environmental factors. Usually this is accomplished by specifying criteria appropriate for the majority of monitoring situations, while at the same time allowing alternatives that are also protective of human health and the environment.

40 CFR Parts 264 and 258 allow the use of other sampling procedures and test methods[2] beyond those explicitly identified in the regulations,[3] subject to approval by the Regional Administrator or state Director. Alternative test methods must be able to meet the performance standards at §264.97(i) or §258.53(h). While these performance standards are occasionally specific, they are much less so in other instances. Accordingly, further guidance is provided concerning the types of procedures that should generally satisfy such performance standards.

Although the Part 264 and 258 regulations explicitly identify five basic formal statistical procedures for testing two- or multiple-sample comparisons characteristic of detection monitoring, the rules are silent on specific tests under compliance or corrective action monitoring when a groundwater protection standard is fixed (a one-sample comparison). The rules also require consideration of data patterns (normality, independence, outliers, non-detects, spatial and temporal dependence), but do not identify specific tests. This document expands the potential statistical procedures to cover these situations identified in earlier guidance, thus providing a comprehensive single EPA reference on statistical methods generally recommended for RCRA groundwater monitoring programs. Not every technique will be appropriate in a given situation, and in many cases more than one statistical approach can be used. The Unified Guidance is meant to be broad enough in scope to cover a high percentage of the potential situations a user might encounter.

The Unified Guidance is not designed as a treatise for statisticians; rather it is aimed at the informed groundwater professional with a limited background in statistics. Most methods discussed are well-known to statisticians, but not necessarily to regulators, groundwater engineers or scientists. A key thrust of the Unified Guidance has been to tailor the standard statistical techniques to the RCRA groundwater arena and its unique constraints. Because of this emphasis, not every variation of each test

[2] For example, §264.97(g)(2), §264.97(h)(5) and §258.53(g)(5)

[3] §264.97(g)(1), §264.97(h)(1-4), and §258.53(g)(1-4) respectively

is discussed in detail. For example, groundwater monitoring in a detection monitoring program is generally concerned with *increases* rather than *decreases* in concentration levels of monitored parameters. Thus, most detection monitoring tests in the Unified Guidance are presented as one-sided upper-tailed tests. In the sections covering compliance and corrective action monitoring (**Chapters 21** and **22** in **Part IV**), either one-sided lower-tail or upper-tail tests are recommended depending on the monitoring program. Users requiring two-tailed tests or additional information may need to consult other guidance or the statistical references listed at the end of the Unified Guidance.

The Unified Guidance is not intended to cover all statistical methods that might be applicable to groundwater. The technical literature is even more extensive, including other published frameworks for developing statistical programs at RCRA facilities. Certain statistical methods and general strategies described in the Unified Guidance are outlined in American Society for Testing and Materials [ASTM] documents entitled ***Standard Guide for Developing Appropriate Statistical Approaches for Groundwater Detection Monitoring Programs*** **(D6312-98[2005])** (ASTM, 2005) and ***Standard Guide for Applying Statistical Methods for Assessment and Corrective Action Environmental Monitoring Programs*** **(D7048-04)** (ASTM, 2004).

The first of these ASTM guidelines primarily covers strategies for detection monitoring, emphasizing the use of prediction limits and control charts. It also contains a series of flow diagrams aimed at guiding the user to an appropriate statistical approach. The second guideline covers statistical strategies useful in compliance/assessment monitoring and corrective action. While not identical to those described in the Unified Guidance, the ASTM guidelines do provide an alternative framework for developing statistical programs at RCRA facilities and are worthy of careful consideration.

EPA's primary consideration in developing the Unified Guidance was to select methods both consistent with the RCRA regulations, as well as straightforward to implement. We believe the methods in the guidance are not only effective, but also understandable and easy to use.

1.2 APPLICABILITY TO OTHER ENVIRONMENTAL PROGRAMS

The Unified Guidance is tailored to the context of the RCRA groundwater monitoring regulations. Some of the techniques described are unique to this guidance. Certain regulatory constraints and the nature of groundwater monitoring limit how statistical procedures are likely to be applied. These include typically small sample sizes during a given evaluation period, a minimum of annual monitoring and evaluation and typically at least semi-annual, often a large number of potential monitoring constituents, background-to-downgradient well comparisons, and a limited set of identified statistical methods. There are also unique regulatory performance constraints such as §264.97(i)(2), which requires a minimum single test false positive α level of 0.01 and a minimum 0.05 level for multiple comparison procedures such as analysis of variance [ANOVA].

There are enough commonalities with other regulatory groundwater monitoring programs (*e.g.*, certain distributional features of routinely monitored background groundwater constituents) to allow for more general use of the tests and methods in the Unified Guidance. Many of these test methods and the consideration of false positive and negative errors in site design are directly applicable to corrective action evaluations of solid waste management units under 40 CFR 264.101 and Comprehensive

Environmental Response, Compensation, and Liability Act [CERCLA] groundwater monitoring programs.

There are also comparable situations involving other environmental media to which the Unified Guidance statistical methods might be applied. Groundwater detection monitoring involves either a comparison between different monitoring stations (***i.e.***, downgradient compliance wells ***vs.*** upgradient wells) or a contrast between past and present data within a given station (***i.e.***, intrawell comparisons). To the extent that an environmental monitoring station is essentially fixed in location (***e.g.***, air quality monitors, surface water stations) and measurements are made over time, the same statistical methods may be applicable.

The Unified Guidance also details methods to compare background data against measurements from regulatory compliance points. These procedures (***e.g.***, Welch's *t*-test, prediction limits with retesting, ***etc.***) are designed to contrast multiple groups of data. Many environmental problems involve similar comparisons, even if the groups of data are not collected at fixed monitoring stations (***e.g.***, as in soil sampling). Furthermore, the guidance describes diagnostic techniques for checking the assumptions underlying many statistical procedures. Testing of normality is ubiquitous in environmental statistical analysis. Also common are checks of statistical independence in time series data, the assumption of equal variances across different populations, and the need to identify outliers. The Unified Guidance addresses each of these topics, providing useful guidance and worked out examples.

Finally, the Unified Guidance discusses techniques for comparing datasets against fixed numerical standards (as in compliance monitoring or corrective action). Comparison of data against a fixed standard is encountered in many regulatory programs. The methods described in **Part IV** of the Unified Guidance could therefore have wider applicability, despite being tailored to the groundwater monitoring data context.

EPA recognizes that many guidance users will make use of either commercially available or proprietary statistical software in applying these statistical methods. Because of their wide range of diversity and coverage, the Unified Guidance does not evaluate software usage or applicability. Certain software is provided with the guidance. The guidance limits itself to describing the basic statistical principles underlying the application of the recommended tests.

CHAPTER 2. REGULATORY OVERVIEW

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This chapter generally summarizes the RCRA groundwater monitoring regulations under 40 CFR Parts 264, 265 and 258 applicable to this guidance. A second section identifies the most critical regulatory statistical issues and how they are addressed by this guidance. Finally, recommendations regarding interim status facilities and certain statistical methods in the regulations are presented at the end of the chapter.

2.1 REGULATORY SUMMARY

Section 3004 of RCRA directs EPA to establish regulations applicable to owners and operators of facilities that treat, store, or dispose of hazardous waste as may be necessary to protect human health and the environment. Section 3005 provides for the implementation of these standards under permits issued to owners and operators by EPA or authorized States. These regulations are codified in 40 CFR Part 264. Section 3005 also provides that owners and operators of facilities in existence at the time of the regulatory or statutory requirement for a permit, who apply for and comply with applicable requirements, may operate until a permit determination is made. These facilities are commonly known as interim status facilities, which must comply with the standards promulgated in 40 CFR Part 265.

EPA first promulgated the groundwater monitoring regulations under Part 265 for interim status surface impoundments, landfills and land treatment units ("regulated units") in 1980.[1] Intended as a temporary system for units awaiting full permit requirements, the rules set out a minimal detection and assessment monitoring system consisting of at least a single upgradient and three downgradient wells. Following collection of the minimum number of samples prescribed in the rule for four indicator parameters — pH, specific conductance, total organic carbon (TOC) and total organic halides (TOX) — and certain constituents defining overall groundwater quality, the owner/operator of a land disposal facility is required to implement a ***detection monitoring*** program. Detection monitoring consists of upgradient-to-downgradient comparisons using the Student's *t*-test of the four indicator parameters at no less than a .01 level of significance (α). The regulations refer to the use of "replicate" samples for contaminant indicator comparisons. Upon failure of a single detection-level test, as well as a repeated

[1] [45 FR 33232ff, May 19, 1980] Interim status regulations; later amended in 1983 and 1985

follow-up test, the facility is required to conduct an ***assessment*** program identifying concentrations of hazardous waste constituents from the unit in groundwater. A facility can return to detection monitoring if none of the latter constituents are detected. These regulations are still in effect today.

Building on the interim status rules, Subtitle C regulations for Part 264 permitted hazardous waste facilities followed in 1982,[2] where the basic elements of the present RCRA groundwater monitoring program are defined. In §264.91, three monitoring programs — ***detection monitoring***, ***compliance monitoring***, and ***corrective action*** — serve to protect groundwater from releases of hazardous waste constituents at certain regulated land disposal units (surface impoundments, waste piles, landfills, and land treatment). In developing permits, the Regional Administrator/State Director establishes groundwater protection standards [GWPS] under §264.92 using concentration limits [§264.94] for certain monitoring constituents [§264.93]. Compliance well monitoring locations are specified in the permit following the rules in §264.95 for the required compliance period [§264.96]. General monitoring requirements were established in §264.97, along with specific detection [§264.98], compliance [§264.99], and corrective action [§264.100] monitoring requirements. Facility owners and operators are required to sample groundwater at specified intervals and to use a statistical procedure to determine whether or not hazardous wastes or constituents from the facility are contaminating the groundwater.

As found in §264.91, detection monitoring is the first stage of monitoring when no or minimal releases have been identified, designed to allow identification of significant changes in the groundwater when compared to background or established baseline levels. Downgradient well observations are tested against established background data, including measurements from upgradient wells. These are known as two- or multiple-sample tests.

If there is statistically significant evidence of a release of hazardous constituents [§264.91(a)(1) and (2)], the regulated unit must initiate compliance monitoring, with groundwater quality measurements compared to the groundwater protection standards [GWPS]. The owner/operator is required to conduct a more extensive Part 261 Appendix VIII (later Part 264 Appendix IX)[3] evaluation to determine if additional hazardous constituents must be added to the compliance monitoring list.

Compliance/assessment as well as corrective action monitoring differ from detection monitoring in that groundwater well data are tested against the groundwater protection standards [GWPS] as established in the permit. These may be fixed health-based standards such as Safe Drinking Water Act [SDWA] maximum concentration limits [MCLs], §264.94 Table 1 values, a value defined from background, or alternate-concentration limits as provided in §264.94(a). Statistically, these are considered single-sample tests against a fixed limit (a background limit can either be a single- or two-sample test depending on how the limit is defined). An exceedance occurs when a constituent level is shown to be significantly greater than the GWPS or compliance standard.

If a hazardous monitoring constituent under compliance monitoring statistically exceeds the GWPS at any compliance well, the facility is subject to corrective action and monitoring under §264.100. Following remedial action, a return to compliance consists of a statistical demonstration that

[2] [47 FR 32274ff, July 26, 1982] Permitting Requirements for Land Disposal Facilities

[3] [52 FR 25942, July 9, 1987] List (Phase I) of Hazardous Constituents for Groundwater Monitoring; Final Rule

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the concentrations of all relevant hazardous constituents lie below their respective standards. Although the rules define a three-tiered approach, the Regional Administrator or State Director can assess available information at the time of permit development to identify which monitoring program is appropriate [§264.91(b)].

Noteworthy features of the 1982 rule included retaining use of the four Part 265 indicator parameters, but allowing for additional constituents in detection monitoring. The number of upgradient and downgradient wells was not specified; rather the requirement is to have a sufficient number of wells to characterize upgradient and downgradient water quality passing beneath a regulated unit. Formalizing the "replicate" approach in the 1980 rules and the use of Student's *t*-test, rules under §264.97 required the use of aliquot replicate samples, which involved analysis of at least four physical splits of a single volume of water. In addition, Cochran's Approximation to the Behrens-Fisher [CABF] Student's *t*-test was specified for detection monitoring at no less than a .01 level of significance (α). Background sampling was specified for a one-year period consisting of four quarterly samples (also using the aliquot approach). The rules allowed use of a repeated, follow-up test subsequent to failure of a detection monitoring test. A minimum of semi-annual sampling was required.

In response to a number of concerns with these regulations, EPA amended portions of the 40 CFR Part 264 Subpart F regulations including statistical methods and sampling procedures on October 11, 1988.[4] Modifications to the regulations included requiring (if necessary) that owners and/or operators more accurately characterize the hydrogeology and potential contaminants at the facility. The rule also identifies specific performance standards in the regulations that all the statistical methods and sampling procedures must meet (discussed in a following section). That is, it is intended that the statistical methods and sampling procedures meeting these performance standards defined in §264.97 have a low probability both of indicating contamination when it is not present (Type I error), and of failing to detect contamination that actually is present (Type II error). A facility owner and/or operator must demonstrate that a procedure is appropriate for the site-specific conditions at the facility, and ensure that it meets the performance standards. This demonstration applies to any of the statistical methods and sampling procedures outlined in the regulation as well as any alternate methods or procedures proposed by facility owners and/or operators.

In addition, the amendments removed the required use of the CABF Student's t-test, in favor of five different statistical methods deemed to be more appropriate for analyzing groundwater monitoring data (discussed in a following section). The CABF procedure is still retained in Part 264, Appendix IV, as an option, but there are no longer specific citations in the regulations for this test. These newer procedures offer greater flexibility in designing a groundwater statistical program appropriate to site-specific conditions. A sixth option allows the use of alternative statistical methods, subject to approval by the Regional Administrator. EPA also instituted new groundwater monitoring sampling requirements, primarily aimed at ensuring adequate statistical sample sizes for use in analysis of variance [ANOVA] procedures, but also allowing alternative sampling plans to be approved by the Regional Administrator. The requirements identify the need for statistically independent samples to be used during evaluation. The Agency further recognizes that the selection of appropriate hazardous

[4] [53 FR 39720, October 11, 1988] 40 CFR Part 264: Statistical Methods for Evaluating Groundwater Monitoring From Hazardous Waste Facilities; Final Rule

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constituent monitoring parameters is an essential part of a reliable statistical evaluation. EPA addressed this issue in a 1987 Federal Register notice.[5]

§264.101 requirements for corrective action at non-regulated units were added in 1985 and later.[6] The Agency determined that since corrective action at non-regulated units would work under a different program, these units are not required to follow the detailed steps of Subpart F monitoring.

In 1991, EPA promulgated Subtitle D groundwater monitoring regulations for municipal solid waste landfills in 40 CFR Part 258.[7] These rules also incorporate a three-tiered groundwater monitoring strategy (detection monitoring, assessment monitoring, and corrective action), and describe statistical methods for determining whether background concentrations or the groundwater protection standards [GWPS] have been exceeded.

The statistical methods and related performance standards in 40 CFR Part 258 essentially mirror the requirements found as of 1988 at 40 CFR Part 264 Subpart F, with certain differences. Minimum sampling frequencies are different than in the Subtitle C regulations. The rules also specifically provide for the GWPS using either current MCLs or standardized risk-based limits as well as background concentrations. In addition, a specific list of hazardous constituent analytes is identified in 40 CFR Part 258, Appendix I for detection-level monitoring, including the use of unfiltered (total) trace elements.

The 1988 and 1991 rule amendments identify certain statistical methods and sampling procedures believed appropriate for evaluating groundwater monitoring data under a variety of situations. Initial guidance to implement these methods was released in 1989 as: ***Statistical Analysis of Groundwater Monitoring Data at RCRA Facilities: Interim Final Guidance*** [IFG]. The IFG covered basic topics such as checking distributional assumptions, selecting one of the methods and sampling frequencies. Examples were provided for applying the recommended statistical procedures and interpreting the results. Two types of compliance tests were provided for comparison to the GWPS — mean/median confidence intervals and upper limit tolerance intervals.

Given additional interest from users of the comparable regulations adopted for Subtitle D solid waste facilities in 1991, and with experience gained in implementing various tests, EPA actively sought to improve existing groundwater statistical guidance. This culminated in a July 1992 publication of: ***Statistical Analysis of Groundwater Monitoring Data at RCRA Facilities: Addendum to Interim Final Guidance*** [Addendum].

The 1992 Addendum included a chapter devoted to retesting strategies, as well as new guidance on several non-parametric techniques not covered within the IFG. These included the Wilcoxon rank-sum test, non-parametric tolerance intervals, and non-parametric prediction intervals. The Addendum also included a reference approach for evaluating statistical power to ensure that contamination could be adequately detected. The Addendum did not replace the IFG — the two documents contained overlapping material but were mostly intended to complement one another based on newer information

[5] [52 FR 25942, July 9, 1987] op. cit.

[6] [50 FR 28747, July 15, 1985] Amended in 1987, 1993, and 1998

[7] [56 FR 50978, October 9, 1991] 40 CFR Parts 257 & 258: Solid Waste Disposal Facility Criteria: Final Rule, especially Part 258 Subpart E Groundwater Monitoring and Corrective Action

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and comments from statisticians and users of the guidance. However, the Addendum changed several recommendations within the IFG and replaced certain test methods first published in the IFG. The two documents provided contradictory guidance on several points, a concern addressed by this guidance.

More recently in April 2006, EPA promulgated further changes to certain 40 CFR Part 264 groundwater monitoring provisions as part of the Burden Reduction Initiative Rule.[8] A brief summary of the regulatory changes and the potential effects on existing RCRA groundwater monitoring programs is provided. Four items of specific interest are:

- Elimination of the requirements to sample four successive times per statistical evaluation under §264.98(d) and §264.99(f) in favor of more flexible, site-specific options as identified in §264.97(g)(1)&(2);
- Removal of the requirements in §264.98(g) and §264.99(g) to annually sample *all* monitoring wells for Part 264 Appendix IX constituents in favor of a specific subset of wells;
- Modifications of these provisions to allow for a specific subset of Part 264 Appendix IX constituents tailored to site needs; and
- A change in the resampling requirement in §264.98(g)(3) from "within a month" to a site-specific schedule.

These changes to the groundwater monitoring provisions require coordination between the regulatory agency and owner/operator with final approval by the agency. Since the regulatory changes are not issued under the 1984 Hazardous and Solid Waste Amendments [HSWA] to RCRA, authorized State RCRA program adoption of these rules is discretionary. States may choose to maintain more stringent requirements, particularly if already codified in existing regulations. Where EPA has direct implementation authority, the provisions would go into effect following promulgation.

The first provision reaffirms the flexible approach in the Unified Guidance for detection monitoring sampling frequencies and testing options. State RCRA programs using the four-successive sampling requirements can still continue to do so under §264.97(g)(1), but the rule now allows for alternate sampling frequencies under §264.97(g)(2) in both detection and compliance monitoring. The second and third provisions provide more site- and waste-specific options for Part 264 Appendix IX compliance monitoring. The final provision provides more flexibility when resampling these Appendix IX constituents.

Since portions of the earlier and the most recent rules are still operative, all are considered in the present Unified Guidance. The effort to create this guidance began in 1996, with a draft release in December 2004, a peer review in 2005, and a final version completed in 2009.

[8] [71 FR 16862-16915] April 4, 2006

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2.2 SPECIFIC REGULATORY FEATURES AND STATISTICAL ISSUES

This section describes critical portions of the RCRA groundwater monitoring regulations which the present guidance addresses. The regulatory language is provided below in bold and italics.[9] A brief discussion of each issue is provided in statistical terms and how the Unified Guidance deals with it.

2.2.1 STATISTICAL METHODS IDENTIFIED UNDER §264.97(h) AND §258.53(g)

The owner or operator will specify one of the following statistical methods to be used in evaluating groundwater monitoring data for each hazardous constituent which, upon approval by the Regional Administrator, will be specified in the unit permit. The statistical test chosen shall be conducted separately for each hazardous constituent in each well…

1. ***A parametric analysis of variance (ANOVA) followed by multiple comparison procedures to identify statistically significant evidence of contamination. The method must include estimation and testing of the contrasts between each compliance well's mean and the background mean levels for each constituent.***

2. ***An analysis of variance (ANOVA) based on ranks followed by multiple comparison procedures to identify statistically significant evidence of contamination. The method must include estimation and testing of the contrasts between each compliance well's median and the background median levels for each constituent.***

3. ***A tolerance interval or prediction interval procedure in which an interval for each constituent is established from the distribution of the background data, and the level of each constituent in each compliance well is compared to the upper tolerance or prediction limit.***

4. ***A control chart approach that gives control limits for each constituent.***

5. ***Another statistical method submitted by the owner or operator and approved by the Regional Administrator.***

Part III of the Unified Guidance addresses these specific tests, as applied to a detection monitoring program. It is assumed that statistical testing will be conducted separately for each hazardous constituent in each monitoring well. The recommended non-parametric ANOVA method based on ranks is identified in this guidance as the Kruskal-Wallis test. ANOVA tests are discussed in **Chapter 17**. Tolerance interval and prediction limit tests are discussed separately in **Chapters 17** and **18**, with particular attention given to implementing prediction limits with retesting when conducting multiple comparisons in **Chapter 19**. The recommended type of control chart is the combined Shewhart-CUSUM control chart test, discussed in **Chapter 20**. Where a groundwater protection standard is based on background levels, application of these tests is discussed in **Part I**, **Chapter 7** and **Part IV**, **Chapter 22.**

[9] The following discussions somewhat condense the regulatory language for ease of presentation and understanding. Exact citations for regulatory text should be obtained from the most recent Title 40 Code of Federal Regulations.

If a groundwater protection standard involves a fixed limit, none of the listed statistical methods in these regulations directly apply. Consequently, a number of other single-sample tests for comparison with a fixed limit are recommended in **Part IV**. Certain statistical limitations encountered when using ANOVA and tolerance level tests in detection and compliance monitoring are also discussed in these chapters. Additional use of ANOVA tests for diagnostic identification of spatial variation or temporal effects is discussed in **Part II**, **Chapters 13** and **14**.

2.2.2 PERFORMANCE STANDARDS UNDER §264.97(i) AND §258.53(h)

Any statistical method chosen under §264.97(h) [or §258.53(g)] for specification in the unit permit shall comply with the following performance standards, as appropriate:

1. ***The statistical method used to evaluate ground-water monitoring data shall be appropriate for the distribution of chemical parameters or hazardous constituents. If the distribution of the chemical parameters or hazardous constituents is shown by the owner or operator to be inappropriate for a normal theory test, then the data should be transformed or a distribution-free test should be used. If the distributions for the constituents differ, more than one statistical method may be needed.***

2. ***If an individual well comparison procedure is used to compare an individual compliance well constituent concentration with background constituent concentrations or a groundwater protection standard, the test shall be done at a Type I error level no less than 0.01 for each testing period. If a multiple comparisons procedure is used, the Type I experiment-wise error rate for each testing period shall be no less than 0.05; however, the Type I error of no less than 0.01 for individual well comparisons must be maintained. This performance standard does not apply to control charts, tolerance intervals, or prediction intervals.***

3. ***If a control chart approach is used to evaluate groundwater monitoring data, the specific type of control chart and its associated parameter values shall be proposed by the owner or operator and approved by the Regional Administrator if he or she finds it to be protective of human health and the environment.***

4. ***If a tolerance interval or a prediction interval is used to evaluate groundwater monitoring data, the levels of confidence, and for tolerance intervals, the percentage of the population that the interval must contain, shall be proposed by the owner or operator and approved by the Regional Administrator if he or she finds it protective of human health and the environment. These parameters will be determined after considering the number of samples in the background data base, the data distribution, and the range of the concentration values for each constituent of concern.***

5. ***The statistical method shall account for data below the limit of detection with one or more procedures that are protective of human health and the environment. Any practical quantification limit (pql) approved by the Regional Administrator under §264.97(h) [or §258.53(g)] that is used in the statistical method shall be the lowest concentration level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions available to the facility.***

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6. If necessary, the statistical method shall include procedures to control or correct for seasonal and spatial variability as well as temporal correlation in the data.

These performance standards pertain to both the listed tests as well as others (such as those recommended in **Part IV** of the guidance for comparison to fixed standards). Each of the performance standards is addressed in **Part I** of the guidance for designing statistical monitoring programs and in **Part II** of the guidance covering diagnostic testing.

The ***first*** performance standard considers distributional properties of sample data; procedures for evaluating normality, transformations to normality, or use of non-parametric (distribution-free) methods are found in **Chapter 10**. Since some statistical tests also require an assumption of equal variances across groups, **Chapter 11** provides the relevant diagnostic tests. Defining an appropriate distribution also requires consideration of possible outliers. **Chapter 12** discusses techniques useful in outlier identification.

The ***second*** performance standard identifies minimum false positive error rates required when conducting certain tests. "Individual well comparison procedures" cited in the regulations include various ANOVA-type tests, Student's *t*-tests, as well as one-sample compliance monitoring/corrective action tests against a fixed standard. Per the regulations, these significance level (α) constraints do not apply to the other listed statistical methods — control charts, tolerance intervals, or prediction intervals.

When comparing an individual compliance well against background, the probability of the test resulting in a false positive or Type I error should be no *less* than 1 in 100 (1%). EPA required a minimum Type I error level for a given test and fixed sample size because false positive and negative rates are inversely related. By limiting Type I error rates to 1%, EPA felt that the risk of incurring false positives would be sufficiently low, while providing sufficient statistical power (i.e., the test's ability to control the false negative rate, that is, the rate of missing or not detecting true changes in groundwater quality).

Though a procedure to test an individual well like the Student's *t*-test may be appropriate for the smallest of facilities, more extensive networks of groundwater monitoring wells and monitoring parameters will generally require a ***multiple comparisons*** procedure. The 1988 regulations recognized this need in specifying a one-way analysis of variance [ANOVA] procedure as the method of choice for replacing the CABF Student's *t*-test. The *F*-statistic in an analysis of variance [ANOVA] does indeed control the site-wide or ***experiment-wise*** error rate when evaluating multiple upgradient and downgradient wells, at least for a single constituent. Using this technique allowed the Type I experiment-wise error rate *for each constituent* to be controlled to about 5% for each testing period.

To maintain adequate statistical power, the regulations also mandate that the ANOVA procedure be run at a *minimum* 5% false positive rate per constituent. But when a full set of well-constituent combinations are considered (particularly large suites of detection monitoring analytes at numerous compliance wells), the site-wide false positive rate can be much greater than 5%. The one-way ANOVA is inherently an interwell technique, designed to simultaneously compare datasets from different well locations. Constituents with significant natural spatial variation are likely to trigger the ANOVA *F*-statistic even in the absence of real contamination, an issue discussed in **Chapter 13**.

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Control charts, tolerance intervals, and prediction intervals provide alternate testing strategies for simultaneously controlling false positive rates while maintaining adequate power to detect contamination during detection monitoring. Although the rules do not require a minimum nominal false positive rate as specified in the **second** performance standard, use of tolerance or prediction intervals combined with a retesting strategy can result in sufficiently low experiment-wise Type I error rates and the ability to detect real contamination. **Chapters 17**, **18** and **20** consider how tolerance limits, control charts, and prediction limits can be designed to meet the **third** and **fourth** performance standards specific to these tests considering the number of samples in background, the data distribution, and the range of concentration values for each constituent of concern [COC]. **Chapters 19** and **20** on multiple comparison procedures using prediction limits or control charts identify how retesting can be used to enhance power and meet the specified false positive objectives.

The ***fifth*** performance standard requires statistical tests to account for non-detect data. **Chapter 15** provides some alternative approaches for either adjusting or modeling sample data in the presence of reported non-detects. Other chapters include modifications of standard tests to properly account for the non-detect portion of data sets.

The ***sixth*** performance standard requires consideration of spatial or temporal (including seasonal) variation in the data. Such patterns can have major statistical consequences and need to be carefully addressed. Most classical statistical tests in this guidance require assumptions of data independence and stationarity. Independence roughly means that observing a given sample measurement does not allow a precise prediction of other sample measurements. Drawing colored balls from an urn at random illustrates and fits this requirement; in groundwater, sample volumes are assumed to be drawn more or less at random from the population of possible same-sized volumes comprising the underlying aquifer. Stationarity assumes that the population being sampled has a constant mean and variance across time and space. Spatial or temporal variation in the well means and/or variances can negate these test assumptions. **Chapter 13** considers the use of ANOVA techniques to establish evidence of spatial variation. Modification of the statistical approach may be necessary in this case; in particular, background levels will need to be established at each compliance well for future comparisons (termed *intrawell* tests). Control chart, tolerance limit, and prediction limit tests can be designed for intrawell comparisons; these topics are considered in **Part III** of this guidance.

Temporal variation can occur for a number of reasons — seasonal fluctuations, autocorrelation, trends over time, *etc*. **Chapter 14** addresses these forms of temporal variation, along with recommended statistical procedures. In order to achieve stationarity and independence, sample data may need to be adjusted to remove trends or other forms of temporal dependence. In these cases, the ***residuals*** remaining after trend removal or other adjustments are used for formal testing purposes. Correlation among monitoring constituents within and between compliance wells can occur, a subject also treated in this chapter.

When evaluating statistical methods by these performance standards, it is important to recognize that the ability of a particular procedure to operate correctly in minimizing unnecessary false positives while detecting possible contamination depends on several factors. These include not only the choice of significance level and test hypotheses, but also the statistical test itself, data distributions, presence or absence of outliers and non-detects, the presence or absence of spatial and temporal variation, sampling requirements, number of samples and comparisons to be made, and frequency of sampling. Since all of these statistical factors interact to determine the procedure's effectiveness, ***any proposed statistical***

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procedure needs to be evaluated in its entirety, not by individual components. **Part I, Chapter 5** discusses evaluation of potential background databases considering all of the performance criteria.

2.2.3 HYPOTHESIS TESTS IN DETECTION, COMPLIANCE/ASSESSMENT, AND CORRECTIVE ACTION MONITORING

The Part 264 Subpart F groundwater monitoring regulations do not specifically identify the test hypotheses to be used in detection monitoring (§264.98), compliance monitoring (§264.99), and corrective action (§264.100). The same is true for the parallel Part 258 regulations for detection monitoring (§258.54), assessment monitoring (§258.55), and assessment of corrective measures (§258.56), as well as for evaluating interim status indicator parameters (§265.93) or Appendix III constituents. However, the language of these regulations as well as accepted statistical principles allow for clear definitions of the appropriate test hypotheses. Two- or multiple-sample comparisons (background *vs*. downgradient well data) are usually involved in detection monitoring (the comparison could also be made against an ACL limit based on background data). Units under detection monitoring are initially presumed not to be contributing a release to the groundwater unless demonstrated otherwise. From a statistical testing standpoint, the population of downgradient well measurements is assumed to be equivalent to or no worse than those of the background population; typically this translates into an initial or null hypothesis that the downgradient population mean is equal to or less than the background population mean. Demonstration of a release is triggered when one or more well constituents indicate statistically significant levels above background.

Compliance and corrective action tests generally compare single sets of sample data to a fixed limit or a background standard. The language of §264.99 indicates that a significant increase above a GWPS will demonstrate the need for corrective action. Consequently, the null hypothesis is that the compliance population mean (or perhaps an upper percentile) is at or below a given standard. The statistical hypothesis is thus quite similar to that of detection monitoring. In contrast, once an exceedance has been established and §264.100 is triggered, the null hypothesis is that a site is contaminated unless demonstrated to be significantly below the GWPS. The same principles apply to Part 258 monitoring programs. In Part 265, the detection monitoring hypotheses apply to an evaluation of the contaminant indicator parameters. The general subject of hypothesis testing is discussed in **Chapter 3**, and specific statistical hypothesis formulations are found in **Parts III** and **IV** of this guidance.

2.2.4 SAMPLING FREQUENCY REQUIREMENTS

Each of the RCRA groundwater monitoring regulations defines somewhat different minimum sampling requirements. §264.97(g)(1) & (2) provides two main options:

1. ***Obtaining a sequence of at least four samples taken at an interval that ensures, to the greatest extent technically feasible, that a statistically independent sample is obtained, by reference to the uppermost aquifer effective porosity, hydraulic conductivity, and hydraulic gradient, and the fate and transport characteristics of potential contaminants; or***

2. ***An alternate sampling procedure proposed by the owner or operator and approved by the Regional Administrator if protective of human health and the environment.***

Additional regulatory language in detection [§264.98(d)] and compliance [§264.99(f)] monitoring reaffirms the first approach:

> ***[A] a sequence of at least four samples from each well (background and compliance wells) must be collected at least semi-annually during detection/compliance monitoring…***

Interim status sampling requirements under §265.92[c] read as follows:

> ***(1) For all monitoring wells, the owner or operator must establish initial background concentrations or values of all parameters specified in paragraph (b) of this section. He must do this quarterly for one year;***
>
> ***(2) For each of the indicator parameters specified in paragraph (b)(3) of this section, at least four replicate measurements must be obtained for each sample and the initial background arithmetic mean and variance must be determined by pooling the replicate measurements for the respective parameter concentrations or values in samples obtained from upgradient wells during the first year.***

The requirements under Subtitle D §258.54(b) are somewhat different:

> ***The monitoring frequency for all constituents listed in Appendix I to this part,... shall be at least semi-annual during the active life of the facility.... A minimum of four independent samples from each well (background and downgradient) must be collected and analyzed for the Appendix I constituents... during the first semi-annual event. At least one sample from each well (background and downgradient) must be collected and analyzed during subsequent semi-annual events...***

The 1980 and 1982 regulations required four analyses of essentially a single physical sample for certain constituents, i.e., the four contaminant indicator parameters. The need for statistically independent data was recognized in the 1988 revisions to Part 264 and in the Part 258 solid waste requirements. In the latter rules, only a minimum single sample is required in successive semi-annual sampling events. Individual Subtitle C programs have also made use of the provision in §264.97(g)(2) to allow for fewer than four samples collected during a given semi-annual period, while other State programs require the four successive sample measurements. As noted, by the recent changes in the April 2006 Burden Reduction Rule, the explicit requirements to obtain at least four samples during the next evaluation period under 40 CFR §264.98(d) and §264.99(f) have been removed, allowing more general flexibility under the §264.97(g) sampling options. Individual State RCRA programs should be consulted as to whether these recent rule changes may be applicable.

The requirements of Parts 264 and 258 were generally intended to provide sufficient data for ANOVA-type tests in detection monitoring. However, control chart, tolerance limit, and prediction limit tests can be applied with as few as one new sample per evaluation, once background data are established. The guidance provides maximum flexibility in offering a range of prediction limit options in **Chapter 18** in order to address these various sample size requirements. Although not discussed in detail, the same conclusions pertain to the use of control charts or tolerance limits.

The use of the term "replicate" in the Part 265 interim status regulations can be a significant problem, if interpreted to mean repeat analyses of splits (or aliquots) of a single physical sample. The

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regulations indicate the need for statistical independence among sample data for testing purposes. This guidance discusses the technical statistical problems that arise if replicate (aliquot) sample data are used with the required Student's *t*-test in Part 265. Thus, the guidance recommends, if possible, that interim status statistical evaluations be based on independent sample data as discussed in **Chapters 13** and **14** and at the end of this chapter. A more standardized Welch's version of the Student-t test for unequal variances is provided as an alternative to the CABF Student's *t*-test.

2.2.5 GROUNDWATER PROTECTION STANDARDS

Part 265 does not use the term groundwater protection standards. A first-year requirement under §265.92(c)(1) is:

> ***For all monitoring wells, the owner or operator must establish background concentrations or values of all parameters specified in paragraph (b) of this section. He must do this quarterly for one year.***

Paragraph (b) includes water supply parameters listed in Part 265 Appendix III, which also provides a Maximum Level for each constituent. If a facility owner or operator does *not* develop and implement an assessment plan under §265.93(d)(4), there is a requirement in §265.94(a)(2) to report the following information to the Regional Administrator:

> ***(i) During the first year when initial background concentrations are being established for the facility: concentrations or values of the parameters listed in §265.92(b)(1) for each groundwater monitoring well within 15 days after completing each quarterly analysis. The owner or operator must separately identify for each monitoring well any parameters whose concentrations or value has been found to exceed the maximum contaminant levels in Appendix III.***

Since the Part 265 regulations are explicit in requiring a one-to-one comparison, no statistical evaluation is needed or possible.

§264.94(a) identifies the permissible concentration limits as a GWPS under §264.92:

> ***The Regional Administrator will specify in the facility permit concentrations limits in the groundwater for hazardous constituents established under §264.93. The concentration of a constituent:***
>
> ***(1) must not exceed the background level of that constituent in the groundwater at the time the limit is specified in the permit; or***
>
> ***(2) for any of the constituents listed in Table 1, must not exceed the respective value given in that table if the background level is below the value given in Table 1; or***
>
> ***(3) must not exceed an alternate limit established by the Regional Administrator under paragraph (b) of this section.***

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The RCRA Subtitle D regulations establish the following standards under §258.55(h) and (i):

> ***(h) The owner or operator must establish a groundwater protection standard for each Appendix II constituent detected in groundwater. The groundwater protection standard shall be:***
>
> > ***(1) For constituents for which a maximum contaminant level (MCL) has been promulgated under Section 1412 of the Safe Drinking Water Act (codified) under 40 CFR Part 141, the MCL for that constituent;***
> >
> > ***(2) for constituents for which MCLs have not been promulgated, the background concentration for the constituent established from wells in accordance with §258.51(a)(1); or***
> >
> > ***(3) for constituents for which the background level is higher than the MCL identified under paragraph (h)(1) of this section or health based levels identified under §258(i)(1), the background concentration.***
>
> ***(i) The Director of an approved State program may establish an alternative groundwater protection standard for constituents for which MCLs have not been established. These groundwater protection standards shall be appropriate health based levels that satisfy the following criteria:***
>
> > ***(1) the level is derived in a manner consistent with Agency guidelines for assessing health risks or environmental pollutants [51 FR 33992, 34006, 34014, 34028, Sept. 24, 1986]***
> >
> > ***(2) to (4)... [other detailed requirements for health risk assessment procedures]***

The two principal alternatives for defining a groundwater protection standard [GWPS] are either a limit based on background data or a fixed health-based value (***e.g.***, MCLs, §264.94 Table 1 values, or a calculated risk limit). The Unified Guidance discusses these two basic kinds of standards in **Chapters 7 and 21**. If a background limit is applied, some definition of how the limit is constructed from prior sample data is required at the time of development. For fixed health-based limits, the regulatory program needs to consider the statistical characteristic of the data (***e.g.***, mean, median, upper percentile) that best represents the standard in order to conduct appropriate statistical comparisons. This subject is also discussed in **Chapter 21**; the guidance provides a number of testing options in this regard.

2.3 UNIFIED GUIDANCE RECOMMENDATIONS

2.3.1 INTERIM STATUS MONITORING

As discussed in **Chapter 14**, replicates required for the four contaminant indicator parameters are not statistically independent when analyzed as aliquots or splits from a single physical sample. This results in incorrect estimates of variance and the degrees of freedom when used in a Student's *t*-test. One of the most important revisions in the 1988 regulations was to require that successive samples be independent. Therefore, at a minimum, the Unified Guidance recommends that only **independent** water quality sample data be applied to the detection monitoring Student's *t*-tests in **Chapter 16**.

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There are other considerations limiting the application of these tests as well. As noted in **Chapter 5**, at least two of the indicator parameters (pH and specific conductance) are likely to exhibit natural spatial differences among monitoring wells. Depending on site groundwater characteristics, TOC and TOX may also vary spatially. TOX analytical limitations described in SW-846[10] also note that levels of TOX are affected by inorganic chloride levels, which themselves can vary spatially by well. In short, all four indicator parameters may need to be evaluated on an intrawell basis, *i.e.*, using historical data from compliance monitoring wells.

Since this option is not identified in existing Part 265 regulations for indicator detection monitoring, a more appropriate strategy is to develop an alternative ***groundwater quality assessment monitoring plan*** under §265.90(d)(3) and (4) and §265.93(d)(3) and (4). These sections of the regulations require evaluation of hazardous waste constituents reasonably derived from the regulated unit (either those which served as a basis for listing in Part 265 Appendix VII or which are found in §261.24 Table 1). Interim status units subject to a permit are also subject to the groundwater contaminant information collection provisions under §270.14[c], which potentially include all hazardous constituents (a wider range of contaminants, *e.g.*, Part 264 Appendix IX) reasonably expected from the unit. While an interim status facility can return to indicator detection monitoring if no hazardous constituent releases have been identified, such a return is itself optional.

EPA recommends that interim status facilities develop the §265.90(d)(3) & (4) alternative groundwater quality assessment monitoring plan, if possible, using principles and procedures found in this guidance for monitoring design and statistical evaluation. Unlike Part 264 monitoring, there are no formal compliance/corrective action steps associated with statistical testing. A regulatory agency may take appropriate enforcement action if data indicate a release or significant adverse effect. The monitoring plan can be applied for an indefinite period until permit development. Multi-year collection of semi-annual or quarterly hazardous constituent data is more determinative of potential releases. The facility or the regulatory agency may also wish to continue evaluation of some or all of the Part 265 water quality indicators. Eventually these groundwater data can be used to establish which monitoring program(s) may be appropriate at the time of permit development under §264.91(b).

2.3.2 PARTS 264 AND 258 DETECTION MONITORING METHODS

As described in **Chapter 13**, many of the commonly monitored inorganic analytes exhibit natural spatial variation among wells. Since the two ANOVA techniques in §264.97(h) and §258.53(g) depend on an assumption of a single common background population, these tests may not be appropriate in many situations. Additionally, at least 50% of the data should be detectable in order to compare either well means or medians. For many hazardous trace elements, detectable percentages are considerably lower. Interwell ANOVA techniques would also not be generally useful in these cases. ANOVA may find limited applicability in detection monitoring with trace organic constituents, especially where downgradient levels are considerably higher than background and there is a high percentage of detects. Based on ranks alone, it may be possible to determine that compliance well(s) containing one or more hazardous constituents exceed background. However, the Unified Guidance recommends avoiding ANOVA techniques in the limiting situations just described.

[10] Test Methods for Evaluating Solid Waste (SW-846), EPA OSWER, 3rd Edition and subsequent revisions, Method 9020B, September 1994

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Another detection monitoring method receiving less emphasis in this guidance is the tolerance limit. In previous guidance, an upper tolerance limit based on background was suggested to identify significant increases in downgradient well concentration levels. While still acceptable by regulation (*e.g.*, under existing RCRA permits), use of prediction limits are preferable to tolerance limits in detection monitoring for the following reasons. The construction of a tolerance limit is nearly identical to that of a prediction limit. In parametric normal distribution applications, both methods use the general formula: $\bar{x} + \kappa s$. The kappa (κ) multiplier varies depending on the coverage and confidence levels desired, but in both cases some multiple of the standard deviation (*s*) is added or subtracted from the sample mean ($\bar{x}$). For non-parametric limits, the similarity is even more apparent. Often the identical statistic (*e.g.*, the maximum observed value in background) can either be used as an upper prediction limit or an upper tolerance limit, with only a difference in statistical interpretation.

More fundamentally, given the wide variety of circumstances in which retesting strategies are now encouraged and even necessary, the mathematical underpinnings of retesting with *prediction limits* are well established while those for retesting with *tolerance limits* are not. Monte Carlo simulations were originally conducted for the 1992 Addendum to develop appropriate retesting strategies involving tolerance limits. Such simulations were found insufficient for the Unified Guidance.[11]

While the simultaneous prediction limits presented in the Unified Guidance consider the actual number of comparisons in defining exact false positive error rates, some tolerance limit approaches (including past guidance) utilized an approximate and less precise pre-selected low level of probability. On balance, there is little practical need for recommending two highly similar (but not identical) methods in the Unified Guidance, both for the reasons just provided and to avoid confusion of which method to use. The final regulation-specified detection monitoring method — *control charts* — is comparable to prediction limits, but possesses some unique benefits and so is also recommended in this guidance.

2.3.3 PARTS 264 AND 258 COMPLIANCE/ASSESSMENT MONITORING

A second use of tolerance limits recommended in earlier guidance was for comparing downgradient monitoring well data to a fixed limit during compliance/assessment monitoring. In this case, an upper tolerance limit constructed on each compliance well data set could be used to identify non-compliance with a fixed GWPS limit. Past guidance also used upper confidence limits around an upper proportion in defining these tolerance limits. A number of problems were identified using this approach.

A tolerance limit makes statistical sense if the limit represents an upper percentile, *i.e.*, when a limit is not to be exceeded by more than, for instance, 1% or 5% or 10% of future individual concentration values. However, GWPS limits can also be interpreted as long-term averages, *e.g.*, chronic risk-based values, which are better approximated by a statistic like the mean or median. **Chapters 7 &**

[11] 1) there were minor errors in the algorithms employed; 2) Davis and McNichols (1987) demonstrated how to compute exact kappa multipliers for prediction limits using a numerical algorithm instead of employing an inefficient simulation strategy; and 3) further research (as noted in **Chapter 19**) done in preparation of the guidance has shown that repeated prediction limits are more statistically powerful than retesting strategies using tolerance limits for detecting changes in groundwater quality.

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22 discuss important considerations when identifying the appropriate statistical parameter to be compared against a fixed GWPS limit.

More importantly, since the upper confidence level of tolerance limit overestimates the true population proportion by design, demonstrating an exceedance of a GWPS by this limit does not necessarily indicate that the corresponding population proportion also exceeds the standard, leading to a high false positive rate. Therefore, the Unified Guidance recommends that the compliance/assessment monitoring null hypothesis be structured so that the compliance population characteristic (***e.g.***, mean, median, upper percentile) is assumed to be less than or equal to the fixed standard unless demonstrated otherwise. The correct test statistic in this situation is then the lower confidence limit. The upper confidence limit is used in corrective action to identify whether a constituent has returned to compliance.

To ensure consistency with the underlying statistical presumptions of compliance/assessment monitoring (see **Chapter 4**) and to maintain control of false positive rates, the Unified Guidance recommends that this tolerance interval approach be replaced with a more coherent and comprehensive strategy based on the use of confidence intervals (see **Chapters 21** and **22**). Confidence intervals can be applied in a consistent fashion to GWPS concentration limits representing either long-term averages or upper percentiles.

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CHAPTER 3. KEY STATISTICAL CONCEPTS

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The success of any discipline rests on its ability to accurately model and explain real problems. Spectacular successes have been registered during the past four centuries by the field of mathematics in modeling fundamental processes in mechanics and physics. The last century, in turn, saw the rise of statistics and its fundamental theory of ***estimation*** and ***hypothesis testing***. All of the tests described in the Unified Guidance are based upon this theory and involve the same key concepts. The purpose of this chapter is to summarize the statistical concepts underlying the methods presented in the Unified Guidance, and to consider each in the practical context of groundwater monitoring. These include:

- Statistical inference: the difference between samples and populations; the concept of sampling.
- Common statistical assumptions used in groundwater monitoring: statistical independence, stationarity, lack of outliers, and normality.
- Frequently-used statistical measures: mean, standard deviation, percentiles, correlation coefficient, coefficient of variation, ***etc.***
- Hypothesis testing: How probability distributions are used to model the behavior of groundwater concentrations and how the statistical evidence is used to "prove" or "disprove" the validity of competing models.
- Errors in hypothesis testing: What false positives (Type I errors) and false negatives (Type II errors) really represent.
- Sampling distributions and the Central Limit Theorem: How the statistical behavior of test statistics differs from that of individual population measurements.
- Statistical power and power curves: How the ability to detect real contamination depends on the size or degree of the concentration increase.
- Type I ***vs.*** Type II errors: The tradeoff between false positives and false negatives; why it is generally impossible to minimize both kinds of error simultaneously.

3.1 INTRODUCTION TO GROUNDWATER STATISTICS

This section briefly covers some basic statistical terms and principles used in this guidance. All of these topics are more thoroughly discussed in standard textbooks. It is presumed that the user already has some familiarity with the following terms and discussions.

Statistics is a branch of applied mathematics, dealing with the description, understanding, and modeling of data. An integral part of statistical analysis is the testing of competing mathematical models and the management of data uncertainty. Uncertainty is present because measurement data exhibit *variability*, with limited knowledge of the medium being sampled. The fundamental aim of almost every statistical analysis is to draw *inferences*. The data analyst must *infer* from the observed data something about the physical world without knowing or seeing all the possible facts or evidence. So the question becomes: how closely do the measured data mimic reality, or put another way, to what extent do the data correctly identify a physical truth (*e.g.*, the compliance well is contaminated with arsenic above regulatory limits)?

One way to ascertain whether an aquifer is contaminated with certain chemicals would be to exhaustively sample and measure every physical volume of groundwater underlying the site of interest. Such a collection of measurements would be impossible to procure in practice and would be infinite in size, since sampling would have to be continuously conducted over time at a huge number of wells and sampling depths. However, one would possess the entire *population* of possible measurements at that site and the exact statistical *distribution* of the measured concentration values.

A statistical *distribution* is an organized summary of a set of data values, sorted into the relative frequencies of occurrence of different measurement levels (*e.g.*, concentrations of 5 ppb or less occur among 30 percent of the values, or levels of 20 ppb or more only occur 1 percent of the time). More generally, a distribution may refer to a mathematical model (known as a *probability distribution*) used to represent the shape and statistical characteristics of a given population and chosen according to one's experience with the type of data involved.

By contrast to the population, a statistical *sample* is a finite subset of the population, typically called a *data set*. Note that the statistical definition of sample is usually different from a geological or hydrological definition of the same term. Instead of a physical volume or mass, a statistical sample is a collection of measurements, *i.e.*, a set of numbers. This collection might contain only a single value, but more generally has a number of measurements denoted as the *sample size*, *n*.

Because a sample is only a partial representation of the population, an inference is usually desired in order to conclude something from the observed data about the underlying population. One or more numerical characteristics of the population might be of interest, such as the true *average* contaminant level or the *upper 95th percentile* of the concentration distribution. Quantities computed from the sample data are known as *statistics*, and can be used to reasonably *estimate* the desired but unknown population characteristics. An example is when testing sample data against a regulatory standard such as a maximum concentration limit [MCL] or background level. *A mean sample estimate* of the average concentration can be used to judge whether the corresponding population characteristic — the true mean concentration (denoted by the Greek letter μ) — exceeds the MCL or background limit.

The accuracy of these estimates depends on how *representative* the sample measurements of the underlying population are. In a representative sample, the distribution of sample values have the best

chance of closely matching the population distribution. Unfortunately, the degree of representativeness of a given sample is almost never known. So it quite important to understand precisely how the sample values were obtained from the population and to explore whether or not they *appear* representative. Though there is no guarantee that a sample will be adequate, the best protection against an unrepresentative sample is to select measurements from the population *at random*. A *random sample* implies that each potential population value has an equivalent chance of being selected depending only on its likelihood of occurrence. Not only does random sampling guard against selection of an unrepresentative portion of the population distribution, it also enables a mathematical estimate to be drawn of the statistical uncertainty associated with the ability of a given sample to represent the desired characteristic of the population. It can be very difficult to gauge the uncertainty surrounding a sample collected haphazardly or by means of professional judgment.

As a simple example, consider an urn filled with red and green balls. By thoroughly mixing the urn and blindly sampling (*i.e.*, retrieving) 10 percent of the balls, a very nearly random sample of the population of balls will be obtained, allowing a fair estimate of the true overall proportion of one color or the other. On the other hand, if one looked into the urn while sampling and only picked red balls or tried to alternate between red and green, the sample would be far from random and likely unrepresentative of the true proportions.

At first glance, groundwater measurements obtained during routine monitoring would not seem to qualify as random samples. The well points are generally not placed in random locations or at random depths, and the physical samples are usually collected at regular, pre-specified intervals. Consequently, further distinctions and assumptions are necessary when performing statistical evaluations of groundwater data. First, the distribution of a given contaminant may not be *spatially uniform* or *homogeneous*. That is, the local distribution of measured values at one well may not be the same as at other wells. Because this is often true for naturally-occurring groundwater constituents, the statistical population(s) of interest may be well-specific. A statistical sample gathered from a particular well must then be treated as potentially representative only of that well's local population. On the other hand, samples drawn from a number of reference background wells for which no significant differences are indicated, may permit the pooled data to serve as an estimate of the overall well field behavior for that particular monitoring constituent.

The distribution of a contaminant may also not be *temporally uniform* or *stationary over time*. If concentration values indicates a trend, perhaps because a plume intensifies or dissipates or natural in-situ levels rise or fall due to drought conditions, *etc.*, the distribution is said to be *non-stationary*. In this situation, some of the measurements collected over time may not be representative of current conditions within the aquifer. Statistical adjustments might be needed or the data partitioned into usable and unusable values.

A similar difficulty is posed by *cyclical* or *seasonal* trends. A long-term constituent concentration average at a well location or the entire site may essentially be constant over time, yet temporarily fluctuate up and down on a seasonal basis. Given a fixed interval between sampling events, some of this fluctuation may go unobserved due to the non-random nature of the sampling times. This could result in a sample that is unrepresentative of the population *variance* and possibly of the population *mean* as well. In such settings, a shorter (*i.e.*, higher frequency) or staggered sampling interval may be needed to better capture key characteristics of the population as a part of the distribution of sample measurements.

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The difficulties in identifying a valid statistical framework for groundwater monitoring highlight a fundamental assumption governing almost every statistical procedure and test. It is the presumption that sample data from a given population should be *independent* and *identically distributed*, commonly abbreviated as *i.i.d.* All of the mathematics and statistical formulas contained in this guidance are built on this basic assumption. If it is not satisfied, statistical conclusions and test results may be invalid or in error. The associated statistical uncertainty may be different than expected from a given test procedure.

Random sampling of a single, fixed, stationary population will guarantee independent, identically-distributed sample data. Routine groundwater sampling typically does not. Consequently, the Unified Guidance discusses both below and in later chapters what assumptions about the sample data must be routinely or periodically checked. Many but not all of these assumptions are a simple consequence of the *i.i.d.* presumption. The guidance also discusses how sampling ought to be conducted and designed to get as close as possible to the *i.i.d.* goal.

3.2 COMMON STATISTICAL ASSUMPTIONS

Every statistical test or procedure makes certain assumptions about the data used to compute the method. As noted above, many of these assumptions flow as a natural consequence of the presumption of *independent, identically-distributed* data (*i.i.d.*). The most common assumptions are briefly described below:

3.2.1 STATISTICAL INDEPENDENCE

A major advantage of truly random sampling of a population is that the measurements will be *statistically independent.* This means that observing or knowing the value of one measurement does not alter or influence the probability of observing any other measurement in the population. After one value is selected, the next value is sampled again at random without regard to the previous measurement, and so on. By contrast, groundwater samples are not chosen at random times or at random locations. The locations are fixed and typically few in number. The intervals between sampling events are fixed and fairly regular. While samples of independent data exhibit no *pairwise correlation* (*i.e.*, no statistical association of similarity or dissimilarity between pairs of sampled measurements), *non-independent* or *dependent* data *do* exhibit pairwise correlation and often other, more complex forms of correlation. Aliquot split sample pairs are generally not independent because of the *positive correlation* induced by the splitting of the same physical groundwater sample. Split measurements tend to be highly similar, much more so than the random pairings of data from distinct sampling events.

In a similar vein, measurements collected close together in time from the same well tend to be more highly correlated than pairs collected at longer intervals. This is especially true when the groundwater is so slow-moving that the same general volume of groundwater is being sampled on closely-spaced consecutive sampling events. Dependence may also be exhibited spatially across a well field. Wells located more closely in space and screened in the same hydrostratigraphic zone may show greater similarity in concentration patterns than wells that are farther apart. For both of these temporal or time-related and spatial dependencies, the observed correlations are a result not only of the non-random nature of the sampling but also the fact that many groundwater populations are not uniform throughout the subsurface. The aquifer may instead exhibit pockets or sub-zones of higher or lower concentration, perhaps due to location-specific differences in natural geochemistry or the dynamics of contaminant plume behavior over time.

As a mathematical construct, statistical independence is essentially impossible to check directly in a set of sample data — other than by ensuring ahead of time that the measurements were collected at random. However, *non-zero pairwise correlation*, a clear sign of dependent data, can be checked and estimated in a variety of ways. The Unified Guidance describes two methods for identifying temporal correlation in **Chapter 14**: the *rank von Neumann ratio* test and the *sample autocorrelation function*. Measurable correlation among consecutive sample pairs may dictate the need for decreasing the sampling frequency or for a more complicated data adjustment.

Defining and modeling wellfield spatial correlation is beyond the scope of this guidance, but is very much the purview of the field of *geostatistics*. The Unified Guidance instead looks for evidence of well-to-well *spatial variation*, *i.e.*, statistically identifiable differences in mean and/or variance levels across the well field. If evident, the statistical approach would need to be modified so that distinct wells are treated as individual populations with statistical testing being conducted separately at each one (*i.e.*, intrawell comparisons).

3.2.2 STATIONARITY

A *stationary* statistical distribution is one whose population characteristics do not change over time and/or space. In a groundwater context, this means that the true population distribution of a given contaminant is the same no matter *where or when* it is sampled. In the strictest form of *stationarity*, the full distribution must be exactly the same at every time and location. However, in practice, a weaker form is usually assumed: that the population mean (μ) and variance (denoted by the Greek symbol σ^2) are the same over time and/or space.

Stationarity is important to groundwater statistical analysis because of the way that monitoring samples must be collected. If a sample set somehow represented the entire population of possible aquifer values, stationarity would not be an issue in theory. A limited number of physical groundwater samples, however, must be individually collected from each sampled location. To generate a statistical sample, the individual measurements must be pooled together over time from multiple sampling events within a well, or pooled together across space by aggregating data from multiple wells, or both.

As long as the contaminant distribution is stationary, such pooling poses no statistical problem. But with a non-stationary distribution, either the mean and/or variance is changing over time in any given well, or the means and variances differ at distinct locations. In either case, the pooled measurements are *not identically-distributed* even if they may be statistically independent.

The effects of non-stationarity are commonly seen in four basic ways in the groundwater context: 1) as spatial variability, 2) in the existence of trends and/or seasonal variation, 3) via other forms of temporal variation, and 4) in the lack of homogeneity of variance. *Spatial variability* (discussed more extensively in **Chapter 13**) refers to statistically identifiable differences in mean and/or variance levels (but usually means) across the well field (*i.e.*, spatial non-stationarity). The existence of such variation often precludes the pooling of data across multiple background wells or the proper upgradient-to-downgradient comparison of background wells against distinct compliance wells. Instead, the usual approach is to perform intrawell comparisons, where well-specific background data is culled from the early sampling history at each well. Checks for spatial variability are conducted graphically with the aid of side-by-side box plots (**Chapter 9**) and through the use of analysis of variance [ANOVA, **Chapter 13**].

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A *trend over time* at a given well location indicates that the mean level is not stationary but is instead rising or falling. A *seasonal trend* is similar in that there are periodic increases and decreases. Pooling several sampling events together thus mixes measurements with differing statistical characteristics. This can violate the identically-distributed presumption of almost all statistical tests and usually leads to an inflated estimate of the current population variance. Trends or seasonal variations identified in (upgradient) background wells or in intrawell background data from compliance wells can severely impact the accuracy and effectiveness of statistical procedures described in this guidance if data are pooled over time to establish background limits. The approach that should be taken will vary with the circumstance. Sometimes the trend component might need to be estimated and removed from the original data, so that what gets tested are the *data residuals* (*i.e.*, values that result from subtracting the estimated trend from the original data) instead of the raw measurements. In other cases, an alternate statistical approach might be needed such as a test for (positive) trend or construction of a confidence band around an estimated trend. More discussion of these options is presented in **Chapters 6**, **7**, **14**, and **21**.

To identify a linear trend, the Unified Guidance describes simple linear regression and the Mann-Kendall test in **Chapter 17**. For seasonal patterns or a combination of linear and seasonal trend effects, the guidance discusses the seasonal Mann-Kendall test and the use of ANOVA tests to identify seasonal effects. These diagnostic procedures are also presented in **Chapter 14**.

Temporal variations are distinguished in this guidance from trends or seasonal effects by the lack of a regular or identifiable pattern. Often a temporal effect will be observed as a temporary shift in concentration levels that is similar in magnitude and direction at multiple wells. This can occur at some sites, for instance, due to rainfall or recharge events. Because the mean level changes at least temporarily, pooling data over time again violates the assumption of identically-distributed data. In this case, the temporal effect can be identified by looking for parallel traces on a time series plot of multiple wells and then more formally by performing a *one-way ANOVA for temporal effects*. These procedures are described in **Chapter 14**. Once identified, the residuals from the ANOVA can be used for compliance testing, since the common temporal effect has been removed.

Lastly, *homogeneity of variance* is important in ANOVA tests, which simultaneously evaluates multiple groups of data each representing a sample from a distinct statistical population. In the latter test, well means need not be the same; the reason for performing the test in the first place is to find out whether the means do indeed differ. But the procedure assumes that all the group variances are equal or *homogeneous*. Lack of homogeneity or stationarity in the variances causes the test to be much less effective at discovering differences in the well means. In extreme cases, the concentration levels would have to differ by large amounts before the ANOVA would correctly register a statistical difference. Lack of homogeneity of variance can be identified graphically via the use of side-by-side box plots and then more formally with the use of Levene's test. Both these methods are discussed further in **Chapter 11**. Evidence of unequal variances may necessitate the use of a transformation to stabilize the variance prior to running the ANOVA. It might also preclude use of the ANOVA altogether for compliance testing, but require intrawell approaches to be considered instead.

ANOVA is not the only statistical procedure which assumes homogeneity of variance. Prediction limits and control charts require a similar assumption between background and compliance well data. But if only one new sample measurement is collected per well per evaluation period (*e.g.*, semi-annually) it can be difficult to formally test this assumption with the diagnostic methods cited above. As

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an alternative, homogeneity of variance can be periodically tested when a sufficient sample size has been collected for each compliance well (see **Chapter 6**).

3.2.3 LACK OF STATISTICAL OUTLIERS

Many authors have noted that *outliers* — extreme, unusual-looking measurements — are a regular occurrence among groundwater data (Helsel and Hirsch, 2002; Gibbons and Coleman, 2001). Sometimes an outlier results from nothing more than a typographical error on a laboratory data sheet or file. In others, the fault is an incorrectly calibrated measuring device or a piece of equipment that was not properly decontaminated. An unusual measurement might also reflect the sampling of a temporary, local 'hot spot' of higher concentration. In each of these situations, outliers in a statistical context represent values that are inconsistent with the distribution of the remaining measurements. Tests for outliers thus attempt to infer whether the suspected outlier could have reasonably been drawn from the same population as the other measurements, based on the sample data observed up to that point. Statistical methods to help identify potential outliers are discussed in **Chapter 12**, including both *Dixon's* and *Rosner's* tests, as well as references to other methods.

The basic problem with including statistical outliers in analyzing groundwater data is that they do not come from the same distribution as the other measurements in the sample and so fail the identically-distributed presumption of most tests. The consequences can be dramatic, as can be seen for instance when considering *non-parametric prediction limits*. In this testing method, one of the largest values observed in the background data such as the maximum, is often the statistic selected as the prediction limit. If a large outlier is present among the background measurements, the prediction limit may be set to this value despite being unrepresentative of the background population. In effect, it arises from another population, *e.g.*, the 'population' of typographical errors. The prediction limit could then be much higher than warranted based on the observed background data and may provide little if any probability that truly contaminated compliance wells will be identified. The test will then have lower than expected *statistical power*.

Overall, it pays to try to identify possible outliers and to either correct the value(s) if possible, or exclude known outliers from subsequent statistical analysis. It is also possible to select a statistical method that is *resistant* to the presence of outliers, so that the test results are still likely to be accurate even if one or more outliers is unidentified. Examples of this last strategy include setting non-parametric prediction limits to values other than the background maximum using repeat testing (see **Chapter 18**) or using Sen's slope procedure to estimate the rate of change in a linear trend (**Chapter 17**).

3.2.4 NORMALITY

Probability distributions introduced in **Section 3.1** are mathematical models used to approximate or represent the statistical characteristics of populations. Knowing the exact form and defining equation of a probability distribution allows one to assess how likely or unlikely it will be to observe particular measurement values (or ranges of values) when selecting or drawing independent, identically distributed [*i.i.d.*] samples from the associated population. This can be done as follows. In the case of a *continuous distributional model*, a curve can be drawn to represent the probability distribution by plotting probability values along the *y*-axis and measurement or concentration values along the *x*-axis. Since the continuum of *x*-values along this curve is infinite, the probability of occurrence of any single possible value is negligible (*i.e.*, zero), and does not equal the height of the curve. Instead, positive probabilities can be computed for *ranges* of possible values by *summing the area under the distributional curve*

associated with the desired range. Since by definition the total area under any probability distribution curve sums to unity, all probabilities are then numbers between 0 and 1.

Probability distributions form the basic building blocks of all statistical testing procedures. Every test relies on comparing one or more statistics computed from the sample data against a *reference distribution*. The reference distribution is in turn a probability distribution summarizing the expected mathematical behavior of the statistic(s) of interest. A formal statistical test utilizes this reference distribution to make inferences about the sample statistic in terms of two contrasting conditions or hypotheses.

In any event, probability distributions used in statistical testing make differing assumptions about how the underlying population of measurements is distributed. A case in point is simultaneous *prediction limits using retesting* (**Chapter 19**). The first and most common version of this test (Davis and McNichols, 1987) is based on an assumption that the sample data are drawn from a *normal probability distribution*. The normal distribution is the well-known bell-shaped curve, perhaps the single most important and frequently-used distribution in statistical analysis. However, it is not the only one. Bhaumik and Gibbons (2006) proposed similar prediction limits for data drawn from a *gamma distribution* and Cameron (2008) did the same for *Weibull-distributed* measurements. This more recent research demonstrates that prediction limits with similar statistical decision error rates can vary greatly in magnitude, depending on the type of data distribution assumed.

Because many tests make an explicit assumption concerning the distribution represented by the sample data, the form and exact type of distribution often has to be checked using a *goodness-of-fit* test. A goodness-of-fit test assesses how closely the observed sample data resemble a proposed distributional model. Despite the wide variety of probability distributions identified in the statistical literature, only a very few goodness-of-fit tests generally are needed in practice. This is because most tests are based on an assumption of *normally-distributed* or *normal* data. Even when an underlying distribution is not normal, it is often possible to use a mathematical transformation of the raw measurements (*e.g.*, taking the *natural logarithm* or *log* of each value) to *normalize* the data set. The original values can be transformed into a set of numbers that behaves as if drawn from a normal distribution. The transformed values can then be utilized in and analyzed with a *normal-theory test* (*i.e.*, a procedure that assumes the input data are normal).

Specific goodness-of-fit tests for checking and identifying data distributions are found in **Chapter 10** of this guidance. These methods all are designed to check the fit to normality of the sample data. Besides the normal, the *lognormal distribution* is also commonly used as a model for groundwater data. This distribution is not symmetric in shape like the bell-shaped normal curve, nor does it have similar statistical properties. However, a simple *log transformation* of lognormal measurements works to normalize such a data set. The *transformed values* can be tested using one of the standard goodness-of-fit tests of *normality* to confirm that the original data were indeed *lognormal*.

More generally, if a sample shows evidence of *non-normality* using the techniques in **Chapter 10**, the initial remedy is to try and find a suitable *normalizing transformation*. A set of useful possible transformations in this regard has been termed the *ladder of powers* (Helsel and Hirsch, 2002). It includes not only the natural logarithm, but also other mathematical power transformations such as the square root, the cube root, the square, *etc*. If none of these transformations creates an adequately normalized data set, a second approach is to consider what are known as *non-parametric* tests. Normal-

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theory and other similar *parametric* statistical procedures assume that the form of the underlying probability distribution is known. They are called parametric because the assumed probability distribution is generally characterized by a small set of *mathematical parameters*. In the case of the normal distribution, the general formula describing its shape and properties is completely specified by two parameters: the *population mean* (μ) and the *population variance* (σ^2). Once values for these quantities are known, the exact distribution representing a particular normal population can be computed or analyzed.

Most parametric tests do not require knowledge of the exact distribution represented by the sample data, but rather just the type of distribution (***e.g.***, normal, lognormal, gamma, Weibull, ***etc***.). In more formal terms, the test assumes knowledge of the *family of distributions* indexed by the characterizing parameters. Every different combination of population mean and variance defines a different normal distribution, yet all belong to the normal family. Nonetheless, there are many data sets for which a known distributional family cannot be identified. Non-parametric methods may then be appropriate, since a known distributional form is not assumed. Non-parametric tests are discussed in various chapters of the Unified Guidance. These tests are typically based on either a *ranking* or an *ordering* of the sample magnitudes in order to assess their statistical performance and accuracy. But even non-parametric tests may make use of a normal approximation to define how expected rankings are distributed.

One other common difficulty in checking for normality among groundwater measurements is the frequent presence of *non-detect* values, known in statistical terms as *left-censored* measurements. The magnitude of these sample concentrations is known only to lie somewhere between zero and the *detection* or *reporting limit*; hence the true concentration is partially 'hidden' or censored on the left-hand side of the numerical concentration scale. Because the most effective normality tests assume that all the sample measurements are known and quantified and not censored, the Unified Guidance suggests two possible approaches in this circumstance. First, it is usually possible to simply assume that the true distributional form of the underlying population cannot be identified, and to instead apply a non-parametric test alternative. This solution is not always ideal, especially when using prediction limits and the background sample size is small, or when using control charts (for which there is no current non-parametric alternative to the Unified Guidance recommended test).

As a second alternative, **Chapter 10** discusses methods for assessing *approximate* normality in the presence of non-detects. If normality can be established, perhaps through a normalizing transformation, **Chapter 15** describes methods for estimating the mean and variance parameters of the specific normal distribution needed for constructing tests (such as prediction limits or control charts), even though the exact value of each non-detect is unknown.

3.3 COMMON STATISTICAL MEASURES

Due to the variety of statistical tests and other methods presented in the Unified Guidance, there are a large number of equations and formulas of relevance to specific situations. The most common statistical measures used in many settings are briefly described below.

Sample mean and standard deviation — the mean of a set of measurements of sample size n is simply the arithmetic average of each of the numbers in the sample (denoted by x_i), described by formula [3.1] below. The sample mean is a common estimate of the center or middle of a statistical distribution. That is, $\bar{x}$ is an estimate of μ, the population mean. The basic formula for the sample standard deviation

is given in equation [3.2]. The sample standard deviation is an estimate of the degree of variability within a distribution, indicating how much the values typically vary from the average value or mean. Thus, the standard deviation *s* is an estimate of the population standard deviation σ. Note that another measure of variability, the sample variance, is simply the square of the standard deviation (denoted by s^2) and serves as an estimate of the population variance σ^2.

$$\bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i \qquad [3.1]$$

$$s = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}\left(x_i - \bar{x}\right)^2} \qquad [3.2]$$

Coefficient of Variation — for positively-valued measurements, the sample coefficient of variation provides a quick and useful indication of the relative degree of variability within a data set. It is computed as $s/\bar{x}$ and so indicates whether the amount of 'spread' in the sample is small or large relative to the average observed magnitude. Sample coefficients of variation can also be calculated for other distributions such as the logarithmic (see discussion on logarithmic statistics below and **Chapter 10**, **Section 10.4**).

Sample percentile — the *p*th percentile of a sample (denoted as $\tilde{x}_p$) is the value such that $p \times 100\,\%$ of the measurements are no greater than $\tilde{x}_p$, while $(1-p)\times 100\,\%$ of the values are no less than $\tilde{x}_p$. Sample percentiles are computed by making an ordered list of the measurements (termed the *order statistics* of the sample) and either selecting an observed value from the sample that comes closest to satisfying the above definition or interpolating between the pair of sample values closest to the definition if no single value meets it.

Slightly different estimates of the sample percentile are used to perform the interpolation depending on the software package or statistics textbook. The Unified Guidance follows Tukey's (1977) method for computing the lower and upper quartiles (*i.e.*, the 25th and 75th sample percentiles, termed *hinges* by Tukey) when constructing box plots (**Chapter 9**). In that setting, the pair of sample values closest to the desired percentile is simply averaged. Another popular method for more generally computing sample percentiles is to set the rank of the desired order statistic as $k = (n+1) \times p$. If k is not an integer, perform linear interpolation between the pair of ordered sample values with ranks just below and just above k.

Median and interquartile range — the sample median is the 50th percentile of a set of measurements, representing the midpoint of an ordered list of the values. It is usually denoted as $\tilde{x}$ or $\tilde{x}_{.5}$, and represents an alternative estimate of the center of a distribution. The interquartile range [IQR] is the difference between the 75th and 25th sample percentiles, thus equal to $(\tilde{x}_{.75} - \tilde{x}_{.25})$. The IQR offers an alternative estimate of variability in a population, since it represents the measurement range of the middle 50% of the ordered sample values. Both the median and the interquartile range are key statistics used to construct box plots (**Chapter 9**).

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The median and interquartile range can be very useful as alternative estimates of data centrality and dispersion to the mean and standard deviation, especially when samples are drawn from a highly skewed (i.e., non-symmetric) distribution or when one or more outliers is present. The table below depicts two data sets, one with an obvious outlier, and demonstrates how these statistical measures compare.

The median and interquartile ranges are not affected by the inclusion of an outlier (perhaps an inadvertent reporting of units in terms of ppb rather than ppm). Large differences between the mean and median, as well as between the standard deviation and interquartile range in the second data set can indicate that an anomalous data point may be present.

Data Set #1	Data Set #2
5	5
10	10
15	15
15	15
15	15
20	20
25	25,000
$\bar{x}$ = 15	$\bar{x}$ > 3,500
$\tilde{x}$ = 15	$\tilde{x}$ = 15
s = 6.5	s > 9,000
IQR = 10	IQR = 10

Log-mean, log-standard deviation and Coefficient of Variation — The lognormal distribution is a frequently-used model in groundwater statistics. When lognormally distributed data are transformed, the normally-distributed measurements can then be input into normal-theory tests. The Unified Guidance frequently makes use of quantities computed on log-transformed values. Two of these quantities, the log-mean and the log-standard deviation, represent the sample mean and standard deviation computed using log-transformed values instead of the raw measurements. Formulas for these quantities — denoted $\bar{y}$ and s_y to distinguish them from the measurement-scale mean ($\bar{x}$) and standard deviation (s) — are given below. Prior to calculating the logarithmic mean and standard deviation, the measurement scale data must first be log-transformed. Taking logarithms of the sample mean ($\bar{x}$) and the sample standard deviation (s) based on the original measurement-scale data, will not give the correct result.

$$\bar{y} = \frac{1}{n}\sum_{i=1}^{n}\log\left(x_i\right) \qquad [3.3]$$

$$s_y = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}\left(\log\left(x_i\right) - \bar{y}\right)^2} \qquad [3.4]$$

A population logarithmic coefficient of variation can be estimated from the logarithmically transformed data as: $CV_{\log} = \sqrt{e^{s_y^2} - 1}$. It is based solely on the logarithmic standard deviation, s_y, and represents the intrinsic variability of the untransformed data. .

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Sample correlation coefficient — correlation is a common numerical measure of the degree of similarity or linear association between two random variables, say x and y. A variety of statistics are used to estimate the correlation depending on the setting and how much is known about the underlying distributions of x and y. Each measure is typically designed to take on values in the range of –1 to +1, where –1 denotes perfect inverse correlation (*i.e.*, as x increases, y decreases, and vice-versa), while +1 denotes perfect correlation (*i.e.*, x and y increase or decrease together), and 0 denotes no correlation (*i.e.*, x and y behave independently of one another). The most popular measure of linear correlation is Pearson's correlation coefficient (r), which can be computed for a set of n sample pairs (x_i, y_i) as:

$$r = \frac{\sum_{i=1}^{n}\left(x_i - \bar{x}\right)\left(y_i - \bar{y}\right)}{\sqrt{\sum_{i=1}^{n}\left(x_i - \bar{x}\right)^2 \sum_{i=1}^{n}\left(y_i - \bar{y}\right)^2}} \qquad [3.5]$$

3.4 HYPOTHESIS TESTING FRAMEWORK

An important component of statistical analysis involves the testing of competing mathematical models, an activity known as *hypothesis testing*. In hypothesis testing, a formal comparison is made between two mutually exclusive possible statements about reality. Usually these statements concern the type or form of underlying statistical population from which the sample data originated, *i.e.*, either the observed data came from one statistical population or from another, but not both. The sample data are used to judge which statistical model identified by the two hypotheses is most consistent with the collected observations.

Hypothesis testing is similar in nature to what takes place in a criminal trial. Just as one of the two statements in an hypothesis test is judged true and the other false, so the defendant is declared either innocent or guilty. The opposing lawyers each develop their theory or model of the crime and what really happened. The jury must then decide whether the available evidence better supports the prosecution's theory or the defense's explanation. Just as a strong presumption of innocence is given to a criminal defendant, one of the statements in a statistical hypothesis is initially favored over the other. This statement, known as the *null hypothesis* [H_0], is only rejected as false if the sample evidence strongly favors the other side of the hypothesis, known as the *alternative hypothesis* [H_A].

Another important parallel is that the same mistakes which can occur in statistical hypothesis testing are made in criminal trials. In a criminal proceeding, the innocent can falsely be declared guilty or the guilty can wrongly be judged innocent. In the same way, if the null hypothesis [H_0] is a true statement about reality but is rejected in favor of the alternative hypothesis [H_A], a mistake akin to convicting the innocent has occurred. Such a mistake is known in statistical terms as a *false positive* or *Type I error*. If the alternative hypothesis [H_A] is true but is rejected in favor of H_0, the mistake is akin to acquitting the guilty. This mistake is known as a *false negative* or *Type II error*.

In a criminal investigation, the test hypotheses can be reversed. A detective investigating a crime might consider a list of probable suspects as potentially guilty (the null hypothesis [H_0]), until substantial evidence is found to exclude one or more suspects [H_A]. The burden of proof for accepting the alternative hypothesis and the kinds of errors which can result are the opposite from a legal trial.

Certain steps are involved in conducting any statistical hypothesis test. First, the null hypothesis H_0 must be specified and is given presumptive weight in the hypothesis testing framework. The observed sample (or a statistic derived from these data) is assumed to follow a known statistical distribution, consistent with the distributional model used to describe reality under H_0. In groundwater monitoring, a null hypothesis might posit that concentration measurements of benzene, for instance, follow a normal distribution with zero mean. This statement is contrasted against the alternative hypothesis, which is constructed as a competing model of reality. Under H_A, the observed data or statistic follows a different distribution, corresponding to a different distributional model. In the simple example above, H_A might posit that benzene concentrations follow a normal distribution, but this time with a mean no less than 20 ppb, representing a downgradient well that has been contaminated.

Complete descriptions of statistical hypotheses are usually not made. Typically, a shorthand formula is used for the two competing statements. Denoting the true population mean as the Greek letter μ and a possible value of this mean as μ_0, a common specification is:

$$H_0 : \mu \leq \mu_0 \text{ vs. } H_A : \mu > \mu_0 \quad [3.6]$$

This formulation clearly distinguishes between the location (*i.e.*, magnitude) of the population mean μ under the two competing models, but it does not specify the *form* of the underlying population itself. In most parametric tests, as explained in **Section 3.2**, the underlying model is assumed to be the normal distribution, but this is not a necessary condition or the basic assumption in all tests. Note also that a *family* of distributions is specified by the hypothesis, not two individual, specific distributions. Any distribution with a true mean no greater than μ_0 satisfies the null hypothesis, while any distribution from the same family with true mean larger than μ_0 satisfies the alternative hypothesis.

Once the statistical hypothesis has been specified, the next step is to actually collect the data and compute whatever test statistic is required based on the observed measurements and the kind of test. The pattern of the observed measurements or the computed test statistic is then compared with the population model predicted or described under H_0. Because this model is specified as a statistical distribution, it can be used to assign probabilities to different results. If the observed result or pattern occurs with very low probability under the null hypothesis model (*e.g.*, with at most a 5% or 1% chance), one of two outcomes is assumed to have occurred. Either the result is a "chance" fluctuation in the data representing a real but unlikely outcome under H_0, or the null hypothesis was an incorrect model to begin with.

A low probability of occurrence under H_0 is cause for rejecting the null hypothesis in favor of H_A, as long as the probability of occurrence under the latter alternative is also not too small. Still, one should be careful to understand that statistics involves the art of *managing uncertainty*. The null hypothesis may indeed be true, even if the measured results seem unlikely to have arisen under the H_0 model. A *small probability* of occurrence is not the same as *no possibility* of occurrence. The judgment in favor of H_A should be made with full recognition that a *false positive mistake* is always possible even if not very likely.

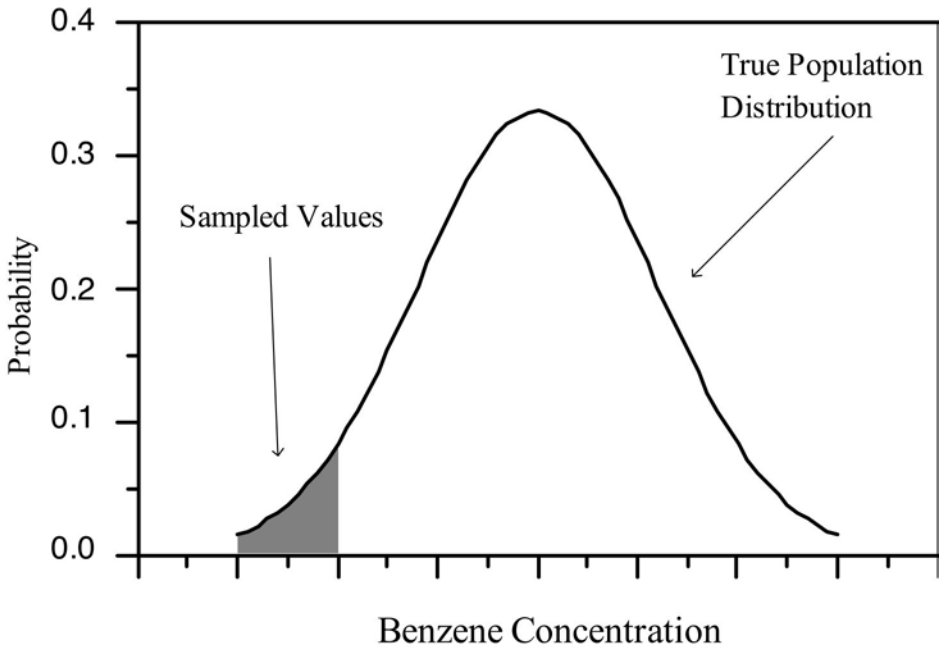
Consider the measurement of benzene in groundwater in the example above. Given natural fluctuations in groundwater composition from week-to-week or month-to-month and the variability introduced in the lab during the measurement process, the fact that one or two samples show either non-detect or very low levels of benzene does not guarantee that the true mean benzene concentration at the

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well is essentially zero. Perhaps the true mean is higher, but the specific sample values collected were gotten from the "lower tail" of the benzene distribution just by chance or were measured incorrectly in the lab. **Figure 3-1** illustrates this possibility, where the full benzene distribution is divided into a lower tail portion that has been sampled and a remaining portion that has not so far been observed. The sampled values are not representative of the entire population distribution, but only of a small part of it.

Along a similar vein, if the observed result or pattern can occur with moderate to high probability under the null hypothesis, the model represented by H_0 is accepted as consistent with the sample measurements. Again, this does not mean the null hypothesis is necessarily true. The alternative hypothesis could be true instead, in which case the judgment to accept H_0 would be considered a *false negative*. Nevertheless the sample data do not provide sufficient evidence or justification to reject the initial presumption.

Figure 3-1. Actual, But Unrepresentative Benzene Measurements



3.5 ERRORS IN HYPOTHESIS TESTING

In order to properly interpret the results of any statistical test, it is important to understand the risks of making a wrong decision. The risks of the two possible errors or mistakes mentioned above are not fixed quantities; rather, false positive and false negative risks are best thought of as statistical parameters that can be adjusted when performing a particular test. This flexibility allows one, in general, to "calibrate" any test to meet specific risk or error criteria. However, it is important to recognize what the different risks represent. RCRA groundwater regulations stipulate that any test procedure maintain a "reasonable balance" between the risks of false positives and false negatives. But how does one decide on a reasonable balance? The answer lies in a proper understanding of the real-life implications attached to wrong judgments.

3.5.1 FALSE POSITIVES AND TYPE I ERRORS

A *false positive* or *Type I error* occurs whenever the null hypothesis [H_0] is falsely rejected in favor of the alternative hypothesis [H_A]. What this means in terms of the underlying statistical models is somewhat different for every test. Many of the tests in the Unified Guidance are designed to address the basic groundwater detection monitoring framework, namely, whether the concentrations at downgradient wells are significantly greater than background. In this case, the null hypothesis is that the background and downgradient wells share the same underlying distribution and that downgradient concentrations should be consistent with background in the absence of any contamination. The alternative hypothesis presumes that downgradient well concentrations are significantly greater than background and come from a distribution with an elevated concentration.

Given this formulation of H_0 and H_A, a Type I error occurs whenever one decides that the groundwater at downgradient locations is significantly higher than background when in reality it is the *same* in distribution. A judgment of this sort concerns the underlying statistical populations and not the observed sample data. The measurements at a downgradient well may indeed be higher than those collected in background. But the disparity must be great enough to decide with confidence that the underlying *populations* also differ. A proper statistical test must account for not just the difference in *observed* mean levels but also variability in the data likely to be present in the underlying statistical populations.

False positive mistakes can cause regulated facilities to incur substantial unnecessary costs and oversight agencies to become unnecessarily involved. Consequently, there is usually a desire by regulators and the regulated community alike to minimize the false positive rate (typically denoted by the Greek letter α). For reasons that will become clear below, the false positive rate is inversely related to the false negative rate for a fixed sample size n. It is impossible to completely eliminate the risk of either Type I or Type II errors, hence the regulatory mandate to minimize the inherent tradeoff by maintaining a "reasonable balance" between false positives and false negatives.

Type I errors are strictly defined in terms of the hypothesis structure of the test. While the conceptual groundwater detection monitoring framework assumes that false positive errors are incorrect judgments of a release when there is none, Type I errors in other statistical tests may have a very different meaning. For instance, in tests of normality (**Chapter 10**) the null hypothesis is that the underlying population is normally-distributed, while the alternative is that the population follows some other, non-normal pattern. In this setting, a false positive represents the mistake of falsely deciding the population to be non-normal, when in fact it *is* normal in distribution. The implication of such an error is quite different, perhaps leading one to select an alternate test method or to needlessly attempt a normalizing transformation of the data.

As a matter of terminology, the false positive rate α is also known as the *significance level* of the test. A test conducted at the $\alpha = .01$ level of significance means there is at most a 1% chance or probability that a Type I error will occur in the results. The test is likely to lead to a false rejection of the null hypothesis at most about 1 out of every 100 times the same test is performed. Note that this last statement says nothing about how well the test will work if H_A is true, when H_0 *should* be rejected. The

false positive rate strictly concerns those cases where H_0 is an accurate reflection of the physical reality, but the test rejects H_0 anyway.

3.5.2 SAMPLING DISTRIBUTIONS, CENTRAL LIMIT THEOREM

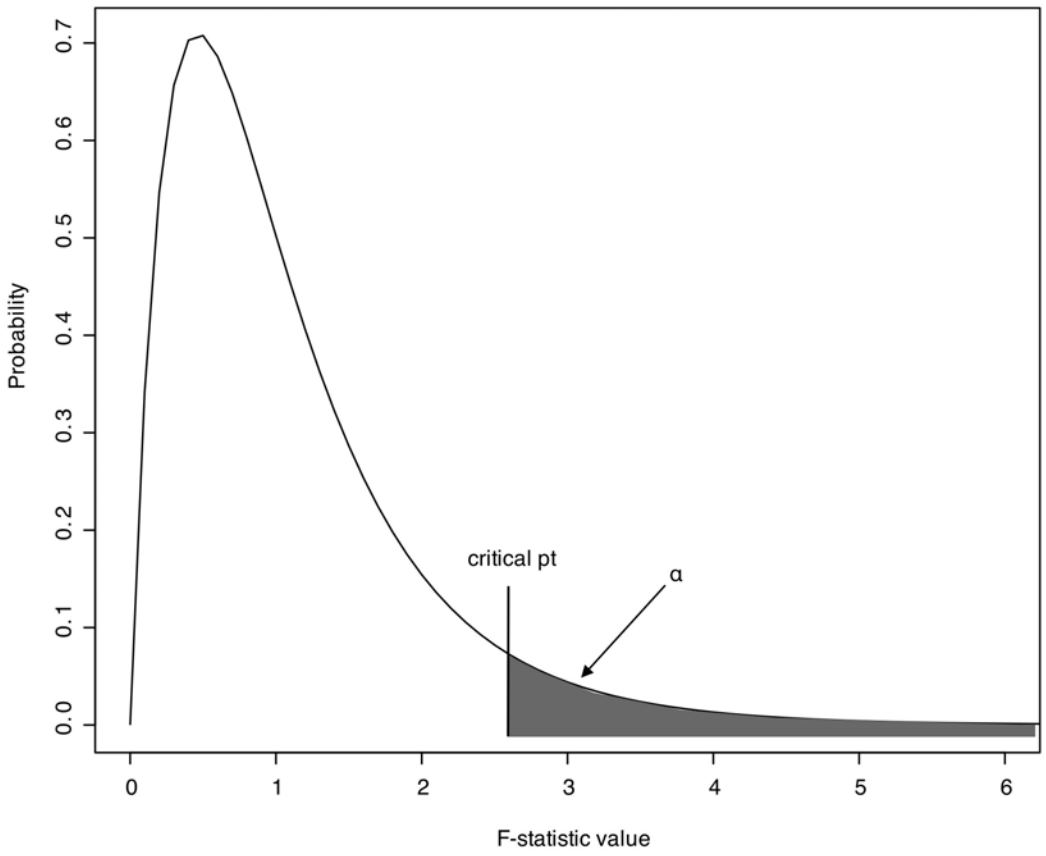
The false positive rate of any statistical test can be calibrated to meet a given risk criterion. To see how this is done, it helps to understand the concept of *sampling distribution*. Most statistical test decisions are based on the magnitude of a particular test statistic computed from the sample data. Sometimes the test statistic is relatively simple, such as the sample mean ($\bar{x}$), while in other instances the statistic is more complex and non-intuitive. In every case, however, the test statistic is formulated as it is for a specific purpose: *to enable the analyst to identify the distributional behavior of the test statistic under the null hypothesis*. Unless one knows the expected behavior of a test statistic, probabilities cannot be assigned to specific outcomes for deciding when the probability is too low to be a chance fluctuation of the data.

The distribution of the test statistic is known as its *sampling distribution*. It is given a special name, in part, to distinguish the behavior of the *test statistic* from the potentially different distribution of the *individual observations or measurements* used to calculate the test. Once identified, the sampling distribution can be used to establish *critical points* of the test associated with specific maximal false positive rates for any given α level of significance. For most tests, a single level of significance is generally chosen.

An example of this idea can be illustrated via the *F*-test. It is used for instance in parametric analysis of variance [ANOVA] to identify differences in the population means at three or more monitoring wells. Although ANOVA assumes that the individual measurements input to the test are normally-distributed, the test statistic under a null hypothesis [H_0] of no differences between the true means follows an *F*-distribution. More specifically, it applies to one member of the *F*-distribution family (an example using 5 wells and 6 measurements per well is pictured in **Figure 3-2**). As seen in the right-hand tail of this distribution by summing the area under the distributional curve, large values of the *F*-statistic become less and less probable as they increase in magnitude. For a given significance level (α), there is a corresponding *F*-statistic value such that the probability of exceeding this cutoff value is α or less. In such situations, there is at most an $\alpha \times 100\%$ chance of observing an F-statistic *under* H_0 that is as large or larger than the cutoff (shaded area in **Figure 3-2**). If α is quite small (*e.g.*, 5% or 1%), one may then judge the null hypothesis to be an untenable model and accept H_A. As a consequence, the cutoff value can be defined as an α-level *critical point* for the *F*-test.

Because test statistics can be quite complicated, there is no easy rule for determining the sampling distribution of a particular test. However, the sampling behavior of some statistics is a consequence of a fundamental result known as the *Central Limit Theorem*. This theorem roughly states that averages or sums of identically-distributed random variables will follow an approximate normal distribution, regardless of the distributional behavior of the individual measurements. This averaged distribution will have the *same* mean μ as the population of individual measurements and whose variance, compared to the underlying population variance σ^2, is scaled by a factor of the sample size *n* on which the average or sum is based. Specifically, the variance is greater by a factor of *n* in the case of a sum $\left(n \cdot \sigma^2\right)$ and smaller by a factor of *n* in the case of an average $\left(\sigma^2/n\right)$. The approximation of the averages or sums to the normal distribution improves as sample size increases (also see the power discussion on page 3-21).

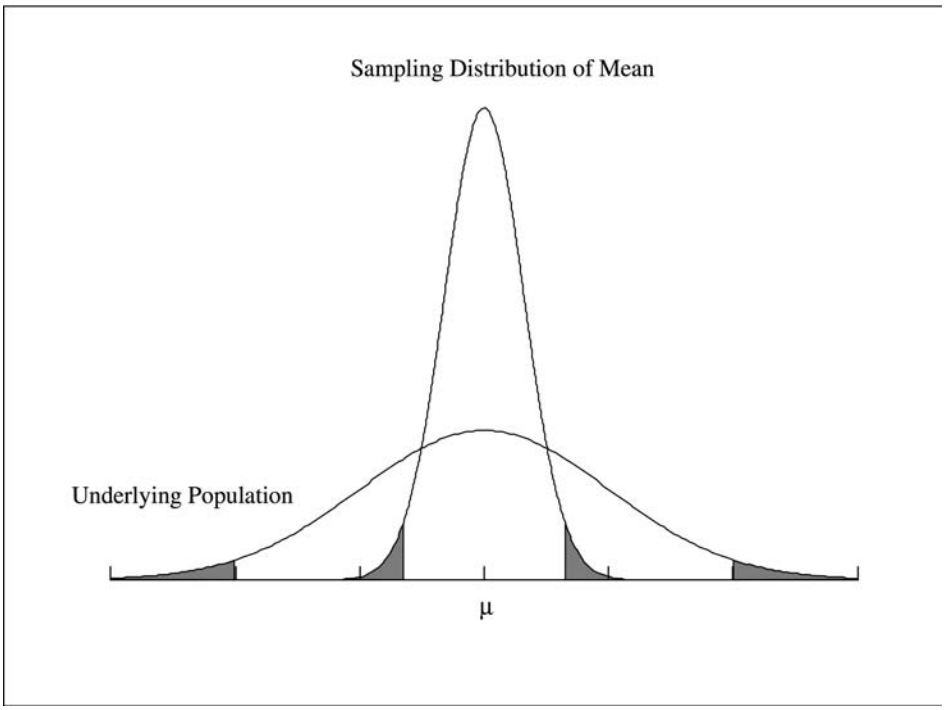
Figure 3-2. F-Distribution with 4 and 25 Degrees of Freedom



Because of the Central Limit Theorem, a number of test statistics at least approximately follow the normal distribution. This allows critical points for these tests to be determined from a table of the standard normal distribution. The Central Limit Theorem also explains why sample means provide a better estimate of the true population mean than individual measurements drawn from the same population (**Figure 3-3**). Since the sampling distribution of the mean is centered on the true average (μ) of the underlying population and the variance is lower by a factor of n, the sample average $\bar{x}$ will tend to be much closer to μ than a typical individual measurement.

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Figure 3-3. Effect of Central Limit Theorem



3.5.3 FALSE NEGATIVES, TYPE II ERRORS, AND STATISTICAL POWER

False negatives or Type II errors are the logical opposites of false positive errors. An error of this type occurs whenever the null hypothesis [H_0] is accepted, but instead the alternative hypothesis [H_A] is true. The false negative rate is denoted by the Greek letter β. In terms of the groundwater detection monitoring framework, a Type II error represents a mistake of judging the compliance point concentrations to be consistent with background, when in reality the compliance point distribution is *higher* on average. False negatives in this context describe the risk of *missing* or *not identifying* contaminated groundwater when it really exists. EPA has traditionally been more concerned with such false negative errors, given its mandate to protect human health and the environment.

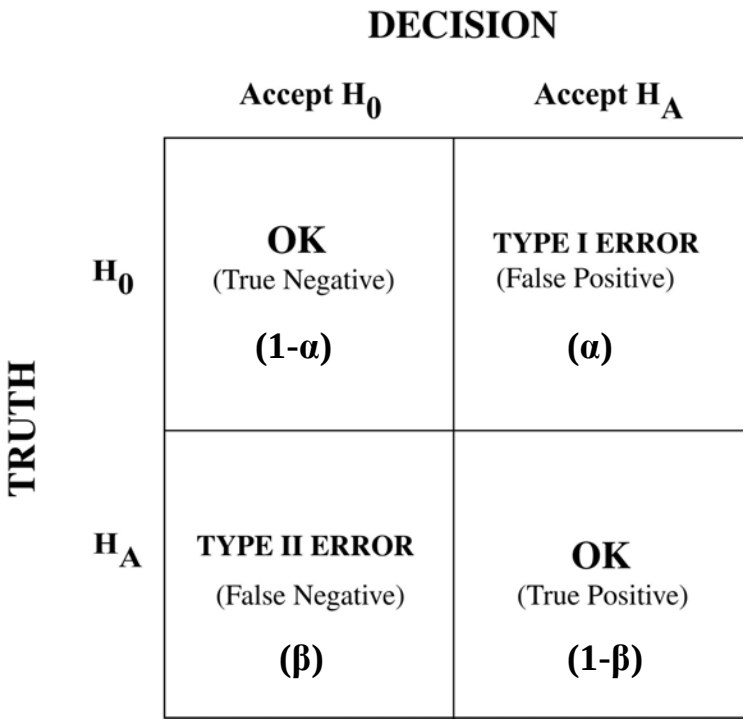
Statistical power is an alternate way of describing false negative errors. Power is merely the complement of the false negative rate. If β is the probability of a false negative, (1–β) is the statistical power of a particular test. In terms of the hypothesis structure, statistical power represents the probability of correctly rejecting the null hypothesis. That is, it is the minimum chance that one will decide to accept H_A, given that H_A is true. High power translates into a greater probability of identifying contaminated groundwater when it really exists.

A convenient way to keep track of the differences between false positives, false negatives, and power is via a Truth Table (**Figure 3-4**). A truth table distinguishes between the *underlying* truth of each hypothesis H_0 or H_A and the *decisions* made on the basis of statistical testing. If H_0 is true, then a decision to accept the alternative hypothesis (H_A) is a false positive error which will occur with a

probability of at most α. Because only one of two decisions is possible, H_0 will also be accepted with a probability of at least (1–α). This is also known as the confidence probability or confidence level of the test, associated with making a 'true negative' *decision*. Similarly if H_A is actually true, making a false negative decision error by accepting the null hypothesis (H_0) has at most a probability of β. Correctly accepting H_A when true then has a probability of at least (1– β) and is labeled a 'true positive' decision. This probability is also known as the statistical power of the test.

For any application of a test to a particular sample, only one of the two types of decision errors can occur. This is because only one of the two mutually exclusive hypotheses will be a true statement. In the detection monitoring context, this means that if a well is *uncontaminated* (*i.e.*, H_0 is true), it may be possible to commit a Type I false positive mistake, but it is *not* possible to make a Type II false negative error. Similarly, if a *contaminated* well is tested (*i.e.*, H_A is true), Type I false positive errors *cannot* occur, but a Type II false negative error might occur.

Figure 3-4. Truth Table in Hypothesis Testing



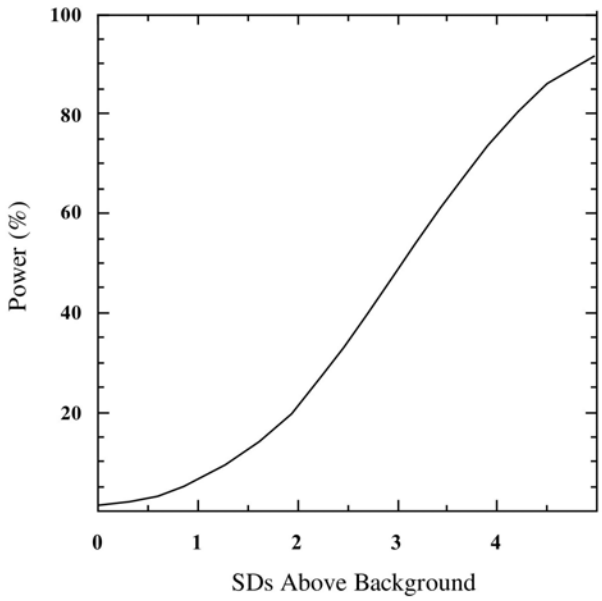
Since the false positive rate can be fixed in advance of running most statistical tests by selecting α, one might think the same could be done with statistical power. Unfortunately, neither statistical power nor the false negative rate can be fixed in advance for a number of reasons. One is that power and the false negative rate depends on the degree to which the true mean concentration level is elevated with respect to the background null condition. Large concentration increases are easier to detect than small increments. In fact, power can be graphed as an increasing function of the true concentration level in what is termed a *power curve* (**Figure 3-5**). A power curve indicates the probability of rejecting H_0 in favor of the alternative H_A for any given alternative to the null hypothesis (*i.e.*, for a range of possible mean-level increases above background).

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In interpreting the power curve below, note that the *x*-axis is labeled in terms of relative background standard deviation units (σ) above the true background population mean (μ). The zero point along the *x*-axis is associated with the background mean itself, while the *k*th positive unit along the axis represents a 'true' mean concentration in the compliance well being tested equal to $\mu + k\sigma$. This mode of scaling the graph allows the same power curve to be potentially applied to any constituent of interest subject to the same test conditions. This is true no matter what the typical background concentration levels of a chemical typically found in groundwater may be. But it also means that the same point along the power curve will represent different absolute concentrations for different constituents. Even if the background means are the same, a two standard deviation increase in a chemical with highly variable background concentrations will correspond to a larger population mean increase at a compliance well than the same relative increase in a less variable constituent.

As a simple example, if the background population averages for arsenic and manganese both happen to be 10 ppb, but the arsenic standard deviation is 5 ppb while that for manganese is only 2 ppb, then a compliance well with a mean equivalent to a three standard deviation increase over background would have an average arsenic level of 25 ppb, but an average manganese level of only 16 ppb. For both constituents, however, there would be approximately a 50% probability of detecting a difference between the compliance well and background.

Figure 3-5. Example Power Curve



Because the power probability depends on the relative difference between the actual downgradient concentration level and background, power cannot typically be fixed ahead of time like the critical false positive rate for a test. The true concentration level (and associated power) in a compliance well is unknown. If it were known, no hypothesis test would be needed. Additionally, it is often not clear what specific magnitude of increase over background is environmentally significant. A two standard deviation increase over the background average might not be protective of human health and/or the

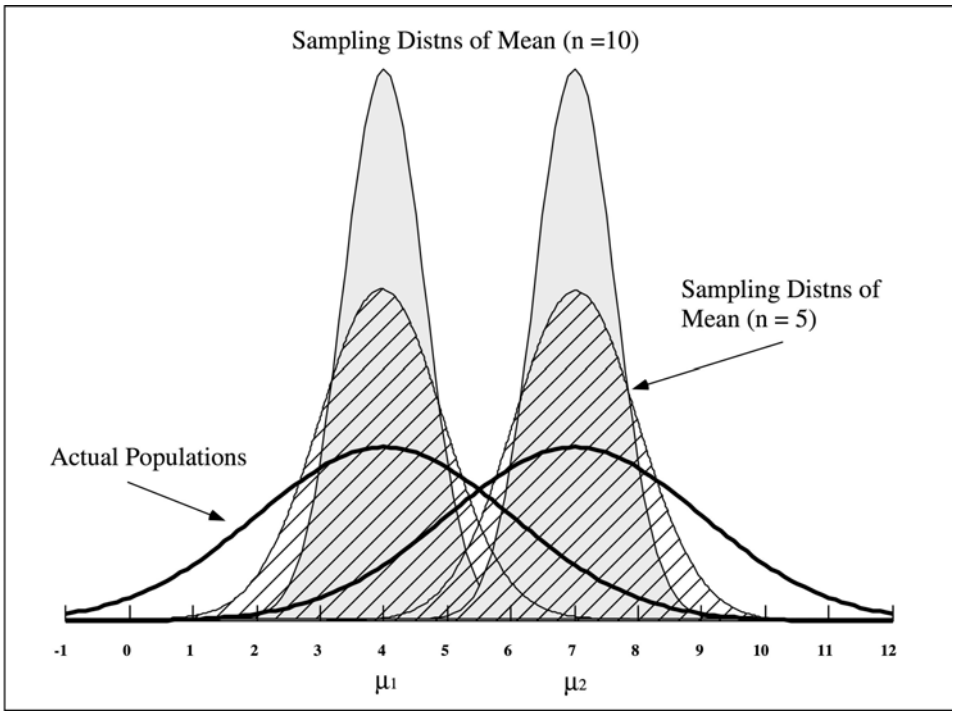
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environment for some monitoring situations. For others, a four standard deviation increase or more may be tolerable before any threat is posed.

Since the exact ramifications of a particular concentration increase are uncertain, it points to the difficulty in setting a minimum power requirement (or a maximum false negative rate) for a given statistical test. Some State statutes contain water quality non-degradation provisions, for which *any* measurable increase might be of concern. By emphasizing relative power as in **Figure 3-5**, all detection monitoring constituents can be evaluated for significant concentration increases on a common footing, subject only to differences in measurement variability.

Another key factor affecting statistical power is sample size. All other test conditions being equal, larger sample sizes provide higher statistical power and the lower the false negative rate (β). Statistical tests perform more accurately with larger data sets, leading to greater power and fewer errors in the process. The Central Limit Theorem illustrates why this is true. Even if a downgradient well mean level is only slightly greater than background, upgradient and downgradient well sample means will have so little variance in their sampling distributions with enough measurements that they will tend to hover very close to their respective population means. True mean differences in the underlying populations can be distinguished with higher probability as sample sizes increase. In **Figure 3-6**, the sampling distributions of means of size 5 and 10 between two different normal populations are provided for illustration. The narrower width of the distribution for the n = 10 sample means are more clearly distinguished from each other than for means of sample size n = 5. This implies higher probability and power to distinguish between the two population means.

Figure 3-6. Why Statistical Power Increases with Sample Size



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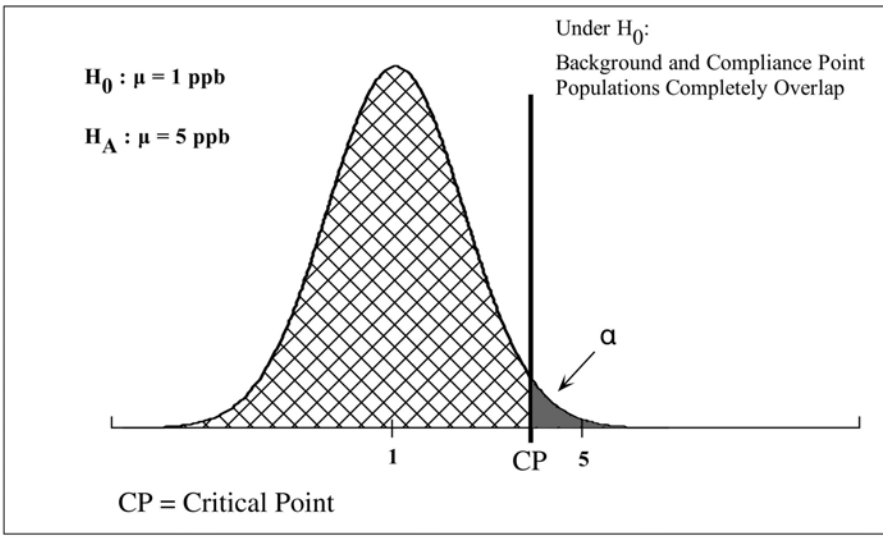
3.5.4 BALANCING TYPE I AND TYPE II ERRORS

In maintaining an appropriate balance between false positive and false negative error rates, one would ideally like to simultaneously minimize both kinds of errors. However, both risks are inherent to any statistical test procedure, and the risk of committing a Type I error is indirectly but inversely related to the risk of a Type II error unless the sample size can be increased. It is necessary to find a *balance* between the two error rates. But given that the false negative rate depends largely on the true compliance point concentrations, it is first necessary to designate what specific mean difference (known as an *effect size*) between the background and compliance point populations should be considered environmentally important. A minimum power requirement can be based on this difference (see **Chapter 6**).

►EXAMPLE 3-1

Consider a simple example of using the downgradient sample mean to test the proposition that the downgradient population mean is 4 ppb larger than background. Assume that extensive sampling has demonstrated that the background population mean is equal to 1 ppb. If the true downgradient mean were the same as the background level, curves of the two sampling distributions would coincide (as depicted in **Figure 3-7**). Then a critical point (e.g., CP = 4.5 ppb) can be selected so that the risk of a false positive mistake is α. The critical point establishes the decision criteria for the test. If the observed sample mean based on randomly selected data from the downgradient sampling distribution exceeds the critical point, the downgradient population will be declared higher in concentration than the background, even though this is not the case. The frequency that such a wrong decision will be made is just the area under the sampling distribution to the right of the critical point equal to α.

Figure 3-7. Relationship Between Type I and Type II Errors, Part A

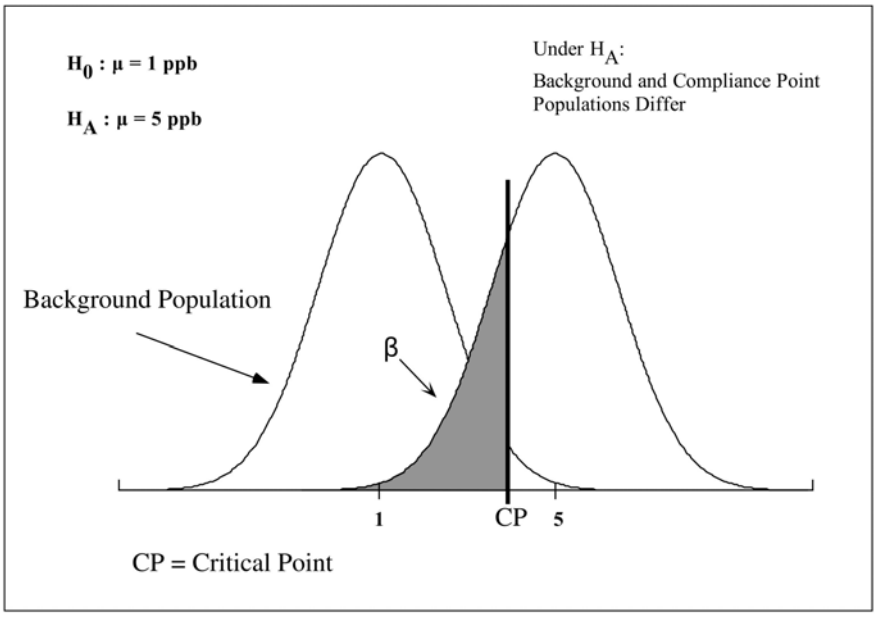


If the true downgradient mean is actually 5 ppb, the sampling distribution of the mean will instead be centered over 5 ppb as in the right-hand curve (*i.e.*, the downgradient population) in **Figure 3-8**. Since there really is a difference between the two populations, the alternative hypothesis and *not* the null

hypothesis is true. Thus, any observed sample mean drawn from the downgradient population then falling below the critical point is a false negative mistake. Consequently, the area under the right-hand sampling distribution in **Figure 3-8** to the *left* of the critical point represents the frequency of Type II errors (β).

The false negative rate (β) in **Figure 3-8** is obviously larger than the false positive rate (α) of **Figure 3-7**. This need not be the case in general, but the key point is to understand that for a fixed sample size, the Type I and Type II error rates cannot be simultaneously minimized. If α is increased, by selecting a lower critical point in **Figure 3-7**, the false negative rate will also be lowered in **Figure 3-8**. Likewise, if α is decreased by selecting a higher critical point, β will be enlarged. If the false positive rate is indiscriminately lowered, the false negative rate (or reduced power) will likely reach unacceptable levels even for mean concentration levels of environmental importance. Such reasoning lay behind EPA's decision to mandate *minimum* false positive rates for *t*-tests and ANOVA procedures in both the revised 1988 and 1991 RCRA rules.

Figure 3-8. Relationship Between Type I and Type II Errors, Part B



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CHAPTER 4. GROUNDWATER MONITORING PROGRAMS AND STATISTICAL ANALYSIS

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This chapter provides an overview of the basic groundwater monitoring framework, explaining the intent of the federal groundwater statistical regulations and offering insight into the key identification mechanism of groundwater monitoring, the ***statistically significant increase*** [SSI]:

- What are statistically significant increases and how should they be interpreted?
- What factors, both statistical and non-statistical can cause SSIs?
- What factors should be considered when demonstrating that an SSI does not represent evidence of actual contamination?

4.1 THE GROUNDWATER MONITORING CONTEXT

The RCRA regulations frame a consistent approach to groundwater monitoring, defining the conditions under which statistical testing takes place. Upgradient and downgradient wells must be installed to monitor the uppermost aquifer in order to identify releases or changes in existing conditions as expeditiously as possible. Geological and hydrological expertise is needed to properly locate the monitoring wells in the aquifer passing beneath the monitored unit(s). The regulations identify a variety of design and sampling requirements for groundwater monitoring (such as measuring well piezometric surfaces and identifying flow directions) to assure that this basic goal is achieved. Indicator or hazardous constituents are measured in these wells at regular time intervals; these sample data serve as the basis for statistical comparisons. For identifying releases under detection monitoring, the regulations generally presume comparisons of observations from downgradient wells against those from upgradient wells (designated as background). The rules also recognize certain situations (***e.g.***, mounding effects) when other means to define background may be necessary.

The Unified Guidance may apply to facility groundwater monitoring programs straddling a wide range of conditions. In addition to units regulated under Parts 264 and 265 Subpart F and Part 258 solid waste landfills, other non-regulated units at Subtitle C facilities or CERCLA sites may utilize similar programs. Monitoring can vary from a regulatory minimum of one upgradient and three downgradient wells, to very large facilities with multiple units, and perhaps 50-200 upgradient and downgradient wells. Although the rules presume that monitoring will occur in the single uppermost aquifer likely to be affected by a release, complex geologic conditions may require sampling and evaluating a number of aquifers or strata.

Detection monitoring constituents may include indicators like common ions and other general measures of water quality, pH, specific conductance, total organic carbon [TOC] and total organic halides [TOX]. Quite often, well monitoring data sets are obtained for filtered or unfiltered trace elements (or both) and sizeable suites of hazardous trace organic constituents, including volatiles, semi-volatiles, and pesticide/herbicides. Measurement and analysis of hazardous constituents using standard methods (in SW-846 or elsewhere) have become fairly routine over time. A large number of analytes may be potentially available as monitoring constituents for statistical testing, perhaps 50-100 or more. Identification of the most appropriate constituents for testing depends to a great extent on the composition of the managed wastes (or their decomposition products) as measured in leachate analyses, soil gas sampling, or from prior knowledge.

Nationally, enough groundwater monitoring experience has been gained in using routine constituent lists and analytical techniques to suggest some common underlying patterns. This is particularly true when defining background conditions in groundwater. Sampling frequencies have also been standardized enough (***e.g.***, semi-annual or quarterly sampling) to enable reasonable computation of the sorts of sample sizes that can be used for statistical testing. Nevertheless, complications can and do occur over time — in the form of changes in laboratories, analytical methods, sampled wells, and sampling frequencies — which can affect the quality and availability of sample data.

Facility status can also affect what data are potentially available for evaluation and testing — from lengthy regulated unit monitoring records under the Part 265 interim status requirements at sites awaiting either operational or post-closure 264 permits or permit re-issuance, to a new solid waste facility located in a zone of uncontaminated groundwater with little prior data. Some combined RCRA/CERCLA facilities may have collected groundwater information under differing program requirements. Contamination from offsite or non-regulated units (or solid waste management units) may complicate assessment of likely contaminant sources or contributions.

Quite often, regulators and regulated parties find themselves with considerable amounts of historical constituent-well monitoring data that must be assessed for appropriate action, such as a permit, closure, remedial action or enforcement decision. Users will need to closely consider the diagnostic procedures in **Part II** of the Unified Guidance, with an eye towards selection of one or more appropriate statistical tests in **Parts III** and **IV**. Selection will depend on key factors such as the number of wells and constituents, statistical characteristics of the observed data, and historical patterns of contamination (if present), and may also reflect preferences for certain types of tests. While the Unified Guidance purposely identifies a range of tests which might fit a situation, it is generally recommended that *one* set of tests be selected for final implementation, in order to avoid "test-shopping" (i.e., selecting tests during permit implementation based on the most favorable outcomes). EPA recognizes that the final permit requirements are approved by the regulatory agency.

All of the above situations share some features in common. A certain number of facility wells will be designated as compliance points, ***i.e.***, those locations considered as significant from a regulatory standpoint for assessing potential releases. Similarly, the most appropriate and critical indicator and/or hazardous constituents for monitoring will be identified. If detection monitoring (***i.e.***, comparative evaluations of compliance wells against background) is deemed appropriate for some or all wells and constituents, definitions of background or reference comparison levels will need to be established. Background data can be obtained either from the upgradient wells or from the historical sampling database as described in **Chapter 5**. Choice of background will depend on how statistically comparable

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the compliance point data are with respect to background and whether individual constituents exhibit spatial or temporal variability at the facility.

Compliance/assessment or corrective action monitoring may be appropriate choices when there is a prior or historical indication of hazardous constituent releases from a regulated unit. In those situations, the regulatory agency will establish GWPS limits. Typically, these limits are found in established tables, in SDWA drinking water MCLs, through risk-based calculations or determined from background data. For remedial actions, site-specific levels may be developed which account not only for risk, but achievability and implementation costs as well. Nationally, considerable experience has been gathered in identifying cleanup targets which might be applicable at a given facility, as well as how practical those targets are likely to be.

Use of the Unified Guidance should thus be viewed in an overall context. While the guidance offers important considerations and suggestions in selecting and designing a statistically-based approach to monitoring, it is important to realize that it is only a part of the overall decision process at a facility. Geologic and hydrologic expertise, risk-based decisions, and legal and practical considerations by the regulated entity and regulatory agency are fundamental in developing the final design and implementation. The guidance does not attempt to address the many other relevant decisions which impact the full design of a monitoring system.

4.2 RCRA GROUNDWATER MONITORING PROGRAMS

Under the RCRA regulations, some form of statistical testing of sample data will generally be needed to determine whether there has been a release, and if so, whether concentration levels lie below or above a protection standard. The regulations frame the testing programs as detection, compliance/assessment, and corrective action monitoring.

Under RCRA permit development and during routine evaluations, all three monitoring program options may need to be simultaneously considered. Where sufficient hazardous constituent data from site monitoring or other evidence of a release exists, the regulatory agency can evaluate which monitoring program(s) are appropriate under §264.91. Statistical principles and testing provided in the Unified Guidance can be used to develop presumptive evidence for one program over another.

In some applications, more than one monitoring program may be appropriate. Both the number of wells and constituents to be tested can vary among the three monitoring programs at a given site. The types of non-hazardous indicator constituents used for detection monitoring might not be applied in compliance or corrective action monitoring. The latter focus is on hazardous constituents. Only a few compliance well constituents may exceed their respective GWPSs. The focus in a corrective action monitoring program might then be placed on the latter, with the remaining well constituents evaluated under the other monitoring schemes. But following the general regulatory structure, the three monitoring systems are presented below and elsewhere in the guidance as an ordered sequence:

Detection monitoring is appropriate either when there is no evidence of a release from a regulated unit, or when the unit situated in a historically contaminated area is not impacted by current RCRA waste management practices. Care must be taken to avoid a situation where the constituents might reasonably have originated offsite or from units not subject to testing, since any adverse change in groundwater quality would be attributed to on-site causes. Whether an observed change in groundwater

quality is in fact due to a release from on-site waste activities at the facility may be open to dispute and/or further demonstration. However, this basic framework underlies each of the statistical methods used in detection monitoring.

A crucial step in setting up a detection monitoring program is to establish a set of *background* measurements, a baseline or reference level for statistical comparisons (see **Chapter 5**). Groundwater samples from compliance wells are then compared against this baseline to measure changes in groundwater quality. If at least one chemical parameter on the monitoring indicates a *statistically significant increase* above the baseline [SSI, see **Section 4.3**], the facility or regulated unit moves into the next phase: compliance or assessment monitoring.

Compliance or assessment monitoring[1] is appropriate when there is reliable statistical evidence that a concentration increase over the baseline has occurred. The purpose of compliance/assessment monitoring is two-fold: 1) to assess the extent of contamination (*i.e.*, the size of the increase, the chemical parameters involved, and the locations on-site where contamination is evident); and 2) to measure compliance with pre-established numerical concentration limits generally referred to as GWPSs. Only the second purpose is fully addressed using formal statistical tests. While important information can be gleaned from compliance well data, more complex analyses (*e.g.*, contaminant modeling) may be needed to address the first goal.

GWPSs can be fixed health- or risk-based limits, against which single-sample tests are made. At some sites, no specific fixed concentration limit may be assigned or readily available for one or more monitoring parameters. Instead, the comparison is made against a limit developed from background data. In this case, an appropriate statistical approach might be to use the background measurements to compute a statistical limit and set it as the GWPS. See **Chapter 7** for further details. Many of the detection monitoring design principles (**Chapter 6**) and statistical tests (**Part III**) can also be applied to a set of constituents defined by a background-type GWPS.

The RCRA Parts 264 and 258 regulations require an expanded analysis of potential hazardous constituents (Part 258 Appendix II for municipal landfills or Part 264 Appendix IX for hazardous waste units) when detection monitoring indicates a release and compliance monitoring is potentially triggered. The purpose is to better gauge which hazardous constituents have actually impacted groundwater. Some detection monitoring programs may require only limited testing of indicator parameters. This additional sampling can be used to determine which wells have been impacted and provide some understanding of the on-site distribution of hazardous constituent concentrations in groundwater. . The course of action decided by the Regional Administrator or State Director will depend on the number of such chemicals that are present in quantifiable levels and the actual concentration levels.

[1] The terms compliance monitoring (§264.99 & 100) and assessment monitoring (§258.55 & 56) are used interchangeably in this document to refer to RCRA monitoring programs. Compliance monitoring is generally used for permitted hazardous waste facilities under RCRA Subtitle C, while assessment monitoring is applied to municipal solid waste landfills regulated under RCRA Subtitle D. The term "assessment" is also used in 40 CFR 265 Subpart F for a second phase of additional analyte testing. Occasional use is also made of the term "compliance wells," which refers to downgradient monitoring wells located at the point(s) of compliance under §264.95 (any of the three monitoring programs may apply when evaluating these wells).

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Following the occurrence of a valid statistically significant increase [SSI] over baseline during detection monitoring, the statistical presumption in compliance/assessment monitoring is quite similar to the detection stage. Given *G* as a fixed compliance or background-derived GWPS, the null hypothesis is that true concentrations (of the underlying compliance point population) are no greater than *G*. This compares to the detection monitoring presumption that concentration levels do not exceed background. One reason for the similarity is that compliance limits may be higher than background levels in some situations. An increase over background in these situations does not necessarily imply an increase over the compliance limit, and the latter must be formally tested. On the other hand, if a health- or risk-based limit is below a background level, the RCRA regulations provide that the GWPS should be based on background.

The Subtitle D regulations for municipal solid waste landfills [MSWLF] stipulate[2] that if "the concentrations of all Appendix II constituents are shown to be at or below background values, using the statistical procedures in §258.53(g), for two consecutive sampling events, the owner or operator... may return to detection monitoring." In other words, assessment monitoring may be exited in favor of detection monitoring when concentrations at the compliance wells are statistically indistinguishable from background for two consecutive sampling periods. While a demonstration that concentration levels are below background would generally not be realistic, it may be possible to show that compliance point levels of contaminants do not exceed an upper limit computed from the background data. Conformance to the limit would then indicate an inability to statistically distinguish between background and compliance point concentration levels.

If a hazardous constituent under compliance or assessment monitoring statistically exceeds a GWPS, the facility is subject to **corrective action.** Remedial activities must be undertaken to remove and/or prevent the further spread of contamination into groundwater. **Monitoring** under corrective action is used to track the progress of remedial activities and to determine if the facility has returned to compliance. Corrective action is usually preceded or accompanied by a formal Remedial Investigation [RI] or RCRA Facility Investigation [RFI] to further delineate the nature and extent of the contaminated plume. Corrective action may be confined to a single regulated unit if only that unit exhibits SSIs above a standard during the detection and compliance/assessment monitoring phases.

Often, clean-up levels are established by the Regional Administrator or State Director during corrective action. Remediation must continue until these clean-up levels are met. The focus of remedial action and monitoring would be on those hazardous constituents and well locations exceeding the GWPSs. If specific clean-up levels have not been met, corrective action must continue until there is evidence of a *statistically significant decrease* [SSD] below the compliance limit for three consecutive years. At this point, corrective action may be exited and compliance monitoring re-started. (As described above and in **Chapter 7**, the protocol for assessing corrective action compliance with a background-type standard can differ). If subsequent concentrations are statistically indistinguishable from background or no detectable concentrations can be demonstrated for three consecutive years in any of the contaminants that triggered corrective measures in the first place, corrective action may be exited in favor of detection monitoring.

[2] [56 FR 51016] October 9, 1991

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4.3 STATISTICAL SIGNIFICANCE IN GROUNDWATER TESTING

The outcome of any statistical test is judged either to be statistically significant or non-significant. In groundwater monitoring, a valid statistically significant result can force a change in the monitoring program, perhaps even leading to remedial activity. Consequently, it is important to understand what statistically significant results represent and what they do not. In the language of groundwater hypothesis testing (**Chapter 3**), a statistically significant test result is a decision to reject the null hypothesis (H_0) and to accept the alternative hypothesis (H_A), based on the observed pattern of the sample data. At the most elementary level, a *statistically significant increase* [SSI] (the kind of result typically of interest under RCRA detection and compliance monitoring) represents an observed increase in concentration at one or more compliance wells. In order to be declared an SSI, the change in concentration must be large enough after accounting for variability in the sample data, that the result is unlikely to have occurred merely by chance. What constitutes a statistically significant result depends on the phase of monitoring and the type of statistical test being employed.

If the detection monitoring statistical test being used is a *t*-test or Wilcoxon rank-sum test (**Chapter 16**), an SSI occurs whenever the *t*-statistic or *W*-statistic is larger than an α-level critical point for the test. If a retesting procedure is chosen using a prediction limit (**Chapter 19**), an SSI occurs only when both the initial compliance sample or initial mean/median and one or more resamples all exceed the upper prediction limit. For control charts (**Chapter 20**), an SSI occurs whenever either the CUSUM or Shewhart portions of the chart exceed their respective control limits. In another variation, an SSI only occurs if one or another of the CUSUM or Shewhart statistics exceeds the control limits when recomputed using one or more resamples. For tests of trend (**Chapter 17**), an SSI is declared whenever the slope is significantly greater than zero at some significance level α.

In compliance/assessment monitoring, tests are often made against a fixed compliance limit or GWPS. In this setting, one can utilize a *confidence interval* around a mean, median, upper percentile or a trend line (**Chapter 21**). A confidence interval is an estimated concentration or measurement range intended to contain a given statistical characteristic of the population from which the sample is drawn. A most common formulation is a two-way confidence interval around a normally-distributed mean μ, as shown below:

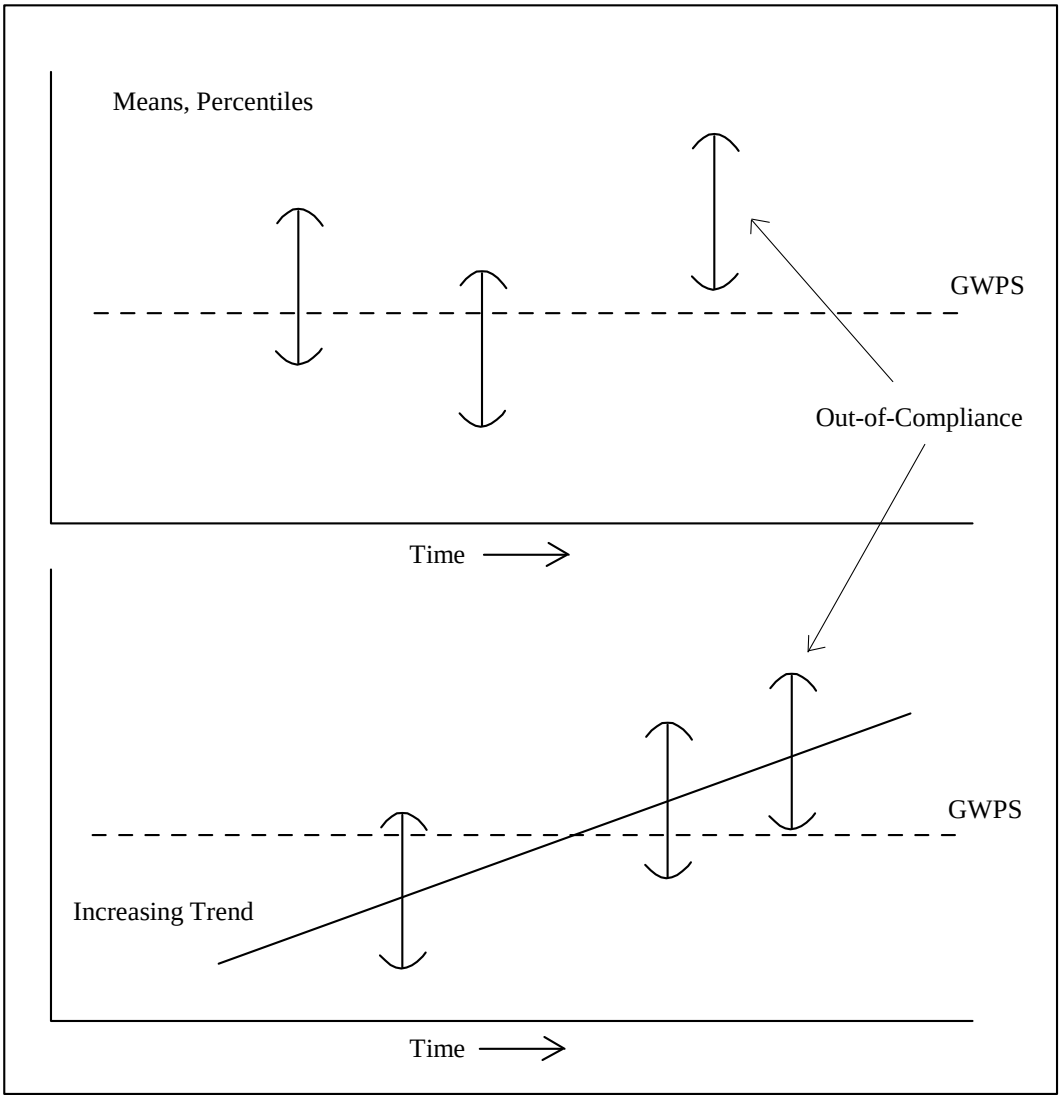
$$\left(\bar{x} - t_{1-\alpha,n-1} \frac{s}{\sqrt{n}} \quad \leq \quad \mu \quad \leq \quad \bar{x} + t_{1-\alpha,n-1} \frac{s}{\sqrt{n}} \right) \qquad [4.1]$$

where $\bar{x}$ is the mean of a sample of size n, s is the sample standard deviation, and $t_{1-\alpha,\, n-1}$ is an upper percentile selected from a Student's *t*-distribution. By constructing a range around the sample mean ($\bar{x}$), this confidence interval is designed to locate the true population mean (μ) with a high degree of *statistical confidence(1-2α)* or conversely, with a low probability of error (2α). If a one-way lower confidence interval is used, the right-hand term in equation [4.1] would be replaced by $+\infty$ at confidence level $1-\alpha$. In a similar fashion, the upper $1-\alpha$ confidence interval would be defined in the range from $-\infty$ for the left-hand term to the right hand term in equation [4.1].

When using a *lower confidence interval* on the mean, median, or upper percentile, an SSI occurs whenever the lower edge of the confidence interval range exceeds the GWPS. For a confidence interval around a trend line, an SSI is declared whenever the lower confidence limit around the estimated trend

line *first* exceeds the GWPS at some point in time. By requiring that a lower confidence limit be used as the basis of comparison, the statistical test will account for data variability and ensure that the apparent violation is unlikely to have occurred by chance. **Figure 4-1** below visually depicts a comparison to a fixed GWPS for both lower confidence intervals for a stationary test like a mean, and around an increasing trend. Where the confidence interval straddles the limit, the test results are inconclusive. In similar fashion, an SSD can be identified by using upper confidence intervals.

Figure 4-1. Confidence Intervals Around Means, Percentiles, or Trend Lines



SSIs offer the primary *statistical* justification for moving from detection monitoring to compliance monitoring, or from compliance/assessment monitoring to corrective action. However, it is important that an SSI be interpreted correctly. Any SSI at a compliance well represents a probable increase in concentration level, but it *does not automatically imply or prove* that contaminated groundwater from the facility is the *cause* of the increase. Due to the complexities of the groundwater medium and the nature of statistical testing, there are numerous reasons why a test may exhibit a statistically significant result. These may or may not be indications of an actual release from a regulated unit.

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It is always reasonable to allow for a separate demonstration once an SSI occurs, to determine whether or not the increase is actually due to a contaminant release. Such a demonstration will rely heavily on hydrological and geochemical evidence from the site, but could include additional statistical factors. Key questions and factors to consider are listed in the following sections.

4.3.1 STATISTICAL FACTORS

- Is the result a false positive? That is, were the data tested simply an unusual sample of the underlying population triggering an SSI? Generally, this can be evaluated with repeat sampling.
- Did the test correctly identify an actual release of an indicator or hazardous constituent?
- Are there corresponding SSIs in upgradient or background wells? If so, there may be evidence of a natural in-situ concentration increase, or perhaps migration from an off-site source.
- Is there evidence of significant concentration differences between separate upgradient or background wells, particularly for inorganic constituents? If so, there may be natural spatial variations between distinct well locations that have not been accounted for. These spatial differences could be local or systematic (*e.g.*, upgradient wells in one formation or zone; downgradient wells in another).
- Could observed SSIs for naturally occurring analytes be due to longer-term (*i.e.*, seasonal or multi-year) variation? Seasonal or other cyclical patterns should be observable in upgradient wells. Is this change occurring in both upgradient and downgradient wells? Depending on the statistical test and frequency of sampling involved, an observed SSI may be entirely due to temporal variation not accounted for in the sampling scheme.
- Do time series plots of the sampling data show parallel "spikes" in concentration levels from both background and compliance well samples that were analyzed at about the same time? Perhaps there was an analytical problem or change in lab methodology.
- Are there substantial correlations among within-well constituents (in both upgradient and downgradient wells)? Highly correlated analytes treated as independent monitoring constituents, may generate incorrect significance levels for individual tests.
- Were trends properly accounted for, particularly in the background data?
- Was a correct assumption made concerning the underlying distribution from which the observations were drawn (*e.g.*, was a normal assumption applied to lognormal data)?
- Was the test computed correctly?
- Were the data input to the test of poor quality? (see various factors below)

4.3.2 WELL SYSTEM DESIGN AND SAMPLING FACTORS

- Were early sample data following well installation utilized in statistical testing? Initial well measurements are sometimes highly variable during a 'break in' sampling and analysis period and potentially less trustworthy.
- Was there an effect attributable to recent well development, perhaps due to the use of hazardous constituent chemicals during development or present in drilling muds?
- Are there multiple geological formations at the site, leading to incorrect well placements?

- Has there been degradation of the well casings and screens (*e.g.*, PVC pipe)? Deteriorating PVC materials can release organic constituents under certain conditions. Occasionally, even stainless steel can corrode and release a number of metallic trace elements.
- Have there been changes in well performance over time?
- Were there excessive holding times or incorrect use of preservatives, cooling, *etc.*
- Was there incorrect calibration or drift in the field instrumentation? This effect should be observable in both upgradient and downgradient data and possibly over a number of sample events. The data itself may be compromised or useless.
- Have there been 'mid-stream' changes in sampling procedures, *e.g.*, increased or decreased well purging? Have sampling or purging techniques been consistently applied from well to well or from sampling event to sampling event?

4.3.3 HYDROLOGICAL FACTORS

- Does the site have a history of previous waste management activity (perhaps prior to RCRA), and is there any evidence of historical groundwater contamination? Previous contamination or waste management contaminant levels can limit the ability to distinguish releases from the regulated unit, particularly for those analytes found in historical contamination.
- Is there evidence of groundwater mounding or other anomalies that could lead to the lack of a reliable, definable gradient? Interwell statistical tests assume that changes in downgradient groundwater quality only affect compliance wells and not upgradient (background) wells. Changes that impact background wells also, perhaps in a complex manner involving seasonal fluctuations, are often best resolved by running intrawell tests instead.
- Is there hydrologic evidence of any migration of contaminants (including DNAPL) from off-site sources or from other non-regulated units? Are any of these contaminants observed upgradient of the regulated units?
- Have there been other prior human or site-related waste management activities which could result in the observed SSI changes for certain well locations (*e.g.*, buried waste materials, pipeline leaks, spills, *etc.*)?
- Have there been unusual changes in groundwater directions and depths? Is there confidence that the SSI did indeed correspond to a potential unit release based on observed groundwater directions, distance of the well from the unit, other well information, *etc.*?
- Is there evidence of migration of landfill gas affecting one or more wells?
- Have there been increases in well turbidity and sedimentation, which could affect observed contaminant levels?
- Are there preferential flow paths in the aquifer that could affect where contaminants are likely to be observed or not observed?
- Are the detected contaminants consistent with those found in the waste or leachate of the regulated unit?
- Are there other nearby well pumping or extraction activities?

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4.3.4 GEOCHEMICAL FACTORS

- Were the measurements that triggered the SSI developed from unfiltered or filtered trace element sample data? If unfiltered, is there any information regarding associated turbidity or total suspended solid measurements? Unusual increases in well turbidity can introduce excess naturally occurring trace elements into the samples. This can be a particularly difficult problem in compliance monitoring when comparing data to a fixed standard, but can also affect detection monitoring well-to-well comparisons if turbidity levels vary.
- Were there changes in associated analytes at the "triggered" well consistent with local geochemistry? For example, given an SSI for total dissolved solids [TDS], did measured cations/anions and pH also show a consistent change? As another example, slight natural geochemical changes can result in large specific conductance changes. Did other constituents demonstrate a consistent change?
- Is there evidence of a simultaneous release of more than one analyte, consistent with the composition of the waste or leachate? In particular, is there corollary evidence of degradation or daughter products for constituents like halogenated organics? For groundwater constituents with identified SSIs, is there a probable relationship to measured concentrations in waste or waste leachate? Are leachate concentrations high enough to be detectable in groundwater?
- If an SSI is observed in one or more naturally occurring species, were organic hazardous constituents not normally present in background and found in the waste or leachate also detected? This could be an important factor in assessing the source of the possible release.
- Have aquifer mobility factors been considered? Certain soluble constituents like sodium, chloride, or conservative volatile organics might be expected to move through the aquifer much more quickly than easily adsorbed heavy metals or 4-5 ring polynuclear aromatic [PNA] compounds.
- Do the observed data patterns (particularly for naturally occurring constituents in upgradient wells or other background conditions) make sense in an overall site geochemical context, especially as compared with other available local or regional site data and published studies? If not, suspect background data may need to be further evaluated for potential errors prior to formal statistical comparisons.
- Do constituents exhibit correlated behavior among both upgradient and downgradient wells due to overall changes in the aquifer?
- Have there been natural changes in groundwater constituents over time and space due to multi-year, seasonal, or cyclical variation?
- Are there different geochemical regimes in upgradient *vs*. downgradient wells?
- Has there been a release of soil trace elements due to changes in pH?

4.3.5 ANALYTICAL FACTORS

- Have there been changes in laboratories, analytical methods, instrumentation, or procedures including specified detection limits that could cause apparent jumps in concentration levels? In some circumstances, using different values for non-detects with different reporting limits has triggered SSIs. Were inexperienced technicians involved in any of the analyses?

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- ❖ Was more than one analytical method used (at different points in time) to generate the measurements?
- ❖ Were there changes in detection/quantification limits for the same constituents?
- ❖ Were there calibration problems, ***e.g.***, drift in instrumentation?
- ❖ Was solvent or other laboratory contamination (***e.g.***, phthalates, methylene chloride extractant, acetone wash) introduced into any of the physical samples?
- ❖ Were there known or probable interferences among the analytes being measured?
- ❖ Were there "spikes" or unusually high values on certain sampling events (either for one constituent among many wells or related analytical constituents) that would suggest laboratory error?

4.3.6 DATA OR ANALYTIC ERRORS

- ❖ Were there data transcription errors (incorrect decimal places, analyte units, or data column entries)? These data can often be identified as being highly improbable.
- ❖ Were there calculation errors in either the analytical (***e.g.***, incorrect trace element valence assumptions or dilution factors) or in the statistical portions (mathematical mistakes, incorrect equation terms) of the analysis?

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CHAPTER 5. ESTABLISHING AND UPDATING BACKGROUND

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This chapter discusses the importance and use of background data in groundwater monitoring. Guidance is provided for the proper identification, review, and periodic updating of background. Key questions to be addressed include:

- How should background be established and defined?
- When should existing background data sets be reviewed?
- How and when should background be updated?
- What impact does retesting have on background updating?

5.1 IMPORTANCE OF BACKGROUND

High quality background data is the single most important key to a successful statistical groundwater monitoring program, especially for detection monitoring. All of the statistical tests listed in the RCRA regulations are predicated on having ***appropriate*** and ***representative*** background measurements. As indicated in **Chapter 3**, a statistical sample is representative if the distribution of the sample measurements best follows the distribution of the population from which the sample is drawn. Representative background data has a similar but slightly different connotation. The most important quality of background is that it reflects the historical conditions unaffected by the activities it is designed to be compared to. These conditions could range from an uncontaminated aquifer to an historically contaminated site baseline unaffected by recent RCRA-actionable contaminant releases. Representative background data will therefore have numerical characteristics closely matching those arising from the site-specific aquifer being evaluated.

Background must also be ***appropriate*** to the statistical test. All RCRA detection monitoring tests involve comparisons of compliance point data against background. If natural groundwater conditions

have changed over time — perhaps due to cycles of drought and recharge — background measurements from five or ten years ago may not reflect current uncontaminated conditions. Similarly, recent background data obtained using improved analytical methods may not be comparable to older data. In each case, older background data may have to be discarded in favor of more recent measurements in order to construct an *appropriate* comparison. If intrawell tests are utilized due to strong evidence of spatial variability, traditional upgradient well background data will not provide an appropriate comparison. Even if the upgradient measurements are reflective of uncontaminated groundwater, appropriate background data must be obtained from each compliance point well. The main point is that compliance samples should be tested against data which best can represent background conditions now and those likely to occur in the future.

5.1.1 TRACKING NATURAL GROUNDWATER CONDITIONS

Background measurements, especially from upgradient wells, can provide essential information for other than formal statistical testing. For one, background data can be used to gauge mean levels and develop estimates of variability in naturally occurring groundwater constituents. They can also be used to confirm the presence or absence of anthropogenic or non-naturally occurring constituents in the site aquifer. Ongoing sampling of upgradient background wells provides a means of tracking natural groundwater conditions. Changes that occur in parallel between the compliance point and background wells may signal site-wide aquifer changes in groundwater quality not specifically attributable to onsite waste management. Such observed changes may also be indicative of analytical problems due to common artifacts of laboratory analysis (*e.g.*, re-calibration of lab equipment, errors in batch sample handling, *etc*.), as well as indications of groundwater mounding, changes in groundwater gradients and direction, migration of contaminants from other locations or offsite, etc.

Fixed GWPS like maximum contaminant levels [MCLs] may be contemplated for compliance/assessment monitoring or corrective action. Background data analysis is important if it is suspected that naturally occurring levels of the constituent(s) in question are higher than the standards or if a given hazardous constituent does not have a health- or risk-based standard. In the first case, concentrations in downgradient wells may indeed exceed the standard, but may not be attributable to onsite waste management if natural background levels *also* exceed the standard. The Parts 264 and 258 regulations recognize these possibilities, and allow for GWPS to be based on background levels.

5.2 ESTABLISHING AND REVIEWING BACKGROUND

Establishing appropriate background depends on the statistical approach contemplated (*e.g.*, interwell *vs*. intrawell). This section outlines the major considerations concerning how to select and develop background data including monitoring constituents and sample sizes, statistical assumptions, and the presence of data outliers, spatial variation or trends. Expanding and reviewing background data are also discussed.

5.2.1 SELECTING MONITORING CONSTITUENTS AND ADEQUATE SAMPLE SIZES

Due to the cost of management, mobilization, field labor, and especially laboratory analysis, groundwater monitoring can be an expensive endeavor. The most efficient way to limit costs and still meet environmental performance requirements is to minimize the total number of samples which must be sampled and analyzed. This will require tradeoffs between the number of monitoring constituents

chosen, and the frequency of background versus compliance well testing. The number of compliance wells and annual frequency of testing also affect overall costs, but are generally site-specific considerations. By limiting the number of constituents and ensuring adequate background sample sizes, it is possible to select certain statistical tests which help minimize future compliance (and total) sample requirements.

Selection of an appropriate number of detection monitoring constituents should be dictated by the knowledge of waste or waste leachate composition and the corresponding groundwater concentrations. When historical background data are available, constituent choices may be influenced by their statistical characteristics. A few representative constituents or analytes may serve to accurately assess the potential for a release. These constituents should stem from the regulated wastes, be sufficiently mobile, stable and occur at high enough concentrations to be readily detected in the groundwater. Depending on the waste composition, some non-hazardous organic or inorganic indicator analytes may serve the same purpose. The guidance suggests that between 10-15 formal detection monitoring constituents should be adequate for most site conditions. Other constituents can still be reported but not directly incorporated into formal detection monitoring, especially when large simultaneously analyzed suites like ICP-trace elements, volatile or semi-volatile organics data are run. The focus of adequate background and future compliance test sample sizes can then be limited to the selected monitoring constituents.

The RCRA regulations do not consistently specify how many observations must be collected in background. Under the Part 265 Interim Status regulations, four quarterly background measurements are required during the first year of monitoring. Recent modifications to Part 264 for Subtitle C facilities require a sequence of at least four observations to be collected in background during an interval approved by the Regional Administrator. On the other hand, at least four measurements must be collected from each background well during the first semi-annual period along with at least one additional observation during each subsequent period, for Subtitle D facilities under Part 258. Although these are minimum requirements in the regulations, are they adequate sample sizes for background definition and use?

Four observations from a population are rarely enough to adequately characterize its statistical features; statisticians generally consider sample sizes of $n \leq 4$ to be insufficient for good statistical analysis. A decent population survey, for example, requires several hundred and often a few to several thousand participants to generate accurate results. Clinical trials of medical treatments are usually conducted on dozens to hundreds of patients. In groundwater tests, such large sample sizes are a rare luxury. However, it is feasible to obtain small sample sets of up to $n = 20$ for individual background wells, and potentially larger sample sizes if the data characteristics allow for pooling of multiple well data.

The Unified Guidance recommends that a minimum of at least 8 to 10 independent background observations be collected before running most statistical tests. Although still a small sample size by statistical standards, these levels allow for minimally acceptable estimates of variability and evaluation of trend and goodness-of fit. However, this recommendation should be considered a temporary minimum until additional background sampling can be conducted and the background sample size enlarged (see further discussions below).

Small sample sizes in background can be particularly troublesome, especially in controlling statistical test false positive and negative rates. False negative rates in detection monitoring, *i.e.*, the

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statistical error of failing to identify a real concentration increase above background, are in part a function of sample size. For a fixed false positive test rate, a smaller sample size results in a higher false negative rate. This means a decreased probability (*i.e.*, *statistical power*) that real increases above background will be detected. With certain parametric tests, control of the false positive rate using very small sample sets comes at the price of extremely low power. Power may be adequate using a non-parametric test, but control of the false positive can be lost. In both cases, increased background sample sizes result in better achievable false positive and false negative errors.

The overall recommendation of the guidance is to establish background sample sizes as large as feasible. The final tradeoff comes in the selection of the type of detection tests to be used. Prediction limit, control chart, and tolerance limit tests can utilize very small future sample sizes per compliance well (in some cases a single initial sample), but require larger background sample sizes to have sufficient power. Since background samples generally are obtained from historical data sets (plus future increments as needed), total annual sample sizes (and costs) can be somewhat minimized in the future.

5.2.2 BASIC ASSUMPTIONS ABOUT BACKGROUND

Any background sample should satisfy the key statistical assumptions described in **Chapter 3**. These include statistical independence of the background measurements, temporal and spatial stationarity, lack of statistical outliers, and correct distribution assumptions of the background sample when a parametric statistical approach is selected. How independence and autocorrelation impact the establishment of background is presented below, with additional discussions on outliers, spatial variability and trends in the following sections. Stationarity assumptions are considered both in the context of temporal and spatial variation.

Both the Part 264 and 258 groundwater regulations require statistically independent measurements (**Chapter 2**). Statistical *independence* is indicated by random data sets. But randomness is only demonstrated by the presence of mean and variance *stationarity* and the lack of evidence for effects such as *autocorrelation, trends, spatial and temporal variation.* These tests (described in **Part II** of this guidance) generally require at least 8 to 10 separate background measurements.

Depending on site groundwater velocity, too-frequent sampling at any given background well can result in highly *autocorrelated*, non-independent data. Current or proposed sampling frequencies can be tested for autocorrelation or other statistical dependence using the diagnostic procedures in **Chapter 14**. Practically speaking, the best way to ensure some degree of statistical independence is to allow as much time as possible to elapse between sampling events. But a balance must be drawn between collecting as many measurements as possible from a given well over a specified time period, and ensuring that the sample measurements are statistically independent. If significant dependence is identified in already collected background, the interval between sampling events may need to be lengthened to minimize further autocorrelation. With fewer sampling events per evaluation period, it is also possible that a change in statistical method may be needed, say from analysis of variance [ANOVA], which requires at least 4 new background measurements per evaluation, to prediction limits or control charts, which may require new background only periodically (*e.g.*, during a biennial update).

5.2.3 OUTLIERS IN BACKGROUND

Outliers or observations not derived from the same population as the rest of the sample violate the basic statistical assumption of identically-distributed measurements. The Unified Guidance recommends that testing of outliers be performed on background data, but they generally not be removed unless some basis for a likely error or discrepancy can be identified. Such possible errors or discrepancies could include data recording errors, unusual sampling and laboratory procedures or conditions, inconsistent sample turbidity, and values significantly outside the historical ranges of background data. Management of potential outliers carries both positive and negative risks, which should be carefully understood.

If an outlier value with much higher concentration than other background observations is not removed from background prior to statistical testing, it will tend to increase both the background sample mean and standard deviation. In turn, this may substantially raise the magnitude of a parametric prediction limit or control limit calculated from that sample. A subsequent compliance well test against this background limit will be much less likely to identify an exceedance. The same is true with non-parametric prediction limits, especially when the maximum background value is taken as the prediction limit. If the maximum is an outlier not representative of the background population, few truly contaminated compliance wells are likely to be identified by such a test, lowering the statistical power of the method and the overall quality of the statistical monitoring program.

Because of these concerns, it may be advisable at times to remove high-magnitude outliers in background even if the reasons for these apparently extreme observations are not known. The overall impact of removal will tend to improve the power of prediction limits and control charts, and thus result in a more environmentally protective program.

But strategies that involve automated evaluation and removal of outliers may unwittingly eliminate the evidence of real and important changes to background conditions. An example of this phenomenon may have occurred during the 1970s in some early ozone depletion measurements over Antarctica (http://www.nas.nasa.gov/About/Education/Ozone/history.html). Automated computer routines for outlier detection apparently removed several measurements indicating a sharp reduction in ozone concentrations, and thus prevented identification of an enlarging ozone hole by many years. Later review of the raw observations revealed that these automated routines had statistically classified measurements as outliers, which were more extreme than most of the data from that time period. Thus, there is some merit in saving and revisiting apparent 'outliers' in future investigations, even if removed from present databases.

In groundwater data collection and testing, background conditions may not be static over time. Caution should be observed in removing observations which may signal a change in natural groundwater quality. Even when conditions have not changed, an apparently extreme measurement may represent nothing more than a portion of the background distribution that has yet to be observed. This is particularly true if the background data set contains fewer than 20 samples.

In balancing these contrasting risks in retaining or removing one or more outliers, analyses of historical data patterns can sometimes provide more definitive information depending on the types of analytes and methods. For example, if a potential order-of magnitude higher outlier is identified in a sodium data set used as a monitoring constituent, cation-anion balances can help determine if this change is geochemically probable. In this case, changes to other intrawell ions or TDS should be

observed. Similarly, if a trace element outlier is identified in a single well sampling event and occurred simultaneously with other trace element maxima measured using the same analytical method (e.g., ICP-AES) either in the same well or groups of wells, an analytical error should be strongly suspected. On the other hand, an isolated increase without any other evidence could be a real but extreme background measurement. Ideally, removal of one or more statistically identified outliers should be based on other technical information or knowledge which can support that decision.

5.2.4 IMPACT OF SPATIAL VARIABILITY

In the absence of contamination, comparisons made between upgradient-to-downgradient wells assume that the concentration distribution is *spatially stationary* across the well field (**Chapter 3**). This implies that every well should have the same population mean and variance, unless a release occurs to increase the concentration levels at one or more compliance wells. At many sites, this is not the case for many naturally occurring constituents. Natural or man-made differences in mean levels — referred to as *spatial variability* or *spatial variation* — impact how background must be established.

Evidence of spatial variation should drive the selection of an *intrawell* statistical approach if observed among wells known to be uncontaminated (*e.g.*, among a group of upgradient background locations). Lack of spatial mean differences and a common variance allow for *interwell* comparisons. Appropriate background differs between the two approaches.

With interwell tests, background is derived from distinct, initially upgradient background wells, which may be enhanced by data from historical compliance wells also shown not to exhibit significant mean and variance differences. Future data from each of these compliance wells are then tested against this common background. On the other hand, intrawell background is derived from and represents historical groundwater conditions in each individual compliance well. When the population mean levels vary across a well field, there is little likelihood that the upgradient background will provide an appropriate comparison by which to judge any given compliance well.

Although spatial variability impacts the choice of background, it does so *only* for those constituents which evidence spatial differences across the well field. Each monitoring constituent should be evaluated on its own statistical merits. Spatial variation in some constituents (*e.g.*, common ions and inorganic parameters) does not preclude the use of interwell background for other infrequently detected or non-naturally occurring analytes. At many sites, a mixture of statistical approaches may be appropriate: interwell tests for part of the monitoring list and intrawell tests for another portion. Distinct background observation sets will need to be developed under such circumstances.

Intrawell background measurements should be selected from the available historical samples at each compliance well and should include only those observations thought to be uncontaminated. Initially, this might result in very few measurements (*e.g.*, 4 to 6). With such a small background sample, it can be very difficult to develop an adequately powerful intrawell prediction limit or control chart, even when *retesting* is employed (**Chapter 19**). Thus, additional background data will be needed to augment the testing power. One option is to periodically augment the existing background data base with recent compliance well samples (discussed in a further section below). Another possible remedy is to *statistically augment* the available sample data by running an analysis of variance [ANOVA] simultaneously on all the sets of intrawell background from the various upgradient and compliance wells (see **Chapter 13**). The *root mean squared error* [RMSE] from this procedure can be used in place of the

background standard deviation in parametric prediction and control limits to substantially increase the *effective background sample size* of such tests, despite the limited number of observations available per well.

This strategy will only work if the key assumptions of ANOVA can be satisfied (**Chapter 17**), particularly the requirement of equal variances across wells. Since natural differences in mean levels often correspond to similar differences in variability, a transformation of the data will often be necessary to homogenize the variances prior to running the ANOVA. For some constituents, no transformation may work well enough to allow the RMSE to be used as a replacement estimate for the intrawell background standard deviation. In that case, it may not be possible to construct reasonably powerful intrawell background limits until background has been updated once or twice (see **Section 5.3**).

5.2.5 TRENDS IN BACKGROUND

A key implication of the independent and identically distributed assumption [*i.i.d.*] is that a series of sample measurements should be *stationary over time* (*i.e.*, stable in mean level and variance). Data that are trending upward or downward violate this assumption since the mean level is changing. Seasonal fluctuations also violate this assumption since both the mean and variance will likely oscillate. The proper handling of trends in background depends on the statistical approach and the cause of the trend. With interwell tests and a common (upgradient) background, a trend can signify several possibilities:

- Contaminated background;
- A 'break-in' period following new well installation;
- Site-wide changes in the aquifer;
- Seasonal fluctuations, perhaps on the order of several months to a few years.

If upgradient well background becomes contaminated, intrawell testing may be needed to avoid inappropriate comparisons. Groundwater flow patterns should also be re-examined to determine if gradients are properly defined or if groundwater mounding might be occurring. With newly-installed background wells, it may be necessary to discard initially collected observations and to wait several months for aquifer disturbances due to well construction to stabilize. Site-wide changes in the underlying aquifer should be identifiable as similar trends in both upgradient and compliance wells. In this case, it might be possible to remove a common trend from both the background and compliance point wells and to perform interwell testing on the *trend residuals*. However, professional statistical assistance may be needed to do this correctly. Another option would be to switch to intrawell *trend tests* (**Chapter 17**).

Seasonal fluctuations in interwell background which are also observed in compliance wells, can be accommodated by modeling the seasonal trend and removing it from all background and compliance well data. Data seasonally-adjusted in this way (see **Chapter 14** for details) will generally be less variable than the unadjusted measurements and lead to more powerful tests than if the seasonal patterns had been ignored. For this adjustment to work properly, the same seasonal trend should be observed across the well field and not be substantially different from well to well.

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Roughly linear trends in *intrawell* background usually signify the need to switch from an intrawell prediction limit or control chart to an explicit trend test, such as *linear regression* or the *Mann-Kendall* (**Chapter 17**). Otherwise the background variance will be overestimated and biased on the high side, leading to higher than expected and ultimately less powerful prediction and control limits. Seasonal fluctuations in intrawell background can be treated in one of two ways. A *seasonal Mann-Kendall* trend test built to accommodate such fluctuations can be employed (**Section 14.3.4**). Otherwise, the seasonal pattern can be estimated and removed from the background data, leaving a set of seasonally-adjusted data to be analyzed with either a prediction limit or control chart. In this latter approach, the same seasonal pattern needs to be extrapolated *beyond* the current background to more recent measurements from the compliance well being tested. These later observations also need to be seasonally-adjusted prior to comparison against the adjusted background, even if there is not enough compliance data yet collected to observe the same seasonal cycles.

When trends are apparent in background, another option is to modify the groundwater monitoring list to include only those constituents that appear to be temporally stable. Only certain analytes may indicate evidence of trends or seasonal fluctuations. More powerful statistical tests might be constructed on constituents that appear to be stationary. All such changes to the monitoring list and method of testing may require approval of the Regional Administrator or State Director.

5.2.6 EXPANDING INITIAL BACKGROUND SAMPLE SIZES

In the initial development of a detection monitoring statistical program under a permit or other legal mechanism, a period of review will identify the appropriate monitoring constituents. For new sites with no prior data, plans for initial background definition need to be developed as part of permit conditions. A more typical situation occurs for interim status or older facilities which have already collected substantial historical data in site monitoring wells. For the most part, the suggestions below cover ways of expanding background data sets from existing information.

Under the RCRA interim status regulations, only a single upgradient well is required as a minimum. Generally speaking, a single background well will not generate observations that are adequately representative of the underlying aquifer. A single background well draws groundwater from only one possible background location. It is accordingly not possible to determine if spatial variation is occurring in the upgradient aquifer. In addition, a single background well can only be sampled so often since measurements that are collected too frequently run the risk of being autocorrelated. Background observations collected from a single well are typically neither representative nor constitute a large enough sample to construct powerful, accurate statistical tests. One way to expand background is to install at least 3-4 upgradient wells and collect additional data under permit.

The early RCRA regulations also allowed for aliquot replicate sampling as a means of expanding background and other well sample sizes. This approach consisted of analyzing splits or aliquots of single water quality samples. As indicated in **Chapter 2**, this approach is not recommended in the guidance. Generally limited analytical variability does not adequately capture the overall variation based on independent water quality sample data, and results in incorrect estimates of variability and degrees of freedom (a function of sample size).

Existing historical groundwater well data under consideration will need to meet the assumptions discussed earlier in this chapter– independence, stationarity, etc., including using statistical methods

which can deal with outliers, spatial and temporal variation including trends. Presuming these conditions are met, it is statistically desirable to develop as large a background sample size as practical. But no matter how many measurements are utilized, a larger sample size is advantageous only if the background samples are both appropriate to the tests selected and representative of baseline conditions.

In limited situations, upgradient-to-downgradient, interwell comparisons may be determined to be appropriate using ANOVA testing of well mean differences. To ensure appropriate and representative background, other conditions may also need to be satisfied when data from separate wells are pooled. First, each background well should be screened at the same hydrostratigraphic position as other background wells. Second, the groundwater chemistry at each of these wells should be similar. This can be checked via the use of standard geochemical bar charts, pie charts, and tri-linear diagrams of the major constituent groundwater ions and cations (Hem, 1989). Third, the *statistical* characteristics of the background wells should be similar — that is, they should be ***spatially stationary***, with approximately the same means and variances. These conditions are particularly important for major water quality indicators, which generally reflect aquifer-specific characteristics. For infrequently detected analytes (***e.g.***, filtered trace elements like chromium, silver, and zinc), even data collected from wells from *different* aquifers and/or geologic strata may be statistically indistinguishable and also eligible for pooling on an interwell basis.

If a one-way ANOVA (**Chapter 13**) on the set of background wells finds significant differences in the mean levels for some constituents, and hence, evidence of spatial variability, the guidance recommends using intrawell tests. The data gathered from the background wells will generally not be used in formal statistical testing, but are still invaluable in ensuring that appropriate background is selected.[1] As indicated in the discussions above and **Chapter 13**, it may be possible to pool constituent data from a number of upgradient and/or compliance wells having a common variance when parametric assumptions allow, even if mean differences exist.

When larger historical databases are available, the data can be reviewed and diagnostically tested to determine which observations best represent natural groundwater conditions suitable for future comparisons. During this review, ***all historical well data*** collected from both upgradient and compliance wells can be evaluated for potential inclusion into background. Wells suspected of prior contamination would need to be excluded, but otherwise each uncontaminated data point adds to the overall statistical picture of background conditions at the site and can be used to enlarge the background database. Measurements can be preferentially selected to establish background samples, so long as a consistent rationale is used (e.g., newer analytical methods, substantial outliers in a portion of a data set, etc.) Changes to an aquifer over time may require selecting newer data representing current groundwater quality over earlier results even if valid.

[1] If the spatial variation is ignored and data are pooled across wells with differing mean levels (and perhaps variances) to run an interwell parametric prediction limit or control chart test, the pooled standard deviation will tend to be substantially larger than expected. This will result in a higher critical limit for the test. Using pooled data with spatial variation will also tends to increase observed maximum values in background, leading to higher and less powerful non-parametric prediction limit tests. In either application, there will be a loss of statistical power for detecting concentration changes at individual compliance wells. Compliance wells with naturally higher mean levels will also be more frequently determined to exceed the limit than expected, while real increases at compliance wells with naturally lower means will go undetected more often.

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5.2.7 REVIEW OF BACKGROUND

As mentioned above, if a large historical database is available, a critical review of the data can be undertaken to help establish initially appropriate and representative background samples. We recommend that other reviews of background also take place periodically. These include the following situations:

- When periodically updating background, say every 1-2 years (see **Section 5.3**)
- When performing a 5-10 year permit review

During these reviews, all observations designated as background should be evaluated to ensure that they still adequately reflect current natural or baseline groundwater conditions. In particular, the background samples should be investigated for apparent trends or outliers. Statistical outliers may need to be removed, especially if an error or discrepancy can be identified, so that subsequent compliance tests can be improved. If trends are indicated, a change in the statistical method or approach may be warranted (see earlier section on "Trends in Background").

If background has been updated or enlarged since the last review, and is being utilized in parametric tests, the assumption of normality (or other distributional fit) should be re-checked to ensure that the augmented background data are still consistent with a parametric approach. The presence of non-detects and multiple reporting limits (especially with changes in analytical methods over time) can prove particularly troublesome in checking distribution assumptions. The methods of **Chapters 10** "Fitting Distributions" and **Chapter 15** "Handling Non-Detects" can be consulted for guidance.

Other periodic checks of the revised background should also be conducted, especially in relation to accumulated knowledge from other sites regarding analyte concentration patterns in groundwater. The following are potential sources for comparison and evaluation:

- reliable regional groundwater data studies or investigations from nearby sites;
- published literature; EPA or other agency groundwater databases like STORET;
- knowledge of typical patterns for background inorganic constituents and trace elements. An example is found in **Table 5-1** at the end of this chapter. Typical surface and groundwater levels for filtered trace elements can also be found in the published literature (***e.g.***, Hem, 1989).

Certain common features of routine groundwater monitoring analytes summarized in **Table 5-1** have been observed in Region 8 and other background data sets, which can have implications for statistical applications. Common water quality indicators like cations and anions, pH, TDS, specific conductance are almost always measurable (detectable) and generally have limited within-well variability. These would be more amenable to parametric applications; however, these measurable analytes are also most likely to exhibit well-to-well spatial variation and various kinds of within- and between-well temporal variation including seasonal and annual trends. Many of these within-well analytes are highly correlated, and would not meet the criterion for independent data if simultaneously used as monitoring constituents.

A second level of common indicator analytes– nitrate/nitrite species, fluoride, TOC and TOX– are less frequently detected and subject to more analytical detection instability (higher and lower

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detection/quantitation limits). As such, these analyte data are somewhat less reliable. There is less likelihood of temporal variation, although they can exhibit spatial well differences.

Among routinely monitored .45µ-filtered trace elements, different groups stand out. Barium is routinely detected with limited variation within most wells, but does exhibit spatial variation. Arsenic and selenium commonly occur in groundwater as oxyanions, and data can range from virtually non-detectable to always detected in different site wells. The largest group of trace elements can be considered colloidal metals (Sb, Al, Be, Cd, Cr, Co, Fe, Hg, Mn, Pb, Ni, Sn, Tl, V and Zn). While Al, Mn and Fe are more commonly detected, variability is often quite high; well-to-well spatial variability can occur at times. The remaining colloidal metals are solubility-limited in most background groundwater, generally <1 to < 10 µg/l. But even with filtration, some natural colloidal geologic solid materials can often be detected in individual samples. Since naturally occurring Al, Mn and Fe soil solid levels are much higher, the effects on measured groundwater levels are more pronounced and variable. For most of the analytically and solubility-limited colloidal metals, there may not be any discernible well spatial differences. Often these data can be characterized by a site-wide lognormal distribution, and may be possible to pool individual well data to form larger background sizes.

With unfiltered trace element data, it is more difficult to generalize even regarding background data. The method of well sample extraction and the aquifer characteristics will determine how much solids material may be present in the samples. Excessive amounts of sample solids can result in higher levels of detection but also elevated average values and variability even for solubility-limited trace elements. The effect is most clearly seen when TSS is simultaneously collected with unfiltered data. Increases are proportional to the amount of TSS and the natural background levels for trace elements in soil/solid materials. It is recommended that TSS always be simultaneously monitored with unfiltered trace elements.

Most trace organic monitoring constituents are absent or non-detectable under clean background conditions. However, with existing up-gradient sources, it is more difficult to generalize. More soluble constituents like benzene or chlorinated hydrocarbons may be amenable to parametric distributions, but changes in groundwater levels or direction can drastically affect observed levels. For sparingly soluble compounds like polynuclear aromatics (e.g., naphthalene), aquifer effects can result in highly variable data less amenable to statistical applications.

Table 5-1 was based on the use of analytical methods common in the 1990's to the present. Detectable filtered trace element data for the most part were limited by the available analytic techniques, generally SW-846 Method 6010 ICP-AES and select AA (atomic absorption) methods with lower detection limits in the 1-10 ppb range. As newer methods are incorporated (particularly Method 6020 ICP-MS capable of parts-per-trillion detection limits for trace elements), higher quantification frequencies may result in data demonstrating more complex spatial and temporal characteristics. Table 5-1 merely provides a rough guide to where various data patterns might occur. Any extension of these patterns to other facility data sets should be determined by the formal guidance tests in **Part II**.

The background database can also be specially organized and summarized to examine common behavior among related analytes (*e.g.*, filtered trace elements using ICP-AES) either over time or across wells during common sampling events. Parallel time series plots (**Chapter 9**) are very useful in this regard. Groups of related analytes can be graphed on the same set of axes, or groups of nearby wells for the same analyte. With either plot, highly suspect sampling events can be identified if a similar spike in

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concentration or other unusual pattern occurs simultaneously at all the wells or in all the analytes. Analytical measurements that appear to be in error might be removed from the background database.

Cation-anion balances and other more sophisticated geochemical analysis programs can also be used to evaluate the reliability of existing water quality background data. A suite of tests like linear or non-parametric correlations, simple or non-parametric ANOVA described in later chapters offer overall methods for evaluating historical data for background suitability.

5.3 UPDATING BACKGROUND

Due both to the complex behavior of groundwater and the need for sufficiently large sample sizes, background once obtained should not be regarded as a single fixed quantity. Background should be sampled regularly throughout the life of the facility, periodically reviewed and revised as necessary. If a site uses traditional, upgradient-to-downgradient comparisons, it might seem that updating of background is conceptually simple: collect new measurements from each background well at each sampling event and add these to the overall background sample. However, significant trends or changes in one or more upgradient wells might indicate problems with individual wells, or be part of a larger site-wide groundwater change. It is worthwhile to consider the following principles for updating, whether interwell or intrawell testing is used.

5.3.1 WHEN TO UPDATE

There are no firm rules on how often to update background data. The Unified Guidance adopts the general principle that updating should occur when enough new measurements have been collected to allow a two-sample statistical comparison between the existing background data and a potential set of newer data. As mentioned in the following section, trend testing might also be used. With quarterly sampling, at least 4 to 8 new measurements should be gathered to enable such a test; this implies that updating would take place every 1-2 years. With semi-annual sampling, the same principle would call for updating every 2-3 years.

Updating should generally not occur more frequently, since adding a new observation to background every one or two sampling rounds does not allow a statistical evaluation of whether the background mean is stationary over time. Enough new data needs to be collected to ensure that a test of means (or medians in the case of non-normal data) can be conducted. Adding individual observations to background can introduce subtle trends that might go undetected and ultimately reduce the statistical power of formal monitoring tests.

Another practical aspect is that when background is updated, all statistical background limits (*e.g.*, prediction and control limits) needs to be recomputed to account for the revised background sample. At complex sites, updating the limits at each well and constituent on the monitoring list may require substantial effort. This includes resetting the cumulative sum [CUSUM] portions of control charts to zero after re-calculating the control limits and prior to additional testing against those limits. Too-frequent updating could thereby reduce the efficacy of control chart tests.

5.3.2 HOW TO UPDATE

Updating background is primarily a concern for intrawell tests, although some of the guidelines apply to interwell data. The common (generally upgradient) interwell background pool can be tested for

trends and/or changes at intervals depending on the sampling frequencies identified above. Those recently collected measurements from the background well(s) can be added to the existing pool if a Student's *t*-test or Wilcoxon rank-sum test (**Chapter 16**) finds no significant difference between the two groups at the $\alpha = 0.01$ level of significance. Individual background wells should also be evaluated in the same manner for their respective newer data. Two-sample tests of the interwell background data are conducted to gauge whether or not background groundwater conditions have changed substantially since the last update, and are ***not*** tests for indicating a potential release under detection monitoring. A significant *t*-test or Wilcoxon rank-sum result should spur a closer investigation and review of the background sample, in order to determine which observations are most representative of the current groundwater conditions.

With intrawell tests using prediction limits or control charts, updating is performed both to enlarge initially small well-specific background samples and to ensure that more recent compliance measurements are not already impacted by a potential release (even if not triggered by the formal detection monitoring tests). A finding of significance using the above two-sample tests means that the most recent data ***should not*** be added to intrawell background. However, the same caveat as above applies: these are not formal tests for determining a potential release and the existing tests and background should continue to be used.

Updating intrawell background should also not occur until at least 4 to 8 new compliance observations have been collected. Further, a potential update is predicated on there being no ***statistically significant increase*** [SSI] recorded for that well constituent, including since the last update. Then a *t*-test or Wilcoxon rank-sum comparison can be conducted at each compliance well between existing intrawell background and the potential set of newer background. A non-significant result implies that the newer compliance data can be re-classified as background measurements and added to the existing intrawell background sample. On the other hand, a determination of significance suggests that the compliance observations should be reviewed to determine whether a gradual trend or other change has occurred that was missed by the intervening prediction limit or control chart tests. If intrawell tests make use of a common pooled variance, the assumption of equal variance in the pooled wells should also be checked with the newer data.

Some users may wish to evaluate historical and future background data for potential trends. If plots of data versus time suggest either an overall trend in the combined data sets or distinct differences in the respective sets, linear or non-parametric trend tests covered in **Chapter 17** might be used. A determination of a significant trend might occur even if the two-sample tests are inconclusive, but individual group sample sizes should be large enough to avoid identifying a significant trend based on too few samples and perhaps randomly occurring. A trend in the newer data may reflect or depart from the historical data conditions. Some form of statistical adjustments may be necessary, but see **Section 5.3.4** below.

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5.3.3 IMPACT OF RETESTING

A key question when updating intrawell background is how to handle the results of retesting.[2] If a retest confirms an SSI, background should not be updated. Rather, some regulatory action at the site should be taken. But what if an initial exceedance of a prediction or control limit is *disconfirmed* by retesting? According to the logic of retesting (**Chapter 19**), the well passes the compliance test for that evaluation and monitoring should continue as usual. But what should be done with the initial exceedance when it comes time to update background at the well?

The initial exceedance may be due to a laboratory error or other anomaly that has caused the observation to be an outlier. If so, the error should be documented and not included in the updated background sample. But if the exceedance is not explainable as an outlier or error, it may represent a portion of the background population that has heretofore not been sampled. In that case, the data value could be included in the updated background sample (along with the repeat sample) as evidence of the expanded but true range of background variation. Ultimately, it is important to characterize the background conditions at the site as completely and accurately as possible, so as to minimize both false positive and false negative decision errors in compliance testing.

The severity and classification of the initial exceedance will depend on the specific retesting strategy that has been implemented (**Chapter 19**). Using the same background data in a parametric prediction limit or control chart test, background limits are proportionately lower as the 1-of-*m* order increases (higher *m*). Thus, a 1-of-4 prediction limit will be lower than a 1-of-3 limit, and similarly the 1-of-3 limit lower than for a 1-of-2 test. An initial exceedance triggered by a 1-of-4 test limit and disconfirmed by a repeat sample, might not trigger a lower order prediction limit test. The initial sample value may represent an upper tail value from the true distribution. Retesting schemes derive much of their statistical power by allowing more frequent initial exceedances, even if some of these represent possible measurements from background. The initial and subsequent resamples *taken together* are designed to identify which initial exceedances truly represent SSIs and which do not. These tests presume that occasional excursions beyond the background limit will occur. Unless the exceedance can be documented as an outlier or other anomaly, it should probably be included in the updated intrawell background sample.

5.3.4 UPDATING WHEN TRENDS ARE APPARENT

An increasing or decreasing trend may be apparent between the existing background and the newer set of candidate background values, either using a time series plot or applying **Chapter 17** trend analyses. Should such trend data be added to the existing background sample? Most detection monitoring tests assume that background is stationary over time, with no discernible trends or seasonal variation. A mild trend will probably make very little difference, especially if a Student-*t* or Wilcoxon rank-sum test between the existing and candidate background data sets is non-significant. More severe or continuing trends are likely to be flagged as SSIs by formal intrawell prediction limit or control chart tests.

[2] With interwell tests, the common (upgradient) background is rarely affected by retests at compliance point wells (unless the latter were included in the common pool). Should retesting fail to confirm an initial exceedance , the initial value can be reported alongside the disconfirming resamples in statistical reports for that facility.

With interwell tests, a stronger trend in the common upgradient background may signify a change in natural groundwater quality across the aquifer or an incomplete characterization of the full range of background variation. If a change is evident, it may be necessary to delete some of the earlier background values from the updated background sample, so as to ensure that compliance testing is based on current groundwater conditions and not on outdated measures of groundwater quality.

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Table 5-1. Typical Background Data Patterns for Routine Groundwater Monitoring Analytes

Analyte Groups	Detection Rates		Between Well Mean Differences	Within Well Variability (CVs)	Between Well Equal Variances	Outlier Problems	Temporal Variation					Typical Distribution within well	Data Grouping
	Frequency of Detection by Well	Multiple Reporting Limiits					Between Well by Analyte	Within Well Among Group	Within Well Auto-correl.	Within Well Seasonal Variation	Within Well Time Correl.		
Inorganic Constituents and Indicators													
Major ions, pH, TDS, Specific Conductance	High to 100%		✓✓✓	Generally low (.1-.5)	✓✓	✓	✓✓	✓✓✓	✓✓	✓✓	✓✓	Normal	Intrawell
CO3, F, NO2,NO3	Some to most detectable	✓✓	✓✓	Moderate (.2-1.5)	Variable	✓✓	✓			✓	✓	Norm, Log or NPM	Intrawell/ Interwell
.45µ Filtered Trace Elements													
Ba	High to 100%	✓✓	✓✓✓	Low (.1-.5)	✓	✓	✓				✓	Normal	Intrawell
As, Se	Some wells high, others low to zero	✓✓	✓✓ (some wells)	Moderate (.2-1.5)	Variable	✓✓	✓				✓	Normal, Log or NPM	Intrawell/ Interwell
Al, Mn, Fe	Low to Moderate	✓✓	✓	Moderate to high (.3->2.0)	✓	✓✓✓	✓				✓	Log or NPM	Intrawell/ Interwell
Sb, Be, Cd, Cr, Cu, Hg, Pb, Ni, Ag, Tl, V, Zn	Zero to low	✓✓✓		Moderate to high (.5->2.0)	✓✓	✓✓✓	✓	✓✓			✓	Log or NPM	Interwell or NDC
Trace Organic and Indicator Analytes (patterns at sites with prior contamination; generally absent in clean sites)													
VOA's-BETX and Cl-Hydrocarbons	Variable, can be high	✓	Variable by site and wells			✓	Variable by site and specific wells					Normal, Log or NPM	Intrawell, Interwell or NDC
BNAs, Other Trace Organics	Generally low-mod	✓✓	" " " " "			✓	" " " "					" "	" "
Indicators: TOX, TPH, TOC, sulfide	Variable	✓✓	" " " " "			✓✓✓	" " " "					" "	" "

NPM– non-parametric methods; **NDC-** never-detected constituents

Checks: **None–** unknown, absent or infrequently occurring; ✓ – Occasionally; ✓✓ – Frequently; ✓✓✓ – Very Frequently

CHAPTER 6. DETECTION MONITORING PROGRAM DESIGN

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6.1 INTRODUCTION

This chapter addresses the *initial statistical design* of a detection monitoring program, prior to routine implementation. It considers what important elements should be specified in site permits, monitoring development plans or during periodic reviews. A good statistical design can be critically important for ensuring that the routine process of detection monitoring meets the broad objective of the RCRA regulations: using statistical testing to accurately evaluate whether or not there is a release to groundwater at one or more compliance wells.

This guidance recommends a *comprehensive* detection monitoring program design, based on two key performance characteristics: adequate *statistical power* and a low predetermined *site-wide false positive rate* [SWFPR]. The design approach presented in **Section 6.2** was developed in response to the *multiple comparisons problem* affecting RCRA and other groundwater detection programs, discussed in **Section 6.2.1**. Greater detail in applying design cumulative false positives and assessing power follows in the next three sub-sections. In **Section 6.3**, consideration is given to data features that impact proper implementation of statistical testing, such as outliers and non-detects, using interwell versus intrawell tests, as well as the presence of spatial variability or trends. **Section 6.4** provides a general discussion of specific detection testing methods listed in the regulations and their appropriate use. Finally, **Section 6.5** applies the design concepts to three hypothetical site examples.

The principles and statistical tests which this chapter covers for a detection monitoring program can also apply to compliance/corrective action monitoring when a background standard is used. Designing a background standards compliance program is discussed in **Chapter 7** (**Section 7.5**).

6.2 ELEMENTS OF THE STATISTICAL PROGRAM DESIGN

6.2.1 THE MULTIPLE COMPARISONS PROBLEM

The foremost goal in detection monitoring is to identify a real release to groundwater when it occurs. Tests must have adequate *statistical power* to identify concentration increases above background. A second critical goal is to avoid *false positive decision errors*, evaluations where one or more wells are falsely declared to be contaminated when in fact their concentration distribution is similar to background. Unfortunately, there is a trade-off (discussed in **Chapter 3**) between maximizing power and minimizing the false positive rate in designing a statistical testing protocol. The statistical power of a given test procedure using a fixed background sample size (*n*) cannot be improved without increasing the risk of false positive error (and vice-versa).

In RCRA and other groundwater detection monitoring programs, most facilities must monitor and test for multiple constituents at all compliance wells one or more times per year. A separate statistical test[1] for each monitoring constituent-compliance well pair is generally conducted semi-annually. Each additional background comparison test increases the accumulative risk of making a false positive mistake, known statistically as the ***multiple comparisons problem***.[2]

The false positive rate α (or *Type I error*) for an individual test is the probability that the test will falsely indicate an exceedance of background. Often, a single fixed low false positive error rate typically found in textbooks or regulation, e.g., $\alpha = .01$ or .05, is applied to each statistical test performed for every well-constituent pair at a facility. Applying such a common false positive rate (α) to each of several tests can result in an acceptable cumulative false positive error if the number of tests is quite small.

But as the number of tests increases, the false positive rate associated with the testing network as a whole (*i.e.*, across all well-constituent pairs) can be surprisingly high. If enough tests are run, at least one test is likely to indicate potential contamination even if a release has not occurred. As an example, if the testing network consists of 20 separate well-constituent pairs and a 99% confidence upper prediction limit is used for each test ($\alpha = .01$), the expected overall *network-wide* false positive rate is about 18%. There is nearly a 1 in 5 chance that one or more tests will *falsely* identify a release to groundwater at uncontaminated wells. For 100 tests and the same statistical procedure, the overall network-wide false positive rate increases to more than 63%, creating additional steps to verify the lack of contamination at falsely triggered wells. This cumulative false positive error is also indicative of <u>at least</u> one well constituent false positive error, but there could be more. Controlling this cumulative false positive error rate is essential in addressing the *multiple comparisons* problem.

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[1] The number of samples collected may not be the same as the number of statistical tests (e.g., a mean test based on 2 individual samples). It is the number of <u>tests</u> which affect the multiple comparisons problem.

[2] To minimize later confusion, note that the Unified Guidance applies the term "comparison" somewhat differently than most statistical literature. In statistical theory, multiple *tests* are synonymous with multiple *comparisons*, regardless of the kind of statistical test employed. But because of its emphasis on retesting and resampling techniques, the Unified Guidance uses "comparison" in referring to the evaluation of a single sample value or sample statistic against a prediction or control chart limit. In many of the procedures described in **Chapters 19** and **20**, a single statistical test will involve two or more such individual comparisons, yet all the comparisons are part of the same (individual) test.

Three main strategies (or their combination) can be used to counter the excessive cumulative false positive error rate-- 1) the number of tests can be reduced; 2) the individual test false positive rate can be lowered, or 3) the type of statistical test can be changed. A fourth strategy to increase background sample sizes may also be appropriate. Under an initial monitoring design, one usually works with fixed historical sample sizes. However, background data can later be updated in periodic program reviews.

To make use of these strategies, a sufficiently low *target* cumulative SWFPR needs to be initially identified for design purposes. The target cumulative error applies to a certain regular time period. The guidance recommends and uses a value of 10% over a year period of testing. Reasons for this particular choice are discussed in **Section 6.2.2**. These strategies have consequences for the overall test power of a well monitoring network, which are considered following control of the false positive error.

The *number of tests* depends on the number of monitoring constituents, compliance wells and periodic evaluations. Statistical testing on a regular basis can be limited to constituents shown to be *reliable* indicators of a contaminant release (discussed further in **Section 6.2.2)**. Depending on site conditions, some constituents may need to be tested only at wells for a single regulated waste unit, rather than across the entire facility well network. The frequency of evaluation is a program decision, but might be modified in certain circumstances.

Monitoring data for other parameters should still be routinely collected and reported to trace the potential arrival of new chemicals into the groundwater, whether from changes in waste management practices or degradation over time into hazardous daughter products. By limiting *statistically evaluated* constituents to the most useful indicators, the overall number of statistical tests can be reduced to help meet the SWFPR objective. Fewer tests also imply a somewhat higher single test false positive error rate, and therefore an improvement in power.

As a second strategy, the Type I error rate (α_{test}) applied to each individual test can be lowered to meet the SWFPR. Using the *Bonferroni adjustment* (Miller, 1981), the individual test error is designed to limit the overall (or *experiment-wise*) false positive rate α associated with n individual tests by conducting each individual test at an adjusted significance level of $\alpha_{test} = \alpha/n$. Computational details for this approach are provided in a later section.

A full Bonferroni adjustment strategy was neither implemented in previous guidance[3] nor allowed by regulation. However, the principle of partitioning individual test error rates to meet an overall cumulative false positive error target is highly recommended as a design element in this guidance. Because of RCRA regulatory limitations, its application is restricted to certain detection monitoring

[3] A Bonferroni adjustment was recommended in the 1989 **Interim Final Guidance** [IFG] as a *post-hoc* (*i.e.*, 'after the fact') testing strategy for individual background-to-downgradient well comparisons following an analysis of variance [ANOVA]. However, the adjustment does not always effectively limit the risks to the intended 5% false positive error for any ANOVA test. If more than 5 compliance wells are tested, RCRA regulations restrict the single test error rate to a minimum of α = 1% for each of the individual post-hoc tests following the *F*-test. This in effect raises the cumulative ANOVA test risk above 5% and considerably higher with a larger number of tested wells. At least one contaminated well would typically be needed to trigger the initial *F*-test prior to *post-hoc* testing. This fact was also noted in the 1989 IFG. Additionally, RCRA regulations mandate a minimum α error rate of 5% *per constituent* tested with this strategy. For sites with extensive monitoring parameter lists, this means a substantial risk of at least one false positive test result during any statistical evaluation.

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tests-- prediction and tolerance limits along with control charts. Where not restricted by regulation, the Bonferroni approach could be used to design workable single-test or post-hoc testing for ANOVAs to meet the overall SWFPR criterion.

Using this strategy of defining individual false positive test rates to meet a cumulative error target, the effect on statistical power is direct. Given a statistical test and fixed sample size, *a lower false positive rate coincides with lower power of the test to detect contamination at the well.* Some improvement in single test power can be gained by increasing background sample sizes at a fixed test error rate. However, the third strategy of utilizing a different or modified statistical test is generally necessary.

This strategy involves choices among certain detection monitoring tests-- prediction limits, control charts and tolerance intervals-- to enhance both power and false positive error control. Except for small sites with a very limited number of tests, any of the three detection monitoring options should incorporate some manner of *retesting*. Through proper design, retesting can simultaneously achieve sufficiently high statistical power while maintaining control of the SWFPR.

RECOMMENDED GUIDANCE CRITERIA

The design of all testing strategies should specifically address the multiple comparisons problem in light of these two fundamental concerns-- an acceptably low false positive site-wide error rate and adequate power. The Unified Guidance accordingly recommends two statistical performance criteria fundamental to good design of a detection monitoring program:

1. **Application of an annual cumulative SWFPR design target, suggested at *10% per year*.**

2. **Use of *EPA reference power curves* [ERPC] to gauge the *cumulative, annual* ability of any individual test to detect contaminated groundwater when it exists. Over the course of a single year assuming normally-distributed background data, any single test performed at the site should have the ability to detect 3 and 4 standard deviation increases above background at specific power levels at least as high as the reference curves**.

False positive rates (or errors) apply both to individual tests and cumulatively to all tests conducted in some time period. Applying the SWFPR annual 10% rate places different sites and state regulatory programs on an equal footing, so that no facility is unfairly burdened by false positive test results. Use of a single overall target allows a proper comparison to be made between alternative test methods in designing a statistical program. Additional details in applying the SWFPR include the following:

- The SWFPR false positive rate should be measured on a *site-wide* basis, partitioned among the total number of annual statistical tests.

- The SWFPR applies to all statistical tests conducted in an *annual* or calendar year period.

- The total number of *annual statistical tests* used in SWFPR calculations depends on the number of valid monitoring constituents, compliance wells and evaluation periods per year. The number of tests may or may not coincide with the number of annual sampling events, for example, if data for a future mean test are collected quarterly and tested semi-annually.

- The Unified Guidance recommends a uniform approach for dealing with monitoring constituents not historically detected in background (e.g., trace organic compounds routinely analyzed in large analytical suites). It is recommended that such constituents *not* be included in SWFPR computations, and an alternate evaluation protocol be used (referred to as the Double Quantification rule) discussed in **Section 6.2.2.**

Statistical power refers to the ability of a test to identify real increases in concentration levels above background (true SSIs). The power of a test is evaluated on population characteristics and represents average behavior defined by repeated or an infinitely large number of samples. Power is reported as a fraction between 0 and 1, representing the probability that the test will identify a *specific level or degree of increase* above background. Statistical power varies with the size of the average population concentration above background-- generally fairly low power to detect small incremental concentrations and substantially increasing power at higher concentrations.

The ERPC describe the cumulative, annual statistical power to detect increasing levels of contamination above a true background mean. These curves are based on specific normal detection monitoring prediction limit tests of single future samples against background conducted once, twice, or four times in a year. Reference curve power is linked to *relative*, not absolute, concentration levels. Actual statistical test power is closely tied to the underlying variability of the concentration measurements. Since individual data set variability will differ by site, constituent, and often by well, the EPA reference power curves provide a generalized ability to estimate power by standardizing variability. By convention, all background concentration data are assumed to follow a standard normal distribution (occasionally referred to in this document as a *Z*-normal distribution) with a true mean $\mu = 0$ and standard deviation $\sigma = 1.0$. Then, increases above background are measured in increasing the k standard deviation units corresponding to $k\sigma$ mean units above baseline. When the background population can be normalized via a transformation, the same normal-based ERPC can be used without loss of generality.

Ideally, actual test power should be assessed using the original concentration data and associated variability, referred to as *effect size* power analysis. The power of any statistical test can be readily computed and compared to the appropriate reference curve, if not analytically, then by Monte Carlo simulation. But the reference power curves laid out in the Unified Guidance offer an important standard by which to judge the adequacy of groundwater statistical programs and tests. They can be universally applied to all RCRA sites and offer a uniform way to assess the environmental and health protection afforded by a particular statistical detection monitoring program.[4]

Consequently, it is recommended that design of any detection monitoring statistical program include an assessment of its ability to meet the power standards set out in the Unified Guidance. The reference power curve approach does not place an undue statistical burden on facility owners or operators, and is believed to be generally protective of human health and the environment.

[4] The ERPCs are specifically intended for comparing background to compliance data in detection monitoring. Power issues in compliance/assessment monitoring and corrective action are considered in **Chapters 7** and **22**.

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Principal features of the ERPC approach include the following:

- Reference curves are based on upper 99% prediction limit tests of single future samples against background. The background sample consists of n = 10 measurements, a minimally adequate background sample size typical of RCRA applications. It is assumed that the background sample and compliance well data are normally distributed and from the same population.

- The three reference curves described below are matched to the *annual* frequency of statistical evaluations: one each for quarterly, semi-annual, and annual evaluations. The annual cumulative false positive testing error is maintained at 1%, testing 1, 2, or 4 single future samples annually against the same background. This represents the ability to identify a release to groundwater in at least one of the 1, 2 or 4 tests over the course of a year. Reporting power on an annual basis was chosen to correspond with the application of a cumulative annual SWFPR.

- In the absence of an acceptable *effect size* increase (**Section 6.2.4**), the Unified Guidance recommends that any statistical test provide at least *55-60% annual power to detecting a 3σ* (*i.e.*, 3 standard deviation) increase above the true background mean and at least *80-85% annual power for detecting increases of 4σ*. The percent power criteria change slightly for the respective reference power curves, depending on the annual frequency of statistical evaluations. For normal populations, a 3σ increase above the background average approximately corresponds to the upper 99th percentile of the background distribution, implying better than a 50% chance of detecting such an increase. Likewise, a 4σ increase corresponds to a true mean greater than the upper 99.99th percentile of the background distribution, with better than a 4-in-5 chance of detecting it.

- A single statistical test is not adequately powerful unless its power matches or betters the appropriate reference curve, at least for mean-level increases of 3 to 4 standard deviation units. The same concept can be applied to the overall detection monitoring test design. It is assumed for statistical design purposes that each individual monitoring well and constituent is of equal importance, and assigned a common test false positive error. *Effective power* then measures the overall ability of the statistical program to identify any single constituent release in any well, assuming all remaining constituents and wells are at background levels. If a number of different statistical methods are employed in a single design, effective power can be defined with respect to the *least powerful* of the methods being employed. Applying effective power in this manner would ensure that every well and constituent is evaluated with adequate statistical power to identify potential contamination, not just those where more powerful tests are applied.

- While the Unified Guidance recommends *effective power* as a general approach, other considerations may outweigh statistical thoroughness. Not all wells and constituents are necessarily of equal practical importance. Specific site circumstances may also result in some anomalous weak test power (e.g., a number of missing samples in a background data set for one or more constituents), which might be remedied by eventually increasing background size. The user needs to consider all factors including effective statistical power criteria in assessing the overall strength of a detection monitoring program.

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6.2.2 SITE-WIDE FALSE POSITIVE RATES [SWFPR]

In this section, a number of considerations in developing and applying the SWFPR are provided. Following a brief discussion of SWFPR computations, the next section explains the rationale for the 10% design target SWFPR. Additional detail regarding the selection of monitoring constituents follows, and a final discussion of the Double Quantification rule for never-detected constituents is included in the last section.

For cumulative false positive error and SWFPR computations, the following approach is used. A cumulative false positive error rate α_{cum} is calculated as the probability of at least one statistically significant outcome for a total number of tests n_T in a calendar year at a single false positive error rate α_{test} using the properties of the Binomial distribution:

$$\alpha_{cum} = 1 - (1 - \alpha_{test})^{n_T}$$

By rearranging to solve for α_{test}, the 10% design SWFPR (.1) can be substituted for α_{cum} and the needed per-test false positive error rate calculated as:

$$\alpha_{test} = 1 - (.9)^{1/n_T}$$

Although these calculations are relatively straightforward and were used to develop certain κ-factor tables in the Unified Guidance (discussed in **Section 6.5** and in later chapters), a further simplification is possible using the Bonferroni approximation. This assumes that cumulative, annual SWFPR is roughly the additive sum of all the individual test errors. For low false positive rates typical of guidance application, the Bonferroni results are satisfactorily close to the Binomial formula for most design considerations.

Using this principle, the design 10% SWFPR can be partitioned among the potential annual statistical tests at a facility in a number of ways. For facilities with different annual monitoring frequencies, the SWFPR can be divided among quarterly or semi-annual period tests. Given $\alpha_{SWFPR} = .1$ and n_E evaluation periods, the quarterly cumulative false positive target rate α_E at a facility conducting quarterly testing would be $\alpha_E = \alpha_{SWFPR}/n_E = .1/4 = .025$ or 2.5% (and similarly for semi-annual testing). The total or sub-divided SWFPR can likewise be partitioned among dedicated monitoring well groupings at a multi-unit facility or among individual monitoring constituents as needed.

DEVELOPMENT AND RATIONALE FOR THE SWFPR

The existing RCRA Part 264 regulations for parametric or non-parametric analysis of variance [ANOVA] procedures mandate a Type I error of at least 1% for any individual test, and at least 5% overall. Similarly, the RCRA Part 265 regulations require a minimum 1% error for indicator parameter tests. The rationale for minimum false positive requirements is motivated by statistical power. If the Type I error is set too low, the power of the test will be unacceptably low for any given test. EPA was historically not able to specify a minimum level of acceptable power within the RCRA regulations. To do so would require specification of a minimum difference of environmental concern between the null and alternative test hypotheses. Limits on current knowledge about the health and/or environmental effects associated with incremental changes in concentration levels of Part 264 Appendix IX or Part 258 Appendix II constituents greatly complicate this task. Tests of non-hazardous or low-hazard indicators

might have different power requirements than for hazardous constituents. Therefore, minimum false positive rates were adopted for ANOVA-type procedures until more specific guidance could be recommended. EPA's main concern was adequate statistical power to detect real contamination of groundwater, and not enforcing commonly-used false positive test rates.

This emphasis is evident in §264.98(g)(6) and §258.54(c)(3) for detection monitoring and §264.99(i) and §258.55(g)(2) for compliance monitoring. Both pairs of provisions allow the owner or operator to demonstrate that any statistically significant difference between background and compliance point wells or between compliance point wells and the GWPS is an artifact caused by an error in sampling, analysis, statistical evaluation, or natural variation in groundwater chemistry. The rules clearly expect that there will be occasional false positive errors, but existing rules are silent regarding the cumulative frequency of false positives at regulated facilities.

As previously noted, it is essentially impossible to maintain a low cumulative SWFPR for moderate to large monitoring networks if the Type I errors for individual tests must be kept at or above 1%. However, the RCRA regulations do not impose similar false positive error requirements on the remaining control chart, prediction limit and tolerance interval tests. Strategies that incorporate prediction limit or control chart *retesting* can achieve very low individual test false positive rates while maintaining adequate power to detect contamination. Based on prediction limit research in the 1990's and after, it became clear that these alternative methods with suitable retesting could also control the overall cumulative false positive error rate to manageable levels.

This guidance suggests the use of an annual SWFPR of .1 or 10% as a fundamental element of overall detection monitoring design. The choice of a 10% annual SWFPR was made in light of the tradeoffs between false positive control and testing power. An annual period was chosen to put different sized facilities on a common footing regardless of variations in scheduled testing. It is recognized that even with such a limited error rate, the probability of false positive outcomes over a number of years (such as in the lifetime of a 5-10 year permit) will be higher. However, such relatively limited eventualities can be identified and adjusted for, since the RCRA regulations do allow for demonstration of a false positive error. State programs may choose to use a different annual rate such as 5% depending on the circumstances. But **some** predefined SWFPR in a given evaluation period is essential for designing a detection monitoring program, which can then be translated into target individual test rates for any alternative statistical testing strategy.

To implement this recommendation, a given facility should identify its yearly evaluation schedule as quarterly, semi-annual, or annual. This designation is used both to select an appropriate EPA reference power curve by which to gauge acceptable power, and to select prediction limit and control chart multipliers useful in constructing detection monitoring tests. Some of the strategies described in the Unified Guidance in later chapters require that more than one observation per compliance well be collected prior to statistical testing. ***The cumulative, annual false positive rate is linked not to the frequency of sampling but rather to the frequency of statistical evaluation***. When resamples (or verification resamples) are incorporated into a statistical procedure (**Chapter 19**), the individual resample comparisons comprise part of a single test. When a single future mean of ***m*** individual observations is evaluated against a prediction limit, this constitutes a test based on one ***mean comparison.***

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NUMBER OF TESTS AND CONSTITUENTS

In designing a detection monitoring program to achieve the target SWFPR, the number of annual statistical tests to be conducted needs to be identified. This number is calculated as the number of distinct monitoring constituents × the number of compliance wells in the network × the number of annual evaluations. Five constituents and 10 well locations statistically evaluated semi-annually constitute 100 annual tests ($5 \times 10 \times 2$), since each distinct well-constituent pair represents a different statistical test that must be evaluated against their respective backgrounds. Even smaller facilities are likely to have a substantial number of such tests, each incrementally adding to the SWFPR.

While the retesting strategies outlined in **Chapters 19** and **20** can aid tremendously in limiting the SWFPR and ensure adequate statistical power, there are practical limits to meeting these goals due to the limited number of groundwater observations that can be collected and/or the number of retests which can feasibly be run. To help balance the risks of false positive and false negative errors, the number of *statistically-tested* monitoring parameters should be limited to constituents thought to be reliable indicators of a contaminant release.

The guidance assumes that data from large suites of trace elements and organics along with a set of inorganic water quality indicators (pH, TDS, common ions, etc.) are routinely collected as part of historical site groundwater monitoring. The number of constituents potentially available for testing can be quite large, perhaps as many as 100 different analytes. At some sites, the full monitoring lists are too large to feasibly limit the SWFPR while maintaining sufficiently high power.

Non-naturally occurring chemicals such as volatile organic compounds [VOC] and semi-volatile organic compounds [SVOC] are often viewed as excellent indicators of groundwater contamination, and are thereby included in the monitoring programs of many facilities. There is a common misperception that the greater the number of VOCs and SVOCs on the monitoring list, the greater the statistical power of the monitoring program. The reasoning is that if none of these chemicals should normally be detected in groundwater — barring a release — testing for more of them ought to improve the chances of identifying contamination.

But including a large suite of VOCs and/or SVOCs among the mix of monitoring parameters ***can be counterproductive*** to the goal of maintaining adequate ***effective power*** for the site as a whole. Because of the trade-off between statistical power and false positive rates (**Chapter 3)**, the power to detect groundwater contamination in one of these wells even with a retesting strategy in place may be fairly low unless background sample sizes are quite large. This is especially true if the regulatory authority only allows for a single retest.

Suppose 40 VOCs and certain inorganic parameters are to be tested semi-annually at 20 compliance wells totaling 1600 annual statistical tests. To maintain a 10% cumulative annual SWFPR, the per-test false positive rate would then need to be set at approximately $\alpha_{test} = .0000625$. If only 10 constituents were selected for formal testing, the per-test rate would be increased to $\alpha_{test} = .00025$. For prediction limits and other detection tests, higher false positive test rates translate to lower κ-factors and improved power.

Some means of reducing the number of tested constituents is generally necessary to design an effective detection monitoring system. Earlier discussions have already suggested one obvious first step,

by eliminating historically non-detected constituents in background from the formal list of detction monitoring constituents (discussed further in the following section). These constituents are still analyzed and informally tested, but do not count against the SWFPR.

Results of waste and leachate testing and possibly soil gas analysis should serve as the initial basis for designating constituents that are reliable leak detection indicators. Such specific constituents actually present in, or derivable from, waste or soil gas samples, should be further evaluated to determine which can be analytically detected a reasonable proportion of the time. This evaluation should include considerations of how soluble and mobile a constituent may be in the underlying aquifer. Additionally, waste or leachate concentrations should be high enough relative to the groundwater levels to allow for adequate detection. By limiting monitoring and statistical tests to fewer parameters with reasonable detection frequencies and that are significant components of the facility's waste, unnecessary statistical tests can be avoided while focusing on the reliable identification of truly contaminated groundwater.

Initial leachate testing should not serve as the sole basis for designating monitoring parameters. At many active hazardous waste facilities and solid waste landfills, the composition of the waste may change over time. Contaminants that initially were all non-detect may not remain so. Because of this possibility, the Unified Guidance recommends that the list of monitoring parameters subject to formal statistical evaluation be periodically reviewed, for example, every three to five years. Additional leachate compositional analysis and testing may be necessary, along with the measurement of constituents not on the monitoring list but of potential health or environmental concern. If previously undetected parameters are discovered in this evaluation, the permit authority should consider revising the monitoring list to reflect those analytes that will best identify potentially contaminated groundwater in the future.

Further reductions are possible in the number of constituents used for formal detection monitoring tests, even among constituents periodically or always detected. EPA's experience at hazardous waste sites and landfills across the country has shown that VOCs and SVOCs detected in a release generally occur in clusters; it is less common to detect only a single constituent at a given location. Statistically, this implies that groups of detected VOCs or SVOCs are likely to be correlated. In effect, the correlated constituents are measuring a release in similar fashion and not providing fully independent measures. At petroleum refinery sites, benzene, toluene, ethylbenzene and xylenes measured in a VOC scan are likely to be detected together Similarly at sites having releases of 1,1,1-trichloroethane, perhaps 10-12 intermediate chlorinated hydrocarbon degradation compounds can form in the aquifer over time. Finally, among water quality indicators like common ions and TDS, there is a great deal of geochemical inter-relatedness. Again, two or three indicators from each of these analyte groups may suffice as detection monitoring constituents.

The overall goal should be to select only the most reliable monitoring constituents for detection monitoring test purposes. Perhaps 10-15 constituents may be a reasonable target, depending on site-specific needs. Those analytes not selected should still continue to be collected and evaluated. In addition to using the informal test to identify previously undetected constituents described in the next section, information on the remaining constituents (e.g., VOCs, SVOCs and trace elements) can still be important in assessing groundwater conditions, including additional confirmation of a detected release.

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DOUBLE QUANTIFICATION RULE

From the previous discussion, a full set of site historical monitoring parameters can be split into three distinct groups: a) those reliable indicators and hazardous constituents selected for formal detection monitoring testing and contributing to the SWFPR; b) other analytes which may be occasionally or even frequently detected and will be monitored for general groundwater quality information but not tested; and c) those meeting the "never-detected" criteria. The last group may still be of considerable interest for eventual formal testing, should site or waste management conditions change and new compounds be detected. All background measurements in the "never-detected" group should be non-detects, whether the full historical set or a subgroup considered most representative (e.g., recently collected background measurements using an improved analytical method.[5]). The following rule is suggested to provide a means of evaluating "never-detected" constituents.

The Double Quantification rule implies that statistical tests should be designed for each of the constituents in the first group. Calculations involving the SWFPR should cover these constituents, but *not* include constituents in second and the third '100% non-detect' categories. Any constituent in this third group should be evaluated by the following simple, quasi-statistical rule[6]:

> ***A confirmed exceedance is registered if any well-constituent pair in the '100% non-detect' group exhibits quantified measurements (i.e., at or above the reporting limit [RL]) in two consecutive sample and resample events.***

It is assumed when estimating an SWFPR using the Bonferroni-type adjustment, that each well-constituent test is at *equal risk* for a *specific, definable* false positive error. As a justification for this Double Quantification rule, analytical procedures involved in identifying a reported non-detect value suggest that the error risk is probably much *lower* for most chemicals analyzed as "never-detected." Reporting limits are set high enough so that if a chemical is *not present at all* in the sample, a detected amount will rarely be recorded on the lab sheet. This is particularly the case since method detection limits [MDLs] are often intended as 99% upper prediction limits on the measured signal of an uncontaminated laboratory sample. These limits are then commonly multiplied by a factor of 3 to 10 to determine the RL.

Consequently, a series of measurements for VOCs or SVOCs on samples of uncontaminated groundwater will tend to be listed as a string of non-detects with possibly a very occasional low-level detection. Because the observed measurement levels (*i.e.*, instrument signal levels) are usually known only to the chemist, an approximate prediction limit for the chemical basically has to be set at the RL. However, the true measurement distribution is likely to be clustered much more closely around zero than the RL (**Figure 6-1**), meaning that the false positive rate associated with setting the RL as the prediction

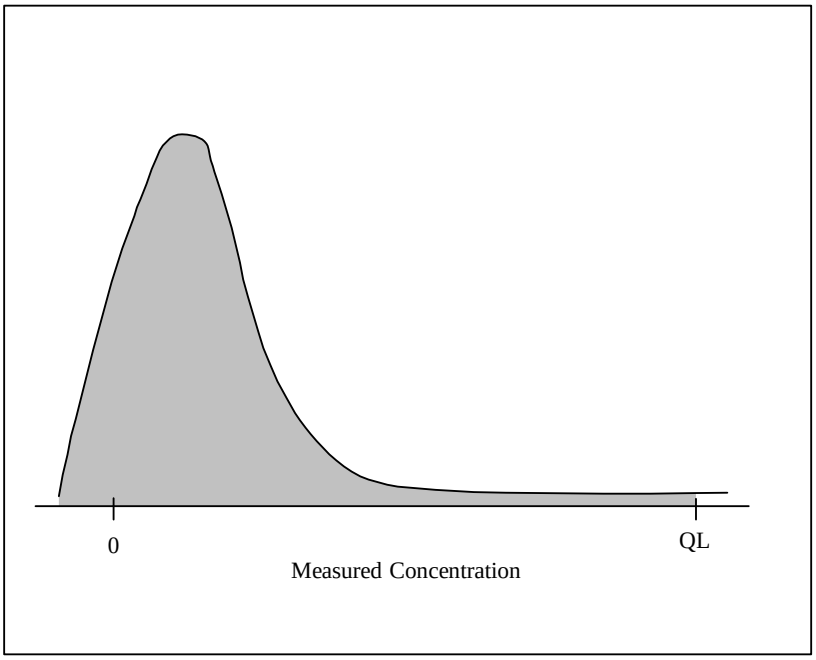
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[5] Note: Early historical data for some constituents (e.g., certain filtered trace elements) may have indicated occasional and perhaps unusual detected values using older analytical techniques or elevated reporting limits. If more recent sampling exhibits no detections at lower reporting limits for a number of events, the background review discussed in **Chapter 5** may have determined that the newer, more reliable recent data should be used as background. These analytes could also be included in the '100% non-detect' group.

[6] The term "quasi-statistical" indicates that although the form is a statistical prediction limit test, only an approximate false positive error rate is implied for the reporting limit critical value. The test form follows 1-of-2 or 1-of-3 non-parametric prediction limit tests using the maximum value from a background data set (**Chapter 19**).

limit is likely already *much lower* than the Bonferroni-adjusted error rate calculated above. A similar chain of reasoning would apply to site-specific chemicals that may be on the monitoring list but have *never* been detected at the facility. Such constituents would also need a prediction limit set at the RL.

Figure 6-1. Hypothetical Distribution of Instrument Signals in Uncontaminated Groundwater



In general, there should be some minimally sufficient sample numbers to justify placing constituents in the "never-detected" category. Even such a recommendation needs to consider individual background well versus pooled well data. Depending on the number of background wells (including historical compliance well data used as background which reflect the same non-detect patterns), certain risks may have to be taken to implement this strategy. With the same total number of non-detects (e.g., 4 each in 5 wells versus 20 from a single well), the relative risk can change. Certain non-statistical judgements may be needed, such as the likelihood of particular constituents arising from the waste or waste management unit. At a minimum, we recommend that at least 6 consecutive non-detect values initially be present in each well of a pooled group, and additional background well sampling should occur to raise this number to 10-15.

Having 10-15 non-detects as a basis, a maximum worst-case probability of a future false positive exceedance under Double Quantification rule testing could be estimated. But it should be kept in mind that the true individual comparison false positive rates based on analytical considerations are likely to be considerably lower. The number of non-detect constituents evaluated under the rule will also play a role. There will be some cumulative false positive error based on the number of comparisons at some true false positive single test error or errors. Since the true false positive test rates cannot be known (and may vary considerably among analytes), it is somewhat problematic to make this cumulative false positive error estimate. Yet there is some likelihood that occasional false positive exceedances will occur under this rule.

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Some flexibility will be required in evaluating such outcomes, particularly if there is doubt that a confirmed exceedance is actually due to a release from the regulated unit. In this circumstance, it might be appropriate to allow for a second resample as more definitive confirmation.

In implementing the Double Quantification rule, consideration should be given to how soon a repeat sample should be taken. Unlike detectable parameters, the question of autocorrelation is immaterial since the compound should not be present in the background aquifer. A sufficiently long interval should occur between the initial and repeat samples to minimize the possibility of a systematic analytical error. But the time interval should be short enough to avoid missing a subsequent real detection due to seasonal changes in the aquifer depth or flow direction. It is suggested that 1-2 months could be appropriate, but will depend on site-specific hydrological conditions.

Using this rule, it should be possible to construct adequately powerful prediction and control limits for naturally-occurring and detectable inorganic and organic chemicals in almost every setting. This is especially helpful at larger sites, since the total number of tests on which the per-test false positive rates (α_{test}) are based will be significantly reduced. Requiring a verified quantification for previously non-detected constituents should ensure that spurious lab results do not falsely trigger a facility into compliance/assessment monitoring, and will more reliably indicate the presence of chemicals that have heretofore not been found in background.

6.2.3 RECOMMENDATIONS FOR STATISTICAL POWER

The second but more important regulatory goal of a testing strategy is to ensure sufficient *statistical power* for detecting contaminated groundwater. Technically, in the context of groundwater monitoring, power refers to the probability that a statistical test will correctly identify a significant increase in concentration above background. Note that power is typically defined with respect to a single test, not a network of tests. In this guidance, cumulative power is assessed for a single test over an *annual* period, depending on the frequency of the evaluation. Since some testing procedures may identify contamination more readily when several wells in the network are contaminated as opposed to just one or two, the Unified Guidance recommends that all testing strategies be compared on the following more stringent common basis.

The *effective power* of a testing protocol across a network of well-constituent pairs is defined as the probability of detecting contamination in the monitoring network when *one and only one* well-constituent pair is contaminated. Effective power is a conservative measure of how a testing regimen will perform across the network, because the set of statistical tests must uncover one contaminated well among many clean ones (*i.e.*, like 'finding a needle in a haystack'). As mentioned above, this initial judgment may need to be qualified with *effect size* and other site-specific considerations.

INTRODUCTION TO POWER CURVES

Perhaps the best way to describe the power function associated with a particular testing procedure is via a graph, such as the example below of the power of a standard normal-based upper prediction limit with 99% confidence (**Figure 6-2**). The power in percent is plotted along the *y*-axis against the standardized mean level of contamination along the *x*-axis. The standardized contamination levels are presented in units of standard deviations above the *baseline* (defined as the true background mean). This

allows different power curves to be compared across constituents, wells, or well-constituent pairs. These standardized units Δ in the case of normally-distributed data may be computed as:

$$\Delta = \frac{(\text{Mean Contamination Level}) - (\text{Mean Background Level})}{(\text{SD of Background Population})} \quad [6.1]$$

In some situations, the probability that contamination will be detected by a particular testing procedure may be difficult if not impossible to derive analytically and will have to be simulated using Monte Carlo analysis on a computer. In these cases, power is typically estimated by generating normally-distributed random values at different mean contamination levels and repeatedly simulating the test procedure. With enough repetitions a reliable *power curve* can be plotted.

In the case of the normal power curve in **Figure 6-2**, the power values were computed analytically, using properties of the *non-central t-distribution.* In particular, the statistical power of a normal 99% prediction limit for the next single future value can be calculated as

$$1-\beta = \Pr\left\{T_{n-1}\left(\delta = \Delta\Big/\sqrt{1+\frac{1}{n}}\right) > t_{n-1,1-\alpha}\right\} \quad [6.2]$$

where Δ is the number of standardized (*i.e.,* standard deviation) units above the background population mean, (1–β) is the fractional power, δ is a non-centrality parameter, and:

$$T_{n-1}\left(\delta = \Delta\Big/\sqrt{1+\frac{1}{n}}\right) \quad [6.3]$$

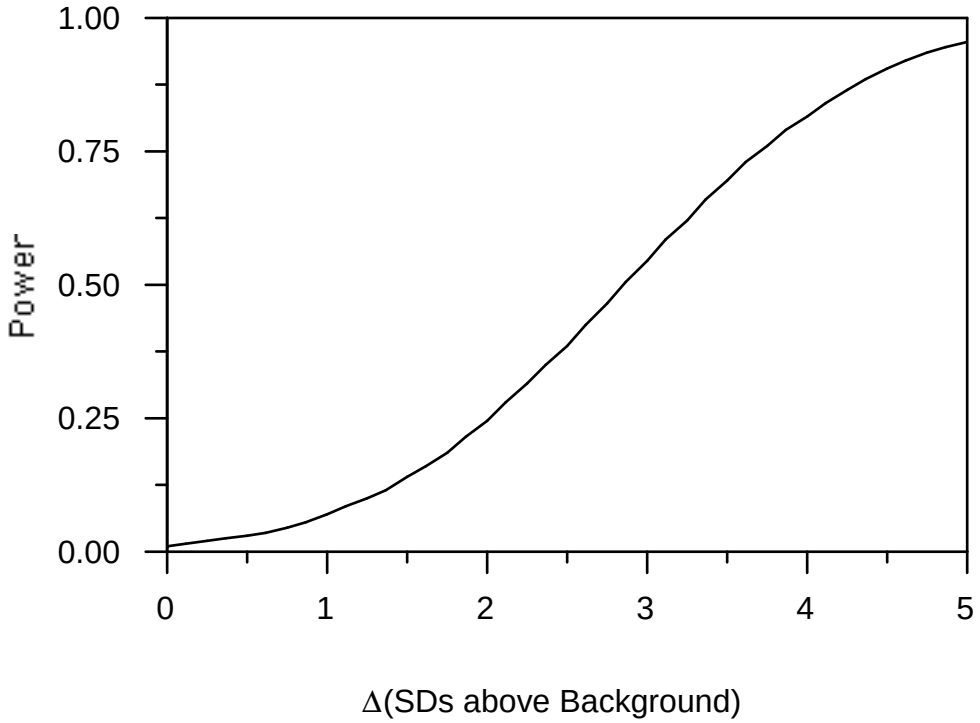
represents a non-central *t*-variate with (*n*–1) degrees of freedom and non-centrality parameter δ. Equation [6.2] was used with $n = 10$ to generate **Figure 6-2**.[7]

On a general power curve, the power at $\Delta = 0$ represents the false positive rate or *size* of the statistical test, because at that point no contamination is actually present (i.e., the background condition), even though the curve indicates how often a significant concentration increase will be detected. One should be careful to distinguish between the SWFPR across many statistical tests and the false positive rate represented on a curve measuring effective power. Since the effective power is defined as the testing procedure's ability to identify a *single* contaminated well-constituent pair, the effective power curve represents an *individual* test, *not* a network of tests. Therefore, the value of the curve at $\Delta = 0$ will only indicate the false positive rate associated with an individual test (α_{test}), not across the network as a whole. For many of the retesting strategies discussed in **Chapters 19** and **20**, the individual per-test false positive rate will be quite small and may appear to be nearly zero on the effective power curve.

[7] For users with access to statistical software containing the non-central T-distribution, this power curve can be duplicated. For example, the $\Delta = 3\sigma$ fractional power can be obtained using the following inputs: a central t-value of $t_{.99,\,9} = 2.821$, 9 df, and $\delta = 3\Big/\sqrt{1+(1/10)} = 2.8604$. The fractional power is .5414. It should be noted that the software may report the

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Figure 6-2. Normal Power Curve (n = 10) for 99% Prediction Limit Test



To properly interpret a power curve, note that not only is the probability greater of identifying a concentration increase above background (shown as a decimal value between 0 and 1 along the vertical axis) as the magnitude of the increase gets bigger (as measured along the horizontal axis), but one can determine the probability of identifying certain kinds of increases. For instance, with effective power equivalent to that in **Figure 6-2**, any mean concentration increase of at least 2 background standard deviations will be detected about 25% percent of the time, while an increase of 3 standard deviations will be detected with approximately 55% probability or better than 50-50 odds. A mean increase of at least 4 standard deviations will be detected with about 80% probability.

An increase of 3 or 4 standard deviations above the baseline may or may not have practical implications for human health or the environment. That will ultimately depend on site-specific factors such as the constituents being monitored, the local hydrogeologic environment, proximity to environmentally sensitive populations, and the observed variability in background concentrations. In some circumstances, more sensitive testing procedures might be warranted. As a general guide especially in the absence of direct site-specific information, the Unified Guidance recommends that when background is approximately normal in distribution,[8] any statistical test should be able to detect a 3

probability as (β) rather than (1-β). For more complex power curves involving multiple repeat samples or multiple tests, integration is necessary to generate the power estimates.

[8] If a non-parametric test is performed, power (or more technically, efficiency) is often measured by Monte Carlo simulation using normally distributed data. So these recommendations also apply to that case.

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standard deviation increase at least 55-60% of the time and a 4 standard deviation increase with at least 80-85% probability.

EPA REFERENCE POWER CURVES

Since effect sizes discussed in the next section often cannot or have not been quantified, the Unified Guidance recommends using the ERPC as a suitable basis of comparison for proposed testing procedures. Each reference power curve corresponds to one of three typical yearly statistical evaluation schedules — quarterly, semi-annual, or annual — and represents the cumulative power achievable during a single year at one well-constituent pair by a 99% upper (normal) prediction limit based on n = 10 background measurements and one new measurement from the compliance well (see **Chapter 18** for discussion of normal prediction limits). The ERPC are pictured in **Figure 6-3** below.

Any proposed statistical test procedure with effective power at least as high as the appropriate ERPC, especially in the range of three or more standard deviations above the background mean, should be considered to have reasonable power.[9] In particular, if the effective power first exceeds the ERPC at a mean concentration increase no greater than 3 background standard deviations (*i.e.*, $\Delta \leq 3$), the power is labeled 'good;' if the effective power first exceeds the ERPC at a mean increase between 3 and 4 standard deviations (*i.e.*, $3 < \Delta \leq 4$), the power is considered 'acceptable;' and if the first exceedance of the ERPC does not occur until an increase greater than 4 standard deviations (*i.e.*, $\Delta > 4$), the power is considered 'low.'

With respect to the ERPCs, one should keep the following considerations in mind:

1. The effective power of any testing method applied to a groundwater monitoring network can be increased merely by relaxing the SWFPR guideline, letting the SWFPR become larger than 10%. This is why a maximum annual SWFPR of 10% is suggested as standard guidance, to ensure fair power comparisons among competing tests and to limit the overall network-wide false positive rate.

2. The ERPCs are based on *cumulative* power over a one-year period. That is, if a single well-constituent pair is contaminated at standardized level Δ during each of the yearly evaluations, the ERPC indicates the probability that a 99% upper prediction limit test will identify the groundwater as impacted during at least one of those evaluations. Because the number of evaluations not only varies by facility, but also impacts the cumulative one-year power, different reference power curves should be employed depending on a facility's evaluation schedule. Quarterly evaluators should utilize the quarterly reference power curve (Q); semi-annual evaluators the semi-annual curve (S); and annual evaluators the annual curve (A).

3. If Monte Carlo simulations are used to evaluate the power of a proposed testing method, it should incorporate every aspect of the procedure, from initial screens of the data to final

[9] When using a retesting strategy in a larger network, the false positive rate associated with a single contaminated well (used to determine the effective power) will tend to be much smaller than the targeted SWFPR. Since the point at which the effective power curve intersects $\Delta = 0$ on the standardized horizontal axis represents the false positive rate for that individual test, the effective power curve by construction will almost always be *less* than the EPA reference power curve for small concentration increases above background. Of more concern is the relative behavior of the effective power curve at larger concentration increases, say two or more standard deviations above background.

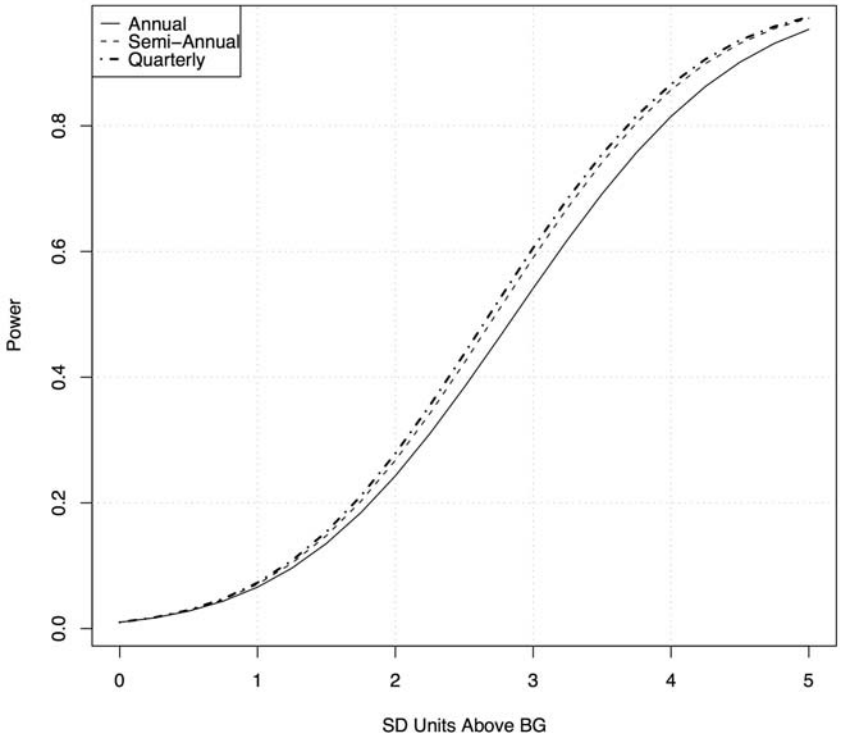
decisions concerning the presence of contamination. This is especially applicable to strategies that involve some form of retesting at potentially contaminated wells.

4. Although monitoring networks incorporate multiple well-constituent pairs, effective power can be gauged by simulating contamination in one and only one constituent at a single well.

5. The ERPCs should be considered a minimal power standard. The prediction limit test used to construct these reference curves does not incorporate retesting of any sort, and is based on evaluating a single new measurement from the contaminated well-constituent pair. In general, both retesting and/or the evaluation of multiple compliance point measurements tend to improve statistical power, so proposed tests that include such elements should be able to match the ERPC.

6. At sites employing multiple types of test procedures (***e.g.***, non-parametric prediction limits for some constituents, control charts for other constituents), effective power should be computed for each type of procedure to determine which type exhibits the least statistical power. Ensuring adequate power across the site implies that the ***least powerful*** procedure should match or exceed the appropriate ERPC, not just the most powerful procedure.

Figure 6-3. EPA Reference Power Curves



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6.2.4 EFFECT SIZES AND DATA-BASED POWER CURVES

EFFECT SIZES

If site-specific or chemical-specific risk/health information is available particularly for naturally-occurring constituents, it can be used in some circumstances to develop an *effect size* of importance. An effect size (φ) is simply the smallest concentration increase above the mean background level that is presumed or known to have a measurable, deleterious impact on human health and/or the environment, or that would clearly signal the presence of contamination.

When an effect size can be quantified for a given constituent and is approved by the regulating authority, the acceptable power of the statistical test can be tailored to that amount. For instance, if an effect size for lead in groundwater at a particular site is φ = 10 ppb, one might require that the statistical procedure have an 80% or 95% chance of detecting such an increase. This would be true regardless of whether the power curve for lead at that site matches the ERPC. In some cases, an agreed-upon effect size will result in a more stringent power requirement compared to the ERPCs. In other cases, the power standard might be less stringent.

Effect sizes are not known or have not been determined for many groundwater constituents, including many inorganic parameters that have detection frequencies high enough to be amenable to effect size calculations. Because of this, many users will routinely utilize the relative power guidelines embodied in the ERPC. Even if a specific effect size cannot be determined, it is helpful to consider the site-specific and test-specific implications of a three or four standard deviation concentration increase above background. Taking the background sample mean ($\bar{x}$) as the estimated baseline, and estimating the underlying population variability by using the sample background standard deviation (s), one can compute the approximate actual concentrations associated with a three, four, five, *etc.* standard deviation increase above the baseline (as would be done in computing a *data-based power curve*; **Section 6.2.4**). These concentration values will only be approximate, since the true background mean (μ) and standard deviation (σ) are unknown. However, conducting this analysis can be useful in at least two ways. Each is illustrated by a simple example.

By associating the standardized units on a reference power curve with specific but approximate concentration levels, it is possible to evaluate whether the anticipated power characteristics of the chosen statistical method are adequate for the site in question. If not, another method with better power might be needed. ***Generally, it is useful to discuss and report statistical power in terms of concentration levels rather than theoretical units***.

►EXAMPLE 6-1

A potential permit GWPS for lead is 15 ppb, while natural background lead levels are normally distributed with an average of 6 ppb and a standard deviation of 2 ppb. The regulatory agency determines that a statistical test should be able to identify an exceedance of this GWPS with high power. Further assume that the power curve for a particular statistical test indicated 40% power at 3 standard deviations and 78% power at 4σ above background (a low power rating).

By comparing the actual standard deviation estimate to the required target increase φ = (15-6)/2 = 4.5 standard units, the power at the critical effect size would be 80% or higher using **Figure 6-2** as a

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rough guide. This might be sufficient for monitoring needs even though the test did not meet the EPA reference criteria. Of course, the results apply only to this specific well-constituent test. ◄

For a given background sample, one can consider the regulatory and environmental impact of using *that particular background* as the basis of comparison in detection monitoring. Especially when deciding between *interwell* and *intrawell* tests at the same site, it is not unusual for the intrawell background from an individual well to exhibit much less variability than a larger set of observations pooled from multiple upgradient wells. This difference can be important since an intrawell test and an interwell test applied to the same site — *using identical relative power criteria* — might be associated with different risks to human health and the environment. A similar type of comparison might also aid in deciding whether the degrees of freedom of an intrawell test ought to be enlarged via a pooled estimate of the intrawell standard deviation (**Chapter 13**), whether a non-adjusted intrawell test is adequate, or whether more background sampling ought to be conducted prior to running intrawell tests.

►EXAMPLE 6-2

The standard deviation of an intrawell background population is σ_{intra} = 5 ppb, but that of upgradient, interwell background is σ_{inter} = 10 ppb. With the increased precision of an intrawell method, it may be possible to detect a 20 ppb increase with high probability (representing a $\Delta = 4\sigma_{intra}$ increase), while the corresponding probability for an interwell test is much lower (*i.e.*, 20 ppb = $2\sigma_{inter} = \Delta$). Of course, even if the intrawell test meets the ERPC target at four standardized units above background, consideration should be given as to whether or not 20 ppb is a meaningful increase.◄

One caveat is that calculation of either effect sizes or data-based power curves (see below) requires a reasonable estimate of the background standard deviation (σ). Such calculations may often be possible only for naturally-occurring inorganics or other constituents with fairly high detection frequencies in groundwater. Otherwise, power computations based on an effect size or the estimated standard deviation (s) are likely to be unreliable due to the presence of left-censored measurements (*i.e.*, non-detects).

A type of effect size calculation is presented in **Chapter 22** regarding methods for compliance/assessment and corrective action monitoring. A comparable effect size is computed by considering changes in mean concentration levels equal to a multiple of a fixed GWPS or clean-up/action level. While the mean level changes are multiples of the concentration limit and in that sense still relative, because they are tied to a fixed concentration standard, the power of the test can be linked to specific concentration levels.

DATA-BASED POWER CURVES

Even if basing power on a specific effect size is impractical for a given facility or constituent, it is still possible to relate power to absolute concentration levels rather than to the standardized units of the ERPC. While exact statistical power depends on the unknown population standard deviation (σ), an approximate power curve can be constructed based on the estimated background standard deviation (s). Instead of an estimate of power at a single effect size (depicted in **Example 6-1**), the actual power over a range of effect sizes can be evaluated. Such a graph is denoted in the Unified Guidance as a ***data-based power curve***, a term first coined by Davis (1998).

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Since the sample standard deviation (*s*) is calculated from actual groundwater measurements, this in turn changes an abstract power curve based on relative concentrations (*i.e.*, $k\sigma$ units above the baseline mean) into one displaying approximate, but absolute, concentrations (*i.e.*, *ks* units above baseline). The advantages of this approach include the following:

- Approximate data-based power curves allow the user to determine statistical power at any desired effect size (ϕ).

- Even if the effect size (ϕ) is unspecified, data-based power curves tie the performance of the statistical test back to actual concentration levels of the population being tested.

- Once the *theoretical* power curve of a particular statistical test is known, a data-based power curve is extremely easy to construct. One merely substitutes the observed background standard deviation (*s*) for σ and multiply by *k* to determine concentration values along the horizontal axis of the power curve. Even if the theoretical power curve is unknown, the same calculations can be made on the reference curve to derive an approximate site-specific, data-based power curve for tests roughly matching the performance of the ERPCs.

- If the choice between an interwell test and an intrawell approach is a difficult one (**Section 6.3.2**), helpful power comparisons can be made between intrawell and interwell tests at the same site using data-based power curves. Even if both tests meet the ERPC criteria, they may be based on different sets of background measurements, implying that the *interwell* standard deviation (s_{inter}) might differ from the *intrawell* standard deviation (s_{intra}). By plotting both data-based power curves on the same set of axes, the comparative performance of the tests can be gauged.

►EXAMPLE 6-3

The following background sample is used to construct a test with theoretical statistical power similar to the ERPC for annual evaluations (see **Figure 6-2**). What will an approximate data-based power curve look like, and what is the approximate power for detecting a concentration increase of 75 ppm?

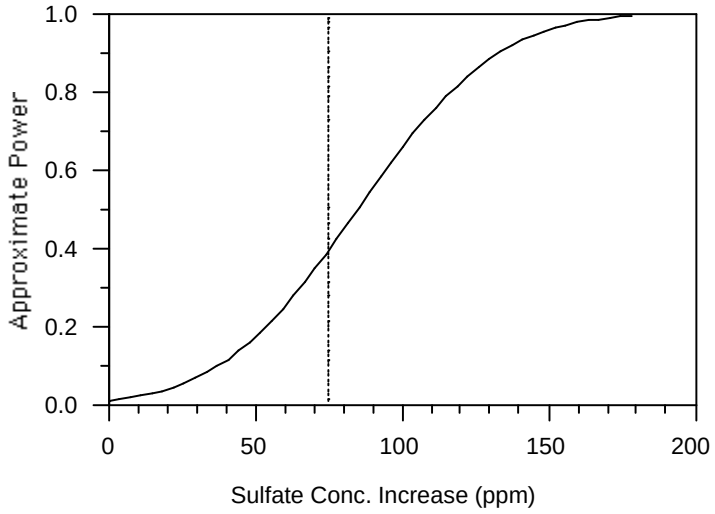
	Sulfate Concentrations (ppm)	
Quarter	BW-1	BW-2
1/95	560	550
4/95	530	570
7/95	568	540
10/95	490	542
1/96	510	590
Mean	545.0 ppm	
SD	29.7 ppm	

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SOLUTION

The sample standard deviation of the pooled background sulfate concentrations is 29.7 ppm. Multiplying this amount by the number of standard deviations above background along the *x*-axis in **Figure 6-2** and re-plotting, the approximate data-based power curve of **Figure 6-3** can be generated. Then the statistical power for detecting an increase of 75 ppm is almost 40%.

Figure 6-3. Approximate *s*-Based Power Curve for Sulfate



Had the pooled sample size been n = 16 using the same test and sample statistics, a different and somewhat more powerful theoretical power curve would result. This theoretical curve can be generated (for a 1-of-1 prediction limit test) using the non-central T-distribution described earlier, if a user has the appropriate statistical software package. The power for a 75 ppm increase can be calculated using $\delta = 75/\sqrt{1+(1/16)} = 2.45$ and $t_{.99,\ 15}$ = 2.602, as closer to 46%. The larger background sample size makes for a more powerful test. ◄

6.2.5 SITES USING MORE THAN ONE STATISTICAL METHOD

There is no requirement that a facility apply one and only one statistical method to its groundwater monitoring program. The RCRA regulations explicitly allow for the use of multiple techniques, depending on the distributional properties of the constituents being monitored and the characteristics of the site. If some constituent data contain a high percentage of non-detect values, but others can be normalized, the statistical approach should vary by constituent.

With interwell testing, parametric prediction limits might be used with certain constituents and non-parametric prediction limits for other highly non-detect parameters. If intrawell testing is used, the most appropriate statistical technique for one constituent might differ at certain groups of wells than for others. Depending on the monitoring constituent, available individual well background, and other site-specific factors, some combination of intrawell prediction limits, control charts, and Wilcoxon rank-sum tests might come into play. At other sites, a mixture of intrawell and interwell tests might be conducted.

The Unified Guidance offers a range of possible methods which can be matched to the statistical characteristics of the observed data. The primary goal is that the statistical program should maximize the

odds of making correct judgments about groundwater quality. The guidance SWFPR and ERPC minimum power criteria serve as comprehensive guides for assessing any of the statistical methods.

One major concern is how statistical power should be compared when multiple methods are involved. Even if each method is so designed as not to exceed the recommended SWFPR, the effective power for identifying contaminated groundwater may vary considerably by technique and specific type of test. Depending on the well network and statistical characteristics of available data, a certain control chart test may or may not be as powerful as normal prediction limits. In turn, a specific non-parametric prediction limit test may be more powerful than some parametric versions. It is important that effective power be defined consistently, even at sites where more than one statistical method is employed.

The guidance encourages employing the *effective power* concept in assessing the ability of the statistical program to correctly identify and flag real concentration increases above background. As already defined, effective power is the probability that such an increase will be identified even if *only* one well-constituent pair is contaminated. Each well-constituent pair being tested should be considered equally at risk of containing a true increase above background. This also implies that the effective power of each statistical test in use should meet the criteria of the EPA reference curves. That is, the test with the *least* power should still have adequate power for identifying mean concentration increases.

The Unified Guidance does not recommend that *a single composite measure of effective power* be used to gauge a program's ability to identify potential contamination. To understand this last recommendation, consider the following hypothetical example. Two constituents exhibiting different subsurface travel times and diffusive potentials in the underlying aquifer are monitored with different statistical techniques. The constituent with the faster travel time might be measured using a test with very low effective power (compared to the ERPC), while the slower moving parameter is measured with a test having very high effective power. Averaging the separate power results into a single composite measure might result in an effective power roughly equivalent to the ERPC. Then the chances of identifying a release in a timely manner would be diminished unless rather large concentrations of the faster constituent began appearing in compliance wells. Smaller mean increases — even if 3 or 4 standard deviation units above background levels — would have little chance of being detected, while the time it took for more readily-identified levels of the slower constituent to arrive at compliance wells might be too long to be environmentally protective. Statistical power results should be reported separately, so that the effectiveness of each distinct test can be adequately judged. Further data-specific power evaluations could still be necessary to identify the appropriate test(s).

The following basic steps are recommended for assessing effective power at sites using multiple statistical methods:

1. Determine the number and assortment of distinct statistical tests. Different power characteristics may be exhibited by different statistical techniques. Specific control charts, *t*-tests, non-parametric prediction limits, *etc.* all tend to vary in their performance. The performance of a given technique is also strongly affected by the data characteristics. Background sample sizes, interwell versus intrawell choices, the number of retests and type of retesting plan, *etc.*, all affect statistical power. Each distinct data configuration and retesting plan will delineate a slightly different statistical test method.

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2. Once the various methods have been identified, gauge the effective power of each.[10] Often the easiest way to measure power is via Monte Carlo simulation. Effective power involves a single well-constituent pair, so the simulation needs to incorporate only one population of background measurements representing the baseline condition and one population of compliance point measurements.

3. To run a Monte Carlo simulation, repeat the following algorithm a large number of times (*e.g.*, N = 10,000). Randomly generate a set of measurements from the background population in order to compute either a comparison limit for a control chart or some type of prediction limit test, or the background portion for a *t*-test or Wilcoxon rank-sum calculation, *etc*. Then generate compliance point samples at successively higher mean concentration levels, representing increases in standard deviation units above the baseline average. Perform each distinct test on the simulated data, recording the result of each iteration. By determining how frequently the concentration increase is identified at each successive mean level (including retests if necessary), the effective power for each distinct method can be estimated and compared.

►EXAMPLE 6-4

As a simple example of measuring effective power, consider a site using two different statistical methods. Assume that most of the constituents will be tested interwell with a 1-of-3 parametric normal prediction limit retesting plan for individual observations (**Chapter 19**). The remaining constituents having low detection rates and small well sample sizes will be tested intrawell with a Wilcoxon rank-sum test.

To measure the effective power of the normal prediction limits, note that the same number of background measurements (n = 30) is likely to be available for each of the relevant constituents. Since the per-constituent false positive rate (α_c) and the number of monitored wells (w) will also be identical for these chemicals, the same κ multiplier can be used for each prediction limit, despite the fact that the background mean and standard deviation will almost certainly vary by constituent.

Because of these identical data and well configurations, the effective power of each normal prediction limit will also be the same,[11] so that only one prediction limit test need be simulated. It is sufficient to assume the background population has a standard normal distribution. The compliance point population at the single contaminated well also has a normal distribution with the same standard deviation but a mean (μ) shifted upward to reflect successive relative concentration increases of 1 standard deviation, 2 standard deviations, 3 standard deviations, *etc*.

Simulate the power by conducting a large number of iterations (*e.g.*, N = 10,000-20,000) of the following algorithm: Generate 30 random observations from background and compute the sample mean

[10] Since power is a property of the statistical method and not linked to a specific data set, power curves are not needed for all well-constituent pairs, but only for each distinct statistical method. For instance, if intrawell prediction limits are employed to monitor barium at 10 compliance wells and the intrawell background sample size is the same for each well, only one power curve needs to be created for this group of tests.

[11] Statistical power measures the likely performance of the *technique* used to analyze the data, and is not a statement about the *data* themselves.

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and standard deviation. Calculate the prediction limit by adding the background mean to κ times the background standard deviation. For a 1-of-3 retesting plan, generate 3 values from the compliance point distribution (*i.e.*, a normal distribution with unit standard deviation but mean equal to μ). If the first of these measurements does not exceed the prediction limit, record a score of zero and move on to the next iteration. If, however, the first value is an exceedance, test the second value and possibly the third. If either resample does not exceed the prediction limit, record a score of zero and move to the next iteration. But if both resamples are also exceedances, record a score of one. The fraction of iterations (*N*) with scores equal to one is an estimate of the effective power at a concentration level of μ standard deviations above the baseline.

In the case of the intrawell Wilcoxon rank-sum test, the power will depend on the number of intrawell background samples available at each well and for each constituent.[12] Assume for purposes of the example that all the intrawell background sizes are the same with $n = 6$ and that two new measurements will be collected at each well during the evaluation period. The power will also depend on the frequency of non-detects in the underlying groundwater population. To simulate this aspect of the distribution for each separate constituent, estimate the proportion (p) of observed non-detects across a series of wells. Then set a RL for purposes of the simulation equal to z_β, the pth quantile of the standard normal distribution.

Finally, simulate the effective power by repeating a large number of iterations of the following algorithm: Generate $n = 6$ samples from a standard normal distribution to represent intrawell background. Also generate two samples from a normal distribution with unit standard deviation and mean equal to μ to represent new compliance point measurements from a distribution with mean level equal to μ standard deviations above background. Classify any values as non-detects that fall below z_β. Then jointly rank the background and compliance values and compute the Wilcoxon rank-sum test statistic, making any necessary adjustments for ties (*e.g.*, the non-detects). If this test statistic exceeds its critical value, record a score of one for the iteration. If not, record a score of zero. Again estimate the effective power at mean concentration level μ as the proportion of iterations (*N*) with scores of one.

As a last step, examine the effective power for each of the two techniques. As long as the power curves of the normal prediction limit and the Wilcoxon rank-sum test ***both*** meet the criteria of the ERPCs, the statistical program taken as a whole should provide acceptable power. ◄

[12] Technically, since the Wilcoxon rank-sum test will often be applied to non-normal data, power will also depend fundamentally on the true underlying distribution at the compliance well. Since there may be no way to determine this distribution, approximate power is measured by assuming the underlying distribution is instead normal.

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6.3 HOW KEY ASSUMPTIONS IMPACT STATISTICAL DESIGN

6.3.1 STATISTICAL INDEPENDENCE

IMPORTANCE OF INDEPENDENT, RANDOM MEASUREMENTS

Whether a facility is in detection monitoring, compliance/assessment, or corrective action, having an appropriate and valid sampling program is critical. All statistical procedures *infer* information about the underlying population from the observed sample measurements. Since these populations are only sampled a few times a year, observations should be carefully chosen to provide accurate information about the underlying population.

As discussed in **Chapter 3**, the mathematical theory behind standard statistical tests assumes that samples were *randomly* obtained from the underlying population. This is necessary to insure that the measurements are *independent* and *identically distributed* [i.i.d.]). Random sampling means that each possible concentration value in the population has an equal or known chance of being selected any time a measurement is taken. Only random sampling guarantees with sufficiently high probability that a set of measurements is adequately representative of the underlying population. It also ensures that human judgment will not bias the sample results, whether by intention or accident.

A number of factors make classical random sampling of groundwater virtually impossible. A typical small number of wells represent only a very small portion of an entire well-field. Wells are screened at specific depths and combine potentially different horizontal and vertical flow regimes. Only a minute portion of flow that passes a well is actually sampled. Sampling normally occurs at fixed schedules, not randomly.

Since a typical aquifer cannot be sampled at random, certain assumptions are made concerning the data from the available wells. It is first assumed that the selected well locations will generate concentration data similar to a randomly distributed set of wells. Secondly, it is assumed that groundwater flowing through the well screen(s) has a concentration distribution identical to the aquifer as a whole. This second assumption is unlikely to be valid unless groundwater is flowing through the aquifer at a pace fast enough and in such a way as to allow adequate mixing of the distinct water volumes over a relatively short (*e.g.*, every few months or so) period of time, so that groundwater concentrations seen at an existing well could also have been observed at other possible well locations.

Adequate sampling of aquifer concentration distributions cannot be accomplished unless enough time elapses between sampling events to allow different portions of the aquifer to pass through the well screen. Most closely-spaced sampling events will tend to exhibit a statistical dependence (*autocorrelation).* This means that pairs of consecutive measurements taken in a series will be positively correlated, exhibiting a stronger similarity in concentration levels than expected from pairs collected at random times. This would be particularly true for overall water quality indicators which are continuous throughout an aquifer and only vary slowly with time.

Another form of statistical dependence is *spatial correlation.* Groundwater concentrations of certain constituents exhibit natural spatial variability, *i.e.*, a distribution that varies depending on the location of the sampling coordinates. Spatially variable constituents exhibit mean and occasionally

variance differences from one well to another. Pairs of spatially variable measurements collected from the same or nearby locations exhibit greater similarity than those collected from distinct, widely-spaced, or distant wells.

Natural spatial variability can result from a number of geologic and hydrological processes, including varying soil composition across an aquifer. Various geochemical, diffusion, and adsorption processes may dominate depending on the specific locations being measured. Differential flow paths can also impact the spatial distribution of contaminants in groundwater, especially if there is limited mixing of distinct groundwater volumes over the period of sampling.

An adequate groundwater monitoring sampling program needs to account for not only site-specific factors such as hydrologic characteristics, projected flow rates, and directional patterns, but also meeting data assumptions such as independence. Statistical adjustments are necessary, such as selecting intrawell comparisons for spatially distinct wells or removing autocorrelation effects in the case of time dependence.

DARCY'S EQUATION AND AUTOCORRELATION

Past EPA guidance recommended the use of Darcy's equation as a means of establishing a minimum time interval between samples. When validly applied as a basic estimate of groundwater travel time in a given aquifer, the Darcy equation ensures that separate volumes of groundwater are being sampled (***i.e.***, physical independence). This increases the probability that the samples will also be statistically independent.

The Unified Guidance in **Chapter 14** also includes a discussion on applying Darcy's equation. Caution is advised in its use, however, since Darcy's equation *cannot guarantee* temporal independence. Groundwater travel time is only one factor that can influence the temporal pattern of aquifer constituents. The measurement process itself can affect time related dependency. An imprecise analytical method might impart enough additional variability to make the measurements essentially uncorrelated even in a short sampling interval. Changes in analytical methods or laboratories and even periodic re-calibration of analytical instrumentation can impart time-related dependencies in a data set regardless of the time intervals between samples.

The overriding interest is in the behavior of chemical contaminants in groundwater, not the groundwater itself. Many chemical compounds do not travel at the same velocity as groundwater. Chemical characteristics such as adsorptive potential, specific gravity, and molecular size can influence the way chemicals move in the subsurface. Large molecules, for example, will tend to travel slower than the average linear velocity of groundwater because of matrix interactions. Compounds that exhibit a strong adsorptive potential will undergo a similar fate, dramatically changing time of travel predictions using the Darcy equation. In some cases, chemical interaction with the matrix material will alter the matrix structure and its associated hydraulic conductivity and may result in an increase in contaminant mobility. This last effect has been observed, for instance, with certain organic solvents in clay units (see Brown and Andersen, 1981).

The Darcy equation is also not valid in turbulent and non-linear laminar flow regimes. Examples of these particular hydrological environments include karst and 'pseudo-karst' (***e.g.***, cavernous basalt and extensively fractured rock) formations. Specialized methods have been investigated by Quinlan (1989)

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for developing alternative monitoring procedures. Dye tracing as described by Quinlan (1989) and Mull, *et al*. (1988) can be useful for identifying flow paths and travel times in these two particular environments; conventional groundwater monitoring wells are often of little value in designing an effective monitoring system in these type of environments.

Thus, we suggest that Darcy's equation not be exclusively relied upon to gauge statistical sampling frequency. At many sites, quarterly or semi-annual sampling often provides a reasonable balance between maintaining statistical independence among observations yet enabling early detection of groundwater problems. The Unified Guidance recommends three tools to explore or test for time-related dependence among groundwater measurements. Time series plots (**Chapter 9**) can be constructed on multiple wells to examine whether there is a time-related dependence in the pattern of concentrations. Parallel traces on such a plot may indicate correlation across wells as part of a natural temporal, seasonal or induced laboratory effect. For longer data series, direct estimates of the autocorrelation in a series of measurements from a single well can be made using either the *sample autocorrelation function* or the *rank von Neumann ratio* (**Section 14.2**).

DATA MIXTURES INCLUDING ALIQUOT REPLICATE SAMPLES

Some facility data sets may contain both single and aliquot replicate groundwater measurements such as duplicate splits. An entire data set may also consist of aliquot replicates from a number of independent water quality samples. The guidance recommends against using aliquot data directly in detection monitoring tests, since they are almost *never* statistically independent. Significant positive correlation almost always exists between such duplicate samples or among aliquot sets. However, it is still possible to utilize some of the aliquot information within a larger water quality data set.

Lab duplicates and field splits can provide valuable information about the level of measurement variability attributable to sampling and/or analytical techniques. However, to use them as separate observations in a prediction limit, control chart, analysis of variance [ANOVA] or other procedure, the test must be specially structured to account for multiple data values per sampling event.

Barring the use of these more complicated methods, one suggested strategy has been to simply average each set of field splits and lab duplicates and treat the resulting mean as a single observation in the overall data set. Despite eliminating the dependence between field splits and/or lab duplicates, *such averaging is not an ideal solution*. The variability in means of two correlated measurements is approximately 30% less than the variability associated with two single independent measurements. If a data set consists of a mixture of single measurements and lab duplicates and/or field splits, the variability of the averaged values will be less than the variability of the single measurements. This would imply that the final data set is not *identically* distributed.

When data are not identically distributed, the actual false positive and false negative rates of statistical tests may be higher or lower than expected. The effect of mixing single measurements and averaged aliquot replicates might be balanced out in a two-sample t-test if sample sizes are roughly equal. However, the impact of non-identically distributed data can be substantial for an upper prediction limit test of a future single sample where the background sample includes a mixture of aliquot replicates and single measurements. Background variability will be underestimated, resulting in a lowered prediction limit and a higher false positive rate.

One statistically defensible but expensive approach is to perform the same number of aliquot replicate measurements on all physical samples collected from background and compliance wells. Aliquot replicates can be averaged, and the same variance reduction will occur in all the final observations. The statistical test degrees of freedom, however, are based on the number of independent, averaged samples.

Mixing single and averaged aliquot data is a serious problem if the component of variability due to field sampling methods and laboratory measurement error is a substantial fraction of the overall sample variance. When natural variability in groundwater concentrations is the largest component, averaging aliquot replicate measurements will do little to weaken the assumption of identically-distributed data. Even when variability due to sampling and analytical methods is a large component of the total variance, if the percentage of samples with aliquot replicate measurements is fairly small (say, 10% or less), the impact of aliquot replicate averaging should usually be negligible. However, consultation with a professional statistician is recommended.

The simplest alternative is to randomly select one value from each aliquot replicate set along with all non-replicate individual measurements, for use in statistical testing. Either this approach or the averaged replicate method described above will result in smaller degrees of freedom than the strategy of using all the aliquots, and will more accurately reflect the statistical properties of the data.

CORRECTING FOR TEMPORAL CORRELATION

The Unified Guidance recommends two general methods to correct for observable temporal correlation. Darcy's equation is mentioned above as a rough guide to physical independence of consecutive groundwater observations. A more generally applicable strategy for yet-to-be-collected measurements involves adjusting the sampling frequency to avoid autocorrelation in consecutive sampling events. Where autocorrelation is a serious concern, the Unified Guidance recommends running a *pilot study* at two or three wells and analyzing the study data by using the sample autocorrelation function (**Section 14.3.1**). The autocorrelation function plots the strength of correlation between consecutive measurements against the time lag between sampling events. When the autocorrelation becomes insignificantly different from zero at a particular sampling interval, the corresponding sampling frequency is the maximum that will ensure uncorrelated sampling events.

Two other strategies are recommended for adjusting already collected data. First, a longer data series at a single well can be corrected for seasonality by estimating and removing the seasonal trend (**Section 14.3.3**). If both a linear trend *and* seasonal fluctuations are evident, the seasonal Mann-Kendall trend test can be run to identify the trend despite the seasonal effects (**Section 14.3.4**). A second strategy is for sites where a temporal effect (*e.g.*, temporal dependence, seasonality) is apparent across multiple wells. This involves estimating a temporal effect via a *one-way* ANOVA and then creating adjusted measurements using the ANOVA residuals (**Section 14.3.3**). The adjusted data can then be utilized in subsequent statistical procedures.

6.3.2 SPATIAL VARIATION: INTERWELL VS. INTRAWELL TESTING

ASSUMPTIONS IN BACKGROUND-TO-DOWNGRADIENT COMPARISONS

The RCRA groundwater monitoring regulations initially presume that detection monitoring background can be defined on the basis of a definable groundwater gradient. In a considerable number of situations, this approach is problematic. No groundwater gradient may be measurable for identifying upgradient and downgradient well locations around a regulated unit. The hydraulic gradient may change in direction, depth or magnitude due to seasonal fluctuations. Groundwater mounding or other flow anomalies can occur. At most locations, significant spatial variability among wells exists for certain constituents. Where spatial variation is a natural artifact of the site-specific geochemistry, differences between upgradient and downgradient wells are unrelated to on-site waste management practices.

Both the Subtitle C and Subtitle D RCRA regulations allow for a determination that background quality may include sampling of wells not hydraulically upgradient of the waste management area. The rules recognize that this can occur either when hydrological information is unable to indicate which wells are hydraulically upgradient or when sampling other wells will be "representative or more representative than that provided by the upgradient wells."

For upgradient-to-downgradient well comparisons, a crucial detection monitoring assumption is that downgradient well changes in groundwater quality are only caused by on-site waste management activity. Up- and down-gradient well measurements are also assumed to be comparable and equal on average unless some waste-related change occurs. If other factors trigger significant increases in downgradient well locations, it may be very difficult to pinpoint the monitored unit as the source or cause of the contaminated groundwater.

Several other critical assumptions apply to the interwell approach. It is assumed that the upgradient and downgradient well samples are drawn from the same aquifer and that wells are screened at essentially the same hydrostratigraphic position. At some sites, more than one aquifer underlies the waste site or landfill, separated by confining layers of clay or other less permeable material. The fate and transport characteristics of groundwater contaminants likely will differ in each aquifer, resulting in unique concentration patterns. Consequently, upgradient and downgradient observations may not be comparable (*i.e.*, drawn from the same statistical population).

Another assumption is that groundwater flows in a definable pathway from upgradient to downgradient wells beneath the regulated unit. If flow paths are incorrectly determined or this does not occur, statistical comparisons can be invalidated. For example, a real release may be occurring at a site known to have groundwater mounding beneath the monitored unit. Since the groundwater may move towards both the downgradient and upgradient wells, it may not be possible to detect the release if both sets of wells become equally or similarly contaminated. One exception to this might occur if certain analytes are shown to exhibit uniform behavior in both historical upgradient and downgradient wells (e.g., certain infrequently detected trace elements). As long as the flow pathway from the unit to the

downgradient wells is assured, then an interwell test based on this combined background could still reflect a real exceedance in the downgradient wells.[13]

Groundwater flow should also move at a sufficient velocity beneath the site, so that the same groundwater observed at upgradient well locations is subsequently monitored at downgradient wells in the course of an evaluation period (*e.g.*, six months or a year). If groundwater flow is much slower, measurements from upgradient and downgradient wells may be more akin to samples from two separate aquifers. Extraneous factors may separately influence the downgradient and background populations, confusing the determination of whether or not a release has occurred.

While statistical testing can determine whether there are significant differences between upgradient and downgradient well measurements, it cannot determine *why* such differences exist. That is primarily the concern of a hydrologist who has carefully reviewed site-specific factors. Downgradient concentrations may be greater than background because contamination of the underlying aquifer has occurred. The increase may be due to other factors, including spatially variable concentration levels attributable to changing soil composition and geochemistry from one well location to another. It could also be due to the migration of contaminants from off-site sources reaching downgradient wells. These and other factors (including those summarized in **Chapter 4** on SSI Increases) should be considered before deciding that statistically significant background-to-downgradient differences represent site-related contamination.

An example of how background-to-downgradient well differences can be misleading is illustrated in **Figure 6-4** below. At this Eastern coastal site, a Subtitle D landfill was located just off a coastal river emptying into the Atlantic Ocean a short distance downstream. Tests of specific conductance measurements comparing the single upgradient well to downgradient well data indicated significant increases at all downgradient wells, with one well indicating levels more than an order of magnitude higher than background concentrations.

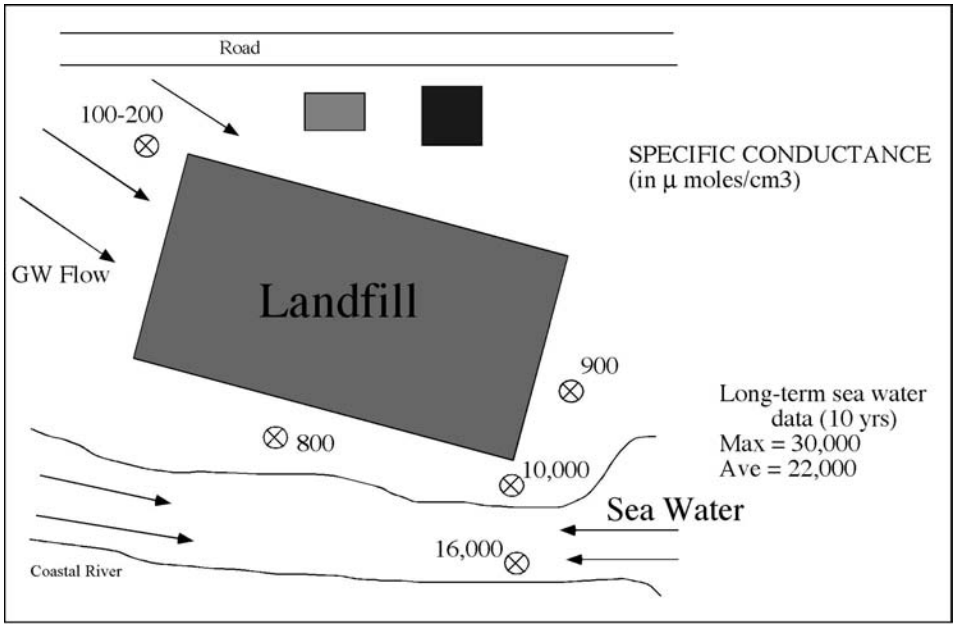
Based on this analysis, it was initially concluded that waste management activities at the landfill had impacted groundwater. However, further hydrologic investigation showed that nearby river water also exhibited elevated levels of specific conductance, even higher than measurements at the downgradient wells. Tidal fluctuations and changes in river discharge caused sea water to periodically mix with the coastal river water at a location near the downgradient wells. Mixed river and sea water apparently seeped into the aquifer, impacting downgradient wells but not at the upgradient location. An off-site source as opposed to the landfill itself was likely responsible for the observed elevations in specific conductance. Without this additional hydrological information, the naive statistical comparison between upgradient and downgradient wells would have reached an incorrect conclusion.

[13] The same would be true of the "never-detected" constituent comparison, which does not depend on the overall flow pathway from upgradient to downgradient wells.

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Figure 6-4. Landfill Site Configuration



TRADEOFFS IN INTERWELL AND INTRAWELL APPROACHES

The choice between interwell and intrawell testing primarily depends on the statistical characteristics of individual constituent data behavior in background wells. It is presumed that a thorough background study described in **Chapter 5** has been completed. This involves selecting the constituents deemed appropriate for detection monitoring, identifying distributional characteristics, and evaluating the constituent data for trends, stationarity, and mean spatial variability among wells. ANOVA tests can be used to assess both well mean spatial variability and the potential for pooled-variance estimates if an intrawell approach is needed.

As discussed in **Chapter 5**, certain classes of potential monitoring constituents are more likely to exhibit *spatial variation*. Water quality indicator parameters are quite frequently spatially variable. Some authors, notably Davis and McNichols (1994) and Gibbons (1994a), have suggested that significant spatial variation is a nearly ubiquitous feature at RCRA-regulated landfills and hazardous waste sites, thus invalidating the use of interwell test methods. The Unified Guidance accepts that interwell tests still have an important role in groundwater monitoring, particularly for certain classes of constituents like non-naturally occurring VOCs and some trace elements. Many sites may best be served by a statistical program which combines interwell and intrawell procedures.

Intrawell testing is an appropriate and recommended alternative strategy for many constituents. Well-specific backgrounds afford intrawell tests certain advantages over the interwell approach. One key advantage is *confounding results due to spatial variability* are eliminated, since all data used in an intrawell test are obtained from a single location. If natural background levels change substantially from

one well to the next, intrawell background provides the most accurate baseline for use in statistical comparisons.

At times, the ***variability*** in a set of upgradient background measurements pooled from multiple wells can be larger than the variation in individual intrawell background wells. Particularly if not checked with ANOVA well mean testing, interwell variability could substantially increase if changes in mean levels from one location to the next are also incorporated. While pooling should not occur among well means determined to be significantly different using ANOVA, a more likely situation is that pooled well true means and variance may be slightly different at each well. The ANOVA test might still conclude that the mean differences were insignificant and satisfy the equal variance assumption. The net result (as explained below) is that intrawell tests can be more statistically powerful than comparable interwell tests using upgradient background, despite employing a smaller background sample size.

Another advantage using intrawell background is that a ***reasonable baseline*** for tests of future observations can be established at historically contaminated wells. In this case, the intrawell background can be used to track the onset of even more extensive contamination in the future. Some compliance monitoring wells exhibit chronic elevated contaminant levels (e.g., arsenic) considerably above other site wells which may not be clearly attributed to a regulated unit release. The regulatory agency has the option of continuing detection monitoring or changing to compliance/corrective action monitoring. Unless the agency has already determined that the pre-existing contamination is subject to compliance monitoring or remedial action under RCRA, the detection monitoring option would be to test for recent or future concentration increases above the historical contamination levels by using intrawell background as a well-specific baseline.

Intrawell tests are not preferable for all groundwater monitoring scenarios. It may be unclear whether a given compliance well was historically contaminated prior to being regulated or more recently contaminated. Using intrawell background to set a baseline of comparison may ignore recent contamination subject to compliance testing and/or remedial action. Even more contamination in the future would then be required to trigger a statistically significant increase [SSI] using the intrawell test. The Unified Guidance recommends the use of intrawell testing only when it is clear that spatial variability is not the result of recent contamination attributable to the regulated unit.

A second concern is that intrawell tests typically utilize a smaller set of background data than interwell methods. Since statistical power depends significantly on background ***sample size***, it may be more difficult to achieve comparable statistical power with intrawell tests than with interwell methods. For the latter, background data can be collected from multiple wells when appropriate, forming a larger pool of measurements than would be available at a single well. However, it may also be possible to enhance intrawell sample sizes for parametric tests using the pooled- variance approach.

Traditional interwell tests can be appropriate for certain constituents if the hydraulic assumptions discussed earlier are verified and there is no evidence of significant spatial variability. Background data from other historical compliance wells not significantly different from upgradient wells using ANOVA may also be used in some cases. When these conditions are met, interwell tests can be preferable as generally more powerful tests. Upgradient groundwater quality can then be more easily monitored in

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parallel to downgradient locations. Such upgradient monitoring can signal changes in natural in-situ concentrations or possible migration from off-site sources. [14]

For most situations, the background constituent data patterns will determine which option is most feasible. Clear indications of spatially distinct well means through ANOVA testing will necessitate some form of intrawell methods. Further choices are then which type of statistical testing will provide the best power.

It may be possible to increase the *effective sample size* associated with a series of intrawell tests. As explained in **Chapters 13 & 19**, the κ-multipliers for intrawell prediction limits primarily depend on the number of background measurements used to estimate the standard deviation. It is first necessary to determine that the intrawell background in a series of compliance wells is both uncontaminated and exhibits similar levels of variability from well to well. Background data from these wells can then be combined to form a *pooled* intrawell standard deviation estimate with larger degrees of freedom, even though individual well means vary. A transformation may be needed to stabilize the well-to-well variances. If one or more of the compliance wells is already contaminated, these should not be mixed with uncontaminated well data in obtaining the pooled standard deviation estimate.

A site-wide constituent pattern of no significant spatial variation will generally favor the interwell testing approach. But given the potential for hydrological and other issues discussed above, further evaluation of intrawell methods may be appropriate. **Example 6-2** provided an illustration of a specific intrawell constituent having a lower absolute standard deviation than an interwell pooled data set, and hence greater relative and absolute power. In making such an interwell-intrawell comparison, the specific test and all necessary design inputs must be considered. Even if a given intrawell data set has a low background standard deviation compared to an interwell counterpart, the advantage in absolute terms over the relative power approach will change with differing design inputs. The simplest way to determine if the intrawell approach might be advantageous is to calculate the actual background limits of a potential test using existing intra- and inter-well data sets. In a given prediction limit test, for example, the actual lower limit will determine the more powerful test.

If desired, approximate data-based power curves (**Section 6.2.4**) can be constructed to evaluate absolute power over a range of concentration level increases. In practice, the method for comparing interwell versus intrawell testing strategies with the same well-constituent pair involves the following basic steps:

1. Given the interwell background sample size (n_{inter}), the statistical test method (including any retesting), and the individual per-test α for that well-constituent pair, compute or simulate the relative power of the test at multiples of ks_{inter} above the baseline mean level. Let k range from 0 to 5 in increments of 0.5, where the interwell population standard deviation (σ_{inter}) has been replaced by the sample background standard deviation (s_{inter}).

[14] The same can be accomplished via intrawell methods if upgradient wells continue to be sampled along with required compliance well locations. Continued tracking of upgradient background groundwater quality is recommended regardless of the testing strategy.

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2. Repeat Step 1 for the intrawell test. Use the intrawell background sample size (n_{intra}), statistical test method, background sample standard deviation (s_{intra}), and the same individual per-test α to generate a relative power curve.

3. On the same graph, plot overlays of the estimated data-based interwell and intrawell power curves (as discussed in **Section 6.2.4**). Use the same range of (absolute, not relative) concentration increases over baseline along the horizontal axis.

4. Visually inspect the data-based power curves to determine which method offers better power over a wider range of possible concentration increases.

The Unified Guidance recommends that users apply the most powerful statistical methods available in detecting and identifying contaminant releases for each well-constituent pair. The ERPC identifies a minimum acceptable standard for judging the relative power of particular tests. However, more powerful methods based on absolute power may be considered preferable in certain circumstances.

As a final concern, very small individual well samples in the early stages of a monitoring program may make it difficult to utilize an intrawell method having both sufficient statistical power and meeting false positive design criteria. One option would be to temporarily defer tests on those well-constituent pairs until additional background observations can be collected. A second option is to use the intrawell approach despite its inadequate power, until the intrawell background is sufficiently large via periodic updates (**Chapter 5**). A third option might be to use a more powerful intrawell test (e.g., a higher order 1-of-*m* parametric or non-parametric prediction limit test). Once background is increased, a lower order test might suffice. Depending on the type of tests, some control of power may be lost (parametric) or the false positive (non-parametric tests). These tradeoffs are considered more fully in **Chapter 19**. For the first two options and the parametric test under the third option, there is some added risk that a release occurring during the period of additional data collection might be missed. For the non-parametric test under the third option, there is an increased risk of a true false positive error. Any of these options might be included as special permit conditions.

6.3.3 OUTLIERS

Evaluation of outliers should begin with historical upgradient and possibly compliance well data considered for defining initial background, as described in **Chapter 5, Section 5.2.3**. The key goal is to select the data most representative of near-term and likely future background. Potentially discrepant or unusual values can occur for many reasons including 1) a contaminant release that significantly impacts measurements at compliance wells; 2) true but extreme background groundwater measurements, 3) inconsistent sampling or analytical chemistry methodology resulting in laboratory contamination or other anomalies; and 4) errors in the transcription of data values or decimal points. While the first two conditions may appear to be discrepant values, they would not be considered outliers.

When appraising extensive background data sets with long periods of acquisition and somewhat uncertain quality, it is recommended that a formal statistical evaluation of outliers not be conducted until a thorough review of data quality (errors, etc.) has been performed. Changes in analytical methodologies, the presence of sample interferences or dilutions can affect the historical data record. Past and current treatment of non-detects should also be investigated, including whether there are multiple reporting limits in the data base. Left-censored values can impact whether or not the sample

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appears normal (**Chapter 15**), especially if the data need to be normalized via a transformation. Techniques for evaluating censored data should be considered, especially those which can properly account for multiple RLs. Censored probability plots (**Chapter 15**) or quasi-nonparametric box plots (**Chapter 12**) adapted by John Tukey (1977) can be used as methods to screen for outliers.

The guidance also recommends that statistical testing of potential outliers also be performed on initial background data, including historical compliance well data potentially considered as additional background data. Recognizing the potential risks as discussed in **Chapter 5**, removal of significant outliers may be appropriate even if no probable error or discrepancy can be firmly identified. The risk is that high values registering as statistical outliers may reflect an extreme, but real value from the background population rather than a true outlier, thereby increasing the likelihood of a false positive error. But the effect of removing outliers from the background data will usually be to improve the odds of detecting upward changes in concentration levels at compliance wells, and thus providing further protection of human health and the environment. *Automated screening and removal* of background data for statistical outliers is not recommended without some consideration of the likelihood of an outlier error.

A *statistical outlier* is defined as a value originating from a different statistical population than the rest of the sample. Outliers or observations not derived from the same population as the rest of the sample violate the basic statistical assumption of identically-distributed measurements. If an outlier is suspected, an initial helpful step is to construct a probability plot of the ordered sample data versus the standardized normal distribution (**Chapter 12**). A probability plot is designed to judge whether the sample data are consistent with a normal population model. If the data can be normalized, a probability plot of the transformed observations should also be constructed. Neither is a formal test, but can still provide important visual evidence as to whether the suspected outlier(s) should be further evaluated.

Formal testing for outliers should be done only if an observation seems particularly high compared to the rest of the sample. The data can be evaluated with either Dixon's or Rosner's tests (**Chapter 12**). These outlier tests assume that the rest of the data except for the suspect observation(s), are normally-distributed (Barnett and Lewis, 1994). It is recommended that tests also be conducted on transformed data, if the original data indicates one or more potential outliers. Lognormal and other skewed distributions can exhibit apparently elevated values in the original concentration domain, but still be statistically indistinguishable when normalized via a transformation. If the latter is the case, the outlier should be retained and the data set treated as fitting the transformed distribution.

Future background and compliance well data may also be periodically tested for outliers. However, removal of outliers should only take place under certain conditions, since a true elevated value may fit the pattern of a release or a change in historical background conditions. If either Dixon's or Rosner's test identifies an observation as a statistical outlier, the measurement should not be treated as such *until* a specific physical reason for the abnormal value can be determined. Valid reasons might include contaminated sampling equipment, laboratory contamination of the sample, errors in transcription of the data values, etc. Records documenting the sampling and analysis of the measurement (*i.e.*, the "chain of custody") should be thoroughly investigated. Based on this review, one of several actions might be taken as a general rule:

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- If an error in transcription, dilution, analytical procedure, *etc.* can be identified and the correct value recovered, the observation should be replaced by its corrected value and further statistical analysis done with the corrected value.

- If it can shown that the observation is in error but the correct value cannot be determined, the observation should be removed from the data set and further statistical analysis performed on the reduced data set. The fact that the observation was removed and the reason for its removal should be documented when reporting results of the analysis.

- If no error in the value can be documented, it should be assumed that the observation is a true but extreme value. In this case, it should not be altered or removed. However, it may helpful to obtain another observation in order to verify or confirm the initial measurement.

6.3.4 NON-DETECTS

Statistically, non-detects are considered 'left-censored' measurements because the concentration of any non-detect is known or assumed only to fall within a certain range of concentration values (*e.g.*, between 0 and the RL). The direct estimate has been censored by limitations of the measurement process or analytical technique.

As noted, non-detect values can affect evaluations of potential outliers. Non-detects and detection frequency also impact what detection monitoring tests are appropriate for a given constituent. A low detection frequency makes it difficult to implement parametric statistical tests, since it may not be possible to determine if the underlying population is normal or can be normalized. Higher detection frequencies offer more options, including *simple substitution* or estimating the mean and standard deviation of samples containing non-detects by means of a *censored estimation technique* (**Chapter 15**).

Estimates of the background mean and standard deviation are needed to construct parametric prediction and control chart limits, as well as confidence intervals. If simple substitution is appropriate, imputed values for individual non-detects can be used as an alternate way to construct mean and standard deviation estimates. These estimates are also needed to update the *cumulative sum* [CUSUM] portion of control charts or to compute means of order *p* compared against prediction limits.

Simple substitution is not recommended in the Unified Guidance unless no more than 10-15% of the sample observations are non-detect. In those circumstances, substituting half the RL for each non-detect is not likely to substantially impact the results of statistical testing. Censored estimation techniques like *Kaplan-Meier* or *robust regression on order statistics* [ROS] are recommended any time the detection frequency is no less than 50% (see **Chapter 15)**.

For lower detection frequencies, non-parametric tests are recommended. Non-parametric prediction limits (**Chapter 18**) can be constructed as an alternative to parametric prediction limits or control charts. The Tarone-Ware two-sample test (**Chapter 16**) is specifically designed to accommodate non-detects and serves as an alternative to the *t*-test. By the same token, the Kruskal-Wallis test (**Chapter 17**) is a non-parametric, rank-based alternative to the parametric ANOVA. These latter tests can be used when the non-detects and detects can be jointly sorted and partially ordered (except for tied values).

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When *all* data are non-detect, the Double Quantification rule (**Section 6.2.2**) can be used to define an approximate non-parametric prediction limit, with the RL as an upper bound. Before doing this, it should be determined whether chemicals never or not recently detected in groundwater should even be formally tested. This will depend on whether the monitored constituent from a large analytical suite is likely to originate in the waste or leachate.

Even if a data set contains only a small proportion of non-detects, care should be taken when choosing between the *method detection limit* [MDL], the quantification limit [QL], and the RL in characterizing 'non-detect' concentrations. Many non-detects are reported with one of three data qualifier flags: "U," "J," or "E." Samples with a U data qualifier represent 'undetected' measurements, meaning that the signal characteristic of that analyte could not be observed or distinguished from 'background noise' during lab analysis. Inorganic samples with an E flag and organic samples with a J flag may or may not be reported with an estimated concentration. If no concentration estimate is reported, these samples represent 'detected, but not quantified' measurements. In this case, the actual concentration is assumed to be positive, falling somewhere between zero and the QL or possibly the RL.

Since the actual concentration is unknown, the suggested imputation when using simple substitution is to replace each non-detect having a qualifier of E or J by one-half the RL. Note, however, that E and J samples reported ***with*** estimated concentrations should be treated as valid measurements for statistical purposes. Substitution of one-half the RL is ***not recommended*** for these measurements, even though the degree of uncertainty associated with the estimated concentration is probably greater than that associated with measurements above the RL.

As a general rule, non-detect concentrations should ***not*** be assumed to be bounded above by the MDL. The MDL is usually estimated on the basis of ideal laboratory conditions with physical analyte samples that may or may not account for matrix or other interferences encountered when analyzing specific field samples. For certain trace element analytical methods, individual laboratories may report detectable limits closer to an MDL than a nominal QL. So long as the laboratory has confidence in the ability to quantify at its lab- or occasionally event-specific detection level, this RL may also be satisfactory. The RL should typically be taken as a more reasonable upper bound for non-detects when imputing estimated concentration values to these measurements.

RLs are sometimes but not always equivalent to a particular laboratory's QLs. While analytical techniques may change and improve over time leading to a lowering of the achievable QL, a contractually negotiated RL might be much higher. Often a multiplicative factor is built into the RL to protect a contract lab against particular liabilities. A good practice is to periodically review a given laboratory's capabilities and to encourage reporting non-detects with actual QLs whenever possible, and providing standard qualifiers with all data measurements as well as ***estimated*** concentrations for E- and J-flagged samples.

Even when no estimate of concentration can be made, a lab should regularly report the distinction between 'undetected' and 'detected, but not quantified' non-detect measurements. Data sets with such delineations can be used to advantage in rank-based non-parametric procedures. Rather than assigning the same tied rank to all non-detects (**Chapter 16**), 'detected but not quantified' measurements should be given larger ranks than those assigned to 'undetected' samples. These two types of non-detects should be treated as two *distinct* groups of tied observations for use in the non-parametric ***Wilcoxon rank-sum*** procedure.

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6.4 DESIGNING DETECTION MONITORING TESTS

In the following sections, the main formal detection monitoring tests covered in this guidance are described in the context of site design choices. Advantages as well as limitations are presented, including the use of certain methods as diagnostic tools in determining the appropriate formal test(s).

6.4.1 T-TESTS

A statistical comparison between two sets of data is known as a two-sample test. When normality of the sample data can be presumed, the parametric Student *t*-test is commonly used (**Section 16.1**). This test compares two distinct populations, represented by two *samples*. These samples can either be individual well data sets, or a common pooled background versus individual compliance well data. The basic goal of the *t*-test is to determine whether there is any statistically significant difference between the two population means. Regulatory requirements for formal use of two-sample t-tests are limited to the Part 265 indicator parameters, and have generally been superseded in the Parts 264 and 258 rules by tests which can account for multiple comparisons.

When the sample data are non-normal and may contain non-detects, the Unified Guidance provides alternative two-sample tests to the parametric t-test. The Wilcoxon rank-sum test (**Section 16.2**) requires that the combined samples be sorted and ranked. This test evaluates potential differences in population *medians* rather than the *means*. The Tarone-Ware test (**Section 16.3**) is specially adapted to handle left-censored measurements, and also tests for differences in population medians.

The *t*-test or a non-parametric variant is recommended as a validation tool when updating intrawell or other background data sets (**Chapter 5**). More recently collected data considered for background addition are compared to the historical data set. A non-significant test result implies no mean differences, and the newer data may be added to the original set. These tests are generally useful for any two-sample diagnostic comparisons.

6.4.2 ANALYSIS OF VARIANCE [ANOVA]

The parametric one-way ANOVA is an extension of the t-test to multiple sample groups. Like its two-sample counterpart, ANOVA tests for significant differences in one or more group (e.g., well) means. If an overall significant difference is found as measured by the F-statistic, *post-hoc* statistical contrasts may be used to determine where the differences lie among individual group means. In the groundwater detection monitoring context, only differences of mean well increases relative to background are considered of importance. The ANOVA test also has wide applicability as a diagnostic tool.

USE OF ANOVA IN FORMAL DETECTION MONITORING TESTS

RCRA regulations under Parts 264 and 258 identify parametric and non-parametric ANOVA as potential detection monitoring tests. Because of its flexibility and power, ANOVA can sometimes be an appropriate method of statistical analysis when groundwater monitoring is based on an *interwell* comparison of background and compliance well data. Two types of ANOVA are presented in the Unified Guidance: parametric and non-parametric one-way ANOVA (**Section 17.1**). Both methods

attempt to assess whether distinct monitoring wells differ in average concentration during a given evaluation period.[15]

Despite the potential attractiveness of ANOVA tests, use in formal detection monitoring is limited by these important factors:

- ❖ Many monitoring constituents exhibit significant spatial variability and cannot make use of interwell comparisons;
- ❖ The test can be confounded by a large number of well network comparisons;
- ❖ A minimum well sample size must be available for testing; and
- ❖ Regulatory false positive error rate restrictions limit the ability to effectively control the overall false positive rate.

As discussed in **Section 6.2.3**, many if not most inorganic monitoring constituents exhibit spatial variability, precluding an interwell form of testing. Since ANOVA is inherently an interwell procedure, the guidance recommends against its use for these constituents and conditions. Spatial variability implies that the average groundwater concentration levels vary from well to well because of existing on-site conditions. Mean differences of this sort can be identified by ANOVA, but the cause of the differences cannot. Therefore, results of a statistically significant ANOVA might be falsely attributed as a regulated unit release to groundwater.

ANOVA testing might be applied to synthetic organic and trace element constituent data. However, spatial variation across a site is also likely to occur from offsite or prior site-related organic releases. An existing contamination plume generally exhibits varying average concentrations longitudinally, as well as in cross-section and depth. For other organic constituents never detected at a site, ANOVA testing would be unnecessary. Certain trace elements like barium, arsenic and selenium do often exhibit some spatial variability. Other trace element data generally have low overall detection rates, which may also preclude ANOVA applications. Overall, very few routine monitoring constituents are measurable (i.e., mostly detectable) yet not spatially distinct to warrant using ANOVA as a formal detection monitoring test. Other guidance tests better serve this purpose.

ANOVA has good power for detecting real contamination provided the network is small to moderate in size. But for large monitoring networks, it may be difficult to identify single well contamination. One explanation is that the ANOVA F-statistic simultaneously combines all compliance well effects into a single number, so that many other uncontaminated wells with their own variability can mask the test effectiveness to detect the contaminated well. This might occur at larger sites with multiple waste units, or if only the edge of a plume happens to intersect one or two boundary wells.

The statistical power of ANOVA depends significantly on having at least 4 observations per well available for testing. Since the measurements must be statistically independent, collection of four well observations may necessitate a wait of several months to a few years if the natural groundwater velocity

[15] Parametric ANOVA assesses differences in means; the non-parametric ANOVA compares ***median*** concentration levels. Both statistical measures are a kind of average.

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is low. In this case, other strategies (e.g., prediction limits) might be considered that allow each new groundwater measurement to be tested as it is collected and analyzed.

The one-way ANOVA test in the RCRA regulations is not designed to control the false positive error rate for multiple constituents. The rules mandate a minimum false positive error rate (α) of 5% per test application. With an overall false positive rate of approximately 5% per constituent, a potentially very high SWFPR can result as the number of constituents tested by ANOVA increases and if tests are conducted more than once per year.

For these reasons, the Unified Guidance does not generally recommend ANOVA for formal detection monitoring. ANOVA might be applicable to a small number of constituents, depending on the site. Prediction limit and control chart strategies using retesting are usually more flexible and offer the ability to accommodate even very large monitoring networks, while meeting the false positive and statistical power targets recommended by the guidance.

USE OF ANOVA IN DIAGNOSTIC TESTING

In contrast, ANOVA is a versatile tool for diagnostic testing, and is frequently used in the guidance for that purpose. Parametric or non-parametric one-way versions are the principal means of identifying prior spatial variability among background monitoring wells (**Chapter 13**). Improving sample sizes using intrawell pooled variances also makes use of ANOVA (**Chapter 13**). Equality of variances among wells is evaluated with ANOVA (**Chapter 11**). ANOVA is also applied when determining certain temporal trends in parallel well sample constituent data (**Chapter 14**).

Tests of natural spatial variability can be made by running ANOVA prior to any waste disposal at a new facility located above an undisturbed aquifer (Gibbons, 1994a). If ANOVA identifies significant upgradient and downgradient well differences when wastes have not yet been managed on-site, natural spatial variability is the likely cause. Prior on-site contamination might also be revealed in the form of significant ANOVA differences.

Sites with multiple upgradient background wells can initially conduct an ANOVA on historical data from just these locations. Where upgradient wells are not significantly different for a given constituent, ANOVA testing can be extended to existing historical compliance well data for evaluating potential additions to the upgradient background data base.

If intrawell tests are chosen because of natural spatial variation, the results of a one-way ANOVA on background data from multiple wells can sometimes be used to improve intrawell background limits (**Section 13.3**). Though the amount of intrawell background at any given well may be small, the ANOVA provides an estimate of the *root mean squared error* [RMSE], which is very close to an estimate of the *average per-well standard deviation*. By substituting the RMSE for the usual well-specific standard deviation (s), a more powerful and accurate intrawell limit can be constructed, at least at those sites where intrawell background across the group of wells can be normalized and the variances approximately equalized using a common transformation.

Although the Unified Guidance primarily makes use of one-way ANOVA, many kinds of ANOVA exist. The one-way ANOVA applications so far discussed— in formal detection monitoring or to assess well mean differences— utilize data from spatial locations as the factor of interest. In some situations,

correlated behavior may exist for a constituent among well samples evaluated in different temporal events. A constituent measured in a group of wells may simultaneously rise or fall in different time periods. Under these conditions, the data are no longer random and independent. ANOVA can be used to assess the significance of such systematic changes, making *time* the factor of interest. Time can also play a role if the sample data exhibit cyclical seasonal patterns or if parallel upward or downward trends are observed both in background and compliance point wells.

If time is an important second factor, a *two-way* ANOVA is probably appropriate. This procedure is discussed in Davis (1994). Such a method can be used to test for and adjust data either for seasonality, parallel trends, or changes in lab performance that cause temporal (*i.e.*, time-related) effects. It is somewhat more complicated to apply than a one-way test. The main advantage of a two-way ANOVA is to separate components of overall data variation into three sources: well-to-well mean-level differences, temporal effects, and random variation or statistical error. Distinguishing the sources of variation provides a more powerful test of whether significant well-to-well differences actually exist compared to using only a one-way procedure.

A significant temporal factor does not necessarily mean that the one-way ANOVA will *not* identify actual well-to-well spatial differences. It merely does not have as strong a chance of doing so. Rarely will the one-way ANOVA identify non-existent well-to-well differences. One situation where this can occur is when there is a strong *statistical interaction* between the well-to-well factor and the time factor in the two-way ANOVA. This would imply that changes in lab performance or seasonal cycles affect certain wells (*e.g.*, compliance point) to a different degree or in a different manner than other wells (*e.g.*, background). If this is the case, professional consultation is recommended before conducting more definitive statistical analyses.

6.4.3 TREND TESTS

Most formal detection monitoring tests in the guidance compare background and compliance point populations under the key assumption that the populations *are stationary over time*. The distributions in each group or well are assumed to be stable during the period of monitoring, with only random fluctuations around a constant mean level. If a significant trend occurs in the background data, these tests cannot be directly used. Trends can occur for several reasons including natural cycles, gradual changes in aquifer parameters or the effects of contaminant migration from off-site sources.

Although not specifically provided for in the RCRA regulations, the guidance necessarily includes a number of tests for evaluating potential trends. **Chapter 17, Section 17.3** covers three basic trend tests. (1) *Linear regression* is a parametric method requiring normal and independent trend residuals, and can be used both to identify a linear trend and estimate its magnitude; (2) For non-normal data (including sample data with left-censored measurements), the *Mann-Kendall* test offers a non-parametric method for identifying trends; and (3) To gauge trend magnitude with non-normal data, the *Theil-Sen* trend line can be used.

Trend analyses are primarily diagnostic tests, which should be applied to background data prior to implementing formal detection monitoring tests. If a significant trend is uncovered, two options may apply. The particular monitoring constituent may be dropped in favor of alternate constituents not exhibiting non-stationary behavior. Alternatively, prediction limit or control chart testing can make use of stationary *trend residuals* for testing purposes. One limitation of the latter approach requires making

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an assumption that the historical trend will continue into future monitoring periods. In addition, future data needs to be de-trended prior to testing. If a trend happened to be of limited duration, this assumption may not be reasonable and could result in identifying a background exceedance when it does not exist. If a trend occurs in future data at a compliance well and prior background data was stationary, other detection monitoring tests are likely to eventually identify it. Trend testing may also be applied to once-future data considered for a periodic background update, although the guidance primarily relies on t-testing of historical and future groups to assess data suitability.

At historically contaminated compliance wells, establishing a proper baseline for a prediction limit or control chart is problematic, since uncontaminated concentration data cannot be collected. Depending on the pattern of contamination, an intrawell background may either have a stable mean concentration level or exhibit an increasing or decreasing trend. Particularly when intrawell background concentrations are rising, the assumption of a static baseline population required by prediction limits and control charts will be violated.

As an alternative, the Unified Guidance recommends a test for trend to measure the extent and nature of the apparent increase. Trend testing can determine if there is a statistically significant positive trend over the period of monitoring and can also determine the magnitude (*i.e.*, slope) of the trend. In identifying a positive trend, it might be possible to demonstrate that the level of contamination has increased relative to historical behavior and indicate how rapidly levels are increasing.

Trend analyses can be used directly as an alternative test against a GWPS in compliance and corrective action monitoring. For typical compliance monitoring, data collected at each compliance well are used to generate a lower confidence limit compared to the fixed standard (**Chapters 7, 21 and 22**). A similar situation occurs when corrective action is triggered, but making use of an upper confidence interval for comparison. For compliance well data containing a trend, the appropriate confidence interval is constructed around a linear regression trend line (or its non-parametric alternative) in order to better estimate the most current concentration levels. Instead of a single confidence limit for stationary tests, the confidence limit (or band) estimate changes with time.

6.4.4 STATISTICAL INTERVALS

Prediction limits, tolerance limits, control chart limits and confidence limits belong to the class of methods known as statistical intervals. The first three are used to define their respective detection monitoring test limits, while the last is used in fixed standard compliance and corrective action tests. When using a background GWPS, either approach is possible (see **Section 7.5**). Intervals are generated as a statistic from reference sample data, and represent a probable range of occurrence either for a future sample statistic or some parameter of the population (in the case of confidence intervals) from which the sample was drawn. A future sample statistic might be one or more single values, as well as a future mean or median of specific size, drawn from one or more sample sets to be compared with the interval (generally an upper limit). Both the reference and comparison sample populations are themselves unknown, with the latter initially presumed to be identical to the reference set population. In the groundwater monitoring context, the initial reference sample is the background data set.

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The key difference in confidence limits[16] is that a statistical interval based on a single sample is used to estimate the probable range of a population parameter like the true mean, median or variance. The three detection monitoring tests use intervals to identify ranges of future sample statistics likely to arise from the background population based on the initial sample, and are hence two- or multiple-sample tests.

Statistical intervals are inherently two-sided, since they represent a finite range in which the desired statistic or population parameter is expected to occur. Formally, an interval is associated with a level of confidence (1-α); by construction, the error rate α represents the remaining likelihood that the interval *does not contain* the appropriate statistic or parameter. In a two-sided interval, the α-probability is associated with ranges both above and below the statistical interval. A one-sided upper interval is designed to contain the desired statistic or parameter at the same (1-α) level of confidence, but the remaining error represents only the range above the limit. As a general rule, detection monitoring options discussed below use one-sided upper limits because of the nature of the test hypotheses.

PREDICTION LIMITS

Upper prediction limits (or intervals) are constructed to contain with (1-α) probability, the next few sample value(s) or sample statistic(s) such as a mean from a background population. Prediction limits are exceptionally versatile, since they can be designed to accommodate a wide variety of potential site monitoring conditions. They have been extensively researched, and provide a straightforward interpretation of the test results. Since this guidance strongly encourages use of a comprehensive design strategy to account for both the cumulative SWFPR and effective power to identify real exceedances, prediction limit options offer a most effective means of accounting for both criteria. The guidance provides test options in the form of parametric normal and non-parametric prediction limit methods. Since a retesting strategy of some form is usually necessary to meet both criteria, prediction limit options are constructed to formally include resampling as part of the overall tests.

Chapters 18 and 19 provide nine parametric normal prediction limit test options: four tests of future values (1-of-2, 1-of-3, 1-of-4 or a modified California plan) and five future mean options (1-of-1, 1-of-2, or 1-of-3 tests of mean size 2, and 1-of-1 or 1-of-2 tests of mean size 3). Non-parametric prediction limit options cover the same future value test options as the parametric versions, as well as two median tests of size 3 (1-of-1 or 1-of-2 tests). **Appendix D** tables provide the relevant κ-factors for each parametric normal test option, the achievable false positive rates for non-parametric tests, and a categorical rating of relative test power for each set of input conditions. Prediction limits can be used both for interwell and intrawell testing. Selecting from among these options should allow the two site design criteria to be addressed for most groundwater site conditions.

The options provided in the guidance are based on a wider class known in the statistical literature as *p-of-m* prediction limit tests. Except for the two modified California plan options, those selected are 1-of-*m* test varieties. The number of future measurements to be predicted (i.e., contained) by the interval is also denoted in the Unified Guidance by *m* and can be as small as $m = 1$. To test for a release to groundwater, compliance well measurements are designated as future observations. Then a limit is constructed on the background sample, with the prediction limit formula based on the number of *m*

[16] Confidence limits are further discussed **in Chapters 7, 21 and 22** for use in compliance and corrective action testing.

future values or statistics to be tested against the limit. As long as the compliance point measurements are similar to background, the prediction limit should contain all *m* of the future values or statistics with high probability (the level of confidence). For a 1-of-*m* test, all *m* values must be larger than the prediction limit to be declared an exceedance, as initial evidence that compliance point concentrations are higher than background.

Prediction limits with retesting are presented in **Chapter 19**. When retesting is part of the procedure, there are significant and instructive differences in statistical performance between parametric and non-parametric prediction limits.

Parametric prediction limits are constructed using the general formula: $PL = \bar{x} + \kappa \cdot s$, where $\bar{x}$ and *s* are the background sample mean and standard deviation, and κ is the specific multiplicative factor for the type of test, background sample size, and the number of annual tests. The number of tests made against a common background is also an input factor for interwell comparison. The **Appendix D** κ-factors are specifically designed to meet the SWFPR objective, but power will vary. Larger background sample sizes and higher order (*m*) tests afford greater power.

When background data cannot be normalized, a non-parametric prediction limit can be used instead. A non-parametric prediction limit test makes use of one or another of the largest sample values from the background data set as the limit. For a given background sample size and test type, the level of confidence of that maximal value is fixed.

Using the absolute maximum of a background data set affords the highest confidence and lowest single-test false positive error. However, even this confidence level may not be adequate to meet the SWFPR objective, especially for lower order 1-of-*m* tests. A higher order future values test using the same maximum and background sample size will provide greater false positive confidence and hence a lower false positive error rate. For a fixed background sample size, a 1-of-4 retesting scheme will have a lower achievable significance level (α) than a 1-of-3 or 1-of-2 plan for any specific maximal value. A larger background sample size using a fixed maximal value for any test also has a higher confidence level (lower α) than a smaller sample.

But for a fixed non-parametric limit of a given background sample size, the power decreases as the test order increases. If the non-parametric prediction limit is set at the maximum, a 1-of-2 plan will be more powerful than a 1-of-4 plan. It is relatively easy to understand why this is the case. A verified exceedance in a 1-of-2 test occurs only if two values exceed the limit, but would require four to exceed for the 1-of-4 plan. As a rule, even the highest order non-parametric test using some maximal background value will be powerful enough to meet the ERPC power criteria, but achieving a sufficiently low single-test error rate to meet the SWFPR is more problematic.

If the SWFPR objective can be attained at a maximum value for higher order 1-of-*m* tests, it may be possible to utilize lower maxima from a large background data base. Lower maxima will have greater power and a somewhat higher false positive rate. Limited comparisons of this type can be made when choosing between the largest or second-largest order statistics in the Unified Guidance **Appendix D Tables 19-19** to **19-24**. A more useful and flexible comparison for 1-of-*m* future value plans can be obtained using the EPA Region 8 *Optimal Rank Values Calculator* discussed in **Chapter 19**. The calculator identifies the lowest ranked maximal value of a background data set for 1-of-1 to 1-of-4 future

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value non-parametric tests which can meet the SWFPR objective, while providing ERPC ratings and fractional power estimates at 2, 3, and 4 standard deviations above background.

TOLERANCE INTERVALS

Tolerance intervals are presented in **Section 17.2**. A tolerance interval is generated from background sample data to contain a pre-specified *proportion* of the underlying population (*e.g.*, 99% of all possible population measurements) at a certain level of confidence. Measurements falling outside the tolerance interval can be judged to be statistically different from background.

While tolerance intervals are an acceptable statistical technique under RCRA as discussed in **Section 2.3**, the Unified Guidance generally recommends prediction limits instead. Both methods can be used to compare compliance point measurements to background in detection monitoring. The same general formula is used in both tests for constructing a parametric upper limit of comparison: $\bar{x} + \kappa s$. For non-parametric upper limit tests, both prediction limits and tolerance intervals use an observed order statistic in background (often the background maximum). But prediction limits are ultimately more flexible and easier to interpret than tolerance intervals.

Consider a parametric upper prediction limit test for the next two compliance point measurements with 95% confidence. If either measurement exceeds the limit, one of two conditions is true: either the compliance point distribution is significantly different and higher than background, or a false positive has been observed and the two distributions are similar. False positives in this case are expected to occur 5% of the time. Using an upper tolerance interval is not so straightforward. The tolerance interval has an extra statistical parameter that must be specified — the coverage (γ) — representing the fraction of background to be contained beneath the upper limit. Since the confidence level (1–α) governs how often a statistical interval contains its target population parameter (**Section 7.4**), the complement α does not necessarily represent the false positive rate in this case.

In fact, a tolerance interval constructed with 95% confidence to cover 80% of background is designed so that as many as 20% of all background measurements will exceed the limit with 95% probability. Here, α = 5% represents the probability that the true coverage will be less than 80%. But less clear is the false positive rate of a tolerance interval test in which as many as 1 in 5 background measurements are expected to exceed the upper background limit. Are compliance point values above the tolerance interval indicative of contaminated groundwater or merely representative of the upper ranges of background?

Besides a more confusing interpretation, there is an added concern. Mathematically valid retesting strategies can be computed for prediction limits, but not yet for tolerance intervals, further limiting their usefulness in groundwater testing. It is also difficult to construct powerful *intrawell* tolerance intervals, especially when the intrawell background sample size is small. Overall, there is little practical need for two similar (but not identical) methods in the Unified Guidance, at least in detection monitoring.

If tolerance intervals ***are*** employed as an alternative to *t*-tests or ANOVA when performing interwell tests, the RCRA regulations allow substantial flexibility in the choice of α. This means that a somewhat arbitrarily high confidence level (1–α) can be specified when constructing a tolerance interval. However, unless the coverage coefficient (γ) is also set to a high value (*e.g.*, ≥ 95%), the test is likely to incur a large risk of false positives despite a small α.

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One setting in which an upper tolerance interval is very appropriate is discussed in **Section 7.5**. Some constituents that must be evaluated under compliance/assessment or corrective action may not have a fixed GWPS. Existing background levels may also exceed a fixed GWPS. In these cases, a background standard can be constructed using an upper tolerance interval on background with 95% confidence and 95% coverage. The standard will then represent a reasonable upper bound on background and an achievable target for compliance and remediation testing.

6.4.5 CONTROL CHARTS

Control charts (**Chapter 20**) are a viable alternative to prediction limits in detection monitoring. One advantage of a control chart over a prediction limit is that control charts allow compliance point data to be viewed and assessed graphically over time. Trends and changes in concentration levels can be easily seen, because the compliance measurements are consecutively plotted on the chart as they are collected, giving the data analyst an historical overview of the concentration pattern. Standard prediction limits allow only *point-in-time comparisons* between the most recent data and background, making long-term trends more difficult to identify.

The guidance recommends use of the combined *Shewhart-CUSUM control chart.* The advantage is that *two* statistical quantities are assessed at every sampling event, both the new individual measurement and the cumulative sum [CUSUM] of past and current measurements. Prediction limits do not incorporate a CUSUM, and this can give control charts comparatively greater sensitivity to gradual (upward) trends and shifts in concentration levels. To enhance false positive error rate control and power, retesting can also be incorporated into the Shewhart-CUSUM control chart. Following the same restrictions as for prediction limits, they may be applied either to interwell or intrawell testing.

A disadvantage in applying control charts to groundwater monitoring data is that less is understood about their statistical performance, *i.e.*, false positive rates and power. The control limit used to identify potential releases to groundwater is not based on a formula incorporating a desired false positive rate (α). Unlike prediction limits, the control limit cannot be precisely set to meet a pre-specified SWFPR, unless the behavior of the control chart is modeled via Monte Carlo simulation. The same is true for assessing statistical power. Control charts usually provide less flexibility than prediction limits in designing a statistical monitoring program for a network.

In addition, Shewhart-CUSUM control charts are a parametric procedure with no existing non-parametric counterpart. Non-parametric prediction limit tests are still generally needed when the background data on which the control chart is constructed cannot be normalized. Control charts are mostly appropriate for analytes with a reasonably high detection frequency in monitoring wells. These include inorganic constituents (*e.g.*, detectable trace elements and geochemical monitoring parameters) occurring naturally in groundwater, and other persistently-found, site-specific chemicals.

6.5 SITE DESIGN EXAMPLES

Three hypothetical design examples consider a small, medium and large facility, illustrating the principles discussed in this chapter. In each example, the goal is to determine what statistical method or methods should be chosen and how those methods can be implemented in light of the two fundamental design criteria. Further design details are covered in respective **Part III** detection monitoring test

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chapters, although very detailed site design is beyond the scope of the guidance. More detailed evaluations and examples of diagnostic tests are found in **Part II** of the guidance.

►EXAMPLE 6-5 SMALL FACILITY

A municipal landfill has 3 upgradient wells and 8 downgradient wells. Semi-annual statistical evaluations are required for five inorganic constituents. So far, six observations have been collected at each well. Exploratory analysis has shown that the concentration measurements appear to be approximately normal in distribution. However, each of the five monitored parameters exhibits significant levels of natural spatial variation from well to well. What statistical approach should be recommended at this landfill?

SOLUTION

Since the inorganic monitoring parameters are measurable and have significant spatial variability, it is recommended that parametric intrawell rather than interwell tests should be considered. Assuming that none of the downgradient wells is recently contaminated, each well has $n = 6$ observations available for its respective intrawell background. Six background measurements may or may not be enough for a sufficiently powerful test.

To address the potential problem of inadequate power, a one-way ANOVA should be run on the combined set of wells (including background locations). If the well-to-well variances are significantly different, individual standard deviation estimates should be made from the six observations at the eight downgradient wells. If the variances are approximately equal, a pooled standard deviation estimate can instead be computed from the ANOVA table. With 11 total wells and 6 measurements per well, the pooled standard deviation has $df = 11 \times 5 = 55$ degrees of freedom, instead of $df = 5$ for each individual well.

Regardless of ANOVA results, the per-test false positive rate is approximately the design SWFPR divided by the annual number of tests. For $w = 8$ compliance wells, $c = 5$ parameters monitored, and $n_E = 2$ statistical evaluations per year, the per-test false positive rate is approximately $\alpha_{test} = SWFPR/(w \times c \times n_E) = 0.00125$. Given normal distribution data, several different parametric prediction limit retesting plans can be examined,[17] using either the combined sample size of $df + 1 = 56$ or the per-well sample size of $n = 6$.

Explained in greater detail in **Chapter 19**, κ-multiples and power ratings for each test type (using the inputs $w = 8$ and $n = 6$ or 56 are obtained from the nine parametric **Appendix D** Intrawell tables labeled *'5 COC, Semi-Annual'*. The following κ-factors were obtained for tests of future values at $n = 6$: $\kappa = 3.46$ (1-of-2 test); $\kappa =$ **2.41** (1-of-3); $\kappa =$ **1.81** (1-of-4); and $\kappa = 2.97$ (modified California) plans. For future means, the corresponding κ-factors were: $\kappa = 4.46$ (1-of-1 mean size 2); $\kappa = 2.78$ (1-of-2 mean size 2); $\kappa = 2.06$ (1-of-3 mean size 2); $\kappa = 3.85$ (1-of-1 mean size 3); and $\kappa = 2.51$ (1-of-2 mean size 3). In these tables, *κ*-factors reported in **Bold** have good power, those *Italicized* have acceptable power and Plain Text indicates low power. For single well intrawell tests, only 1-of-3 or 1-of-4 plans for future values, 1-of-2 or 1-of-3 mean size 2 or 1-of-2 mean size 3 plans meet the ERPC criteria.

[17] Intrawell control charts with retesting are also an option, though the control limits associated with each retesting scheme need to be simulated.

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Although each of these retesting plans is adequately powerful, a final choice would be made by balancing 1) the cost of sampling and chemical analysis at the site; 2) the ability to collect statistically independent samples should the sampling frequency be increased; and 3) a comparison of the actual power curves of the three plans. The last can be used to assess how differences in power might impact the rapid identification of a groundwater release. Since a 1-of-3 test for future observations has good power, it is unnecessary to make use of a 1-of-4 test. Similarly, the 1-of-3 test for mean size 2 and a 1-of-2 test for mean size 3 might also be eliminated, since a 1-of-2 test of a mean size 2 is more than adequate. This leaves the 1-of-3 future values and 1-of-2 mean 2 tests as the final prediction limit options to consider.

Though prediction limits around future means are more powerful than plans for observations, only 3 independent measurements might be required for a 1-of-3 test, while 4 might be necessary for the 1-of-2 test for mean size 2. For most tests at background, a single sample might suffice for the 1-of-3 test and 2 independent samples for the test using a 1-of-2 mean size 2.

Much greater flexibility is afforded if the pooled intrawell standard deviation estimate can be used. For this example, any of the nine parametric intrawell retesting plans is sufficiently powerful, including a 1-of-2 prediction limit test on observations and a 1-of-1 test of mean size 2. In order to make this assessment using the pooled-variance approach, a careful reading of **Chapter 13, Section 13.3**. is necessary to generate comparative κ-factors.

Less overall sampling is needed with the 1-of-2 plan on observations, since only a single sample may be needed for most background conditions. Two observations are always required for the 1-of-1 mean size 2 test. More prediction limit testing options are generally available for a small facility. ◄

►EXAMPLE 6-6 MEDIUM FACILITY

A medium-sized hazardous waste facility has 4 upgradient background wells and 20 downgradient compliance wells. Ten initial measurements have been collected at each upgradient well and 8 at downgradient wells. The permitted monitoring list includes 10 inorganic parameters and 30 VOCs. No VOCs have yet been detected in groundwater. The remaining 10 inorganic constituents are normal or can be normalized, and five show evidence of significant spatial variation across the site. Assume that pooled-variances cannot be obtained from the historical upgradient or downgradient well data. If one statistical evaluation must be conducted each year, what statistical method and approach are recommended?

SOLUTION

At this site, there are potentially 800 distinct well-constituent pairs that might be tested. But since none of the VOCs has been detected in groundwater in background wells, all 30 of the VOCs should be handled using the *double quantification rule* (**Section 6.2.2).** A second confirmatory resample should be analyzed at those compliance wells for any of the 30 VOC constituents initially detected. Two successive quantified detections above the RL are considered significant evidence of groundwater contamination at that well and VOC constituent. To properly limit the SWFPR, the 30 VOC constituents are excluded from further SWFPR calculations, which is now based on $w \times c \times n_E = 20 \times 10 \times 1 = 200$ annual tests.

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The five inorganic constituent background data sets indicate insignificant spatial variation and can be normalized. The observations from the four upgradient wells can be pooled to form background data sets with an n = 40 for each of these five constituents. Future samples from the 20 compliance wells are then compared against the respective *interwell* background data. With one annual evaluation, c = 10 constituents, w = 20 wells and n = 40 background samples, the Interwell *'10 COC, Annual'* tables for parametric prediction limits with retesting can be searched in **Appendix D**. Alternatively, control chart limits can be fit to this configuration via Monte Carlo simulations. Even though only five constituents will be tested this way, all of the legitimate constituents (c) affecting the SWFPR calculation, are used in applying the tables.

Most of the interwell prediction limit retesting plans, whether for observations or means, offer good power relative to the annual evaluation ERPC. The final choice of a plan may be resolved by a consideration of sampling effort and cost, as well as perhaps a more detailed power comparison using simulated curves. For prediction limits, a 1-of-2 test for observations (κ = **2.18**) and the 1-of-1 prediction limit for a mean of order 2 (κ = **2.56**) both offer good power. These two plans also require the least amount of sampling to identify a potential release (as discussed in Example 6-6). Beyond this rationale, the more powerful 1-of-1 test of a future mean size 2 might be selected. Full power curves could be constructed and overlaid for several competing plans.

The remaining 5 inorganic constituents must be managed using intrawell methods based on individual compliance well sizes of n = 8. For the same c, w, and n_E inputs as above, the Appendix D Intrawell '10 COC, Annual' tables should be used. Only four of the higher order prediction limit tests have acceptable or good power: 1-of-4 future values (κ = **1.84**); 1-of-2 mean size 2 (κ = *2.68*); 1-of-3 mean size 2 (κ = **2.00**); and 1-of-2 mean size 3 (κ = **2.39**) tests. The 1-of-2 mean size 2 has only acceptable power. The first two tests require the fewest samples under most background conditions and in total, with the 1-of-4 test having superior power. ◄

►EXAMPLE 6-7 LARGE FACILITY

A larger solid waste facility must conduct two statistical evaluations per year at two background wells and 30 compliance wells. Parameters on the monitoring list include five trace metals with a high percentage of non-detect measurements, and five other inorganic constituents. While the inorganic parameters are either normal or can be normalized, a significant degree of spatial variation is present from one well to the next. If 12 observations were collected from each background well, but only 4 quarterly measurements from each compliance well, what statistical approach is recommended?

SOLUTION

Because the two groups of constituents evidence distinctly different statistical characteristics, each needs to be separately considered. Since the trace metals have occasional detections or 'hits,' they cannot be excluded from the SWFPR computation. Because of their high non-detect rates, parametric prediction limits or control charts may not be appropriate or valid unless a non-detect adjustment such as Kaplan-Meier or robust regression on order statistics is used (**Chapter 15**). Assuming for this example that parametric tests cannot be applied, the trace metals should be analyzed using non-parametric prediction limits. The presence of frequent non-detects may substantially limit the potential degree of spatial variation, making an *interwell* non-parametric test potentially feasible. The Kruskal-Wallis non-parametric ANOVA (**Chapter 17**) could be used to test this assumption.

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In this case, the number of background measurements is n = 24, and this value along with w = 30 compliance wells would be used to examine possible non-parametric retesting plans in the **Appendix D** tables for non-parametric prediction limits. As these tables offer achievable per-evaluation, per-constituent false positive rates for each configuration of compliance wells and background levels, the target α level must be determined. Given semi-annual evaluations, the per-evaluation false positive rate is approximately $\alpha_E = 0.10/n_E = 0.05$. Then, with 10 constituents altogether, the approximate per-constituent false positive rate for each trace metal becomes $\alpha_{const} = 0.05/10 = 0.005$.

Only one retesting plan meets the target false positive rate, a 1-of-4 non-parametric prediction limit using the maximum value in background as the comparison limit. This plan has 'acceptable' power relative to the ERPC. Other more powerful plans all have higher-than-targeted false positive rates.

For the remaining 5 inorganic constituents, the presence of significant spatial variation and the fact that the observations can be normalized, suggests the use of parametric intrawell prediction or control limits. As in the previous **Example 6-6**, interwell prediction limit tables in **Appendix D** are used by identifying κ multipliers and power ratings based on *all* 10 constituents subject to the SWFPR calculations. This is true even though these parametric options only pertain to 5 constituents. The total number of well-constituent pair tests per year is equal to $w \times c \times n_E = 30 \times 10 \times 2 = 600$ annual tests.

Assuming none of the observed spatial variation is due to already contaminated compliance wells, the number of measurements that can be used as intrawell background per well is small (n = 4). A quick scan of the intrawell prediction limit retesting plans in **Appendix D** *'10COC, Semi-Annual'* tables indicates that none of the plans offer even acceptable power for identifying a potential release. A one-way ANOVA should be run on the combined set of w = 30 compliance wells to determine if a pooled intrawell standard deviation estimate can be used.

If levels of variance across these wells are roughly the same, the pooled standard deviation will have $df = w(n-1) = 30 \times 3 = 90$ degrees of freedom, making each intrawell prediction or control limit much more powerful. Using the **R** script provided in **Appendix C** for intrawell prediction limits with a pooled standard deviation estimate (see **Section 13.3**), based on n = 4 and df = 90, all of the relevant intrawell prediction limits are sufficiently powerful compared to the semi-annual ERPC. With the exception of the 1-of-2 future values test at acceptable power, the other tests have good power. The final choice of retesting plan can be made by weighing the costs of required sampling versus perhaps a more detailed comparison of the full power curves. Plans with lower sampling requirements may be the most attractive. ◄

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CHAPTER 7. STRATEGIES FOR COMPLIANCE/ASSESSMENT AND CORRECTIVE ACTION

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This chapter covers the fundamental design principles for compliance/assessment and corrective action statistical monitoring programs. One important difference between these programs and detection monitoring is that a fixed external GWPS is often used in evaluating compliance. These GWPS can be an MCL, risk-based or background limit as well as a remedial action goal. Comparisons to a GWPS in compliance/assessment and corrective action are generally *one-sample* tests as opposed to the two- or multi-sample tests in detection monitoring. Depending on the program design, *two- or multiple-sample* detection monitoring strategies can be used with well constituents subject to background compliance/corrective action testing. While a general framework is presented in this chapter, specific test applications and strategies are presented in **Chapters 21 and 22** for fixed GWPS comparisons. **Sections 7.1** through **7.4** discuss comparisons to fixed GWPSs, while **Section 7.5** covers background GWPS testing (either as a fixed limit or based on a background statistic). Discussions of regulatory issues are generally limited to 40 CFR Part 264, although they also apply to corresponding sections of the 40 CFR Part 258 solid waste rules.

7.1 INTRODUCTION

The RCRA regulatory structure for compliance/assessment and corrective action monitoring is outlined in **Chapter 2**. In detection and compliance/assessment monitoring phases, a facility is presumed not to be 'out of compliance' until significant evidence of an impact or groundwater release can be identified. In corrective action monitoring, the presumption is reversed since contamination of the groundwater has already been identified and confirmed. The null hypothesis of onsite contamination is rejected only when there is significant evidence that the clean-up or remediation strategy has been successful.

Compliance/assessment monitoring is generally begun when statistically significant concentration exceedances above background have been confirmed for one or more detection monitoring constituents. *Corrective action* is undertaken when at least one exceedance of a *hazardous* constituent GWPS has been identified in compliance/assessment monitoring. The suite of constituents subject to compliance/assessment monitoring is determined from Part 264 Appendix IX or Part 258 Appendix II testing, along with prior hazardous constituent data evaluated under the detection monitoring program. Following a compliance monitoring statistical exceedance, only a few of these constituents may require

the change in hypothesis structure to corrective action monitoring. This formal corrective action testing will need to await completion of remedial activities, while continued monitoring can track progress in meeting standards.

The same general statistical method of *confidence interval testing against a fixed GWPS* is recommended in both compliance/assessment and corrective action programs. As discussed more fully below and in **Chapter 21**, confidence intervals provide a flexible and statistically accurate method to test how a parameter estimated from a single sample compares to a fixed numerical limit. Confidence intervals explicitly account for variation and uncertainty in the sample data used to construct them.

Most decisions about a statistical program under §264.98 detection monitoring are tailored to facility conditions, other than selecting a target site-wide cumulative false positive rate and a scheme for evaluating power. Statistical design details are likely to be site-specific, depending on the available data, observed distributions and the scope of the monitoring network. For compliance/assessment and corrective action testing under §264.99 and §264.100 or similar tests against fixed health-based or risk-based standards, the testing regimen is instead likely to be determined in advance by the regulatory agency. The Regional Administrator or State Director is charged with defining the nature of the tests, constituents to be tested, and the wells or compliance points to be evaluated. Specific decisions concerning false positive rates and power may also need to be defined at a regulatory program level.

The advantage of a consistent approach for compliance/assessment and corrective action monitoring tests is that it can be applied across all Regional or State facilities. Facility-specific input is still needed, including the observed distributions of key constituents and the selection of statistical power and false positive criteria for permits. Because of the asymmetric nature of the risks involved, regulatory agency and facility perspectives may differ on which statistical risks are most critical. Therefore, we recommend that the following issues be addressed for compliance/assessment and corrective action monitoring (both §264.99 and §264.100), as well as for other programs involving comparisons to fixed standards:

- What are the appropriate hypothesis testing structures for making comparisons to a fixed standard?
- What do fixed GWPS represent in statistical terms and which population parameter(s) should be tested against them?
- What is a desirable frequency of sampling and testing, which test(s), and for what constituents?
- What statistical power requirements should be included to ensure protection of health and the environment?
- What confidence level(s) should be selected to control false positive error rates, especially considering sites with multiple wells and/or constituents?

Decisions regarding these five questions are complex and interrelated, and have not been fully addressed by previous RCRA guidance or existing regulations. This chapter addresses each of these points for both §264.99 and §264.100 testing. By developing answers at a regulatory program level, the necessity of re-evaluating the same questions at each specific site may be avoided.

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7.2 HYPOTHESIS TESTING STRUCTURES

Compliance testing under §264.99 specifically requires a determination that one or more well constituents exceeds a permit-specific GWPS. The correct statistical hypothesis during compliance/assessment monitoring is that groundwater concentrations are presumed *not* to exceed the fixed standard unless sampling data from one or more well constituents indicates otherwise. The null hypothesis, H_0, assumes that downgradient well concentration levels are less than or equal to a standard, while the alternative hypothesis, H_A, is accepted only if the standard is significantly exceeded. Formally, for some parameter (Θ) estimated from sample data and representing a standard G, the relevant hypotheses under §264.99 compliance monitoring are stated as:

$$H_0 : \Theta \le G \; vs. \; H_A : \Theta > G \qquad [7.1]$$

Once a positive determination has been made that at least one compliance well constituent exceeds the fixed standard (*i.e.*, GWPS), the facility is subject to corrective action requirements under §264.100. At this point, the regulations imply and statistical principles dictate that the hypothesis structure should be *reversed* (for those compliance wells and constituents indicating exceedances). Other compliance constituents (*i.e.*, those not exceeding their respective GWPSs) may continue to be tested using equation 7.1 hypotheses. It is then assumed that contamination equal to or in excess of the GWPS exists and is presumed to be the case unless demonstrated otherwise. A positive determination that groundwater concentrations are below the standard is necessary to demonstrate regulatory compliance for any wells and constituents under remediation. In statistical terms, the relevant hypotheses for §264.100 are:

$$H_0 : \Theta \ge G \; vs. \; H_A : \Theta < G \qquad [7.2]$$

The reasoning behind this approach is as follows. Background exceedances by one or more well constituents under §264.98 detection monitoring do not predetermine any particular relationship of these increased concentration levels to fixed limits used as GWPS. Standards for different constituents vary over orders of magnitude. The actual concentration level triggering a statistically significant increase above background can vary considerably and bear little or no relationship to risk-based standards. Use of the initial compliance monitoring hypothesis framework in [7.1] ensures positive evidence that at least one hazardous constituent is truly above a GWPS. Since corrective action can be expensive and difficult, this provides important assurance that site program monitoring decisions are made correctly.

This guidance recognizes that not all regulatory programs are constructed alike. Objectives and regulatory interpretations may differ as to the basic goals of compliance/assessment or corrective action monitoring. When large numbers of sites with available hazardous constituent data are being screened to determine their need for remediation (perhaps outside the formal RCRA regulatory framework), the assessment may be conducted with the ***explicit presumption*** that contamination exists onsite. Presumably, elevated hazardous constituent concentrations have already been detected at these facilities. For these assessments, the compliance/assessment statistical hypothesis framework follows that presented in Equation 7.2. Instead of a *lower* confidence limit as recommended below, the appropriate statistical approach involves an ***upper*** confidence limit, as is appropriate for corrective action.

Non-RCRA programs seeking to use methods presented in the Unified Guidance may also presume a different statistical hypothesis structure from that presented here. The primary goal is to ensure that the statistical approach matches the appropriate hypothesis framework. It is also allowable under RCRA regulations to define GWPS based on background data, discussed further in **Section 7.5**.

Whatever the population parameter (Θ) selected as representative of the GWPS, testing consists of a confidence interval derived from the compliance point data at some choice of significance level (α), and then compared to the standard *G*. The confidence intervals describe the probable distribution of the sample statistic, θ, employed to estimate the true parameter Θ. For testing under compliance/assessment monitoring, a lower confidence limit around the true parameter — LCL(Θ) — is utilized. If LCL(Θ) exceeds the standard, there is statistically significant evidence in favor of the alternative hypothesis, H_A: $\Theta > G$, that the compliance standard has been violated. If not, the confidence limit test is inconclusive and the null hypothesis accepted.

When the corrective action hypothesis of [7.2] is employed, an *upper* confidence limit UCL(Θ) is generated from the compliance point data and compared to the standard *G*. In this case, the UCL(Θ) should lie *below* the standard to accept the alternative hypothesis that concentration levels are in compliance, H_A: $\Theta < G$. If the UCL(Θ) is larger than the standard, the test is inconclusive. It should be recognized that once corrective action or remediation activities are initiated, there will be a considerable time during which the GWPS may still be exceeded. As provided in the RCRA regulations, it is at the conclusion of remediation activities that formal corrective action monitoring evaluation is appropriate. However, in the intervening period of remedial activity, well constituents can still be monitored and the relative efficacy of remediation measures tracked. The same corrective action statistical hypotheses can be assumed for the targeted constituents; techniques such as trend testing may be appropriate interim applications.

If the entire confidence interval (considering both the lower and upper confidence limits) lies below the fixed standard *G* in either a compliance/assessment or corrective action setting, there is statistically significant evidence that the true parameter or characteristic (*e.g.*, the mean) is less than the standard. The constituent concentrations at the well are considered to be in compliance. Conversely, if the confidence interval lies entirely above *G*, the evidence suggests that the true parameter or characteristic exceeds the standard, and that concentrations at the well are out of compliance.

When the confidence interval straddles the standard *G* (as with the example confidence interval around the upper 95th percentile in **Figure 7-1** below), the correct decision is uncertain. When the population mean is being tested, and a confidence interval around the mean has accurately estimated its location, the true mean lies somewhere between the lower and upper confidence limits. But the *precise* value of the population mean within that range is unknown. The mean might be less than *G* or it might be greater than *G*. No clear decision with high statistical confidence is possible. ***When testing the compliance/assessment monitoring hypothesis of* [7.1]*, we recommend that the null hypothesis should not be rejected unless the entire confidence interval defined by and including the lower confidence limit exceeds the GWPS. By the same token, when testing the corrective action hypothesis of equation* [7.2]*, we recommend that the null hypothesis not be rejected unless the entire upper confidence interval and limit lies below the GWPS***.

These ideas can be illustrated with a normal confidence interval around the arithmetic mean. In this case, the population parameter Θ equals μ, the true population mean of a given compliance well

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constituent. The statistic used to estimate μ is the sample mean ($\bar{x}$). With this statistic and normally-distributed data, the lower and upper confidence limits are symmetric:

$$LCL(\mu) = \bar{x} - t_{1-\alpha,n-1}\frac{s}{\sqrt{n}} \quad [7.3]$$

$$UCL(\mu) = \bar{x} + t_{1-\alpha,n-1}\frac{s}{\sqrt{n}} \quad [7.4]$$

for a selected significance level (α) and sample size *n*. Note in these formulas that *s* is the sample standard deviation, and $t_{1-\alpha,n-1}$ is a central Student's *t*-value with *n*–1 degrees of freedom.

The two hypothesis structures and tests are defined as follows:

Case A. Test of non-compliance (§264.99) *vs*. a fixed standard (compliance/assessment monitoring):

Test Hypothesis: $H_0 : \mu \le G \; vs. \; H_A : \mu > G$

Test Statistic: $LCL_{1-\alpha} = \bar{x} - t_{1-\alpha,n-1}\frac{s}{\sqrt{n}}$

Rejection Region: Reject null hypothesis (H_0) if $LCL_{1-\alpha} > G$; otherwise, accept null hypothesis

Case B. Test of compliance (§264.100) *vs*. a fixed standard (corrective action):

Test Hypothesis: $H_0 : \mu \ge G \; vs. \; H_A : \mu < G$

Test Statistic: $UCL_{1-\alpha} = \bar{x} + t_{1-\alpha,n-1}\frac{s}{\sqrt{n}}$

Rejection Region: Reject null hypothesis (H_0) if $UCL_{1-\alpha} < G$; otherwise, accept null hypothesis

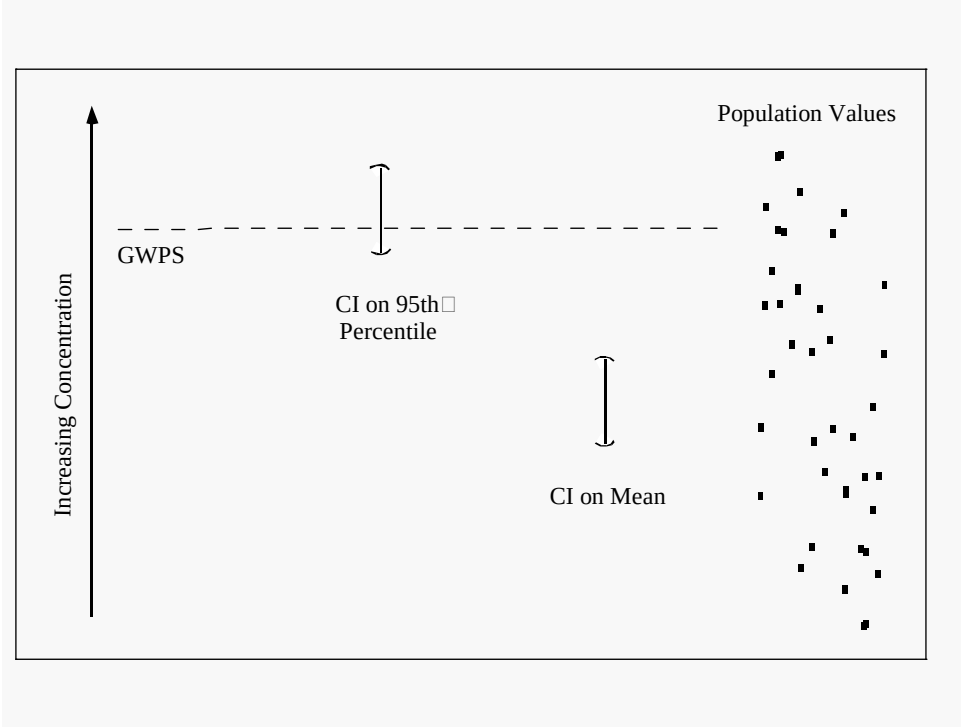
For all confidence intervals and tests presented in **Chapters 21** and **22**, the test structures are similar to those above. But not every pair of lower and upper confidence limits (*i.e.*, LCL and UCL) will be symmetric, particularly for skewed distributions and in non-parametric tests on upper percentiles. For a non-parametric technique such as a confidence interval around the median, exact confidence levels will depend on the available sample size and which *order statistics* are used to estimate the desired population parameter. In these cases, an exact target confidence level may or may not be attainable.

When calculating confidence intervals, assignment of the false positive error (α) differs between a one-sided and two-sided confidence interval test. The symmetric upper and lower confidence intervals are shown in **Figure 7-1** largely for illustration purposes. If the *lower* confidence interval for some tested parameter Θ is the critical limit, all of the α error is assigned to the region below the LCL(Θ). Hence, a 1-α confidence level covers the range from the lower limit to positive infinity. Similarly, all of the α error for an upper confidence limit UCL(Θ) is assigned to the region above this value. For a two-

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sided interval, the error rate is equally partitioned on both sides of the respective confidence interval limits. A 95% lower confidence limit implies that a 5% chance of an error exists for values lying below the limit. In contrast, a two-sided 95% confidence interval implies a 2.5% chance above and a 2.5% chance of an error below the confidence level. Depending on how confidence intervals are defined, the appropriate statistical adjustment (e.g., the *t*-value in **Equations 7-3** and **7-4**) needs to take this into account.

Figure 7-1. Confidence Interval on Mean vs. Fixed Upper Percentile Limit



7.3 GROUNDWATER PROTECTION STANDARDS

A second essential design step is to identify the appropriate population parameter and its associated statistical estimate. This is primarily a determination of what a given fixed GWPS represents in statistical terms. Not all fixed concentration standards are meant to represent the same statistical quantities. A distinction is drawn between 1) those central tendency standards designed to represent a mean or average concentration level and 2) those which represent either an upper percentile or the maximum of the concentration distribution. If the fixed standard represents an average concentration, it is assumed in the Unified Guidance that the ***mean*** concentration (or possibly the ***median*** concentration) in groundwater should not exceed the limit. When a fixed standard represents an ***upper percentile*** or ***maximum***, no more than a small, specified fraction of the individual concentration measurements should exceed the limit.

The choice of confidence interval should be based on the type of fixed standard to which the groundwater data will be compared. A fixed limit best representing an upper percentile concentration (***e.g.***, the upper 95th percentile) should not be compared to a confidence interval constructed around the arithmetic mean. Such an interval only estimates the location of the population mean, but says nothing about the specific upper percentile of the concentration distribution. The ***average*** concentration level

could be substantially less than the standard even though a significant fraction of the individual measurements exceeds the standard (see **Figure 7-1**).

There are a variety of fixed standards to which different statistical measures apply. Alternative GWPSs based on Agency risk-assessment protocols are cited as an option in the solid waste regulations at §258.55(i)(1). Many of the risk-assessment procedures identified in the CERCLA program make use of chronic, long-term exposure models for ingestion or inhalation. These procedures are identified in the (EPA, 1989b) Risk Assessment Guidance for Superfund (RAGS) and the Supplemental Guidance for Calculating the Concentration Term (EPA, 1992c), and serve as guidance for other EPA programs. In the latter document, the *arithmetic mean* is identified as the appropriate parameter for identifying environmental exposure levels. The levels are intended to identify chronic, time-weighted *concentration averages* based on lifetime exposure scenarios.

The primary *maximum contaminant levels* [MCL] promulgated under the Safe Drinking Water Act (SDWA) follow the same exposure evaluation principles. An MCL is typically based on 70-year risk-exposure scenarios (for carcinogenic compounds), assuming an ingestion rate of 2 liters of water per day at the average concentration over time. Similarly, long-term risk periods (*e.g.*, 6-years) are used for non-carcinogenic constituents, assuming average exposure concentrations. The promulgated levels also contain a safety multiplicative factor and are applied at the end-user tap. Calculations for ingestion exposure risk to soil contaminants by an individual randomly traversing a contaminated site are based on the average estimated soil concentration. It is expected that an exposed individual drinking the water or ingesting the soil is not afforded any protection in the form of prior treatment.

Other standards which may represent a population mean include some RCRA site permits that include comparisons against an *alternate concentration limit* [ACL] based on the average value of background data. In addition, some standards represent time-weighted averages used for carcinogenic risk assessments such as the *lifetime average daily dose* [LADD].

Fixed limits based explicitly on the *median concentration* include *fish ingestion exposure factors*, used in testing fish tissue for certain contaminants. The exposure factors represent the allowable concentration level below which at least half of the fish sample concentrations should lie, the 50th percentile of the observed concentration distribution. If this distribution is symmetric, the mean and median will be identical. For positively skewed populations, the mean concentration could exceed the exposure factor even though the median (and hence, a majority of the individual concentrations) is below the limit. It would therefore not be appropriate to compare such exposure factors against a confidence interval around the mean contaminant level, unless one could be certain the distribution was symmetric.

Fixed standards are sometimes based on *upper percentiles*. Scenarios of this type include risk-based standards designed to limit acute effects that result from short-term exposures to certain chemicals (*e.g.*, chlorine gas leaking from a rail car or tanker). There is greater interest in possible acute effects or transient exposures having a significant short-term risk. Such exposure events may not happen often, but can be important to track for monitoring and/or compliance purposes.

When even short exposures can result in deleterious health or environmental effects, the fixed limit can be specified as a maximum allowable concentration. From a statistical standpoint, the standard identifies a level which can only be exceeded a small fraction of the time (*e.g.*, the upper 90th percentile). If a larger than allowable fraction of the individual exposures exceeds the standard, action is

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likely warranted, even if the average concentration level is below the standard. Certain MCLs are interpreted in this same manner; the term 'maximum' in maximum contaminant level would be treated statistically as an upper percentile limit. Examples include criteria for bacterial counts and nitrate/nitrite concentrations, best regarded as upper percentile limits.

As an example, exposure of infants to nitrate concentrations in excess of 10 mg/L (NO_3^- as N) in drinking water is a case where greater concern surrounds acute effects resulting from short-term exposure. The flora in the intestinal tract of infant humans and animals does not fully develop until the age of about six months. This results in a lower acidity in the intestinal tract, which permits the growth of nitrate reducing bacteria. These bacteria convert nitrate to nitrite. When absorbed into the bloodstream, nitrite interferes with the absorption of oxygen. Suffocation by oxygen starvation in this manner produces a bluish skin discoloration — a condition known as "blue baby" syndrome (or methemoglobinemia) — which can result in serious health problems, even death. In such a scenario, suppose that acute effects resulting from short-term exposure above some critical level should normally occur in no more than 10 percent of all exposure events. Then the critical level so identified would be equivalent to the upper 90th percentile of all exposure events.

Another example is the so-called 20-year flood recurrence interval for structural design. Flood walls and drainage culverts are designed to handle not just the average flood level, but also flood levels that have a 1 in 20 chance of being equaled or exceeded in any single year. A 20-year flood recurrence level is essentially equivalent to estimating the upper 95th percentile of the distribution of flood levels (***e.g.***, a flood of this magnitude is expected to occur only 5 times every 100 years).

The various limits identified as potential GWPS in **Chapter 2** pose some interpretation problems. §264.94 Table 1 values are identified as "Maximum Concentration[s] of Constituents for Groundwater Protection" for 14 hazardous constituents, originating from earlier Federal Water Pollution Control Administration efforts. While not a definitive protocol for comparison, it was indicated that the limits were intended to represent a concentration level that should not be exceeded most of the time. In an early Water Quality Criteria report (USDI, 1968), the language is as follows:

> "It is clearly not possible to apply these (drinking water) criteria solely as maximum single sample values. The criteria should *not be exceeded over substantial portions* of time."

Similarly, the more current MCLs promulgated under the SDWA are identified as "maximum contaminant limits". Even if the limits were derived from chronic, risk-based assessments, the same implication is that these limits should not be exceeded.

Individual EPA programs make sample data comparisons to MCLs using different approaches. For small-facility systems monitored under the SDWA, only one or two samples a year might be collected for comparison. Anything other than direct comparisons isn't possible. Some Clean Water Act programs use arithmetic comparisons (means or medians) rather than a fully statistical approach. CERCLA typically utilizes these standards in mean statistical comparisons, consistent with other chronic health-based levels derived from their program risk assessment equations. In short, EPA nationwide does not have a single operational definition or measure for assessing MCLs with sample data.

The Unified Guidance cannot directly resolve these issues. Since the regulations promulgated under RCRA presume the use of fully statistical measures for groundwater monitoring program

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evaluations, the guidance provides a number of options for both centrality-based and upper limit tests. It falls upon State or Regional programs to determine which is the most appropriate parameter for comparison to a GWPS. As indicated above, the guidance does recommend that any operational definition of the appropriate parameter of comparison to GWPS's be applied uniformly across a program.

If a mean- or median-based centrality parameter is chosen, the guidance offers fairly straightforward confidence interval testing options. For a parameter representing some infrequent level of exceedance to address the "maximum" or "most" criteria, the program would need to identify a specific upper proportion and confidence level that the GWPS represents. Perhaps a proportion of 80 to 95% would be appropriate, at 90-95% confidence. It is presumed that the same standard would apply to both compliance and corrective action testing under §264.99 and §264.100. If non-parametric upper proportion tests must be used for certain data, very high proportions make for especially difficult tests to determine a return to compliance (**Chapter 22**) because of the number of samples required.

7.4 DESIGNING A STATISTICAL PROGRAM

7.4.1 FALSE POSITIVES AND STATISTICAL POWER IN COMPLIANCE/ASSESSMENT

As discussed in **Chapters 3 and 6**, the twin criteria in designing an acceptable detection monitoring statistical program are the site-wide false positive rate [SWFPR] and the effective power of the testing regimen. Both statistical measures are crucial to good statistical design, although from a regulatory perspective, ensuring adequate power to detect contaminated groundwater is of primary importance.

In compliance/assessment monitoring, statistical power is also of prime concern to EPA. There should be a high probability that the statistical test will positively identify concentrations that have exceeded a fixed, regulatory standard. In typical applications where a confidence interval is compared against a fixed standard, a low false positive error rate (α) is chosen without respect to the power of the test. Partly this is due to a natural desire to have high *statistical confidence* in the test, where ($1-\alpha$) designates the confidence level of the interval. But statistical confidence is *not* the same as power. The confidence level merely indicates how often — in repeated applications — the interval will contain the true population parameter (Θ); not how often the test will indicate an exceedance of a fixed standard. It has historically been much easier to select a single value for the false positive rate (α) than to measure power, especially since power is not a single number but a *function* of the level of contamination (as discussed in **Section 3.5**).

The power to detect increases above a fixed standard using a lower confidence limit can be negligible when contaminant variability is high, the sample size is small and especially when a high degree of confidence has been selected. To remedy this problem, the Unified Guidance recommends reversing the usual sequence: first select a desired level of power for the test ($1-\beta$), and then compute the associated (maximum) false positive rate (α). In this way, a pre-specified power can be maintained even if the sample size is too low to simultaneously minimize the risks of both Type I and Type II errors (*i.e.*, false positives and false negatives).

Specific methods for choosing power and computing false positive rates with confidence interval tests are presented in **Chapter 22**. Detailed applications of confidence interval tests are provided in **Chapter 21**. The focus here is on setting a basic framework and consistent strategies.

As noted above, selecting false positive error rates in compliance or assessment testing (§264.99) has traditionally been accomplished under RCRA by choosing a fixed, individual test α. This strategy is attractive if only for the sake of simplicity. Individual test-wise false positive rates in the range of α = .01 to α = .10 are traditional and easily understood. In addition, the Part 264 regulations in §264.97(i)(2) require a minimum individual false positive rate of α = .01 in both compliance and corrective action testing against a fixed standard, as well as in those tests not specifically exempted under detection monitoring.[1]

Given a *fixed* sample size and constant level of variation, the statistical power of a test method drops as the false positive rate decreases. A low false positive rate is often associated with low power. Since statistical power is of particular concern to EPA in compliance/assessment monitoring, somewhat higher false positive rates than the minimum α = .01 RCRA requirement may be necessary to maintain a pre-specified power over the range of sample sizes and variability likely to be encountered in RCRA testing situations. The key is sample variability. When the true population coefficient of variation [CV] is no greater than 0.5 (whether the underlying distribution is normal or lognormal), almost all lower confidence limit tests exhibit adequate power. When the variation is higher, the risk of false negative error is typically much greater (and thus the power is lower), which may necessitate setting a larger than usual individual α.

Based on the discussion regarding false positives in detection monitoring in **Chapter 6**, some might be concerned about the use of relatively high individual test-wise false positive rates (α) in order to meet a pre-specified power, especially when considering the cumulative false positive error rate across multiple wells and/or constituents (*i.e.*, SWFPR). Given that a number of compliance wells and constituents might need to be tested, the likelihood of occurrence of at least one false positive error increases dramatically. However, several factors specific to compliance/assessment monitoring need to be considered. Unlike detection monitoring where the number of tests is easily identified, the issue is less obvious for compliance/assessment or corrective action testing. The RCRA regulations do not clearly specify which wells and constituents must be compared to the GWPS in compliance/assessment monitoring other than wells at the 'compliance point.' In some situations, this has been interpreted to mean all compliance wells; in other instances, only at those wells with a documented exceedance.

While all hazardous constituents including additional ones detected in Part 264 Appendix IX monitoring are potentially subject to testing, many may still be at concentration levels insignificantly different from onsite background. Constituents without health-based limits may or may not be included in compliance testing. The latter would be tested against background levels, using perhaps an ACL computed as a *tolerance limit on background* (see **Section 7.5**). This also tends to complicate derivation of SWFPRs in compliance testing. It was also noted in **Section 7.2** that the levels at which contaminants are released bear no necessary relationship to fixed, health-based standards. In a typical release, some constituent levels from a suite of analytical parameters may lie orders of magnitude below their GWPS, while certain carcinogenic compounds may easily exceed their standards.

[1] In some instances, a test with "reasonable confidence" (that is, having adequate statistical power) for identifying compliance violations can be designed even if α < 0.01. This is particularly the case when the sample coefficient of variation is quite low, indicating small degrees of sample variability.

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The simple example below illustrates typical low-level aquifer concentrations following a release of four common petrochemical facility hazardous organic constituents often detected together:

Analyte	Aquifer Concentration (ug/l)		MCL (ug/l)
	Mean	SD	
Benzene	20	10	5
Toluene	35	15	1,000
Ethylbenzene	40	20	700
Xylene	100	35	10,000

While benzene as a carcinogen has a very low health standard, the remaining three constituents have aquifer concentrations orders of magnitude lower than their respective MCLs. Realistically, only benzene is likely to impact the cumulative false positive rate in LCL testing. Similar relationships occur in releases measured by trace element and semi-volatile organic suites.

Even though the null hypotheses in detection and compliance/assessment monitoring are similar (and compound) in nature (see [7.1]), it is reasonable to presume in detection monitoring that the compliance wells have average concentrations *no less* than mean background levels.[2] Since it is these background levels to which the compliance point data are compared in the absence of a release, the compound null hypothesis in detection monitoring (H_0: $\mu_C \leq \mu_{BG}$) can be reformulated practically as (H_0: $\mu_C = \mu_{BG}$). In this framework, individual concentration measurements are likely to occasionally exceed the background average and at times cause false positives to be identified even when there has been no change in average groundwater quality.

In compliance/assessment monitoring, the situation is generally different. The compound null hypothesis (H_0: $\mu_C \leq$ GWPS) will include some wells and constituents where the sample mean equals or nearly equals the GWPS when testing begins. But many well-constituent pairs may have true means considerably less than the standard, making false positives much less likely for those comparisons and lowering the overall SWFPR. How much so will depend on both the variability of each individual constituent and the degree to which the true mean (or relevant statistical parameter Θ) is lower than the GWPS for that analyte.

Because of this, determining the relevant number of comparisons with non-negligible false positive error rates may be quite difficult. The SWFPR in this situation would be defined as the probability that at least one or more lower confidence limits exceeded the fixed standard *G*, when the true parameter Θ (usually the mean) was actually below the standard. However, the relevant number of comparisons will depend on the nature and extent of the release. For a more extensive release, there is greater likelihood that the null hypothesis is no longer true at one or more wells. Instead of computing false positive rates, the focus should shift to minimizing false negative errors (*i.e.*, the risk of missing contamination above the GWPS).

[2] Note that background might consist of early intrawell measurements from compliance wells when substantial spatial variability exists.

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On balance, the Unified Guidance considers computation of cumulative SWFPRs in compliance/assessment testing to be problematic, and reliance on individual test false positive rates preferable. The above arguments also suggest that flexibility in setting individual test-wise α levels may be appropriate.

7.4.2 FALSE POSITIVES AND STATISTICAL POWER IN CORRECTIVE ACTION

When contamination above a GWPS is confirmed, corrective action is triggered. Following a period of remediation activity, formal statistical testing will usually involve an *upper* confidence limit around the mean or an upper percentile compared against a GWPS. EPA's overriding concern in corrective action is that remediation efforts not be declared successful without sufficient statistical proof. Since groundwater is now presumed to be impacted at unacceptable levels, a facility should not exit corrective action until there is sufficient evidence that contamination has been abated.

Given the reversal of test hypotheses from compliance/assessment monitoring to corrective action (*i.e.*, comparing equation [7.1] with [7.2]), there is an asymmetry in regulatory considerations of false positive and false negative rates depending on the stage of monitoring. In compliance/assessment monitoring using tests of the lower confidence limit, the principal regulatory concern is that a given test has adequate statistical power to detect exceedances above the GWPS.

Permitted RCRA monitoring is likely to involve small annual well sample sizes based on quarterly or semi-annual sampling. To meet a pre-specified level of power by controlling the false negative rate (β) necessitates varying the false positive rate (α) for individual tests. Controlling an SWFPR for these tests (using a criterion like the SWFPR) is usually not practical because of the ambiguity in identifying the relevant number of potential tests and the difficulty of properly assigning via the subdivision principle (**Chapter 19**) individual fractions of a targeted SWFPR.

By contrast under corrective action using an *upper* confidence limit for testing, the principal regulatory and environmental concern is that one or more constituents might falsely be declared below a GWPS in concentration. Under the corrective action null hypothesis [7.2] this would be a *false positive error*, implying that α should be minimized during this sort of testing, instead of β. Specific methods for accomplishing this goal are presented in **Chapter 22**.

A remaining question is whether SWFPRs should be controlled during corrective action. While potentially desirable, the number of well-constituent pairs exceeding their respective GWPS and subject to corrective action testing is likely to be small relative to compliance testing. Not all compliance wells or constituents may have been impacted, and some may not be contaminated to levels exceeding the GWPS, depending on the nature, extent, and intensity of the plume. Remediation efforts would focus on those constituents exceeding their GWPS.

As noted in **Section 7.4.1**, the tenuous relationship between ambient background levels, contaminant magnitudes, and risk-based health standards implies that most GWPS exceedances are likely to be carcinogens, usually representing a small portion of all monitored constituents. Some exceedances may also be related compounds, for instance, chlorinated hydrocarbon daughter degradation products.

Statistically, the fact that some wells are contaminated while others may not be makes it difficult to define SWFPRs in corrective action. Instead, the Unified Guidance attempts to limit the individual test-wise α at those wells where exceedances have been confirmed and that are undergoing remediation. Since the most important consideration is to ensure that the true population parameter (Θ) is actually below the clean-up standard before declaring remediation a success, this guidance recommends the use of a reasonably low, *fixed* test-wise false positive rate (*e.g.*, α = .05 or .10). Under this framework, there will be a 5% to 10% chance of incorrectly declaring any single well-constituent pair of being in compliance when its concentrations are truly above the remedial standard.

The regulatory position in corrective action concerning statistical power is one of relative indifference. Although power under [7.2] represents the probability that the confidence interval test will correctly identify concentrations to be below the regulatory standard when in fact they are, the onus of proof for demonstrating that remediation has succeeded (*e.g.*, μ_C < GWPS) falls on the regulated facility. As it is the facility's interest to demonstrate compliance, it may wish to develop statistical power criteria which would enhance this possibility (including increasing test sample sizes).

7.4.3 RECOMMENDED STRATEGIES

As noted in **Section 7.1**, the Unified Guidance recommends the use of confidence intervals in both compliance/assessment and corrective action testing. In compliance/assessment, the lower confidence limit is the appropriate statistic of interest, while in corrective action it is the upper confidence limit. In either case, the confidence limit is compared against a fixed, regulatory standard as a one-sample test. These recommendations are consistent with good statistical practice, as well as literature in the field, such as Gibbons and Coleman (2001).

The type of confidence interval test will initially be determined by the choice of parameter(s) to represent the GWPS (**Section 7.2**). While this discussion has suggested that the mean may be the most appropriate parameter for chronic, health-based limits, other choices are possible. **Chapter 21** identifies potential test statistical tests of a mean, median or upper percentile as the most appropriate parameters for comparison to a GWPS. In turn, data characteristics will determine whether parametric or non-parametric test versions can be used. Depending on whether normality can be assumed for the original data or following transformation, somewhat different approaches may be needed. Finally, the presence of data trends affects how confidence interval testing can be applied.

Some regulatory programs prefer to compare each *individual* measurement against *G*, identifying a well as out-of-compliance if any of the individual concentrations exceeds the standard. However, the false positive rate associated with such strategies tends to be quite high if the parameter choice has not been clearly specified. Using this individual comparison approach and assuming a mean as the parameter of choice, is of particular concern. If the true mean is *less than but close to* the standard, chances are very high that one or more individual measurements will be greater than the limit even though the hypothesis in [7.1] has not been violated. Corrective action could then be initiated on a false premise. To evaluate whether a limited number of sample data exceed a standard, a lower confidence interval test would need to be based on a pre-specified upper percentile assumed to be the appropriate parameter for comparison to the GWPS.

Small individual well sample sizes and data uncertainty can rarely be avoided in compliance/assessment and corrective action. Given the nature of RCRA permits, sampling frequencies

in compliance/assessment or corrective action monitoring are likely to be established in advance. Relatively small sample sizes per well-constituent pair each year are likely to be the rule; the Unified Guidance assumes that quarterly and semi-annual sampling will be very typical.

For small and highly variable sample data sets, compliance/assessment monitoring and corrective action tests will have low statistical power either to detect exceedances above fixed standards or to demonstrate compliance in corrective action. One way to both enhance statistical power and control false positive error rates is through *incremental* or *sequential pooling* of compliance point data over time. Adding more data into a test of non-compliance or compliance will generally result in narrower confidence intervals and a clearer decision with respect to a compliance standard.

The Unified Guidance recommends accumulating compliance data over time at each well, by allowing construction of confidence limits on *overlapping* as opposed to *distinct* or *mutually exclusive* data sets. If the lower confidence limit [LCL] exceeds the GWPS in compliance/assessment, a clear exceedance can be identified. If the upper confidence limit [UCL] is below the GWPS in corrective action, remediation at that well can be declared a success. If neither of these respective events occurs, further sampling should continue. A confidence interval can be recomputed after each additional 1 or 2 measurements and a determination made whether the position of the confidence limit has changed relative to the compliance standard.

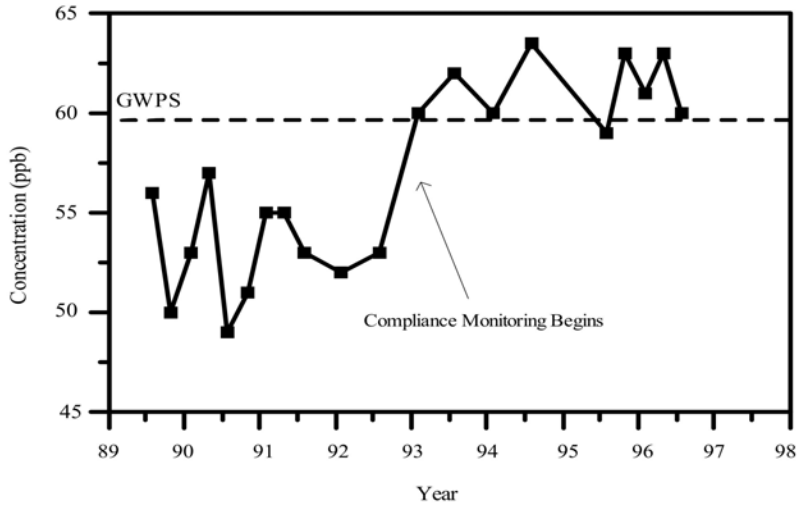
Tests constructed in this way at each successive evaluation period will not be statistically independent; instead, the proposed testing strategy falls into the realm of *sequential analysis*. But it should help to minimize the possibility that a small group of spurious values will either push a facility into needless corrective action or prevent a successful remedial effort from being identified.

One caveat with this approach is that it must be reasonable to assume that the population parameter Θ is stable over time. If a release has occurred and a contaminant plume is spreading through the aquifer, concentration shifts in the form of increasing trends over time may be more likely at contaminated wells. Likewise under active remediation, decreasing trends for a period of time may be more likely. Therefore, it is recommended that the sequential testing approach be used *after* aquifer conditions have stabilized to some degree. While concentration levels are actively changing with time, use of confidence intervals around a trend line should be pursued (see **Section 7.4.4** and **Chapter 21**).

7.4.4 ACCOUNTING FOR SHIFTS AND TRENDS

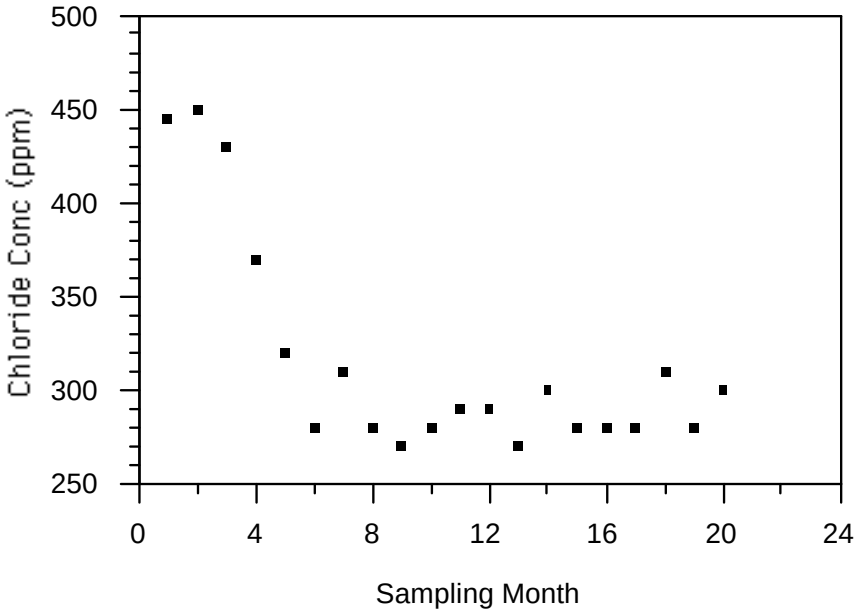
While accumulating compliance point data over time and successively re-computing confidence limits is appropriate for stable (*i.e.*, stationary) populations, it can give misleading or false results when the underlying population is changing. Should a release create an expanding contaminant plume within the aquifer, concentration levels at some or all of the compliance wells will tend to shift upward, either in discrete jumps (as illustrated in **Figure 7-2**) or an increasing trend over time. In these cases, a lower confidence limit constructed on accumulated data will be overly wide (due to high sample variability caused by combining pre- and post-shift data) and not be reflective of the more recent upward shift in the contaminant distribution.

Figure 7-2. Effect on Confidence Intervals of Stable Contamination Level



A similar problem can arise with corrective action data. Aquifer modifications as part of contaminant removals are likely to result in observable declines in constituent concentrations during the active treatment phase. At some point following cessation of remedial action, a new steady-state equilibrium may be established (**Figure 7-3**).

Figure 7-3. Decreasing Trend During Corrective Action



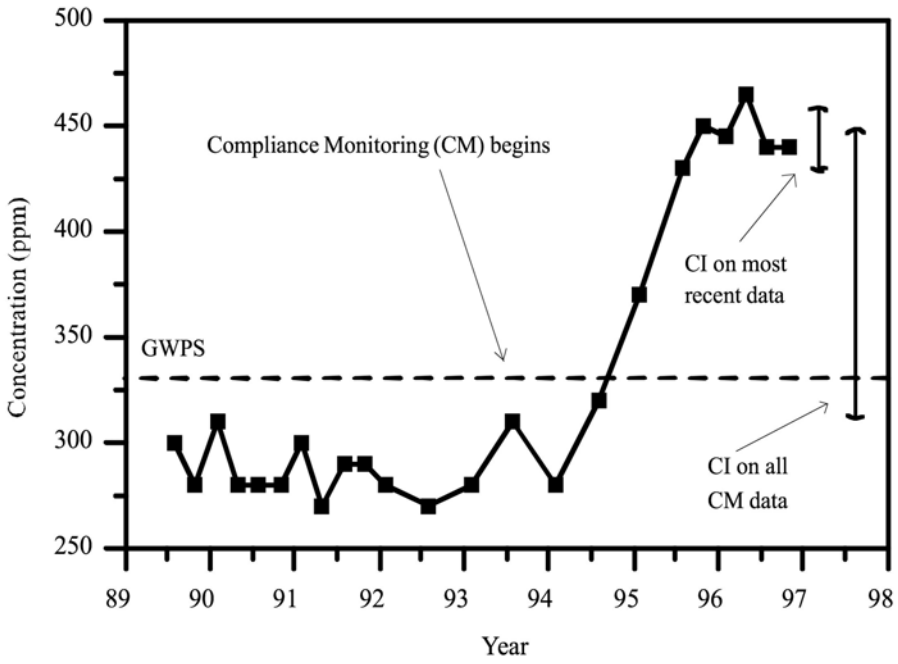
Until then, it is inappropriate to use a confidence interval test around the mean or an upper percentile to evaluate remedial success with respect to a clean-up standard. During active treatment phases and under non-steady state conditions, other forms of analysis such as confidence bands around a trend (see below), are recommended and should be pursued.

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The Unified Guidance considers two basic types of non-stationary behavior: shifts and (linear) trends. A shift refers to a significant mean concentration increase or decrease departing from a roughly stable mean level. A trend refers to a series of consecutive measurements that evidence successively increasing or decreasing concentration levels. More complicated non-random data patterns are also possible, but beyond the scope of this guidance. With these two basic scenarios, the strategy for constructing an appropriate confidence interval differs.

An important preliminary step is to track the individual compliance point measurements on a time series plot (**Chapter 9**). If a discrete shift in concentration level is evident, a confidence limit should be computed on the most recent stable measurements. Limiting the observations in this fashion to a specific time period is often termed a 'moving window.' The reduction in sample size will often be more than offset by the gain in statistical power. More recent measurements may exhibit less variation around the shifted mean value, resulting in a shorter confidence interval (**Figure 7-4**). The sample size included in the moving window should be sufficient to achieve the desired statistical power (compliance/assessment) or false positive rate (corrective action). However, measurements that are clearly unrepresentative of the newly shifted distribution should not be included, even if the sample size suffers. Once a stable mean can be assumed, the strategy of sequential pooling can be used.

Figure 7-4. Effect on Confidence Intervals of Concentration Shift

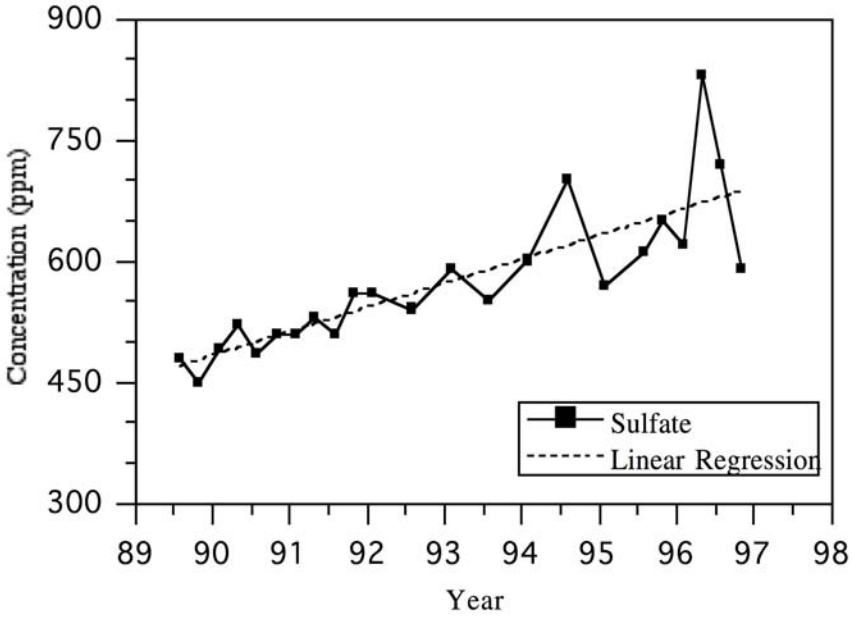


If well concentration levels exhibit an increasing or decreasing trend over time (such as the example in **Figure 7-5**) and the pattern is reasonably linear or monotone, the trend can be identified using the methods detailed in **Chapter 17**. To measure compliance or non-compliance, a *confidence band* can be constructed around the estimated trend line, as described in **Chapter 21**. A confidence band is essentially a continuous series of confidence intervals estimated along every point of the trend. Using this technique, the appropriate upper or lower confidence limits at one or more points in the most recent

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portion of the end of the sampling record can be compared against the fixed standard. The lower band is used to determine whether or not an exceedance has occurred in compliance/assessment, and an upper confidence band to determine if remedial success has been achieved in corrective action.

Figure 7-5. Rising Trend During Compliance Monitoring



By explicitly accounting for the trend, the confidence interval in **Chapter 21** will adjust upward or downward with the trend and thus more accurately estimate the current true concentration levels. Trend techniques are not just used to track progress towards exceeding or meeting a fixed standard. Confidence bands around the trend line can also provide an estimate of confidence in the average concentration as it changes over time. This subject is further covered in the Comprehensive Environmental Response, Compensation, and Liability Act [CERCLA] guidance ***Methods for Evaluating the Attainment of Cleanup Standards — Volume 2: Groundwater*** (EPA, 1992a).

A final determination of remedial success should not solely be a statistical decision. In many hydrologic settings, contaminant concentrations tend to rise after groundwater pumping wells are turned off due to changes in well drawdown patterns. Concentration levels may exhibit more complicated behavior than the two situations considered above. Thus, on balance, it is recommended that determining achievement of corrective action goals be done in consultation with the site manager, geologist, and/or remedial engineer.

7.4.5 IMPACT OF SAMPLE VARIABILITY, NON-DETECTS, AND NON-NORMAL DATA

Selection of hazardous constituents to be monitored in compliance/assessment or corrective action is largely determined by permit decisions. Regulatory requirements (*e.g.*, Part 264, Appendix IX) may also dictate the number of constituents. As a practical matter, the most reliable indicators of contamination should be favored. Occasionally, constituents subject to degradation and transformation in the aquifer (*e.g.*, chlorinated hydrocarbon suites) may result in additional, related constituents of concern.

Since health-based considerations are paramount in this type of monitoring, the most sensitive constituents from a health risk standpoint could be selected. But even with population parameters (Θ), sample sizes, and constituents determined, selecting an appropriate confidence interval test from **Chapter 21** can be problematic. For mildly variable sample data, measured at relatively stable levels, tests based on the normal distribution should be favored, whether constructed around a mean or an upper percentile. With highly variable sample data, selection of a test is less straightforward. If the observed data happen to be lognormal, Land's confidence interval around the arithmetic mean is a valid option; however, it has low power to measure compliance as the observations become more variable, and upward adjustment of the false positive rate (α) may be necessary to maintain sufficient power.

In addition, the extreme variability of an upper confidence limit using Land's technique can severely restrict its usage in tests of compliance during corrective action. Depending on the data pattern observed, degree of variability, and how closely the sample mimics the lognormal model, consultation with a professional statistician should be considered to resolve unusual cases. When the lognormal coefficient of variation is quite high, one alternative is to construct an upper confidence limit around the lognormal geometric mean (**Chapter 21**). Although such a confidence limit does not fully account for extreme concentration values in the right-hand tail of the lognormal distribution, a bound on the geometric mean will account for the bulk of possible measurements. Nonetheless, use of a geometric mean as a surrogate for the population arithmetic mean leads to distinctly different statistical test characteristics in terms of power and false positive rates.

In sum, excessive sample variability can severely limit the effectiveness of traditional compliance/assessment and corrective action testing. On the other hand, if excessive variability is primarily due to trends observable in the data, confidence bands around a linear trend can be constructed (**Section 7.4.4**).

LEFT-CENSORED SAMPLES

For compliance point data sets containing left-censored measurements (*i.e.*, non-detects), parametric confidence intervals cannot be computed directly without some adjustment. All of the parametric confidence intervals described in **Chapter 21** require estimates of the population mean μ and standard deviation σ. A number of adjustment strategies are presented in **Chapter 15.** If the percentage of non-detects is small — no more than 10-15% — *simple substitution* of half the reporting limit [RL] for each non-detect will generally work to give an approximately correct confidence interval.

For samples of at least 8-10 measurements and up to 50% non-detects, the *Kaplan-Meier* or *robust regression on order statistics* [ROS] methods can be used. Data should first be assessed via a *censored probability plot* whether the sample can be normalized. If so, these techniques can be used to compute estimates of the mean μ and standard deviation σ adjusted for the presence of left-censored values. These adjusted estimates can be used in place of the sample mean ($\bar{x}$) and standard deviation (s) listed in the confidence interval formulas of **Chapter 21** around either a mean or upper percentile.

If none of these adjustments is appropriate, non-parametric confidence intervals on either the median or an upper percentile (**Section 21.2**) can be calculated. Larger sample sizes are needed than with parametric confidence interval counterparts, especially for intervals around an upper percentile, to ensure a high level of confidence and a sufficiently narrow interval. The principal advantage of non-parametric

intervals is their flexibility. Not only can large fractions of non-detects be accommodated, but non-parametric confidence intervals can also be applied to data sets which cannot be normalized.

For heavily censored small data sets of 4-6 observations, the options are limited. One approach is to replace each non-detect by half its RL and compute the confidence interval *as if* the sample were normal. Though the resulting interval will be approximate, it can provide a preliminary indication of the well's compliance with the standard until further sampling data can be accumulated and the confidence interval recomputed.

Confidence bands around a trend can be constructed with censored data using a bootstrapped Theil-Sen non-parametric trend line (**Section 21.3.2**). In this method, the Theil-Sen trend is first computed using the sample data, accounting for the non-detects. Then a large number bootstrap resamples are drawn from the original sample, and an alternate Theil-Sen trend is conducted on each bootstrap sample. Variability in these alternate trend estimates is then used to construct a confidence band around the original trend.

LOGNORMAL AND OTHER NORMALIZED DATA

Lognormal data may require special treatment when building a confidence interval around the mean. Land's method (**Section 21.1.3**) can offer a reasonable way to accommodate the transformation bias associated with the logarithm, particularly when computing a lower confidence limit as recommended in compliance/assessment monitoring. For data normalized by transformations other than the logarithm, one option is to calculate a normal-based confidence interval around the mean using the transformed measurements, then back-transform the limits to the original concentration scale. The resulting interval will *not* represent a confidence interval around the arithmetic mean of the original data, but rather will estimate the confidence intervals of the *median* and/or *geometric mean*.

If the difference between the arithmetic mean and median is not considered important for a given GWPS, this strategy will be the easiest to implement. A wide range of results can occur with Land's method on highly skewed lognormal populations especially when computing an upper confidence limit around the arithmetic mean (Singh *et al.*, **1997**). It may be better to either construct a confidence interval around the lognormal *geometric* mean (**Section 21.1.2**) or to use the technique of *bootstrapping* (Efron, 1979; Davison and Hinkley, 1997) to create a non-parametric interval around the arithmetic mean.[3]

For confidence intervals around an upper percentile, no bias is induced by data that have been normalized via a transformation. Whatever the transformation used (*e.g.*, logarithm, square root, cube, *etc.*), a confidence interval can be constructed on the transformed data. The resulting limits can then be back-transformed to provide confidence limits around the desired upper percentile in the concentration domain.

[3] Bootstrapping is widely available in statistical software, including the open source **R** computing environment and EPA's free-of-charge **ProUCL** package. In some cases, setting up the procedure correctly may require professional statistical consultation.

7.5 COMPARISONS TO BACKGROUND DATA

Statistical tests in compliance/assessment and corrective action monitoring will often involve a comparison between compliance point measurements and a promulgated fixed health-based limit or a risk-based remedial action goal as the GWPS, described earlier. But a number of situations arise where a GWPS must be based on a background limit. The Part 264 regulations presume such a standard as one of the options under §264.94(a); an ACL may also be determined from background under §264.94(b). More recent Part 258 rules specify a background GWPS where a promulgated or risk-based standard is not available or if the historical background is greater than an MCL [§258.55(h)(2) & (3)].

Health-based risk standards bear no necessary relationship to site-specific aquifer concentration levels. At many sites this poses no problem, since the observed levels of many constituents may be considerably lower than their GWPS. However, either naturally-occurring or pre-existing aquifer concentrations of certain analytes can exceed promulgated standards. Two commonly monitored trace elements in particular-- arsenic and selenium-- are occasionally found at uncontaminated background well concentrations exceeding their respective MCLs. The regulations then provide that a GWPS based on background levels is appropriate.

A number of factors should be considered in designing a background-type GWPS testing program for compliance/assessment or corrective action monitoring. The most fundamental decision is whether to base such comparisons on *two- (or multiple-) sample* versus *single-sample* tests. For the first, many of the design factors discussed for detection monitoring in **Chapter 6** will be appropriate; for single sample comparisons to a fixed background GWPS, a confidence level approach similar to that discussed earlier for testing fixed health standards in this **Chapter 7** would be applied. This basic decision then determines how the GWPS is defined, the appropriate test hypotheses, types of statistical tests, what the background GWPS represents in statistical terms, and the relevance of individual test and cumulative false positive error rates. Such decisions may also be constrained by State groundwater anti-degradation policies. Other design factors to consider are the number of wells and constituents tested, interwell versus intrawell options, background sample sizes, and power. Unlike a single fixed standard like an MCL, background GWPS's may be uniquely defined for a given monitoring well constituent by a number of these factors.

SINGLE- VERSUS TWO-SAMPLE TESTING

One of two fundamental testing approaches can be used with site-specific background GWPSs. Either 1) a GWPS is defined as the critical limit from a pre-selected detection-level statistical test (e.g., a prediction limit) based on background measurements, or 2) background data are used to generate a fixed GWPS somewhat elevated above current background levels. In both cases, the resulting GWPS will be constituent- and possibly compliance well- specific. The first represents a *two-sample test* of two distinct populations (or more if a multiple-sample test) similar to those utilized in detection monitoring. As such, the individual test false positive rate, historical background sample size, cumulative false positive considerations, number of annual tests and desired future sample size will uniquely determine the limit. Whatever the critical value for a selected background test, it becomes the GWPS under compliance/assessment or corrective action monitoring.

The only allowable hypothesis test structure for the two-sample approach follows that of detection and compliance monitoring [7.1]. Once exceeded and in corrective action, a return to compliance is through evidence that future samples lie below the GWPS using the same hypothesis structure.

The second option uses a fixed statistic from the background data as the GWPS in a ***single-sample*** confidence interval test. Samples from a single population are compared to the fixed limit. In other respects, the strategy follows that outlined in **Chapter 7** for fixed health- or risk-based GWPS tests. The compliance/assessment test hypothesis structure also follows [7.1], but the hypotheses are reversed as in [7.2] for corrective action testing.

The choice of the single-sample GWPS deserves careful consideration. In the past, many such standards were simply computed as multiples of the background sample average (***i.e.***, GWPS = $2 \cdot \bar{x}$). However, this approach may not fully account for natural variation in background levels and lead to higher than expected false positive rates. If the GWPS were to be set at the historical background sample mean, even higher false positive rates would occur during compliance monitoring, and demonstrating corrective action compliance becomes almost impossible.

In the recommendations which follow below, an upper tolerance limit based on both background sample size and sample variability is recommended for identifying the background GWPS at a suitably high enough level above current background to allow for reversal of the test hypotheses. Although a somewhat arbitrary choice, a GWPS based on this method allows for a variety of confidence interval tests (e.g., a one-way normal mean confidence interval identified in equations [7.3] and [7.4]).

WHAT A BACKGROUND GWPS REPRESENTS

If the testing protocol involves two-sample comparisons, the background GWPS is an upper limit statistical interval derived from a given set of background data based on one or another detection monitoring tests discussed in **Chapter 6** and detailed in **Part III**. In these cases, the appropriate testing parameter is the true *mean* for the parametric tests, and the true *median* for non-parametric tests. This would include 1-of-*m* prediction limit detection tests involving future values. If a single-sample comparison against a fixed background GWPS is used, the appropriate parameter will also depend upon the type of confidence interval test to be used (**Part IV**). Except for parametric or non-parametric upper percentile comparisons, the likely statistical parameter would again be a mean (arithmetic, logarithmic, geometric) or the median. A background GWPS could be defined as an upper percentile parameter, making use of normal test confidence interval structures found in **Section 21.1.4**. Non-parametric percentile options would likely require test sample sizes too large for most applications. The Unified Guidance recommended approaches for defining single-sample GWPSs discussed later in this section presume a central tendency test parameter like the mean or median.

NUMBER OF MONITORED WELLS AND CONSTITUENTS

Compliance/assessment or corrective action monitoring tests against a fixed health- or risk-based standard (including single-sample background GWPSs) are not affected in a significant manner by the number of annual tests. But this would not be true for two- or multiple-sample background GWPS testing. In similar fashion to detection monitoring, the total number of tests is an important consideration in defining the appropriate false positive error test rate (α_{test}). The total number of annual tests is determined by how many compliance wells, constituents and evaluations occur per year.

Regulatory agency interpretations will determine the number and location of compliance monitoring wells. These can differ depending on whether the wells are unit-specific, and if a reasonable subset can be shown to be affected by a release. Perhaps only those compliance wells containing detectable levels of a compliance monitoring constituent need be included. Formal annual tests are generally required semi-annually, but other approaches may be applied.

The number of constituents subject to two-sample background GWPS testing will also depend on several factors. Only ***hazardous*** constituents not having a health- or risk-based standard are considered here. The basic criterion in interpreting required Part 264 Appendix IX or Part 258 Appendix II analyses is to identify those hazardous constituents found in downgradient compliance wells. Some initially detected common laboratory or sampling contaminants might be eliminated following a repeat scan. The remainder of the qualifying constituents will then require some form of background GWPS's. Along with the number of wells and annual evaluations, the total annual number of background tests will then be used in addressing an overall design cumulative design false positive rate.

In corrective action testing (for either the one- or two-sample approaches), the number of compliance wells and constituents may differ. Only those wells and constituents showing a significant compliance test exceedance might be used. However, from a standpoint of eventually demonstrating compliance under corrective action, it might be appropriate to still use the compliance/assessment GWPS for two-sample tests. With single-sample tests, the GWPS is compared individually by well and constituent as described.

BACKGROUND SAMPLE SIZES and INTERWELL vs. INTRAWELL TESTING

Some potential constituents may already have been monitored during the detection phase, and have a reasonable background size. Others identified under Part 264 Appendix IX or part 258 Appendix II testing may have no historical background data bases and require a period of background sampling.

Historical constituent well data patterns and the results of this testing may help determine if an interwell or intrawell approach should be used for a given constituent. For example, if arsenic and selenium were historical constituents in detection monitoring, they might also be identified as candidates for compliance background GWPS testing. There may already be indications that individual well spatial differences will need to be taken into account and an intrawell approach followed. In this case, individual compliance well background GWPSs need to be established and tested. On the other hand, certain hazardous trace elements and organics may only be detected and confirmed in one or more compliance wells with non-detects in background upgradient wells and possibly historical compliance well data. Under the latter conditions, the simpler Double Quantification Rule (**Section 6.2.2**.) might be used with the GWPS set at a quantification limit. However, this could pose some interpretation problems. Subsequent testing against the background GWPS at the same compliance well concentration levels causing the initial detection monitoring exceedance, might very likely result in further excursions above the background GWPS. The more realistic option would be to collect and use additional compliance well data to establish a specific minimum intrawell background, and only apply the Double Quantification Rule at other wells not exhibiting detections. Even this approach might be unnecessarily stringent if a contaminant plume were to expand in size and gradually affect other compliance wells (now subject to GWPS testing).

CUMULATIVE & INDIVIDUAL TEST FALSE POSITIVE RATES

Each of the independent two-sample tests against background standards will have a roughly equal probability of being exceeded by chance alone. Since an exceedance in the compliance monitoring mode based on background can result in a need for corrective action, it is recommended that the individual test false positive rate be set sufficiently low. Much of the discussion in **Chapter 6**, **Section 6.2.2** is relevant here. An *a priori,* cumulative error design rate must first be identified. To allow for application of the Unified Guidance detection monitoring strategies and **Appendix D** tables, it is suggested that the .1 *SWFPR* value also be applied to two-sample background GWPS testing. In similar fashion to **Chapter 6** and **Part III**, this can be translated into individual test configurations.

If the single-sample confidence interval option will be used with an elevated GWPS, the compliance level test will have a very low probability of being exceeded by truly background data. Cumulative false positive error considerations are generally negligible. For testing compliance/assessment or corrective action hypotheses, there is still a need to identify an appropriately low single test false positive rate which meets the regulatory goals. Generally, a single test false positive error rate of .1 to .05 will be suitable with the recommended approach for defining the background GWPS.

UNIFIED GUIDANCE RECOMMENDATIONS

Two-Sample GWPS Definition and Testing

As indicated above, any of the detection monitoring tests described in **Chapter 6** might be selected for two- or multiple- sample background compliance testing. One highly recommended statistical test approach is a prediction limit. Either a parametric prediction limit for a future mean (**Section 18.2.2**) or a non-parametric prediction limit for a future median (**Section 18.3.2**) can be used, depending on the constituent being tested and its statistical and distributional characteristics (*e.g.*, detection rate, normality, *etc*.). It would be equally possible to utilize one of the 1-of-*m* future value prediction limit tests, on an interwell or intrawell basis. Use of repeat samples as part of the selected test is appropriate, although the expected number of annual compliance/corrective action samples may dictate which tests can apply.

One parametric example is the 1-of-1 future mean test. If the background data can be normalized, background observations are used to construct a parametric prediction limit with (1–α) confidence around a mean of order *p*, using the equation:

$$PL = \bar{x} + t_{1-\alpha,n-1} \cdot s \cdot \sqrt{\frac{1}{p} + \frac{1}{n}} \qquad [7.5]$$

The next *p* measurements from each compliance well are averaged and the future mean compared to the background prediction limit, *PL* (considered the background GWPS). In compliance/assessment monitoring, if any of the means exceeds the limit, those well-constituent pairs are deemed to be out of compliance. In corrective action, if the future mean is no greater than *PL*, it can be concluded that the well-constituent pair is sufficiently similar to background to be within the remediation goal. In both monitoring phases, the prediction limit is constructed to represent a reasonable upper limit on the

background distribution. Compliance point means above this limit are statistically different from background; means below it are similar to background.

If the background sample cannot be normalized perhaps due to a large fraction of non-detects, two-sample non-parametric upper prediction limit detection monitoring tests (**Chapters 18 & 19**) can be used. As an example, a maximal order statistic (often the highest or second-highest value) can be selected from background as a non-parametric 1-of-1 upper prediction limit test of the median. **Table 18-2** is used to guide the choice based on background sample size (n) and the achievable confidence level (α). The median of the next 3 measurements from each compliance well is compared to the upper prediction limit. As with the parametric case in compliance/assessment, if any of the medians exceeds the limit, those well-constituent pairs would be considered out of compliance. In corrective action, well-constituent pairs with medians no greater than the background prediction limit would be considered as having met the standard.

If background measurements for a particular constituent are all non-detect, the GWPS should be set equal to the highest RL. In similar fashion to detection monitoring, 1-of-2 or 1-of-3 future value prediction limit tests can be applied (**Section 6.2.2** Double Quantification rule).

Single-Sample GWPS Definition and Testing

For single-sample testing, the Unified Guidance recommendation is to define a fixed GWPS or ACL based on a background *upper tolerance limit* with 95% confidence and 95% coverage (**Chapter 17**). For normal background, the appropriate formula for the GWPS would be the same as that given in **Section 17.2.1**, namely:

$$GWPS = \bar{x} + \tau(n,.95,.95)\cdot s \qquad [7.6]$$

where n = number of background measurements, $\bar{x}$ and s represent the background sample mean and standard deviation, and τ is a tolerance factor selected from **Table 17-3**. If the background sample is a mixture of detects and non-detects, but the non-detect fraction is no more than 50%, a censored estimation method such as Kaplan-Meier or robust regression on order statistics [ROS] (**Chapter 15**) can be attempted to compute adjusted estimates of the background mean μ and standard deviation σ in equation [7.5].

For larger fractions of non-detects, a non-parametric tolerance limit can be constructed, as explained in **Section 17.2.2**. In this case, the GWPS median will often be set to the largest or second-largest observed value in background. **Table 17-4** can be used to determine the achieved confidence level ($1-\alpha$) associated with a 95% coverage GWPS constructed in this way. Ideally, enough background measurements should be used to set the tolerance limit as close to the target of 95% coverage, 95% confidence as possible. However, this could require very large background sample sizes ($n \geq 60$).

Multiple independent measurements are used to form either a mean or median confidence interval for comparison with the background GWPS. Preferably at least 4 distinct compliance point measurements should be used to define the mean confidence interval in the parametric case, and 3-7 values should be used with a non-parametric median test. The guidance does not recommend retesting in single-sample background GWPS compliance/assessment monitoring. An implicit kind of retesting is built in to any test of a sample mean or median as explained in **Section 19.3.2.**

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In essence, the background tolerance limit is used to set a somewhat higher mean target GWPS which can accommodate both compliance and corrective action testing under background conditions. The GWPS in equation [7.6] can be interpreted as an approximation to the upper 95th percentile of the background distribution. It is designed to be a reasonable maximum on the likely range of background concentrations. It is high enough that compliance wells exceeding the GWPS via a confidence interval test (*i.e.*, LCL > GWPS) are probably impacted and not mere false positives. At the same time, successful remedial efforts must show that concentrations at contaminated wells have decreased to levels similar to background. The GWPS above represents an upper bound on background but is not so low as to make proof of remediation via an upper confidence limit [GWPS] impossible.

To ensure that the GWPS in equation [7.6] sets a reasonable target, the Unified Guidance recommends that at least 8 to 10 background measurements (*n*) be utilized, and more if available. If the background sample is not normal, but can be normalized via a transformation, the tolerance limit should be computed on the transformed measurements and the result ***back-transformed*** to obtain a limit in the concentration scale (see **Chapter 17** for further details).

TRADEOFFS IN BACKGROUND GWPS TESTING METHODS

A two-sample GWPS approach offers a stricter test of background exceedances. There is also greater flexibility in designing tests for a variety of future comparison values (single with repeat, small sample means, etc.). The true test parameter is explicitly defined by the type of test chosen. Non-parametric upper prediction limit tests also allow for greater flexibility when data sets include significant non-detect values or are not transformable to a normal distribution assumption. The approach suggested in this section accounts for the cumulative false positive error rate.

One negative feature of two-sample GWPS testing is that the test hypotheses cannot be reversed for correction action monitoring. The trigger for compliance/assessment testing may also be quite small, resulting in important consequences (the need to move to corrective action). It may also be difficult to demonstrate longer-term compliance following remedial activities, if the actual background is somewhat elevated.

Single-sample GWPS testing, by contrast, does allow for the reversal of test hypotheses. Using a suitable definition of the somewhat elevated GWPS takes into account background sample variability and size. Cumulative false positive error rates for compliance or corrective action testing are not considered, and standardized alpha error levels (.1 or .05) can be used. Exceedances under compliance monitoring also offer clear evidence of a considerable increase above background.

But applying an arbitrary increase above background recommended for single-sample testing may conflict with State anti-degradation policy. Defining the GWPS as a specific population parameter is also somewhat arbitrary. Using the suggested guidance approach for defining the GWPS in equation [7.6] above, may result in very high values if the data are not normal (including logarithmic or non-parametric applications). There is also less flexibility in identifying testing options, especially with data sets containing significant non-detect values. Annual testing with quarterly sampling may be the only realistic choice.

A possible compromise might utilize both approaches. That is, initially apply the two-sample approach for compliance/assessment testing. Then evaluate the single-sample approach with reversed

hypotheses. Some of the initially significant increases under the two-sample approach may also meet the upper confidence level limit when tested against the higher GWPS. Those well constituents that cannot meet this limit can then be subjected to corrective action remediation and full post-treatment testing. This implies that the background GWPS would be a range based on the two testing methods rather than a single value.

►EXAMPLE 7-1

A facility has triggered a significant increase under detection monitoring. One hazardous constituent (arsenic) was identified which must be tested against a background GWPS at six different compliance wells, since background well levels were above the appropriate arsenic MCL of 10 ug/l. Two semi-annual tests are required for compliance/assessment monitoring. Assume that arsenic had been detected in both background and downgradient wells, but was significantly higher in one of the compliance wells. It must be determined whether any of the compliance wells have exceeded their background GWPS, and might require corrective action.

Design a background GWPS monitoring system for the following arsenic data from the elevated Well #1, consisting of eight hypothetical historical intrawell background samples and four future annual values for two different simulated data distribution cases shown in the table below. Sample means and standard deviations are provided in the bottom row:

Compliance Well #1 Arsenic (μg/l)

Historical Well Data		Case 1	Case2
74.1	41.5	61.5	95.0
10.8	41.0	58.7	73.4
32.8	30.8	76.8	73.3
25.0	40.0	81.3	90.0
$\bar{x}$ = 37.0		$\bar{x}$ = 69.58	$\bar{x}$ = 82.93
s = 18.16		s = 11.15	s = 11.24

Background values were randomly generated from a normal distribution with a true mean of μ = 40 and a population standard deviation of σ = 16. Case 1 future data were from a normal distribution with a mean 1.5 times higher, while Case 2 data were from a normal distribution twice as high as the background true mean. Both cases used the same background population standard deviation. The intent of these simulated values is to allow exploration of both of the Unified Guidance recommended background GWPS methods when background increases are relatively modest and sample sizes small.

The two-sample background GWPS approach is first evaluated. Assume that the background data are normal and stationary (no evidence of spatial or temporal variation and other forms of statistical dependence). Given a likely limit of future quarterly sampling and required semi-annual evaluations, two guidance prediction limit options would seem appropriate—either a 1-of-2 future values or a 1-of-1 future mean size 2 test conducted twice a year. The 1-of-2 future values option is chosen.

Since there are a total of 6 compliance wells, one background constituent and two annual evaluations, there are a total of 12 annual background tests to be conducted. Either the Unified Guidance tables in **Appendix D** or R-script can be used to identify the appropriate prediction limit κ-

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factor. For the 1-of-2 future values test, κ = **1.83** (found by interpolation from the second table on page D-118), based on w = 6, COC = 1, and two tests per year. The calculated prediction limit using the background data set statistics and κ-factor is 70.2 µg/l, serving as the background GWPS.

When the future values from the table above are tested against the GWPS, the following results are obtained. A "Pass" indicates that the compliance/assessment null hypothesis was achieved, while a "Fail" indicates that the alternative hypothesis (the GWPS has been exceeded) is accepted.

Well #1 As Compliance Comparisons
1-of-2 Future Values Test (µg/l)

Case 1 (data)	Result	Case 2 (data)	Result
61.5		95.0	
58.7	Pass	73.4	Fail
76.8		73.3	
81.3	Fail	90.0	Fail

GWPS = 70.2

Both cases indicate at least one GWPS exceedance using the 1-of-2 future values tests. These may be indications of a statistically significant increase above background, but the outcome for Case 1 is somewhat troubling. While a 50% increase above background (based on the simulated population parameters) is potentially significant, more detailed power evaluations indicate that such a detected exceedance would only be expected about 24% of the time (using R-script power calculations with a Z-value of 1.25 standard deviations above background for the 1-of-2 future values test). In contrast, the 2.5 Z-value for Case 2 would be expected to be exceeded about 76% of the time. In order to further evaluate the extent of significance of these results, the single-sample GWPS method is also considered.

Following the guidance above, define the single-sample mean GWPS using equation [7.6] for the upper 95% confidence, 95% proportion tolerance limit. Then apply upper and lower normal mean confidence intervals tests of the Case 1 and 2 n = 4 sample data using equations [7.3] and [7.4].

From **Table 21-9** on page D-246, a τ-factor of 3.187 is used with the background mean and standard deviation to generate the GWPS = 94.9. One-way upper and lower mean confidence levels are evaluated at 90 or 95% confidence for the tests and compared to the fixed background GWPS.

LCL test Pass/Fail results are the same as above for the two-sample compliance test. However, a "Pass" for the UCL test implies that the alternative hypothesis (less than the standard) is accepted while a "Fail" implies greater than or equal to the GWPS under corrective action monitoring hypotheses:

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As Mean Confidence Interval Tests Against Background GWPS (μg/l)

LCL Test				UCL Test			
90% LCL	Result	95% LCL	Result	90% UCL	Result	95% UCL	Result
			Case 1 Data				
60.5	Pass	56.5	Pass	78.7	Pass	82.7	Pass
			Case 2 Data				
73.7	Pass	69.7	Pass	92.1	Pass	96.2	Fail

GWPS = 94.9

For either chosen significance level, the Case 1 90% and 95% UCLs of 78.7 and 82.7 are below the GWPS and the alternative corrective action hypothesis (the mean is less than the standard) can be accepted. For Case 2, the 90% UCL of 92.1 is below the GWPS, but the 95% UCL of 96.2 is above. If a higher level of test confidence is appropriate, the Case 2 arsenic values can be considered indicative of the need for corrective action.

If only the single-sample background GWPS approach were applied to the same data as above in compliance/assessment monitoring tests, neither case mean LCLs would exceed the standard, and no corrective action monitoring would be necessary. However, it should be noted from the example that this approach does allow for a significant increase above the reference background level before any action would be indicated. ◄

The approaches provided above presume that well constituent data subject to background GWPS testing are *stationary* over time. If sampling data show evidence of a trend, the situation becomes more complicated in making compliance or corrective action test decisions. Two- and single-sample stationary scenarios for identifying standards may not be appropriate. Trend behavior can be determined by applying one of the methods provided in **Chapter 17** (e.g., linear regression or Mann-Kendall trend tests) to historical data. A significant increasing slope can be indicative of a background exceedance, although it should be clear that the increase is not due to natural conditions. A decreasing or non-significant slope can be considered evidence for compliance with historical background. The most problematic standard would be setting an eventual background target for compliance testing under corrective action. To a great extent, it will depend on site-specific conditions including the behavior of specific constituent subject to remediation. A background GWPS might be determined following the period of remediation and monitoring when aquifer conditions have hopefully stabilized.

Setting and applying background GWPSs have not received a great deal of attention in previous guidance. The discussions and example above help illustrate the somewhat difficult regulatory choices that need to be made. A regulatory agency needs to determine what levels, if any, above background can be considered acceptable. A further consideration is the degree of importance placed on background GWPS exceedances, particularly when tested along with constituents having health-based limits. Existing regulatory programs may have already developed procedures to deal with many of the issues discussed in this section.

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CHAPTER 8. SUMMARY OF RECOMMENDED METHODS

8.1 SELECTING THE RIGHT STATISTICAL METHODS 8-1
8.2 TABLE 8.1 INVENTORY OF RECOMMENDED METHODS 8-4
8.3 METHOD SUMMARIES 8-9

This chapter provides a quick guide to the statistical procedures discussed within the Unified Guidance. The first section is a basic road map designed to encourage the user to ask a series of key questions. The other sections offer thumbnail sketches of each method and a matrix of options to help in selecting the right procedure, depending on site-specific characteristics and constraints.

8.1 SELECTING THE RIGHT STATISTICAL METHODS

Choosing appropriate statistical methods is important in developing a sound groundwater monitoring statistical program. The statistical test(s) should be selected to match basic site-specific characteristics such as number and configuration of wells, the water quality constituents being measured, and general hydrology. Statistical methods should also be selected with reference to the statistical characteristics of the monitored parameters — proportion of non-detects, type of concentration distribution (***e.g.***, normal, lognormal), presence or absence of spatial variability, ***etc.***

Because site conditions and permit requirements vary considerably, no single "cookbook" approach is readily available to select the right statistical method. The best strategy is to consider site-specific conditions and ask a series of questions. A table of recommended options (**Table 8-1**) and summary descriptions is presented in **Section 8.2** to help select an appropriate basic approach.

The first question is: what stage of monitoring is required? Detection monitoring is the first stage of any groundwater monitoring program and typically involves comparisons between measurements of background and compliance point groundwater. Most of the methods described in this document (***e.g.***, prediction limits, control charts, tests for trend, ***etc.***) are designed for facilities engaged in detection monitoring. However, it must be determined whether an interwell (***e.g.***, upgradient-to-downgradient) or an intrawell test is warranted. This entails consideration of the site hydrology, constituent detection rates, and deciding whether separate (upgradient) wells or past intrawell data serves as the most appropriate and representative background.

Compliance/assessment monitoring is required for facilities that no longer meet the requirements of a detection monitoring program by exhibiting statistically significant indications of a release to groundwater. Once in compliance/assessment, compliance point measurements are typically tested against a fixed GWPS. Examples of fixed standards include Maximum Concentration Limits [MCL], risk-derived limits or a single limit derived from background data. The most appropriate statistical method for tests against GWPS is a lower confidence limit. The type of confidence limit will depend on whether the regulatory standard represents an average concentration; an absolute maximum, ceiling, or upper percentile; or whether the compliance data exhibit a trend over time.

In cases where no fixed GWPS is specified for a particular constituent, compliance point data may be directly compared against background data. In this situation, the most appropriate statistical method is

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one or another detection monitoring two- or multiple-sample tests using the critical design limit as the GWPS (discussed in **Section 7.5**).

Corrective action is reserved for facilities where evidence of a groundwater release is confirmed above a GWPS. In these situations, the facility is required to submit an appropriate remediation plan to the Regional Administrator and to institute steps to insure adequate containment and/or clean-up of the release. Remediation of groundwater can be very costly and also difficult to measure. EPA has not adopted a uniform approach in the setting of clean-up standards or how one should determine whether those clean-up standards have been attained. Some guidance on this issue is given in the EPA document, ***Methods for Evaluating the Attainment of Cleanup Standards, Volume II: Groundwater*** (EPA, 1992).

The null hypothesis in corrective action testing is reversed from that of detection and compliance/assessment monitoring. Not only is it assumed that contamination is above the compliance or clean-up standard, but corrective action should continue until the average concentration level is below the clean-up limit for periods specified in the regulations. For any fixed-value standard (e.g., the GWPS or a remediation goal) a reasonable and consistent statistical test for corrective action is an *upper* confidence limit. The type of confidence limit will depend on whether the data have a stable mean concentration or exhibit a trend over time. For those well constituents requiring remediation, there will be a period of activity before formal testing can take place. A number of statistical techniques (e.g. trend testing) can be applied to the data collected in this interim period to gauge prospects for eventual GWPS compliance. **Section 7.5** describes corrective action testing limitations involving a two-sample GWPS.

Another major question involves the statistical distribution most appropriate to the observed measurements. Parametric tests are those which assume the underlying population follows a known and identifiable distribution, the most common examples in groundwater monitoring being the normal and the lognormal. If a specific distribution cannot be determined, non-parametric test methods can be used. Non-parametric tests do not require a known statistical distribution and can be helpful when the data contain a substantial proportion of non-detects. All of the parametric tests described in the Unified Guidance, except for control charts, have non-parametric counterparts that can be used when the underlying distribution is uncertain or difficult to test.

A special consideration in fitting distributions is the presence of non-detects, also known as left-censored measurements. As long as a sample contains a small fraction of non-detects (*i.e.*, no more than 10-15%), simple substitution of half the reporting limit [RL] is generally adequate. If the proportion of non-detects is substantial, it may be difficult or impossible to determine whether a specific parametric distributional model provides a good fit to the data. For some tests, such as the *t*-test, one can switch to a non-parametric test with little loss of power or accuracy. Non-parametric interval tests, however, such as prediction and tolerance limits, require substantially more data before providing statistical power equivalent to *parametric* intervals. Partly because of this drawback, the Unified Guidance discusses methods to adjust datasets with significant fractions of non-detects so that parametric distributional models may still be used (**Chapter 15**).

The Unified Guidance now recommends a single, consistent D*ouble Quantification rule* approach for handling constituents that have either never been detected or have not been recently detected. Such constituents are *not* included in cumulative annual *site-wide false positive error rate* [SWFPR] computations; and no special adjustment for non-detects is necessary. Any confirmed quantification (*i.e.*,

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two consecutive detections above the RL) at a compliance point provides sufficient evidence of groundwater contamination by that parameter.

A key question when picking a test for detection monitoring is whether traditional background-to-downgradient interwell or single-well intrawell tests are appropriate. If intrawell testing is appropriate, historical measurements form the individual compliance well's own background while future values are tested against these data. Intrawell tests eliminate any natural spatial differences among monitoring wells. They can also be used when the groundwater flow gradient is uncertain or unstable, since all samples being tested are collected from the same well.

Possible disadvantages to intrawell tests also need to be considered. First, if the compliance well has already been impacted, intrawell background will also be impacted. Such contaminated background may provide a skewed comparison to later data from the same well, making it difficult to identify contaminated groundwater in the future. Secondly, if intrawell background is constructed from only a few early measurements, considerable time may be needed to accumulate a sufficient number of background observations (via periodic updating) to run a statistically powerful test.

If a compliance well has already been impacted by previous contamination, trend testing can still indicate whether conditions have deteriorated since intrawell background was collected. For sites historically contaminated above background, the only way to effectively monitor compliance wells may be to establish an historical intrawell baseline and measure increases above this baseline.

Besides trend tests, techniques recommended for intrawell comparisons include intrawell prediction limits, control charts, and sometimes the Wilcoxon rank-sum test. The best choice between these methods is not always clear. Since there is no non-parametric counterpart to control charts, the choice will depend on whether the data is normal or can be normalized via a transformation. New guidance for control charts shows they also can be designed to incorporate retesting. For sites with a large number of well-constituent pairs, intrawell prediction limits can incorporate retesting to meet specific site-wide false positive rate and statistical power characteristics. Parametric intrawell prediction limits can be used with background that is normal or transformable to normality; non-parametric versions can also be applied for many other data sets.

If interwell, upgradient-to-downgradient tests are appropriate, the choice of statistical method depends primarily on the number of compliance wells and constituents being monitored, the number of observations available from each of these wells, and the detection rates and distributional properties of these parameters. If a very small number of comparisons must be tested (*i.e.*, two or three compliance wells versus background, for one or two constituents), a *t*-test or Wilcoxon rank-sum test may be appropriate if there are a sufficient number of compliance measurements (*i.e.*, at least two per well).

For other cases, the Unified Guidance recommends a prediction limit or control chart constructed from background. Whenever more than a few statistical tests must be run, retesting should be incorporated into the procedure. If multiple observations per compliance well can be collected during a given evaluation period, either a prediction limit for 'future' observations, a prediction limit for means or medians, or a control chart can be considered, depending on which option best achieves statistical power and SWFPR targets, while balancing the site-specific costs and feasibility of sampling. If only one observation per compliance well can be collected per evaluation, the only practical choices are a prediction limit for individual observations or a control chart.

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8.2 TABLE 8-1 INVENTORY OF RECOMMENDED METHODS

Chapter 9. Exploratory Tools		
Statistical Method	Chapter	Use
Time Series Plot	**§9.1**	Plot of measurement levels over time; Useful for assessing trends, data inconsistencies, etc.
Box Plot	**§9.2**	Graphical summary of sample distribution; Useful for comparing key statistical characteristics in multiple wells
Histogram	**§9.3**	Graphical summary of sample distribution; Useful for assessing probability density of single data set
Scatter Plot	**§9.4**	Diagnostic tool; Plot of one variable vs. another; Useful for exploring statistical associations
Probability Plot	**§9.5**	Graphical fit to normality; Useful for raw or transformed data
Chapter 10. Fitting Distributions		
Statistical Method	Chapter	Use
Skewness Coefficient	**§10.4**	Measures symmetry/asymmetry in distribution; Screening level test for plausibility of normal fit
Coefficient of Variation	**§10.4**	Measures symmetry/asymmetry in distribution; Screening tool for plausibility of normal fit; Only for non-negative data
Shapiro-Wilk Test	**§10.5.1**	Numerical normality test of a single sample; for $n \leq 50$
Shapiro-Francía Test	**§10.5.2**	Numerical test of normality for a single sample; Supplement to Shapiro-Wilk; Use with $n > 50$
Filliben's Probability Plot Correlation Coefficient	**§10.6**	Numerical test of normality for a single sample; Interchangeable with Shapiro-Wilk; Use with $n \leq 100$; Good supplement to probability plot
Shapiro-Wilk Multiple Group Test	**§10.7**	Extension of Shapiro-Wilk test for multiple samples with possibly different means and/or variances; Good check to use with Welch's *t*-test
Chapter 11. Equality of Variance		
Statistical Method	Chapter	Use
Box Plots (side-by-side)	**§11.1**	Graphical test of differences in population variances; Good screening tool for equal variance assumption in ANOVA
Levene's Test	**§11.2**	Numerical, robust ANOVA-type test of equality of variance for ≥ 2 populations; Useful for testing assumptions in ANOVA
Mean-SD Scatter Plot	**§11.3**	Visual test of association between SD and mean levels across group of wells; Use to check for proportional effect or if variance-stabilizing transformation is needed
Chapter 12. Outliers		
Statistical Method	Chapter	Use
Probability Plot	**§12.1**	Graphical fit of distribution to normality; Useful for identifying extreme points not coinciding with predicted tail of distribution
Box Plot	**§12.2**	Graphical screening tool for outliers; quasi-non-parametric, only requires rough symmetry in distribution
Dixon's Test	**§12.3**	Numerical test for single low or single high outlier; Use when $n \leq 25$
Rosner's Test	**§12.4**	Numerical test for up to 5 outliers in single dataset; Recommended when $n \geq 20$; User must identify a specific number of possible outliers before running

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Chapter 13. Spatial Variation		
Statistical Method	Chapter	Use
Box Plots (side-by-side)	**§13.2.1**	Quick screen for spatial variability; Look for noticeably staggered boxes
One-Way Analysis of Variance [ANOVA] for Spatial Variation	**§13.2.2**	Test to compare means of several populations; Use to identify spatial variability across a group of wells and to estimate pooled (background) standard deviation for use in intrawell tests; Data must be normal or normalized; Assumption of equal variances across populations
Chapter 14. Temporal Variability		
Statistical Method	Chapter	Use
Time Series Plot (parallel)	**§14.2.1**	Quick screen for temporal (and/or spatial) variation; Look for parallel movement in the graph traces at several wells over time
One-way ANOVA for Temporal Effects	**§14.2.2**	Test to compare means of distinct sampling events, in order to assess systematic temporal dependence across wells; Use to get better estimate of (background) variance and degrees of freedom in data with temporal patterns; Residuals from ANOVA also used to create stationary, adjusted data
Sample Autocorrelation Function	**§14.2.3**	Plot of autocorrelation by lag between sampling events; Requires approximately normal data; Use to test for temporal correlation and/or to adjust sampling frequency
Rank von Neumann Ratio	**§14.2.4**	Non-parametric numerical test of dependence in time-ordered data series; Use to test for first-order autocorrelation in data from single well or population
Darcy Equation	**§14.3.2**	Method to approximate groundwater flow velocity; Use to determine sampling interval guaranteeing physical independence of consecutive groundwater samples; Does not ensure statistical independence
Seasonal Adjustment (single well)	**§14.3.3**	Method to adjust single data series exhibiting seasonal correlations (*i.e.*, cyclical fluctuations); At least 3 seasonal cycles must be evident on time series plot
Temporally-Adjusted Data Using ANOVA	**§14.3.3**	Method to adjust multiple wells for a common temporal dependence; Use adjusted data in subsequent tests
Seasonal Mann-Kendall Test	**§14.3.4**	Extension of Mann-Kendall trend test when seasonality is present; At least 3 seasonal cycles must be evident
Chapter 15. Managing Non-Detect Data		
Statistical Method	Chapter	Use
Simple Substitution	**§15.2**	Simplest imputation scheme for non-detects; Useful when ≤ 10-15% of dataset is non-detect
Censored Probability Plot	**§15.3**	Probability plot for mixture of non-detects and detects; Use to check normality of left-censored sample
Kaplan-Meier	**§15.3**	Method to estimate mean and standard deviation of left-censored sample; Use when ≤ 50% of dataset is non-detect; Multiple detects and non-detects must originate from same distribution
Robust Regression on Order Statistics	**§15.4**	Method to estimate mean and standard deviation of left-censored sample; Use when ≤ 50% of dataset is non-detect; Multiple detects and non-detects must originate from same distribution
Cohen' Method and Parametric Regression on Order Statistics	**§15.5**	Other methods to estimate mean and standard deviation of left-censored sample; Use when ≤ 50% of dataset is non-detect; Detects and non-detects must originate from same distribution and there must be a single censoring limit

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Chapter 16. Two-sample Tests		
Statistical Method	Chapter	Use
Pooled Variance *t*-Test	**§16.1.1**	Test to compare means of two populations; Data must be normal or normalized, with no significant spatial variability; Useful at very small sites in upgradient-to-downgradient comparisons; Also useful for updating background; Population variances must be equal
Welch's *t*-Test	**§16.1.2**	Test to compare means of two populations; Data must be normal or normalized, with no significant spatial variability; Useful at very small sites in interwell comparisons; Also useful for updating background; Population variances can differ
Wilcoxon Rank-Sum Test	**§16.2**	Non-parametric test to compare medians of two populations; Data need not be normal; Some non-detects OK; Should have no significant spatial variability; Useful at very small sites in interwell comparisons and for certain intrawell comparisons; Also useful for updating background
Tarone-Ware Test	**§16.3**	Extension of Wilcoxon rank-sum; non-parametric test to compare medians of two populations; Data need not be normal; Designed to accommodate left-censored data; Should have no significant spatial variability; Useful at very small sites in interwell comparisons and for certain intrawell comparisons; Also useful for updating background
Chapter 17. ANOVA, Tolerance Limits, & Trend Tests		
Statistical Method	Chapter	Use
One-Way ANOVA	**§17.1.1**	Test to compare means across multiple populations; Data must be normal or normalized; Should have no significant spatial variability if used as interwell test; Assumes equal variances; Mandated in some permits, but generally superceded by other tests; Useful for identifying spatial variation; RMSE from ANOVA can be used to improve intrawell background limits
Kruskal-Wallis Test	**§17.1.2**	Test to compare medians across multiple populations; Data need not be normal; some non-detects OK; Should have no significant spatial variability if used as interwell test; Useful alternative to ANOVA for identifying spatial variation
Tolerance Limit	**§17.2.1**	Test to compare background vs. ≥ 1 compliance well; Data must be normal or normalized; Should have no significant spatial variability if used as interwell test; Alternative to ANOVA; Mostly superceded by prediction limits; Useful for constructing alternate clean-up standard in corrective action
Non-parametric Tolerance Limit	**§17.2.2**	Test to compare background vs. ≥ 1 compliance well; Data need not be normal; Non-Detects OK; Should have no significant spatial variability if used as interwell test; Alternative to Kruskal-Wallis; Mostly superceded by prediction limits
Linear Regression	**§17.3.1**	Parametric estimate of linear trend; Trend residuals must be normal or normalized; Useful for testing trends in background or at already contaminated wells; Can be used to estimate linear association between two random variables
Mann-Kendall Trend Test	**§17.3.2**	Non-parametric test for linear trend; Non-detects OK; Useful for documenting upward trend at already contaminated wells or where trend already exists in background
Theil-Sen Trend Line	**§17.3.3**	Non-parametric estimate of linear trend; Non-detects OK; Useful for estimating magnitude of an increasing trend in conjunction with Mann-Kendall test

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Chapter 18. Prediction Limit Primer		
Statistical Method	Chapter	Use
Prediction Limit for m Future Values	**§18.2.1**	Test to compare m measurements from compliance well against background; Data must be normal normalized; Useful in retesting schemes; Can be adapted to either intrawell or interwell tests; No significant spatial variability allowed if used as interwell test
Prediction Limit for Future Mean	**§18.2.2**	Test to compare mean of compliance well against background; Data must be normal or normalized; Useful alternative to traditional ANOVA; Can be useful in retesting schemes; Most useful for interwell (*e.g.*, upgradient to downgradient) comparisons; No significant spatial variability allowed if used as interwell test
Non-Parametric Prediction Limit for m Future Values	**§18.3.1**	Non-parametric test to compare m measurements from compliance well against order statistics of background; Non-normal data and/or non-detects OK; Useful in non-parametric retesting schemes; Should have no significant spatial variability if used as interwell test
Non-parametric Prediction Limit for Future Median	**§18.3.2**	Test to compare median of compliance well against order statistics of background; Non-normal data and/or non-detects OK; Useful in non-parametric retesting schemes; Most useful for interwell (*e.g.*, upgradient to downgradient) comparisons; No significant spatial variability allowed if used as interwell test
Chapter 19. Prediction Limit Strategies with Retesting		
Statistical Method	Chapter	Use
Prediction Limits for Individual Observations With Retesting	**§19.3.1**	Tests individual compliance point measurements against background; Data must be normal or normalized; Assumes common population variance across wells; No significant spatial variability allowed if used as interwell test; Replacement for traditional ANOVA, extends Dunnett's multiple comparison with control (MCC) procedure; Allows control of SWFPR across multiple well-constituent pairs; Retesting explicitly incorporated; Useful at any size site
Prediction Limits for Means With Retesting	**§19.3.2**	Tests compliance point means against background; Data must be normal or normalized; Assumes common population variance across wells; No significant spatial variability allowed if used as interwell test; Replacement for traditional ANOVA, extends Dunnett's multiple comparison with control (MCC) procedure; More flexible than a series of intrawell t-tests if used as intrawell test; Allows control of SWFPR across multiple well-constituent pairs; Must be feasible to collect ≥2 resamples per evaluation period to incorporate retesting; 1-of-1 scheme does not require explicit retesting
Non-Parametric Prediction Limits for Individual Observations With Retesting	**§19.4.1**	Non-parametric test of individual compliance point observations against background; Non-normal data and/or non-detects OK; No significant spatial variability allowed if used as interwell test; Retesting explicitly incorporated; Large background sample size helpful
Non-Parametric Prediction Limits for Medians With Retesting	**§19.4.2**	Non-parametric test of compliance point medians against background; Non-normal and/or non-detects OK; No significant spatial variability allowed if used as interwell test; Large background sample size helpful; Must be feasible to collect ≥ 3 resamples per evaluation period to incorporate retesting; 1-of-1 scheme does not require explicit retesting

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Chapter 20. Control Charts		
Statistical Method	Chapter	Use
Shewhart-CUSUM Control Chart	**§20.2**	Graphical test of significant increase above background; Data must be normal or normalized; Some non-detects OK if left-censored adjustment made; At least 8 background observations recommended; Viable alternative to prediction limits; Retesting can be explicitly incorporated; Control limits can be set via published literature or Monte Carlo simulation
Chapter 21. Confidence Intervals		
Statistical Method	Chapter	Use
Confidence Interval Around Normal Mean	**§21.1.1**	Data must be normal; Some non-detects OK if left-censored adjustment made; Used in compliance/assessment or corrective action to compare compliance well against fixed, mean-based groundwater standard; Should be no significant trend; 4 or more observations recommended
Confidence Interval Around Lognormal Geometric Mean	**§21.1.2**	Data must be lognormal; Some non-detects OK if left-censored adjustment made; Used in compliance/assessment or corrective action to compare compliance well against fixed, mean-based groundwater standard; Should be no significant trend; 4 or more observations recommended; Geometric mean equivalent to lognormal median, smaller than lognormal mean
Confidence Interval Around Lognormal Arithmetic Mean	**§21.1.3**	Data must be lognormal; Some non-detects OK if left-censored adjustment made; Used in compliance/assessment or corrective action to compare compliance well against fixed, mean-based groundwater standard; Should be no significant trend; 4 or more observations recommended; Lognormal arithmetic mean larger than lognormal geometric mean
Confidence Interval Around Upper Percentile	**§21.1.4**	Data must be normal or normalized; Some non-detects OK if left-censored adjustment made; Used in compliance/assessment to compare compliance well against percentile-based or maximum groundwater standard; Should be no significant trend
Non-Parametric Confidence Interval around Median	**§21.2**	For non-normal, non-lognormal data; Non-detects OK; Used in compliance/assessment or corrective action to compare compliance well against fixed, mean-based groundwater standard; Should be no significant trend; 7 or more observations recommended
Non-Parametric Confidence Interval Around Upper Percentile	**§21.2**	For non-normal, non-lognormal data; Non-detects OK; Used in compliance/assessment or corrective action to compare compliance well against percentile-based or maximum groundwater standard; Should be no significant trend; Large background sample size helpful
Confidence Band Around Linear Regression	**§21.3.1**	Use on data with significant trend; Trend residuals must be normal or normalized; Used in compliance/assessment or corrective action to compare compliance well against fixed groundwater standard; ≥ 8 observations recommended
Non-parametric Confidence Band Around Theil-Sen Line	**§21.3.2**	Use on data with significant trend; Non-normal data and/or non-detects OK; Used in compliance/assessment or corrective action to compare compliance well against fixed groundwater standard; Bootstrapping of Theil-Sen trend line used to construct confidence band

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8.3 METHOD SUMMARIES

TIME SERIES PLOT (SECTIONS 9.1 AND 14.2.1)

Basic purpose: Diagnostic and exploratory tool. It is a graphical technique to display changes in concentrations at one or more wells over a specified period of time or series of sampling events.

Hypothesis tested: Not a formal statistical test. Time series plots can be used to informally gauge the presence of temporal and/or spatial variability in a collection of distinct wells sampled during the same time frame.

Underlying assumptions: None.

When to use: Given a collection of wells with several sampling events recorded at each well, a time series plot can provide information not only on whether the mean concentration level changes from well to well (an indication of possible spatial variation), but also on whether there exists time-related or temporal dependence in the data. Such temporal dependence can be seen in parallel movement on the time series plot, that is, when several wells exhibit the same pattern of up-and-down fluctuations over time.

Steps involved: 1) For each well, make a plot of concentration against time or date of sampling for the sampling events that occurred during the specified time period; 2) Make sure each well is identified on the plot with a distinct symbol and/or connected line pattern (or trace); 3) To observe possible spatial variation, look for well traces that are substantially separated from one another in concentration level; 4) To look for temporal dependence, look for well traces that rise and fall together in roughly the same (parallel) pattern; 5) To ensure that artificial trends due to changing reporting limits are not reported, plot any non-detects with a distinct symbol, color, and/or fill.

Advantages/Disadvantages: Time series plots are an excellent tool for examining the behavior of one or more samples over time. Although, they do not offer the compact summary of distributional characteristics that, say, box plots do, time series plots display each and every data point and provide an excellent initial indication of temporal dependence. Since temporal dependence affects the underlying variability in the data, its identification is important so adjustments can be made to the estimated standard deviation.

BOX PLOT (SECTIONS 9.2, 12.2, AND 13.2.1)

Basic purpose: Diagnostic and exploratory tool. Graphical summary of data distribution; gives compact picture of central tendency and dispersion.

Hypothesis tested: Although not a formal statistical test, a side-by-side box plot of multiple datasets can be used as a rough indicator of either unequal variances or spatial variation (via unequal means/medians). Also serves as a quasi-non-parametric screening tool for outliers in a symmetric population.

Underlying assumptions: When used to screen outliers, underlying population should be approximately symmetric.

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When to use: Can be used as a quick screen in testing for unequal variances across multiple populations. Box lengths indicate the range of the central 50% of sample data values. Substantially different box lengths suggest possibly different population variances. It is useful as a rough indication of spatial variability across multiple well locations. Since the median (and often the mean) are graphed on each box, significantly staggered medians and/or means on a multiple side-by-side box plot can suggest possibly different population means at distinct well locations. Can also be used to screen for outliers: values falling beyond the 'whiskers' on the box plot are labeled as potential outliers.

Steps involved: 1) Compute the median, mean, lower and upper quartiles (*i.e.*, 25th and 75th percentiles) of each dataset; 2) Graph each set of summary statistics side-by-side on the same set of axes. Connect the lower and upper quartiles as the ends of a box, cut the box in two with a line at the median, and use an 'X' or other symbol to represent the mean. 3) Compute the 'whiskers' by extending lines below and above the box by an amount equal to 1.5 times the interquartile range [IQR].

Advantages/Disadvantages: The box plot is an excellent screening tool and visual aid in diagnosing either unequal variances for testing the assumptions of ANOVA, the possible presence of spatial variability, or potential outliers. It is not a formal statistical test, however, and should generally be used in conjunction with numerical test procedures.

HISTOGRAM (SECTION 9.3)

Basic purpose: Diagnostic and exploratory tool. It is a graphical summary of an entire data distribution.

Hypothesis tested: Not a formal statistical test.

Underlying assumptions: None.

When to use: Can be used as a rough estimate of the probability density of a single sample. Shape of histogram helps determine whether the distribution is symmetric or skewed. For larger data sets, histogram can be visually compared to a normal distribution or other known model to assess whether the shapes are similar.

Steps involved: 1) Sort and bin the data set into non-overlapping concentration segments that span the range of measurement values; 2) Create a bar chart of the bins created in **Step 1**: put the height of each bar equal to the number or fraction of values falling into each bin.

Advantages/Disadvantages: The histogram is a good visual aid in exploring possible distributional models that might be appropriate. Since it is not a formal test, there is no way to judge possible models solely on the basis of the histogram; however, it provides a visual 'feel' for a data set.

SCATTER PLOT (SECTION 9.4)

Basic purpose: Diagnostic tool. It is a graphical method to explore the association between two random variables or two paired statistical samples.

Hypothesis tested: None.

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Underlying Assumptions: None.

When to use: Useful as an exploratory tool for discovering or identifying statistical relationships between pairs of variables. Graphically illustrates the degree of correlation or association between two quantities.

Steps involved: Using Cartesian pairs of the variables of interest, graph each pair on the scatter plot, using one symbol per pair.

Advantages/Disadvantages: A scatter plot is not a formal test, but rather an excellent exploratory tool. Helps identify statistical relationships.

PROBABILITY PLOT (SECTIONS 9.5 AND 12.1)

Basic purpose: Diagnostic tool. A graphical method to compare a dataset against a particular statistical distribution, usually the normal. Designed to show how well the data match up to or 'fit' the hypothesized distribution. An absolutely straight line fit indicates perfect consistency with the hypothesized model.

Hypothesis tested: Although not a formal test, the probability plot can be used to graphically indicate whether a dataset is normal. The straighter the plot, the more consistent the dataset with a null hypothesis of normality; significant curves, bends, or other non-linear patterns suggest a rejection of the normal model as a poor fit.

Underlying Assumptions: All observations come from a single statistical population.

When to use: Can be used as a graphical indication of normality on a set of raw measurements or, by first making a transformation, as an indication of normality on the transformed scale. It should generally be supplemented by a formal numerical test of normality. It can be used on the residuals from a one-way ANOVA to test the joint normality of the groups being compared. The test can also be used to help identify potential outliers (*i.e.*, individual values not part of the same basic underlying population).

Steps involved: 1) Order the dataset and determine matching percentiles (or quantiles) from the hypothesized distribution (typically the standard normal); 2) Plot the ordered data values against the matching percentiles; 3) Examine the plot for a straight line fit.

Advantages/Disadvantages: Not a formal test of normality; however, the probability plot is an excellent graphical supplement to any goodness-of-fit test. Because each data value is depicted, specific departures from normality can be identified (*e.g.*, excessive skewness, possible outliers, *etc.*).

SKEWNESS COEFFICIENT (SECTION 10.4)

Basic purpose: Diagnostic tool. Sample statistic designed to measure the degree of symmetry in a sample. Because the normal distribution is perfectly symmetric, the skewness coefficient can provide a quick indication of whether a given dataset is symmetric enough to be consistent with the normal model. Skewness coefficients close to zero are consistent with normality; skewness values large in absolute value suggest the underlying population is asymmetric and non-normal.

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Hypothesis tested: The skewness coefficient is used in groundwater monitoring as a screening tool rather than a formal hypothesis test. Still, it can be used to roughly test whether a given sample is normal by using the following rule of thumb: if the skewness coefficient is no greater than one in absolute value, accept a null hypothesis of normality; if not, reject the normal model as ill-fitting.

Underlying Assumptions: None

Steps involved: 1) Compute skewness coefficient; 2) Compare to cutoff of 1; 3) If skewness is greater than 1, considering running a formal test of normality.

Advantages/Disadvantages: Fairly simple calculation, good screening tool. Skewness coefficient can be positive or negative, indicating positive or negative skewness in the dataset, respectively. Measures symmetry rather than normality, per se; since other non-normal distributions can also be symmetric, might give a misleading result. Not as powerful or accurate a test of normality as either the Shapiro-Wilk or Filliben tests, but a more accurate indicator than the coefficient of variation, particularly for data on a transformed scale.

COEFFICIENT OF VARIATION [CV] (SECTION 10.4)

Basic purpose: Diagnostic tool. Sample statistic used to measure skewness in a sample of positively-valued measurements. Because the CV of positively-valued normal measurements must be close to zero, the CV provides an easy indication of whether a given sample is symmetric enough to be normal. Coefficients of variation close to zero are consistent with normality; large CVs indicate a skewed, non-normal population.

Hypothesis tested: The coefficient of variation is not a formal hypothesis test. Still, it can be used to provide a 'quick and easy' gauge of non-normality: if the CV exceeds 0.5, the population is probably not normal.

Underlying Assumptions: Sample must be positively-valued for CV to have meaningful interpretation.

Steps involved: 1) Compute sample mean and standard deviation; 2) Divide standard deviation by mean to get coefficient of variation.

Advantages/Disadvantages: Simple calculation, good screening tool. It measures skewness and variability in positively-valued data. Not an accurate a test of normality, especially if data have been transformed.

SHAPIRO-WILK AND SHAPIRO-FRANCÍA TESTS (SECTION 10.5)

Basic purpose: Diagnostic tool and a formal numerical goodness-of-fit test of normality. Shapiro-Francía test is a close variant of the Shapiro-Wilk useful when the sample size is larger than 50.

Hypothesis tested: H_0 — the dataset being tested comes from an underlying normal population. H_A — the underlying population is non-normal (note that the form of this alternative population is not specified).

Underlying assumptions: All observations come from a single normal population.

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When to use: To test normality on a set of raw measurements or following transformation of the data. It can also be used with the residuals from a one-way ANOVA to test the joint normality of the groups being compared.

Steps involved (for Shapiro-Wilk): 1) Order the dataset and compute successive differences between pairs of extreme values (*i.e.*, most extreme pair = maximum – minimum, next most extreme pair = 2nd largest – 2nd smallest, *etc.*); 2) Multiply the pair differences by the Shapiro-Wilk coefficients and compute the Shapiro-Wilk test statistic; 3) Compare the test statistic against an α-level critical point; 4) Values higher than the critical point are consistent with the null hypothesis of normality, while values lower than the critical point suggest a non-normal fit.

Advantages/Disadvantages: The Shapiro-Wilk procedure is considered one of the very best tests of normality. It is much more powerful than the skewness coefficient or chi-square goodness-of-fit test. The Shapiro-Wilk and Shapiro-Francía test statistics will tend to be large (and more indicative of normality) when a probability plot of the same data exhibits a close-to-linear pattern. Special Shapiro-Wilk coefficients are available for sample sizes up to 50. For larger sample sizes, the Shapiro-Francía test does not require a table of special coefficients, just the ability to compute inverse normal probabilities.

FILLIBEN'S PROBABILITY PLOT CORRELATION COEFFICIENT TEST (SECTION 10.6)

Basic purpose: Diagnostic tool and a formal numerical goodness-of-fit procedure to test for normality.

Hypothesis tested: H_0 — the dataset being tested comes from an underlying normal population. H_A — the underlying population is non-normal (note that the form of this alternative population is not specified).

Underlying assumptions: All observations come from a single normal population.

When to use: To test normality on a set of raw measurements or following transformation of the data on the transformed scale. It can also be used on the residuals from a one-way ANOVA to test the joint normality of the groups being compared.

Steps involved: 1) Construct a normal probability plot of the dataset; 2) Calculate the correlation between the pairs on the probability plot; 3) Compare the test statistic against an α-level critical point; 4) Values higher than the critical point are consistent with the null hypothesis of normality, while values lower than the critical point suggest a non-normal fit.

Advantages/Disadvantages: Filliben's procedure is an excellent test of normality, with very similar characteristics to the Shapiro-Wilk test. As a correlation on a probability plot, the Filliben's test statistic will tend to be close to one (and more indicative of normality) when a probability plot of the same data exhibits a close-to-linear pattern. Critical points for Filliben's test are available for sample sizes up to 100. A table of special coefficients is not needed to run Filliben's test, only the ability to compute inverse normal probabilities.

SHAPIRO-WILK MULTIPLE GROUP TEST (SECTION 10.7)

Basic purpose: Diagnostic tool and a formal normality goodness-of-fit test for multiple groups.

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Hypothesis tested: H_0 — datasets being tested all come from underlying normal populations, possibly with different means and/or variances. H_A — at least one underlying population is non-normal (note that the form of this alternative population is not specified).

Underlying assumptions: The observations in each group all come from, possibly different, normal populations.

When to use: Can be used to test normality on multiple sets of raw measurements or, by first making a transformation, to test normality of the data groups on the transformed scale. It is particularly helpful when used in conjunction with Welch's *t*-test.

Steps involved: 1) Compute Shapiro-Wilk statistic (**Section 10.5**) on each group separately; 2) Transform the Shapiro-Wilk statistics into *z*-scores and combine into an omnibus *z*-score; 3) Compare the test statistic against an α-level critical point; 4) Values higher than the critical point are consistent with the null hypothesis of normality for all the populations, while values lower than the critical point suggest a non-normal fit of one or more groups.

Advantages/Disadvantages: As an extension of the Shapiro-Wilk test, the multiple group test shares many of its desirable properties. Users should be careful, however, not to assume that a result consistent with the hypothesis of normality implies that all groups follow the ***same*** normal distribution. The multiple group test does not assume that all groups have the same means or variances. Special coefficients are needed to convert Shapiro-Wilk statistics into *z*-scores, but once converted, no other special tables needed to run test besides a standard normal table.

LEVENE'S TEST (SECTION 11.2)

Basic purpose: Diagnostic tool. Levene's test is a formal numerical test of equality of variances across multiple populations.

Hypothesis tested: H_0 — The population variances across all the datasets being tested are equal. H_A — One or more pairs of population variances are unequal.

Underlying assumptions: The data set from each population is assumed to be roughly normal in distribution. Since Levene's test is designed to work well even with somewhat non-normal data (***i.e.***, it is fairly robust to non-normality), precise normality is not an overriding concern.

When to use: Levene's method can be used to test the equal variance assumption underlying one-way ANOVA for a group of wells. Used in this way, the test is run on the absolute values of the residuals after first subtracting the mean of each group being compared. If Levene's test is significant, the original data may need to be transformed to stabilize the variances before running an ANOVA.

Steps involved: 1) Compute the residuals of each group by subtracting the group mean; 2) conduct a one-way ANOVA on the absolute values of the residuals; and 3) if the ANOVA *F*-statistic is significant at the 5% α-level, conclude the underlying population variances are unequal. If not, conclude the data are consistent with the null hypothesis of equal variances.

Advantages/Disadvantages: As a test of equal variances, Levene's test is reasonably robust to non-normality. It is much more so than for Bartlett's test (recommended within the 1989 ***Interim Final***

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Guidance [IFG]). In addition, Levene's method uses the same basic equations as those needed to run a one-way ANOVA.

MEAN-STANDARD DEVIATION SCATTER PLOT (SECTION 11.3)

Basic purpose: Diagnostic tool. It is a graphical method to examine degree of association between mean levels and standard deviations at a series of wells. Positive correlation or association between these quantities is known as a 'proportional effect' and is characteristic of skewed distributions such as the lognormal.

Hypothesis tested: Though not a formal test, the mean-standard deviation scatter plot provides a visual indication of whether variances are roughly equal from well to well, or whether the variance depends on the well mean.

Underlying Assumptions: None.

When to use: Useful as a graphical indication of 1) equal variances or 2) proportional effects between the standard deviation and mean levels. A positive correlation between well means and standard deviations may signify that a transformation is needed to stabilize the variances.

Steps involved: 1) Compute the sample mean and standard deviation for each well; 2) plot the mean-standard deviation pairs on a scatter plot; and 3) examine the plot for any association between the two quantities.

Advantages/Disadvantages: Not a formal test of homoscedasticity (*i.e.*, equal variances). It is helpful in assessing whether a transformation might be warranted to stabilize unequal variances.

DIXON'S TEST (SECTION 12.3)

Basic purpose: Diagnostic tool. It is used to identify (single) outliers within smaller datasets.

Hypothesis tested: H_0 — Outlier(s) comes from same normal distribution as rest of the dataset. H_A — Outlier(s) comes from different distribution than rest of the dataset.

Underlying assumptions: Data without the suspected outlier(s) are normally distributed. Test recommended only for sample sizes up to 25.

When to use: Try Dixon's test when one value in a dataset appears anomalously low or anomalously high when compared to the other data values. Be cautious about screening apparent high outliers in compliance point wells. Even if found to be statistical outliers, such extreme concentrations may represent contamination events. A safer application of outlier tests is with background or baseline samples. Even then, always try to establish a physical reason for the outlier if possible (*e.g.*, analytical error, transcription mistake, *etc.*).

Steps involved: 1) Remove the suspected outlier and test remaining data for normality. If non-normal, try a transformation to achieve normality; 2) Once remaining data are normal, calculate Dixon's statistic, depending on the sample size n; 3) Compare Dixon's statistic against an α-level critical point; and 4) If Dixon's statistic exceeds the critical point, conclude the suspected value is a statistical outlier. Investigate this measurement further.

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Advantages/Disadvantages: Dixon's test is only recommended for sample sizes up to 25. Furthermore, if there is more than one outlier, Dixon's test may lead to masking (*i.e.*, a non-significant result) where two or more outliers close in value 'hide' one another. If more than one outlier is suspected, always test the *least* extreme value first.

ROSNER'S TEST (SECTION 12.4)

Basic purpose: Diagnostic tool. It is used to identify multiple outliers within larger datasets.

Hypothesis tested: H_0 — Outliers come from same normal distribution as the rest of the dataset. H_A — Outliers come from different distribution than the rest of the dataset.

Underlying assumptions: Data without the suspected outliers are normally distributed. Test recommended for sample sizes of at least 20.

When to use: Try Rosners's test when multiple values in a dataset appear anomalously low or anomalously high when compared to the other data values. As Dixon's test, be cautious about screening apparent high outliers in compliance point wells. Always try to establish a physical reason for an outlier if possible (*e.g.*, analytical error, transcription mistake, *etc.*).

Steps involved: 1) Identify the maximum number of possible outliers ($r_0 \leq 5$) and the number of suspected outliers ($r \leq r_0$). Remove the suspected outliers and test the remaining data for normality. If non-normal, try a transformation to achieve normality; 2) Once remaining data are normal, successively compute the mean and standard deviation, removing the next most extreme value each time until r_0 possible outliers have been removed; 3) Compute Rosner's statistic based on the number (r) of suspected outliers; and 4) If Rosner's statistic exceeds an α-level critical point, conclude there are r statistical outliers. Investigate these measurements further. If Rosner's statistic does not exceed the critical point, recompute the test for (r–1) possible outliers, successively reducing r until either the critical point is exceeded or $r = 0$.

Advantages/Disadvantages: Rosner's test is only recommended for sample sizes of 20 or more, but can be used to identify up to 5 outliers per use. It is more complicated to use than some other outlier tests, but does not require special tables other than to determine α-level critical points.

ONE-WAY ANALYSIS OF VARIANCE [ANOVA] FOR SPATIAL VARIATION (SECTION 13.2.2)

Basic purpose: Diagnostic tool. Test to compare population means at multiple wells, in order to gauge the presence of spatial variability.

Hypothesis tested: H_0 — Population means across all tested wells are equal. H_A — One or more pairs of population means are unequal.

Underlying assumptions: 1) ANOVA residuals at each well or group must be normally distributed using the original data or after transformation. Residuals should be tested for normality using a goodness-of-fit procedure; 2) population variances across all wells must be equal. This assumption can be tested with box plots and Levene's test; and 3) each tested well should have at least 3 to 4 separate observations.

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When to use: The one-way ANOVA procedure can be used to identify significant spatial variation across a group of distinct well locations. The method is particularly useful for a group of multiple upgradient wells, to determine whether or not there are large average concentration differences from one location to the next due to natural groundwater fluctuations and/or differences in geochemistry. If downgradient wells are included in an ANOVA, the downgradient groundwater should not be contaminated, at least if a test of *natural* spatial variation is desired. Otherwise, a significant difference in population means could reflect the presence of either recent or historical contamination.

Steps involved: 1) Form the ANOVA residuals by subtracting from each measurement its sample well mean; 2) test the ANOVA residuals for normality and equal variance. If either of these assumptions is violated, try a transformation of the data and retest the assumptions; 3) compute the one-way ANOVA *F*-statistic; 4) if the *F*-statistic exceeds an α-level critical point, conclude the null hypothesis of equal population means has been violated and that there is some (perhaps substantial) degree of spatial variation; 5) if the *F*-statistic does not exceed the critical point, conclude that the well averages are close enough to treat the combined data as coming from the same statistical population.

Advantages/Disadvantages: One-way ANOVA is an excellent technique for identifying differences in separate well populations, as long as the assumptions are generally met. However, a finding of significant spatial variability does not specify the reason for the well-to-well differences. Additional information or investigation may be necessary to determine why the spatial differences exist. Be especially careful when (1) testing a combination of upgradient and downgradient wells that downgradient contamination is not the source of the difference found with ANOVA; and 2) when ANOVA identifies significant spatial variation and intrawell tests are called for. In the latter case, the ANOVA results can sometimes be used to estimate more powerful intrawell prediction and control limits. Such an adjustment comes directly from the ANOVA computations, requiring no additional calculation.

ANALYSIS OF VARIANCE [ANOVA] FOR TEMPORAL EFFECTS (SECTIONS 14.2.2 & 14.3.3)

Basic purpose: Diagnostic tool. It is a test to compare population means at multiple sampling events, after pooling the event data across wells. The test can also used to adjust data across multiple wells for common temporal dependence.

Hypothesis tested: H_0 — Population means across all sampling events are equal. H_A — One or more pairs of population means are unequal.

Underlying assumptions: 1) ANOVA residuals from the population at each sampling event must be normal or normalized. These should be tested for normality using a goodness-of-fit procedure; 2) the population variances across all sampling events must be equal. Test this assumption with box plots and Levene's test; and 3) each tested well should have at least 3 to 4 observations per sampling event.

When to use: 1) The ANOVA procedure for temporal effects should be used to identify significant temporal variation over a series of distinct sampling events. The method assumes that spatial variation by well location is not a significant factor (this should have already been tested). ANOVA for temporal effects should be used when a time series plot of a group of wells exhibits roughly parallel traces over time, indicating a time-related phenomenon affecting all the wells in a similar

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way on any given sampling event. If a significant temporal effect is found, the results of the ANOVA can be employed to adjust the standard deviation estimate and the degrees of freedom quantities needed for further upgradient-to-downgradient comparisons; 2) compliance wells can be included in ANOVA for temporal effects, since the temporal pattern is assumed to affect all the wells on-site, regardless of gradient; and 3) residuals from ANOVA for temporal effects can be used to create adjusted, temporally-stationary measurements in order to eliminate the temporal dependence.

Steps involved: 1) Compute the mean (across wells) from data collected on each separate sampling event; 2) form the ANOVA residuals by subtracting from each measurement its sampling event mean; 3) test the ANOVA residuals for normality and equal variance. If either of these assumptions is violated, try a transformation of the data and retest the assumptions; 4) compute the one-way ANOVA *F*-statistic; 5) if the *F*-statistic exceeds an α-level critical point, conclude the null hypothesis of equal population means has been violated and that there is some (perhaps substantial) degree of temporal dependence; 6) compute the degrees of freedom adjustment factor and the adjusted standard deviation for use in *interwell* comparisons; 7) if the *F*-statistic does not exceed the critical point, conclude that the sampling event averages are close enough to treat the combined data as if there were no temporal dependence; and use the residuals, if necessary, to create adjusted, temporally-stationary measurements, regardless of the significance of the *F*-test (**Section 14.3.3**).

Advantages/Disadvantages: 1) One-way ANOVA for temporal effects is a good technique for identifying time-related effects among a group of wells. The procedure should be employed when a strong temporal dependence is indicated by parallel traces in time series plots; 2) if there is both temporal dependence and strong spatial variability, the ANOVA for temporal effects may be non-significant due to the added spatial variation. A two-way ANOVA for temporal and spatial effects might be considered instead; and 3) even if the ANOVA is non-significant, the ANOVA residuals can still be used to adjust data for apparent temporal dependence.

SAMPLE AUTOCORRELATION FUNCTION (SECTION 14.2.3)

Basic purpose: Diagnostic tool. This is a parametric estimate and test of autocorrelation (*i.e.*, time-related dependence) in a data series from a single population.

Hypothesis tested: H_0 — Measurements from the population are independent of sampling events (*i.e.*, they are not influenced by the time when the data were collected). H_A — The distribution of measurements is impacted by the time of data collection.

Underlying assumptions: Data should be approximately normal, with few non-detects. Sampling events represented in the sample should be fairly regular and evenly spaced in time.

When to use: When testing a data series from a single population (*e.g.*, a single well), the sample autocorrelation function (also known as the correlogram) can determine whether there is a significant temporal dependence in the data.

Steps involved: 1) Form overlapping ordered pairs from the data series by pairing measurements 'lagged' by a certain number of sampling events (*e.g.*, all pairs with measurements spaced by $k = 2$ sampling events); 2) for each distinct lag (k), compute the sample autocorrelation; 3) plot the

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autocorrelations from **Step 2** by lag (*k*) on a scatter plot; and 4) count any autocorrelation as significantly different from zero if its absolute magnitude exceeds $2/\sqrt{n}$, where *n* is the sample size.

Advantages/Disadvantages: 1) The sample autocorrelation function provides a graphical test of temporal dependence. It can be used not only to identify autocorrelation, but also as a planning tool for adjusting the sampling interval between events. The smallest lag (*k*) at which the autocorrelation is insignificantly different from zero is the minimum sampling interval ensuring temporally uncorrelated data; 2) the test only applies to a single population at a time and cannot be used to identify temporal effects that span across groups of wells simultaneously. In that scenario, use a one-way ANOVA for temporal effects; and 3) tests for significant autocorrelation depend on the data being approximately normal; use the rank von Neumann ratio for non-normal samples.

RANK VON NEUMANN RATIO (SECTION 9.4)

Basic purpose: Diagnostic tool. It is a non-parametric test of first-order autocorrelation (*i.e.*, time-related dependence) in a data series from a single population.

Hypothesis tested: H_0 — Measurements from the population are independent of sampling events (*i.e.*, they are not influenced by the time when the data were collected). H_A — The distribution of measurements is impacted by the time of data collection.

Underlying assumptions: Data need not be normally distributed. However, it is assumed that the data series can be uniquely ranked according to concentration level. Ties in the data (*e.g.*, non-detects) are not technically allowed. Although a mid-rank procedure (as used in the Wilcoxon rank-sum test) to rank tied values might be considered, the available critical points for the rank von Neumann ratio statistic only directly apply to cases where a unique ranking is possible.

When to use: When testing a data series from a single population (*e.g.*, a single well) for use in, perhaps, an intrawell prediction limit, control chart, or test of trend, the rank von Neumann ratio can determine whether there is a significant temporal dependence in the data. If the dependence is seasonal, the data may be adjusted using a seasonal correction (**Section 14.3.3**). If the dependence is a linear trend, remove the estimated trend and re-run the rank von Neumann ratio on the trend residuals before concluding there are additional time-related effects. Complex dependence may require consultation with a professional statistician.

Steps involved: 1) Rank the measurements by concentration level, but then list the ranks in the order the samples were collected; 2) using the ranks, compute the von Neumann ratio; 3) if the rank von Neumann ratio exceeds an α-level critical point, conclude the data exhibit no significant temporal correlation. Otherwise, conclude that a time-related pattern does exist. Check for seasonal cycles or linear trends using time series plots. Consult a professional statistician regarding possible statistical adjustments if the pattern is more complex.

Advantages/Disadvantages: The rank von Neumann ratio, as opposed to other common time series methods for determining autocorrelation, is a non-parametric test based on using the ranks of the data instead of the actual concentration measurements. The test is simple to compute and can be used as a formal confirmation of temporal dependence, even if the autocorrelation appears fairly obvious on a time series plot. As a limiting feature, the test only applies to a single population at a time and

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cannot be used to identify temporal effects that span across groups of wells simultaneously. In that scenario, a one-way ANOVA for temporal effects is a better diagnostic tool. Because critical points for the rank von Neumann ratio have not been developed for the presence of ties, the test will not be useful for datasets with substantial portions of non-detects.

DARCY EQUATION (SECTION 14.3.2)

Basic purpose: Method to determine a sampling interval ensuring that distinct physical volumes of groundwater are sampled on any pair of consecutive events.

Hypothesis tested: Not a statistical test or formal procedure.

Underlying assumptions: Flow regime is one in which Darcy's equation is approximately valid.

When to use: Use Darcy's equation to gauge the minimum travel time necessary for distinct volumes of groundwater to pass through each well screen. Physical independence of samples does not guarantee statistical independence, but it increases the likelihood of statistical independence. Use to design or plan for a site-specific sampling frequency, as well as what formal statistical tests and retesting strategies are possible given the amount of temporally-independent data that can be collected each evaluation period.

Steps involved: 1) Using knowledge of the site hydrogeology, calculate the horizontal and vertical components of average groundwater velocity with Darcy's equation; 2) Determine the minimum travel time needed between field samples to ensure physical independence; 3) Specify a sampling interval during monitoring no less than the travel time obtained via the Darcy computation.

Advantages/Disadvantages: Darcy's equation is relatively straightforward, but is not a statistical procedure. It is not applicable to certain hydrologic environments. Further, it is not a substitute for a direct estimate of autocorrelation. Statistical independence is not assured using Darcy's equation, so caution is advised.

SEASONAL CORRECTION (SECTION 14.3.3)

Basic purpose: Method to adjust a longer data series from a single population for an obvious seasonal cycle or fluctuation pattern. By removing the seasonal pattern, the remaining residuals can be used in further statistical procedures (*e.g.*, prediction limits, control charts) and treated as independent of the seasonal correlation.

Hypothesis tested: The seasonal correction is not a formal statistical test. Rather, it is a statistical adjustment to data for which a definite seasonal pattern has been identified.

Underlying assumptions: There should be enough data so that at least 3 full seasonal cycles are displayed on a time series plot. It is also assumed that the seasonal component has a stationary (*i.e.*, stable) mean and variance during the period of data collection.

When to use: Use the seasonal correction when a longer series of data must be examined, but a time series plot indicates a clearly recurring, seasonal fluctuation of concentration levels. If not removed, the seasonal dependence will tend to upwardly bias the estimated variability and could lead to inaccurate or insufficiently powerful tests.

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Steps involved: 1) Using a time series plot of the data series, separate the values into common sampling events for each year (*e.g.*, all January measurements, all third quarter values, *etc.*); 2) compute the average of each subgroup and the overall mean of the dataset; and 3) adjust the data by removing the seasonal pattern.

Advantages/Disadvantages: The seasonal correction described in the Unified Guidance is relatively simple to perform and offers a more accurate standard deviation estimates compared to using unadjusted data. Removal of the seasonal component may reveal other previously unnoticed features of the data, such as a slow-moving trend. A fairly long data series is required to confirm the presence of a recurring seasonal cycle. Furthermore, many complex time-related patterns cannot be handled by this simple correction. In such cases, consultation with a professional statistician may be necessary.

SEASONAL MANN-KENDALL TEST FOR TREND (SECTION 14.3.4)

Basic purpose: Method for detection monitoring. It is used to identify the presence of a significant (upward) trend at a compliance point when data also exhibit seasonal fluctuations. It may also be used in compliance/assessment and corrective action monitoring to track upward or downward trends.

Hypothesis tested: H_0 — No discernible linear trend exists in the concentration data over time. H_A — A non-zero, (upward) linear component to the trend does exist.

Underlying assumptions: Since the seasonal Mann-Kendall trend test is a non-parametric method, the underlying data need not be normal or follow a particular distribution. No special adjustment for ties is needed.

When to use: Use when 1) upgradient-to-downgradient comparisons are inappropriate so that intrawell tests are called for; 2) a control chart or intrawell prediction limit cannot be used because of possible trends in the intrawell background, and 3) the data also exhibit seasonality. A trend test can be particularly helpful at sites with recent or historical contamination where it is uncertain if background is already contaminated. An upward trend in these cases will document the changing concentration levels more accurately than either a control chart or intrawell prediction limit, both of which assume a stationary background mean concentration.

Steps involved: 1) Divide the data into separate groups representing common sampling events from each year; 2) compute the Mann-Kendall test statistic (S) and its standard deviation ($SD[S]$) on each group; 3) sum the separate Mann-Kendall statistics into an overall test statistic; 4) compare this statistic against an α-level critical point; and 5) if the statistic exceeds the critical point, conclude that a significant upward trend exists. If not, conclude there is insufficient evidence for identifying a significant, non-zero trend.

Advantages/Disadvantages: 1) The seasonal Mann-Kendall test does not require any special treatment for non-detects, only that all non-detects be set to a common value lower than any of the detected values; and 2) the test is easy to compute and reasonably efficient for detecting (upward) trends in the presence of seasonality. Approximate critical points are derived from the standard normal distribution.

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SIMPLE SUBSTITUTION (SECTION 15.2)

Basic purpose: A simple adjustment for non-detects in a dataset. One-half the reporting limit [RL] is substituted for each non-detect to provide a numerical approximation to the unknown true concentration.

Hypothesis tested: None.

Underlying assumptions: The true non-detect concentration is assumed to lie somewhere between zero and the reporting limit. Furthermore, that the probability of the true concentration being less than half the RL is about the same as the probability of it being greater than half the RL.

When to use: In general, simple substitution should be used when the dataset contains a relatively small proportion of non-detects, say no more than 10-15%. Use with larger non-detect proportions can result in biased estimates, especially if most of the detected concentrations are recorded at low levels (*e.g.*, at or near RL).

Steps involved: 1) Determine the reporting limit; and 2) replace each non-detect with one-half RL as a numerical approximation.

Advantages/Disadvantages: Simple substitution of half the RL is the easiest adjustment available for non-detect data. However, it can lead to biased estimates of the mean and particularly the variance if employed when more than 10-15% of the data are non-detects.

CENSORED PROBABILITY PLOT (SECTIONS 15.3 AND 15.4)

Basic purpose: Diagnostic tool. It is a graphical fit to normality of a mixture of detected and non-detect measurements. Adjustments are made to the plotting positions of the detected data under the assumption that all measurements come from a common distributional model.

Hypothesis tested: As a graphical tool, the censored probability plot is not a formal statistical test. However, it can provide an indication as to whether a dataset is consistent with the hypothesis that the mixture of detects and non-detects come from the same distribution and that the non-detects make up the lower tail of that distribution.

Underlying assumptions: Dataset consists of a mixture of detects and non-detects, all arising from a common distribution. Data must be normal or normalized.

When to use: Use the censored probability plot to check the viability of the Kaplan-Meier or robust regression on order statistics [ROS] adjustments for non-detect measurements. If the plot is linear, the data are consistent with a model in which the unobserved non-detect concentrations comprise the lower tail of the underlying distribution.

Steps involved: 1) Using either Kaplan-Meier or ROS, construct a partial ranking of the detected values to account for the presence of non-detects; 2) determine standard normal quantiles that match the ranking of the detects; and 3) graph the detected values against their matched normal quantiles on a probability plot and examine for a linear fit.

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Advantages/Disadvantages: The censored probability plot offers a visual indication of whether a mixture of detects and non-detects come from the same (normal) distribution. There are, however, no formal critical points to aid in deciding when the fit is 'linear enough.' Correlation coefficients can be computed to informally aid the assessment. Censored probability plots can also be constructed on transformed data to help select a normalizing transformation.

KAPLAN-MEIER ADJUSTMENT (SECTION 15.3)

Basic purpose: Diagnostic tool. It is used to adjust a mixture of detected and non-detect data for the unknown concentrations of non-detect values. The Kaplan-Meier procedure leads to adjusted estimates for the mean and standard deviation of the underlying population.

Hypothesis tested: As a statistical adjustment procedure, the Kaplan-Meier method is not a formal statistical test. Rather, it allows estimation of characteristics of the population by assuming the combined group of detects and non-detects come from a common distribution.

Underlying assumptions: Dataset consists of a mixture of detects and non-detects, all arising from the same distribution. Data must be normal or normalized in the context of the Unified Guidance. Kaplan-Meier should not be used when more than 50% of the data are non-detects.

When to use: Since the Kaplan-Meier adjustment assumes all the measurements arise from the same statistical process, but that some of these measurements (*i.e.*, the non-detects) are unobservable due to limitations in analytical technology, Kaplan-Meier should be used when this model is the most realistic or reasonable choice. In particular, when constructing prediction limits, confidence limits, or control charts, the mean and standard deviation of the underlying population must be estimated. If non-detects occur in the dataset (but do not account for more than half of the observations), the Kaplan-Meier adjustment can be used to determine these estimates, which in turn can be utilized in constructing the desired statistical test.

Steps involved: 1) Sort the detected values and compute the 'risk set' associated with each detect; 2) using the risk set, compute the Kaplan-Meier cumulative distribution function [CDF] estimate associated with each detect; 3) calculate adjusted estimates of the population mean and standard deviation using the Kaplan-Meier CDF values; and 4) use these adjusted population estimates in place of the sample mean and standard deviation in prediction limits, confidence limits, and control charts.

Advantages/Disadvantages: Kaplan-Meier offers a way to adjust for significant fractions of non-detects without having to know the actual non-detect concentration values. It is more difficult to use than simple substitution, but avoids the biases inherent in that method.

ROBUST REGRESSION ON ORDER STATISTICS [ROS] (SECTION 15.4)

Basic purpose: Diagnostic tool. It is a method to adjust mixture of detects and non-detects for the unknown concentrations of non-detect values. Robust ROS leads to adjusted estimates for the mean and standard deviation of the underlying population by imputing a distinct estimated value for each non-detect.

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Hypothesis tested: As a statistical adjustment procedure, robust ROS is not a formal statistical test. Rather, it allows estimation of characteristics of the population by assuming the combined group of detects and non-detects come from a common distribution.

Underlying assumptions: Dataset consists of a mixture of detects and non-detects, all arising from the same distribution. Data must be normal or normalized in the context of the Unified Guidance. Robust ROS should not be used when more than 50% of the data are non-detects.

When to use: Since robust regression on order statistics assumes all the measurements arise from the same statistical process, robust ROS should be used when this model is reasonable. In particular, when constructing prediction limits, confidence limits, or control charts, the mean and standard deviation of the underlying population must be estimated. If non-detects occur in the dataset (but do not account for more than half of the observations), robust ROS can be used to determine these estimates, which in turn can be utilized to construct the desired statistical test.

Steps involved: 1) Sort the distinct reporting limits [RL] for non-detect values and compute 'exceedance probabilities' associated with each RL; 2) using the exceedance probabilities, compute 'plotting positions' for the non-detects, essentially representing CDF estimates associated with each RL; 3) impute values for individual non-detects based on their RLs and plotting positions; 4) compute adjusted mean and standard deviation estimates via the sample mean and standard deviation of the combined set of detects and imputed non-detects; and 5) use these adjusted population estimates in place of the (unadjusted) sample mean and standard deviation in prediction limits, confidence limits, and control charts.

Advantages/Disadvantages: Robust ROS offers an alternative to Kaplan-Meier to adjust for significant fractions of non-detects without having to know the actual non-detect concentration values. It is more difficult to use than simple substitution, but avoids the biases inherent in that method.

COHEN'S METHOD AND PARAMETRIC ROS (SECTION 15.5)

Basic purpose: Diagnostic tools. These are other methods to adjust mixture of detects and non-detects to obtain the unknown mean and standard deviation for the entire data set

Hypothesis tested: **N**either technique is a formal statistical test. Rather, they allow estimation of characteristics of the population by assuming the combined group of detects and non-detects come from a common distribution.

Underlying assumptions: Dataset consists of a mixture of detects and non-detects, all arising from the same distribution. Data must be normal or normalized in the context of the Unified Guidance. Neither should be used when more than 50% of the data are non-detects nor when data contain multiple non-detect levels.

When to use: Since these methods assume that all the measurements arise from the same statistical process, they should be used when this model is reasonable. In particular, when constructing prediction limits, confidence limits, or control charts, the mean and standard deviation of the underlying population must be estimated. If non-detects occur in the dataset (but do not account for more than half of the observations), they can be used to determine these estimates, which in turn can be utilized to construct the desired statistical test.

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Steps involved: Cohen's Method: 1) data are sorted into non-detect and detected portions; 2) detect mean and standard deviation estimates are calculated; 3) intermediate quantities of the ND% and a factor γ are calculated and used to locate the appropriate λ value from a table; and 4) full data set mean and standard deviation estimates are then obtained using formulas based on the detected mean, standard deviation, the detection limit and λ. Parametric ROS: 1) detected data are sorted in ascending order; 2) standardized normal distribution Z-values are generated from the full set of ranked values. Those corresponding to the sorted detected values are retained; 3) the detected values are then regressed against the Z-values; and 4) the resulting regression intercept and slope are the estimates of the mean and standard deviation for the full data set.

Advantages/Disadvantages: These two methods offer alternatives to Kaplan-Meier and robust ROS. The key limitation is that only data containing a single censoring limit can be used. In some situations using logarithmic data, their application can lead to biased estimates of the mean and standard deviation. Where appropriate, these methods are less computationally intensive that either Kaplan-Meier or robust ROS.

POOLED VARIANCE T-TEST (SECTION 16.1.1)

Basic purpose: Method for detection monitoring. This test compares the means of two populations.

Hypothesis tested: H_0 — Means of the two populations are equal; H_A — Means of the two populations are unequal (for the usual one-sided alternative, the hypothesis would state that the mean of the second population is greater than the mean of the first population).

Underlying assumptions: 1) The data from each population must be normal or normalized; 2) when used for interwell tests, there should be no significant spatial variability; 3) at least 4 observations per well should be available before applying the test; and 4) the two group variances are equal.

When to use: The pooled variance *t*-test can be used to test for groundwater contamination at very small sites, those consisting of maybe 3 or 4 wells and monitoring for 1 or 2 constituents. Site configurations with larger combinations of wells and constituents should employ a retesting scheme using either prediction limits or control charts. The pooled variance *t*-test can also be used to test proposed updates to intrawell background. A ***non-significant*** *t*-test in this latter case suggests the two sets of data are sufficiently similar to allow the initial background to be updated by augmenting with more recent measurements.

Steps involved: 1) Test the combined residuals from each population for normality. Make a data transformation if necessary; 2) test for equal variances, and if equal, compute a pooled variance estimate; 3) compute the pooled variance *t*-statistic and the degrees of freedom; 3) compare the *t*-statistic against a critical point based on both the α-level and the degrees of freedom; and 4) if the *t*-statistic exceeds the critical point, conclude the null hypothesis of equal means has been violated.

Advantages/Disadvantages: 1) The pooled variance *t*-test is one of the easiest to compute *t*-test procedures, but requires an assumption of equal variances across both populations; 2) because the *t*-test is a well-understood statistical procedure, the Unified Guidance recommends its use at very small groundwater monitoring facilities. For larger sites, however, repeated use of the *t*-test at a given α-level will lead to an unacceptably high risk of false positive error; and 3) if substantial spatial variability exists, the use of any *t*-test for upgradient-to-downgradient comparisons may lead

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to inaccurate conclusions. A significant difference in the population averages could also indicate the presence of natural geochemical factors differentially affecting the concentration levels at different wells. In these situations, consider an intrawell test instead.

WELCH'S T-TEST (SECTION 16.1.2)

Basic purpose: Method for detection monitoring. This test compares the means of two populations.

Hypothesis tested: H_0 — Means of the two populations are equal; H_A — Means of the two populations are unequal (for the usual one-sided alternative, the hypothesis would state that the mean of the second population is greater than the mean of the first population).

Underlying assumptions: 1) The data from each population must be normal or normalized; 2) when used for interwell tests, there should be no significant spatial variability; and 3) At least 4 observations per well should be available before applying the test.

When to use: Welch's *t*-test can be used to test for groundwater contamination at very small sites, those consisting of maybe 3 or 4 wells and monitoring for 1 or 2 constituents. Site configurations with larger combinations of wells and constituents should employ a retesting scheme using either prediction limits or control charts. Welch's *t*-test can also be used to test proposed updates to intrawell background data. A ***non-significant*** *t*-test in this latter case suggests the two sets of data are sufficiently similar to allow the initial background to be updated by augmenting with the more recent measurements.

Steps involved: 1) Test the combined residuals from each population for normality. Make a data transformation if necessary; 2) compute Welch's *t*-statistic and approximate degrees of freedom; 3) compare the *t*-statistic against a critical point based on both the α-level and the estimated degrees of freedom; and 4) if the *t*-statistic exceeds the critical point, conclude the null hypothesis of equal means has been violated.

Advantages/Disadvantages: 1) Welch's *t*-test is slightly more difficult to compute than other common *t*-test procedures, but has the advantage of ***not*** requiring equal variances across both populations. Furthermore, it has been shown to perform statistically as well or better than other *t*-tests; 2) it can be used at very small groundwater monitoring facilities, but should be avoided at larger sites. Repeated use of the *t*-test at a given α-level will lead to an unacceptably high risk of false positive error; and 3) if there is substantial spatial variability, use of Welch's *t*-test for interwell tests may lead to inaccurate conclusions. A significant difference in the population averages may reflect the presence of natural geochemical factors differentially affecting the concentration levels at different wells. In these situations, consider an intrawell test instead.

WILCOXON RANK-SUM TEST (SECTION 16.2)

Basic purpose: Method for detection monitoring. This test compares the medians of two populations.

Hypothesis tested: H_0 — Both populations have equal medians (and, in fact, are identical in distribution). H_A — The two population medians are unequal (in the usual one-sided alternative, the hypothesis would state that the median of the second population is larger than the median of the first).

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Underlying assumptions: 1) While the Wilcoxon rank-sum test does not require normal data, it does assume both populations have the same distributional form and that the variances are equal. If the data are non-normal but there at most a few non-detects, the equal variance assumption may be tested through the use of box plots and/or Levene's test. If non-detects make-up a large fraction of the observations, equal variances may have to be assumed rather than formally verified; 2) use of the Wilcoxon rank-sum procedure for interwell tests assumes there is no significant spatial variability. This is more likely to be the case in precisely those circumstances where the Wilcoxon procedure might be used: when there are high fractions of non-detects, so that most of the concentration measurements at any location are at low levels; and 3) there should be at least 4 background measurements and at least 2-4 compliance point values.

When to use: The Wilcoxon rank-sum test can be used to test for groundwater contamination at very small sites, those consisting of maybe 3 or 4 wells and monitoring for 1 or 2 constituents. Site configurations with larger combinations of wells and constituents should employ a retesting scheme using non-parametric prediction limits. Note, however, that non-parametric prediction limits often require large background sample sizes to be effective. The Wilcoxon rank-sum can be useful when a high percentage of the data is non-detect, but the amount of available background data is limited. Indeed, an *intrawell* Wilcoxon procedure may be helpful in some situations where the false positive rate would otherwise be too high to run intrawell prediction limits.

Steps involved: 1) Rank the combined set of values from the two datasets, breaking ties if necessary by using midranks; 2) compute the sum of the ranks from the compliance point well and calculate the Wilcoxon test statistic; 3) compare the Wilcoxon test statistic against an α-level critical point; and 4) if the test statistic exceeds the critical point, conclude that the null hypothesis of equal medians has been violated.

Advantages/Disadvantages: 1) The Wilcoxon rank-sum test is an excellent technique for small sites with constituent non-detect data. Compared to other possible methods such as the test of proportions or exact binomial prediction limits, the Wilcoxon rank-sum does a better job overall of correctly identifying elevated groundwater concentrations while limiting false positive error; 2) because the Wilcoxon rank-sum is easy to compute and understand, the Unified Guidance recommends its use at very small groundwater monitoring facilities. For larger sites, repeated use of the Wilcoxon rank-sum at a given α-level will lead to an unacceptably high risk of false positive error; and 3) if substantial spatial variability exists, the use of the Wilcoxon rank-sum for interwell tests may lead to inaccurate conclusions. A significant difference in the population medians may signal the presence of natural geochemical differences rather than contaminated groundwater. In these situations, consider an intrawell test instead.

TARONE-WARE TEST (SECTION 16.3)

Basic purpose: Non-parametric method for detection monitoring. This is an extension of Wilcoxon rank-sum, an alternative test to compare the medians in two populations when non-detects are prevalent.

Hypothesis tested: H_0 — Both populations have equal medians (and, in fact, are identical in distribution). H_A — The two population medians are unequal (in the usual one-sided alternative, the hypothesis would state that the median of the second population is larger than the median of the first).

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Underlying assumptions: 1) The Tarone-Ware test does not require normal data, but does assume both populations have the same distributional form and that the variances are equal; and 2) use of the Tarone-Ware procedure for interwell tests assumes there is no significant spatial variability. This is more likely to be the case when there are high fractions of data non-detects, so that most of the concentration measurements at any location are at low and similar levels.

When to use: The Tarone-Ware test can be used to test for groundwater contamination at very small sites, those consisting of perhaps 3 or 4 wells and monitoring for 1 or 2 constituents. Site configurations with larger combinations of wells and constituents should employ a retesting scheme using non-parametric prediction limits. Note, however, that non-parametric prediction limits often require large background sample sizes to be effective. The Tarone-Ware test can be useful when a high percentage of the data is non-detect, but the amount of available background data is limited. The Tarone-Ware test is also an alternative to the Wilcoxon rank-sum when there are multiple reporting limits and/or it is unclear how to fully rank the data as required by the Wilcoxon.

Steps involved: 1) Sort the distinct detected values in the combined data set; 2) count the 'risk set' associated with each distinct value from **Step 1** and compute the expected number of compliance point detections within each risk set; 3) form the Tarone-Ware test statistic from the expected counts in **Step 2**; 4) compare the test statistic against a standard normal α-level critical point; and 5) if the test statistic exceeds the critical point, conclude that the null hypothesis of equal medians has been violated.

Advantages/Disadvantages: The Tarone-Ware test is an excellent technique for small sites with constituent non-detect data having multiple reporting limits. If substantial spatial variability exists, use of the Tarone-Ware test for interwell tests may lead to inaccurate conclusions. A significant difference in the population medians may signal the presence of natural geochemical differences rather than contaminated groundwater. In these situations, consider an intrawell test instead.

ONE-WAY ANALYSIS OF VARIANCE [ANOVA] (SECTION 17.1.1)

Basic purpose: Formal interwell detection monitoring test and diagnostic tool. It compares population means at multiple wells, in order to detect contaminated groundwater when tested against background.

Hypothesis tested: H_0 — Population means across all tested wells are equal. H_A — One or more pairs of population means are unequal.

Underlying assumptions: 1) ANOVA residuals at each well or population must be normally distributed or transformable to normality. These should be tested for normality using a goodness-of-fit procedure; 2) the population variances across all wells must be equal. This assumption can be tested with box plots and Levene's test; and 3) each tested well should have at least 3 to 4 separate observations.

When to use: The one-way ANOVA can sometimes be used to identify to simultaneously test for contaminated groundwater across a group of distinct well locations. As an inherently interwell test, ANOVA should be utilized only on constituents exhibiting little to no spatial variation. Most uses of ANOVA have been superseded by prediction limits and control charts, although it is commonly employed to identify spatial variability or temporal dependence across a group of wells.

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Steps involved: 1) Form the ANOVA residuals by subtracting from each measurement its sample well mean; 2) tcst the ANOVA residuals for normality and equal variance. If either of these assumptions is violated, try a transformation of the data and retest the assumptions; 3) compute the one-way ANOVA *F*-statistic; 4) if the *F*-statistic exceeds an α-level critical point, conclude the null hypothesis of equal population means has been violated and that at least one pair of wells shows a significant difference in concentration levels; and 5) test each compliance well individually to determine which one or more exceeds background.

Advantages/Disadvantages: ANOVA is only likely to be infrequently used to make upgradient-to-downgradient comparisons in formal detection monitoring testing. The regulatory restrictions for per-constituent α-levels using ANOVA make it difficult to adequately control site-wide false positive rates [SWFPR]. Even if spatial variability is not a significant problem, users are advised to consider interwell prediction limits or control charts, and to incorporate some form of retesting

KRUSKAL-WALLIS TEST (SECTION 17.1.2)

Basic purpose: Formal interwell detection monitoring test and diagnostic tool. It compares population medians at multiple wells, in order to detect contaminated groundwater when tested against background. It is also useful as a non-parametric alternative to ANOVA for identifying spatial variability in constituents with non-detects or for data that cannot be normalized.

Hypothesis tested: H_0 — Population medians across all tested wells are equal. H_A — One or more pairs of population medians are unequal.

Underlying assumptions: 1) As a non-parametric alternative to ANOVA, data need not be normal; 2) the population variances across all wells must be equal. This assumption can be tested with box plots and Levene's test if the non-detect proportion is not too high; and 3) each tested well should have at least 3 to 4 separate observations.

When to use: The Kruskal-Wallis test can sometimes be used to identify to simultaneously test for contaminated groundwater across a group of distinct well locations. As an inherently interwell test, Kruskal-Wallis should be utilized for this purpose only with constituents exhibiting little to no spatial variation. Most uses of the Kruskal-Wallis (similar to ANOVA) have been superseded by prediction limits, although it can be used to identify spatial variability and/or temporal dependence across a group of wells when the sample data are non-normal or have higher proportions of non-detects.

Steps involved: 1) Sort and form the ranks of the combined measurements; 2) compute the rank-based Kruskal-Wallis test statistic (*H*); 3) if the *H*-statistic exceeds an α-level critical point, conclude the null hypothesis of equal population medians has been violated and that at least one pair of wells shows a significant difference in concentration levels; and 5) test each compliance well individually to determine which one or more exceeds background.

Advantages/Disadvantages: 1) The Kruskal-Wallis test is only likely to be infrequently used to make upgradient-to-downgradient comparisons in formal detection monitoring testing. The regulatory restrictions for per-constituent α-levels using ANOVA make it difficult to adequately control the SWFPR. Even if spatial variability is not a significant problem, users are advised to consider

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interwell prediction limits, and to incorporate some form of retesting; and 2) the Kruskal-Wallis test can be used to test for spatial variability in constituents with significant fractions of non-detects.

TOLERANCE LIMIT (SECTION 17.2.1)

Basic purpose: Formal interwell detection monitoring test of background versus one or more compliance wells. Tolerance limits can be used as an alternative to one-way ANOVA. These can also be used in corrective action as an alternative clean-up limit.

Hypothesis tested: H_0 — Population means across all tested wells are equal. H_A — One or more pairs of population means are unequal.

Underlying assumptions: 1) Data should be normal or normalized; 2) the population variances across all wells are assumed to be equal. This assumption can be difficult to test when comparing a single new observation from each compliance well against a tolerance limit based on background; and 3) there should be a minimum of 4 background measurements, preferably 8-10 or more.

When to use: A tolerance limit can be used in place of ANOVA for detecting contaminated groundwater. It is more flexible than ANOVA since 1) as few as one new measurement per compliance well is needed to run a tolerance limit test, and 2) no post-hoc testing is necessary to identify which compliance wells are elevated over background. Most uses of tolerance limits (similar to ANOVA) have been superseded by prediction limits, due to difficulty of incorporating retesting into tolerance limit schemes. If a hazardous constituent requires a background-type standard in compliance/assessment or corrective action, a tolerance limit can be computed on background and used as a fixed GWPS.

Steps involved: 1) Compute background sample mean and standard deviation; 2) calculate upper tolerance limit on background with high confidence and high coverage; 3) collect one or more observations from each compliance well and test each against the tolerance limit; and 4) identify a well as contaminated if any of its observations exceed the tolerance limit.

Advantages/Disadvantages: Tolerance limits are likely to be used only infrequently to be used as either interwell or intrawell tests. Prediction limits or control charts offer better control of false positive rates, and less is known about the impact of retesting on tolerance limit performance.

NON-PARAMETRIC TOLERANCE LIMIT (SECTION 17.2.2)

Basic purpose: Formal interwell detection monitoring test of background versus one or more compliance wells. Non-parametric tolerance limits can be used as an alternative to the Kruskal-Wallis test. They may also be used in compliance/assessment or corrective action to define a background GWPS.

Hypothesis tested: H_0 — Population medians across all tested wells are equal. H_A — One or more pairs of population medians are unequal.

Underlying assumptions: 1) As a non-parametric test, non-normal data with non-detects can be used; and 2) there should be a minimum of 8-10 background measurements and preferably more.

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When to use: A non-parametric tolerance limit can be used in place of the Kruskal-Wallis test for detecting contaminated groundwater. It is more flexible than Kruskal-Wallis since 1) as few as one new measurement per compliance well is needed to run a tolerance limit test, and 2) no post-hoc testing is necessary to identify which compliance wells are elevated over background. Most uses of tolerance limits have been superseded by prediction limits, due to difficulty of incorporating retesting into tolerance limit schemes. However, when a clean-up limit cannot or has not been specified in corrective action, a tolerance limit can be computed on background and used as a site-specific alternate concentration limit [ACL].

Steps involved: 1) Compute a large order statistic from background and set this value as the upper tolerance limit; 2) calculate the confidence and coverage associated with the tolerance limit; 3) collect one or more observations from each compliance well and test each against the tolerance limit; and 4) identify a well as contaminated if any of its observations exceed the tolerance limit.

Advantages/Disadvantages: 1) Tolerance limits are likely to be used only infrequently to be used as either interwell or intrawell tests. Prediction limits or control charts offer better control of false positive rates, and less is known about the impact of retesting on tolerance limit performance; and 2) non-parametric tolerance limits have the added disadvantage of generally requiring large background samples to ensure adequate confidence and/or coverage. For this reason, it is strongly recommended that a parametric tolerance limit be constructed whenever possible.

LINEAR REGRESSION (SECTION 14.4)

Basic purpose: Method for detection monitoring and diagnostic tool. It is used to identify the presence of a significantly increasing trend at a compliance point or any trend in background data sets.

Hypothesis tested: H_0 — No discernible linear trend exists in the concentration data over time. H_A — A non-zero, (upward) linear component to the trend does exist.

Underlying assumptions: Trend residuals should be normal or normalized, equal in variance, and statistically independent. If a small fraction of non-detects exists (≤10-15%), use simple substitution to replace each non-detect by half the reporting limit [RL]. Test homoscedasticity of residuals with a *scatter plot* (**Section 9.1**).

When to use: Use a test for trend when 1) upgradient-to-downgradient comparisons are inappropriate so that intrawell tests are called for, and 2) a control chart or intrawell prediction limit cannot be used because of possible trends in the intrawell background. A trend test can be particularly helpful at sites with recent or historical contamination where it is uncertain to what degree intrawell background is already contaminated. The presence of an upward trend in these cases will document the changing nature of the concentration data much more accurately than either a control chart or intrawell prediction limit, both of which assume a stable baseline concentration.

Steps involved: 1) If a linear trend is evident on a time series plot, construct the linear regression equation; 2) subtract the estimated trend line from each observation to form residuals; 3) test residuals for assumptions listed above; and 4) test regression slope to determine whether it is significantly different from zero. If so and the slope is positive, conclude there is evidence of a significant upward trend.

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Advantages/Disadvantages: Linear regression is a standard statistical method for identifying trends and other linear associations between pairs of random variables. However, it requires approximate normality of the trend residuals. Confidence bands around regression trends can be used in compliance/assessment and corrective action to determine compliance with fixed standards even when concentration levels are actively changing (*i.e.*, when a trend is apparent).

MANN-KENDALL TEST FOR TREND (SECTION 17.3.2)

Basic purpose: Method for detection monitoring and diagnostic tool. It is used to identify the presence of a significant (upward) trend at a compliance point or any trend in background data.

Hypothesis tested: H_0 — No discernible linear trend exists in the concentration data over time. H_A — A non-zero, (upward) linear component to the trend does exist.

Underlying assumptions: Since the Mann-Kendall trend test is a non-parametric method, the underlying data need not be normal or follow any particular distribution. No special adjustment for ties is needed.

When to use: Use a test for trend when 1) interwell tests are inappropriate so that intrawell tests are called for, and 2) a control chart or intrawell prediction limit cannot be used because of possible trends in intrawell background. A trend test can be particularly helpful at sites with recent or historical contamination where it is uncertain if intrawell background is already contaminated. An upward trend in these cases documents changing concentration levels more accurately than either a control chart or intrawell prediction limit, both of which assume a stationary background mean concentration.

Steps involved: 1) Sort the data values by time of sampling/collection; 2) consider all possible pairs of measurements from different sampling events; 3) score each pair depending on whether the later data point is higher or lower in concentration than the earlier one, and sum the scores to get Mann-Kendall statistic; 4) compare this statistic against an α-level critical point; and 5) if the statistic exceeds the critical point, conclude that a significant upward trend exists. If not, conclude there is insufficient evidence for identifying a significant, non-zero trend.

Advantages/Disadvantages: The Mann-Kendall test does not require any special treatment for non-detects, only that all non-detects can be set to a common value lower than any of the detects. The test is easy to compute and reasonably efficient for detecting (upward) trends. Exact critical points are provided in the Unified Guidance for $n \leq 20$; a normal approximation can be used for $n > 20$. 3) A version of the Mann-Kendall test (the seasonal Mann-Kendall, **Section 14.3.4**) can be used to test for trends in data that exhibit seasonality.

THEIL-SEN TREND LINE (SECTION 17.3.3)

Basic purpose: Method for detection monitoring. This is a non-parametric alternative to linear regression for estimating a linear trend.

Hypothesis tested: As presented in the Unified Guidance, the Theil-Sen trend line is not a formal hypothesis test but rather an estimation procedure. The algorithm can be modified to formally test whether the true slope is significantly different from zero, but this question will already be answered if used in conjunction with the Mann-Kendall procedure.

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Underlying assumptions: Like the Mann-Kendall trend test, the Theil-Sen trend line is non-parametric, so the underlying data need not be normal or follow a particular distribution. Furthermore, data ranks are not used, so no special adjustment for ties is needed.

When to use: It is particularly helpful when used in conjunction with the Mann-Kendall test for trend. The latter test offers information about whether a trend exists, but does not estimate the trend line itself. Once a trend is identified, the Theil-Sen procedure indicates how quickly the concentration level is changing with time.

Steps involved: 1) Sort the data set by date/time of sampling; 2) for each pair of distinct sampling events, compute the simple pairwise slope; 3) sort the list of pairwise slopes and set the overall slope estimate (Q) as the median slope in this list; 4) compute the median concentration and the median date/time of sampling; and 5) construct the Theil-Sen trend as the line passing through the median scatter point from **Step 4** with slope Q.

Advantages/Disadvantages: Although non-parametric, the Theil-Sen slope estimator does not use data ranks but rather the concentrations themselves. The method is non-parametric because the median pairwise slope is utilized, thus ignoring extreme values that might otherwise skew the slope estimate. The Theil-Sen trend line is as easy to compute as the Mann-Kendall test and does not require any special adjustment for ties (***e.g.***, non-detects).

PREDICTION LIMIT FOR *M* FUTURE VALUES (SECTION 18.2.1)

Basic purpose: Method for detection monitoring. This technique estimates numerical bound(s) on a series of m independent future values. The prediction limit(s) can be used to test whether the mean of one or more compliance well populations are equal to the mean of a background population.

Hypothesis tested: H_0 — The true mean of m future observations arises from the same population as the mean of measurements used to construct the prediction limit. H_A — The m future observations come from a distribution with a different mean than the population of measurements. Since an upper prediction limit is of interest in detection monitoring, the alternative hypothesis would state that the future observations are distributed with a larger mean than the background population.

Underlying assumptions: 1) Data used to construct the prediction limit must be normal or normalized. Adjustments for small to moderate fractions of non-detects can be made, perhaps using Kaplan-Meier or robust ROS; 2) although the variances of both populations (background and future values) are assumed to be equal, rarely will there be enough data from the future population to verify this assumption except during periodic updates to background; and 3) if used for upgradient-to-downgradient comparisons, there should be no significant spatial variability.

When to use: Prediction limits on individual observations can be used as an alternative in detection monitoring to either one-way ANOVA or Dunnett's multiple comparison with control [MCC] procedure. Assuming there is insignificant natural spatial variability, an interwell prediction limit can be constructed using upgradient or other representative background data. The number of future samples (m) should be chosen to reflect a single new observation collected from each downgradient or compliance well prior to the next statistical evaluation, plus a fixed number (m–1) of possible resamples. The initial future observation at each compliance point is then compared against the prediction limit. If it exceeds the prediction limit, one or more resamples are collected from the

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'triggered' well and also tested against the prediction limit. If substantial spatial variability exists, prediction limits for individual values can be constructed on a well-specific basis using intrawell background. The larger the intrawell background size, the better. To incorporate retesting, it must be feasible to collect up to (m–1) additional, but independent, resamples from each well.

Steps involved: 1) Compute the estimated mean and standard deviation of the background data; 2) considering the type of prediction limit (*i.e.*, interwell or intrawell), the number of future samples m, the desired site-wide false positive rate, and the number of wells and monitoring parameters, determine the prediction limit multiplier (κ); 3) compute the prediction limit as the background mean plus κ times the background standard deviation; and 4) compare each initial future observation against the prediction limit. If both the initial measurement and resample(s) exceed the limit, conclude the null hypothesis of equal means has been violated.

Advantages/Disadvantages: Prediction limits for individual values offer several advantages compared to the traditional one-way ANOVA and Dunnett's multiple comparison with control [MCC] procedures. Prediction limits are not bound to a minimum 5% per-constituent false positive rate and can be constructed to meet a target site-wide false positive rate [SWFPR] while maintaining acceptable statistical power. Unlike the one-way ANOVA F-test, only the comparisons of interest (*i.e.*, each compliance point against background) are tested. This gives the prediction limit more statistical power. Prediction limits can be designed for intrawell as well as interwell comparisons.

PREDICTION LIMIT FOR FUTURE MEAN (SECTION 18.2.2)

Basic purpose: Method for detection monitoring or compliance monitoring. It is used to estimate numerical limit(s) on an independent mean constructed from p future values. The prediction limits(s) can be used to test whether the mean of one population is equal to the mean of a separate (background) population.

Hypothesis tested: H_0 — The true mean of p future observations arise from the same population as the mean of measurements used to construct the prediction limit. H_A — The p future observations come from a distribution with a different mean than the population of background measurements. Since an upper prediction limit is of interest in both detection and compliance monitoring, the alternative hypothesis would state that the future observations are distributed with a larger mean than that of the background population.

Underlying assumptions: 1) Data used to construct the prediction limit must be normal or normalized. Adjustments for small to moderate fractions of non-detects can be made, perhaps using Kaplan-Meier or robust ROS; 2) although the variances of both populations (background and future values) are assumed to be equal, rarely will there be enough data from the future population to verify this assumption; and 3) if used for upgradient-to-downgradient comparisons, there should be no significant spatial variability.

When to use: Prediction limits on means can be used as an alternative in detection monitoring to either one-way ANOVA or Dunnett's multiple comparison with control [MCC] procedure. Assuming there is insignificant natural spatial variability, an interwell prediction limit can be constructed using upgradient or other representative background data. The number of future samples p should be chosen to reflect the number of samples that will be collected at each compliance well prior to the next statistical evaluation (*e.g.*, 2, 4, *etc.*). The average of these p observations at each compliance

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point is then compared against the prediction limit. If it is feasible to collect at least *p* additional, but independent, resamples from each well, retesting can be incorporated into the procedure by using independent mean(s) of *p* samples as confirmation value(s).

If substantial spatial variability exists, prediction limits for means can be constructed on a well-specific basis using intrawell background. At least two future values must be available per well. Larger intrawell background size are preferable. To incorporate retesting, it must be feasible to collect at least *p* independent resamples from each well, in addition to the initial set of *p* samples. A prediction limit can also be used in some compliance monitoring settings when a fixed compliance health based limit cannot be use and the compliance point data must be compared directly to a background GWPS. In this case, the compliance point mean concentration is tested against an upper prediction limit computed from background. No retesting would be employed for this latter kind of test.

Steps involved: 1) Compute the background sample mean and standard deviation; 2) considering the type of prediction limit (*i.e.*, interwell or intrawell), the number of future samples *p*, use of retesting, the desired site-wide false positive rate, and the number of wells and monitoring parameters, determine the prediction limit multiplier (κ); 3) compute the prediction limit as the background mean plus κ times the background standard deviation; 4) compare each future mean of order *p* (*i.e.*, a mean constructed from *p* values) against the prediction limit; and 5) if the future mean exceeds the limit and retesting is not feasible (or if used for compliance monitoring), conclude the null hypothesis of equal means has been violated. If retesting is feasible, conclude the null hypothesis has been violated only when the resampled mean(s) of order *p* also exceeds the prediction limit.

Advantages/Disadvantages: Prediction limits on means offer several advantages compared to the traditional one-way ANOVA and Dunnett's multiple comparison with control [MCC] procedure: Prediction limits are not bound to a minimum 5% per-constituent false positive rate. As such, prediction limits can be constructed to meet a target SWFPR, while maintaining acceptable statistical power. Unlike the one-way *F*-test, only the comparisons of interest (*i.e.*, each compliance point against background) are tested, giving the prediction limit more statistical power. Prediction limits can be designed for intrawell as well as interwell comparisons. One slight disadvantage is that ANOVA combines compliance point data with background to give a somewhat better per-well estimate of variability. But even this disadvantage can be overcome when using an interwell prediction limit by first running ANOVA on the combined background and compliance point data to generate a better variance estimate with a larger degree of freedom. A disadvantage compared to prediction limits on individual future values is that two or more new compliance point observations per well must be available to run the prediction limit on means. If only one new measurement per evaluation period can be collected, the user should instead construct a prediction limit on individual values.

NON-PARAMETRIC PREDICTION LIMIT FOR *M* FUTURE VALUES (SECTION 18.3.1)

Basic purpose: Method for detection monitoring. It is a non-parametric technique to estimate numerical limits(s) on a series of *m* independent future values. The prediction limit(s) can be used to test whether two samples are drawn from the same or different populations.

Hypothesis tested: H_0 — The *m* future observations come from the same distribution as the measurements used to construct the prediction limit. H_A — The *m* future observations come from a

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different distribution than the population of measurements used to build the prediction limit. Since an upper prediction limit is of interest in detection monitoring, the alternative hypothesis is that the future observations are distributed with a larger median than the background population.

Underlying assumptions: 1) The data used to construct the prediction limit need not be normal; however, the forms of the both the background distribution and the future distribution are assumed to be the same. Since the non-parametric prediction limit is constructed as an order statistic of background, high fractions of non-detects are acceptable; 2) although the variances of both populations (background and future values) are assumed to be equal, rarely will there be enough data from the future population to verify this assumption; and 3) if used for upgradient-to-downgradient comparisons, there should be no significant spatial variability. Spatial variation is less likely to be significant in many cases where constituent data are primarily non-detect, allowing the use of a non-parametric interwell prediction limit test.

When to use: Prediction limits on individual values can be used as a non-parametric alternative in detection monitoring to either one-way ANOVA or Dunnett's multiple comparison with control [MCC] procedure. Assuming there is insignificant natural spatial variability, an interwell prediction limit can be constructed using upgradient or other representative background data. The number of future samples m should be chosen to reflect a single new observation collected from each compliance well prior to the next statistical evaluation, plus a fixed number (m–1) of possible resamples. The initial future observation at each compliance point is then compared against the prediction limit. If it exceeds the prediction limit, one or more resamples are collected from the 'triggered' well and also compared to the prediction limit.

Steps involved: 1) Determine the maximum, second-largest, or other highly ranked value in background and set the non-parametric prediction limit equal to this level; 2) considering the number of future samples m, and the number of wells and monitoring parameters, determine the achievable site-wide false positive rate [SWFPR]. If the error rate is not acceptable, consider possibly enlarging the pool of background data used to construct the limit or increasing the number of future samples m; 3) compare each initial future observation against the prediction limit; and 4) if both the initial measurement and resample(s) exceed the limit, conclude the null hypothesis of equal distributions has been violated.

Advantages/Disadvantages: Non-parametric prediction limits on individual values offer distinct advantages compared to the Kruskal-Wallis non-parametric ANOVA test. Prediction limits are not bound to a minimum 5% per-constituent false positive rate. As such, prediction limits can be constructed to meet a target SWFPR, while maintaining acceptable statistical power. Unlike the Kruskal-Wallis test, only the comparisons of interest (*i.e.*, each compliance point against background) are tested, giving the prediction limit more statistical power. Non-parametric prediction limits have the disadvantage of generally requiring fairly large background samples to effectively control false positive error and ensure adequate power.

PREDICTION LIMIT FOR FUTURE MEDIAN (SECTION 18.3.2)

Basic purpose: Method for detection monitoring and compliance monitoring. This is a non-parametric technique to estimate numerical limits(s) on the median of p independent future values. The prediction limit(s) is used to test whether the median of one or more compliance well populations is equal to the median of the background population.

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Hypothesis tested: H_0 — The true median of p future observations arise from the same population as the median of measurements used to construct the prediction limit. H_A — The p future observations come from a distribution with a different median than the background population of measurements. Since an upper prediction limit is of interest in both detection monitoring and compliance monitoring, the alternative hypothesis is that the future observations are distributed with a larger median than the background population.

Underlying assumptions: 1) The data used to construct the prediction limit need not be normal; however, the forms of the both the background distribution and the future distribution are assumed to be the same. Since the non-parametric prediction limit is constructed as an order statistic of background, high fractions of non-detects are acceptable: 2) although the variances of both populations (background and future values) are assumed to be equal, rarely will there be enough data from the future population to verify this assumption; and 3) if used for upgradient-to-downgradient comparisons, there should be no significant spatial variability.

When to use: Prediction limits on medians can be used as a non-parametric alternative in detection monitoring to either one-way ANOVA or Dunnett's multiple comparison with control [MCC] procedure. Assuming there is insignificant natural spatial variability, an interwell prediction limit can be constructed using upgradient or other representative background data. The number of future samples p should be odd and chosen to reflect the number of samples that will be collected at each compliance well prior to the next statistical evaluation (*e.g.*, 3). The median of these p observations at each compliance point is then compared against the prediction limit. If it is feasible to collect at least p additional, but independent, resamples from each well, retesting can be incorporated into the procedure by using independent median(s) of p samples as confirmation value(s). A prediction limit for a compliance point median can also be constructed in certain compliance monitoring settings, when no fixed health-based compliance limit can be used and the compliance point data must be directly compared against a background GWPS. In this case, the compliance point median concentration is compared to an upper prediction limit computed from background. No retesting is employed for this latter kind of test.

Steps involved: 1) Determine the maximum, second-largest, or other highly ranked value in background and set the non-parametric prediction limit equal to this level; 2) considering the number of future samples p, whether or not retesting will be incorporated, and the number of wells and monitoring parameters, determine the achievable SWFPR. If the error rate is not acceptable, increase the background sample size or consider a non-parametric prediction limit on individual future values instead; 3) compare each future median of order p (*i.e.*, a median of p values) against the prediction limit; and 4) if the future median exceeds the limit and retesting is not feasible (or if the test is used for compliance monitoring), conclude the null hypothesis of equal medians has been violated. If retesting is feasible, conclude the null hypothesis has been violated only when the resampled median(s) of order p also exceeds the prediction limit.

Advantages/Disadvantages: Non-parametric prediction limits on medians offer distinct advantages compared to the Kruskal-Wallis test (a non-parametric one-way ANOVA). Prediction limits are not bound to a minimum 5% per-constituent false positive rate. As such, prediction limits can be constructed to meet a target SWFPR, while maintaining acceptable statistical power. Unlike the Kruskal-Wallis test, only the comparisons of interest (*i.e.*, each compliance point against background) are tested, giving the prediction limit more statistical power. A disadvantage in

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detection monitoring compared to non-parametric prediction limits on individual future values is that at least three new compliance point observations per well must be available to run the prediction limit on medians. If only one new observation per evaluation period can be collected, construct instead a non-parametric prediction limit for individual values. All non-parametric prediction limits have the disadvantage of usually requiring fairly large background samples to effectively control false positive error and ensure adequate power.

SHEWHART-CUSUM CONTROL CHART (SECTION 20.2)

Basic purpose: Method for detection monitoring. These are used to quantitatively and visually track concentrations at a given well over time to determine whether they exceed a critical threshold (*i.e.*, control limit), thus implying a significant increase above background conditions.

Hypothesis tested: H_0 — Data plotted on the control chart follow the same distribution as the background data used to compute the baseline chart parameters. H_A — Data plotted on the chart follow a different distribution with higher mean level than the baseline data.

Underlying assumptions: Data used to construct the control chart must be approximately normal or normalized. Adjustments for small to moderate fractions of non-detects, perhaps using Kaplan-Meier or ROS, can be acceptable. There should be no discernible trend in the baseline data used to calculate the control limit.

When to use: Use control charts as an alternative to parametric prediction limits, when 1) there are enough uncontaminated baseline data to compute an accurate control limit, and 2) there are no trends in intrawell background. Retesting can be incorporated into control charts by judicious choice of control limit. This may need to be estimated using Monte Carlo simulations.

Steps involved: 1) Compute the intrawell baseline mean and standard deviation; 2) calculate an appropriate control limit from these baseline parameters, the desired retesting strategy and number of well-constituent pairs in the network; 3) construct the chart, plotting the control limit, the compliance point observations, and the cumulative sums [CUSUM]; and 4) determine that the null hypothesis is violated when either an individual concentration measurement or the cumulative sum exceeds the control limit.

Advantages/Disadvantages: Unlike prediction limits, control charts offer an explicit visual tracking of compliance point values over time and provide a method to judge whether these concentrations have exceeded a critical threshold. The Shewhart portion of the chart is especially good at detecting sudden concentration increases, while the CUSUM portion is preferred for detecting slower, steady increases over time. No non-parametric version of the combined Shewhart-CUSUM control chart exists, so non-parametric prediction limits should be considered if the data cannot be normalized.

CONFIDENCE INTERVAL AROUND NORMAL MEAN (SECTION 21.1.1)

Basic purpose: Method for compliance/assessment monitoring or corrective action. This is a technique for estimating a range of concentration values from sample data, in which the true mean of a normal population is expected to occur at a certain probability.

Hypothesis tested: In compliance monitoring, H_0 — True mean concentration at the compliance point is no greater than the predetermined groundwater protection standard [GWPS]. H_A — True mean

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concentration is greater than the GWPS. In corrective action, H_0 — True mean concentration at the compliance point is greater than or equal to the fixed GWPS. H_A — True mean concentration is less than or equal to the fixed standard.

Underlying assumptions: 1) Compliance point data are approximately normal in distribution. Adjustments for small to moderate fractions of non-detects, perhaps using Kaplan-Meier or ROS, are encouraged; 2) data do not exhibit any significant trend over time; 3) there are a minimum of 4 observations for testing. Generally, at least 8 to 10 measurements are recommended; and 4) the fixed GWPS is assumed to represent a true mean average concentration, rather than a maximum or upper percentile.

When to use: A mean confidence interval can be used for normal data to determine whether there is statistically significant evidence that the average is either above a fixed GWPS (in compliance monitoring) or below the fixed standard (in corrective action). In either case, the null hypothesis is rejected only when the *entire* confidence interval lies on one or the other side of the GWPS. The key determinant in compliance monitoring is whether the *lower* confidence limit exceeds the GWPS, while in corrective action the *upper* confidence limit lies below the clean-up standard. Because of bias introduced by transformations when estimating a mean, this approach should not be used for highly-skewed or non-normal data. Instead consider a confidence interval around a lognormal mean or a non-parametric confidence interval. It is also not recommended for use when the data exhibit a significant trend. In that case, the estimate of variability will likely be too high, leading to an unnecessarily wide interval and possibly little chance of deciding the hypothesis. When a trend is present, consider instead a confidence interval around a trend line.

Steps involved: 1) Compute the sample mean and standard deviation; 2) based on the sample size and choice of a confidence level ($1-\alpha$), calculate either the lower confidence limit (for use in compliance monitoring) or the upper confidence limit (for use in corrective action); 3) compare the confidence limit against the GWPS or clean-up standard; and 4) if the lower confidence limit exceeds the GWPS in compliance monitoring or the upper confidence limit is below the clean-up standard, conclude that the null hypothesis should be rejected.

Advantages/Disadvantages: Use of a confidence interval instead of simply the sample mean for comparison to a fixed standard accounts for both the level of statistical variation in the data and the desired or targeted confidence level. The same basic test can be used both to document contamination above the compliance standard in compliance/assessment and to show a sufficient decrease in concentration levels below the clean-up standard in corrective action.

CONFIDENCE INTERVAL ON LOGNORMAL GEOMETRIC MEAN (SECTION 21.1.2)

Basic purpose: Method for compliance/assessment monitoring or corrective action. It is a technique to estimate the range of concentration values from sample data, in which the true geometric mean of a lognormal population is expected to occur at a certain probability.

Hypothesis tested: In compliance monitoring, H_0 — True mean concentration at the compliance point is no greater than the fixed compliance or groundwater protection standard [GWPS]. H_A — True mean concentration is greater than the GWPS. In corrective action, H_0 — True mean concentration at the compliance point is greater than the fixed compliance or clean-up standard. H_A — True mean concentration is less than or equal to the fixed standard.

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Underlying assumptions: 1) Compliance point data are approximately lognormal in distribution. Adjustments for small to moderate fractions of non-detects, perhaps using Kaplan-Meier or ROS, are encouraged; 2) data do not exhibit any significant trend over time; 3) there are a minimum of 4 observations. Generally, at least 8 to 10 measurements are recommended; and 4) the fixed GWPS is assumed to represent a true geometric mean average concentration following a lognormal distribution, rather than a maximum or upper percentile. The GWPS also represents the true median.

When to use: A confidence interval on the geometric mean can be used for lognormal data to determine whether there is statistically significant evidence that the geometric average is either above a fixed numerical standard (in compliance monitoring) or below a fixed standard (in corrective action). In either case, the null hypothesis is rejected only when the *entire* confidence interval is to one side of the compliance or clean-up standard. Because of this fact, the key question in compliance monitoring is whether the *lower* confidence limit exceeds the GWPS, while in corrective action the user must determine whether the *upper* confidence limit is below the clean-up standard. Because of bias introduced by transformations when estimating the arithmetic lognormal mean, and the often unreasonably high upper confidence limits generated by Land's method for lognormal mean confidence intervals (see below), this approach is an alternative approach for lognormal data. One could also consider a non-parametric confidence interval. It is also not recommended for use when data exhibit a significant trend. In that case, the estimate of variability will likely be too high, leading to an unnecessarily wide interval and possibly little chance of deciding the hypothesis. When a trend is present, consider instead a confidence interval around a trend line.

Steps involved: 1) Compute the sample log-mean and log-standard deviation; 2) based on the sample size and choice of confidence level ($1-\alpha$), calculate either the lower confidence limit (for use in compliance monitoring) or the upper confidence limit (for use in corrective action) using the logged measurements and exponentiate the result; 3) compare the confidence limit against the GWPS or clean-up standard; and 4) if the lower confidence limit exceeds the GWPS in compliance monitoring or the upper confidence limit is below the clean-up standard, conclude that the null hypothesis should be rejected.

Advantages/Disadvantages: Use of a confidence interval instead of simply the sample geometric mean for comparison to a fixed standard accounts for both statistical variation in the data and the targeted confidence level. The same basic test can be used both to document contamination above the compliance standard in compliance/assessment and to show a sufficient decrease in concentration levels below the clean-up standard in corrective action.

CONFIDENCE INTERVAL ON LOGNORMAL ARITHMETIC MEAN (SECTION 21.1.3)

Basic purpose: Test for compliance/assessment monitoring or corrective action. This is a method by Land (1971) used to estimate the range of concentration values from sample data, in which the true arithmetic mean of a lognormal population is expected to occur at a certain probability.

Hypothesis tested: In compliance monitoring, H_0 — True mean concentration at the compliance point is no greater than the fixed compliance or groundwater protection standard [GWPS]. H_A — True mean concentration is greater than the GWPS. In corrective action, H_0 — True mean concentration at the compliance point is greater than the fixed compliance or clean-up standard. H_A — True mean concentration is less than or equal to the fixed standard.

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Underlying assumptions: 1) Compliance point data are approximately lognormal in distribution. Adjustments for small to moderate fractions of non-detects, perhaps using Kaplan-Meier or ROS, are encouraged; 2) data do not exhibit any significant trend over time; 3) there are a minimum of 4 observations. Generally, at least 8 to 10 measurements are strongly recommended; and 4) the fixed GWPS is assumed to represent the true arithmetic mean average concentration, rather than a maximum or upper percentile.

When to use: Land's confidence interval procedure can be used for lognormally-distributed data to determine whether there is statistically significant evidence that the average is either above a fixed numerical standard (in compliance monitoring) or below a fixed standard (in corrective action). In either case, the null hypothesis is rejected only when the *entire* confidence interval is to one side of the compliance or clean-up standard. Because of this fact, the key question in compliance monitoring is whether the *lower* confidence limit exceeds the GWPS, while in corrective action the user must determine whether the *upper* confidence limit is below the clean-up standard. Because the lognormal distribution can have a highly skewed upper tail, this approach should only be used when the data fit the lognormal model rather closely, especially if used in corrective action. Consider instead a confidence interval around the lognormal geometric mean or a non-parametric confidence interval if this is not the case. It is also not recommended for data that exhibit a significant trend. In that situation, the estimate of variability will likely be too high, leading to an unnecessarily wide interval and possibly little chance of deciding the hypothesis. When a trend is present, consider instead a confidence interval around a trend line.

Steps involved: 1) Compute the sample log-mean and log-standard deviation; 2) based on the sample size, magnitude of the log-standard deviation and choice of confidence level ($1-\alpha$), determine Land's adjustment factor; 3) then calculate either the lower confidence limit (for use in compliance monitoring) or the upper confidence limit (for use in corrective action); 4) compare the confidence limit against the GWPS or clean-up standard; and 5) if the lower confidence limit exceeds the GWPS in compliance montoring or the upper confidence limit is below the clean-up standard, conclude that the null hypothesis should be rejected.

Advantages/Disadvantages: Use of a confidence interval instead of simply the sample mean for comparison to a fixed standard accounts for both statistical variation in the data and the targeted confidence level. The same basic test can be used both to document contamination above the compliance standard in compliance/assessment and to show a sufficient decrease in concentration levels below the clean-up standard in corrective action. Since the upper confidence limit on a lognormal mean can be extremely high for some populations, the user may need to consider a non-parametric upper confidence limit on the median concentration as an alternative or use a program such as **Pro-UCL** to determine an alternate upper confidence limit.

CONFIDENCE INTERVAL ON UPPER PERCENTILE (SECTION 21.1.4)

Basic purpose: Method for compliance monitoring. It is used to estimate the range of concentration values from sample data in which a pre-specified true proportion of a normal population is expected to occur at a certain probability. The test can also be used to identify the range of a true proportion or percentile (*e.g.*, the 95th) in population data which can be normalized.

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Hypothesis tested: H_0 — True upper percentile concentration at the compliance point is no greater than the fixed compliance or groundwater protection standard [GWPS]. H_A — True upper percentile concentration is greater than the fixed GWPS.

Underlying assumptions: 1) Compliance point data are either normal in distribution or can be normalized. Adjustments for small to moderate fractions of non-detects, perhaps using Kaplan-Meier or ROS, are encouraged; 2) data do not exhibit any significant trend over time; 3) there are a minimum of at least 8 to 10 measurements; and 4) the fixed GWPS is assumed to represent a maximum or upper percentile, rather than an average concentration.

When to use: A confidence interval around an upper percentile can be used to determine whether there is statistically significant evidence that the percentile is above a fixed numerical standard. The null hypothesis is rejected only when the *entire* confidence interval is greater than the compliance standard. Because of this fact, the key question in compliance monitoring is whether the *lower* confidence limit exceeds the GWPS. This approach is not recommended for use when the data exhibit a significant trend. The estimate of variability will likely be too high, leading to an unnecessarily wide interval and possibly little chance of deciding the hypothesis.

Steps involved: 1) Compute the sample mean and standard deviation; 2) based on the sample size, pre-determined true proportion and test confidence level (1–α), calculate the lower confidence limit; 3) compare the confidence limit against the GWPS; and 4) if the lower confidence limit exceeds the GWPS, conclude that the true upper percentile is larger than the compliance standard.

Advantages/Disadvantages: If a fixed GWPS is intended to represent a 'not-to-be-exceeded' maximum or an upper percentile, statistical comparison requires the prior definition of a true or expected upper percentile against which sample data can be compared. Some standards may explicitly identify the expected percentile. The appropriate test then must estimate the confidence interval in which this true proportion is expected to lie. Either an upper or lower confidence limit can be generated, depending on whether compliance or corrective action hypothesis testing is appropriate. Whatever the interpretation of a given limit used as a GWPS, it should be determined in advance what a given standard represents before choosing which type of confidence interval to construct.

NON-PARAMETRIC CONFIDENCE INTERVAL ON MEDIAN (SECTION 21.2)

Basic purpose: Test for compliance/assessment monitoring or corrective action. It is a non-parametric method used to estimate the range of concentration values from sample data in which the true median of a population is expected to occur at a certain probability.

Hypothesis tested: In compliance monitoring, H_0 — True median concentration at the compliance point is no greater than the fixed compliance or groundwater protection standard [GWPS]. H_A — True median concentration is greater than the GWPS. In corrective action, H_0 — True median concentration at the compliance point is greater than the fixed compliance or clean-up standard. H_A — True median concentration is less than or equal to the fixed standard.

Underlying assumptions: 1) Compliance data need not be normal in distribution; up to 50% non-detects are acceptable; 2) data do not exhibit any significant trend over time; 3) there are a *minimum* of at least 7 measurements; and 4) the fixed GWPS is assumed to represent a true median average concentration, rather than a maximum or upper percentile.

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When to use: A confidence interval on the median can be used for non-normal data (*e.g.*, samples with non-detects) to determine whether there is statistically significant evidence that the average (*i.e.*, median) is either above a fixed numerical standard (in compliance monitoring) or below a fixed standard (in corrective action). In either case, the null hypothesis is rejected only when the *entire* confidence interval is to one side of the compliance or clean-up standard. Because of this fact, the key question in compliance monitoring is whether the *lower* confidence limit exceeds the GWPS, while in corrective action the user must determine whether the *upper* confidence limit is below the clean-up standard. This approach is not recommended for use when data exhibit a significant trend. In that case, the variation in the data will likely be too high, leading to an unnecessarily wide interval and possibly little chance of deciding the hypothesis. It is also possible that the apparent trend is an artifact of differing detection or reporting limits that have changed over time. The trend may disappear if all non-detects are imputed at a common value or RL. If a trend is still present after investigating this possibility, but a significant portion of the data are non-detect, consultation with a professional statistician is recommended.

Steps involved: 1) Order and rank the data values; 2) pick tentative interval endpoints close to the estimated median concentration; 3) using the selected endpoints, compute the achieved confidence level of the lower confidence limit for use in compliance monitoring or that of the upper confidence limit for corrective action; 4) iteratively expand the interval until either the selected endpoints achieve the targeted confidence level or the maximum or minimum data value is chosen as the confidence limit; and 5) compare the confidence limit against the GWPS or clean-up standard. If the lower confidence limit exceeds the GWPS in compliance monitoring or the upper confidence limit is below the clean-up standard, conclude that the null hypothesis should be rejected.

Advantages/Disadvantages: Use of a confidence interval instead of simply the sample median for comparison to a fixed limit accounts for both statistical variation in the data and the targeted confidence level. The same basic test can be used both to document contamination above the compliance standard in compliance/assessment and to show a sufficient decrease in concentration levels below the clean-up standard in corrective action. By not requiring normal or normalized data, the non-parametric confidence interval can accommodate a substantial fraction of non-detects. A minor disadvantage is that a non-parametric confidence interval estimates the location of the median, instead of the mean. For symmetric populations, these quantities will be the same, but for skewed distributions they will differ. So if the compliance or clean-up standard is designed to represent a mean concentration, the non-parametric interval around the median may not provide a completely fair and/or accurate comparison. In some cases, the non-parametric confidence limit will not achieve the desired confidence level even if set to the maximum or minimum data value, leading to a higher risk of false positive error.

NON-PARAMETRIC CONFIDENCE INTERVAL ON UPPER PERCENTILE (SECTION 21.2)

Basic purpose: Non-parametric method for compliance monitoring. It is used to estimate the range of concentration values from sample data in which a pre-specified true proportion of a population is expected to occur at a certain probability. Exact probabilities will depend upon sample data ranks.

Hypothesis tested: H_0 — True upper percentile concentration at the compliance point is no greater than the fixed compliance or groundwater protection standard [GWPS]. H_A — True upper percentile concentration is greater than the GWPS.

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Underlying assumptions: 1) Compliance point data need not be normal; large fractions of non-detects can be acceptable; 2) data do not exhibit any significant trend over time; 3) there are a minimum of at least 8 to 10 measurements; and 4) the fixed GWPS is assumed to represent a true upper percentile of the population, rather than an average concentration.

When to use: A confidence interval on an upper percentile can be used to determine whether there is statistically significant evidence that the percentile is above a fixed numerical standard. The null hypothesis is rejected only when the *entire* confidence interval is greater than the compliance standard. Because of this fact, the key determinant in compliance/assessment monitoring is whether the *lower* confidence limit exceeds the GWPS. This approach is not recommended for use when data exhibit a significant trend. In that case, the estimate of variability will likely be too high, leading to an unnecessarily wide interval and possibly little chance of deciding the hypothesis.

Steps involved: 1) Order and rank the data values; 2) select tentative interval endpoints close to the estimated upper percentile concentration; 3) using the selected endpoints, compute the achieved confidence level of the lower confidence limit; 4) iteratively expand the interval until either the selected lower endpoint achieves the targeted confidence level or the minimum data value is chosen as the confidence limit; and 5) compare the confidence limit against the GWPS. If the lower confidence limit exceeds the GWPS, conclude that the population upper percentile is larger than the compliance standard.

Advantages/Disadvantages: If a fixed GWPS is intended to represent a 'not-to-be-exceeded' maximum or an upper percentile, statistical comparison requires the prior definition of a true or expected upper percentile against which sample data can be compared. Some standards may explicitly identify the expected percentile. The appropriate test then must estimate the confidence interval in which this true proportion is expected to lie. Either an upper or lower confidence limit can be generated, depending on whether compliance or corrective action hypothesis testing is appropriate. Whatever the interpretation of a given limit used as a GWPS, it should be determined in advance what a given standard represents before choosing which type of confidence interval to construct. However, precise non-parametric estimation of upper percentiles often requires much larger sample sizes than the parametric option (**Section 21.1.4**). For this reason, a *parametric* confidence interval for upper percentile tests is recommended whenever possible, especially if a suitable transformation can be found or adjustments made for non-detect values.

CONFIDENCE BAND AROUND LINEAR REGRESSION (SECTION 21.3.1)

Basic purpose: Method for compliance/assessment monitoring or corrective action when stationarity cannot be assumed. It is used to estimate ranges of concentration values from sample data around each point of a predicted linear regression line at a specified probability. The prediction line (based on regression of concentration values against time) represents the best estimate of gradually changing true mean levels over the time period.

Hypothesis tested: In compliance monitoring, H_0 — True mean concentration at the compliance point is no greater than the fixed compliance or groundwater protection standard [GWPS]. H_A — True mean concentration is greater than the GWPS. In corrective action, H_0 — True mean concentration at the compliance point is greater than the fixed compliance or clean-up standard. H_A — True mean concentration is less than or equal to the fixed standard.

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Underlying assumptions: 1) Compliance point values exhibit a linear trend with time, with normally distributed residuals. Use simple substitution with small (≤10-15%) fractions of non-detects. Non-detect adjustment methods are not recommended; 2) there are a minimum of 4 observations. Generally, at least 8 to 10 measurements are recommended; and 3) the fixed GWPS is assumed to represent an average concentration, rather than a maximum or upper percentile.

When to use: A confidence interval around a trend line should be used in cases where a linear trend is apparent on a time series plot of the compliance point data. Even if observed well concentrations are either increasing under compliance monitoring or decreasing in corrective action, it does not necessarily imply that the true mean concentration at the current time is either above or below the fixed GWPS. While the trend line properly accounts for the fact that the mean is changing with time, the null hypothesis is rejected only when the *entire* confidence interval is to one side of the compliance or clean-up standard at the most recent point(s) in time. The key determinant in compliance monitoring is whether the *lower* confidence limit at a specified point in time exceeds the GWPS, while in corrective action the *upper* confidence limit at a specific time must lie below the clean-up standard to be considered in compliance.

Steps involved: 1) Check for presence of a trend on a time series plot; 2) estimate the coefficients of the best-fitting linear regression line; 3) compute the trend line residuals and check for normality; 4) if data are non-normal, try re-computing the regression and residuals after transforming the data; 5) compute the lower confidence limit band around the trend line for compliance monitoring or the upper confidence limit band around the trend line for corrective action; and 6) compare the confidence limit at each sampling event against the GWPS or clean-up standard. If the lower confidence limit exceeds the GWPS in compliance/assessment or the upper confidence limit is below the clean-up standard on one or more recent sampling events, conclude that the null hypothesis should be rejected.

Advantages/Disadvantages: Use of a confidence interval around the trend line instead of simply the regression line itself for comparison to a fixed standard accounts for both statistical variation in the data and the targeted confidence level. The same basic test can be used both to document contamination above the compliance standard in compliance/assessment and to show a sufficient decrease in concentration levels below the clean-up standard in corrective action. By estimating the trend line first and then using the residuals to construct the confidence interval, variation due to the trend itself is removed, providing a more powerful test (via a narrower interval) of whether or not the true mean is on one side of the fixed standard. This technique can only be used when the identified trend is reasonably linear and the trend residuals are approximately normal.

NON-PARAMETRIC CONFIDENCE BAND AROUND THEIL-SEN TREND (SECTION 21.3.1)

Basic purpose: Non-parametric method for compliance/assessment or corrective action when stationarity cannot be assumed. It is used to estimate ranges of concentration values from sample data around each point of a predicted Theil-Sen trend line at a specified probability. The prediction line represents the best estimate of gradually changing true median levels over the time period.

Hypothesis tested: In compliance monitoring, H_0 — True mean concentration at the compliance point is no greater than the fixed compliance or groundwater protection standard [GWPS]. H_A — True mean concentration is greater than the GWPS. In corrective action, H_0 — True mean concentration at the

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compliance point is greater than the fixed compliance or clean-up standard. H_A — True mean concentration is less than or equal to the fixed standard.

Underlying assumptions: 1) Compliance point values exhibit a linear trend with time; 2) non-normal data and substantial levels of non-detects up to 50% are acceptable; 3) there are a minimum of 8-10 observations available to construct the confidence band; and 4) the fixed GWPS is assumed to represent a median average concentration, rather than a maximum or upper percentile.

When to use: A confidence interval around a trend line should be used in cases where a linear trend is apparent on a time series plot of the compliance point data. Even if observed well concentrations are either increasing under compliance monitoring or decreasing in corrective action, it does not necessarily imply that the true mean concentration at the current time is either above or below the fixed GWPS. While the trend line properly accounts for the fact that the mean is changing with time, the null hypothesis is rejected only when the *entire* confidence interval is to one side of the compliance or clean-up standard at the most recent point(s) in time. The key determinant in compliance monitoring is whether the *lower* confidence limit at a specified point in time exceeds the GWPS, while in corrective action the *upper* confidence limit at a specific time must lie below the clean-up standard to be considered in compliance.

Steps involved: 1) Check for presence of a trend on a time series plot; 2) construct a Theil-Sen trend line; 3) use bootstrapping to create a large number of simulated Theil-Sen trends on the sample data; 4) construct a confidence band by selecting lower and upper percentiles from the set of bootstrapped Theil-Sen trend estimates; and 5) compare the confidence band at each sampling event against the GWPS or clean-up standard. If the lower confidence band exceeds the GWPS in compliance/assessment or the upper confidence band is below the clean-up standard on one or more recent sampling events, conclude that the null hypothesis should be rejected.

Advantages/Disadvantages: Use of a confidence band around the trend line instead of simply the Theil-Sen trend line itself for comparison to a fixed standard accounts for both statistical variation in the data and the targeted confidence level. The same basic test can be used both in compliance/assessment and in corrective action. By estimating the trend line first and then using bootstrapping to construct the confidence band, variation due to the trend itself is removed, providing a more powerful test (via a narrower interval) of whether or not the true mean is on one side of the fixed standard. This technique can only be used when the identified trend is reasonably linear. The Theil-Sen trend estimates the change in median level rather than the mean. For roughly symmetric populations, this will make little difference; for highly skewed populations, the trend in the median may not accurately reflect changes in mean concentration levels.

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PART II: DIAGNOSTIC METHODS AND TESTING

Part II covers diagnostic evaluations of historical facility data for checking key assumptions implicit in the recommended statistical tests and for making appropriate adjustments to the data (e.g., consideration of outliers, seasonal autocorrelation, or non-detects). Also included is a discussion of groundwater sampling and how hydrologic factors such as flow and gradient can impact the sampling program.

Chapter 9 provides a number of exploratory data tools and examples, which can generally be used in data evaluations. Approaches for fitting data sets to normal and other parametric distributions follows in **Chapter 10**. The importance of the normal distribution and its potential uses is also discussed. **Chapter 11** provides methods for assessing the equality of variance necessary for some formal testing. The subject of outliers and means of testing for them is covered in **Chapter 12**. **Chapter 13** addresses spatial variability, with particular emphasis on ANOVA means testing. In **Chapter 14**, a number of topics concerning temporal variation are provided. In addition to providing tests for identifying the presence of temporal variation, specific adjustments for certain types of temporal dependence are covered. The final **Chapter 15** of **Part II** discusses non-detect data and offers several methods for estimating missing data. In particular, methods are provided to deal with data containing multiple non-detection limits.

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CHAPTER 9. COMMON EXPLORATORY TOOLS

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9.5 PROBABILITY PLOTS 9-16

Graphs are an important tool for exploring and understanding patterns in any data set. Plotting the data visually depicts the structure and helps unmask possible relationships between variables affecting the data set. Data plots which accompany quantitative statistical tests can better demonstrate the reasons for the results of a formal test. For example, a Shapiro-Wilk test may conclude that data are not normally distributed. A probability plot or histogram of the data can confirm this conclusion graphically to show why the data are not normally distributed (e.g., heavy skewness, bimodality, a single outlier, etc.).

Several common exploratory tools are presented in **Chapter 9**. These graphical techniques are discussed in statistical texts, but are presented here in detail for easy reference for the data analyst. An example data set is used to demonstrate how each of the following plots is created.

- Time series plots (**Section 9.1**)
- Box plots (**Section 9.2**)
- Histograms (**Section 9.3**)
- Scatter plots (**Section 9.4**)
- Probability plots (**Section 9.5**)

9.1 TIME SERIES PLOTS

Data collected over specific time intervals (e.g., monthly, biweekly, or hourly) have a temporal component. For example, air monitoring measurements of a pollutant may be collected once a minute or once a day. Water quality monitoring measurements may be collected weekly or monthly. Typically, groundwater sample data are collected quarterly from the same monitoring wells, either for detection monitoring testing or demonstrating compliance to a GWPS. An analyst examining temporal data may be interested in the trends over time, correlation among time periods, or cyclical patterns. Some graphical techniques specific to temporal data are the time plot, lag plot, correlogram, and variogram. The degree to which some of these techniques can be used will depend in part on the frequency and number of data collected over time.

A data sequence collected at regular time intervals is called a time series. More sophisticated time series data analyses are beyond the scope of this guidance. If needed, the interested user should consult with a statistician or appropriate statistical texts. The graphical representations presented in this section are recommended for any data set that includes a temporal component. Techniques described below will help identify temporal patterns that need to be accounted for in any analysis of the data. The analyst examining temporal environmental data may be interested in seasonal trends, directional trends, serial correlation, or stationarity. ***Seasonal trends*** are patterns in the data that repeat over time, i.e., the data

rise and fall regularly over one or more time periods. Seasonal trends may occur over long periods of time (large scale), such as a yearly cycle where the data show the same pattern of rising and falling from year to year, or the trends may be over a relatively short period of time (small scale), such as a daily cycle. Examples of seasonal trends are quarterly seasons (winter, spring, summer and fall), monthly seasons, or even hourly (e.g., air temperature rising and falling over the course of a day). ***Directional trends*** are increasing or decreasing patterns over time in monitored constituent data, which may be of importance in assessing the levels of contaminants. ***Serial correlation*** is a measure of the strength in the linear relationship of successive observations. If successive observations are related, statistical quantities calculated without accounting for the serial correlation may be biased. A time series is ***stationary*** if there is no systematic change in the mean (i.e., no trend) and variance across time. Stationary data look the same over all time periods except for random behavior. Directional trends or a change in the variability in the data imply non-stationarity.

A time series plot of concentration data versus time makes it easy to identify lack of randomness, changes in location, change in scale, small scale trends, or large-scale trends over time. Small-scale trends are displayed as fluctuations over smaller time periods. For example, ozone levels over the course of one day typically rise until the afternoon, then decrease, and this process is repeated every day. Larger scale trends such as seasonal fluctuations appear as regular rises and drops in the graph. Ozone levels tend to be higher in the summer than in the winter, so ozone data tend to show both a daily trend and a seasonal trend. A time plot can also show directional trends or changing variability over time.

A time plot is constructed by plotting the measurements on the vertical axis versus the actual time of observation or the order of observation on the horizontal axis. The points plotted may be connected by lines, but this may create an unfounded sense of continuity. It is important to use the actual date, time or number at which the observation was made. This can create discontinuities in the plot but are needed as the data that should have been collected now appear as "missing values" but do not disturb the integrity of the plot. Plotting the data at equally spaced intervals when in reality there were different time periods between observations is not advised.

For environmental data, it is also important to use a different symbol or color to distinguish non-detects from detected data. Non-detects are often reported by the analytical laboratory with a "U" or "<" analytical qualifier associated with the reporting limit [RL]. In statistical terminology, they are left-censored data, meaning the actual concentration of the chemical is known only to be below the RL. Non-detects contrast with detected data, where the laboratory reports the result as a known concentration that is statistically higher than the analytical limit of detection. For example, the laboratory may report a trichloroethene concentration in groundwater of "5 U" or "< 5" µg/L, meaning the actual trichloroethene concentration is unknown, but is bounded between zero and 5 µg/L. This result is different than a detected concentration of 5 µg/L which is unqualified by the laboratory or data validator. Non-detects are handled differently than detected data when calculating summary statistics. A statistician should be consulted on the proper use of non-detects in statistical analysis. For radionuclides negative and zero concentrations should be plotted as reported by the laboratory, showing the detection status.

The scaling of the vertical axis of a time plot is of some importance. A wider scale tends to emphasize large-scale trends, whereas a narrower scale tends to emphasize small-scale trends. A wide scale would emphasize the seasonal component of the data, whereas a smaller scale would tend to

emphasize the daily fluctuations. The scale needs to contain the full range of the data. Directions for constructing a time plot are contained in **Example 9-1** and **Figure 9-1**.

►EXAMPLE 9-1

Construct a time series plot using trichloroethene groundwater data in **Table 9-1** for each well. Examine the time series for seasonality, directional trends and stationarity.

Table 9-1. Trichloroethene (TCE) Groundwater Concentrations

	Well 1		Well 2	
Date Collected	**TCE (mg/L)**	**Data Qualifier**	**TCE (mg/L)**	**Data Qualifier**
1/2/2005	0.005	U	0.10	U
4/7/2005	0.005	U	0.12	
7/13/2005	0.004	J	0.125	
10/24/2005	0.006		0.107	
1/7/2006	0.004	U	0.099	U
3/30/2006	0.009		0.11	
6/28/2006	0.017		0.13	
10/2/2006	0.045		0.109	
10/17/2006	0.05		NA	
1/15/2007	0.07		0.10	U
4/10/2007	0.12		0.115	
7/9/2007	0.10		0.14	
10/5/2007	NA		0.17	
10/29/2007	0.20		NA	
12/30/2007	0.25		0.11	

NA = Not available (missing data).

U denotes a non-detect.

J denotes an estimated detected concentration.

SOLUTION

Step 1. Import the data into data analysis software capable of producing graphics.

Step 2. Sort the data by date collected.

Step 3. Determine the range of the data by calculating the minimum and maximum concentrations for each well, shown in the table below:

	Well 1		Well 2	
	TCE (mg/L)	**Data Qualifier**	**TCE (mg/L)**	**Data Qualifier**
Min	0.004	U	0.099	U
Max	0.25		0.17	

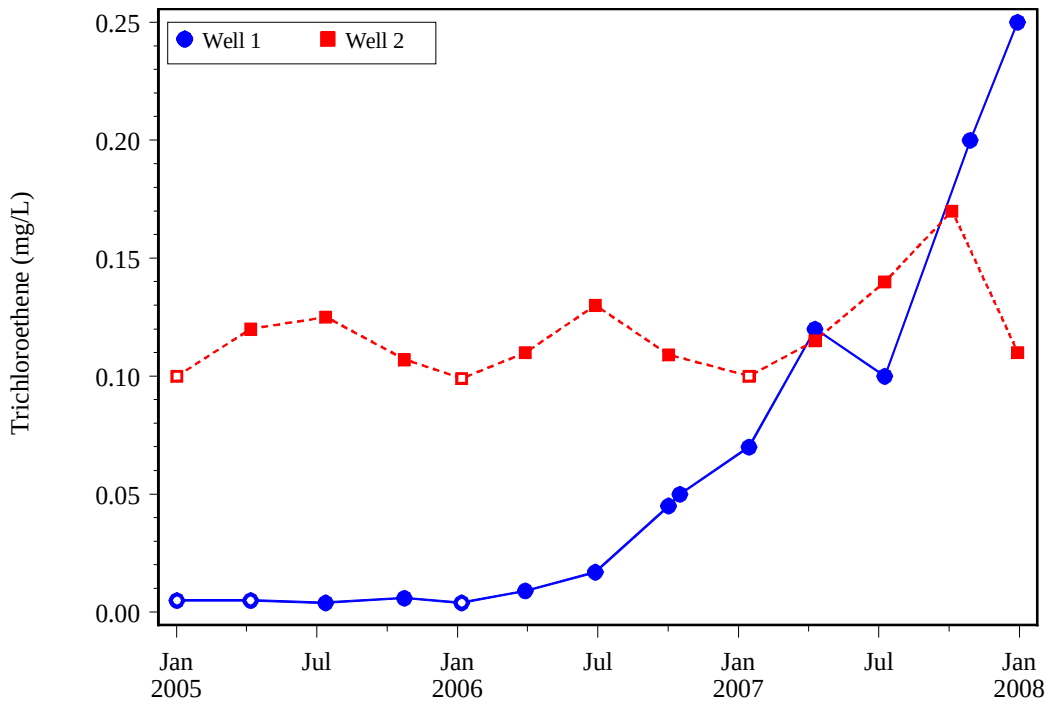
Step 4. Plot the data using a scale from 0 to 0.25 if data from both wells are plotted together on the same time series plot. Use separate symbols for non-detects and detected concentrations. One suggestion is to use "open" symbols (whose centers are white) for non-detects and "closed" symbols for detects.

Step 5. Examine each series for directional trends, seasonality and stationarity. Note that Well 1 demonstrates a positive directional trend across time, while Well 2 shows seasonality within each year. Neither well exhibits stationarity.

Step 6. Examine each series for missing values. Inquire from the project laboratory why data are missing or collected at unequal time intervals. A response from the laboratory for this data set noted that on 10/5/2007 the sample was accidentally broken in the laboratory from Well 1, so Well 1 was resampled on 10/29/2007. Well 1 was resampled on 10/17/2006 to confirm the historically high concentration collected on 10/2/2006. Well 2 was not sampled on 10/17/2006 because the data collected on 10/2/2006 from Well 2 did not merit a resample, as did Well 1.

Step 7. Examine each series for elevated detection limits. Inquire why the detection limits for Well 2 are much larger than detection limits for Well 1. A reason may be that different laboratories analyzed the samples from the two wells. The laboratory analyzing samples from Well 1 used lower detection limits than did the laboratory analyzing samples from Well 2.◄

Figure 9-1. Time Series Plot of Trichloroethene Groundwater for Wells 1 and 2 from 2005-2007.



Open symbols denote non-detects. Closed symbols denote detected concentrations.

9.2 BOX PLOTS

Box plots (also known as Box and Whisker plots) are useful in situations where a picture of the distribution is desired, but it is not necessary or feasible to portray all the details of the data. A box plot displays several percentiles of the data set. It is a simple plot, yet provides insight into the location, shape, and spread of the data and underlying distribution. A simple box plot contains only the 0^{th} (minimum data value), 25^{th}, 50^{th}, 75^{th} and 100^{th} (maximum data value) percentiles. A box-plot divides the data into 4 sections, each containing 25% of the data. Whiskers are the lines drawn to the minimum and maximum data values from the 25^{th} and 75^{th} percentiles. The box shows the interquartile range (IQR) which is defined as the difference between the 75^{th} and the 25^{th} percentiles. The length of the central box indicates the spread of the data (the central 50%), while the length of the whiskers shows the breadth of the tails of the distribution. The 50^{th} percentile (median) is the line within the box. In addition, the mean and the 95% confidence limits around the mean are shown. Potential outliers are categorized into two groups:

- data points between 1.5 and 3 times the IQR above the 75^{th} percentile or between 1.5 and 3 times the IQR below the 25^{th} percentile, and
- data points that exceed 3 times the IQR above the 75^{th} percentile or exceed 3 times the IQR below the 25^{th} percentile.

The mean is shown as a star, while the lower and upper 95% confidence limits around the mean are shown as bars. Individual data points between 1.5 and 3 times the IQR above the 75th percentile or below the 25th percentile are shown as circles. Individual data points at least 3 times the IQR above the 75th percentile or below the 25th percentile are shown as squares.

Information from box plots can assist in identifying potential data distributions. If the upper box and whisker are approximately the same length as the lower box and whisker, with the mean and median approximately equal, then the data are distributed symmetrically. The normal distribution is one of a number that is symmetric. If the upper box and whisker are longer than the lower box and whisker, with the mean greater than the median, then the data are right-skewed (such as lognormal or square root normal distributions in original units). Conversely, if the upper box and whisker are shorter than the lower box and whisker with the mean less than the median, then the data are left-skewed.

A box plot showing a normal distribution will have the following characteristics: the mean and median will be in the center of the box, whiskers to the minimum and maximum values are the same length, and there would be no potential outliers. A box plot showing a lognormal distribution (in original units) typical of environmental applications will have the following characteristics: the mean will be larger than the median, the whisker above the 75th percentile will be longer than the whisker below the 25th percentile, and extreme upper values may be indicated as potential outliers. Once the data have been logarithmically transformed, the pattern should follow that described for a normal distribution. Other right-skewed distributions transformable to normality would indicate similar patterns.

It is often helpful to show box plots of different sets of data side by side to show differences between monitoring stations (see **Figure 9-2**). This allows a simple method to compare the locations, spreads and shapes of several data sets or different groups within a single data set. In this situation, the width of the box can be proportional to the sample size of each data set. If the data will be compared to a standard, such as a preliminary remediation goal (PRG) or maximum contaminant level (MCL), a line on the graph can be drawn to show if any results exceed the criteria.

It is important to plot the data as reported by the laboratory for non-detects or negative radionuclide data. Proxy values for non-detects should not be plotted since we want to see the distribution of the original data. Different symbols can be used to display non-detects, such as the open symbols described in **Section 9.1**. The mean will be biased high if using the RL of non-detects in the calculation, but the purpose of the box plot is to assess the distribution of the data, not quantifying a precise estimate of an unbiased mean. Displaying the frequency of detection (number of detected values / number of total samples) under the station name is also useful. Unlike time series plots, box plots cannot use missing data, so missing data should be removed before producing a box plot.

Directions for generating a box plot are contained in **Example 9-2**, and an example is shown in **Figure 9-2.** It is important to remove lab and field duplicates from the data before calculating summary statistics such as the mean and UCL since these statistics assume independent data. The box plot assumes the data are statistically independent.

►EXAMPLE 9-2

Construct a box plot using the trichloroethene groundwater data in **Table 9-1** for each well. Examine the box plot to assess how each well is distributed (normal, lognormal, skewed, symmetric, etc.). Identify possible outliers.

SOLUTION

Step 1. Import the data into data analysis software capable of producing box plots.

Step 2. Sort the data from smallest to largest results by well.

Step 3. Compute the 0^{th} (minimum value), 25^{th}, 50^{th} (median), 75^{th} and 100^{th} (maximum value) percentiles by well.

Step 4. Plot these points vertically. Draw a box around the 25^{th} and 75^{th} percentiles and add a line through the box at the 50^{th} percentile. Optionally, make the width of the box proportional to the sample size. Narrow boxes reflect smaller sample sizes, while wider boxes reflect larger sample sizes.

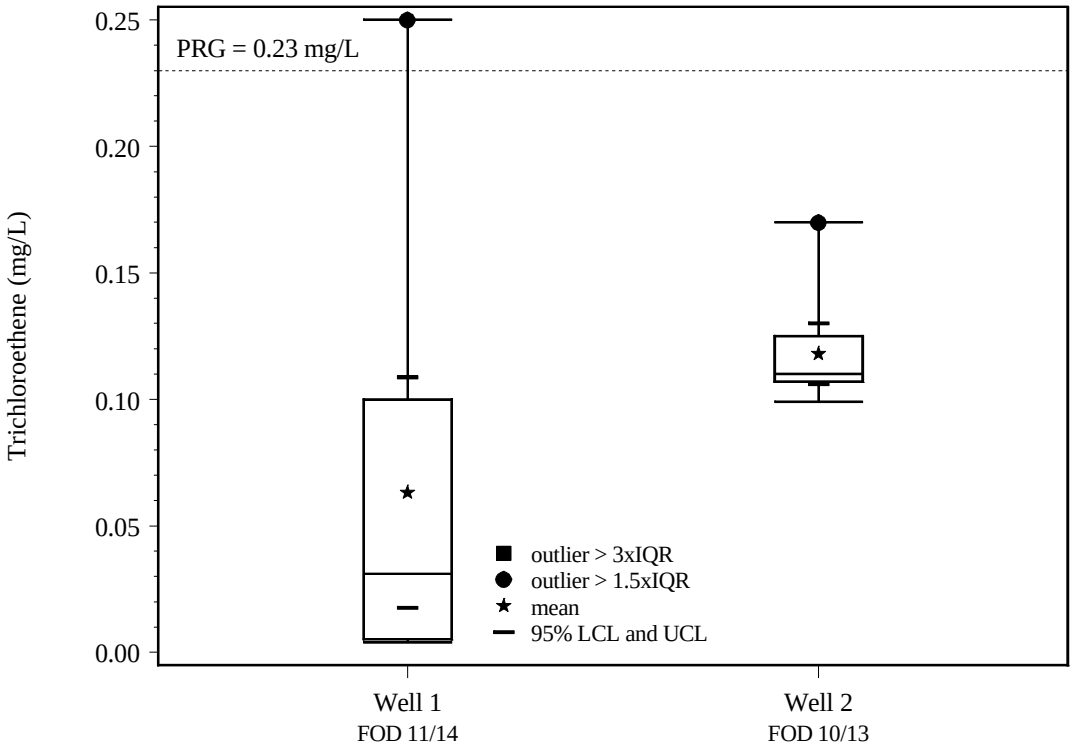
Step 5. Compute the mean and the lower and upper 95% confidence limits. Denote the mean with a star and the confidence limits as bars. Also, identify potential outliers between 1.5×IQR and 3×IQR beyond the box with a circle. Identify potential outliers exceeding 3×IQR beyond the box with a ` square.

Step 6. Draw the whiskers from each end of the box to the furthest data point to show the full range of the data.

INTERPRETATION

The box plots in **Figure 9-2** show the similarities and differences in the distributions of trichloroethene in Wells 1 and 2. The mean of trichloroethene in Well 1 is significantly lower than the mean in Well 2. The variance of the data from Well 1 is significantly larger than the variance from Well 2. A parametric t-test or nonparametric Wilcoxon Rank Sum test can quantitatively confirm these conclusions. Since the mean exceeds the median for both wells and the whiskers at the top of each box are much longer than the whiskers at the bottom of each box, we can conclude both distributions are skewed to the right, resembling a lognormal distribution. In fact, the Shapiro-Wilk test quantitatively confirms that both distributions are lognormally distributed. Both wells have their largest concentrations between 1.5 and 3 times the IQR, as denoted by a black circle. No data point lies outside 3 times the IQR. Since the data for both wells are lognormally distributed, the maximum concentrations in each well should not be removed just because they exceed 1.5 times the IQR. Long tails are expected for the lognormal distribution. The width of the 95% confidence limits confirms the large variability in Well 1 compared to the width of the confidence limits in Well 2. Well 1 has one concentration exceeding the PRG of 0.23 mg/L, while Well 2 has all concentrations below the PRG. The width of each box is similar since the sample size as shown in the frequency of detection (FOD) are nearly the same (11 detects out of 14 samples for Well 1 and 10 detects out of 13 samples for Well 2). ◄

Figure 9-2. Box Plots of Trichloroethene Data for Wells 1 & 2



9.3 HISTOGRAMS

A histogram is a visual representation of the data collected into groups. This graphical technique provides a visual method of identifying the underlying distribution of the data. The data range is divided into several bins or classes and the data is sorted into the bins. A histogram is a bar graph conveying the bins and the frequency of data points in each bin. Other forms of the histogram use a normalization of the bin frequencies for the heights of the bars. The two most common normalizations are relative frequencies (frequencies divided by sample size) and densities (relative frequency divided by the bin width). **Figure 9-3** is an example of a histogram using frequencies and **Figure 9-4** is a histogram of densities. Histograms provide a visual method of accessing location, shape and spread of the data. Also, extreme values and multiple modes can be identified. The details of the data are lost, but an overall picture of the data is obtained. A stem and leaf plot offers the same insights into the data as a histogram, but the data values are retained.

The visual impression of a histogram is sensitive to the number of bins selected. A large number of bins will increase data detail, while fewer bins will increase the smoothness of the histogram. A good starting point when choosing the number of bins is the square root of the sample size n. The minimum number of bins for any histogram should be at least 4. Another factor in choosing bins is the choice of endpoints. When feasible, using simple bin endpoints can improve the readability of the histogram. Simple bin endpoints include multiples of $5k$ units for some integer $k > 0$ (e.g., 0 to <5, 5 to <10, etc. or 1 to <1.5, 1.5 to <2, etc.). Finally, when plotting a histogram for a continuous variable (e.g.,

concentration), it is necessary to decide on an endpoint convention; that is, what to do with data points that fall on the boundary of a bin. Also, use the data as reported by the laboratory for non-detects and eliminate any missing values, since histograms cannot include missing data. With discrete variables, (e.g., family size) the intervals can be centered in between the variables. For the family size data, the intervals can span between 1.5 and 2.5, 2.5 and 3.5, and so on. Then the whole numbers that relate to the family size can be centered within the box. Directions for generating a histogram are contained in **Example 9-3**.

►EXAMPLE 9-3

Construct a histogram using the trichloroethene groundwater data in **Table 9-1** for each well. Examine the histogram to assess how each well is distributed (normal, lognormal, skewed, symmetric, etc.).

SOLUTION

Step 1. Import the data into data analysis software capable of producing histograms.

Step 2. Sort the data from smallest to largest results by well.

Step 3. With n = 14 concentrations for Well 1, a rough estimate of the number of bins is $\sqrt{14}$ = 3.74 or 4 bins. Since the data from Well 1 range from 0.004 to 0.25, the suggested bin width is calculated as (maximum concentration – minimum concentration) / number of bins = (0.25 – 0.004) / 4 = 0.0615. Therefore, the bins for Well 1 are 0.004 to <0.0655, 0.0655 to <0.127, 0.127 to <0.1885, and 0.1885 to 0.25 mg/L.

Similarly, with n = 13 concentrations for Well 2, the number of bins is $\sqrt{13}$ = 3.61 or 4 bins. Since the data from Well 2 range from 0.099 to 0.17, the suggested bin width is calculated as (maximum concentration – minimum concentration) / number of bins = (0.17 – 0.099) / 4 = 0.01775. Therefore, the bins for Well 2 are 0.099 to <0.11675, 0.11675 to <0.1345, 0.1345 to <0.15225, and 0.15225 to 0.17 mg/L.

Step 4. Construct a frequency table using the bins defined in Step 3. **Table 9-2** shows the frequency or number of observations within each bin defined in Step 3 for Wells 1 and 2. The third column shows the relative frequency which is the frequency divided by the sample size n. The final column of the table gives the densities or the relative frequencies divided by the bin widths calculated in Step 3.

Step 5. The horizontal axis for the data is from 0.004 to 0.25 mg/L for Well 1 and 0.099 to 0.17 for Well 2. The vertical axis for the histogram of frequencies is from 0 to 9 and the vertical axis for the histogram of relative frequencies is from 0% - 70%.

Step 6. The histograms of frequencies are shown in **Figure 9-3**. The histograms of relative frequencies or densities are shown in **Figure 9-4**. Note that frequency, relative frequency and density histograms all show the same shape since the scale of the vertical axis is divided by

the sample size or the bin width. These histograms confirm the data are not normally distributed for either well, but are closer to lognormal.

Table 9-2. Histogram Bins for Trichloroethene Groundwater Data

Bin	Frequency	Relative Frequency (%)	Density
Well 1			
0.0040 to <0.0655 mg/L	9	64.3	10.5
0.0655 to <0.1270 mg/L	3	21.4	3.5
0.1270 to <0.1885 mg/L	0	0	0
0.1885 to 0.2500 mg/L	2	14.3	2.3
Well 2			
0.099 to <0.11675 mg/L	8	61.5	34.7
0.11675 to <0.1345 mg/L	3	23.1	13.0
0.1345 to <0.15225 mg/L	1	7.7	4.3
0.15225 to 0.17 mg/L	1	7.7	4.3

◄

Figure 9-3. Frequency Histograms of Trichloroethene by Well.

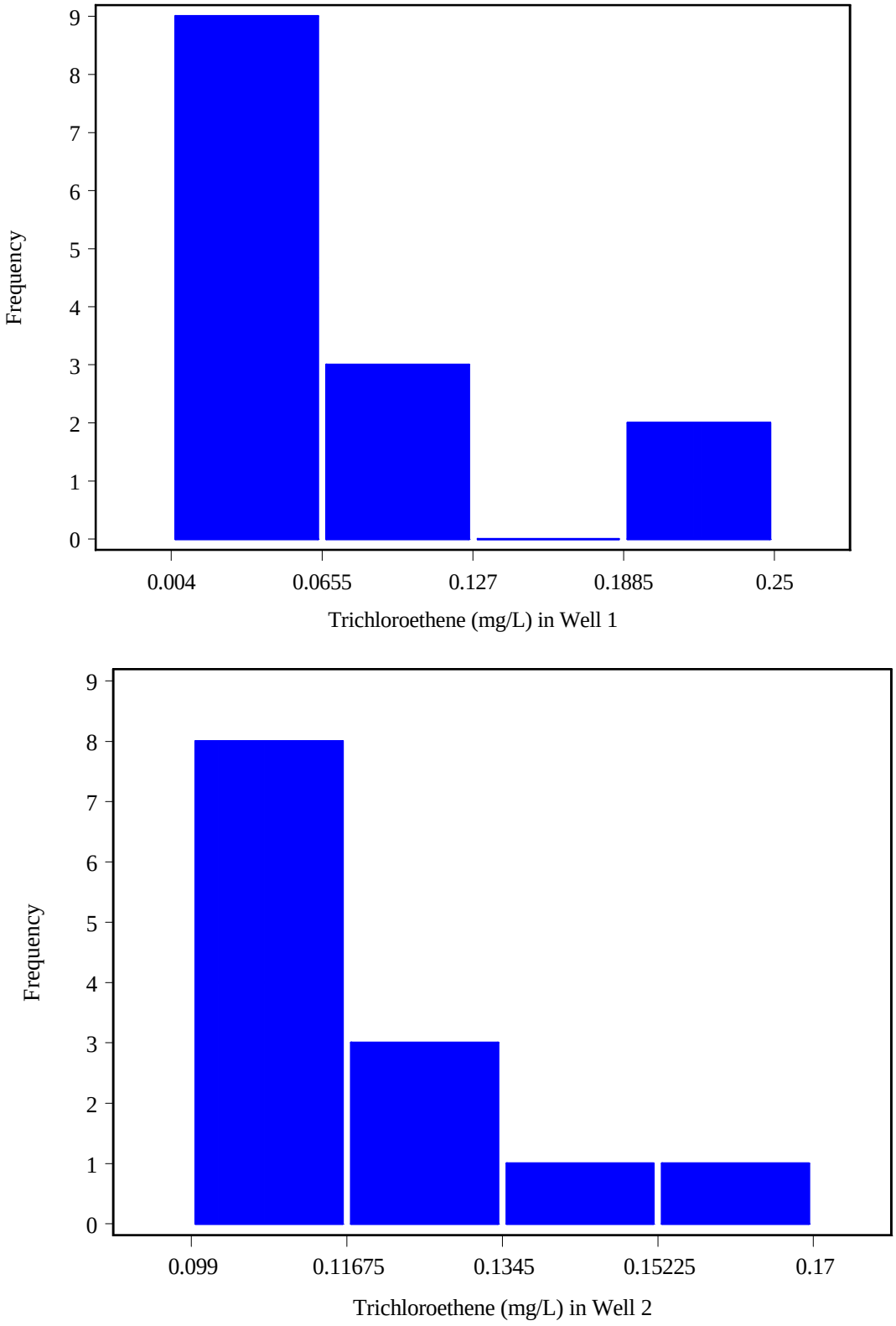
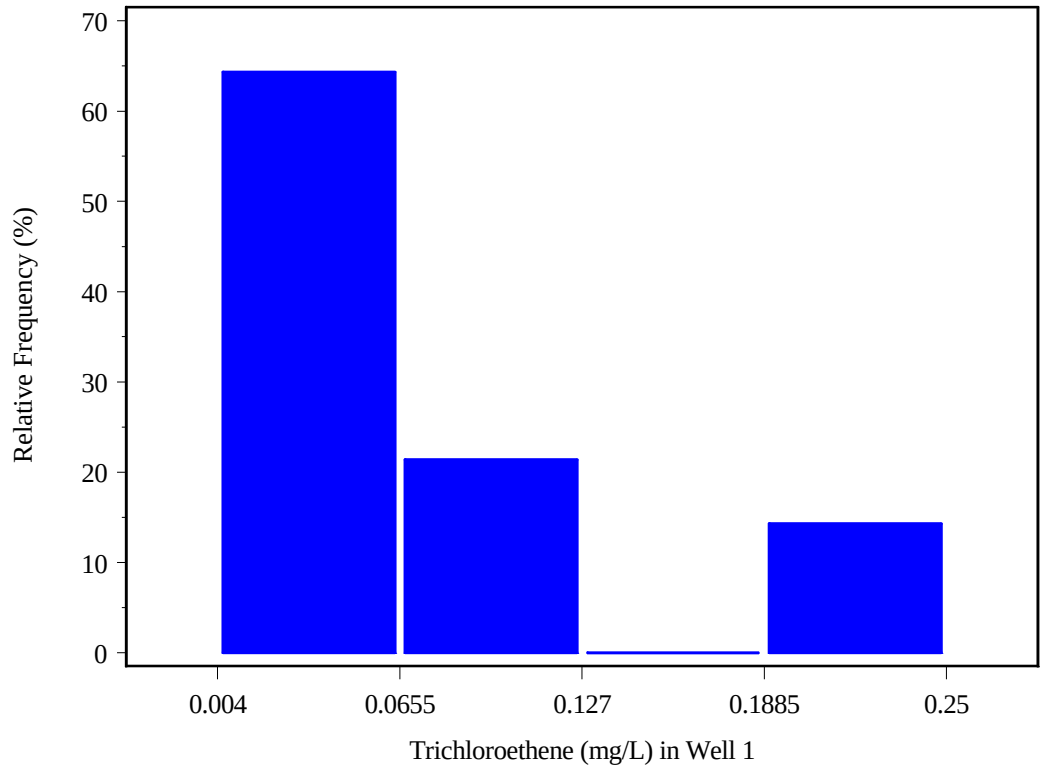
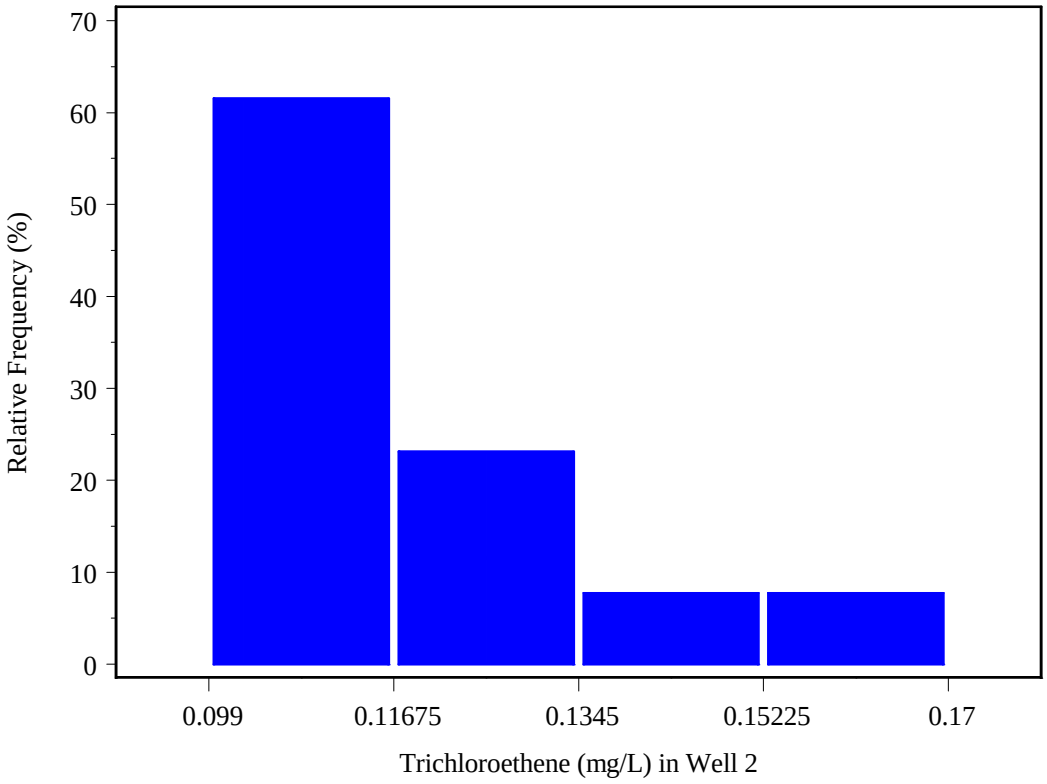


Figure 9-4. Relative Frequency Histograms of Trichloroethene by Well.





9.4 SCATTER PLOTS

For data sets consisting of multiple observations per sampling point, a scatter plot is one of the most powerful graphical tools for analyzing the relationship between two or more variables. Scatter plots are easy to construct for two variables, and many software packages can construct 3-dimensional scatter plots. A scatter plot can clearly show the relationship between two variables if the data range is sufficiently large. Truly linear relationships can always be identified in scatter plots, but truly nonlinear relationships may appear linear (or some other form) if the data range is relatively small. Scatter plots of linearly correlated variables cluster about a straight line.

As an example of a nonlinear relationship, consider two variables where one variable is approximately equal to the square of the other. With an adequate range in the data, a scatter plot of this data would display a partial parabolic curve. Other important modeling relationships that may appear are exponential or logarithmic. Two additional uses of scatter plots are the identification of potential outliers for a single variable or for the paired variables and the identification of clustering in the data. Directions for generating a scatter plot are contained in **Example 9-4**.

►EXAMPLE 9-4

Construct a scatter plot using the groundwater data in **Table 9-3** for arsenic and mercury from a single well collected approximately quarterly across time. Examine the scatter plot for linear or quadratic relationships between arsenic and mercury, correlation, and for potential outliers.

Table 9-3. Groundwater Concentrations from Well 3

	Arsenic		Mercury		Strontium	
Date Collected	Conc. (mg/L)	Data Qualifier	Conc. (mg/L)	Data Qualifier	Conc. (mg/L)	Data Qualifier
1/2/2005	0.01	U	0.02	U	0.10	
4/7/2005	0.01	U	0.03		0.02	U
7/13/2005	0.02		0.04	U	0.05	U
10/24/2005	0.04		0.06		0.11	
1/7/2006	0.01		0.02		0.05	
3/30/2006	0.05		0.07		0.07	
6/28/2006	0.09		0.10		0.03	
10/2/2006	0.07		0.08		0.04	
10/17/2006	0.10		NA		0.02	U
1/15/2007	0.02	U	0.03	U	0.15	
4/10/2007	0.15		0.11		0.03	
7/9/2007	0.12		0.08		0.10	
10/5/2007	0.10		0.07		0.09	
10/29/2007	0.30		0.29		0.05	
12/30/2007	0.25		0.23		0.22	

NA = Not available (missing data).

U denotes a non-detect.

SOLUTION

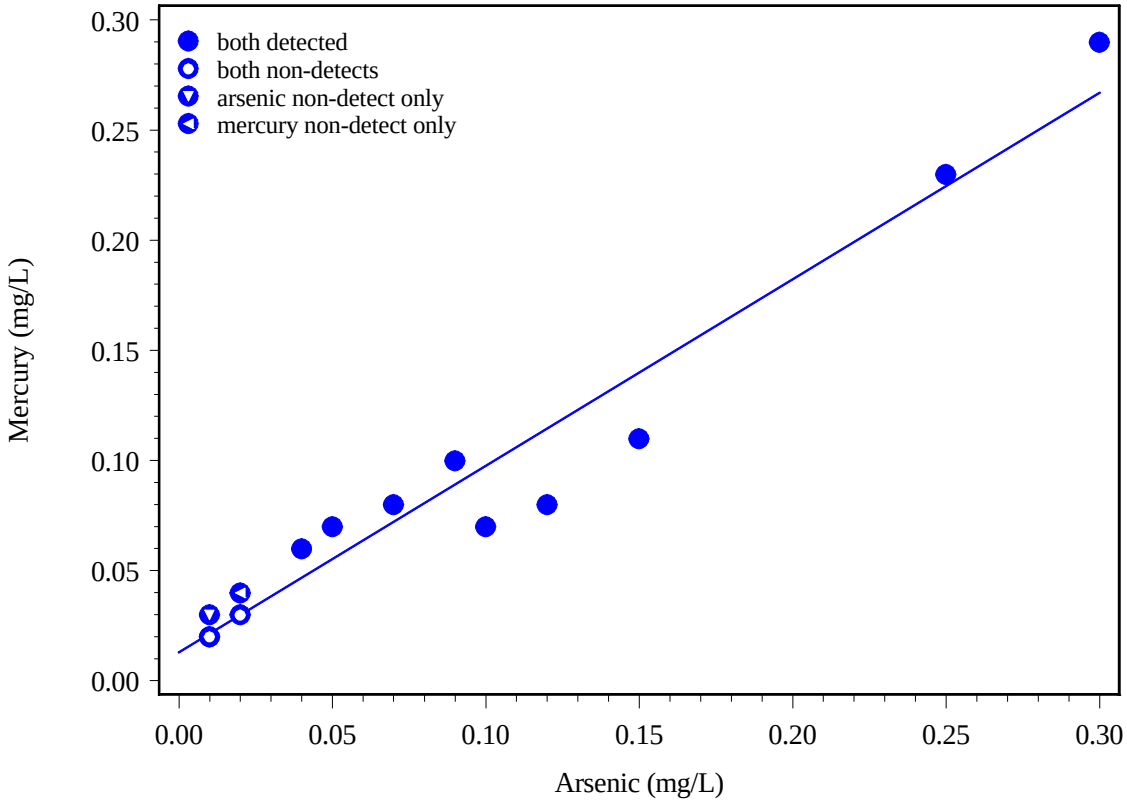
Step 1. Import the data into data analysis software capable of producing scatter plots.

Step 2. Sort the data by date collected.

Step 3. Calculate the range of concentrations for each constituent. If the range of both constituents are similar, then scale both the X and Y axes from the minimum to the maximum concentrations of both constituents. If the range of concentrations are very different (e.g., two or more orders of magnitude), then perhaps the scales for both axes should be logarithmic ($\log_{10}$). The data will be plotted as pairs from (X_1, Y_1) to (X_n, Y_n) for each sampling date, where n = number of samples.

Step 4. Use separate symbols to distinguish detected from non-detected concentrations. Note that the concentration for one constituent may be detected, while the concentration for the other constituent may not be detected for the same sampling date. If the concentration for one constituent is missing, then the pair (X_i, Y_i) cannot be plotted since both concentrations are required. **Figure 9-5** shows a linear correlation between arsenic and mercury with two possible outliers. The Pearson correlation coefficient is 0.97, indicating a significantly high correlation. The linear regression line is displayed to show the linear correlation between arsenic and mercury.◀

Figure 9-5. Scatter Plot of Arsenic with Mercury from Well 3



Many software packages can extend the 2-dimensional scatter plot by constructing a 3-dimensional scatter plot for 3 constituents. However, with more than 3 variables, it is difficult to construct and interpret a scatter plot. Therefore, several graphical representations have been developed that extend the idea of a scatter plot for data consisting of more than 2 variables. The simplest of these graphical techniques is a coded scatter plot. All possible two-way combinations are given a symbol and the pairs of data are plotted on one 2-dimensional scatter plot. The coded scatter plot does not provide information on three way or higher interactions between the variables since only two dimensions are plotted. If the data ranges for the variables are comparable, then a single set of axes may suffice. If the data ranges are too dissimilar (e.g., at least two orders of magnitude), different scales may be required.

►EXAMPLE 9-5

Construct a coded scatter plot using the groundwater data in **Table 9-3** for arsenic, mercury, and strontium from Well 3 collected approximately quarterly across time. Examine the scatter plot for linear or quadratic relationships between the three inorganics, correlation, and for potential outliers.

SOLUTION

Step 1. Import the data into data analysis software capable of producing scatter plots.

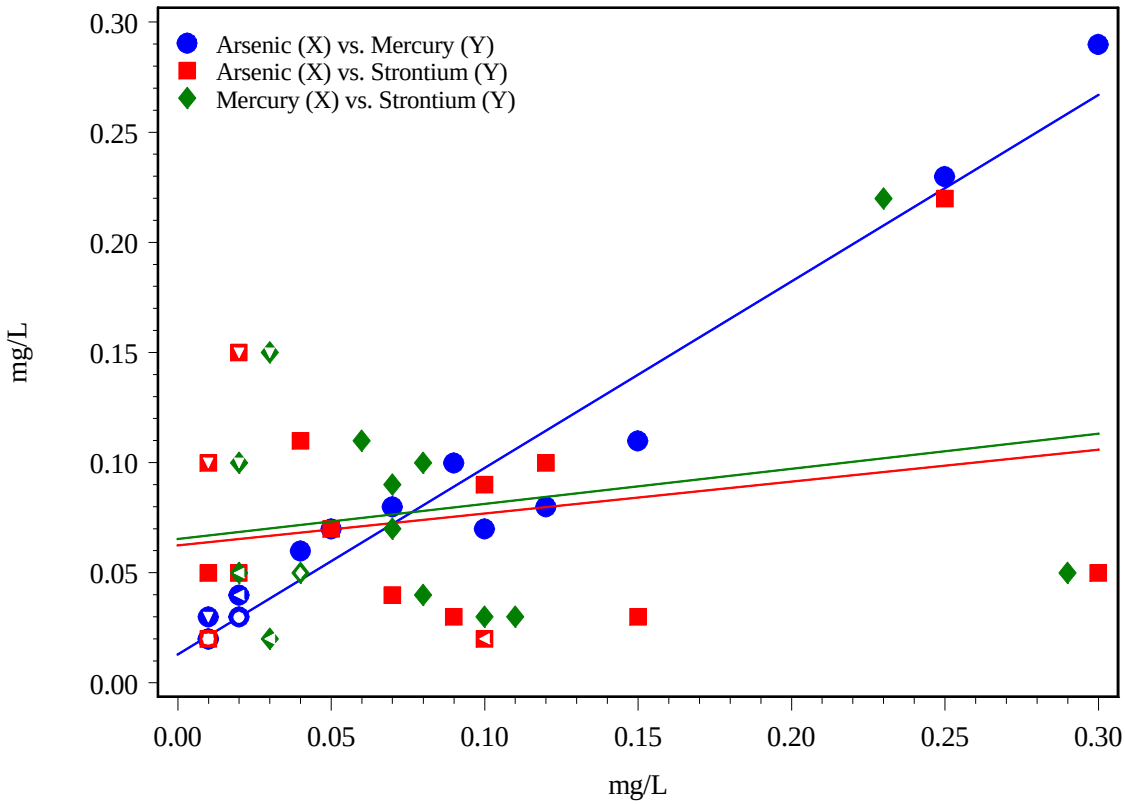
Step 2. Sort the data by date collected.

Step 3. Calculate the range of concentrations for each constituent. If the ranges of both constituents are similar, then scale both the X and Y axes from the minimum to the maximum concentrations of all three constituents. Since the ranges of concentrations are very similar, the minimum to the maximum concentrations of all three constituents will be used for both axes.

Step 4. Let each arsenic concentration be denoted by X_i, each mercury concentration be denoted by Y_i, and each strontium concentration be denoted by Z_i. The arsenic and mercury paired data will be plotted as pairs (X_i, Y_i) with solid blue circles for $1 \leq i \leq n$. The arsenic and strontium paired data will be plotted as pairs (X_i, Z_i) with solid red squares. The mercury and strontium paired data will be plotted as pairs (Y_i, Z_i) with solid green diamonds. If either concentration in each pair is a non-detect, then the non-detects will be displayed similar to **Figure 9-5**.

Step 5. Interpret the plot. **Figure 9-6** shows the linear correlation between arsenic and mercury with two possible outliers. The Pearson correlation coefficient is 0.97, indicating a significantly high correlation. The approximate 45º slope of the regression line indicates a strong correlation between arsenic and mercury. However, the nearly zero slope of the regression line between arsenic and strontium indicates little or no correlation between arsenic and strontium. There are two possible outliers for arsenic and strontium. Similarly, the nearly zero slope of the regression line between mercury and strontium indicates little or no correlation between mercury and strontium. There are also two possible outliers for mercury and strontium. The Pearson correlation coefficients for both arsenic with strontium and mercury with strontium are 0.23 which are not significantly different from zero.◄

Figure 9-6. Coded Scatter Plot of Well 3 Arsenic, Mercury, and Strontium



9.5 PROBABILITY PLOTS

A simple, but extremely useful visual assessment of normality is to graph the data as a probability plot. The *y*-axis is scaled to represent quantiles or *z*-scores from a standard normal distribution and the concentration measurements are arranged in increasing order along the *x*-axis. As each observed value is plotted on the *x*-axis, the *z*-score corresponding to the proportion of observations less than or equal to that measurement is plotted as the *y*-coordinate. Often, the *y*-coordinate is computed by the following formula:

$$y_i = \Phi^{-1}\left(\frac{i}{n+1}\right) \qquad [9.1]$$

where Φ^{-1} denotes the inverse of the cumulative standard normal distribution, n represents the sample size, and i represents the rank position of the i^{th} ordered concentration. The plot is constructed so that, if the data are normal, the points when plotted will lie on a straight line. Visually apparent curves or bends indicate that the data do not follow a normal distribution.

Probability plots are particularly useful for spotting irregularities within the data when compared to a specific distributional model (usually, but not always, the normal). It is easy to determine whether departures from normality are occurring more or less in the middle ranges of the data or in the extreme

tails. Probability plots can also indicate the presence of possible outlier values that do not follow the basic pattern of the data and can show the presence of significant positive or negative skewness.

If a (normal) probability plot is constructed on the combined data from several wells and normality is accepted, it suggests — but does not prove — that all of the data came from the same normal distribution. Consequently, each subgroup of the data set (*e.g.*, observations from distinct wells) probably has the same mean and standard deviation. If a probability plot is constructed on the data residuals (each value minus its subgroup mean) and is not a straight line, the interpretation is more complicated. In this case, either the residuals are not normally-distributed, or there is a subgroup of the data with a normal distribution but a different mean or standard deviation than the other subgroups. The probability plot will indicate a deviation from the underlying assumption of a common normal distribution in either case. It would be prudent to examine normal probability plots by well on the same plot if the ranges of the data are similar. This would show how the data are distributed by well to determine which wells may depart from normality.

The same probability plot technique may be used to investigate whether a set of data or residuals follows a lognormal distribution. The procedure is generally the same, except that one first replaces each observation by its natural logarithm. After the data have been transformed to their natural logarithms, the probability plot is constructed as before. The only difference is that the natural logarithms of the observations are used on the *x*-axis. If the data are lognormal, the probability plot of the logged observations will approximate a straight line.

►EXAMPLE 9-6

Determine whether the dataset in **Table 9-4** is normal by using a probability plot.

SOLUTION

Step 1. After combining the data into a single group, list the measured nickel concentrations in order from lowest to highest.

Step 2. The cumulative probabilities, representing for each observation (x_i) the proportion of values less than or equal to x_i, are given in the third column of the table below. These are computed as $i / (n + 1)$ where n is the total number of samples ($n = 20$).

Step 3. Determine the quantiles or *z*-scores from the standard normal distribution corresponding to the cumulative probabilities in Step 2. These can be found by successively letting P equal each cumulative probability and then looking up the entry in **Table 10-1 (Appendix D)** corresponding to P. Since the standard normal distribution is symmetric about zero, for cumulative probabilities $P < 0.50$, look up the entry for $(1–P)$ and give this value a negative sign.

Step 4. Plot the normal quantile (*z*-score) versus the ordered concentration for each sample, as in the plot below (**Figure 9-7**). The curvature found in the probability plot indicates that there is evidence of non-normality in the data. ◄

Table 9-4. Nickel Concentrations from a Single Well

Nickel Concentration (ppb)	Order (*i*)	Cumulative Probability [*i*/(*n*+1)]	Normal Quantile (*z*-score)
1.0	1	0.048	–1.668
3.1	2	0.095	–1.309
8.7	3	0.143	–1.068
10.0	4	0.190	–0.876
14.0	5	0.238	–0.712
19.0	6	0.286	–0.566
21.4	7	0.333	–0.431
27.0	8	0.381	–0.303
39.0	9	0.429	–0.180
56.0	10	0.476	–0.060
58.8	11	0.524	0.060
64.4	12	0.571	0.180
81.5	13	0.619	0.303
85.6	14	0.667	0.431
151.0	15	0.714	0.566
262.0	16	0.762	0.712
331.0	17	0.810	0.876
578.0	18	0.857	1.068
637.0	19	0.905	1.309
942.0	20	0.952	1.668

PROBABILITY PLOTS FOR LOG TRANSFORMED DATA

Step 1. List the natural logarithms of the measured nickel concentrations in **Table 9-4** in order from lowest to highest. These are shown in **Table 9-5**.

Step 2. The cumulative probabilities representing the proportion of values less than or equal to x_i for each observation (x_i), are given in the third column of **Table 9-4**. These are computed as i / (n + 1) where n is the total number of samples (n = 20).

Step 3. Determine the quantiles or *z*-scores from the standard normal distribution corresponding to the cumulative probabilities in Step 2. These can be found by successively letting P equal each cumulative probability and then looking up the entry in **Table 10-1 Appendix D** corresponding to P. Since the standard normal distribution is symmetric about zero, for cumulative probabilities $P < 0.50$, look up the entry for (1–P) and give this value a negative sign.

Table 9-5. Nickel Log Concentrations from a Single Well

Order (*i*)	Log Nickel Concentration log(ppb)	Cumulative Probability [*i*/(*n*+1)]	Normal Quantile (*z*-score)
1	0.00	0.048	–1.668
2	1.13	0.095	–1.309
3	2.16	0.143	–1.068
4	2.30	0.190	–0.876
5	2.64	0.238	–0.712
6	2.94	0.286	–0.566
7	3.06	0.333	–0.431
8	3.30	0.381	–0.303
9	3.66	0.429	–0.180
10	4.03	0.476	–0.060
11	4.07	0.524	0.060
12	4.17	0.571	0.180
13	4.40	0.619	0.303
14	4.45	0.667	0.431
15	5.02	0.714	0.566
16	5.57	0.762	0.712
17	5.80	0.810	0.876
18	6.36	0.857	1.068
19	6.46	0.905	1.309
20	6.85	0.952	1.668

Step 4. Plot the normal quantile (*z*-score) versus the ordered logged concentration for each sample, as in the plot below (**Figure 9-8**). The reasonably linear trend found in the probability plot indicates that the log-scale data closely follow a normal pattern, further suggesting that the original data closely follow a lognormal distribution.

Figure 9-7. Nickel Normal Probability Plot

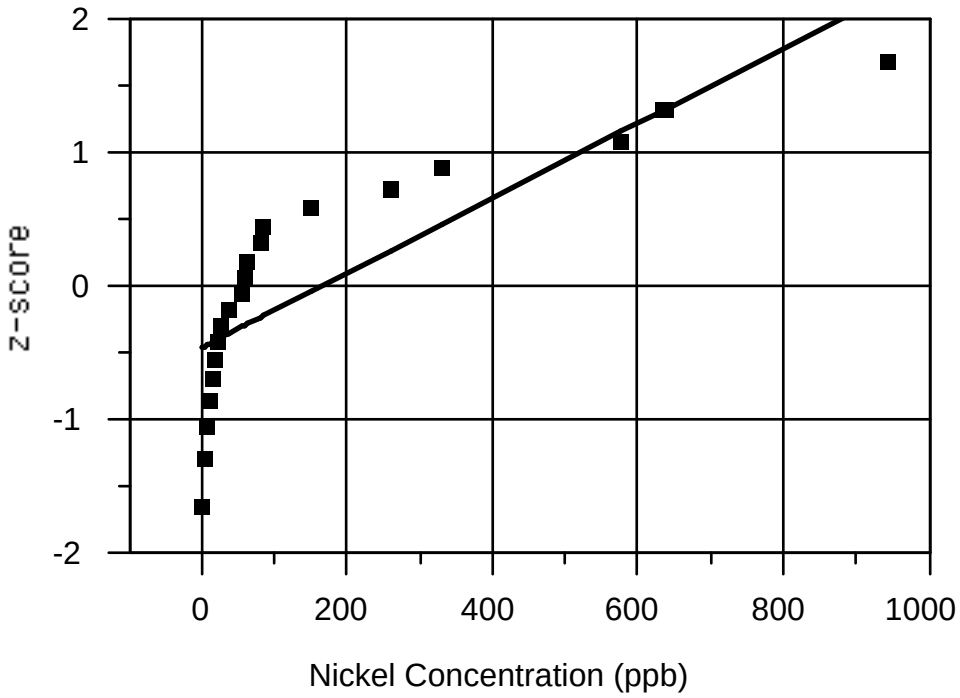
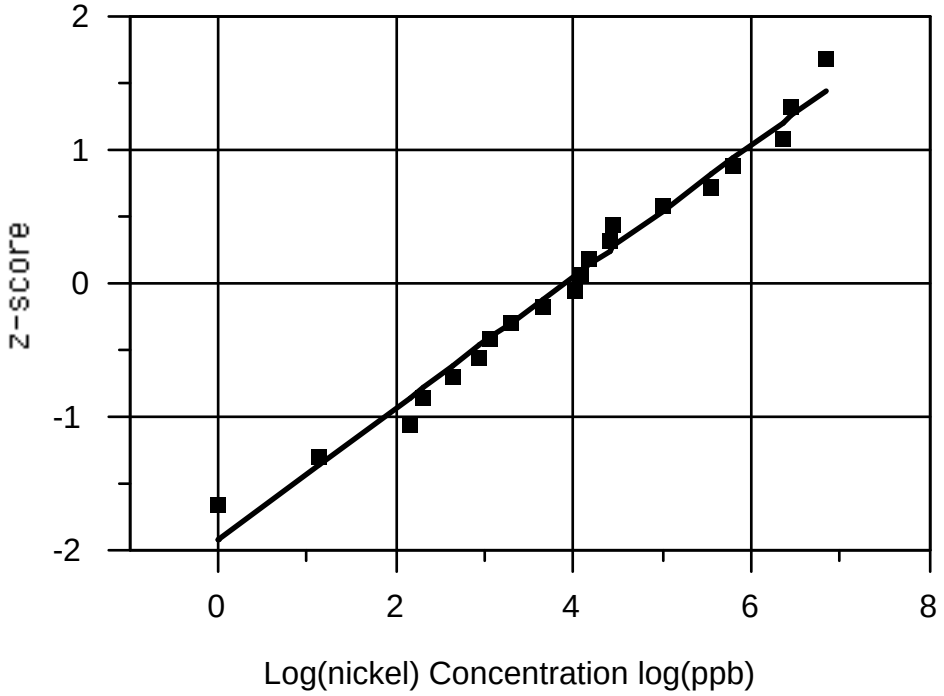


Figure 9-8. Probability Plot of Log Transformed Nickel Data



CHAPTER 10. FITTING DISTRIBUTIONS

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Because a statistical or mathematical model is at best an approximation of reality, all statistical tests and procedures require certain assumptions for the methods to be used correctly and for the results to be properly interpreted. Many tests make an assumption regarding the underlying distribution of the observed data; in particular, that the original or transformed sample measurements follow a normal distribution. Data transformations are discussed in **Section 10.2** while considerations as to whether the normal distribution should be used as a 'default' are explored in **Section 10.3**. Several techniques for assessing normality are also examined, including:

- The skewness coefficient (**Section 10.4**)
- The Shapiro-Wilk test of normality and its close variant, the Shapiro-Francía test (**Section 10.5**)
- Filliben's probability plot correlation coefficient test (**Section 10.6**)
- The Shapiro-Wilk multiple group test of normality (**Section 10.7**)

10.1 IMPORTANCE OF DISTRIBUTIONAL MODELS

As introduced in **Chapter 3**, all statistical testing relies on the critical assumption that the sample data are *representative* of the population from which they are selected. The statistical distribution of the *sample* is assumed to be similar to the distribution of the mostly unobserved *population* of possible measurements. Many *parametric* testing methods make a further assumption: that the form or type of the underlying population is at least approximately known or can be identified through diagnostic testing. Most of these parametric tests assume that the population is *normal* in distribution; the validity or accuracy of the test results may be in question if that assumption is violated.

Consequently, an important facet of choosing among appropriate test methods is determining whether a commonly-used statistical distribution such as the normal, adequately models the observed sample data. A large variety of possible distributional models exist in the statistical literature; most are not typically applied to groundwater measurements and often introduce additional statistical or mathematical complexity in working with them. So groundwater statistical models are usually confined to the gamma distribution, the Weibull distribution, or distributions that are normal or can be normalized via a transformation (e.g., the logarithmic or square root).

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Although the Unified Guidance will occasionally reference procedures that assume an underlying gamma or Weibull distribution, the presentation in this guidance will focus on distributions that can be normalized and diagnostic tools for assessing normality. The principal reasons for limiting the discussion in this manner are: 1) the same tools useful for testing normality can be utilized with any distribution that can be normalized-- the only change needed is perform the normality test after first making a data transformation; 2) if no transformation works to adequately normalize the sample data, a non-parametric test can often be used as an alternative statistical approach; and 3) addressing more complicated scenarios is outside the scope of the guidance and may require professional statistical consultation.

Understanding the statistical behavior of groundwater measurements can be very challenging. The constituents of interest may occur at relatively low concentrations and frequently be left-censored because of current analytical method limitations. Sample data are often positively skewed and asymmetrical in distributional pattern, perhaps due to the presence of outliers, inhomogeneous mixing of contaminants in the subsurface, or spatially variable soils deposition affecting the local groundwater geochemistry. For some constituents, the distribution in groundwater is not stationary over time (*e.g.*, due to linear or seasonal trends) or not stationary across space (due to spatial variability in mean levels from well to well). A set of these measurements pooled over time and/or space may appear highly non-normal, even if the underlying population at any fixed point in time or space *is* normal.

Because of these complexities, fitting a distributional model to a set of sample data cannot be done in isolation from checks of other key statistical assumptions. The data must also be evaluated for outliers (**Chapter 12**), since the presence of even one extreme outlier may cause an otherwise recognizable distribution from being correctly identified. For data grouped across wells, the possible presence of spatial variability must be considered (**Chapter 13**). If identified, the Shapiro-Wilk multiple group test of normality may be needed to account for differing means and/or variances at distinct wells. Data pooled across sampling events (*i.e.*, over time) must be examined for the presence of trends or seasonal patterns (**Chapter 14**). A clearly identified pattern may need to be removed and the *data residuals* tested for normality, instead of the raw measurements.

A frequently encountered problem involves testing normality on data sets containing non-detect values. The best goodness-of-fit tests attempt to assess whether the sample data closely resemble the *tails* of the candidate distributional model. Since non-detects represent *left-censored observations* where the exact concentrations are unknown for the lower tail of the sample distribution, standard normality tests cannot be run without some estimate or *imputation* of these unknown values. For a small fraction of non-detects in a sample (10-15% or less) censored at a single reporting limit, it may be possible to apply a normality test by simply replacing each non-detect with an imputed value of half the RL. However, more complicated situations arise when there is a combination of multiple RLs (detected values intermingled with different non-detect levels), or the proportion of non-detects is larger. The Unified Guidance recommends different strategies in these circumstances.

Properly *ordering* the sample observations (*i.e.*, from least to greatest) is critical to *any* distributional goodness-of-fit test. Because the concentration of a non-detect measurement is only known to be in the range from zero to the RL, it is generally impossible to construct a full ordering of the

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sample.[1] There are methods, however, to construct *partial orderings* of the data that allow the assignment of relative rankings to each of the detected measurements and which account for the presence of censored values. In turn, a partial ordering enables construction of an approximate normality test. This subject is covered in **Chapter 15**.

10.2 TRANSFORMATIONS TO NORMALITY

Guidance users will often encounter data sets indicating significant evidence of non-normality. Due to the presumption of most parametric tests that the underlying population is normal, a common statistical strategy for apparently non-normal observations is to search for a normalizing mathematical transformation. Because of the complexities associated with interpreting statistical results from data that have been transformed to another scale, some care must be taken in applying statistical procedures to transformed measurements. In questionable or disputable circumstances, it may be wise to analyze the same data with an equivalent non-parametric version of the same test (if it exists) to see if the same general conclusion is reached. If not, the data transformation and its interpretation may need further scrutiny.

Particularly with prediction limits, control charts, and some of the confidence intervals described in **Chapters 18**, **20,** and **21**, the parametric versions of these procedures are especially advantageous. Here, a transformation may be warranted to approximately normalize the statistical sample. Transformations are also often useful when combining or pooling intrawell background from several wells in order to increase the degrees of freedom available for intrawell testing (**Chapter 13**). Slight differences in the distributional pattern from well to well can skew the resulting pooled dataset, necessitating a transformation to bring about approximate normality and to equalize the variances.

The interpretation of transformed data is straightforward in the case of prediction limits for individual observations or when building a confidence interval around an upper percentile. An interval with limits constructed from the transformed data and then re-transformed (or *back-transformed*) to the original measurement domain will retain its original probabilistic interpretation. For instance, if the data are approximately normal under a square root transformation and a 95% confidence prediction limit is constructed on the square roots of the original measurements, *squaring* the resulting prediction limit allows for a 95% confidence level when applied to the original data.

The same ease of interpretation does not apply to prediction limits for a future arithmetic mean (**Chapter 18**) or to confidence intervals around an arithmetic mean compared to a fixed GWPS (**Chapter 21**). A back-transformed confidence interval constructed around the mean of log-transformed data (*i.e.*, the log-mean) corresponds to a confidence interval around the *geometric mean* of the raw (untransformed) data. For the lognormal distribution, the geometric mean is equal to the median, but it is *not* the same as the arithmetic mean. Using this back-transformation to bracket the location of the true arithmetic population mean will result in an incorrect interval.

For these particular applications, a similar problem of *scale bias* occurs with other potential normality transformations. Care is needed when applying and interpreting transformations to a data set

[1] Even when all the non-detects represent the lowest values in the sample, there is still no way to determine how this subset is internally ordered.

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for which either a confidence interval around the mean or a prediction limit for a future mean is desired. The interpretation depends on which statistical parameter is being estimated or predicted. The geometric mean or median in some situations may be a satisfactory alternative as a central tendency parameter, although that decision must be weighed carefully when making comparisons against a GWPS.

Common normalizing transformations include the natural logarithm, the square root, the cube root, the square, the cube, and the reciprocal functions, as well as a few others. More generally, one might consider the "ladder of powers" (Helsel and Hirsch, 2002) technically known as the set of Box-Cox transformations (Box and Cox, 1964). The heart of these transformations is a power transformation of the original data, expressed by the equations:

$$y_\lambda = \begin{cases} \left(x^\lambda - 1\right) \big/ \lambda & \text{for } \lambda \neq 0 \\ \log x & \text{for } \lambda = 0 \end{cases} \qquad [10.1]$$

The goal of a Box-Cox analysis is to find the value λ that best transforms the data to approximate normality, using a procedure such as maximum likelihood. Such algorithms are beyond the scope of this guidance, although an excellent discussion can be found in Helsel and Hirsch (2002). In practice, slightly different equation formulations can be used:

$$y_\lambda = \begin{cases} x^\lambda & \text{for } \lambda \neq 0 \\ \log x & \text{for } \lambda = 0 \end{cases} \qquad [10.2]$$

where the parameter λ can generally be limited to the choices 0, -1, 1/4, 1/3, 1/2, 1, 2, 3, and 4, except for unusual cases of more extreme powers.

As noted in **Section 10.1**, checking normality with transformed data does not require any additional tools. Standard normality tests can be applied using the transformed scale measurements. Only the interpretation of the test changes. A goodness-of-fit test can assess the normality of the raw measurements. Under a transformation, the same test checks for normality on the transformed scale. The data will still follow the non-normal distribution in the original concentration domain. So if a cube root transformation is attempted and the transformed data are found to be approximately normal, the original data are not normal but rather cube-root normal in distribution. If a log transformation is successfully used, the original measurements are not normal but lognormal instead. In sum, a series of non-normal distributions can be fitted to data with the goodness-of-fit tests described in this chapter without needing specific tests for other potential distributions.

Finding a reasonable transformation in practice amounts to systematically 'climbing' the "ladder of powers" described above. In other words, different choices of the power parameter λ would be attempted — beginning with λ = 0 and working upward from -1 toward more extreme power transformations — until a specific λ normalizes the data or all choices have been attempted. If no transformation seems to work, the user should instead consider a non-parametric test alternative.

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10.3 USING THE NORMAL DISTRIBUTION AS A DEFAULT

Normal and lognormal distributions are frequently applied models in groundwater data because of their general utility. One or the other of these models might be chosen as a *default distribution* when designing a statistical approach, particularly when relatively little data has been collected at a site. Since the statistical behavior of these two models is very different and can lead to substantially different conclusions, the choice is not arbitrary. The type of test involved, the monitoring program, and the sample size can all affect the decision. For many data sets and situations, however, the normal distribution can be assumed as a default unless and until a better model can be pinpointed through specific *goodness-of-fit* testing provided in this chapter.

Assumptions of normality are most easily made with regard to naturally-occurring and measurable inorganic parameters, particularly under background conditions. Many ionic and other inorganic water quality analyte measurements exhibit decent symmetry and low variability within a given well data set, making these data amenable to assumptions of normality. Less frequently detected analytes (*e.g.*, certain colloidal trace elements) may be better fit either by a site-wide lognormal or another distribution that can be normalized, as well as evaluated with non-parametric methods.

Where contamination in groundwater is known to exist *a priori* (whether in background or compliance wells), default distributional assumptions become more problematic. At a given well, organic or inorganic contaminants may exhibit high or low variability, depending on local hydrogeologic conditions, the pattern of release from the source, the degree of solid phase absorption, degradability of a given constituent, and the variation in groundwater flow direction and depths. Non-steady state releases may result in a historical, occasionally non-linear pattern of trend increases or decreases. Such data might be fit by an apparent lognormal distribution, although removal of the trend may lead to normally-distributed residuals.

Sample size is also a consideration. With fewer than 8 samples in a data set, formal goodness-of-fit tests are often of limited value. Where larger sample sizes are available, goodness-of-fit tests should be conducted. The Shapiro-Wilk multiple group well test (**Section 10.7**) — even with small sample sizes — can sometimes be used to identify individual anomalous wells which might otherwise be presumed to meet the criterion of normality. Under compliance/assessment or corrective action monitoring, one might anticipate only four samples per well in the first year after instituting such monitoring. Under these conditions, a default assumption of normality for testing of the mean against a fixed standard is probably necessary. Aggregation of multi-year data when conducting compliance tests (see **Chapter 7**) may allow large enough sample sizes to warrant formal goodness-of-fit testing. With 8 (or more) samples, it may be possible to determine that a lognormal distribution is an appropriate fit for the data. Even in this latter approach, caution may be needed in applying Land's confidence interval for a lognormal mean (**Chapter 21**) if the sample variability is large and especially if the upper confidence limit is used in the comparison (*i.e.*, in corrective action monitoring).

The normal distribution may also serve as a reasonable default when it is not critical to ensure that sample data closely follow a specific distribution. For example, statistical tests on the mean are generally considered more *robust* with respect to departures from normality than procedures which involve upper or lower limits of an assumed distribution. Even if the data are not quite normal, tests on the mean such

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as a Student's *t*-test will often still provide a valid result. However, one might need to consider transformations of the data for other reasons. Analysis of variance [ANOVA] can be run with small individual well samples (*e.g.*, $n = 4$), and as a comparison of means, it is fairly robust to departures from normality. A logarithmic or other transformation may be needed to stabilize or equalize the well-to-well variability (*i.e.*, achieve *homoscedasticity*), a separate and more critical assumption of the test.

Given their importance in statistical testing and the risks that sometimes occur in trying to interpret tests on other data transformation possibilities, it is useful to briefly consider the logarithmic transformation in more detail. As noted in **Section 10.1**, groundwater data can frequently be normalized using a logarithmic distribution model. Despite this, objections are sometimes raised that the log transformation is merely used to "make large numbers look smaller."

To better understand the log transformation, it should be recognized that logarithms are, in fact, exponents to some unit base. Given a concentration-scale variable *x*, re-expressed as $x = 10^y$ or $x = e^y$, the logarithm *y* is the exponent of that base (10 or the natural base *e*). It is the behavior of the resultant *y values* that is assessed when data are log-transformed. When data relationships are multiplicative in the original arithmetic domain ($x_1 \times x_2$), the relationships between exponents (*i.e.*, logarithms) are additive ($y_1 + y_2$). Since the logarithmic distribution by mathematical definition is normal in a log-transformed domain, working with the logarithms instead of the original concentration measurements may offer a sample distribution much closer to normal.

Similar to a unit scale transformation (ppm to ppb or Fahrenheit to Centigrade), the relative ordering of log-transformed measurements does not change. When non-parametric tests based on ranks (*e.g.*, the Wilcoxon rank-sum test) are applied to data transformed either to a different unit scale or by logarithms, the outcomes are identical. However, other relationships among the log-transformed data *do* change, so that the log-scale numerical 'spacing' between lower values is more similar to the log-scale spacing between higher values. While parametric tests like prediction limits, *t*-tests, *etc.*, are not affected by unit scale transformations, these tests may have different outcomes depending on whether raw concentrations or log-transformed measurements are used. The justification for utilizing log-transformed data is that the transformation helps to normalize the data so that these tests can be properly applied.

There is also a plausible physical explanation as to why pollutant concentrations often follow a logarithmic pattern (Ott, 1990). In Ott's model, pollutant sources are randomly dispersed through the subsurface or atmosphere in a multiplicative fashion through repeated dilutions when mixing with volumes of (uncontaminated) water or air, depending on the medium. Such random and repeated dilutions can mathematically lead to a lognormal distribution. In particular, if a final concentration (c_0) is the product of several random dilutions (c_i) as suggested by the following equation:

$$c_0 = \prod_{i=1}^{n} c_i = (c_1 \times c_2 \times \ldots \times c_n) \qquad [10.3]$$

the logarithm of this concentration is equivalent to the *sum* of the logarithms of the individual dilutions:

$$\log(c_0) = \sum_{i=1}^{n} \log(c_i) \qquad [10.4]$$

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The Central Limit Theorem (**Chapter 3**) can be applied to conclude that the logged concentration in equation [10.4] should be approximately normal, implying that the original concentration (c_0) should be approximately lognormal in distribution. Contaminant fate-and-transport models more or less follow this same approach, using successive multiplicative dilutions (while accounting for absorption and degradation effects) across grids in time and space.

Despite the mathematical elegance of the Ott model, experience with groundwater monitoring data has shown that the lognormal model alone is not adequate to account for observed distribution patterns. While contaminant modeling might predict a lognormal contaminant distribution in space (and often in time at a fixed point during transient phases), individual well location points fixed in space and at rough contaminant equilibrium are more likely to be subject to a variety of local hydrologic and other factors, and the observed distributions can be almost limitless in form. Since most of the tests within the Unified Guidance presume a stationary population over time at a given well location (subject to identification and removal of trends), the resultant distributions may be other than lognormal in character. Individual constituents may also exhibit varying aquifer-related distributional characteristics.

A practical issue in selecting a default transformation is ease of use. Distributions like the lognormal usually entail more complicated statistical adjustments or calculations than the normal distribution. A confidence interval around the arithmetic mean of a lognormal distribution utilizes Land's *H*-factor, which is a function of both log sample data variability and sample size, and is only readily available for specific confidence levels. By contrast, a normal confidence interval around the sample mean based on the *t*-statistic can easily be defined for virtually any confidence level. As noted earlier, correct use of these confidence intervals depends on selecting the appropriate parameter and statistical measure (arithmetic mean versus the geometric mean).

While a transformation does not always necessitate using a different statistical formula to ensure unbiased results, use of a transformation *does* assume that the underlying population is non-normal. Since the true population will almost never be known with certainty, it may not be advantageous to simply default to a lognormal assumption for a variety of reasons. Under detection monitoring, the presumption is made that a statistically significant increase above background concentrations will trigger a monitoring exceedance. But the larger the prediction limit computed from background, the less *statistical power* the test will have for detecting true increases. An important question to answer is what the consequences are when incorrectly applying statistical techniques based on one distributional assumption (normal or lognormal), when the underlying distribution is in fact the other. More specifically, what is the impact on statistical power and accuracy of assuming the wrong underlying distribution? The general effects of violating underlying test assumptions can be measured in terms of false positive and negative error rates (and therefore power). These questions are particularly pertinent for prediction limit and control chart tests in detection monitoring. Similar questions could be raised regarding the application of confidence interval tests on the mean when compared against fixed standards.

To answer these questions, a series of Monte Carlo simulations was generated for the Unified Guidance to evaluate the impacts on prediction limit false positive error rates and statistical power of using normal and lognormal distributions (correctly and incorrectly applied to the underlying distributions). Detailed results of this study are provided in **Appendix C, Section C.1**.

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The conclusions of the Monte Carlo study are summarized as follows:

- If an underlying population is truly normal, *treating the sample data as lognormal* in constructing a prediction limit can have significant consequences. With no retesting, the lognormal prediction limits were in every case considerably larger and thus less powerful than the normal prediction limits. Further, the lognormal limits consistently exhibited less than the expected (nominal) false positive rate, while the normal prediction limits tended to have slightly higher than nominal error rates.
- When retesting was added to the procedure, both types of prediction limits improved. While power uniformly improved compared to no retest, the normal limits were still on average about 13% shorter than the lognormal limits, leading again to a measurable loss of statistical power in the lognormal case.
- On balance, *misapplication* of logarithmic prediction limits to normally-distributed data consistently resulted in (often considerably) lower power and false positive rates that were lower than expected. The results argue *against* presuming the underlying data to be lognormal without specific goodness-of-fit testing.
- The highest penalties from misapplying lognormal prediction limits occurred for smaller background sizes. Since goodness-of-fit tests are least able to distinguish between normal and lognormal data with small samples, small background samples should not be presumed to be lognormal *as a default* unless other evidence from the site suggests otherwise. For larger samples, goodness-of-fit tests have much better discriminatory power, enabling a better indication of which model to use.
- If the underlying population is truly lognormal but the sample data *are treated as normal*, the penalty in overall statistical performance is substantial *only* if no retesting is conducted. With no retesting, the false positive rates of normal-based limits were often substantially higher than the expected rate. Under conditions of no retesting, *misapplying* normal prediction limits to lognormal data would result in an excessive site-wide false positive rate (SWFPR).
- If at least one retest was added, the achieved false positive rates for the misapplied normal limits tended to be *less* than the expected rates, especially for moderate to larger sample sizes. Except for highly skewed lognormal distributions, the power of the normal limits was comparable or greater than the power of the lognormal limits.

Overall, the Monte Carlo study indicated that adding a retest to the testing procedure significantly minimized the penalty of misapplying normal prediction limits to lognormal data, as long as the sample size was at least 8 and the distribution was not too skewed. Consequently, there is *less* penalty associated with making a default assumption of *normality* than in making a default assumption of *lognormality* under most situations. With highly skewed data, goodness-of-fit tests tend to better discriminate between the normal and lognormal models. The Unified Guidance therefore recommends that such diagnostic testing be done *explicitly* rather than simply assuming the data to be normal or lognormal.

The most problematic cases in the study occurred for very small background sample sizes, where a misapplication of prediction limits in either direction often resulted in poorer statistical performance, even with retesting. In some situations, compliance testing may need to be conducted on an interim basis until enough data has been collected to accurately identify a distributional model. The Unified Guidance does not recommend an automatic default assumption of lognormality.

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In summary, during detection and compliance/assessment monitoring, data sets should be treated initially as normal in distribution unless a better model can be pinpointed through specific testing. The normal distribution is a fairly safe assumption for background distributions, particularly for naturally occurring, measurable constituents and when sample sizes are small. Goodness-of-fit tests provided in this chapter can be used to more closely identify the appropriate distributions for larger sample sizes. If the initial assumption of normality is not rejected, further statistical analyses should be performed on the raw observations. If the normal distribution *is* rejected by a goodness-of-fit test, one should generally test the normality of the logged data, in order to check for lognormality of the original observations. If this test also fails, one can either look for an alternate transformation to achieve approximate normality (**Section 10.2**) or use a non-parametric technique.

Since tests of normality have low power for rejecting the null hypothesis when the data are really lognormal but the sample size and degree of skewness are small, it is reassuring that a "wrong" default assumption of normality will infrequently lead to an incorrect statistical conclusion. In fact, the statistical power for detecting real concentration increases will generally be better than if the data were assumed to be lognormal. If the data *are* truly lognormal, there *is* a risk of greater-than-expected site-wide false positive error rates.

When the population is more skewed, normality tests in the Unified Guidance have much greater power for correctly rejecting the normal model in favor of the lognormal distribution. Consequently, an initial assumption of normality will not, in most cases, lead to an incorrect final conclusion, since the presumed normal model will tend to be rejected before further testing is conducted.

These recommendations do not apply to corrective action monitoring or other programs where it either known or reasonable to presume that groundwater is already impacted or has a non-normal distribution. In such settings, a default presumption of lognormality could be made, or a series of normalizing transformations could be attempted until a suitable fit is determined. Furthermore, even in detection monitoring, there are situations that often require the use of alternate transformations, for instance when pooling intrawell background across several wells to increase the degrees of freedom available for intrawell testing (**Chapter 13**).

Whatever the circumstance, the Unified Guidance recommends whenever possible that site-specific data be used to test the distributional presumption. If no data are initially available to do this, "referencing" may be employed to justify the use of, say, a normal or lognormal assumption in developing statistical tests at a particular site. Referencing involves the use of historical data or data from sites in similar hydrologic settings to justify the assumptions applied to the proposed statistical regimen. These initial assumptions should be checked when data from the site become available, using the procedures described in the Unified Guidance. Subsequent changes to the initial assumptions should be made if goodness-of-fit testing contradicts the initial hypothesis.

10.4 COEFFICIENT OF VARIATION AND COEFFICIENT OF SKEWNESS

PURPOSE AND BACKGROUND

Because the normal distribution has a symmetric 'bell-shape,' the normal mean and median coincide and random observations drawn from a normal population are just as likely to occur below the mean as above it. More generally, in any symmetric distribution the distributional pattern below the

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mean is a mirror-image of the pattern above the mean. By definition, such distributions have no degree of *skewness* or asymmetry.

Since the normal distribution has zero skewness, one way to look for non-normality is to estimate the degree of skewness. Non-zero values of this measure imply that the population is asymmetric and therefore something different from normal. Two exploratory screening tools useful for this task are the *coefficient of variation* and the *coefficient of skewness*.

The coefficient of variation [CV] is extremely easy to compute, but only indirectly offers an estimate of skewness and hence normality/non-normality. A more direct estimate can be determined via the coefficient of skewness. Furthermore, better, formal tests can be used instead of either coefficient to directly assess normality. Nevertheless, the CV provides a measure of intrinsic variability in positive-valued data sets. Although approximate, CVs can indicate the relative variability of certain data, especially with small sample sizes and in the absence of other formal tests (*e.g.*, see **Chapter 22**, when comparing confidence limits on the mean to a fixed standard in compliance monitoring).

The CV is also a valid measure of the multiplicative relationship between the population mean and the standard deviation for positively-valued random variables. Using sample statistics for the mean ($\bar{x}$) and standard deviation (s), the true CV for non-negative normal populations can be reasonably estimated as:

$$CV = s / \bar{x} \qquad [10.5]$$

In lognormal populations, the CV is also used in evaluations of statistical power. In this latter case, the population CV works out to be:

$$CV = \sqrt{\exp\left(\sigma_y^2\right) - 1} \qquad [10.6]$$

where σ_y is the population log-standard deviation. Instead of a ratio between the original scale standard deviation and the mean, the lognormal CV is estimated with the equation:

$$CV = \sqrt{\exp\left(s_y^2\right) - 1} \qquad [10.7]$$

where s_y is the sample log-standard deviation. The estimate in equation [10.7] is usually more accurate than the simple CV ratio of the arithmetic standard deviation-to-mean, especially when the underlying population coefficient of variation is high. Similar to using the normal CV as a formal indicator of normality, the lognormal coefficient of variation estimator in equation [10.7] will have little relevance *as a test of lognormality* of the data. Using it for that purpose is not recommended in the Unified Guidance. But it can provide a sense of how variable a data set is and whether a lognormal assumption might need to be tested.

While others have reported a ratio CV on logged measurements as $CV = s_y / \bar{y}$ for the transformation $y = \log x$, the result is essentially meaningless. The actual logarithmic CV in equations [10.6] and [10.7] is solely determined by the logarithmic variability of σ_y or s_y. Negative logarithmic mean values are always possible, and the log ratio statistic is not invariant under a unit scale

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transformation (*e.g.*, ppb to ppm or ppt). Similar problems in interpretation occur when CV estimators are applied to any variable which can be negatively valued, such as following a *z*-transformation to a standard normal distribution. This log ratio statistic is not recommended for any application in the guidance.

The coefficient of skewness (γ_1) directly indicates to what degree a dataset is skewed or asymmetric with respect to the mean. Sample data from a normal distribution will have a skewness coefficient near zero, while data from an asymmetric distribution will have a positive or negative skewness depending on whether the right- or left-hand tail of the distribution is longer and skinnier than the opposite tail.

Since groundwater monitoring concentrations are inherently non-negative, such data often exhibit skewness. A small degree of skewness is not likely to affect the results of statistical tests that assume normality. However, if the skewness coefficient is larger than 1 (in absolute value) and the sample size is small (*e.g.*, $n < 25$), past research has shown that standard normal theory-based tests are much less powerful than when the absolute skewness is less than 1 (Gayen, 1949).

Calculating the skewness coefficient is useful and only slightly more difficult than computing the CV. It provides a quick indication of whether the skewness is minimal enough to assume that the data are roughly symmetric and hopefully normal in distribution. If the original data exhibit a high skewness coefficient, the normal distribution will provide a poor approximation to the dataset. In that case — and unlike the CV — γ_1 can be computed on the log-transformed data to test for symmetry of the logged measurements, or similarly for other transformations.

PROCEDURE

The CV is calculated simply by taking the ratio of the sample standard deviation to the sample mean, $CV = s/\bar{x}$ or its corresponding logarithmic version $CV = \sqrt{\exp\left(s_y^2\right) - 1}$.

The skewness coefficient may be computed using the following equation:

$$\gamma_1 = \frac{1}{n}\sum_{i=1}^{n}\left(x_i - \bar{x}\right)^3 \Bigg/ \left[\frac{1}{n}\sum_{i=1}^{n}\left(x_i - \bar{x}\right)^2\right]^{3/2} = n^{1/2}\sum_{i=1}^{n}\left(x_i - \bar{x}\right)^3 \Bigg/ \left(n-1\right)^{3/2} s^3 \qquad [10.8]$$

where the numerator represents the average cubed residual after subtracting the sample mean.

►EXAMPLE 10-1

Using the following data, compute the CVs and the coefficient of skewness to test for approximate symmetry. Assume that the individual well data sets can be shown to arise from a single common population distribution:

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Month	Nickel Concentration (ppb)			
	Well 1	Well 2	Well 3	Well 4
Jan	58.8	19	39	3.1
Mar	1.0	81.5	151	942
Jun	262	331	27	85.6
Aug	56	14	21.4	10
Oct	8.7	64.4	578	637

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SOLUTION

Step 1. Compute the mean, standard deviation (s), and sum of the cubed residuals for the nickel concentrations:

$$\bar{x} = \frac{1}{20}(58.8+1+\ldots+637)=169.52 \; ppb$$

$$s=\sqrt{\frac{1}{19}\left[(58.8-169.52)^2+(1-169.52)^2+\ldots+(637-169.52)^2\right]} = 259.7175 \; ppb$$

$$\sum_{i=1}^{n}(x_i-\bar{x})^3 = \left[(58.8-169.52)^3+\ldots+(637-169.52)^3\right]=5.97845791\times10^8 \; ppb^3$$

Step 2. Compute the arithmetic normal coefficient of variation following equation [10.5]: $CV = 259.7175/169.52 = 1.53$

Step 3. Calculate the coefficient of skewness using equation [10.8]:

$$\gamma_1 = (20)^{1/2}\left(5.97845791\times10^8\right)/(19)^{3/2}(259.7175)^3 = 1.84$$

Both the CV and the coefficient of skewness are much larger than 1, so the data appear to be significantly positively skewed. Do not assume that the underlying population is normal.

Step 4. Since the original data evidence a high degree of skewness, one can instead compute the skewness coefficient and corresponding sample CV with equation [10.7] on the logged nickel concentrations. The logarithmic CV equals 4.97, a much more variable data set than suggested by the arithmetic CV. The skewness coefficient works out to be $|\gamma_1| = 0.24 < 1$, indicating that the logged data values are slightly skewed but not enough to clearly reject an assumption of normality in the logged data. In other words, the original nickel values may be lognormally distributed. ◄

10.5 SHAPIRO-WILK AND SHAPIRO-FRANCÍA NORMALITY TESTS

10.5.1 SHAPIRO-WILK TEST (N ≤ 50)

PURPOSE AND BACKGROUND

The Shapiro-Wilk test is based on the premise that if a data set is normally distributed, the ordered values should be highly correlated with corresponding *quantiles* (*z*-scores) taken from a normal distribution (Shapiro and Wilk, 1965). In particular, the Shapiro-Wilk test gives substantial weight to evidence of non-normality in the tails of a distribution, where the robustness of statistical tests based on the normality assumption is most severely affected. A variant of this test, the Shapiro-Francía test, is useful for sample sizes greater than 50 (see **Section 10.5.2**).

The Shapiro-Wilk test statistic (*SW*) will tend to be large when a probability plot of the data indicates a nearly straight line. Only when the plotted data show significant bends or curves will the test statistic be small. The Shapiro-Wilk test is considered one of the best tests of normality available (Miller, 1986; Madansky, 1988).

PROCEDURE

Step 1. Order and rank the dataset from least to greatest, labeling the observations as x_i for rank i = 1…n. Using the notation $x_{(i)}$, let the ith rank statistic from a data set represent the ith smallest value.

Step 2. Compute differences $\left[x_{(n-i+1)} - x_{(i)} \right]$ for each i = 1…n. Then determine k as the greatest integer less than or equal to (n/2).

Step 3. Use **Table 10-2** in **Appendix D** to determine the Shapiro-Wilk coefficients, a_{n-i+1} , for i = 1…k. Note that while these coefficients depend only on the sample size (n), the order of the coefficients must be preserved when used in Step 4. The coefficients can be determined for any sample size from n = 3 up to n = 50.

Step 4. Compute the quantity b given by the following equation:

$$b = \sum_{i=1}^{k} b_i = \sum_{i=1}^{k} a_{n-i+1}(x_{(n-i+1)} - x_{(i)}) \qquad [10.9]$$

Note that the values b_i are simply intermediate quantities represented by the terms in the sum of the right-hand expression in equation [10.9].

Step 5. Calculate the standard deviation (s) of the dataset. Then compute the Shapiro-Wilk test statistic using the equation:

$$SW = \left[\frac{b}{s\sqrt{n-1}} \right]^2 \qquad [10.10]$$

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Step 6. Given the significance level (α) of the test, determine the critical point of the Shapiro-Wilk test with n observations using **Table 10-3** in **Appendix D**. To maximize the utility and power of the test, choose $\alpha = .10$ for very small data sets ($n < 10$), $\alpha = .05$ for moderately sized data sets ($10 \leq n < 20$), and $\alpha = .01$ for larger sized data sets ($n \geq 20$). Compare the SW against the critical point (sw_c). If the test statistic exceeds the critical point, accept normality as a reasonable model for the underlying population. However, if $SW < sw_c$, reject the null hypothesis of normality at the α-level and decide that another distributional model might provide a better fit.

►EXAMPLE 10-2

Use the nickel data of **Example 10-1** to compute the Shapiro-Wilk test of normality.

SOLUTION

Step 1. Order the data from smallest to largest, rank in ascending order and list, as shown in columns 1 and 2 of the table below. Next list the data in reverse order in a third column.

i	$x_{(i)}$	$x_{(n-i+1)}$	$x_{(n-i+1)} - x_{(i)}$	a_{n-i+1}	b_i
1	1.0	942.0	941.0	.4734	445.47
2	3.1	637.0	633.9	.3211	203.55
3	8.7	578.0	569.3	.2565	146.03
4	10.0	331.0	321.0	.2085	66.93
5	14.0	262.0	248.0	.1686	41.81
6	19.0	151.0	132.0	.1334	17.61
7	21.4	85.6	64.2	.1013	6.50
8	27.0	81.5	54.5	.0711	3.87
9	39.0	64.4	25.4	.0422	1.07
10	56.0	58.8	2.8	.0140	0.04
11	58.8	56.0	−2.8		b = 932.88
12	64.4	39.0	−25.4		
13	81.5	27.0	−54.5		
14	85.6	21.4	−64.2		
15	151.0	19.0	−132.0		
16	262.0	14.0	−248.0		
17	331.0	10.0	−321.0		
18	578.0	8.7	−569.3		
19	637.0	3.1	−633.9		
20	942.0	1.0	−941.0		

Step 2. Compute the differences $\left[x_{(n-i+1)} - x_{(i)} \right]$ in column 4 of the table by subtracting column 2 from column 3. Since the total sample size is $n = 20$, the largest integer less than or equal to (n/2) is $k = 10$.

Step 3. Look up the coefficients a_{n-i+1} from **Table 10-2** in **Appendix D** and list in column 4.

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Step 4. Multiply the differences in column 3 by the coefficients in column 4 and add the first k products (b_i) to get quantity b, using equation [10.9].

$$b = [.4734(941.0) + .3211(633.9) + \ldots + .0140(2.8)] = 932.88$$

Step 5. Compute the standard deviation of the sample, s = 259.72. Then use equation [10.10] to calculate the SW:

$$SW = \left[\frac{932.88}{259.72\sqrt{19}} \right]^2 = 0.679$$

Step 6. Use **Table 10-3** in **Appendix D** to determine the 0.01-level critical point for the Shapiro-Wilk test when n = 20. This gives sw_c = 0.868. Then compare the observed value of SW = 0.679 to the 1% critical point. Since SW < 0.868, the sample shows significant evidence of non-normality by the Shapiro-Wilk test. The data should be transformed using logarithms or another transformation on the ladder of powers and re-checked using the Shapiro-Wilk test before proceeding with further statistical analysis. ◄

10.5.2 SHAPIRO-FRANCÍA TEST (N > 50)

The Shapiro-Wilk test of normality can be used for sample sizes up to 50. When n is larger than 50, a slight modification of the procedure called the Shapiro-Francía test (Shapiro and Francia, 1972) can be used instead. Like the Shapiro-Wilk test, the Shapiro-Francía test statistic (SF) will tend to be large when a probability plot of the data indicates a nearly straight line. Only when the plotted data show significant bends or curves will the test statistic be small.

To calculate the test statistic SF, one can use the following equation:

$$SF = \left[\sum_{i=1}^{n} m_i x_{(i)} \right]^2 \Bigg/ \left[(n-1) s^2 \sum_{i=1}^{n} m_i^2 \right] \qquad [10.11]$$

where $x_{(i)}$ represents the ith ranked value of the sample and where m_i denotes the approximate expected value of the ith rank normal quantile (or z-score). The values for m_i are approximately equal to

$$m_i = \Phi^{-1}\left(\frac{i}{n+1} \right) \qquad [10.12]$$

where Φ^{-1} denotes the inverse of the standard normal distribution with zero mean and unit variance. These values can be computed by hand using the normal distribution in **Table 10-1** of **Appendix D** or via simple commands found in many statistical computer packages.

Normality of the data should be rejected if the Shapiro-Francía statistic is too low when compared to the critical points provided in **Table 10-4** of **Appendix D**. Otherwise one can assume the data are approximately normal for purposes of further statistical analysis.

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10.6 PROBABILITY PLOT CORRELATION COEFFICIENT

BACKGROUND AND PURPOSE

Another test for normality that is essentially equivalent to the Shapiro-Wilk and Shapiro-Francía tests is the *probability plot correlation coefficient* test described by Filliben (1975). This test meshes perfectly with the use of probability plots, because the essence of the test is to compute the usual *correlation coefficient* for points on a probability plot. Since the correlation coefficient is a measure of the linearity of the points on a scatterplot, the probability plot correlation coefficient, like the *SW* test statistic, will be high when the plotted points fall along a straight line and low when there are significant bends and curves in the probability plot. Comparison of the Shapiro-Wilk and probability plot correlation coefficient tests has indicated very similar statistical power for detecting non-normality (Ryan and Joiner, 1990).

It should be noted that although some statistical software may not compute Filliben's test directly, the usual Pearson's correlation coefficient computed on the data pairs used to construct a probability plot will provide a very close approximation to the Filliben statistic. Some users may find this latter correlation easier to compute or more accessible in their software.

PROCEDURE

Step 1. List the observations in order from smallest to largest, denoting $x_{(i)}$ as the ith smallest rank statistic in the data set. Then let n = sample size and compute the sample mean ($\bar{x}$) and the standard deviation (s).

Step 2. Consider a random sample drawn from a standard normal distribution. The ith rank statistic of this sample is fixed once the sample is drawn, but beforehand it can be considered a random variable, denoted as $X_{(i)}$. Likewise, by considering all possible datasets of size n that might be drawn from the normal distribution, one can think of the sampling distribution of the statistic $X_{(i)}$. This sampling distribution has its own mean and variance, and, of importance to the probability plot correlation coefficient, its own *median*, which can be denoted M_i.

To compute the median of the ith rank statistic, first compute intermediate probabilities m_i for $i = 1 \ldots n$ using the equation:

$$m_i = \begin{cases} 1-(.5)^{1/n} & \text{for } i = 1 \\ (i-.3175)/(n+.365) & \text{for } 1 < i < n \\ (.5)^{1/n} & \text{for } i = n \end{cases} \qquad [10.13]$$

Then compute the medians M_i as the standard normal quantiles or z-scores associated with the intermediate probabilities m_i. These can be determined from **Table 10-1** in **Appendix D** or computed according to the following equation, where Φ^{-1} represents the inverse of the standard normal distribution:

$$M_i = \Phi^{-1}(m_i) \qquad [10.14]$$

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Step 3. With the rank statistic medians in hand, calculate the arithmetic mean of the M_i's, denoted $\bar{M}$, and the intermediate quantity C_n, given by the equation:

$$C_n = \sqrt{\sum_{i=1}^{n} M_i^2 - n\bar{M}^2} \qquad [10.15]$$

Note that when the dataset is "complete" (meaning it contains no non-detects, ties, or censored values), the mean of the order statistic medians reduces to $\bar{M} = 0$. This in turn reduces the calculation of C_n to:

$$C_n = \sqrt{\sum_{i=1}^{n} M_i^2} \qquad [10.16]$$

Step 4. Finally compute Filliben's probability plot correlation coefficient:

$$r = \frac{\sum_{i=1}^{n} x_{(i)} M_i - n\bar{x}\bar{M}}{C_n \cdot s\sqrt{n-1}} \qquad [10.17]$$

When the dataset is complete, the equation for the probability plot correlation coefficient also has a simplified form:

$$r = \sum_{i=1}^{n} x_{(i)} M_i \Big/ \left[C_n \cdot s\sqrt{n-1} \right] \qquad [10.18]$$

Step 5. Given the level of significance (α), determine the critical point (r_{cp}) for Filliben's test with sample size n from **Table 10-5** in **Appendix D**. Compare the probability plot correlation coefficient (r) against the critical point (r_{cp}). If $r \geq r_{cp}$, conclude that normality is a reasonable model for the underlying population at the α-level of significance. If, however, $r < r_{cp}$, reject the null hypothesis and conclude that another distributional model would provide a better fit.

►EXAMPLE 10-3

Use the data of **Example 10-1** to compute Filliben's probability plot correlation coefficient test at the $\alpha = .01$ level of significance.

SOLUTION

Step 1. Order and rank the nickel data from smallest to largest and list, as in the table below. The sample size is $n = 20$, with sample mean $\bar{x} = 169.52$ and the standard deviation $s = 259.72$.

Step 2. Compute the intermediate probabilities m_i from equation [10.13] for each i in column 3 and the rank statistic medians, M_i, in column 4 by applying the inverse normal transformation to column 3 using equation [10.14] and **Table 10-1** of **Appendix D**.

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Step 3. Since this sample contains no non-detects or ties, the simplified equations for C_n in equation [10.16] and for r in equation [10.18] may be used. First compute C_n using the squared order statistic medians in column 5:

$$C_n = \sqrt{[3.328 + 1.926 + \ldots + 3.328]} \quad = \quad 4.138$$

Step 4. Next compute the products $x_{(i)} \times M_i$ in column 6 and sum to get the numerator of the correlation coefficient (equal to 3,836.81 in this case). Then compute the final correlation coefficient:

$$r = 3{,}836.81 \Big/ \left[4.138 \times 259.72\sqrt{19} \right] = 0.819$$

i	$x_{(i)}$	m_i	M_i	$(M_i)^2$	$x_{(i)} \times M_i$
1	1.0	.03406	−1.8242	3.328	−1.824
2	3.1	.08262	−1.3877	1.926	−4.302
3	8.7	.13172	−1.1183	1.251	−9.729
4	10.0	.18082	−0.9122	0.832	−9.122
5	14.0	.22993	−0.7391	0.546	−10.347
6	19.0	.27903	−0.5857	0.343	−11.129
7	21.4	.32814	−0.4451	0.198	−9.524
8	27.0	.37724	−0.3127	0.098	−8.444
9	39.0	.42634	−0.1857	0.034	−7.242
10	56.0	.47545	−0.0616	0.004	−3.448
11	58.8	.52455	0.0616	0.004	3.621
12	64.4	.57366	0.1857	0.034	11.959
13	81.5	.62276	0.3127	0.098	25.488
14	85.6	.67186	0.4451	0.198	38.097
15	151.0	.72097	0.5857	0.343	88.445
16	262.0	.77007	0.7391	0.546	193.638
17	331.0	.81918	0.9122	0.832	301.953
18	578.0	.86828	1.1183	1.251	646.376
19	637.0	.91738	1.3877	1.926	883.941
20	942.0	.96594	1.8242	3.328	1718.408

Step 5. Compare Filliben's test statistic of $r = 0.819$ to the 1% critical point for a sample of size 20 in **Table 10-5** of **Appendix D**, namely $r_{cp} = 925$. Since $r < 0.925$, the sample shows significant evidence of non-normality by the probability plot correlation coefficient. The data should be transformed and the correlation coefficient re-calculated before proceeding with further statistical analysis. ◄

10.7 SHAPIRO-WILK MULTIPLE GROUP TEST OF NORMALITY

BACKGROUND AND PURPOSE

The main purpose for including the multiple group test normality (Wilk and Shapiro, 1968) in the Unified Guidance is to serve as a check for normality when using a Student's *t*-test (**Chapter 16**) or

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when assessing the joint normality of multiple intrawell data sets. The multiple group test is an extension of the Shapiro-Wilk procedure for assessing the joint normality of several independent samples. Each sample may have a different mean and/or variance, but as long as the underlying distribution of each group is normal, the multiple group test statistic will tend to be non-significant. Conversely, the multiple group test is designed to identify when at least one of the groups being tested is definitely non-normal.

This test extends the Shapiro-Wilk procedure for a single sample, using individual *SW* test statistics computed separately for each group or sample. Then the individual *SW* statistics are transformed and combined into an overall or "omnibus" statistic (*G*). Like the single sample procedure — where non-normality is indicated when the test statistic *SW* is too low — non-normality in one or more groups is indicated when *G* is too low. However, instead of a special table of critical points, *G* is constructed to follow a standard normal distribution under the null hypothesis of normality. The value of *G* can simply be compared to an α-level *z*-score or normal quantile to decide whether the null or alternative hypothesis is better supported.

Since it may be unclear which one or more of the groups is actually non-normal when the *G* statistic is significant, Wilk and Shapiro recommend that a probability plot (**Chapter 9**) be examined on the intermediate quantities, G_i (at least for the case where several groups are being simultaneously tested). One of these statistics is computed for each separate sample/group and is designed to follow a standard normal distribution under H_0. Because of this, the G_i statistics for non-normal groups will tend to look like outliers on a normal probability plot (see **Chapter 12**).

The multiple group test can also be used to check normality when performing Welch's *t*-test, a two-sample procedure in which the underlying data of both groups are assumed to be normal, but no assumption is made that the means or variances are the same. This is different from either the pooled variance *t*-test or the one-way analysis of variance [ANOVA], both of which assume *homoscedasticity* (*i.e.*, equal variances across groups). If the group variances can be shown to be equal, the single sample Shapiro-Wilk test can be run on the combined residuals, where the residuals of each group are formed by subtracting off the group mean from each of the individual measurements. However, if the group variances are possibly different, testing the residuals as a single group using the *SW* statistic may give an inaccurate or misleading result. Consequently, since a test of homoscedasticity is not required for Welch's *t*-test, it is suggested to first use the multiple group test to check normality.

Although the Shapiro-Wilk multiple group method is an attractive procedure for accommodating several groups of data at once, the user is cautioned against indiscriminate use. While many of the methods described in the Unified Guidance assume underlying normality, they also assume homoscedasticity. Other parametric multi-sample methods recommended for detection monitoring — prediction limits in **Chapter 18** and control charts in **Chapter 20** — all assume that each group has the same variance. Even if normality of the joint data can be demonstrated using the Shapiro-Wilk multiple group test, it says nothing about whether the assumption of equal variances is also satisfied. Generally speaking, except for Welch's *t*-test, a separate test of homoscedasticity may also be needed. Such tests are described in **Chapter 11**.

PROCEDURE

Step 1. Assuming there are *K* groups to be tested, let the sample size of the *i*th group be denoted n_i. Then compute the SW_i test statistic for each of the *K* groups using equation [10.10].

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Step 2. Transform the SW_i statistics to the intermediate quantities (G_i). If the sample size (n_i) of the ith group is at least 7, compute G_i with the equation:

$$G_i = \gamma + \delta \ln\left(\frac{SW_i - \varepsilon}{1 - SW_i}\right) \quad [10.19]$$

where the quantities γ, δ, and ε can be found in **Table 10-6** of **Appendix D** for $7 \le n_i \le 50$. If the sample size (n_i) is less than 7, determine G_i directly from **Table 10-7** in **Appendix D** by first computing the intermediate value

$$u_i = \ln\left(\frac{SW_i - \varepsilon}{1 - SW_i}\right) \quad [10.20]$$

(obtaining ε from the top of **Table 10-7**), and then using linear interpolation to find the closest value G_i associated with u_i.

Step 3. Once the G_i statistics are derived, compute the Shapiro-Wilk multiple group statistic with the equation:

$$G = \frac{1}{\sqrt{K}} \sum_{i=1}^{K} G_i \quad [10.21]$$

Step 4. Under the null hypothesis that all K groups are normally-distributed, G will follow a standard normal distribution. Given the significance level (α), determine an α-level critical point from **Table 10-1** of **Appendix D** as the *lower* $\alpha \times 100th$ normal quantile (z_α). Then compare G to z_α. If $G < z_\alpha$, there is significant evidence of non-normality at the α level. Otherwise, the hypothesis of normality cannot be rejected.

►EXAMPLE 10-4

The previous examples in this chapter pooled the data of **Example 10-1** into a single group before testing for normality. This time, treat each well separately and compute the Shapiro-Wilk multiple group test of normality at the $\alpha = .05$ level.

SOLUTION

Step 1. The nickel data in **Example 10-1** come from $K = 4$ wells with $n_i = 5$ observations per well. Using equation [10.10], the SW_i individual well test statistics are calculated as:

Well 1: $SW_1 = 0.7577$

Well 2: $SW_2 = 0.7396$

Well 3: $SW_3 = 0.7065$

Well 4: $SW_4 = 0.8149$

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Step 2. Since $n_i = 5$ for each well, use **Table 10-7** of **Appendix D** to find $\varepsilon = .5521$. First calculating u_1 with equation [10.20]:

$$u_1 = \ln\left(\frac{.7577-.5521}{1-.7577}\right) = -.1641$$

Then performing this step for each well group and using linear interpolation on u in **Table 10-7**, the approximate G_i statistics are:

Well 1: $u_1 = -.1641$ $G_1 = -1.783$

Well 2: $u_2 = -.3280$ $G_2 = -1.932$

Well 3: $u_3 = -.6425$ $G_3 = -2.200$

Well 4: $u_4 = .3502$ $G_4 = -1.254$

Step 3. Compute the multiple group test statistic using equation [10.21]:

$$G = \frac{1}{\sqrt{4}}[(-1.783)+(-1.932)+(-2.200)+(-1.254)] = -3.585$$

Step 4. Since $\alpha = 0.05$, the lower $\alpha \times 100th$ critical point from the standard normal distribution in **Table 10-1** of **Appendix D** is $z_{.05} = -1.645$. Clearly, $G < z_{.05}$; in fact G is equivalent to a Z-value probability of .0002. Thus, there is significant evidence of non-normality in at least one of these wells (and perhaps all of them). ◄

►EXAMPLE 10-5

The data in **Example 10-1** showed significant evidence of non-normality. In this example, use the same nickel data applying the coefficient of skewness, Shapiro-Wilk and the Probability Plot Correlation Coefficient tests to determine whether the combined well measurements better follow a lognormal distribution by first log-transforming the measurements. Computing the natural logarithms of the data gives the table below:

	Logged Nickel Concentrations log(ppb)			
Month	Well 1	Well 2	Well 3	Well 4
1	4.07	2.94	3.66	1.13
2	0.00	4.40	5.02	6.85
3	5.57	5.80	3.30	4.45
4	4.03	2.64	3.06	2.30
5	2.16	4.17	6.36	6.46

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SOLUTION

METHOD 1. COEFFICIENT OF SKEWNESS

Step 1. Compute the log-mean ($\bar{y}$), log-standard deviation (s_y), and sum of the cubed residuals for the logged nickel concentrations (y_i):

$$\bar{y} = \frac{1}{20}(4.07 + 0.00 + \ldots + 6.46) \quad = \quad 3.918 \log(ppb)$$

$$s_y \quad = \quad \sqrt{\frac{1}{19}\left[(4.07 - 3.918)^2 + (0.00 - 3.918)^2 + \ldots + (6.46 - 3.918)^2\right]} \quad = \quad 1.8014 \log(ppb)$$

$$\sum_{i=1}^{n}\left(y_i - \bar{y}\right)^3 \quad = \quad \left[(4.07 - 3.918)^3 + \ldots + (6.46 - 3.918)^3\right] = -26.528 \log^3(ppb)$$

Step 2. Calculate the coefficient of skewness using equation [10.8] with Step 1 values as:

$$\gamma_1 = (20)^{1/2}(-26.528)\Big/(19)^{3/2}(1.8014)^3 = -0.245$$

Since the absolute value of the skewness is less than 1, the data do not show evidence of significant skewness. Applying a normal distribution to the log-transformed data may therefore be appropriate, but this model should be further checked. The logarithmic CV of 4.97 computed in Example 10-1 was also suggestive of a highly skewed distribution, but can be difficult to interpret in determining if measurements, in fact, follow a logarithmic distribution.

METHOD 2. SHAPIRO-WILK TEST

Step 1. Order and rank the data from smallest to largest and list, as in the table below. List the data in reverse order alongside the first column. Denote the *i*th logged observation by $y_i = \log(x_i)$.

Step 2. Compute differences $\left[y_{(n-i+1)} - y_{(i)}\right]$ in column 4 of the table by subtracting column 2 from column 3. Since $n = 20$, the largest integer less than or equal to $(n/2)$ is $k = 10$.

Step 3. Look up the coefficients a_{n-i+1} from **Table 10-2** of **Appendix D** and list in column 5.

Step 4. Multiply the differences in column 4 by the coefficients in column 5 and add the first k products (b_i) to get quantity b, using equation [10.9].

$$b = [.4734(6.85) + .3211(5.33) + \ldots + .0140(.04)] = 7.77$$

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i	$y_{(i)}$	$y_{(n-i+1)}$	$y_{(n-i+1)} - y_{(i)}$	a_{n-i+1}	b_i
1	0.00	6.85	6.85	.4734	3.24
2	1.13	6.46	5.33	.3211	1.71
3	2.16	6.36	4.20	.2565	1.08
4	2.30	5.80	3.50	.2085	0.73
5	2.64	5.57	2.93	.1686	0.49
6	2.94	5.02	2.08	.1334	0.28
7	3.06	4.45	1.39	.1013	0.14
8	3.30	4.40	1.10	.0711	0.08
9	3.66	4.17	0.51	.0422	0.02
10	4.03	4.07	0.04	.0140	0.00
11	4.07	4.03	−0.04		b = 7.77
12	4.17	3.66	−0.51		
13	4.40	3.30	−1.10		
14	4.45	3.06	−1.39		
15	5.02	2.94	−2.08		
16	5.57	2.64	−2.93		
17	5.80	2.30	−3.50		
18	6.36	2.16	−4.20		
19	6.46	1.13	−5.33		
20	6.85	0.00	−6.85		

Step 5. Compute the log-standard deviation of the sample, $s_y = 1.8014$. Then use [10.10] to calculate the *SW* test statistic:

$$SW = \left[\frac{7.77}{1.8014\sqrt{19}}\right]^2 = 0.979$$

Step 6. Use **Table 10-3** of **Appendix D** to determine the .01-level critical point for the Shapiro-Wilk test when $n = 20$. This gives $sw_{cp} = 0.868$. Then compare the observed value of $SW = 0.979$ to the 1% critical point. Since $SW > 0.868$, the sample shows no significant evidence of non-normality by the Shapiro-Wilk test. Proceed with further statistical analysis using the log-transformed data or by assuming the underlying population is lognormal.

METHOD 3. PROBABILITY PLOT CORRELATION COEFFICIENT

Step 1. Order and rank the logged nickel data from smallest to largest and list, as in the table below. Again let the *i*th logged value be denoted by $y_i = \log(x_i)$. The sample size is $n = 20$, the log-mean is $\bar{y} = 3.918$, and the log-standard deviation is $s_y = 1.8014$.

Step 2. Compute the intermediate probabilities m_i from equation [10.13] for each *i* in column 3 and the rank statistic medians, M_i , in column 4 by applying the inverse normal transformation to column 3 using equation [10.14] and **Table 10-1** of **Appendix D**.

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i	$y_{(i)}$	m_i	M_i	$(M_i)^2$	$y_{(i)} \times M_i$
1	0.00	.03406	−1.8242	3.328	0.000
2	1.13	.08262	−1.3877	1.926	−1.568
3	2.16	.13172	−1.1183	1.251	−2.416
4	2.30	.18082	−0.9122	0.832	−2.098
5	2.64	.22993	−0.7391	0.546	−1.951
6	2.94	.27903	−0.5857	0.343	−1.722
7	3.06	.32814	−0.4451	0.198	−1.362
8	3.30	.37724	−0.3127	0.098	−1.032
9	3.66	.42634	−0.1857	0.034	−0.680
10	4.03	.47545	−0.0616	0.004	−0.248
11	4.07	.52455	0.0616	0.004	0.251
12	4.17	.57366	0.1857	0.034	0.774
13	4.40	.62276	0.3127	0.098	1.376
14	4.45	.67186	0.4451	0.198	1.981
15	5.02	.72097	0.5857	0.343	2.940
16	5.57	.77007	0.7391	0.546	4.117
17	5.80	.81918	0.9122	0.832	5.291
18	6.36	.86828	1.1183	1.251	7.112
19	6.46	.91738	1.3877	1.926	8.965
20	6.85	.96594	1.8242	3.328	12.496

Step 3. Since this sample contains no non-detects or ties, the simplified equations for C_n in [10.16] and for r in [10.18] may be used. First compute C_n using the squared order statistic medians in column 5:

$$C_n = \sqrt{[3.328 + 1.926 + \ldots + 3.328]} \quad = \quad 4.138$$

Step 4. Next compute the products $y_{(i)} \times M_i$ in column 6 and sum to get the numerator of the correlation coefficient (equal to 32.226 in this case). Then compute the final correlation coefficient:

$$r = 32.226 \Big/ \left[4.138 \times 1.8014 \sqrt{19} \right] = 0.992$$

Step 5. Compare the Filliben's test statistic of $r = 0.992$ to the 1% critical point for a sample of size 20 in **Table 10-5** in **Appendix D**, namely $r_{cp} = 925$. Since $r > 0.925$, the sample shows no significant evidence of non-normality by the probability plot correlation coefficient test. Therefore, lognormality of the original data can be assumed in subsequent statistical procedures.

Note: the Shapiro-Wilk and Filliben's Probability Plot Correlation Coefficient tests for normality on a single data set perform quite comparably. Only one of these tests need be run in routine applications. ◄

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CHAPTER 11. TESTING EQUALITY OF VARIANCE

11.1 BOX PLOTS 11-2
11.2 LEVENE'S TEST 11-4
11.3 MEAN-STANDARD DEVIATION SCATTER PLOT 11-8

Many of the methods described in the Unified Guidance assume that the different groups under comparison have the same variance (***i.e.***, are ***homoscedastic***). This chapter covers procedures for assessing homoscedasticity and its counterpart, ***heteroscedasticity*** (***i.e.***, unequal variances). Equality of variance is assumed, for instance, when using prediction limits to make either upgradient-to-downgradient or intrawell comparisons. In the former case, the method assumes that the upgradient variance is equal to the variance in each downgradient well. In the latter case, the presumption is that the well variance is stable over time (***i.e.***, stationary) when comparing intrawell background versus more recent measurements.

If a prediction limit is constructed on a single new measurement at each downgradient well, it isn't feasible to test the variance equality assumption prior to each statistical evaluation. Homoscedasticity ***can*** be tested after several new rounds of compliance sampling by pooling collected compliance measurements within a well. The Unified Guidance recommends periodic testing of the presumption of equal variances by comparing newer data to historical background (**Chapter 6**).

Equality of variance between different groups (***e.g.***, different wells) is also an important assumption for an analysis of variance [ANOVA]. If equality of variance does not hold, the power of the *F*-test (its ability to detect differences among the group means) is reduced. Mild differences in variance are generally acceptable. But the effect becomes noticeable when the largest and smallest group variances differ by a ratio of about 4, and becomes quite severe when the ratio is 10 or more (Milliken and Johnson, 1984).

Three procedures for assessing or testing homogeneity of variance are described in the Unified Guidance, two of which that are more robust to departures from normality (***i.e.***, less sensitive to non-normality). These include:

1. The box plot (**Chapter 9**), a graphical method useful not only for checking equality of variance but also as an exploratory tool for visualizing the basic statistical characteristics of data sets. It can also provide a rough indication of differences in mean or median concentration levels across several wells;
2. Levene's test (**Section 11.2**), a formal ANOVA-type procedure for testing variance inequality; and
3. The mean-standard deviation scatter plot (**Chapter 9** and **Section 11.3**), a visual tool for assessing whether the degree of variability in a set of data groups or wells is correlated with the mean levels for those groups. This could potentially indicate whether a ***variance stabilizing transformation*** might be needed.

11.1 BOX PLOTS

PURPOSE AND BACKGROUND

Box plots are described in **Chapter 9**. In the context of variance testing, one can construct a box plot for each well group and compare the boxes to see if the assumption of equal variances is reasonable. The comparison is not a formal test procedure, but is easier to perform and is often sufficient for checking the group variance assumption.

Box plots for each data group simultaneously graphed side-by-side provide a direct visual comparison of the dispersion in each group. As a rule of thumb, if the box length for each group is less than 1.5–2 times the length of the shortest box, the sample variances may be close enough to assume equal group variances. If the box length for any group is greater than 1.5–2 times the length of the box for another group, the variances may be significantly different. A formal test such as Levene's might be needed to more accurately decide. Sample data sets with unequal variances may need a ***variance stabilizing transformation, i.e.***, one in which the transformed measurements have approximately equal variances.

Most statistical software packages will calculate the statistics needed to draw a box plot, and many will construct side-by-side box plots directly. Usually a box plot will also be shown with two "whiskers" extending from the edges of the box. These lines indicate either the positions of extreme minimum or maximum values in the data set. In Tukey's original formulation (Tukey, 1977), they indicate the most extreme lower and upper data points outside the box but falling within a distance of 1.5 times the interquartile range (that is, the length of the box) from either edge. The whiskers should generally *not* be used to approximate the overall variance under either formulation.

A convenient tactic when using box plots to screen for heteroscedasticity is to plot the *residuals* of each data group rather than the measurements themselves. This will line the boxes up at roughly a common level (close to zero), so that a visual comparison of box lengths is easier.

REQUIREMENTS AND ASSUMPTIONS

The requirements and assumptions for box plots are discussed in **Section 9.2.**

PROCEDURE

Step 1. For each of j wells or data groups, compute the sample mean of that group $\bar{x}_j$. Then compute the residuals (r_{ij}) for each group by subtracting the group mean from each individual measurement: $r_{ij} = x_{ij} - \bar{x}_j$.

Step 2. Use the procedure outlined in **Section 9.2** to create side-by-side box plots of the residuals formed in Step 1. Then compare the box lengths to check for possibly unequal variances.

►EXAMPLE 11-1

Construct box plots on the residuals for each of the following well groups to check for homoscedasticity.

	Arsenic Concentration (ppb)					
Month	Well 1	Well 2	Well 3	Well 4	Well 5	Well 6
1	22.9	2.0	2.0	7.8	24.9	0.3
2	3.1	1.2	109.4	9.3	1.3	4.8
3	35.7	7.8	4.5	25.9	0.8	2.8
4	4.2	52	2.5	2.0	27	1.2

SOLUTION

Step 1. Form the residuals for each well by subtracting the sample well mean from each observation, as shown in the table below.

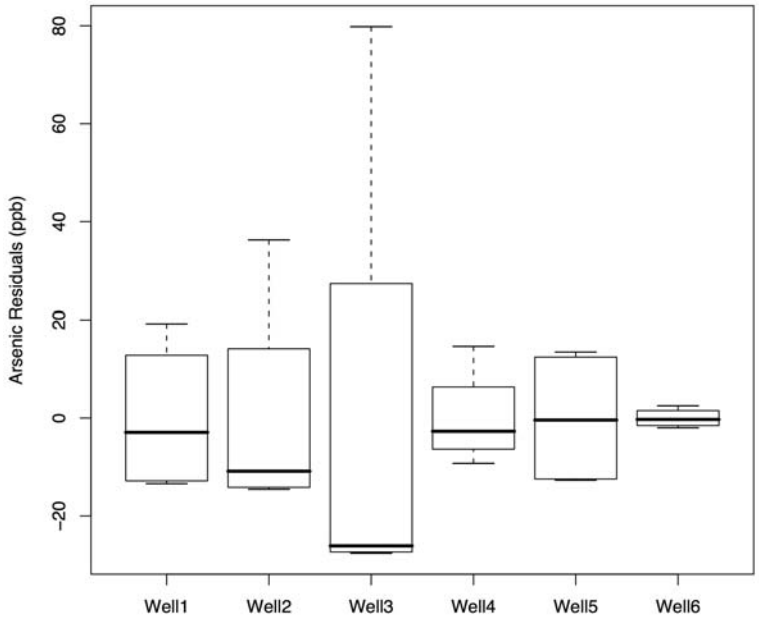
	Arsenic Residuals (ppb)					
Month	Well 1	Well 2	Well 3	Well 4	Well 5	Well 6
1	6.43	−13.75	−27.6	−3.45	11.4	−1.98
2	−13.38	−14.55	79.8	−1.95	−12.2	2.52
3	19.22	−7.95	−25.1	14.65	−12.7	0.52
4	−12.28	36.25	−27.1	−9.25	13.5	−1.08
Mean	16.48	15.75	29.6	11.25	13.5	2.28

Step 2. Follow the procedure in **Section 9.2** to compute a box plot of the residuals for each well. Line these up side by side on the same graph, as in **Figure 11-1**.

Step 3. Compare the box lengths. Since the box length for Well 3 is more than three times the box lengths of Wells 4 and 6, there is informal evidence that the population group variances may be different. These data should be further checked using a formal test and perhaps a variance stabilizing transformation attempted. ◄

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Figure 11-1. Side-by-Side Box Plots of Arsenic Residuals



11.2 LEVENE'S TEST

PURPOSE AND BACKGROUND

Levene's test is a formal procedure for testing homogeneity of variance that is fairly robust (i.e., not overly sensitive) to non-normality in the data. It is based on computing the new variables:

$$z_{ij} = \left| x_{ij} - \bar{x}_{i\bullet} \right| \qquad [11.1]$$

where x_{ij} represents the *j*th sample value from the *i*th group (*e.g.*, well) and $\bar{x}_{i\bullet}$ is the *i*th group sample mean. The symbol $(\bullet)$ in the notation for the group sample mean represents an averaging over subscript *j*. The values z_{ij} then represent the absolute values of the *residuals*. Levene's test involves running a standard one-way ANOVA (**Chapter 17**) on the variables z_{ij}. If the *F*-test is significant, reject the hypothesis of equal group variances and perhaps seek a variance stabilizing transformation. Otherwise, proceed with analysis of the original x_{ij}'s.

Levene's test is based on a one-way ANOVA and contrasts the means of the groups being tested. This implies a comparison between averages of the form:

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$$\bar{z}_i = \frac{1}{n_i}\sum_{j=1}^{n_i}\left|x_{ij} - \bar{x}_{i\bullet}\right| \qquad [11.2]$$

Such averages of the z_{ij}'s are very similar to the standard deviations of the original data groups, given by the formula:

$$s_i = \sqrt{\frac{1}{n_i - 1}\sum_{j=1}^{n_i}\left(x_{ij} - \bar{x}_{i\bullet}\right)^2} \qquad [11.3]$$

In both cases, the statistics are akin to an average absolute residual. Therefore, the comparison of means in Levene's test is closely related to a direct comparison of the group standard deviations, the underlying aim of any test of variance equality.

REQUIREMENTS AND ASSUMPTIONS

The requirements and assumptions for Levene's test are essentially the same as the one-way ANOVA in **Section 17.1**, but applied to the absolute residuals instead of the raw measurements.

PROCEDURE

Step 1. Suppose there are p data groups to be compared. Because there may be different numbers of observations per well, denote the sample size of the ith group by n_i and the total number of data points across all groups by N.

Denote the observations in the ith group by x_{ij} for $i = 1\ldots p$ and $j = 1\ldots n_i$. The first subscript then designates the well, while the second denotes the jth value in the ith well. After computing the sample mean ($\bar{x}_i$) for each group, calculate the absolute residuals (z_{ij}) using equation [11.1].

Step 2. Utilizing the absolute residuals — and not the original data — compute the mean of each group along with the overall (grand) mean of the combined data set using the formula:

$$\bar{z}_{\bullet\bullet} = \frac{1}{N}\sum_{i=1}^{p}\sum_{j=1}^{n_i} z_{ij} \qquad [11.4]$$

Step 3. Compute the sum of squares of differences between the group means and the grand mean, denoted SS_{grps}:

$$SS_{grps} = \sum_{i=1}^{p} n_i\left(\bar{z}_{i\bullet} - \bar{z}_{\bullet\bullet}\right)^2 = \sum_{i=1}^{p} n_i\bar{z}_{i\bullet}^2 - N\bar{z}_{\bullet\bullet}^2 \qquad [11.5]$$

The formula on the far right is usually the most convenient for calculation. This sum of squares has (p–1) degrees of freedom associated with it and is a measure of the variability *between* groups. It constitutes the numerator of the F-statistic.

Step 4. Compute the corrected total sum of squares, denoted by SS_{total}:

$$SS_{total} = \sum_{i=1}^{p}\sum_{j=1}^{n_i}\left(z_{ij} - \bar{z}_{\bullet\bullet}\right)^2 = \sum_{i=1}^{p}\sum_{j=1}^{n_i} z_{ij}^2 - N\bar{z}_{\bullet\bullet}^2 \quad [11.6]$$

Again, the formula on the far right is usually the most computationally convenient. This sum of squares has (N–1) associated degrees of freedom.

Step 5. Compute the sum of squares of differences between the absolute residuals and the group means. This is known as the within-groups component of the total sum of squares or, equivalently, as the sum of squares due to error. It is easiest to obtain by subtracting SS_{grps} from SS_{total} and is denoted SS_{error}:

$$SS_{error} = \sum_{i=1}^{p}\sum_{j=1}^{n_i}\left(z_{ij} - \bar{z}_{i\bullet}\right)^2 = SS_{total} - SS_{grps} = \sum_{i=1}^{p}\sum_{j=1}^{n_i} z_{ij}^2 - \sum_{i=1}^{p} n_i\bar{z}_{i\bullet}^2 \quad [11.7]$$

SS_{error} is associated with (N–p) degrees of freedom and is a measure of the variability *within* groups. This quantity goes into the denominator of the F-statistic.

Step 6. Compute the mean sum of squares for both the between-groups and within-groups components of the total sum of squares, denoted by MS_{grps} and MS_{error}. These quantities are obtained by dividing each sum of squares by its corresponding degrees of freedom:

$$MS_{grps} = SS_{grps}/\left(p-1\right) \quad [11.8]$$

$$MS_{error} = SS_{error}/\left(N-p\right) \quad [11.9]$$

Step 7. Compute the F-statistic by forming the ratio between the mean sum of squares for wells and the mean sum of squares due to error, as in **Figure 11-2** below. This layout is known as the one-way parametric ANOVA table and illustrates each sum of squares component of the total variability, along with the corresponding degrees of freedom, the mean squares components, and the final F-statistic calculated as $F = MS_{grps}/MS_{error}$. Note that the first two rows of the one-way table sum to the last row.

Step 8. **Figure 11-2** is a generalized ANOVA table for Levene's test. To test the hypothesis of equal variances across all p well groups, compare the F-statistic in **Figure 11-2** to the α-level critical point found from the F-distribution with (p–1) and (N–p) degrees of freedom in **Appendix D Table 17-1**. When testing variance equality, only severe levels of difference typically impact test performance in a substantial way. For this reason, the Unified Guidance recommends setting α = .01 when screening multiple wells and/or constituents using Levene's test. In that case, the needed critical point equals the upper 99th percentage point of the F-distribution. If the observed F-statistic exceeds the critical point ($F_{.99,p-1,N-p}$), reject the hypothesis of equal group population variances. Otherwise, conclude that there is insufficient evidence of a significant difference between the variances.

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Figure 11-2. ANOVA Table for Levene's Test

Source of Variation	Sums of Squares	Degrees of Freedom	Mean Squares	*F*-Statistic
Between Wells	SS_{grps}	$p-1$	$MS_{grps} = SS_{grps}/(p-1)$	$F = MS_{grps}/MS_{error}$
Error (within wells)	SS_{error}	$N-p$	$MS_{error} = SS_{error}/(N-p)$	
Total	SS_{total}	$N-1$		

►EXAMPLE 11-2

Use the data from **Example 11-1** to conduct Levene's test of equal variances at the $\alpha = 0.01$ level of significance.

SOLUTION

Step 1. Calculate the group arsenic mean for each well ($\bar{x}_{i\bullet}$):

Well 1 mean = 16.47 ppm Well 4 mean = 11.26 ppm

Well 2 mean = 15.76 ppm Well 5 mean = 13.49 ppm

Well 3 mean = 29.60 ppm Well 6 mean = 2.29 ppm

Then compute the absolute residuals z_{ij} in each well using equation [11.1] as in the table below.

	Absolute Arsenic Residuals (z_{ij})					
Month	Well 1	Well 2	Well 3	Well 4	Well 5	Well 6
1	6.43	13.76	27.6	3.42	11.41	1.95
2	13.38	14.51	79.8	1.96	12.19	2.49
3	19.23	7.96	25.1	14.64	12.74	0.56
4	12.29	36.24	27.1	9.26	13.51	1.09
Well Mean ($\bar{z}_{i\bullet}$)	12.83	18.12	39.9	7.32	12.46	1.52
Overall Mean ($\bar{z}_{\bullet\bullet}$)	15.36					

Step 2. Compute the mean absolute residual ($\bar{z}_{i\bullet}$) in each well and then the overall grand mean using equation [11.4]. These results are listed above.

Step 3. Compute the between-groups sum of squares for the absolute residuals using equation [11.5]:

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$$SS_{grps} = \left[4(12.83)^2 + 4(18.12)^2 + \ldots + 4(1.52)^2\right] - 24 \cdot (15.36)^2 = 3{,}522.90$$

Step 4. Compute the corrected total sum of squares using equation [11.6]:

$$SS_{total} = \left[(6.43)^2 + (13.38)^2 + \ldots + (1.09)^2\right] - 24 \cdot (15.36)^2 = 6{,}300.89$$

Step 5. Compute the within-groups or error sum of squares using equation [11.7]:

$$SS_{error} = 6{,}300.89 - 3{,}522.90 = 2{,}777.99$$

Step 6. Given that the number of groups is p = 6 and the total sample size is N = 24, calculate the mean squares for the between-groups and error components using formulas [11.8] and [11.9]:

$$MS_{grps} = 3{,}522.90 \big/ (6-1) = 704.58$$

$$MS_{error} = 2{,}777.99 \big/ (24-6) = 154.33$$

Step 7. Construct an ANOVA table following **Figure 11-2** to calculate the *F*-statistic. The numerator degrees of freedom [*df*] is computed as (p–1) = 5, while the denominator *df* is equal to (N–p) = 18.

Source of Variation	Sums of Squares	Degrees of Freedom	Mean Squares	*F*-Statistic
Between Well Grps	3,522.90	5	704.58	4.56
Error (within grps)	2,777.99	18	154.33	
Total	6,300.89	23		

Step 8. Determine the .01-level critical point for the *F*-test with 5 and 18 degrees of freedom from **Table 17-1**. This gives $F_{.99,5,18}$ = 4.25. Since the *F*-statistic of 4.56 exceeds the critical point, the assumption of equal variances should be rejected. Since the original concentration data are used in this example, a transformation such as the natural logarithm might be tried and the transformed data retested. ◄

11.3 MEAN-STANDARD DEVIATION SCATTER PLOT

BACKGROUND AND PURPOSE

The mean-standard deviation scatter plot is described in **Chapter 9**. It is useful as an exploratory tool for multiple groups of data (*e.g.*, wells) to aid in identifying relationships between mean levels and variability. It is also helpful in providing a visual assessment of variance homogeneity across data groups. Like side-by-side box plots, the mean-standard deviation scatter plot graphs a measure of variability for each well. In the latter, however, the standard deviation is plotted rather than the interquartile range, so a more direct assessment of variance equality can be made. Since standard

deviations (and consequently variances) are often positively correlated with sample mean levels in skewed populations, the observed pattern on the mean-standard deviation scatter plot can offer valuable clues as to what sort of variance stabilizing transformation if any might work.

REQUIREMENTS AND ASSUMPTIONS

The requirements for the mean-standard deviation scatter plot are listed in **Section 9.4.**

PROCEDURE

See **Section 9.4.**

►EXAMPLE 11-3

Use the data from **Example 11-1** to construct a mean-standard deviation scatter plot.

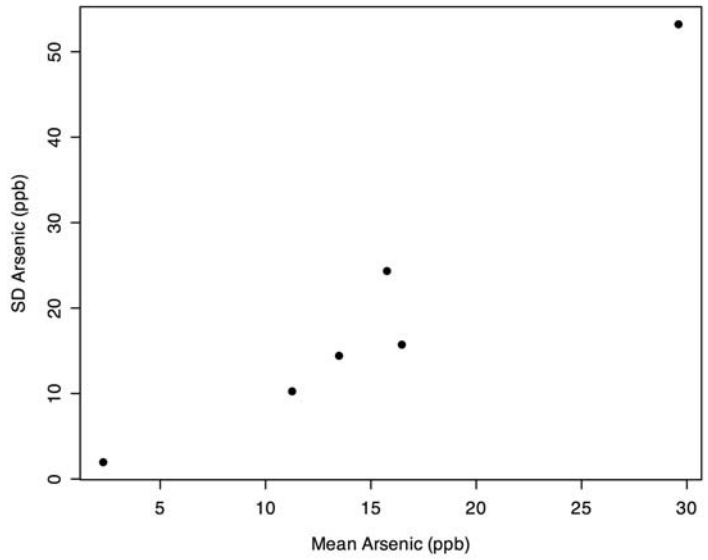
SOLUTION

Step 1. First compute the sample mean ($\bar{x}$) and standard deviation (s) of each well, as listed below.

Well	Mean	Std Dev
1	16.468	15.718
2	15.762	24.335
3	29.600	53.211
4	11.260	10.257
5	13.488	14.418
6	2.292	1.958

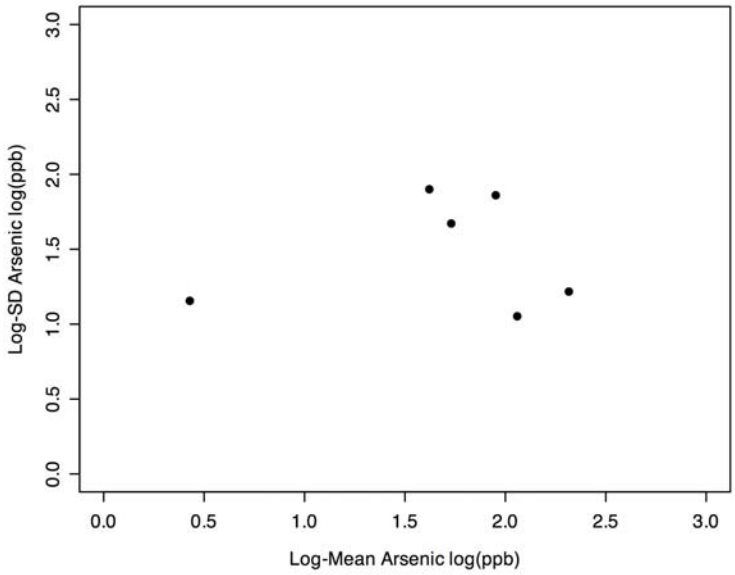
Step 2. Plot the well means versus the standard deviations as in **Figure 11-3** below. Note the roughly linear relationship between the magnitude of the standard deviations and their corresponding means. The data suggest unequal variances among the wells, as indicated by the large range in the standard deviations.

Figure 11-3. Arsenic Mean-Standard Deviation Plot



Step 3. Because lognormal data groups will tend to show a linear association between the sample means and standard deviations, apply a log transformation to the original arsenic measurements and reconstruct the mean-standard deviation scatter plot on the log scale. Computing the log-means and log-standard deviations and then re-plotting gives **Figure 11-4**. Now the apparent trend between the means and standard deviations is gone. Further, on the log scale, the standard deviations are much more similar in magnitude, all with values between 1 and 2. The log transformation thus appears to roughly stabilize the arsenic variances. ◄

Figure 11-4. Log(Arsenic) Mean-Standard Deviation Plot



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CHAPTER 12. IDENTIFYING OUTLIERS

12.1 SCREENING WITH PROBABILITY PLOTS 12-1
12.2 SCREENING WITH BOX PLOTS 12-5
12.3 DIXON'S TEST 12-8
12.4 ROSNER'S TEST 12-10

This chapter discusses screening tools and formal tests for identifying statistical outliers. Two screening tools are first presented: probability plots (**Section 12.1**) and box plots (**Section 12.2**). These are followed by two formal outlier tests:

- Dixon's test (**Section 12.3**) for a single outlier in smaller data sets, and
- Rosner's test (**Section 12.4**) for up to five separate outliers in larger data sets.

A statistical determination of one or more statistical outliers does not indicate *why* the measurements are discrepant from the rest of the data set. The Unified Guidance does not recommend that outliers be removed *solely* on a statistical basis. The outlier tests can provide supportive information, but generally a reasonable rationale needs to be identified for removal of suspect outlier values (usually limited to background data**).** At the same time there must be some level of confidence that the data are representative of ground water quality. A number of factors and considerations in removing outliers from potential background data are discussed in **Section 5.2.3.**

12.1 SCREENING WITH PROBABILITY PLOTS

BACKGROUND AND PURPOSE

Probability plots (**Chapter 9**) are helpful in identifying outliers in at least two ways. First, since the straightness of the plot indicates how closely the data fit the pattern of a normal distribution, values that appear "out of line" with the remaining data can be visually identified as possible outliers. Secondly, the two formal outlier tests presented in the Unified Guidance assume that the underlying population minus the suspected outlier(s) is normal. Probability plots can provide visual evidence for this assumption. Data that appear non-normal after the suspected outliers have been removed from the probability plot may need to be transformed (e.g., via the natural logarithm) and re-examined on the transformed scale to see if potential outliers are still apparent.

As an aid to the interpretation of a given probability plot, the Unified Guidance recommends computation of the probability plot correlation coefficient, using either Filliben's procedure (**Chapter 10**) or the simple (Pearson) correlation (**Chapter 3**) between the numerical pairs plotted on the graph. The higher the correlation, the more linear the pattern is on the probability plot and therefore a better fit to normality. Note that while the Filliben correlation coefficient can be compared to critical points derived for that test of normality (**Chapter 10**), a low correlation may be related to other causes of non-normality besides the presence of outliers. The correlation coefficient is not a substitute for a formal outlier test, but can be useful as a screening tool.

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REQUIREMENTS AND ASSUMPTIONS

Probability plots are primarily a tool to assess normality, and not to identify outliers *per se*. It is critical that the remaining data without potential outliers is either normal in distribution or can be normalized via a transformation. Otherwise, the probability plot may appear non-linear and non-normal for reasons unrelated to the presence of outliers. Right-skewed lognormal distributions can appear to have one or more outliers on a probability plot unless the original data are first log-transformed. As a general rule, probability plots should be constructed on the original (or raw) measurements and one or more transformed data sets (*e.g.*, log or square root), in order to avoid mistaking inherent data skewness for outliers.

If the raw and transformed-data probability plots both indicate one or more values inconsistent with the pattern of the remaining values, continue with a second level of screening by temporarily removing the suspected outlier(s) and re-constructing the probability plots. If the raw-scale plot is reasonably linear, consider running a formal outlier test on the original measurements. On the other hand, if the raw-scale plot is skewed but the transformed-scale plot is linear, consider conducting a formal outlier test on the transformed measurements.

A related difficulty occurs when sample data includes censored or non-detect values. If simple substitution is used to estimate a value for each non-detect prior to plotting, the resulting probability plot may appear non-linear simply because the censored observations were not properly handled. In this case, a censored probability plot (**Chapter 15**) should be constructed instead of an uncensored, complete sample plot (**Chapter 9**). The same caveats apply to normalizing the sample data, perhaps by attempting at least one transformation. The only difference is that each probability plot constructed must appropriately account for the observed censoring in the sample.

PROCEDURE

Step 1. After identifying one or more possible outliers (*e.g.*, values much higher in concentration than the remaining measurements), construct a probability plot on the entire sample using the procedure described in **Section 9.5**. Construct a *censored probability plot* from **Section 15.3** if the sample contains non-detects. If the data including the suspected outlier(s) follow a reasonably linear pattern, a formal outlier test is probably unnecessary. However, if one or more values are out of line compared to the pattern of the remaining data, construct a similar probability plot after applying one or more transformations. If one or more suspected outliers is still inconsistent, proceed to Step 2.

Step 2. Compute a probability plot correlation coefficient for each plot constructed in Step 1. Use these correlations as an aid to interpreting the degree of linearity in each probability plot.

Step 3. Reconstruct the probability plots from Step 1 after removing the suspected outlier(s). Recompute the correlation coefficients from Step 2 on this reduced sample.

Step 4. If the 'outlier-deleted' probability plot on the raw concentration scale indicates a linear pattern with high correlation, consider running a formal outlier test on the original measurements. When the pattern is distinctly non-linear but the corresponding probability plot on the transformed-scale is fairly linear (and higher in correlation), conduct the outlier test on the transformed values.

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►EXAMPLE 12-1

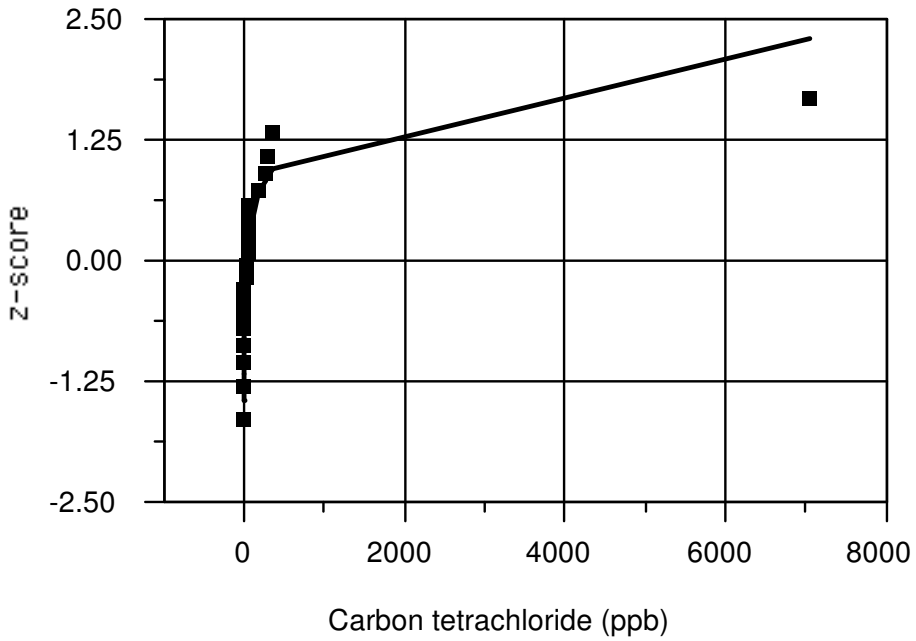
The table below contains data from five background wells measured over a four month period. The value 7,066 is found in the second month at Well 3. Use probability plots on the combined sample to determine whether or not a formal outlier test is warranted.

Carbon Tetrachloride Concentrations (ppb)				
Well 1	Well 2	Well 3	Well 4	Well 5
1.7	302	16.2	199	275
3.2	35.1	7066	41.6	6.5
7.3	15.6	350	75.4	59.7
12.1	13.7	70.1	57.9	68.4

SOLUTION

Step 1. Examine the probability plots of the entire sample first using the raw measurements and then log-transformed values (**Figures 12-1** and **12-2**). Both these plots indicate that the suspected outlier does not follow the pattern of the remaining observations, but seems 'out of line.' The Pearson correlation coefficients for these probability plots are, respectively, r = 0.502 and 0.973, indicating that the fit to normality overall is much closer using log-transformed measurements.

Figure 12-1. Probability Plot on Raw Concentrations (r = .502)



Step 2. Next remove the suspected outlier and reconstruct the probability plots on both the original and logged observations (**Figures 12-3** and **12-4**). The plot on the original scale indicates heavy positive (or right-) skewness and a non-linear pattern, while the plot on the log-scale exhibits a fairly linear pattern. The respective correlation coefficients now become r = 0.854 and 0.987, again favoring the log-transformed sample. On the basis of these plots, the

underlying data should be modeled as lognormal and the observations logged prior to running a formal outlier test. ◄

Figure 12-2. Probability Plot on Logged Observations (r = .973)

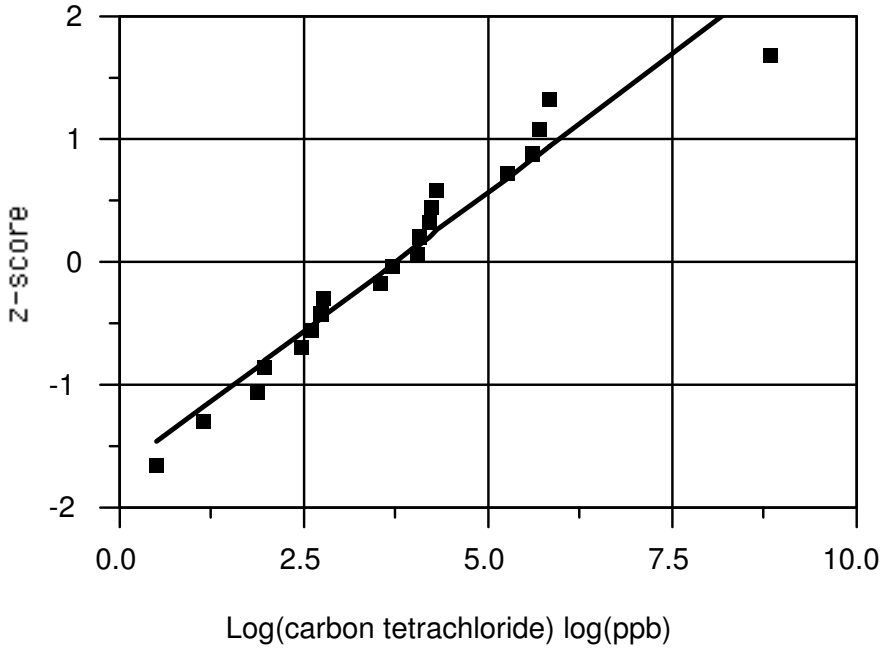
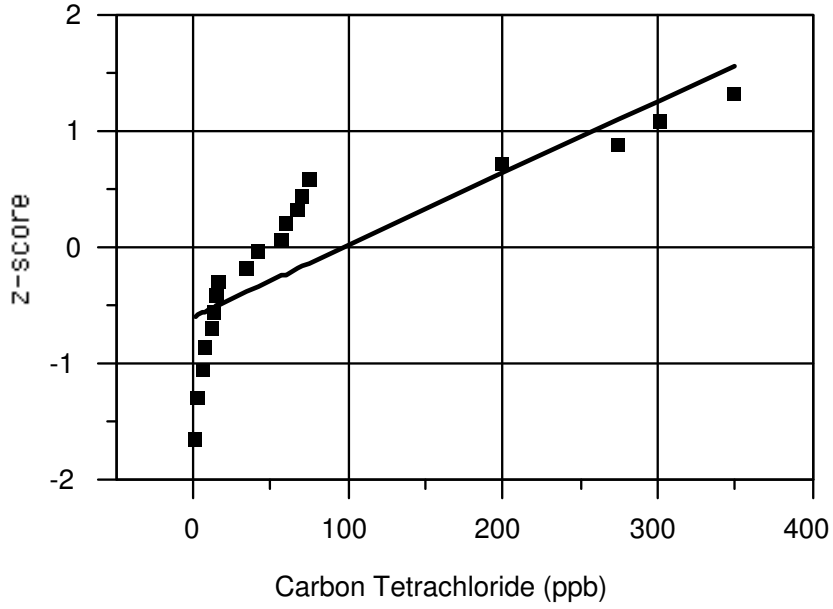
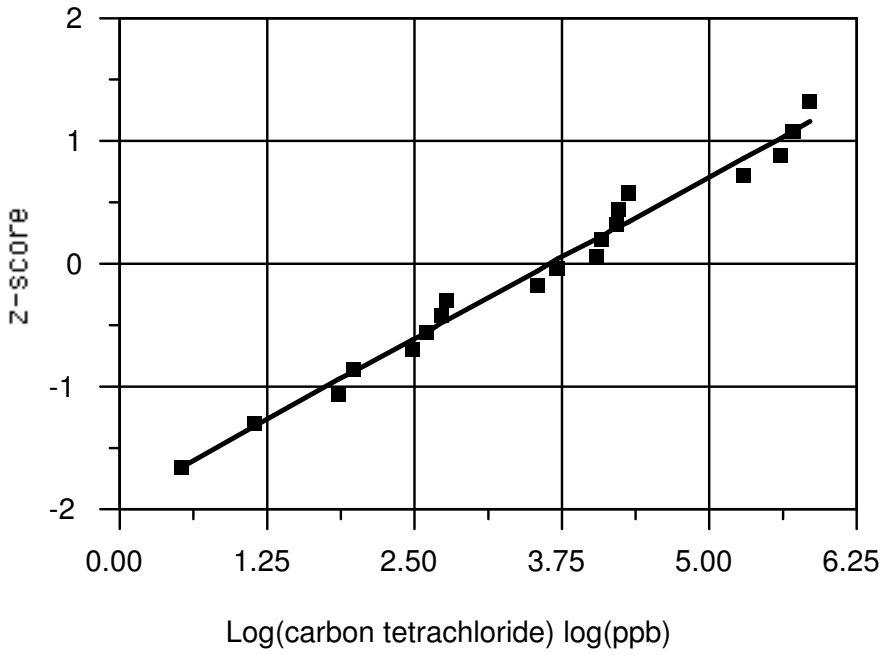


Figure 12-3. Outlier-Deleted Probability Plot on Original Scale (r = .854)



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Figure 12-4. Outlier-Deleted Probability Plot on Logarithmic Scale (r = .987)



12.2 SCREENING WITH BOX PLOTS

BACKGROUND AND PURPOSE

Probability plots as described in **Section 12.1** require the remaining observations following removal of one or more suspected outliers to be either approximately normal or normalized via transformation. Box plots (**Chapter 9**) provide an alternate method to perform outlier screening, one not dependent on normality of the underlying measurement population. Instead of looking for points inconsistent with a linear pattern on a probability plot, the box plot flags as possible outliers values that are located in either or both of the *extreme tails* of the sample.

To define the extreme tails, Tukey (1977) proposed the concept of 'hinges' that would 'swing' off either end of a box plot, defining the range of concentrations consistent with the bulk of the data. Data points outside this concentration range could then be identified as potential outliers. Tukey defined the hinges, i.e., the lower and upper edges of the box plot, essentially as the lower and upper quartiles of the data set. Then multiples of the interquartile range [IQR] (*i.e.*, the range represented by the middle half of the sample) were added to or subtracted from these hinges as potential outlier boundaries. Any observation from 1.5 × IQR to 3 × IQR below the lower edge of the box plot was labeled a 'mild' low outlier; any value more than 3 × IQR below the lower edge of the box plot was labeled an 'extreme' low outlier. Similarly, values greater than the upper edge of the box plot in the range of 1.5 to 3 times the IQR were labeled 'mild' higher outliers, and 'extreme' high outliers if more than 3 times the IQR beyond the upper box plot edge.

REQUIREMENTS AND ASSUMPTIONS

By using hinges and multiples of the interquartile range, Tukey's box plot method utilizes statistics (*i.e.*, the lower and upper quartiles) that are generally not or minimally affected by one or a few outliers

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in the sample. Consequently, it isn't necessary to first delete possible outliers before constructing the box plot.

Screening for outliers with box plots is a very simple technique. Since no assumption of normality is needed, Tukey's procedure can be considered quasi-non-parametric. But note that rough symmetry of the underlying distribution is implicitly assumed. Legitimate observations from highly skewed distributions could be flagged as potential outliers on a box plot if no transformation of the data is first attempted. It may be necessary to first conduct multiple data transformations in order to achieve approximate symmetry before applying and evaluating potential outliers with box plots.

PROCEDURE

Step 1. Construct a box plot on the sample using the method given in **Section 9.2**. Using the IQR from that calculation, along with the lower and upper quartiles ($\tilde{x}_{.25}$ and $\tilde{x}_{.75}$), compute the first pair of lower and upper boundaries as:

$$LB_1 = \tilde{x}_{.25} - 1.5 \times IQR \quad (12.1)$$

$$UB_1 = \tilde{x}_{.75} + 1.5 \times IQR \quad (12.2)$$

Step 2. Construct the second pair of lower and upper boundaries as:

$$LB_2 = \tilde{x}_{.25} - 3 \times IQR \quad (12.3)$$

$$UB_2 = \tilde{x}_{.75} + 3 \times IQR \quad (12.4)$$

Step 3. Label any sample measurement lower than the first lower boundary (LB_1) but no less than the second lower boundary (LB_2) as a mild low outlier. Label any measurement greater than the first upper boundary (UB_1) but no greater than the second upper boundary (UB_2) as a mild high outlier.

Step 4. Label any sample measurement lower than the second lower boundary (LB_2) as an extreme low outlier. Label any value higher than the second upper boundary (UB_2) as an extreme high outlier.

►EXAMPLE 12-2

Use the carbon tetrachloride data from **Example 12-1** to screen for possible outliers using Tukey's box plot.

SOLUTION

Step 1. Using the procedure described in **Section 9.2**, the upper and lower quartiles of carbon tetrachloride sample are found to be $\tilde{x}_{.25} = 12.9$ and $\tilde{x}_{.75} = 137.2$, leading to an IQR = 124.3.

Step 2. Compute the two pairs of lower and upper boundaries using equations (12.1), (12.2), (12.3), and (12.4):

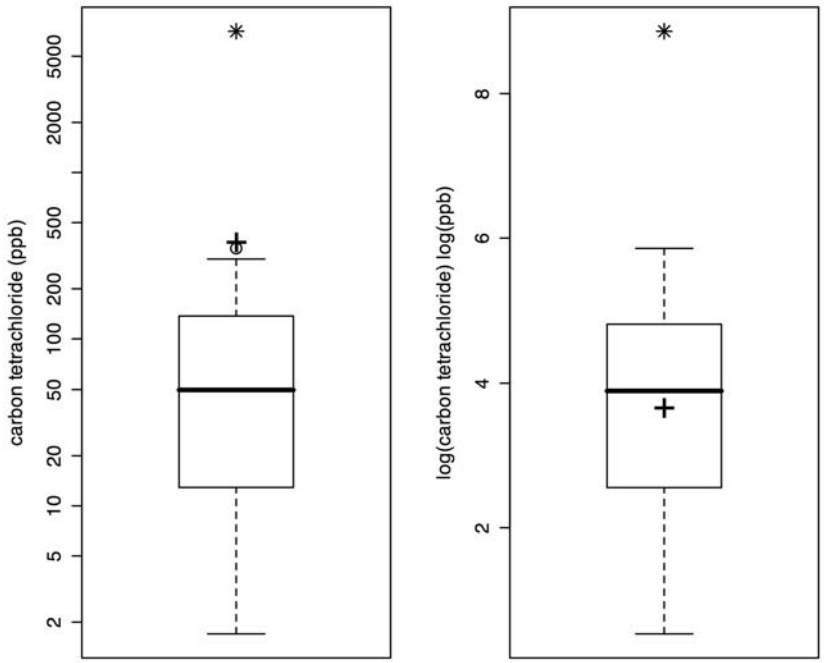
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$$LB_1 = 12.9 - 1.5 \times 124.3 = -173.55$$
$$UB_1 = 137.2 + 1.5 \times 124.3 = 323.65$$
$$LB_2 = 12.9 - 3 \times 124.3 = -360$$
$$UB_2 = 137.2 + 3 \times 124.3 = 510.1$$

Step 3. Scan the list of carbon tetrachloride measurements and compare against the boundaries of **Step 2**. It can be seen that the value of 350 from Well 3 is greater than UB_1 but lower than UB_2, thus qualifying as a mild high outlier. Also, the measurement 7,066 from the same well is higher than UB_2 and so qualifies as an extreme high outlier.

Step 4. Because the box plot outlier screening method assumes roughly symmetric data, recompute the box plot on the log-transformed measurements (as shown in **Figure 12-5** alongside a similar box plot of the raw concentrations). Transforming the sample to the log-scale does result in much greater symmetry compared to the original measurement scale. This can be seen in the close similarity between the mean and median on the log-scale box plot. With a more symmetric data set, the mild high outlier from Step 3 disappears, but the extreme high value is still classified as an outlier. ◄

Figure 12-5. Comparative Carbon Tetrachloride Box Plots Indicating Outliers



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12.3 DIXON'S TEST

BACKGROUND AND PURPOSE

Dixon's test is helpful for documenting statistical outliers in smaller data sets (*i.e.*, $n \leq 25$). The test is particularly designed for cases where there is only a single high or low outlier, although it can also be adapted to test for multiple outliers. The test falls in the general class of tests for *discordancy* (Barnett and Lewis, 1994). The test statistic for such procedures is generally a ratio: the numerator is the difference between the suspected outlier and some summary statistic of the data set, while the denominator is always a measure of spread within the data. In this version of Dixon's test, the summary statistic in the numerator is an order statistic nearby to the potential outlier (*e.g.*, the second or third most extreme value). The measure of spread is essentially the observed sample range.

If there is more than one outlier in the data set, Dixon's test can be vulnerable to *masking*, at least for very small samples. Masking in the statistical literature refers to the problem of an extreme outlier being missed because one or more additional extreme outliers are also present. For instance, if the data consist of the values {2, 4, 10, 12, 15, 18, 19, 22, 200, 202}, identification of the maximum value (202) as an outlier might fail since the maximum by itself is not extreme with respect to the next highest value (200). However, both of these values are clearly much higher than the rest of the data set and might jointly be considered outliers.

If more than one outlier is suspected, the user is encouraged to consider Rosner's test (**Section 12.4**) as an alternative to Dixon's test, at least if the sample size is 20 or more. If the data set is smaller, Dixon's test should be modified so that the *least extreme* of the suspected outliers is tested first. This will help avoid the risk of masking. The same equations given below can be used, but the data set and sample size should be temporarily reduced to exclude any suspected outliers that are *more* extreme than the one being tested. If a less extreme value is found to be an outlier, then that observation and any more extreme values can also be regarded as outliers. Otherwise, add back the next most extreme value and test it in the same way.

REQUIREMENTS AND ASSUMPTIONS

Dixon's test is only recommended for sample sizes $n \leq 25$. It assumes that the data set (minus the suspected outlier) is normally-distributed. This assumption should be checked prior to running Dixon's test using a goodness-of-fit technique such as the probability plots described in **Section 12.2**.

PROCEDURE

Step 1. Order the data set and label the ordered values, $x_{(i)}$.

Step 2. If a "low" outlier is suspected (*i.e.*, $x_{(1)}$), compute the test statistic C using the appropriate equation [12.5] depending on the sample size (n):

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$$C = \begin{cases} \left(x_{(2)} - x_{(1)}\right) \Big/ \left(x_{(n)} - x_{(1)}\right) \text{ for } 3 \le n \le 7 \\ \left(x_{(2)} - x_{(1)}\right) \Big/ \left(x_{(n-1)} - x_{(1)}\right) \text{ for } 8 \le n \le 10 \\ \left(x_{(3)} - x_{(1)}\right) \Big/ \left(x_{(n-1)} - x_{(1)}\right) \text{ for } 11 \le n \le 13 \\ \left(x_{(3)} - x_{(1)}\right) \Big/ \left(x_{(n-2)} - x_{(1)}\right) \text{ for } 14 \le n \le 25 \end{cases} \quad [12.5]$$

Step 3. If a "high" outlier is suspected (*i.e.*, $x_{(n)}$), and again depending on the sample size (n), compute the test statistic C using the appropriate equation [12.6] as:

$$C = \begin{cases} \left(x_{(n)} - x_{(n-1)}\right) \Big/ \left(x_{(n)} - x_{(1)}\right) \text{ for } 3 \le n \le 7 \\ \left(x_{(n)} - x_{(n-1)}\right) \Big/ \left(x_{(n)} - x_{(2)}\right) \text{ for } 8 \le n \le 10 \\ \left(x_{(n)} - x_{(n-2)}\right) \Big/ \left(x_{(n)} - x_{(2)}\right) \text{ for } 11 \le n \le 13 \\ \left(x_{(n)} - x_{(n-2)}\right) \Big/ \left(x_{(n)} - x_{(3)}\right) \text{ for } 14 \le n \le 25 \end{cases} \quad [12.6]$$

Step 4. In either case, given the significance level (α), determine a critical point for Dixon's test with n observations from **Table 12-1** in **Appendix D**. If C exceeds this critical point, the suspected value should be declared a statistical outlier and investigated further (see discussion in **Chapter 6**).

►EXAMPLE 12-3

Use the data from **Example 12-1** in Dixon's test to determine if the anomalous high value is a statistical outlier at an $\alpha = 0.05$ level of significance.

SOLUTION

Step 1. In **Example 12-1**, probability plots of the carbon tetrachloride data indicated that the highest value might be an outlier, but that the distribution of the measurements was more nearly lognormal than normal. Since the sample size $n = 20$, Dixon's test can be used on the logged observations. Logging the values and ordering them leads to the following table:

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Order	Concentration (ppb)	Logged Concentration
1	1.7	0.531
2	3.2	1.163
3	6.5	1.872
4	7.3	1.988
5	12.1	2.493
6	13.7	2.617
7	15.6	2.747
8	16.2	2.785
9	35.1	3.558
10	41.6	3.728
11	57.9	4.059
12	59.7	4.089
13	68.4	4.225
14	70.1	4.250
15	75.4	4.323
16	199.0	5.293
17	275.0	5.617
18	302.0	5.710
19	350.0	5.878
20	7066.0	8.863

Step 2. Because a high outlier is suspected and n = 20, use the last option of equation [12.6] to calculate the test statistic C:

$$C = \frac{8.863 - 5.710}{8.863 - 1.872} = 0.451$$

Step 3. With n = 20 and α = .05, the critical point from **Table 12-1** in **Appendix D** is equal to 0.450. Since the test statistic C exceeds this critical point, the extreme high value can be declared a statistical outlier. Before excluding this value from further analysis, however, a valid explanation for this unusually high value should be sought. Otherwise, the outlier may need to be treated as an extreme but valid concentration measurement. ◄

12.4 ROSNER'S TEST

BACKGROUND AND PURPOSE

Rosner's test (Rosner, 1975) is a useful method for identifying multiple outliers in moderate to large-sized data sets. The approach developed in Rosner's method is known as a *block*-style test. Instead of testing for outliers one-by-one in a consecutive manner from most extreme to least extreme (*i.e.*, most to least suspicious), the data are examined first to identify the total number of possible outliers, k. Once k is determined, the set of possible outliers is tested together as a block. If the test is significant, all k measurements are regarded as statistical outliers. If not, the set of possible outliers is reduced by one and the test repeated on the smaller block. This procedure is iterated until either a set of outliers is identified

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or none of the observations are labeled an outlier. By testing outliers in blocks instead of one-by-one, Rosner's test largely avoids the problem of *masking* of one outlier by another (as discussed in **Section 12.3** regarding Dixon's test).

Although Rosner's test avoids the problem of masking when multiple outliers are present in the same data set, it is not immune to the related problem of *swamping*. A good discussion is found in Barnett and Lewis, 1994, Outliers in Statistical Data (3rd Edition), p. 236. Swamping refers to a block of measurements all being *labeled* as outliers even though only *some* of the observations are actually outliers. This can occur with Rosner's test especially if all the outliers tend to be at one end of the data set (*e.g.*, as upper extremes). The difficulty is in properly identifying the total number of possible outliers (k), which can be low outliers, high outliers, or some combination of the two extremes. If k is made too large, swamping may occur. Again, the user is reminded to always do a preliminary screening for outliers via box plots (**Section 12.2**) and probability plots (**Section 12.1**).

REQUIREMENTS AND ASSUMPTIONS

Rosner's test is recommended when the sample size (n) is 20 or larger. The critical points provided in **Table 12-2** in **Appendix D** can be used to identify from 2 to 5 outliers in a given data set. Like Dixon's test, Rosner's method assumes the underlying data set (minus any outliers) is normally distributed. If a probability plot of the data exhibits significant bends or curves, the data should first be transformed (*e.g.*, via a logarithm) and then re-plotted. The formal test for outliers should only be performed on (outlier-deleted) data sets that have been approximately normalized.

A potential drawback of Rosner's test is that the user must first identify the maximum number of potential outliers (k) prior to running the test. Therefore, this requirement makes the test ill-advised as an automatic outlier screening tool, and somewhat reliant on the user to identify candidate outliers.

PROCEDURE

Step 1. Order the data set and denote the ordered values $x_{(i)}$. Then by simple inspection, identify the maximum number of possible outliers, r_0.

Step 2. Compute the sample mean and standard deviation of all the data; denote these values by $\bar{x}^{(0)}$ and $s^{(0)}$. Then determine the measurement furthest from $\bar{x}^{(0)}$ and denote it $y^{(0)}$. Note that $y^{(0)}$ could be either a potentially low or a high outlier.

Step 3. Delete $y^{(0)}$ from the data set and compute the sample mean and standard deviation from the remaining observations. Label these new values $\bar{x}^{(1)}$ and $s^{(1)}$. Again find the value in this reduced data set furthest from $\bar{x}^{(1)}$ and label it $y^{(1)}$.

Step 4. Delete $y^{(1)}$, recompute the mean and standard deviation, and continue this process until all r_0 potential outliers have been removed. At this point, the following set of statistics will be available:

$$\left[\bar{x}^{(0)}, s^{(0)}, y^{(0)}\right], \left[\bar{x}^{(1)}, s^{(1)}, y^{(1)}\right], \ldots, \left[\bar{x}^{(r_0-1)}, s^{(r_0-1)}, y^{(r_0-1)}\right] \quad [12.7]$$

Step 5. Now test for r outliers (where $r \leq r_0$) by iteratively computing the test statistic:

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$$R_{r-1} = \left| y^{(r-1)} - \bar{x}^{(r-1)} \right| \Big/ s^{(r-1)} \qquad [12.8]$$

First test for r_0 outliers. If the test statistic R_{r_0-1} in equation [12.8] exceeds the first critical point from **Table 12-2** in **Appendix D** based on sample size (n) and the Type I error (α), conclude there are r_0 outliers. If not, test for r_0–1 outliers in the same fashion using the next critical point, continuing until a certain number of outliers have either been identified or Rosner's test finds no outliers at all.

►EXAMPLE 12-4

Consider the following series of 25 background napthalene measurements (in ppb). Use Rosner's test to determine whether any of the values should be deemed statistical outliers.

	Naphthalene Concentrations (ppb)				
Qtr	BW-1	BW-2	BW-3	BW-4	BW-5
1	3.34	5.59	1.91	6.12	8.64
2	5.39	5.96	1.74	6.05	5.34
3	5.74	1.47	23.23	5.18	5.53
4	6.88	2.57	1.82	4.43	4.42
5	5.85	5.39	2.02	1.00	35.45

SOLUTION

Step 1. Screening with probability plots of the combined data indicates a less than linear fit with both the raw measurements and log-transformed data (see **Figures 12-6 and 12-7**); two points appear rather discrepant from the rest. Correlation coefficients for these plots are 0.740 on the concentration scale and 0.951 on the log-scale. Re-plotting after removing the two possible outliers gives a substantially improved correlation on the concentration scale of 0.958 but reduces the log-scale correlation to 0.929. Normality appears to be a slightly better default distribution for the outlier-deleted data set. Run Rosner's test on the original data with $k = 2$ possible outliers.

Step 2. Compute the mean and standard deviation of the complete data set. Then identify the observation farthest from the mean. These results are listed, along with the ordered data, in the table below. After removing the farthest value (35.45), recompute the mean and standard deviation on the remaining values and again identify the most discrepant observation (23.23). Repeat this process one more time so that both suspected outliers have been removed (see table below).

Step 3. Now test for 2 joint outliers by computing Rosner's statistic on subset $SS_{k-1} = SS_1$ using equation [12.8]:

$$R_1 = \frac{23.23 - 5.23}{4.326} = 4.16$$

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Figure 12-6. Napthalene Probability Plot

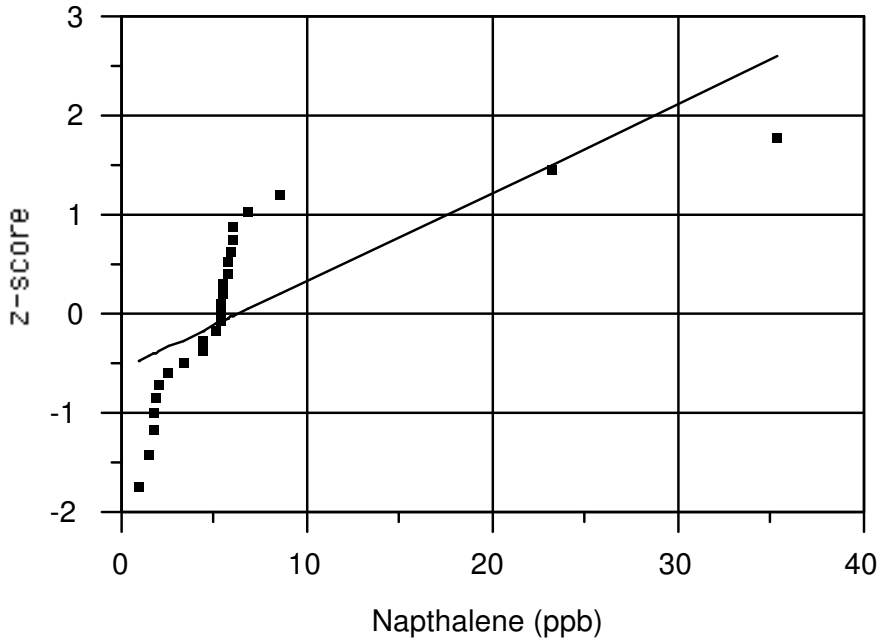
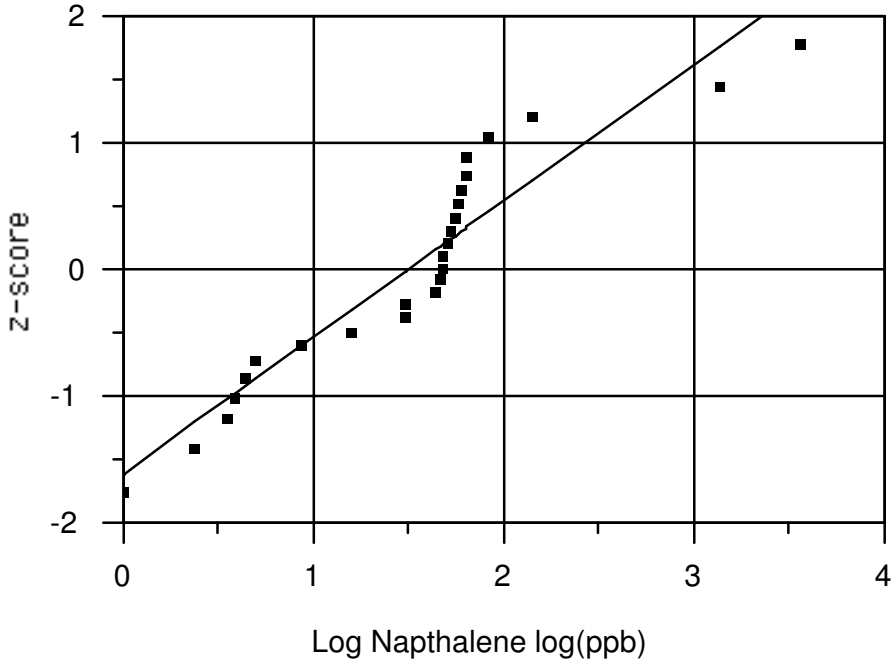


Figure 12-7. Log Napthalene Probability Plot



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Successive Naphthalene Subsets (SS_i)		
SS_0	SS_1	SS_2
1.00	1.00	1.00
1.47	1.47	1.47
1.74	1.74	1.74
1.82	1.82	1.82
1.91	1.91	1.91
2.02	2.02	2.02
2.57	2.57	2.57
3.34	3.34	3.34
4.42	4.42	4.42
4.43	4.43	4.43
5.18	5.18	5.18
5.34	5.34	5.34
5.39	5.39	5.39
5.39	5.39	5.39
5.53	5.53	5.53
5.59	5.59	5.59
5.74	5.74	5.74
5.85	5.85	5.85
5.96	5.96	5.96
6.05	6.05	6.05
6.12	6.12	6.12
6.88	6.88	6.88
8.64	8.64	8.64
23.23	23.23	
35.45		
$\bar{x}_0$ = 6.44	$\bar{x}_1$ = 5.23	$\bar{x}_2$ = 4.45
s_0 = 7.379	s_1 = 4.326	s_2 = 2.050
y_0 = 35.45	y_1 = 23.23	y_2 = 8.64

Step 4. Given $\alpha = 0.05$, a sample size of $n = 25$, and $k = 2$, the first critical point in **Table 12-2** in **Appendix D** equals 2.83 for $n = 20$ and 3.05 for $n = 30$. The value R_1 in Step 3 is larger than either of these critical points, so both suspected values may be declared statistical outliers by Rosner's test at the 5% significance level. Before excluding these values from further analysis, however, a valid explanation for them should be found. Otherwise, treat the outliers as extreme but valid concentration measurements.

Note: had R_1 been *less* than these values, a test could still be run for a *single* outlier using the second critical point for each sample size (or a critical point interpolated between them). ◄

The guidance considers Dixon's and Rosner's outlier evaluation methods preferable for groundwater monitoring data situations, when assumptions of normality are reasonable and data are quantified. We did not include the older method found in the 1989 guidance based on ASTM paper E178-75, which can still be used as an alternative. Where data do not appear to be fit by a normal or transformably normal distribution, other robust outlier evaluation methods can be considered from the wider statistical literature. The literature will also need to be consulted when data contains non-detect values along with potential outliers.

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CHAPTER 13. SPATIAL VARIABILITY

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This chapter discusses a type of *statistical dependence* in groundwater monitoring data known as *spatial variability*. Spatial variability exists when the distribution or pattern of concentration measurements changes from well location to well location (most typically in the form of differing mean levels). Such variation may be natural or *synthetic*, depending on whether it is caused by natural or anthropogenic factors. Methods for *identifying* spatial variation are detailed via the use of box plots (**Section 13.2.1**) and analysis of variance [ANOVA] (**Section 13.2.2**). Once identified, ANOVA can sometimes be employed to construct more powerful intrawell background limits. This topic is addressed in **Section 13.3**.

13.1 INTRODUCTION TO SPATIAL VARIATION

Spatial dependence, *spatial variation* or *variability*, and *spatial correlation* are closely related concepts. All refer to the notion of measurement levels that vary in a structured way as a function of the *location* of sampling. Although spatial variation can apply to any statistical characteristic of the underlying population (including the population variance or upper percentiles), the usual sense in groundwater monitoring is that *mean* levels of a given constituent vary from one well to the next.

Standard geostatistical models posit that an area exhibits positive spatial correlation if any two sampling locations share a greater similarity in concentration level the closer the distance between them, and more dissimilarity the further apart they are. Such models have been applied to both groundwater and soil sampling problems, but are not applicable in all geological configurations. It may be, for instance, that mean concentration levels differ across wells but vary in a seemingly random way with no apparent connection to the distance between the sampling points. In that case, the concentrations between pairs of wells are not correlated with distance, yet the measurements within each well are strongly associated with the mean level at that particular location, whether due to a change in soil composition, hydrological characteristics or some other factor. In other words, spatial *variation* may exist even when spatial *correlation* does not.

Spatial variation is important in the guidance context since substantial differences in mean concentration levels between different wells can *invalidate* interwell, upgradient-to-downgradient comparisons and point instead toward *intrawell* tests (**Chapter 6**). Not all spatial variability is natural. Average concentration levels can vary from well to well for a variety of reasons.

In this guidance, a distinction is occasionally made between *natural* versus *synthetic* spatial variation. Natural spatial variability refers to a pattern of changing mean levels in groundwater associated with normal geochemical behavior unaffected by human activities. Natural spatial variability

is not an indication of groundwater contamination, even if concentrations at one or more compliance wells exceed (upgradient) background. In contrast, synthetic spatial variability is related to human activity. Sources can include recent releases affecting compliance wells, migration of contaminants from off-site sources, or historic contamination at certain wells due to past industrial activity or pre-RCRA waste disposal. Whether natural or synthetic, techniques and test methods for dealing with spatial variation will still be identical from a purely statistical standpoint. It is interpreting the testing outcomes which will necessitate a consideration of why the spatial variation occurs.

The goal of groundwater analysis is not simply to identify significant concentration differences among monitoring wells at compliance point locations. It is also to determine *why* those differences exist. Especially with prior groundwater contamination, regulatory decisions outside the scope of this guidance need to address the problem. In some cases, compliance/assessment monitoring or remedial action may be warranted. In other cases, chronic contamination from offsite sources may simply have to be considered as the current background condition at a given location. At least the ability to attribute certain mean differences to *natural* spatial variation allows the range of potential concerns to be somewhat narrowed. Of course, deciding that an observed pattern of spatial variation is natural and not synthetic may not be easy. Ultimately, expert judgment and knowledge concerning site hydrology, geology and geochemistry are important in providing more definitive answers.

One statistical approach to use when a site has multiple, non-impacted background wells is to conduct a one-way ANOVA for inorganic constituents on those wells. Substantial differences among the mean levels at a set of *uncontaminated* sampling locations are suggestive of natural spatial variability. At a true 'greenfield' site, ANOVA can be run on all the wells — both background and compliance — after a few preliminary sampling rounds have been collected.

The Unified Guidance offers two basic tools to explore and test for spatial correlation. The first, side-by-side box plots (**Section 13.2.1**), provides a quick screen for possible spatial variation. When multiple well data are plotted on the same concentration axis, noticeably staggered boxes are often an indication of significantly different mean levels.

A more formal test of spatial variation is the one-way ANOVA (**Section 13.3.2**). When significant spatial variation exists and an intrawell test strategy is pursued, one-way ANOVA can also be used to adjust the standard deviation estimate used in forming intrawell prediction and control chart limits, and to increase the effective sample size of the test, via the *degrees of freedom*. This is discussed in **Section 13.3**.

13.2 IDENTIFYING SPATIAL VARIABILITY

13.2.1 SIDE-BY-SIDE BOX PLOTS

BACKGROUND AND PURPOSE

Box plots for graphing side-by-side statistical summaries of multiple wells were introduced in **Chapter 9**. They are also discussed in **Chapter 11** as an initial screen for differences in population variances and as a tool to check the assumption of equal variances in ANOVA. They can further be employed to screen for possible spatial variation in mean levels. While variability in a sample from a given well is roughly indicated by the length of the box, the average concentration level is indicated by the position of the box relative to the concentration axis. Many standard box plot software routines

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display both the sample median value and the sample mean on each box, so these values may be compared from well to well. A high degree of staggering in the box positions is then indicative of potentially significant spatial variation.

Since side-by-side box plots provide a picture of the variability at each well, the extent to which apparent differences in mean levels seem to be real rather than chance fluctuations can be examined. If the boxes are staggered but there is substantial overlap between them, the degree of spatial variability may not be significant. A more formal ANOVA might still be warranted as a follow-up test, but side-by-side box plots will offer a initial sense of how spatially variable the groundwater data appear.

REQUIREMENTS, ASSUMPTIONS AND PROCEDURE

Requirements, assumptions and the procedure for box plots are outlined in **Chapter 9, Section 9.2**.

►EXAMPLE 13-1

Quarterly dissolved iron concentrations measured at each of six upgradient wells are listed below. Construct side-by-side box plots to initially screen for the presence of spatial variability.

	Iron Concentrations (ppm)					
Date	Well 1	Well 2	Well 3	Well 4	Well 5	Well 6
Jan 1997	57.97	46.06	100.48	34.12	60.95	83.10
Apr 1997	54.05	76.71	170.72	93.69	72.97	183.09
Jul 1997	29.96	32.14	39.25	70.81	244.69	198.34
Oct 1997	46.06	68.03	52.98	83.10	202.35	160.77
Mean	47.01	55.74	90.86	70.43	145.24	156.32
Median	50.06	57.04	76.73	76.96	137.66	171.93
SD	12.40	20.34	59.35	25.95	92.16	51.20

SOLUTION

Step 1. Determine the median, mean, lower and upper quartiles of each well. Then plot these against a concentration axis to form side-by-by side box plots (**Figure 13-1**) using the procedure in **Section 9.2**. .

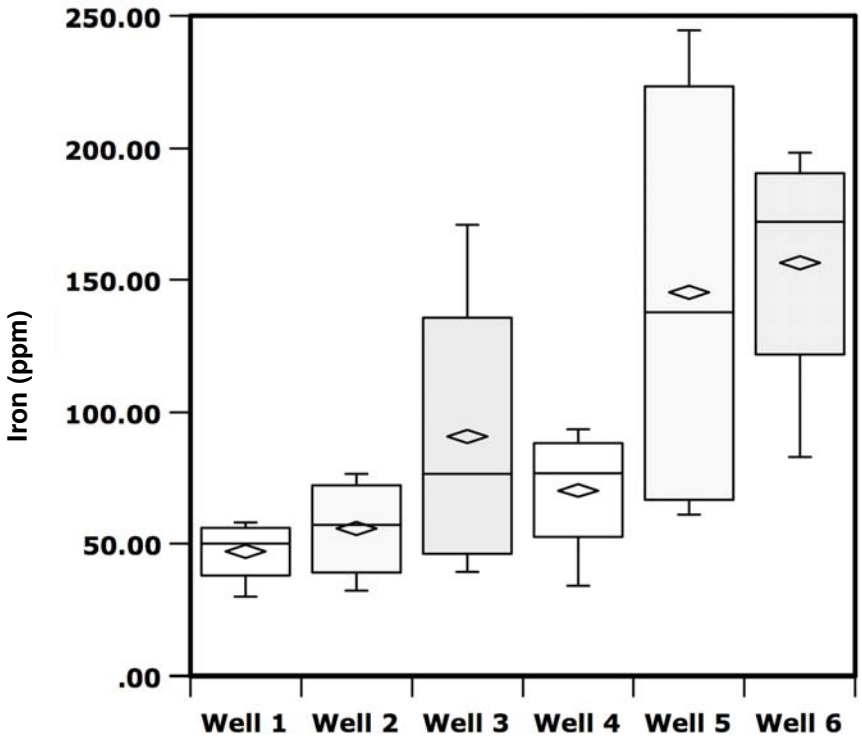
Step 2. From this plot, the means and medians at the last two wells (Wells 5 and 6) appear elevated above the rest. This is a possible indication of spatial variation. However, the variances as represented by the box lengths also appear to differ, with the highest means associated with the largest boxes. A transformation of the data should be attempted and the data re-plotted. Spatial variability is only a significant problem if it is apparent on the scale of the data actually used for statistical analysis.

Step 3. Take the logarithm of each measurement as in the table below. Recompute the mean, median, lower and upper quartiles, and then re-construct the box plot as in **Figure 13-2**.

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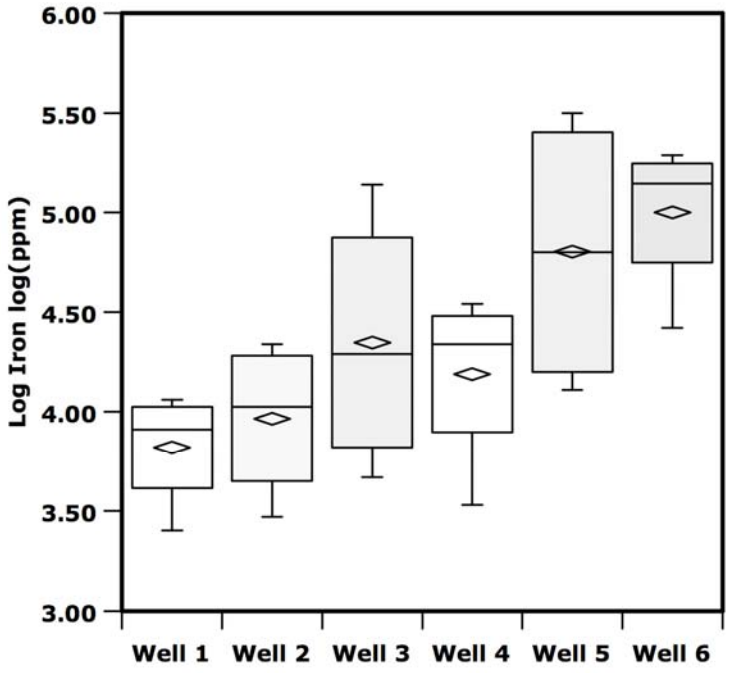
Date	Log Iron Concentrations log(ppm)					
	Well 1	Well 2	Well 3	Well 4	Well 5	Well 6
Jan 1997	4.06	3.83	4.61	3.53	4.11	4.42
Apr 1997	3.99	4.34	5.14	4.54	4.29	5.21
Jul 1997	3.40	3.47	3.67	4.26	5.50	5.29
Oct 1997	3.83	4.22	3.97	4.42	5.31	5.08
Mean	3.82	3.96	4.35	4.19	4.80	5.00
Median	3.91	4.02	4.29	4.34	4.80	5.14

Figure 13-1. Side-by-Side Iron Box Plots



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Figure 13-2. Side-by-Side Log(Iron) Box Plots



Step 4. While more nearly similar on the log-scale, the means and medians are still elevated in Wells 5 and 6. Since the differences in box lengths are much less on the log-scale, the log transformation has worked to somewhat stabilize the variances. These data should be tested formally for significant spatial variation using an ANOVA, probably on the log-scale. ◄

13.2.2 ONE-WAY ANALYSIS OF VARIANCE FOR SPATIAL VARIABILITY

PURPOSE AND BACKGROUND

Chapter 17 presents Analysis of Variance [ANOVA] in greater detail. When using ANOVA to check for spatial variability, the observations from each well are taken as a single group. Significant differences between data groups represent monitoring wells with different mean concentration levels. The lack of significant well mean differences may afford an opportunity to pool the data for larger background sizes and conduct interwell detection monitoring tests.

ANOVA used for this purpose should be performed either on a set of multiple non-impacted upgradient wells, or on historically uncontaminated compliance and upgradient background wells. If significant mean differences exist among naturally occurring constituent data at upgradient wells, natural spatial variability is the likely reason. Synthetic consitituents in upgradient wells might also exhibit spatial differences if affected by an offsite- plume. Presumably, if the flow gradient has been correctly

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assessed and no migration of contaminants from off-site has occurred, differences in mean levels across upgradient wells ought to signal the influence of factors not attributable to a monitored release. A similar, but potentially weaker, argument can be made if spatial differences exist between uncontaminated historical data at compliance wells. The lack of spatial differences between uncontaminated compliance and upgradient background well data, may again allow for even larger background sample sizes.

REQUIREMENTS AND ASSUMPTIONS

The basic assumptions and data requirements for one-way ANOVA are presented in **Section 17.1**. If the assumption that the observations are statistically independent over time is not met, both identifying spatial variability using ANOVA as well as improving intrawell prediction limits and control charts can be impacted. It is usually difficult to verify that the measurements are temporally independent with only a limited number of observations per well. This potential problem can be somewhat minimized by collecting samples far enough apart in time to guard against autocorrelation. Another option is to construct a parallel time series plot (**Chapter 14**) to look for time-related effects or dependencies occurring simultaneously across the set of wells.

If a significant temporal dependence or autocorrelation exists, the one-way ANOVA can still identify well-to-well mean level differences. But the power of the test to do so is lessened. If a parallel time series plot indicates a potentially strong time-related effect, a two-way ANOVA including temporal effects can be performed to test and correct for a significant temporal factor. This slightly more complicated procedure is discussed in Davis (1994).

Another key assumption of parametric ANOVA is that the residuals are normal or can be normalized. If a normalizing transformation cannot be found, a test for spatial variability can be made using the Kruskal-Wallis non-parametric ANOVA (**Chapter 17**). As long as the measurements can be ranked, average ranks that differ significantly across wells provide evidence of spatial variation.

PROCEDURE

Step 1. Assuming there are p distinct wells to test, designate the measurements from each well as a separate group for purposes of computing the ANOVA. Then follow **Steps 1** through **7** of the procedure in **Section 17.1.1** to compute the overall F-statistic and the quantities of the ANOVA table in **Figure 13-3** below.

Figure 13-3. One-Way Parametric ANOVA Table

Source of Variation	Sums of Squares	Degrees of Freedom	Mean Squares	*F*-Statistic
Between Wells	SS_{wells}	$p-1$	$MS_{wells} = SS_{wells}/(p-1)$	$F = MS_{wells}/MS_{error}$
Error (within wells)	SS_{error}	$n-p$	$MS_{error} = SS_{error}/(n-p)$	
Total	SS_{total}	$n-1$		

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Step 2. To test the hypothesis of equal means for all p wells, compare the F-statistic from Step 1 to the α-level critical point found from the F-distribution with $(p-1)$ and $(n-p)$ degrees of freedom in **Table 17-1** of **Appendix D**. Usually α is taken to be 5%, so that the needed comparison value equals the upper 95th percentage point of the F-distribution. If the observed F-statistic exceeds the critical point ($F_{.95,p-1,n-p}$), reject the hypothesis of equal well population means and conclude there is significant spatial variability. Otherwise, the evidence is insufficient to conclude there are significant differences between the means at the p wells.

►EXAMPLE 13-2

The iron concentrations in **Example 13-1** show evidence of spatial variability in side-by-side box plots. Tested for equal variances and normality, these same data are best fit by a lognormal distribution. The statistics for natural logarithms of the iron measurements are shown below; individual log data are provided in the **Example 13-1** second table. Compute a one-way parametric ANOVA to determine whether there is significant spatial variation at the $\alpha = .05$ significance level.

	Log Iron Concentration Statistics log(ppm)					
Date	Well 1	Well 2	Well 3	Well 4	Well 5	Well 6
N	4	4	4	4	4	4
Mean	3.820	3.965	4.348	4.188	4.802	5.000
SD	0.296	0.395	0.658	0.453	0.704	0.396
	Grand Mean = 4.354					

SOLUTION

Step 1. With 6 wells and 4 observations per well, $n_i = 4$ for all the wells. The total sample size is $n = 24$ and $p = 6$. Compute the (overall) grand mean and the sample mean concentrations in each of the well groups using equations [17.1] and [17.2]. These values are listed (along with each group's standard deviation) in the above table.

Step 2. Compute the sum of squares due to well-to-well differences using equation [17.3]:

$$SS_{wells} = \left[4(3.820)^2 + 4(3.965)^2 + \ \ldots \ + 4(5.000)^2\right] - 24(4.354)^2 = 4.331$$

This quantity has $(6 - 1) = 5$ degrees of freedom.

Step 3. Compute the corrected total sum of squares using equation [17.4] with $(n - 1) = 23$ df:

$$SS_{total} = \left[(4.06)^2 + \ \ldots \ + (5.08)^2\right] - 24(4.354)^2 = 8.935$$

Step 4. Obtain the within-well or error sum of squares by subtraction using equation [17.5]:

$$SS_{error} = 8.935 - 4.331 = 4.604$$

This quantity has $(n - p) = 24–6 = 18$ degrees of freedom.

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Step 5. Compute the well and error mean sum of squares using equations [17.6] and [17.7]:

$$MS_{wells} = 4.331/5 = .866$$

$$MS_{error} = 4.604/18 = .256$$

Step 6. Construct the *F*-statistic and the one-way ANOVA table, using **Figure 13-3** as a guide:

Source of Variation	Sums of Squares	Degrees of Freedom	Mean Squares	*F*-Statistic
Between Wells	4.331	5	0.866	*F* = 0.866/0.256=3.38
Error (within wells)	4.604	18	0.256	
Total	8.935	23		

Step 7. Compare the observed *F*-statistic of 3.38 against the critical point taken as the upper 95th percentage point from the *F*-distribution with 5 and 18 degrees of freedom. Using **Table 17-1** of **Appendix D**, this gives a value of $F_{.95,5,18}$ = 2.77. Since the *F*-statistic exceeds the critical point, the null hypothesis of equal well means can be rejected, suggesting the presence of significant spatial variation. ◄

13.3 USING ANOVA TO IMPROVE PARAMETRIC INTRAWELL TESTS

BACKGROUND AND PURPOSE

Constituents that exhibit significant spatial variability usually should be formally tested with intrawell procedures such as a prediction limit or control chart. Historical data from each compliance well are used as background for these tests instead of from upgradient wells. At an early stage of intrawell testing, there may only be a few measurements per well which can be designated as background. Depending on the number of statistical tests that need to be performed across the monitoring network, available intrawell background at individual compliance wells may not provide sufficient statistical power or meet the false positive rate criteria (**Chapter 19**).

One remedy first suggested by Davis (1998) can increase the *degrees of freedom* of the test by using one-way ANOVA results (**Section 13.2**) from a number of wells to provide an alternate estimate of the average intrawell variance. In constructing a parametric intrawell prediction limit for a single compliance well, the intrawell background of sample size *n* is used to compute a well-specific sample mean ($\bar{x}$). The intrawell standard deviation (*s*) is replaced by the root mean squared error [RMSE] component from an ANOVA of the intrawell background associated with a series of compliance and/or background wells.[1] This raises the degrees of freedom from (*n*–1) to (*N*–*p*), where *N* is the total sample size across the group of wells input to the ANOVA and *p* is the number of distinct wells.

[1] RMSE is another name for the square root of the mean error sum of squares (MS_{error}) in the ANOVA table of **Figure 13-3**.

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As an example of the difference this adjustment can make, consider a site with 6 upgradient wells and 15 compliance wells. Assuming $n = 6$ observations per well that have been collected over the last year, a total of 36 potential background measurements are available to construct an interwell test. If there is significant natural spatial variation in the mean levels from well to well, an interwell test is probably not appropriate. Switching to an intrawell method is the next best solution, but with only six observations per compliance well, either the power of an intrawell test to identify contaminated groundwater is likely to be quite low (even with retesting) or the site-wide false positive rate [SWFPR] will exceed the recommended target.

If the six upgradient wells were tested for spatial variability using a one-way ANOVA (presuming that the equal variance assumption is met), the degrees of freedom [*df*] associated with the mean error sum of squares term is (6 wells × 5 *df* per well) = 30 *df* (see **Section 13.2**). Thus by substituting the RMSE in place of each compliance well's intrawell standard deviation (*s*), the degrees of freedom for the modified intrawell prediction or control chart limit is 30 instead of 5.

ANOVA can be usefully employed in this manner since the RMSE is very close to being a weighted average of the individual well sample standard deviations. As such, it can be considered a measure of average within-well variability across the wells input to the ANOVA. Substituting the RMSE for *s* at an individual well consequently provides a better estimate of the typical within-well variation, since the RMSE is based on levels of fluctuation averaged across several wells. In addition, the number of observations used to construct the RMSE is much greater than the *n* values used to compute the intrawell sample standard deviation (*s*). Since both statistical measures are estimates of within-well variation, the RMSE with its larger degrees of freedom is generally a superior estimate if certain assumptions are met.

REQUIREMENTS AND ASSUMPTIONS

Using ANOVA to bolster parametric intrawell prediction or control chart limits will not work at every site or for every constituent. Replacement of the well-specific, intrawell sample standard deviation (s) by the RMSE from ANOVA assumes that the true within-well variability is *approximately the same* at all the wells for which an intrawell background limit (*i.e.*, prediction or control chart) will be constructed, and not just those wells tested in the ANOVA procedure. This last assumption can be difficult to verify if the ANOVA includes only background or upgradient wells. But to the extent that uncontaminated intrawell background measurements from compliance point wells can be included, the ANOVA should be run on all or a substantial fraction of the site's wells (excluding those which might already be contaminated). Whatever mix of upgradient and downgradient wells are included in the ANOVA, the purpose of the procedure is *not* to identify groundwater contamination, but rather to compute a better and more powerful estimate of the average intrawell standard deviation.

For the ANOVA to be valid and the RMSE to be a reasonable estimate of average within-well variability, a formal check of the equal variance assumption should be conducted using **Chapter 11** methods. A spatially variable constituent will often exhibit well-specific standard deviations that increase with the well-specific mean concentration. Equalizing the variances in these cases will require a data transformation, with an ANOVA conducted on the transformed data. Ultimately, any transformation applied to the wells in the ANOVA *also* need to be applied to intrawell background before computing intrawell prediction or control chart limits. The *same transformation* has to be appropriate for *both* sets

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of data (*i.e.*, wells included in ANOVA *and* intrawell background at wells for which background limits are desired).

Even when the ANOVA procedure described in this section is utilized, the resulting intrawell limits should also be designed to incorporate retesting. When intrawell background is employed to estimate both a well-specific background mean ($\bar{x}$) and well-specific standard deviation (s), the **Appendix D** tables associated with **Chapters 19** and **20** can be used to look up the intrawell sample size (n) and number of wells (w) in the network in order to find a prediction or control chart multiplier that meets the targeted SWFPR and has acceptable statistical power. However, these tables implicitly assume that the degrees of freedom [df] associated with the test is equal to (n–1). The ANOVA method of this section results in a much larger df, and more importantly, in a df that does not 'match' the intrawell sample size (n).

Consequently, the parametric multipliers in the **Appendix D** tables cannot be directly used when constructing prediction or control chart limits with retesting. Instead, a multiplier must be computed for the specific combination of n and df computed as a result of the ANOVA. Tabulating all such possibilities would be prohibitive. For prediction limits, the Unified Guidance recommends the free-of-charge, open source **R** statistical computing environment. A pre-scripted program is included in **Appendix C** that can be run in **R** to calculate appropriate prediction limit multipliers, once the user has supplied an intrawell sample size (n), network size (w), and type of retesting scheme.

If guidance users are unable to utilize the **R-script** approach, the following approximation for the well-specific prediction limit κ-factors is suggested based on EPA Region 8 Monte Carlo evaluations. Given a per- test confidence level of $1\text{-}\alpha$, r total tests of $w \cdot c$ well-constituents, an individual well size n_i, a pooled variance sample size of $n_{df} = df + 1$, and $\kappa_{ndf,1-\alpha}$ obtained from annual intrawell Unified Guidance tables, the individual well $\kappa_{ni,1-\alpha}$ factor can be estimated using the following equation:

$$\kappa_{n_i,1-\alpha} = \kappa_{n_{df},1-\alpha} \cdot \left[\frac{(n_i + \mu) \cdot n_{df}}{n_i \cdot (n_{df} + \mu)} \right]^{m^* = \frac{A \cdot n_i^b}{r^c}}$$

where $\mu = 1$ for future $1{:}m$ observations or μ is the size of a future mean. The value of m^* is specific to each of the nine parametric prediction limit tests and is a function of the three coefficients A, b and c, individual well sample size n_i and r tests. For a 1:1 test of future means or observations, the equation is exact; for higher order 1:m tests, the results are approximate.[2] The equation is also useful in

[2] For each of the nine prediction limit tests, the following coefficients (A, b & c) are recommended: a 1:2 future values test (1.01, .0524 & .0158); a 1:3 test (1.63, .108 & .0407); a 1:4 test (2.41, .157 & .0668); the modified California plan (1.36, .103 & .0182); a 1:1 mean size 2 test (.5, 0 & 0); a 1:2 mean size 2 test (.898, .0856 & .0172); a 1:3 mean size 2 test (1.27, .168 & .0363); a 1:1 mean size 3 test (.5, 0 & 0); and a 1:2 mean size 3 test (.817, .108 & .0158). %. The coefficients were obtained from regression analysis; approximation values were compared with R-script values for κ-factors. In 1260 comparisons of the seven tests using repeat values ($m > 1$), 86% of the approximations lay within or equal to ± 1% of the true value and 96% within or equal to ± 2%. The 1:4 test had the greatest variability, but all values lay within ± 4%. 81% of the values lay within or equal to ± .01 κ-units and 93% less than or equal to ± .02 units.

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gauging **R-script** method results. Another virtue of this equation is that it can be readily applied to different individual well sample sizes based on the common $\kappa_{ndf,1-\alpha}$ for pooled variance data.

A less elegant solution is available for intrawell control charts. Currently, an appropriate multiplier needs to be simulated via Monte Carlo methods. The approach is to simulate separate normally-distributed data sets for the background mean based on n measurements, and the background standard deviation based on $df + 1$ measurements. Statistical independence of the sample mean ($\bar{x}$) and standard deviation (s) for normal populations allows this to work. With the background mean and standard deviation available, a series of possible multipliers (h) can be investigated in simulations of control chart performance. The multiplier which meets the targeted SWFPR and provides acceptable power should be selected. Further detail is presented in **Chapter 20**. **R** can also be used to conduct these simulations.

►EXAMPLE 13-3

The logged iron concentrations from **Example 13-2** showed significant evidence of spatial variability. Use the results of the one-way ANOVA to compute adjusted intrawell prediction limits (without retesting) for each of the wells in that example and compare them to the unadjusted prediction limits.

SOLUTION

Step 1. Summary statistics by well for the logged iron measurements are listed in the table below. With $n = 4$ measurements per well, use equation [13.1] and $t_{1-\alpha,n-1} = t_{.99,3} = 4.541$ from **Table 16-1** in **Appendix D** to compute at each well an unadjusted 99% intrawell prediction limit for the next single measurement, based on lognormal data:

$$PL_{1-\alpha} = \exp\left[\bar{y} + s_y t_{1-\alpha,n-1}\sqrt{1+\frac{1}{n}}\right] \qquad [13.1]$$

	Unadjusted 99% Prediction Limits for Iron (ppm)					
	Well 1	Well 2	Well 3	Well 4	Well 5	Well 6
Log-mean	3.820	3.965	4.348	4.188	4.802	5.000
Log-SD	0.296	0.395	0.658	0.453	0.704	0.396
n	4	4	4	4	4	4
$t_{.99,3}$	4.541	4.541	4.541	4.541	4.541	4.541
99% PL	204.9	391.6	2183.0	657.0	4341.5	1108.1

Step 2. Use the RMSE (*i.e.*, square root of the mean error sum of squares [MS_{error}] component) of the ANOVA in **Example 13-2** as an estimate of the adjusted, pooled standard deviation, giving $\sqrt{MS_{error}} = \sqrt{.256} = .506$. The degrees of freedom (df) associated with this pooled standard deviation is $p(n-1) = 6(3) = 18$, the same as listed in the ANOVA table of **Example 13-2**.

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Step 3. Use equation [13.2], along with the adjusted pooled standard deviation and its associated *df*, to compute an adjusted 99% prediction limit for each well, as given in the table below. Note that the adjusted t-value based on the larger *df* is $t_{1-\alpha,\mathrm{df}} = t_{.99,18} = 2.552$.

$$PL_{1-\alpha} = \exp\left[\overline{y} + t_{1-\alpha,df}\sqrt{MS_{error}\left(1+\frac{1}{n}\right)}\right] \qquad [13.2]$$

	Adjusted 99% Prediction Limits for Iron (ppm)					
	Well 1	Well 2	Well 3	Well 4	Well 5	Well 6
Log-mean	3.820	3.965	4.348	4.188	4.802	5.000
RMSE	0.5079	0.5079	0.5079	0.5079	0.5079	0.5079
df	18	18	18	18	18	18
$t_{.99,18}$	2.552	2.552	2.552	2.552	2.552	2.552
99% PL	193.2	223.3	327.5	279.1	515.8	628.7

Step 4. Compare the adjusted and unadjusted lognormal prediction limits. By estimating the average intrawell standard deviation using ANOVA, the adjusted prediction limits are significantly lower and thus more powerful than the unadjusted limits, especially at Wells 3, 5, and 6.

In this example, use of the **R**-script approach was unnecessary, since the corresponding κ-multiple used in 1-of-1 prediction limit tests can be directly derived analytically. ◄

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CHAPTER 14. TEMPORAL VARIABILITY

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This chapter discusses the importance of *statistical independence* in groundwater monitoring data with respect to *temporal variability*. Temporal variability exists when the distribution of measurements varies with the times at which sampling or analytical measurement occurs. This variation can be caused by seasonal fluctuations in the groundwater itself, changes in the analytical method used, the re-calibration of instruments, anomalies in sampling method, *etc*.

Methods to *identify* temporal variability are discussed for both groups of wells (parallel time series plots; one-way analysis of variance [ANOVA] for temporal effects) and single data series (sample autocorrelation function; rank von Neumann ratio). Procedures are also presented for correcting or accommodating temporal effects. These include guidance on adjusting the sampling frequency to avoid temporal correlation, choosing a sampling interval using the Darcy equation, removing seasonality or other temporal dependence, and finally testing for trends with seasonal data.

14.1 TEMPORAL DEPENDENCE

A key assumption underlying most statistical tests is that the sample data are independent and identically distributed [*i.i.d.*] (**Chapter 3**). In part, this means that measurements collected over a period of time should not exhibit a clear *time dependence* or significant *autocorrelation*. Time dependence refers to the presence of trends or cyclical patterns when the observations are graphed on a time series plot. The closely related concept of autocorrelation is essentially the degree to which measurements collected later in a series can be predicted from previous measurements. Strongly autocorrelated data are highly predictable from one value to the next. Statistically independent values vary in a random, unpredictable fashion.

While temporal independence is a complex topic, there are several common types of temporal dependence. Some of these include: 1) correlation across wells over time in the concentration pattern of a single constituent (*i.e.*, concentrations tending to jointly rise or fall at each of the wells on common sampling events); 2) correlation across multiple constituents over time in their concentration patterns (*i.e.*, a parallel rise or fall in concentration across several parameters on common sampling events); 3) seasonal cycles; 4) trends, linear or otherwise; and 5) serial dependence or autocorrelation (*i.e.*, greater correlation between sampling events more closely spaced in time).

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Any of these patterns can invalidate or weaken the results of statistical testing. In some cases, a statistical method can be chosen that specifically accounts for temporal dependence (e.g., seasonal Mann-Kendall trend test). In other instances, the sample data need to be adjusted for the dependence. Future data might also need to be collected in a manner that avoids temporal correlation. The goal of this chapter is to present straightforward tools that can be used to first identify temporal dependence and then to adjust for this correlation.

To better understand why most statistical tests depend on the assumption of statistical independence, consider a hypothetical series of groundwater measurements exhibiting an obvious pattern of seasonal fluctuation (**Figure 14-1**). These data demonstrate regular and repeated cycles of higher and lower values. Even though fluctuating predictably and highly dependent, the characteristics of the entire groundwater population will be observed over a long period of monitoring. This provides an estimate of the full range of concentrations and an accurate gauge of total variability.

The same is not true for data collected from the same population over a much shorter span, say in five to six months. A much narrower range of sample concentrations would be observed due to the cyclical pattern. Depending on when the sampling was conducted, the average concentration level would either be much higher or much lower than the overall average; no single sampling period is likely to accurately estimate either the true population mean or its variance.

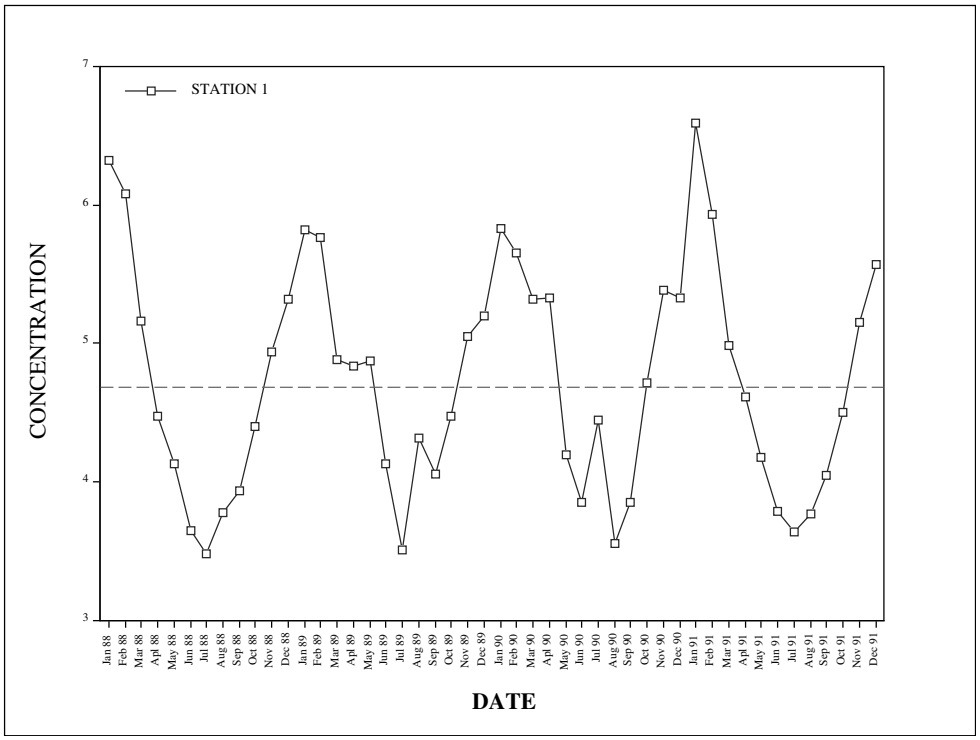
From this example, an important lesson can be drawn about temporally dependent data. Variance estimates in a sample of dependent, positively autocorrelated data are likely to be biased low. This is important because the guidance methods require and assume that an accurate and unbiased estimate of the sample standard deviation be available. A case in point was the practice of using aliquot replicates of a single physical sample for comparison with other combined replicate aliquot samples from a number of individual physical water quality samples (*e.g.*, in a Student-*t* test). Aliquot replicate values are much more similar to each other than to measurements made on physically discrete groundwater samples. Consequently, the estimate of variance was too low and the *t*-test frequently registered false positives.

Using physically discrete samples is not always sufficient. If the sampling interval ensures that discrete volumes of groundwater are being sampled on consecutive sampling events, the observations can be described as *physically independent*. However, they are not necessarily *statistically* independent. Statistical independence is based not on the physical characteristics of the sample data, but rather on the statistical pattern of measurements.

Temporally dependent and autocorrelated data generally contain both a truly random and non-random component. The relative strength of the latter effect is a measured by one or more correlation techniques. The degree of correlation among dependent sample measurements lies on a continuum. Sample pairs can be mildly correlated or strongly correlated. Only strong correlations are likely to substantially impact the results of further statistical testing.

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Figure 14-1. Seasonal Fluctuations



14.2 IDENTIFYING TEMPORAL EFFECTS AND CORRELATION

14.2.1 PARALLEL TIME SERIES PLOTS

BACKGROUND AND PURPOSE

Time series plots were introduced in **Chapter 9**. A time series plot such as **Figure 14-1** is a simple graph of concentration versus time of sample collection. Such plots are useful for identifying a variety of temporal patterns. These include identifying a trend over time, one or more sampling events that may signal contaminant releases, measurement outliers resulting in anomalous 'spikes' due to field handling or analytical problems, cyclical and seasonal fluctuations, as well as the presence of other time-related dependencies.

Time series plots can be used in two basic ways to identify temporal dependence. By graphing single constituent data from multiple wells together on a time series plot, potentially significant temporal components of variability can be identified. For example, seasonal fluctuations can cause the mean concentration levels at a number of wells to vary with the time of sampling events. This dependency will show up in the time series plot as a pattern of *parallel traces*, in which the individual wells will tend to rise and fall together across the sequence of sampling dates. The parallel pattern may be the result of the measurement process such as mid-stream changes in field handling or sample collection procedures, periodic re-calibration of analytical instrumentation, and changes in laboratory or analytical methods. It could also be the result from significant autocorrelation present in the groundwater population itself. Hydrologic factors such as drought, recharge patterns or regular (*e.g.*, seasonal) water table fluctuations may be responsible. In these cases, it may be useful to test for the presence of a significant temporal

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effect by first constructing a parallel time series plot and then running a formal one-way ANOVA for temporal effects (**Section 14.2.2**).

The second way time series plots can be helpful is by plotting multiple constituents over time for the same well, or averaging values for each constituent across wells on each sampling event and then plotting the averages over time. In either case, the plot can signify whether the general concentration pattern over time is simultaneously observed for different constituents. If so, it may indicate that a group of constituents is highly correlated in groundwater or that the same artifacts of sampling and/or lab analysis impacted the results of several monitoring parameters.

REQUIREMENTS AND ASSUMPTIONS

The requirements for time series plots were discussed in **Chapter 9**. Two very useful recommendations follow from that discussion. First, a different plot symbol should be used to display any non-detect measurements (*e.g.*, solid symbols for detected values, hollow symbols for non-detects). This can help prevent mistaking a change over time in reporting limits as a trend, since detected and non-detected data are clearly distinguished on the plot. It also allows one to determine whether non-detects are more prevalent during certain portions of the sample record and less prevalent at other times. Secondly, when multiple constituents are plotted on the same graph, it may be necessary to *standardize* each constituent prior to plotting to avoid trying to simultaneously visualize high-valued and low-valued traces on the same *y*-axis (*i.e.*, concentration axis). The goal of such a plot is to identify parallel concentration patterns over time. This can be done most readily by subtracting each constituent's sample mean ($\bar{x}$) from the measurements for that constituent and dividing by the standard deviation (s), so that every constituent is plotted on roughly the same scale.

PROCEDURE FOR MULTIPLE WELLS, ONE CONSTITUENT

Step 1. For each well to be plotted, form data pairs by matching each concentration value with its sampling date.

Step 2. Graph the data pairs for each well on the same set of axes, the horizontal axis representing time and the vertical axis representing concentration. Connect the points for each individual well to form a 'trace' for that well.

Step 3. Look for parallel movement in the traces across the wells. Even if all the well concentrations tend to rise on a given sampling event, but not to the same magnitude or degree, this is evidence of a possible temporal effect.

PROCEDURE FOR MULTIPLE CONSTITUENTS, ONE OR MANY WELLS

Step 1. For each constituent to be plotted, compute the constituent-specific sample mean ($\bar{x}$) and standard deviation (s). Form standardized measurements (z_i) by subtracting the mean from each concentration (x_i) and dividing by the standard deviation, using the equation:

$$z_i = \frac{x_i - \bar{x}}{s} \qquad [14.1]$$

Form data pairs by matching each standardized concentration with its sampling event.

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Step 2. If correlation is suspected in a group of wells, average the standardized concentrations for each given constituent *across wells* for each specific sampling event. Otherwise, form a multi-constituent time series plot separately for each well.

Step 3. Graph the data pairs for each constituent on the same set of axes, the horizontal axis representing time and the vertical axis representing standardized concentrations. Connect the points for each constituent to form a trace for that parameter.

Step 4. Look for parallel movement in the traces across the constituents. A strong degree of parallelism indicates a high degree of correlation among the monitoring parameters.

►EXAMPLE 14-1

The following well sets of manganese measurements were collected over a two-year period. Construct a time series plot of these data to check for possible temporal effects.

	Manganese Concentrations (ppm)			
Qtr	BW-1	BW-2	BW-3	BW-4
1	28.14	31.41	27.15	30.46
2	29.33	30.27	30.24	30.60
3	30.45	32.57	29.14	30.96
4	32.42	32.77	30.59	30.70
5	34.37	33.03	34.88	32.71
6	33.25	32.18	30.53	31.76
7	31.02	28.85	30.33	31.85
8	28.50	32.88	30.42	29.58

SOLUTION

Step 1. Graph each well's concentrations versus sampling event on the same set of axes to construct the following time series plot (**Figure 14-2**).

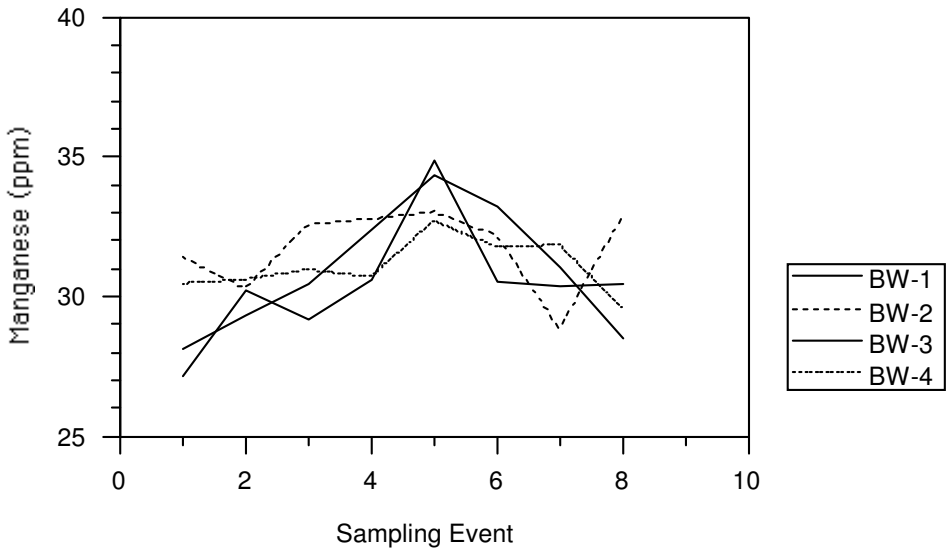


Figure 14-2. Manganese Parallel Time Series Plot

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Step 2. Examining the traces on the plot, there is some degree of parallelism in the pattern over time. Particularly for the fifth quarter, there is an across-the-board increase in the manganese level, followed by a general decline the next two quarterly events. Note, however, that there is little evidence of differences in mean levels by *well location*. ◄

14.2.2 ONE-WAY ANALYSIS OF VARIANCE FOR TEMPORAL EFFECTS

PURPOSE AND BACKGROUND

Parametric ANOVA is a comparison of means among a set of populations. The one-way ANOVA for temporal effects is no exception. A one-way ANOVA for spatial variation (**Chapter 13**) uses well data sets to represent *locations* as the statistical factor of interest. In contrast, a one-way ANOVA for temporal effects considers multiple well data sets for individual *sampling events* or *seasons* as the relevant statistical factor. A significant temporal factor implies that the average concentration depends to some degree on *when* sampling takes place.

Three common examples of temporal factors include: 1) an irregular, but consistent shift of average concentrations over time perhaps due to changes in laboratories or analytical method interferences; 2) cyclical seasonal patterns; or 3) parallel upward or downward trends. These can occur in both upgradient and downgradient well data.

If event-specific analytical differences or seasonality appear to be an important temporal factor, the one-way ANOVA for temporal effects can be used to formally identify seasonality, parallel trends, or changes in lab performance that affect other temporal effects. Results of the ANOVA can also be used to create temporally *stationary residuals*, where the temporal effect has been 'subtracted from' the original measurements. These stationary residuals may be used to replace the original data in subsequent statistical testing.

The one-way ANOVA for a temporal factor described below can be used for an additional purpose when interwell testing is appropriate. For this situation, *there can be no significant spatial variability*. If a group of upgradient or other background wells indicates a significant temporal effect, an interwell prediction limit can be designed which properly accounts for this temporal dependence. A more powerful interwell test of upgradient-to-downgradient differences can be developed than otherwise would be possible. This can occur because the ANOVA separates or 'decomposes' the overall data variation into two sources: a) temporal effects and b) random variation or statistical error. It also estimates how the background mean is changing from one sampling event to the next. The final prediction limit is formed by computing the background mean, using the separate structural and random variation components of the ANOVA to better estimate the standard deviation, and then adjusting the effective sample size (via the degrees of freedom) to account for these factors.

REQUIREMENTS AND ASSUMPTIONS

Like the one-way ANOVA for spatial variation (**Chapter 13**), the one-way ANOVA for temporal effects assumes that the data groups are normally-distributed with constant variance. This requirement means that the group residuals should be tested for normality (**Chapter 10**) and also for equality of

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variance (**Chapter 11**). It is also assumed that for each of a series of background wells, measurements are collected at each well on sampling events or dates *common* to all the wells.

Two variations in the basic procedure are described below. For cases of temporal effects *excluding* seasonality, each sampling event is treated as a separate population. The ANOVA residuals are grouped and tested *by sampling event* to test for equality of variance. In cases of apparent seasonality, each *season* is treated as a distinct population. The difference is that seasons contain multiple sampling events across a span of multiple years, with sampling events collected at the same time of year assigned to one of the seasons (*e.g.*, all January or first quarter measurements). Here, the ANOVA residuals are grouped by season to test for homoscedasticity.

If the assumption of equal variances or normal residuals is violated, a data transformation should be considered. This should be followed by testing of the assumptions on the transformed scale. The one-way ANOVA for a non-seasonal effect should include a minimum of four wells and at least 4 observations (*i.e.*, distinct sampling dates) per well. In the seasonal case, there should be a minimum of 3-4 sampling events per distinct season, with the events thus spanning at least three years (*i.e.*, one per year per season). Larger numbers of both wells and observations are preferable. Sampling dates should also be approximately the *same* for each well if a temporal effect is to be tested.

If the data cannot be normalized, a similar test for a temporal or seasonal effect can be performed using the Kruskal-Wallis test (**Chapter 17**). The only difference from the procedure outlined in **Section 17.1.2** is that the roles of wells/groups and sampling events have to be reversed. That is, each sampling event should be treated as a separate 'well,' while each well is treated as a separate 'sampling event.' Then the same equations can be applied to the reversed data set to test for a significant temporal dependence. If testing for a seasonal effect, the wells in the notation of **Section 17.1.2** become the groups of common sampling events from different years, while the sampling events are again the distinct wells.

Even when a temporal effect exists and is apparent on a time series plot, the variation between well locations (*i.e.*, spatial variability) may overshadow the temporal variability. This could result in a non-significant one-way ANOVA finding for the temporal factor. In these cases, a two-way ANOVA can be considered where both well location and sampling event/season are treated as statistical factors. This procedure is described in Davis (1994). Evidence for a temporal effect can be documented using this last technique, although the two-way ANOVA isn't necessary if the goal is simply to construct temporally stationary residuals. That can be accomplished with a one-way ANOVA even when significant spatial variability exists.

PROCEDURE

Step 1. Given a set of W wells and measurements from each of T sampling events at each well on each of K years, label the observations as x_{ijk}, for $i = 1$ to W, $j = 1$ to T, and $k = 1$ to K. Then x_{ijk} represents the measurement from the ith well on the jth sampling event during the kth year.

Step 2. When testing for a *non-seasonal* temporal effect, form the set of event means ($x_{\bullet jk}$) and the grand mean ($x_{\bullet\bullet\bullet}$) using equations [14.2] and [14.3] respectively:

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$$x_{\bullet jk} = \frac{1}{W}\sum_{i=1}^{W} x_{ijk} \text{ for } j = 1 \text{ to } T \text{ and } k = 1 \text{ to } K \quad [14.2]$$

$$x_{\bullet\bullet\bullet} = \sum_{i=1}^{W}\sum_{j=1}^{T}\sum_{k=1}^{K} x_{ijk} \Big/ WTK \quad [14.3]$$

Step 2a. If testing for a seasonal effect common to all wells, form the seasonal means ($x_{\bullet j\bullet}$) instead of the event means of **Step 2**, using the equation:

$$x_{\bullet j\bullet} = \frac{1}{WK}\sum_{i=1}^{W} x_{ijk} \text{ for } j = 1 \text{ to } T \quad [14.4]$$

Step 3. Compute the set of residuals for each sampling event or season using either equation [14.5] or equation [14.6] respectively:

$$r_{ijk} = x_{ijk} - x_{\bullet jk} \text{ for } i = 1 \text{ to } W \quad [14.5]$$

$$r_{ijk} = x_{ijk} - x_{\bullet j\bullet} \text{ for } i = 1 \text{ to } W \text{ and } k = 1 \text{ to } K \quad [14.6]$$

Step 4. Test the residuals for normality (**Chapter 10**). If significant non-normality is evident, consider transforming the data and re-doing the computations in **Steps 1** through **4** on the transformed scale.

Step 5. Test the sets of residuals grouped either by sampling event or season for equal variance (**Chapter 11**). If the variances are significantly different, consider transforming the data and re-doing the computations in **Steps 1** through **5** on the transformed data.

Step 6. If testing for a non-seasonal temporal effect, compute the mean error sum of squares term (MS_E) using equation:

$$MS_E = \sum_{i=1}^{W}\sum_{j=1}^{T}\sum_{k=1}^{K} r_{ijk}^2 \Big/ TK(W-1) \quad [14.7]$$

This term is associated with $TK(W–1)$ degrees of freedom. Also compute the mean sum of squares for the temporal effect (MS_T) with degrees of freedom ($TK–1$), using equation:

$$MS_T = W\sum_{j=1}^{T}\sum_{k=1}^{K}\left(x_{\bullet jk} - x_{\bullet\bullet\bullet}\right)^2 \Big/ (TK-1) \quad [14.8]$$

Step 6a. If testing for a seasonal effect, compute the mean error sum of squares (MS_E) using equation:

$$MS_E = \sum_{i=1}^{W}\sum_{j=1}^{T}\sum_{k=1}^{K} r_{ijk}^2 \Big/ T(WK-1) \quad [14.9]$$

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This term is associated with $T(WK-1)$ degrees of freedom. Also compute the mean sum of squares for the seasonal effect (MS_T) with degrees of freedom ($T-1$), using equation:

$$MS_T = WK\sum_{j=1}^{T}\left(x_{\bullet j\bullet} - x_{\bullet\bullet\bullet}\right)^2 \Big/ \left(T-1\right) \qquad [14.10]$$

Step 7. Test for a significant event-to-event or seasonal effect by computing the ratio of the mean sum of squares for time and the mean error sum of squares:

$$F_T = MS_T \big/ MS_E \qquad [14.11]$$

Step 8. If testing for a non-seasonal temporal effect, the test statistic F_T under the null hypothesis (*i.e.*, of no significant time-related variability among the sampling events) will follow an *F*-distribution with $(TK-1)$ and $TK(W-1)$ degrees of freedom. Therefore, using a significance level of $\alpha = 0.05$, compare F_T against the critical point $F_{.05,\ TK-1,TK(W-1)}$ taken from the *F*-distribution in **Table 17-1** in **Appendix D**. If the critical point is exceeded, conclude there is a significant temporal effect.

Step 8a. If testing for a seasonal effect, the test statistic F_T under the null hypothesis (*i.e.*, of no seasonal pattern) will follow an *F*-distribution with $(T-1)$ and $T(WK-1)$ degrees of freedom. Therefore, using a significance level of $\alpha = 0.05$, compare F_T against the critical point $F_{.05,\ T-1,T(WK-1)}$ taken from the *F*-distribution in **Table 17-1** of **Appendix D**. If the critical point is exceeded, conclude there is a significant seasonal pattern.

Step 9. If there is no spatial variability but a significant temporal effect exists among a set of background wells, compute an appropriate *interwell* prediction or control chart limit as follows. First replace the background sample standard deviation (s) with the following estimate built from the one-way ANOVA table:

$$\hat{\sigma} = \sqrt{\frac{1}{W}\left[MS_T + (W-1)\,MS_E\right]} \qquad [14.12]$$

Then calculate the effective sample size for the prediction limit as:

$$n^* = 1 + \left\{\left[TK\cdot(TK-1)\cdot\left(F_T + W - 1\right)^2\right] \Big/ \left[TK\cdot F_T^2 + (TK-1)\cdot(W-1)\right]\right\} \qquad [14.13]$$

►EXAMPLE 14-2

Some parallelism was found in the time series plot of **Example 14-1**. Test those same manganese data for a significant, non-seasonal temporal effect using a one-way ANOVA at the 5% significance level.

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Qtr	Manganese Concentrations (ppm)				
	Event Mean	BW-1	BW-2	BW-3	BW-4
1	29.290	28.14	31.41	27.15	30.46
2	30.110	29.33	30.27	30.24	30.60
3	30.780	30.45	32.57	29.14	30.96
4	31.620	32.42	32.77	30.59	30.70
5	33.747	34.37	33.03	34.88	32.71
6	31.930	33.25	32.18	30.53	31.76
7	30.513	31.02	28.85	30.33	31.85
8	30.345	28.50	32.88	30.42	29.58
	Grand mean = 31.042				

SOLUTION

Step 1. First compute the means for each sampling event and the grand mean of all the data. These values are listed in the table above. With four wells and eight quarterly events per well, $W = 4$, $T = 4$, and $K = 2$.

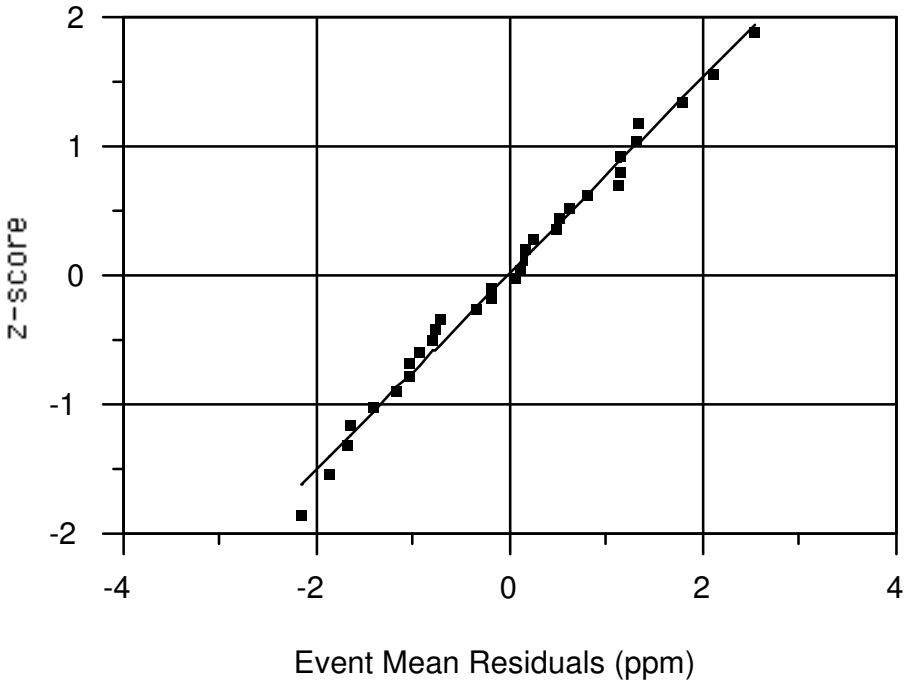
Step 2. Determine the residuals for each sampling event by subtracting off the event mean. These values are listed in the table below.

Qtr	Manganese Event Residuals (ppm)			
	BW-1	BW-2	BW-3	BW-4
1	-1.150	2.120	-2.140	1.170
2	-0.780	0.160	0.130	0.490
3	-0.330	1.790	-1.640	0.180
4	0.800	1.150	-1.030	-0.920
5	0.622	-0.718	1.132	-1.038
6	1.320	0.250	-1.400	-0.170
7	0.508	-1.662	-0.182	1.338
8	-1.845	2.535	0.075	-0.765

Step 3. Test the residuals for normality. A probability plot of these residuals is given in **Figure 14-3**. An adequate fit to normality is suggested by Filliben's probability plot correlation coefficient test.

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Figure 14-3. Probability Plot of Manganese Sampling Event Residuals



Step 4. Next, test the groups of residuals for equal variance across sampling events. Levene's test (**Chapter 11**) gives an *F*-statistic of 1.30, well below the 5% critical point with 7 and 24 degrees of freedom of $F_{.95,7,24} = 2.42$. Therefore, the group variances test out as adequately homogeneous.

Step 5. Compute the mean error sum of squares term using equation [14.7]:

$$MS_E = \left[(-1.150)^2 + (-.780)^2 + \ldots + (1.338)^2 + (-.765)^2\right] / (4 \cdot 2)(3) = 1.87$$

Step 6. Compute the mean sum of squares term for the time effect using equation [14.8]:

$$MS_T = 4\left[(29.290 - 31.042)^2 + (30.11 - 31.042)^2 + \ldots + (30.345 - 31.042)^2\right] / 7 = 7.55$$

Step 7. Test for a significant temporal effect, computing the *F*-statistic in equation [14.11]:

$$F_T = 7.55 / 1.87 = 4.04$$

The degrees of freedom associated with the numerator and denominator respectively are (TK–1) = 7 and $TK(W–1)$ = 24. Just as with Levene's test run earlier, the 5% level critical point for the test is $F_{.95,7,24} = 2.42$. Since F_T exceeds this value, there is evidence of a significant temporal effect in the manganese background data.

Step 8. Assuming a lack of spatial variation, the presence of a temporal effect can be used to compute a standard deviation estimate and effective background sample size appropriate for an

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interwell prediction limit test, using equations [14.12] and [14.13] respectively. The adjusted standard deviation becomes:

$$\hat{\sigma} = \sqrt{\frac{1}{4}\left[7.55 + 3\cdot(1.87)\right]} = 1.814\ ppm$$

while the effective sample size is:

$$n^* = 1 + \left\{\left[8\cdot 7\cdot(4.04+4-1)^2\right] / \left[8\cdot(4.04)^2 + 7\cdot 3\right]\right\} = 19.31 \approx 19$$

If the background data had simply been pooled together and the sample standard deviation computed, s = 1.776 ppm with a sample size of n = 32. So the adjustments based on the temporal effect alter the final prediction limit by enlarging it and reducing the effective sample size to account for the additional component of variation. ◄

14.2.3 SAMPLE AUTOCORRELATION FUNCTION

BACKGROUND AND PURPOSE

The sample autocorrelation function enables a test of temporal autocorrelation in a single data series (*e.g.*, from a single well over time). When a time-related dependency affects several wells simultaneously, parallel time series plots (**Section 14.2.1**) and one-way ANOVA for temporal effects (**Section 14.2.2**) should be considered. But when a longer data series is to be used for an intrawell test such as a prediction limit or control chart, the autocorrelation function does an excellent job of identifying temporal dependence.

Given a sequence of consecutively-collected measurements, x_1, x_2,…, x_n, form the set of overlapping pairs (x_i, x_{i+1}) for i = 1,…, n–1. The approximate first-order sample autocorrelation coefficient is then computed from these pairs as (Chatfield, 2004):

$$r_1 = \frac{\sum_{i=1}^{n-1}\left(x_i - \bar{x}\right)\left(x_{i+1} - \bar{x}\right)}{\sum_{i=1}^{n}\left(x_i - \bar{x}\right)^2} \qquad [14.14]$$

Equation [14.14] estimates the *first-order autocorrelation*, that is, the correlation between pairs of sample measurements collected one event apart (*i.e.*, consecutive events). The number of sampling events separating each pair is called the *lag*, representing the temporal distance between the pair measurements.

Autocorrelation can also be computed at other lags. The general approximate equation for the kth lag is given by:

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$$r_k = \frac{\sum_{i=1}^{n-k}\left(x_i - \bar{x}\right)\left(x_{i+k} - \bar{x}\right)}{\sum_{i=1}^{n}\left(x_i - \bar{x}\right)^2} \qquad [14.15]$$

which estimates the *k*th-order autocorrelation for pairs of measurements separated in time by *k* sampling events. Note that the number of pairs used to compute r_k decreases with increasing *k* due to the fact that fewer and fewer sample pairs can be formed which are separated by that many lags.

By computing the first few sample autocorrelation coefficients and defining $r_0 = 1$, the sample autocorrelation function can be formed by plotting r_k against *k*. Since the autocorrelation coefficients are approximately normal in distribution with zero mean and variance equal to $1/n$, a test of significant autocorrelation at the 95% significance level can be made by examining the sample autocorrelation function to see if any coefficients exceed $2/\sqrt{n}$ in absolute value ($\pm 2/\sqrt{n}$ represent approximate upper and lower confidence limits).

The sample autocorrelation function is a valuable visual tool for assessing different types of autocorrelation (Chatfield, 2004). For instance, a stationary (*i.e.*, stable, non-trending) but non-random series of measurements will often exhibit a large value of r_1 followed by perhaps one or two other significantly non-zero coefficients. The remaining coefficients will be progressively smaller and smaller, tending towards zero. A series with a clear seasonal pattern will exhibit a seasonal (i.e., approximately sinusoidal) autocorrelation function. If the series tends to alternate between high and low values, the autocorrelation function will also alternate, with r_1 being negative to reflect that consecutive measurements tend to be on 'opposite sides' of the sample mean. Finally, if the series contains a trend, the sample autocorrelation function will not drop to zero as the lag *k* increases. Rather, there will a persistent autocorrelation even at very large lags.

REQUIREMENTS AND ASSUMPTIONS

The approximate distribution of the sample autocorrelation coefficients is predicated on the sample measurements following a normal distribution. A test for significant autocorrelation may therefore be inaccurate unless the sample measurements are roughly normal. Non-normal data series should be tested for temporal autocorrelation using the non-parametric rank Von Neumann ratio (**Section 14.2.4**).

Outliers can drastically affect the sample autocorrelation function (Chatfield, 2004). Before assessing autocorrelation, check the sample for possible outliers, removing those that are identified. A series of at least 10-12 measurements is minimally recommended to construct the autocorrelation function. Otherwise, the number of lagged data pairs will be too small to reliably estimate the correlation, especially for larger lags. Sampling events should be regularly spaced so that pairs lagged by the same number of events (*k*) represent the same approximate time interval.

PROCEDURE

Step 1. Given a series of *n* measurements, $x_1,\ldots, x_n$, form sets of lagged data pairs (x_i, x_{i+k}), $i = 1,\ldots, n–k$, for $k \leq [n/3]$, where the notation $[c]$ represents the largest integer no greater than *c*. For longer series, computing lags to a maximum of $k = 15$ is generally sufficient.

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Step 2. For each set of lagged pairs from **Step 1**, compute the sample autocorrelation coefficient, r_k, using equation [14.15]. Also define $r_0 = 1$.

Step 3. Graph the sample autocorrelation function by plotting r_k versus k for $k = 0,\ldots,$ [n/3], generally up to a maximum lag of 15. Also plot horizontal lines at levels equal to: $\pm 2/\sqrt{n}$.

Step 4. Examine the sample autocorrelation function. If any coefficient r_k exceeds $2/\sqrt{n}$ in absolute value, conclude that the sample has significant autocorrelation.

►EXAMPLE 14-3

The following series of monthly total alkalinity measurements were collected from leachate at a solid waste landfill during a four and a half year period. Use the sample autocorrelation function to test for significant temporal dependence in this series.

Date	Total Alkalinity (mg/L)	Date	Total Alkalinity (mg/L)	Date	Total Alkalinity (mg/L)
01/26/96	1400	07/01/97	2400	01/15/99	1350
02/20/96	1700	08/15/97	3500	02/02/99	1560
03/19/96	1900	09/15/97	3100	03/02/99	1220
04/22/96	1800	10/15/97	3300	04/15/99	1390
05/22/96	1300	11/15/97	2100	05/04/99	1940
06/24/96	2000	12/15/97	2100	06/02/99	2160
07/15/96	2300	01/15/98	1500	07/07/99	1990
08/21/96	2500	02/15/98	710	08/03/99	2540
09/15/96	1700	03/15/98	1100	09/02/99	2250
10/15/96	1600	04/15/98	1900	10/07/99	1630
11/11/96	1400	05/08/98	2100	11/02/99	1710
12/10/96	1600	06/15/98	2000	12/07/99	1210
01/22/97	1800	07/15/98	2500	01/06/00	1170
02/11/97	1000	08/15/98	2700	02/02/00	1330
03/04/97	720	09/02/98	2400	03/02/00	1540
04/07/97	1400	10/06/98	3000	04/04/00	1670
05/01/97	1600	11/03/98	2700	05/02/00	1520
06/09/97	990	12/15/98	2680	06/06/00	2080

SOLUTION

Step 1. Create a time series plot of the $n = 54$ alkalinity measurements, as in **Figure 14-4**. The series indicates an apparent seasonal fluctuation.

Step 2. Form lagged data pairs from the alkalinity series for each lag k = 1,…, [n/3] = 18. The first two pairs for k = 1 (i.e., first order lag) are (1400, 1700) and (1700, 1900). For k = 2, the first two pairs are (1400, 1900) and (1700, 1800), etc.

Step 3. At each lag (k), compute the sample autocorrelation coefficient using equation [14.15]. Note that the denominator of this equation equals $(n-1)s^2$. For the alkalinity data, the sample mean and variance are $\bar{x} = 1865.93$ and $s^2 = 392349.1$ respectively. The lag-1 autocorrelation is thus:

$$r_1 = \frac{(1400 - 1865.93)\cdot(1700 - 1865.93) + \ldots + (1520 - 1865.93)\cdot(2080 - 1865.93)}{(54 - 1)\cdot 392349.1} = .64$$

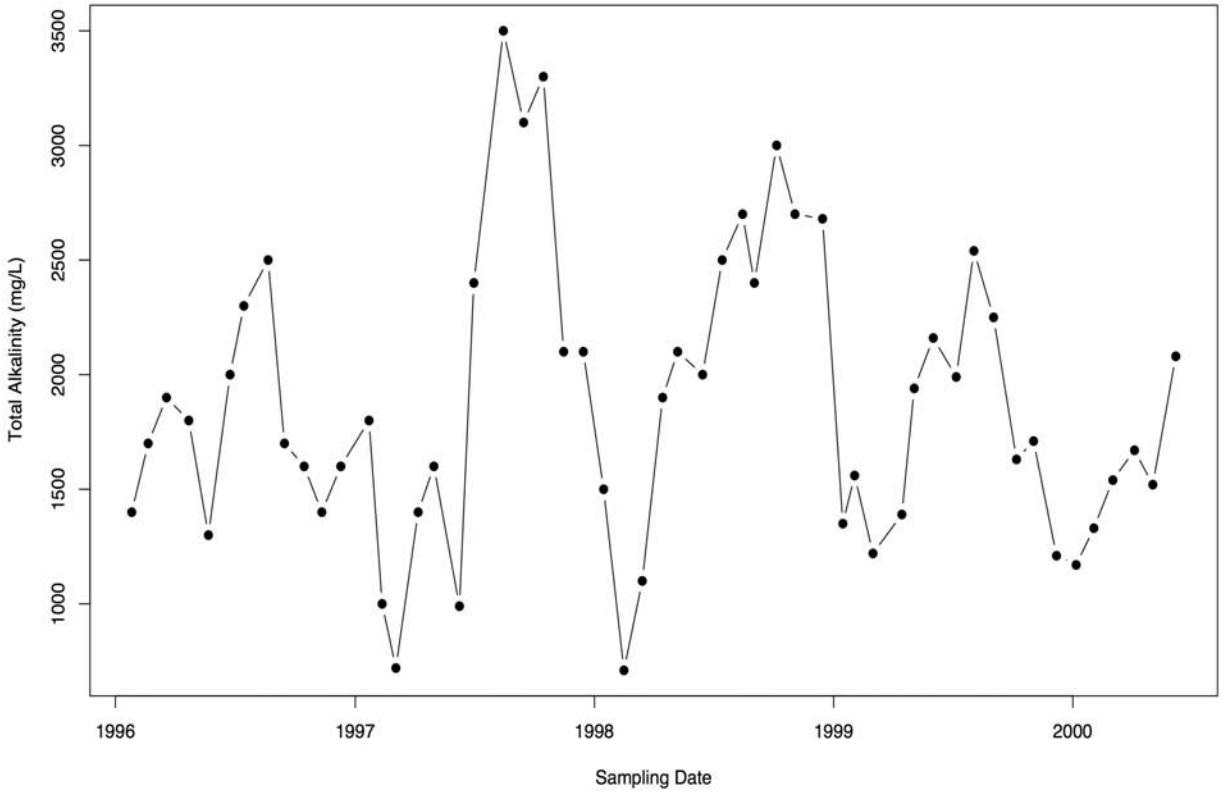
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Other lags are computed similarly.

Step 4. Plot the sample autocorrelation function as in **Figure 14-5**. Overlay the plot with 95% confidence limits (dotted lines) shown at $\pm 2/\sqrt{n} = \pm 2/\sqrt{54} = 0.27$.

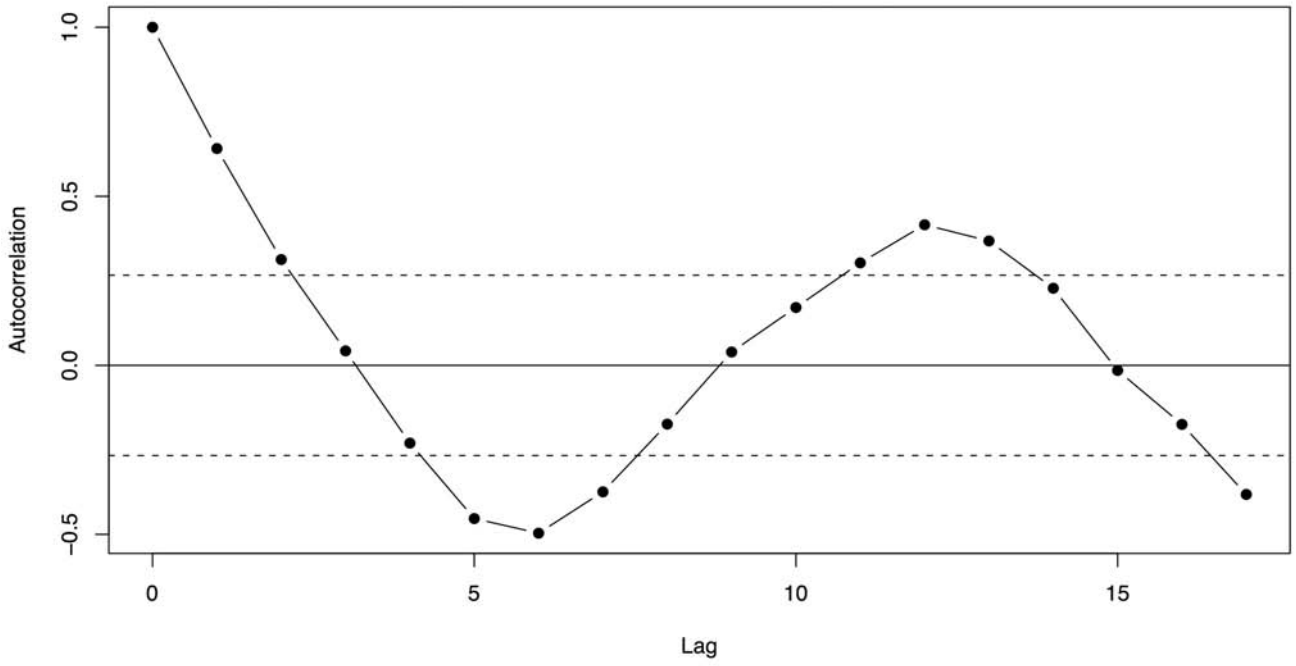
Step 5. The autocorrelation function indicates coefficients at several lags that lie outside the 95% confidence limits, confirming the presence of temporal dependence. Further, the shape of autocorrelation function is sinusoidal, suggesting a strong seasonal fluctuation in the alkalinity levels. ◄

Figure 14-4. Time Series Plot of Total Alkalinity (mg/L)



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Figure 14-5. Sample Autocorrelation Function for Total Alkalinity



14.2.4 RANK VON NEUMANN RATIO TEST

BACKGROUND AND PURPOSE

The rank von Neumann ratio is a non-parametric test of first-order temporal autocorrelation in a single data series (*e.g.*, from a single well over time). It can be used as an alternative to the sample autocorrelation function (**Section 14.2.3**) for non-normal data, and is both easily computed and effective.

The rank von Neumann ratio is based on the idea that a truly independent series of data will vary in an unpredictable fashion as the list is examined sequentially. The first order or lag-1 autocorrelation will be approximately zero. By contrast, the first-order autocorrelation in *dependent* data will tend to be positive (or negative), implying that lag-1 data pairs in the series will tend to be more similar (or dissimilar) in magnitude than would expected by chance.

Not only will the concentrations of lag-1 data pairs tend to be similar (or dissimilar) when the series is autocorrelated, but the *ranks* of lag-1 data pairs will share that similarity or dissimilarity. Although the test is non-parametric and rank-based, the ranks of non-independent data still follow a discernible pattern. Therefore, the rank von Neumann ratio is constructed from the sum of differences between the *ranks* of lag-1 data pairs. When these differences are *small*, the ranks of consecutive data measurements need to be fairly similar, implying that the pattern of observations is somewhat predictable. Given the relative position and magnitude of one observation, the approximate relative position and magnitude of the next sample measurement can be predicted. Low values of the rank von Neumann ratio are therefore indicative of temporally dependent data series.

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Compared to other tests of statistical independence, the rank von Neumann ratio has been shown to be more powerful than non-parametric methods such as the Runs up-and-down test (Madansky, 1988). It is also a reasonable test when the data follow a normal distribution. In that case, the efficiency of the test is always close to 90 percent when compared to the von Neumann ratio computed on concentrations instead of the ranks. Thus, very little effectiveness is lost by using the ranks in place of the original measurements. The rank von Neumann ratio will correctly detect dependent data and do so over a variety of underlying data distributions. The rank von Neumann ratio is also fairly robust to departures from normality, such as when the data derive from a skewed distribution like the lognormal.

REQUIREMENTS AND ASSUMPTIONS

An unresolved problem with the rank von Neumann ratio test is the presence of a substantial fraction of tied observations. Like the Wilcoxon rank-sum test (**Chapter 16**), Bartels (1982) recommends replacing each tied value by its mid-rank (*i.e.*, the average of all the ranks that would have been assigned to that set of ties). However, no explicit adjustment of the ratio for ties has been developed. The rank von Neumann critical points may not be appropriate (or at best very approximate) when a large portion of the data consists of non-detects or other tied values. Especially in the case of frequent non-detects, too much information is lost regarding the pattern of variability to use the rank von Neumann ratio as an accurate indication of autocorrelation. In fact, no test is likely to provide a good estimate of temporal correlation, whether non-parametric or parametric.

While the rank von Neumann ratio test is recommended in the Unified Guidance for its ease of use and robustness when applied to either normal or non-normal distributions, the literature on time series analysis and temporal correlation is extensive with respect to other potential tests. Many other tests of autocorrelation are available, especially when either the original measurements or the residuals of the data are normally distributed after a trend has been removed. Chatfield (2004) and (Madansky, 1988) are two good references for some of these alternate tests.

PROCEDURE

Step 1. Order the sample from least to greatest and assign a unique rank to each measurement. If some data values are tied, replace tied values with their mid-ranks as in the Wilcoxon rank-sum test (**Chapter 16**). Then list the observations and their corresponding ranks in the order that they were collected (*i.e.*, by sampling event or time order).

Step 2. Using the list of ranks, R_i, for the sampling events $i = 1 \ldots n$, compute the rank von Neumann ratio with the equation:

$$v = \sum_{i=2}^{n} \left(R_i - R_{i-1}\right)^2 \Big/ \left[n\left(n^2 - 1\right)/12 \right] \qquad [14.16]$$

Step 3. Given sample size (n) and desired significance level (α), find the lower critical point of the rank von Neumann ratio in **Table 14-1** of **Appendix D**. In most cases, a choice of $\alpha = .01$ should be sufficient, since only substantial non-independence is likely to affect subsequent statistical testing. If the computed ratio, v, is *smaller* than this critical point, conclude that the data series is strongly autocorrelated. If not, there is insufficient evidence to reject the

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hypothesis of independence; treat the data as temporally independent in subsequent statistical testing.

►EXAMPLE 14-4

Use the rank von Neumann ratio test on the following series of 16 quarterly measurements of arsenic (ppb) to determine whether or not the data set should be treated as temporally independent in subsequent tests. Compute the test at the $\alpha = .01$ level of significance.

Sample Date	Arsenic (ppb)	Rank (R_i)
Jan 1990	4.0	5
Apr 1990	7.2	15
Jul 1990	3.1	2
Oct 1990	3.5	3
Jan 1991	4.4	8
Apr 1991	5.1	9
Jul 1991	2.2	1
Oct 1991	6.3	13
Jan 1992	6.5	14
Apr 1992	7.5	16
Jul 1992	5.8	11
Oct 1992	5.9	12
Jan 1993	5.7	10
Apr 1993	4.1	6
Jul 1993	3.8	4
Oct 1993	4.3	7

SOLUTION

Step 1. Assign ranks to the data values as in the table above. Then list the data in chronological order so that each rank value occurs in the order sampled.

Step 2. Compute the von Neumann ratio using the set of ranks in column 3 using equation [14.16], being sure to take squared differences of successive, *overlapping* pairs of rank values:

$$\nu = \frac{\left[(15-5)^2 + (2-15)^2 + \ldots + (7-4)^2\right]}{16 \cdot \left(16^2 - 1\right)/12} = 1.67$$

Step 3. Look up the lower critical point (v_{cp}) for the rank von Neumann ratio in **Table 14-1** of **Appendix D**. For $n = 16$ and $\alpha = .01$, the lower critical point is equal to 0.93. Since the test statistic v is larger than v_{cp}, there is insufficient evidence of autocorrelation at the $\alpha = .01$ level of significance. Therefore, treat these data as statistically independent in subsequent testing. ◄

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14.3 CORRECTING FOR TEMPORAL EFFECTS AND CORRELATION

14.3.1 ADJUSTING THE SAMPLING FREQUENCY AND/OR TEST METHOD

If a data series is temporally correlated, a simple remedy (if allowable under program rules) is to change the sampling frequency and/or statistical method used to analyze the data. In some cases, increasing the sampling interval will effectively eliminate the statistical dependence exhibited by the series. This may happen because the longer time between sampling events allows more groundwater to flow through the well screen, further differentiating measurements of consecutive volumes of groundwater and lessening the impact of seasonal fluctuations or other time-dependent patterns in the underlying concentration distribution.

Many authors including Gibbons (1994a) and ASTM (1994) have recommended that sampling be conducted no more often than quarterly to avoid temporal dependence. If the sampling frequency is reduced, there are obviously fewer measurements available for statistical analysis during any given evaluation period. A *t*-test or ANOVA cannot realistically be run with fewer than four measurements per well. A prediction limit for a future mean requires at least two new observations, and a prediction limit for a future median requires at least three measurements, not counting any resamples. Depending on the length of the evaluation period (i.e., quarterly, semi-annual, annual), a change of statistical method may also be necessary when groundwater measurements are autocorrelated.

When sufficient background data have been collected over a longer period of time, a prediction limit test for future values can be run with as few as one or two new measurements per compliance well. The same is true for control charts. Therefore, if a low groundwater flow velocity and/or evidence of statistical dependence suggest a reduction in sampling frequency, certain prediction limits and control charts should be strongly considered as alternate statistical procedures.

RUNNING A PILOT STUDY

An optional approach to adjusting the sampling frequency is to run a site-specific *pilot study* of autocorrelation. Such a study can be conducted in several ways, but perhaps the easiest is to pick two or three wells from the network (perhaps one background well and one or two compliance wells) and then conduct weekly sampling at these wells over a one year period. For each well in the study, construct the sample autocorrelation function (**Section 14.2.3**) for a variety of constituents, and determine from these graphs the smallest lagged interval at which the autocorrelation coefficient becomes insignificantly different from zero for most of the study constituents.

Since an autocorrelation of zero is equivalent to temporal independence for practical purposes, finding the smallest lag between sampling events with no correlation indicates the minimum sampling frequency needed to approximately ensure statistical independence. If the sample autocorrelation function does not drop down to zero with increasing lag (k), there may be a strong seasonal component or a trend involved. In these circumstances, lengthening the sampling frequency may do little to lessen the temporal dependence. A seasonal pattern may need to be estimated instead and regularly removed from the data prior to statistical testing. Likewise, any apparent trends should be investigated to determine if there is evidence of increasing concentration levels indicative of a possible release.

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14.3.2 CHOOSING A SAMPLING INTERVAL VIA DARCY'S EQUATION

Another strategy for determining an appropriate sampling interval is to use Darcy's equation. The goal of this approach is to calculate groundwater flow velocity and the time needed to ensure that physically independent or distinct volumes of groundwater are collected on each sampling trip. As noted in **Chapter 6**, physical independence does not guarantee statistical independence. However, statistical independence may be more likely if the same general volume of groundwater is not re-sampled on multiple occasions.

This section discusses the important hydrological parameters to consider when choosing a sampling interval. The *Darcy equation* is used to determine the horizontal component of the average linear velocity of ground water for confined, semi-confined, and unconfined aquifers. This value provides a good estimate of travel time for most soluble constituents in groundwater, and can be used to determine a minimal sampling interval. Example calculations are provided to further assist the reader. Alternative methods should be employed to determine a sampling interval in groundwater environments where Darcy's law is invalid. Karst, cavernous basalt, fractured rocks, and other 'pseudo-karst' terranes usually require specialized monitoring approaches.

Section 264.97(g) of 40 CFR Part 264 Subpart F allows the owner or operator of a RCRA facility to choose a sampling procedure that will reflect site-specific concerns. It specifies that the owner or operator shall obtain a sequence of at least four samples from each well collected at least semi-annually. The interval is determined after evaluating the uppermost aquifer's effective porosity, hydraulic conductivity, and hydraulic gradient, and the fate and transport characteristics of potential contaminants. The intent of this provision is to set a sampling frequency that allows sufficient time between sampling events to ensure, to the greatest extent technically feasible, that independent groundwater observations are taken from each well.

The sampling frequency required in Part 264 Subpart F can be based on estimates using the average linear velocity of ground water. Two forms of the Darcy equation stated below relate groundwater velocity (V) to effective porosity (Ne), hydraulic gradient (i), and hydraulic conductivity (K):

$$V_h = \left(K_h \cdot i\right) \Big/ Ne \qquad [14.17]$$

$$V_v = \left(K_v \cdot i\right) \Big/ Ne \qquad [14.18]$$

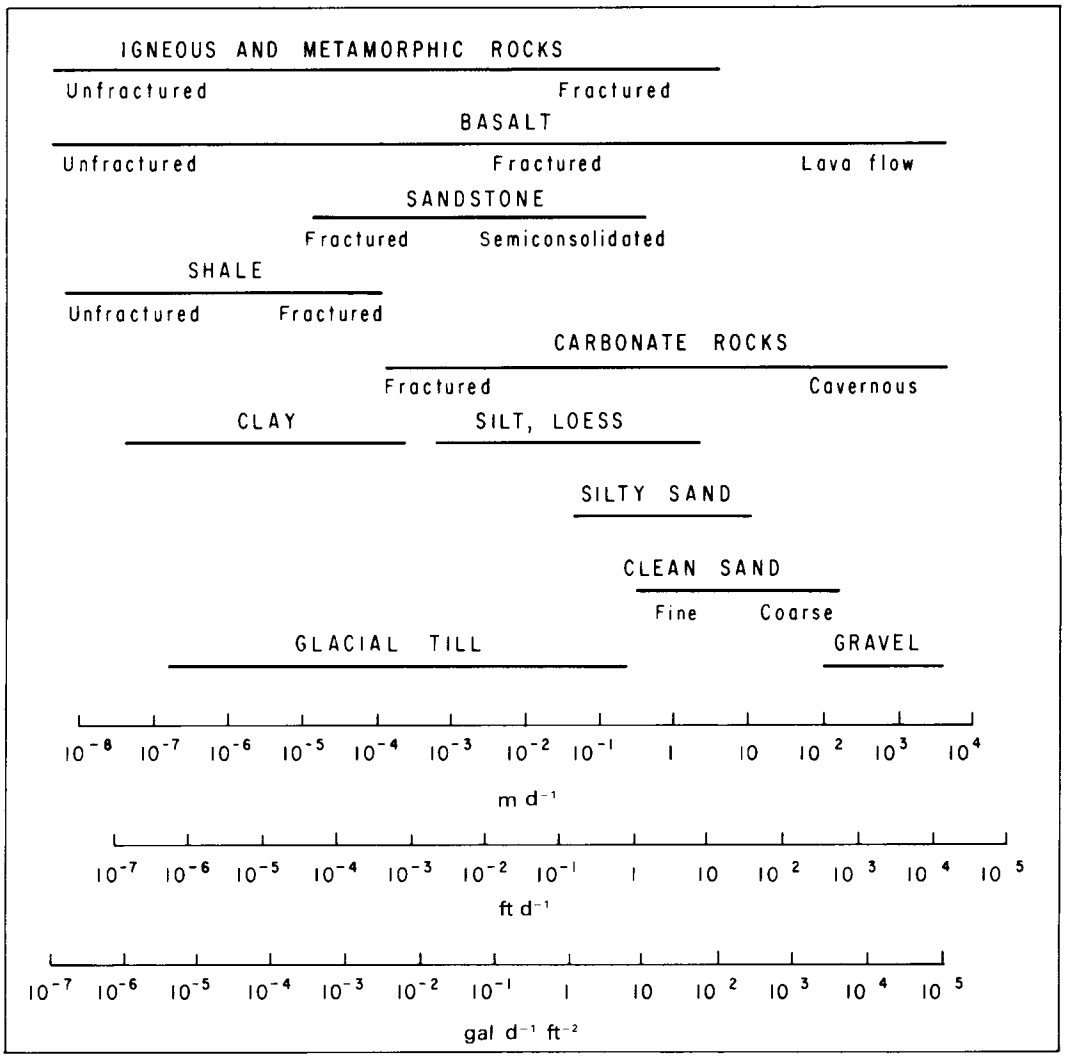
where V_h and V_v are the horizontal and vertical components of the average linear velocity of groundwater, respectively; K_h and K_v are the horizontal and vertical components of hydraulic conductivity, respectively; i is the head gradient; and Ne is the effective porosity.

In applying these equations to ground-water monitoring, the horizontal component of the average linear velocity (V_h) can be used to determine an appropriate sampling interval. Usually, field investigations will yield bulk values for hydraulic conductivity. In most cases, the bulk hydraulic conductivity determined by a pump test, tracer test, or a slug test will be sufficient for these calculations. The vertical component (V_v), however, should be considered in estimating flow velocities in areas with significant components of vertical velocity such as recharge and discharge zones.

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To apply the Darcy equation to groundwater monitoring, the parameters *K*, *i*, and *Ne* need to be determined. The hydraulic conductivity, *K*, is the volume of water at the existing kinematic viscosity that will move in unit time under a unit hydraulic gradient through a unit area measured at right angles to the direction of flow. "[E]xisting kinematic viscosity" refers to the fact that hydraulic conductivity is not only determined by the media (aquifer), but also by fluid properties (groundwater or potential contaminants). Thus, it is possible to have several hydraulic conductivity values for different chemical substances present in the same aquifer. The lowest velocity value calculated using the Darcy equation should be used to determine sampling intervals, ensuring physical independence of consecutive sample measurements.

Figure 14-6. Hydraulic Conductivity of Selected Rocks



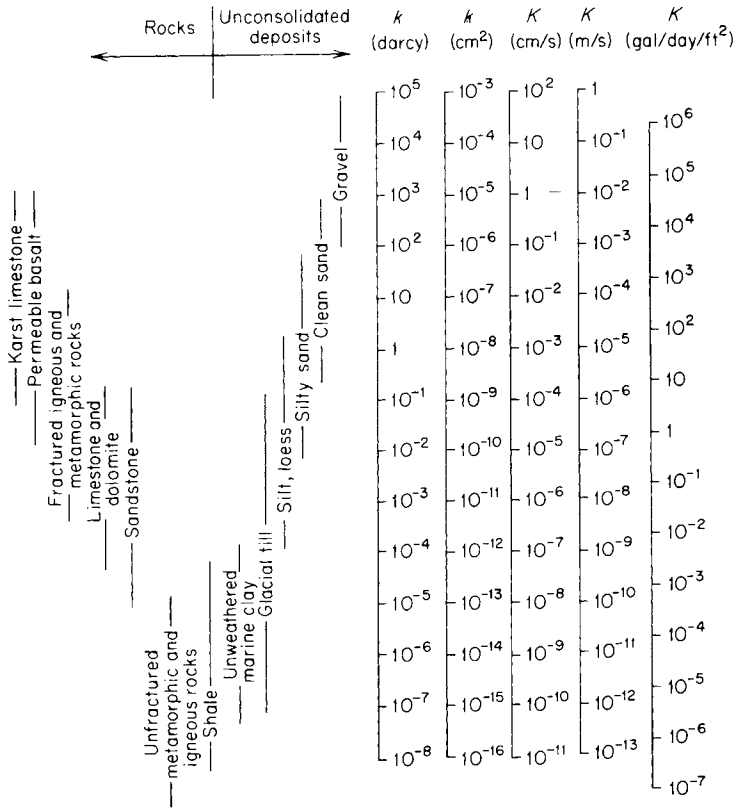
Source: Heath, R.C. 1987. Basic Ground-Water Hydrology. U.S. Geological Survey Water Supply Paper, 2220, 13 pp.

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A range of hydraulic conductivities (the transmitted fluid is water) for various aquifer materials is given in **Figures 14-6** and **14-7**. The conductivities are given in several units. **Figure 14-8** lists conversion factors to change between various permeability and hydraulic conductivity units.

The hydraulic gradient, *i*, is the change in hydraulic head per unit of distance in a given direction. It can be determined by dividing the difference in head between two points on a potentiometric surface map by the orthogonal distance between those two points (see calculation in **Example 14-5**). Water level measurements are normally used to determine the natural hydraulic gradient at a facility. However, the effects of mounding in the event of a release may produce a steeper local hydraulic gradient in the vicinity of the monitoring well. These local changes in hydraulic gradient should be accounted for in the velocity calculations.

Figure 14-7. Range of Values of Hydraulic Conductivity and Permeability



Source: Freeze, R.A., and J.A. Cherry. 1979. Ground Water. Prentice Hall, Inc., Englewood Cliffs, New Jersey. p. 29.

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Figure 14-8. Conversion Factors for Permeability and Hydraulic Conductivity Units

	Permeability, *k**			Hydraulic conductivity, *K*		
	cm^2	ft^2	darcy	m/s	ft/s	$gal/day/ft^2$
cm^2	1	1.08×10^{-3}	1.01×10^{8}	9.80×10^{2}	3.22×10^{3}	1.85×10^{9}
ft^2	9.29×10^{2}	1	9.42×10^{10}	9.11×10^{5}	2.99×10^{6}	1.71×10^{12}
darcy	9.87×10^{-9}	1.06×10^{-11}	1	9.66×10^{-6}	3.17×10^{-5}	1.82×10^{1}
m/s	1.02×10^{-3}	1.10×10^{-6}	1.04×10^{5}	1	3.28	2.12×10^{6}
ft/s	3.11×10^{-4}	3.35×10^{-7}	3.15×10^{4}	3.05×10^{-1}	1	6.46×10^{5}
$gal/day/ft^2$	5.42×10^{-10}	5.83×10^{-13}	5.49×10^{-2}	4.72×10^{-7}	1.55×10^{-6}	1

*To obtain *k* in ft^2, multiply *k* in cm^2 by 1.08×10^{-3}

Source: Freeze, R.A., and J.A. Cherry (1979). *Ground Water*. Prentice Hall, Inc., Englewood Cliffs, New Jersey, p. 29.

The effective porosity, *Ne*, is the ratio, usually expressed as a percentage, of the total volume of voids available for fluid transmission to the total volume of the porous medium de-watered. It can be estimated during a pump test by dividing the volume of water removed from an aquifer by the total volume of aquifer dewatered (see calculation in **Example 14-5**). **Figure 14-9** presents approximate effective porosity values for a variety of aquifer materials. In cases where the effective porosity is unknown, specific yield may be substituted into the equation. Specific yields of selected rock units are given in **Figure 14-10**. In the absence of measured values, drainable porosity is often used to approximate effective porosity. **Figure 14-11** illustrates representative values of drainable porosity and total porosity as a function of aquifer particle size. If available, field measurements of effective porosity are preferred.

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Figure 14-9. Default Values of Effective Porosity (*Ne*) For Travel Time Analyses

Soil textural classes	Effective porosity of saturation[a]
Unified soil classification system	
GS, GP, GM, GC, SW, SP, SM, SC	0.20 (20%)
ML, MH	0.15 (15%)
CL, OL, CH, OH, PT	0.01 (1%)[b]
USDA soil textural classes	
Clays, silty clays, sandy clays	0.01 (1%)b
Silts, silt loams, silty clay loams	0.10 (10%)
All others	0.20 (20%)
Rock units (all)	
Porous media (non-fractured rocks such as sandstone and some carbonates)	0.15 (15%)
Fractured rocks (most carbonates, shales, granites, etc.)	0.0001 (0.01%)

Source: Barari, A., and L. S. Hedges (1985). Movement of Water in Glacial Till. *Proceedings of the 17th International Congress of the International Association of Hydrogeologists*, pp. 129-134.

[a]These values are estimates and there may be differences between similar units. For example, recent studies indicate that weathered and unweathered glacial till may have markedly different effective porosities (Barari and Hedges, 1985; Bradbury et al., 1985).

[b]Assumes *de minimus* secondary porosity. If fractures or soil structure are present, effective porosity should be 0.001 (0.1%).

Figure 14-10. Specific Yield Values for Selected Rock Types

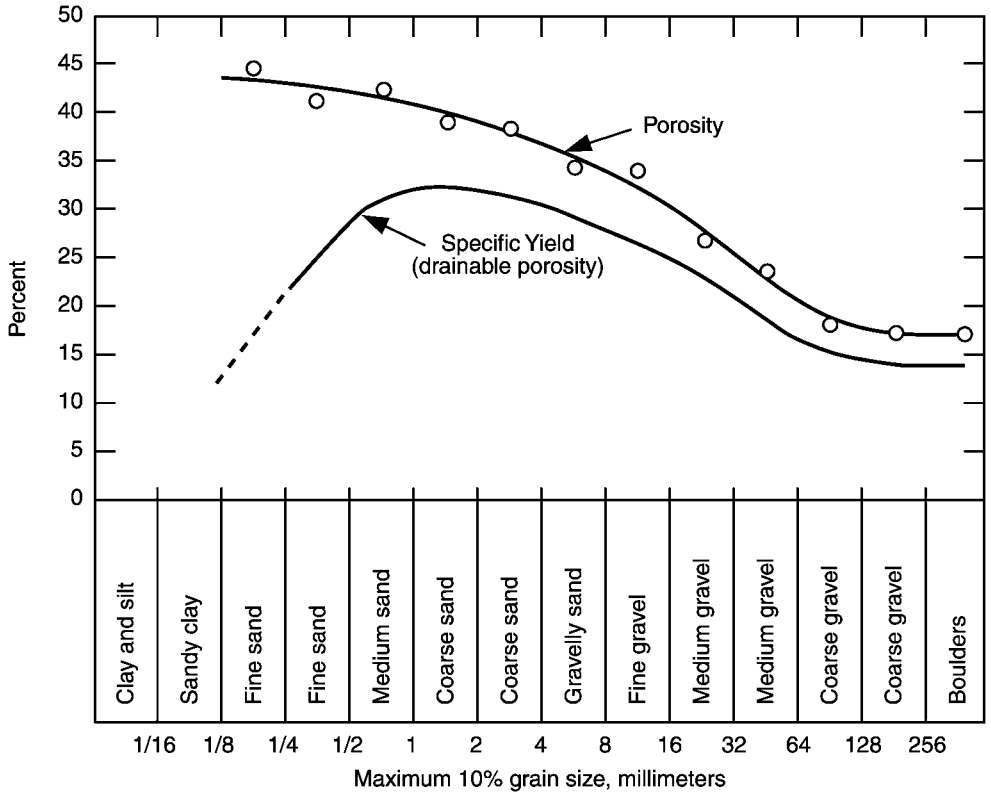
Rock Type	Specific Yield (%)
Clay	2
Sand	22
Gravel	19
Limestone	18
Sandstone (*semi-consolidated*)	6
Granite	0.09
Basalt (*young*)	8

Source: Heath, R.C. (1983). *Basic Ground-Water Hydrology*. U.S. Geological Survey, Water Supply Paper 2220, 84 pp.

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Once the values for *K*, *i*, and *Ne* are determined, the horizontal component of average linear groundwater velocity can be calculated. Using the Darcy equation [14.17], the time required for groundwater to pass through the complete monitoring well diameter can be determined by dividing the well diameter by the horizontal component of the average linear groundwater velocity. If considerable exchange of water occurs during well purging, the diameter of the filter pack may be used rather than the well diameter. This value represents the *minimum* time interval required between sampling events yielding a physically independent (*i.e.*, distinct) ground-water sample. Note that three-dimensional mixing of groundwater in the vicinity of the monitoring well is likely to occur when the well is purged before sampling. Partly for that reason, this method can only provide an estimated travel time.

Figure 14-11. Total Porosity and Drainable Porosity for Typical Geologic Materials



Source: Todd, D.K. 1980. Ground Water Hydrology. John Wiley and Sons, New York, 534 pp.

In determining these sampling intervals, many chemical compounds do not travel at the same velocity as groundwater. Chemical characteristics such as adsorptive potential, specific gravity, and molecular size influence the way chemicals travel in the subsurface. Large molecules, for example, tend to travel slower than the average linear groundwater velocity because of matrix interactions. Compounds that exhibit a strong adsorptive potential undergo a similar fate that dramatically changes time of travel predictions using the Darcy equation. In some cases chemical interaction with the matrix material alters the matrix structure and its associated hydraulic conductivity and may result in an increase in contaminant mobility. This effect has been observed with certain organic solvents in clay units (see Brown and Andersen, 1981). Contaminant fate and transport models may be useful in determining the influence of these effects on movement in the subsurface.

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►EXAMPLE 14-5

Compute the effective porosity, *Ne*, expressed as a percent (%), using results obtained during a pump test.

SOLUTION

Step 1. Compute the effective porosity using the following equation:

$$Ne = 100\% \times \text{volume of water removed} / \text{volume of aquifer dewatered} \quad [14.19]$$

Step 2. Based on a pumping rate of 50 gal/min and a pumping duration of 30 min, compute the volume of water removed as:

$$\text{volume of water removed} = 50 \text{ gal/min} \times 30 \text{ min} = 1{,}500 \text{ gal}$$

Step 3. To calculate the volume of aquifer de-watered, use the equation:

$$V = \frac{1}{3}\pi h r^2 \quad [14.20]$$

where r is the radius (in ft) of the area affected by pumping and h (ft) is the drop in the water level. If, for example, h = 3 ft and r = 18 ft, then:

$$V = \frac{1}{3}\left(3.14 \times 3 \times 18^2\right) = 1{,}018 \text{ ft}^3$$

Next, converting cubic feet of water to gallons of water,

$$V = 1{,}018 \text{ ft}^3 \times 7.48 \text{ gal/ft}^3 = 7{,}615 \text{ gal}$$

Step 4. Finally, substitute the two volumes from **Step 3** into equation [14.19] to obtain the effective porosity:

$$Ne = 100\% \times \left(1{,}500 \text{ gal}/7{,}615 \text{ gal}\right) = 19.7\% \text{ ◄}$$

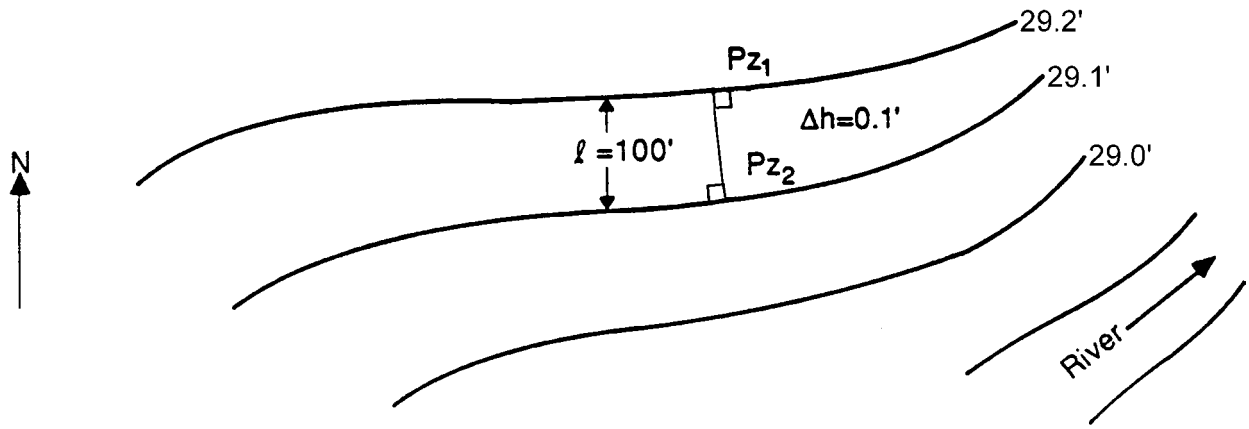
►EXAMPLE 14-6

Determine the hydraulic gradient, *i*, from a potentiometric surface map.

SOLUTION

Step 1. Consider the potentiometric surface map in **Figure 14-12**. The hydraulic gradient can be constructed as $i = \Delta h/l$, where Δh is the difference measured in the gradient at piezometers Pz_1 and Pz_2,and l is the orthogonal distance between the two piezometers.

Figure 14-12. Potentiometric Surface Map for Computation of Hydraulic Gradient



Step 2. Using the values given in **Figure 14-12**, the hydraulic gradient is computed as:

$$i = \Delta h / l = \left(29.2 \text{ ft} - 29.1 \text{ ft}\right) / 100 \text{ ft} = 0.001 \text{ ft/ft}$$

Step 3. Note that this method provides only a very general estimate of the natural hydraulic gradient existing in the vicinity of the two piezometers. Chemical gradients are known to exist and may override the effects of the hydraulic gradient. A detailed study of the effects of multiple chemical contaminants may be necessary to determine the actual average linear groundwater velocity (horizontal component) in the vicinity of the monitoring wells. ◄

►EXAMPLE 14-7

Determine the horizontal component of the average linear groundwater velocity (V_h) at a land disposal facility which has monitoring wells screened in an unconfined silty sand aquifer.

SOLUTION

Step 1. Slug tests, pump tests, and tracer tests conducted during a hydrologic site investigation have revealed that the aquifer has a horizontal hydraulic conductivity (K_h) of 15 ft/day and an effective porosity (Ne) of 15%. Using a potentiometric map (as in **Example 14-6**), the regional hydraulic gradient (i) has been determined to be 0.003 ft/ft.

Step 2. To estimate the minimum time interval between sampling events enabling the collection of physically independent samples of ground water, calculate the horizontal component of the average linear groundwater velocity (V_h) using Darcy's equation [14.17]. With K_h = 15 ft/day, Ne = .15 (15%), and i = 0.003 ft/ft, the velocity becomes:

$$V_h = \left(15 \, ft/day \times .003 \, ft/ft\right) / .15 = .3 \, ft/day \; or \; 3.6 \, in/day$$

Step 3. Based on these calculations, the horizontal component of the average linear groundwater velocity, V_h, is equal to 3.6 in/day. Since monitoring well diameters at this particular facility are 4 inches, the minimum time interval between sampling events enabling a physically

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independent groundwater sample can be computed by dividing the horizontal component into the monitoring well diameter:

$$\text{Minimum time interval} = \left(4 \text{ in}\right) \Big/ \left(3.6 \text{ in/day}\right) = 1.1 \text{ days}$$

As a result, the facility could theoretically sample every other day. However, this may be unwise because velocity can seasonally vary with recharge rates. It is also emphasized that *physical* independence does not guarantee *statistical* independence. **Figure 14-13** gives results for common situations. The overriding point is that it may not be necessary to set the minimum sampling frequency to quarterly at every site. Some hydrologic environments may allow for more frequent sampling, some less. ◄

Figure 14-13. Typical Darcy Equation Results in Determining a Sampling Interval

Unit	K_h (ft/day)	*Ne* (%)	V_h (in/mo)	Sampling Interval
Gravel	10^4	19	9.6×10^4	Daily
Sand	10^2	22	8.3×10^2	Daily
Silty Sand	10	14	1.3×10^2	Weekly
Till	10^{-3}	2	9.1×10^{-2}	Monthly
Silty Sand (semi-consolidated)	1	6	30	Weekly
Basalt	10^{-1}	8	2.28	Monthly

14.3.3 CREATING ADJUSTED, STATIONARY MEASUREMENTS

When an existing data set exhibits temporal correlation or other variability, it is sometimes possible to *remove* the temporal pattern and thereby create a set of adjusted data which are uncorrelated and stationary over time in mean level. As long as the same temporal pattern seems to affect both background and the compliance point data to be tested, the effect (*e.g.*, regular seasonal fluctuation) can be estimated and removed from both data sets prior to statistical testing. Testing the adjusted data instead of the raw measurements in this way results in a more powerful and accurate test. An extraneous source of variation *not related* to identifying a contaminant release has been removed from the sample data.

The general topic of stationary, adjusted data is complex, contained within the extensive literature on time series. The Unified Guidance discusses two simple cases below: removing a seasonal pattern from a single well and creating adjusted data from a one-way ANOVA for temporal effects across several wells. More complicated situations may need professional consultation.

14.3.3.1 CORRECTING FOR SEASONAL PATTERN IN A SINGLE WELL

BACKGROUND AND PURPOSE

Sometimes an obvious cyclical seasonal pattern can be seen in a time series plot. Such data are not statistically independent. They do not fluctuate randomly but rather in a predictable way from one sampling event to the next. Data from such patterns can be adjusted to correct for or remove the seasonal fluctuation, but only if a longer series of data is available. This is also known as *deseasonalizing* the data. Seasonal correction should be done both to minimize the chance of mistaking a seasonal effect for

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evidence of contaminated groundwater, and also to build more powerful background-to-compliance point tests.

Problems can arise, for instance, from measurement variations associated with changing recharge rates during different seasons. Compliance point concentrations can exceed a groundwater protection standard [GWPS] for a portion of the year, but on average lie below. If the long-term average is of regulatory concern, the data should first be de-seasonalized before comparing it against a GWPS.

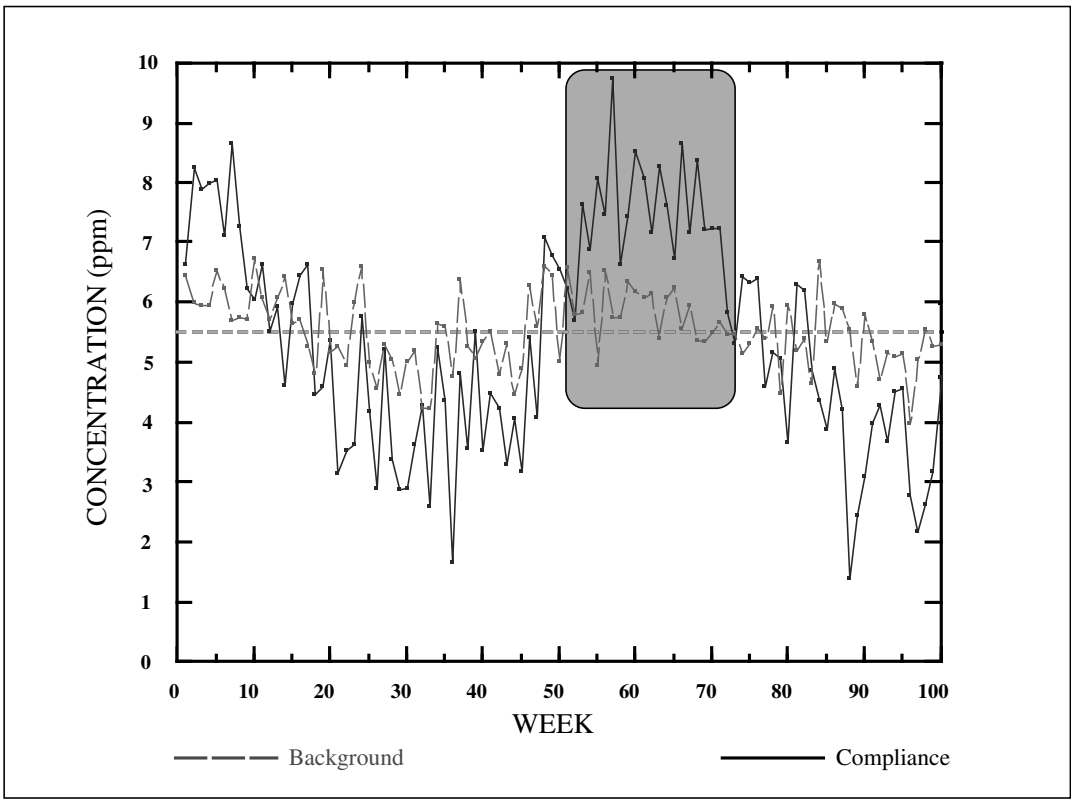
If *point-in-time, interwell comparisons* are being made between simultaneously collected background and downgradient data, a correction may not be necessary even when seasonal fluctuations exist. A temporal cycle may cover a period of several years so that both the background and downgradient values are observed on essentially the same parts of the overall cycle. In this case, the short-term averages in both data sets will be fairly stable and the seasonal or cyclical effect may equivalently impact both sets of data.

For intrawell tests, the data need to be collected sequentially at each well, with background formed from the earliest measurements in the series. The point-in-time argument would not apply and the presence of seasonality should be checked and accounted for.

Even with interwell testing, it is sometimes difficult to verify whether or not a seasonal pattern is impacting upgradient and compliance point wells similarly. If the groundwater velocity is low, the lag between the time groundwater passes through a background well screen and then travels downgradient may create a noticeable shift as to when corresponding portions of the seasonal cycle are observed in compliance point locations. It also may be the case that differences in geochemistry from well to well may cause the same seasonal pattern to differentially impact concentration levels at distinct wells (**Figure 14-14**).

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Figure 14-14. Differential Seasonal Effects: Background vs. Compliance Wells



If the timing of the cycle and the relative *magnitude* of the concentration swings are essentially the same in upgradient and downgradient wells, both data sets should be deseasonalized prior to statistical analysis. If the seasonal effects are ignored, real differences in mean levels between upgradient and downgradient well data may not be observed, simply because the short-term seasonal fluctuations add variability that can mask the difference being tested. In this case, the non-independent nature of the seasonal pattern adds unwanted noise to the observations, obscuring statistical evidence of groundwater contamination.

REQUIREMENTS AND ASSUMPTIONS

Seasonal correction is only appropriate for wells where a cyclical pattern is clearly present and very regular over time. Many approaches to deseasonalizing data exist. If the seasonal pattern is highly regular, it may be modeled with a sine or cosine function. Often, moving averages and/or lag-based differences (of order 12 for monthly data, for example) are used. General time series models may include these and other more complicated methods for deseasonalizing the data.

The simple method described in the Unified Guidance has the advantage of being easy to understand and apply, and of providing natural estimates of the monthly or quarterly seasonal effects via the monthly or quarterly means. The method can be applied to any seasonal or recurring cycle-- perhaps an annual cycle for monthly or quarterly data or a longer cycle for certain kinds of geologic environments. In some cases, recharge rates are linked to drought cycles that may be on the order of

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several years long. For these situations, the 'seasonal' cycle may not correspond to typical fluctuations over the course of a single year.

Corrections for seasonality should be used cautiously, as they represent extrapolation into the future. There should be a good physical explanation for the seasonal fluctuation as well as good empirical evidence for seasonality before corrections are made. Higher than average rainfall for two or three Augusts in a row does not justify the belief that there will never be a drought in August, and this idea extends directly to groundwater quality. At least three complete cycles of the seasonal pattern should be observed on a time series plot before attempting the adjustment below. If seasonality is suspected but the pattern is complicated, the user should seek the help of a professional statistician.

PROCEDURE

Step 1. If a time series plot clearly shows at least 3 full cycles of the seasonal pattern, determine the length of time to complete one full cycle. Since the correction presumes a regular sampling schedule, determine the number of observations (k) in each full cycle (this number should be the *same* for each cycle). Then, assuming that N complete cycles of data are available, let x_{ij} denote the raw, unadjusted measurement for the ith sampling event during the jth complete cycle. Note that this could represent monthly data over an annual cycle, quarterly data over a biennial cycle, semi-annual data over a 10-year cycle, *etc.*

Step 2. Compute the mean concentration for sampling event i over the N-cycle period:

$$\bar{x}_i = \left(x_{i1} + x_{i2} + \ldots + x_{iN}\right)/N \qquad [14.21]$$

This is the average of all observations taken in different cycles, but during the same sampling event. For instance, with monthly data over an annual cycle, one would calculate the mean concentrations for all Januarys, the mean for all Februarys, and so on for each of the 12 months.

Step 3. Calculate the grand mean, $\bar{x}$, of all $N \times k$ observations:

$$\bar{x} = \sum_{i=1}^{k}\sum_{j=1}^{N}\frac{x_{ij}}{N \times k} = \sum_{i=1}^{k}\frac{\bar{x}_i}{k} \qquad [14.22]$$

Step 4. Compute seasonally-corrected, adjusted concentrations using the equation:

$$z_{ij} = x_{ij} - \bar{x}_i + \bar{x} \qquad [14.23]$$

Computing $x_{ij} - \bar{x}_i$ removes the average seasonal effect of sampling event i from the data series. Adding back the overall mean, $\bar{x}$, gives the adjusted z_{ij} values the same mean as the raw, unadjusted data. Thus, the overall mean of the corrected values, $\bar{z}$, equals the overall mean value, $\bar{x}$.

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►EXAMPLE 14-8

Consider the monthly unadjusted concentrations of an analyte over a 3-year period graphed in **Figure 14-15** and listed in the table below. Given the clear and regular seasonal pattern, use the above method to produce a deseasonalized data set.

	Unadjusted Concentrations				**Adjusted Concentrations**		
	1983	1984	1985	Monthly Average	1983	1984	1985
January	1.99	2.01	2.15	2.05	2.11	2.13	2.27
February	2.10	2.10	2.17	2.12	2.14	2.14	2.21
March	2.12	2.17	2.27	2.19	2.10	2.15	2.25
April	2.12	2.13	2.23	2.16	2.13	2.14	2.24
May	2.11	2.13	2.24	2.16	2.12	2.14	2.25
June	2.15	2.18	2.26	2.20	2.12	2.15	2.23
July	2.19	2.25	2.31	2.25	2.11	2.17	2.23
August	2.18	2.24	2.32	2.25	2.10	2.16	2.24
September	2.16	2.22	2.28	2.22	2.11	2.17	2.23
October	2.08	2.13	2.22	2.14	2.10	2.15	2.24
November	2.05	2.08	2.19	2.11	2.11	2.14	2.25
December	2.08	2.16	2.22	2.15	2.09	2.17	2.23
Overall 3-year average = 2.17							

SOLUTION

Step 1. From **Figure 14-15**, there are $N = 3$ full cycles represented, each lasting approximately a year. With monthly data, the number of sampling events per cycle is $k = 12$.

Step 2. Compute the monthly averages across the 3 years for each of the 12 months using equation [14.21]. These values are shown in the fifth column of the table above.

Step 3. Calculate the grand mean over the 3-year period using equation [14.22]:

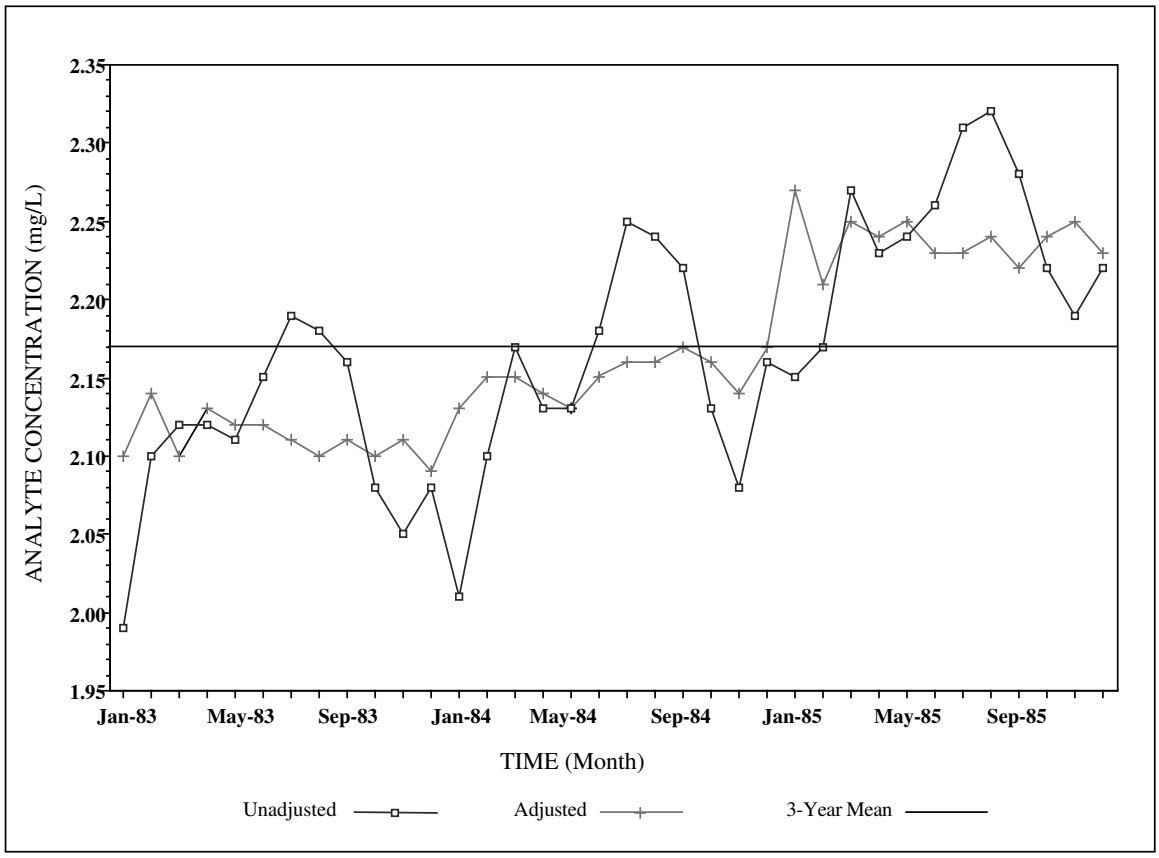
$$\bar{x} = \frac{1}{3 \cdot 12}(1.99 + 2.01 + 2.15 + 2.10 \quad + \ldots + 2.22) = 2.17$$

Step 4. Within each month and year, subtract the average monthly concentration for that month and add-in the grand mean, using equation [14.23]. As an example, for January 1983, the adjusted concentration becomes:

$$z_{11} = 1.99 - 2.05 + 2.17 = 2.11$$

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Figure 14-15. Seasonal Time Series Over a Three-Year Period



The adjusted concentrations are shown in the last three columns of the table above. The average of all 36 adjusted concentrations equals 2.17, the same as the mean *unadjusted* concentration. **Figure 14-15** shows the adjusted data superimposed on the unadjusted data. The raw data exhibit seasonality, as well as an upward trend. The adjusted data, on the other hand, no longer exhibit a seasonal pattern, although the upward trend still remains. From a statistical standpoint, the trend is much more easily identified by a trend test on the adjusted data than with the raw data. ◄

14.3.3.2 Correcting For A Temporal Effect Across Several Wells

BACKGROUND AND PURPOSE

When a significant temporal dependence or correlation is identified across a group of wells using one-way ANOVA for temporal effects (**Section 14.2.2**), results of the ANOVA can be used to create stationary adjusted data similar to the seasonal correction described in **Section 14.3.3.1**. The difference is that the adjustment is not applied to a data series at a single well, but rather simultaneously to several well sets.

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The adjustment works in the same way as a correction for seasonality. First, the mean for each sampling event or season (averaged across wells) is computed along with the grand mean. Then each individual measurement is adjusted by subtracting off the event/seasonal mean and adding the overall or grand mean. In practice, this process is identical to adding the one-way ANOVA residual to the grand mean, so the already-computed results of the ANOVA can be used. By removing or correcting for a significant temporal effect, the adjusted data will have a temporally stationary mean and less overall variation. This allows for more powerful and accurate detection monitoring tests.

Temporal dependence (*e.g.*, seasonality) is sometimes observed as parallel traces on a time series plot across multiple wells (**Section 14.2.1**), although the one-way ANOVA for temporal effects is *non-significant*. This can occur due to the simultaneous presence of strong spatial variability (**Chapter 13**). Differences in mean levels from well to well can be large enough to 'swamp' the added variation due to the temporal dependence. The one-way ANOVA for temporal effects will not identify the dependence because the mean error sum of squares will then include the spatial variation component and not just random error.

Two remedies are possible when the ANOVA for temporal effects is non-significant. First, if a strong parallelism is evident on time series plots, the residuals from the ANOVA can still be used to create a set of adjusted, temporally-stationary measurements. The adjustment will not eliminate or remove any existing spatial variation, but it may not matter. Intrawell tests are needed anyway when such spatial variability is evident, and those tests assume temporal independence of the measurements collected at each well.

A second remedy is to perform a *two-way* ANOVA, testing for both spatial variation and temporal effects. This procedure is discussed in Davis (1994). Not only will a two-way ANOVA more readily identify a significant temporal effect even when there is simultaneous spatial variability, but the *F*-statistic used to test for the temporal dependence can be utilized to further adjust the appropriate degrees of freedom in intrawell background limits, such as prediction limits and control charts.

REQUIREMENTS AND ASSUMPTIONS

The key requirement to correct for a temporal effect using ANOVA is that the same effect must be present in all wells to which the adjustment is applied. Otherwise, the adjustment will tend to skew or bias measurements at wells with no observable temporal dependence. Parallel time series plots (**Section 14.2.1**) should be examined to determine whether all the wells under consideration exhibit a similar temporal pattern.

The parametric one-way ANOVA assumes the data are normal or can be normalized. If the data cannot be normalized, a Kruskal-Wallis non-parametric ANOVA can be conducted to test for the presence of a temporal dependence. In this case, no residuals can be computed since the Kruskal-Wallis test employs ranks of the data rather than the measurements themselves. So the adjustment presented below is only applicable for data sets that can be normalized.

PROCEDURE

Step 1. Given a set of W wells and measurements from each of T sampling events at each well on each of K years, label the observations as x_{ijk}, for $i = 1$ to W, $j = 1$ to T, and $k = 1$ to K. Then x_{ijk} represents the measurement from the ith well on the jth sampling event during the kth year.

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Step 2. Using the one-way ANOVA for temporal effects (**Section 14.2.2**), compute the sampling event or seasonal means (whichever is appropriate), along with the grand (overall) mean. Also construct the ANOVA residuals using either equation [14.5] or [14.6].

Step 3. Add each residual to the grand mean to form adjusted values $z_{ijk} = x_{\bullet\bullet\bullet} + r_{ijk}$. Use these adjusted values in subsequent statistical testing instead of the original measurements.

►EXAMPLE 14-9

The manganese data of **Examples 14-1** and **14-2** were found to have a significant temporal dependence using ANOVA for temporal effects. Adjust these data to remove the temporal pattern.

Qtr	Manganese Residuals (ppm)				
	Event Mean	BW-1	BW-2	BW-3	BW-4
1	29.290	-1.15	2.12	-2.14	1.17
2	30.110	-0.78	0.16	0.13	0.49
3	30.780	-0.33	1.79	-1.64	0.18
4	31.620	0.80	1.15	-1.03	-0.92
5	33.747	0.6225	-0.7175	1.1325	-1.0375
6	31.930	1.32	0.25	-1.40	-0.17
7	30.513	0.5075	-1.6625	-0.1825	1.3375
8	30.345	-1.845	2.535	0.075	-0.765
	Grand mean = 31.042				

SOLUTION

Step 1. The mean of each sampling event taken across the four background wells was computed in **Example 14-2**, along with the grand mean. These results are listed in the table above, along with the individual residuals which were also computed in that example.

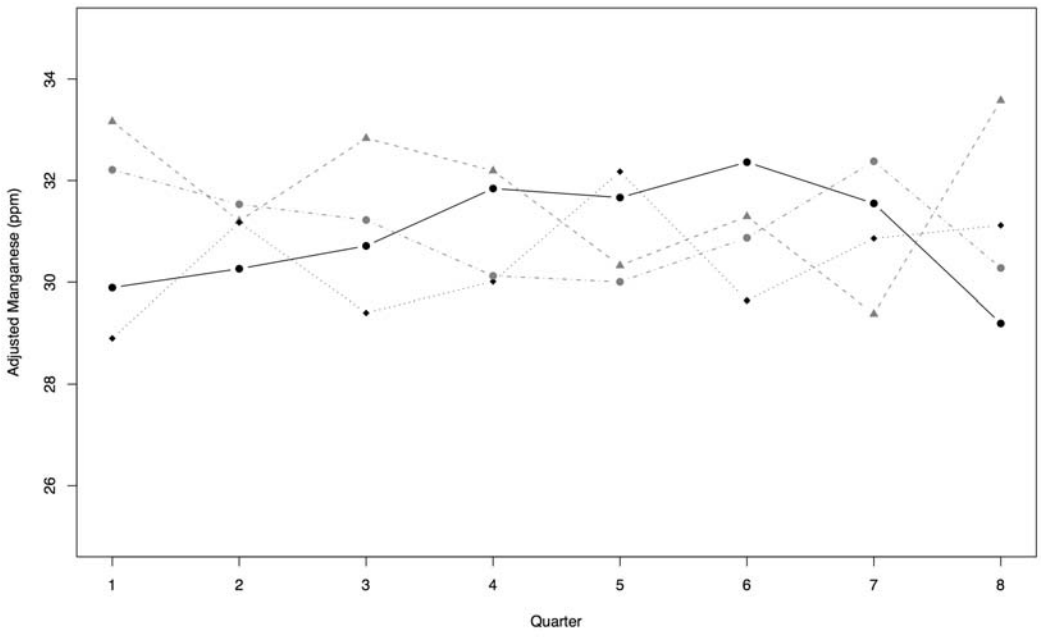
Step 2. Add the grand mean to each residual to form the adjusted manganese concentrations, as in the table below.

Qtr	Adjusted Manganese (ppm)				
	Event Mean	BW-1	BW-2	BW-3	BW-4
1	29.290	29.89	33.16	28.90	32.21
2	30.110	30.26	31.20	31.17	31.53
3	30.780	30.71	32.83	29.40	31.22
4	31.620	31.84	32.19	30.01	30.12
5	33.747	31.66	30.32	32.17	30.00
6	31.930	32.36	31.29	29.64	30.87
7	30.513	31.55	29.38	30.86	32.38
8	30.345	29.20	33.58	31.12	30.28
	Grand mean = 31.042				

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Step 3. Plot a time series of the adjusted manganese values, as in **Figure 14-16**. The 'hump-like' temporal pattern evident in **Figure 14-2** is no longer apparent. Instead, the overall mean is stationary across the 8 quarters. ◄

Figure 14-16. Parallel Time Series Plot of Adjusted Manganese Concentrations



14.3.3.3 CORRECTING FOR LINEAR TRENDS

If a data series exhibits a linear trend, the sample will exhibit temporal dependence when tested via the sample autocorrelation function (**Section 14.2.3**), the rank von Neumann ratio (**Section 14.2.4**), or similar procedure. These data can be de-trended, much like the data in the previous example were deseasonalized. Probably the easiest way to de-trend observations with a linear trend is to compute a linear regression on the data (**Section 17.3.1**) and then use the regression *residuals* instead of the original measurements in subsequent statistical analysis.

But no matter how tempting it may be to automatically de-trend data of this sort, the user is strongly cautioned to consider what a linear trend may represent. Often, an upward trend is indicative of changing groundwater conditions at a site, perhaps due to the increasing presence of contaminants during a gradual waste release. The trend in this case may itself be statistically significant evidence of groundwater contamination, particularly if it occurs at compliance wells but not at upgradient background wells. The trend tests of **Chapter 17** are useful for such determinations. Trends in background may signal other important factors, including migration of contaminants from off-site sources, changes in the regional aquifer, or possible groundwater mounding.

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The overriding point is that data should be deseasonalized when a cyclical pattern might obscure the random deviations around an otherwise stable average concentration level, or to more clearly identify an existing trend. However, a linear trend is inherently indicative of a changing mean level. Such data should not be de-trended before it is determined what the trend likely represents, and whether or not it is itself *prima facie* evidence of possible groundwater contamination.

A similar trend both in direction and slope may be exhibited by background wells *and* compliance wells, perhaps suggestive of sitewide changes in natural groundwater conditions. Residuals from a one-way ANOVA for temporal effects (**Section 14.2.2**) can be used to simultaneously create adjusted values across the well network (**Section 14.3.3.2**). Linear trends are just as easily identified and adjusted in this way as are parallel seasonal fluctuations or other temporal effects.

14.3.4 IDENTIFYING LINEAR TRENDS AMIDST SEASONALITY: SEASONAL MANN-KENDALL TEST

BACKGROUND AND PURPOSE

Corrections for seasonality or other cyclical patterns over time in a single well are discussed in **Section 14.3.3.1**. These adjustments work best when the long-term mean at the well is stationary. In cases where a test for trend is desired and there are also seasonal fluctuations, **Chapter 17** tests may not be sensitive enough to detect a real trend due to the added seasonal variation.

One possible remedy is to use the seasonal correction in **Section 14.3.3.1** and illustrated in **Example 14-8**. The seasonal component of the trend is removed prior to conducting a formal trend test. A second option is the seasonal Mann-Kendall test (Gilbert, 1987).

The seasonal Mann-Kendall is a simple modification to the Mann-Kendall test for trend (**Section 17.3.2**) that accounts for apparent seasonal fluctuations. The basic idea is to divide a longer multi-year data series into subsets, each subset representing the measurements collected on a common sampling event (*e.g.*, all January events or all fourth quarter events). These subsets then represent different points along the regular seasonal cycle, some associated with peaks and others with troughs. The usual Mann-Kendall test is performed on each subset separately and a Mann-Kendall test statistic S_i formed for each. Then the separate S_i statistics are summed to get an overall Mann-Kendall statistic S.

Assuming that the same basic trend impacts each subset, the combined statistic S will be powerful enough to identify a trend despite the seasonal fluctuations.

REQUIREMENTS AND ASSUMPTIONS

The basic requirements of the Mann-Kendall trend test are discussed in **Section 17.3.2**. The only differences with the seasonal Mann-Kendall test are that 1) the sample should be a multi-year series with an observable seasonal pattern each year; 2) each 'season' or subset of the overall series should include at least three measurements in order to compute the Mann-Kendall statistic; and 3) a normal approximation to the overall Mann-Kendall test statistic must be tenable. This will generally be the case if the series has at least 10-12 measurements.

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PROCEDURE

Step 1. Given a series of measurements from each of T sampling events on each of K years, label the observations as x_{ij}, for $i = 1$ to T, and $j = 1$ to K. Then x_{ij} represents the measurement from the ith sampling event during the jth year.

Step 2. For each distinct sampling event (i), form a seasonal subset by grouping together observations $x_{i1}, x_{i2},...., x_{iK}$. This results in T separate seasons.

Step 3. For each seasonal subset, use the procedure in **Section 17.3.2** to compute the Mann-Kendall statistic S_i and its standard deviation $SD[S_i]$. Form the overall seasonal Mann-Kendall statistic (S) and its standard deviation with the equations:

$$S = \sum_{i=1}^{T} S_i \qquad [14.24]$$

$$SD\left[S\right] = \sqrt{\sum_{i=1}^{T} SD^2\left[S_i\right]} \qquad [14.25]$$

Step 4. Compute the normal approximation to the seasonal Mann-Kendall statistic using the equation:

$$Z = \left(\left|S\right| - 1\right) \Big/ SD\left[S\right] \qquad [14.26]$$

Step 5. Given significance level, α, determine the critical point z_{cp} from the standard normal distribution in **Table 10-1** of **Appendix D**. Compare Z against this critical point. If $Z > z_{cp}$, conclude there is statistically significant evidence at the α-level of an increasing trend. If $Z < -z_{cp}$, conclude there is statistically significant evidence of a decreasing trend. If neither, conclude that the sample evidence is insufficient to identify a trend.

►EXAMPLE 14-10

The data set in **Example 14-8** replicated below indicated both clear seasonality and an apparent increasing trend. Use the seasonal Mann-Kendall procedure to test for a significant trend with $\alpha = 0.01$ significance.

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	Analyte Concentrations				
	1983	1984	1985	S_i	$SD[S_i]$
January	1.99	2.01	2.15	3	1.915
February	2.10	2.10	2.17	2	1.633
March	2.12	2.17	2.27	3	1.915
April	2.12	2.13	2.23	3	1.915
May	2.11	2.13	2.24	3	1.915
June	2.15	2.18	2.26	3	1.915
July	2.19	2.25	2.31	3	1.915
August	2.18	2.24	2.32	3	1.915
September	2.16	2.22	2.28	3	1.915
October	2.08	2.13	2.22	3	1.915
November	2.05	2.08	2.19	3	1.915
December	2.08	2.16	2.22	3	1.915
				S = 35	$SD[S]$= 6.558

SOLUTION

Step 1. Form a seasonal subset for each month by grouping all the January measurements, all the February measurements, and so on, across the 3 years of sampling. This gives 12 seasonal subsets with n = 3 measurements per season. Note there are no tied values in any of the seasons except for February.

Step 2. Use equations [17.30] and [17.31] in **Section 17.3.2** to compute the Mann-Kendall statistic (S_i) for each subset. These values are listed in the table above. Also compute their sum to form the overall seasonal Mann-Kendall statistic, giving S = 35.

Step 3. Use equation [17.28] from **Section 17.3.2** for all months but February to compute the standard deviation of S_i. Since n = 3 for each of these subsets, this gives

$$SD\left[S_i\right] = \sqrt{\frac{1}{18}n\left(n-1\right)\left(2n+5\right)} = \sqrt{\frac{1}{18}3\cdot 2\cdot 11} = 1.915$$

For the month of February, one pair of tied values exists. Use equation [17.27] to compute the standard deviation for this subset:

$$SD\left[S_i\right] = \sqrt{\frac{1}{18}\left[n\left(n-1\right)\left(2n+5\right) - \sum_{j=1}^{g} t_j\left(t_j-1\right)\left(2t_j+5\right)\right]} = \sqrt{\frac{1}{18}\left[3\cdot 2\cdot 11 - 2\cdot 1\cdot 9\right]} = 1.633$$

List all the subset standard deviations in the table above. Then use equation [14.25] to compute the overall standard deviation:

$$SD\left[S\right] = \sqrt{\sum_{i=1}^{12} SD^2\left[S_i\right]} = \sqrt{11\cdot\left(1.915\right)^2 + \left(1.633\right)^2} = 6.558$$

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Step 4. Compute a normal approximation to *S* with equation [17.29]:

$$Z = (35 - 1) \Big/ 6.558 = 5.18$$

Step 5. Compare *Z* against the 1% critical point from the standard normal distribution in **Table 10-1** of **Appendix D**, $z_{.01} = 2.33$. Since *Z* is clearly larger than $z_{.01}$, the increasing trend evidence in **Figure 14-15** is highly significant. ◄

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CHAPTER 15. MANAGING NON-DETECT DATA

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This chapter considers strategies for accommodating non-detect measurements in groundwater data analysis. Five particular methods are described for incorporating non-detects into parametric statistical procedures. These include:

- Simple substitution (**Section 15.2**);
- Kaplan-Meier (**Section 15.3**);
- Robust Regression on Order Statistics (**Section 15.4**);
- Cohen's Method (**Section 15.5.1**); and
- Parametric Regression on Order Statistics (**Section 15.5.2**).

15.1 GENERAL CONSIDERATIONS FOR NON-DETECT DATA

Non-detects commonly reported in groundwater monitoring are statistically known as "left-censored" measurements, because the concentration of any non-detect either cannot be estimated or is not reported directly. Rather, it is known or assumed only to fall within a certain range of concentration values (*e.g.*, between zero and the *quantitation limit* [QL]). The direct estimate has been censored by the limitations of the measurement process or analytical technique, and is deemed too uncertain to be considered reliable. Groundwater non-detect data are censored on the low or left end of a sample concentration range. Other kinds of threshold data, particularly survival rates in the medical literature, are often reported as right-censored values.

Historically, there has been inconsistent treatment of non-detects in groundwater analysis. Often, easily applied techniques have been favored over more sophisticated methods of handling non-detects. This may primarily be due to the lack of familiarity and difficulties with software that can incorporate such methods. Even at present, most statistical packages include analysis routines for right-censored values but not left-censored ones (Helsel, 2005). Left-censored data needs to be converted to right-censored data for analysis and then back again. Despite these limitations, the more sophisticated methods are almost always superior to the methods of simple substitution.

The past twenty years has seen considerable research on statistical aspects of non-detect data analysis. Helsel (2005) provides a detailed summary of available methods for non-detects, and

concludes that simple substitution usually leads to greater statistical bias and inaccuracy than with better technical methods. Gibbons (1994b) and Gibbons & Coleman (2001) offer a broad review of some of the same research, not all of it directly relating to groundwater data. Both Gibbons and McNichols & Davis (1988) note that most of the existing studies focus on an ***estimation of parameters*** such as the mean and variance of an underlying population from which the censored and detected data originate. For these tasks, simple substitution methods tend to perform poorly, especially when the non-detect percentages are high (Gilliom & Helsel, 1986).

Much less attention has been given to how left-censored data impact the ***results of statistical tests***, the actual data-based conclusions that are drawn when using detection, compliance, or corrective action monitoring tests. Closely estimating the true mean and variance of the underlying background population may be important, but does not directly answer how well a given test performs (in achieving the nominal false positive error rate and correctly identifying true significant differences). McNichols & Davis (1988) performed a limited study to address these concerns. They found that simple substitution methods were among the best performers in simulated prediction limit tests even with fairly high rates of censoring, ***so long as*** the prediction limit procedure incorporated a verification resample.

Gibbons (1994b; also Gibbons and Coleman, 2001) conducted a similar limited simulation of prediction limit testing performance incorporating a verification resample. They, too, found that a type of simple substitution was one of the best performers when either an average of 20% or 50% of the data was non-detect. The Gibbons study concluded that substituting zero for each non-detect worked better to keep the false positive rate low than by substituting half the method detection limit [MDL].

Both studies primarily focused on the achievable false positive rate when censored data are present, rather than the statistical power of these tests to identify contaminated groundwater. In addition, both only considered parametric prediction limits. For data sets with fairly low detection frequencies (***e.g.***, <50%), parametric prediction limits may not accurately accommodate left-censored measurements, with or without retesting. The McNichols & Davis study in particular found that ***none*** of the simpler methods for handling non-detects did well when the underlying data came from a skewed distribution and the non-detect percentage was over 50%.

On balance, there are four general strategies for handling non-detects: 1) employing a test specifically designed to accommodate non-detects, such as the Tarone-Ware two-sample alternative to the *t*-test (**Section 16.3**); 2) using a rank-based, non-parametric test such as the Kruskal-Wallis alternative to analysis of variance [ANOVA] (**Section 17.1.2**) when the non-detects and detects can be jointly sorted and ordered (except for tied values); 3) estimating the mean and standard deviation of samples containing non-detects by means of a ***censored estimation technique***; and 4) ***imputing an estimated value*** for each non-detect prior to further statistical manipulation.

The first two strategies mentioned above are discussed in **Chapters 16** and **17** of the Unified Guidance as alternative testing procedures for evaluating left-censored data when parametric distribution assumptions cannot be made. Tests that can accommodate non-detects are typically non-parametric and thus carry both the advantages and disadvantages of non-parametric methods. The third and fourth strategies — presented in this chapter — are often employed as an ***intermediate step*** in parametric analyses. Estimates of the background mean and standard deviation are needed to construct parametric prediction and control chart limits, as well as confidence intervals. Imputed values for individual non-detects can be used as an alternate way to construct mean and standard deviation estimates, which are

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needed to update the *cumulative sum* [CUSUM] portion of control charts or to compute the means of order *p* that get compared against prediction limits.

The guidance generally favors the use of the more sophisticated Kaplan-Meier or Robust ROS methods which can address the problem of multiple detection limits. Two older techniques-- Cohen's method and parametric ROS-- are also included as somewhat easier methods which can work in some circumstances. Applying any of the four estimation techniques as well as simple substitution does rely on a fundamental underlying assumption. Both the detectable and non-detect portions of a data set are assumed to arise from a single distribution, and in particular this underlying population is expected to be stable or *stationary* during the period of the sampling record.

However, if an underlying distribution is subject to a trend over time, applying any of these techniques including simple substitution is more problematic. If data indicating a decreasing trend also happen to contain multiple detection limit data (perhaps the result of improved analytical methods), it may be very difficult to determine whether there is truly a trend or analytical problems are the apparent cause of the observed decreases. None of the techniques provided in this chapter can directly address this issue. As discussed in **Chapter 5**, careful exploratory review of the historical data sets, particularly those which might serve as background, need to consider which data including non-detects are most representative of present or near-term future conditions. In some cases, removal of the older, less reliable data may also resolve multiple detection limit problems. If non-detect values higher than other quantified data at reasonable detection limits are included in a data set (especially if dictated by reporting policy rather than analytical considerations), these will almost invariably need to be removed. Even sophisticated multiple detection limit techniques cannot realistically address these particular information-limited data values. But presuming valid and reliable data are selected, the four estimation techniques are provided to address the management of non-detects.

A data set may also not be defined by a single distribution. If observed data are the result of two or more different generative processes and indicate one or more separate peaks, it is referred to as a mixture distribution. One example might be trace organics data in a release subject to changes in the flow direction of the aquifer, which can result in very high to absent values. The subject is a complex one and generally beyond the scope of this guidance. Aitchison's method can be used in limited situations where detectable data form one discrete distribution, and the remainder are non-detect. The following discussion also addresses when Aitchison's method might be appropriate. The non-detect data are simply considered as some single value, another form of simple substitution.

15.2 IMPUTING NON-DETECT VALUES BY SIMPLE SUBSTITUTION

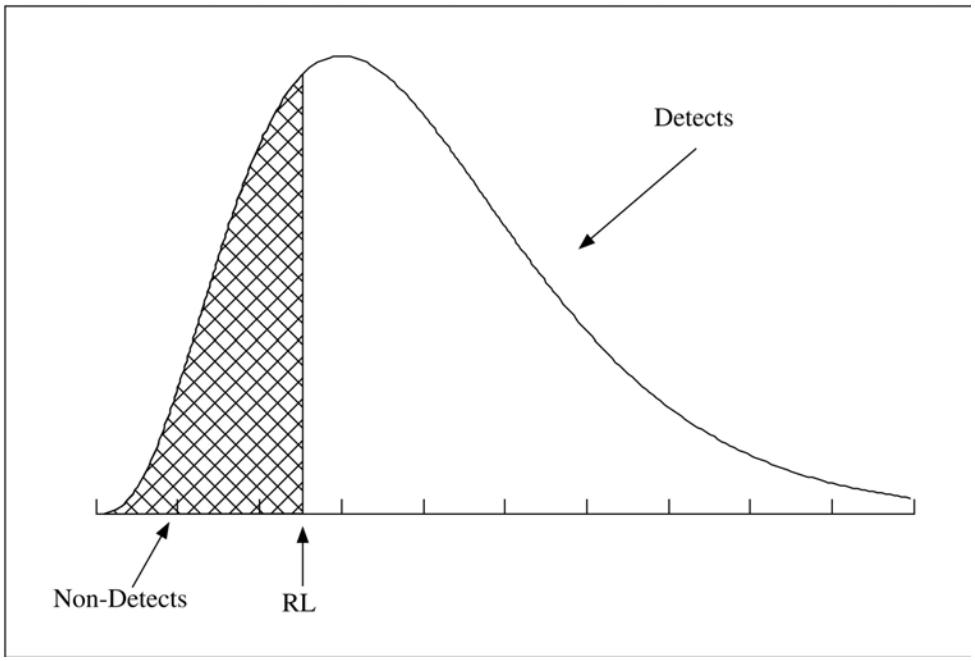
The simplest approach in managing non-detects is to substitute an *imputed value* for each prior to subsequent statistical analysis. The imputation is intended to be a 'reasonable estimate' of the true, but unknown concentration, usually a fraction (*e.g.*, 0, ½, 1) of the reporting limit [RL]. If non-detects represent an *absence* of the contaminant being measured, replacing a reported 'less than' value by zero may make sense. If the true concentration is completely unknown, but believed to be between zero and the RL, half the RL, or RL/2, may be a reasonable substitution, since this choice is the *maximum likelihood estimate* [MLE] of the mean or median for a population of measurement values *uniformly*

distributed along the interval [0, RL].[1] In other cases, a conservative choice might be made to maximize the *possible* concentration levels present in non-detects by selecting the RL itself as the imputation.

Any of these substitution choices is imperfect since they ignore two realities about left-censored measurements. First, non-detects are a product of ***both*** the underlying distribution of actual concentrations ***and*** the measurement process used to estimate these concentrations. In particular, the measurement technique may impart random or not so random bias to the 'true' concentration levels, causing the reported values to be 'shifted away from' the true values. As an example, simple substitution of zero for each non-detect ignores the fact that only the ***measurements*** can be observed and analyzed, not the actual concentration levels. Physical groundwater samples that are completely devoid of a given chemical may not receive ***measurements*** of zero, even if the actual amount is zero. Simple substitution by zero thereby ignores the ***measurement distribution*** in favor of an ***a priori*** assumption about what non-detects might represent.

A second reality is that non-detects must be considered with respect to other, detected measurements, as well as the physical process that generated the data. In many cases, the entire sample is drawn from a single statistical distribution (representing a common physical process) but some portion of the lower tail has been censored during measurement, as illustrated in **Figure 15-1**. In this situation, the overall distribution (and especially the shape of the lower tail) dictates how likely it is that a given non-detect would have an ***uncensored*** measurement close to zero or close to the RL. Substitution by half the RL or by the RL itself ignores the larger distributional pattern, especially since this distribution will rarely be uniform in the interval [0, RL].

Figure 15-1. Single Distributional Model For Detects and Non-Detects



[1] The uniform distribution places equal probability along every point of a finite concentration or measurement range. This model implies that a true value close to zero is just as likely as a true value close to RL or any other point along the interval.

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These realities can lead to severe biases in statistical parameter estimates made from censored data when simple substitution methods are used (Helsel, 2005). Even if only 20% of the data are censored, Gibbons (1994b) found that the false positive rate of a prediction limit test was far above the *nominal* (*i.e.*, expected or targeted) rate of $\alpha = .05$ when a simple imputation strategy was employed. For that reason, the Unified Guidance recommends imputation by simple substitution only in select circumstances described below:

❖ ***When the sample size is too small to do anything else***.

With only a handful of measurements (*e.g.*, 5 or less), it will be almost impossible to accurately apply a censored estimation technique, such as those described in **Sections 15-3 to 15-5**. Instead, simple substitution of half the RL is recommended, perhaps until enough data has been collected to allow a more sophisticated analysis. Three situations where simple substitution might commonly be needed include:

1. Plotting cumulative sums [CUSUM] on control charts (**Chapter 20**). While there should be enough background data to allow for a more sophisticated estimate of the control limit, the CUSUM must be updated with each single new compliance observation ($n = 1$). If the new measurement is a non-detect, the value must be imputed for the CUSUM to be calculated.

2. Constructing future means for prediction limits (**Chapter 19**). Again, if censored data exist in background, the prediction limit for a future mean can be computed with the help of a censored estimation technique. But with only 2 or 3 new measurements per compliance well ($p = 2, 3$), the same strategy will not work for computing a mean of order p.

3. Construction of confidence intervals in compliance monitoring or corrective action. Especially in the early months or years after the onset of compliance monitoring or a corrective action plan, there may be too few compliance point measurements to allow for a statistically refined treatment of non-detects. Until more data has been collected that is representative of the conditions under which these phases of monitoring have been triggered, simple substitution of non-detects will probably be needed. Furthermore, if groundwater conditions are in a state of flux, it may be impossible — even with a larger sample size — to postulate a single, stationary distributional model (similar to **Figure 15-1**) on which to base a censored estimation technique.

❖ ***When non-detects comprise no more than 10-15% of the total sample***.

If the percentage of non-detects is small enough, results of parametric *t*-tests and ANOVA are usually not significantly affected if non-detects are first replaced by half their reporting limits [RLs]. A similar statement can be made for parametric prediction limits, tolerance limits, control charts, and confidence intervals. However, because *t*-tests and ANOVA involve a comparison of means utilizing multiple data points per mean estimate,[2] while prediction limits for individual observations, tolerance limits, and control charts focus on single measurements, it is important that *retesting* be included in the statistical procedure whenever simple substitution is utilized with these latter methods.

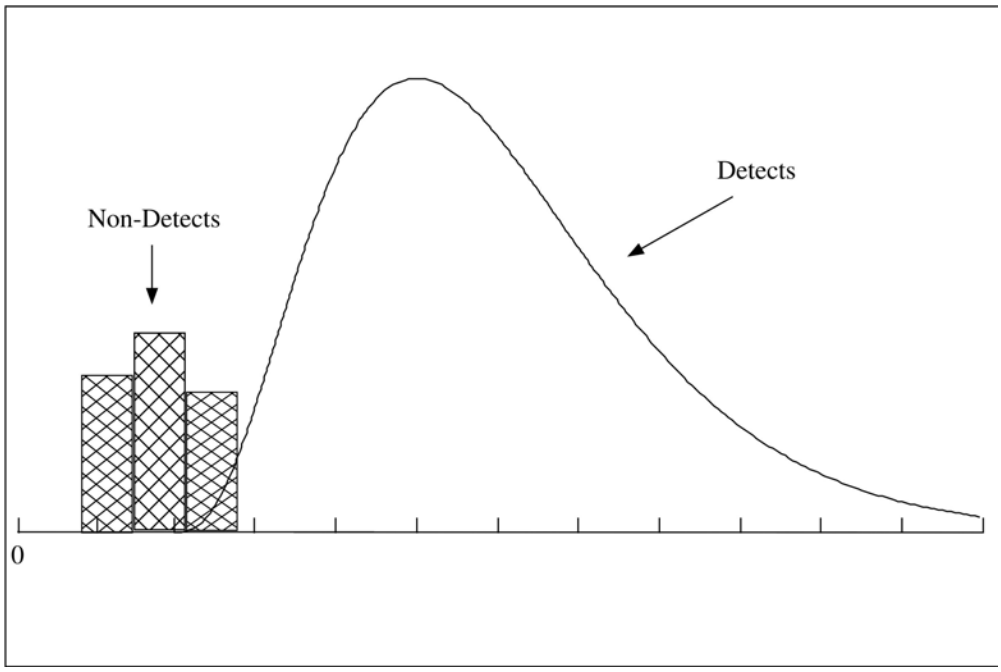
[2] Parametric confidence intervals around the mean also involve an estimate of the population average using multiple data points.

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- ***When non-detects are generated by a different physical process than the detected values, and thus represent a distinct statistical distribution***.

One non-detect treatment recommended in past EPA guidance — Aitchison's method (1955), as applied to groundwater[3] — assumed that non-detects were actually *free* of the contaminant being measured, so that all non-detects could be regarded as zero concentrations. In some cases, if an analyte has been detected infrequently or not at all in background measurements, and/or all non-detects are qualified as "U" (*i.e.*, undetected) values, this assumption may be practical, even if it cannot be directly verified. Another example might be seasonal changes in groundwater elevation at wells located on the edges of a contaminant plume. Parameters detectable at certain times of the year may be non-detect during other seasons, even within the same well. Such non-detects may result from a different data-generating mechanism, due to seasonal changes in groundwater chemistry, and so may not follow the same distribution as detects.

Figure 15-2. Modified Delta Model For Mixture Distribution of Detects/Non-Detects



More generally, Aitchison's original model posited a 'spike' of zero-valued measurements, combined with a lognormal distribution governing the detected values. A modification to Aitchison's model known as the *modified delta method*[4] (USEPA, 1993) has been found to be more practical and realistic in many circumstances (**Figure 15-2**). Instead of assuming that all non-detects represent zero

[3] Aitchison's model was not originally applied to concentration data. More typical applications were in the fields of economics and demographics.

[4] The original Aitchison model was termed the *delta-lognormal*, so called because it presumed that the data consisted of a mixture of two distinct populations: 1) a lognormal distribution representing the observed continuous measurements, and 2) a 'spike' of values, known as a delta function, located at zero.

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concentrations, the modified delta method assumes that non-detects constitute a separate, discrete distribution. When combined with the detected values, a ***mixture distribution*** is formed consisting of a continuous detected portion (usually the normal or lognormal distribution) and a discrete non-detect portion. Rather than assuming that all non-detects are zeros, the modified delta model assigns all non-detects at half the reporting limit [RL]. (Note: this might be a method detection limit [MDL], a quantitation limit [QL], or a contract RL). This method can accommodate multiple reporting limits since each non-detect is assigned half of its possibly sample-specific RL. It can also accommodate low-valued detects ***intermingled*** with the non-detects, since the non-detects and detects are modeled by distinct distributions.

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15.3 ESTIMATION BY KAPLAN-MEIER

BACKGROUND AND PURPOSE

When a sample contains both detects and non-detects generated by a common process and governed by a single underlying distribution (**Figure 15-1**), a more reliable strategy is to attempt to fit the sample to a known distribution (***e.g.***, normal, lognormal) and then to estimate the mean and standard deviation of this distribution via a *censored estimation technique*. These adjusted estimates can be input into standard equations for parametric prediction, tolerance, and control chart limits, as well parametric confidence intervals around the mean.

Two censored estimation methods which can address the multiple detection limit problem are discussed in the Unified Guidance: the Kaplan-Meier estimator and *robust regression on order statistics* [ROS] (**Section 15.4**). Both involve initially fitting a left-censored sample to a known distribution. After that, the procedures differ. The Kaplan-Meier creates an estimate of the population mean and standard deviation adjusted for data censoring, based on the fitted distributional model, whereas the Robust ROS uses the fitted model to construct a *model-based imputation* for each non-detect. Once the imputations are made, the adjusted mean and standard deviation are estimated using standard equations for the sample mean ($\bar{x}$) and standard deviation (s).

The key to either method is finding a single distributional model that adequately fits the joint sample of detects and non-detects. While each procedure does the fitting in a slightly different fashion, both utilize the notion of *partial ranking*. As discussed in **Section 16.2** on "Handling Non-Detects," the presence of left-censored measurements, particularly when there are multiple RLs and/or an *intermingling* of detects and non-detects, prevents a full and complete ranking of the sample. Both Kaplan-Meier and ROS construct a partial ranking of the data, accounting for the non-detects and assigning explicit ranks to each of the detected values. These detected values can then be graphed on a *censored probability plot* and fitted against a known distribution.

The Kaplan-Meier technique estimates the approximate proportion of concentrations below each observed level by sorting and ordering the distinct sample values, although the exact concentrations of non-detects are unknown. In particular, the probability of observing a concentration no greater than a given level (x_i) depends on the relative proportion of the sample greater than x_i. Any detects larger than x_i obviously fall into this latter proportion, while non-detects with RLs of at most x_i do not. On balance, the proportion of the sample greater than x_i cannot be precisely calculated for every x_i, but it can be estimated.

The Kaplan-Meier estimator for left-censored data thus depends on a series of *conditional* probabilities, where the frequency of lower concentrations depends on how many larger concentrations have already been observed. The final result is an estimate of the *cumulative distribution function* [CDF] for each distinct concentration level in the sample.

In mathematical notation, suppose there are m distinct values in the sample (out of a total of n measurements), including distinct reporting limits. Order these values from least to greatest and denote them as $x_{(1)}, x_{(2)}, \ldots, x_{(m)}$. Let n_i for $i = 1$ to m denote the 'risk set' associated with value $x_{(i)}$. The *risk set* represents the total number of measurements — both detects and non-detects — no greater than $x_{(i)}$. Since a non-detect with a RL larger than $x_{(i)}$ is *potentially* (but not necessarily) larger than $x_{(i)}$, non-detects with RL > $x_{(i)}$ are *not* included in n_i. A further term d_i identifies the number of detected measurements exactly equal to $x_{(i)}$.

With these definitions in place and letting X denote a random variable concentration from the true underlying distribution, the Kaplan-Meier estimator is constructed from the pair of probabilities:

$$\Pr\left(X \le x_{(m)}\right) = 1 \qquad [15.1]$$

$$\Pr\left(X \le x_{(i)} \middle| X \le x_{(i+1)}\right) = 1 - \frac{d_{i+1}}{n_{i+1}} \quad \textit{for } i = 1 \textit{ to } m \qquad [15.2]$$

where $x_{(m+1)} = +\infty$, $d_{m+1} = 0$, and $n_{m+1} = n$ all by definition. Equation [15.2] represents the conditional probability that the concentration does not exceed $x_{(i)}$ given that it does not exceed $x_{(i+1)}$. The final Kaplan-Meier CDF estimate (F_{KM}) for each $i = 1$ to m–1 (each distinct detected value) is given by a product of these conditional probabilities and can be expressed as:

$$F_{KM}\left(x_{(i)}\right) = \Pr\left(X \le x_{(i)}\right) = \left(1 - \frac{d_{i+1}}{n_{i+1}}\right) \times \left(1 - \frac{d_{i+2}}{n_{i+2}}\right) \times \ldots \times \left(1 - \frac{d_m}{n_m}\right) = \prod_{k=i}^{m-1}\left(1 - \frac{d_{k+1}}{n_{k+1}}\right) \qquad [15.3]$$

Once the CDF is estimated using equation [15.3], two additional steps are made possible. One is to use the distinct values ($x_{(i)}$) and their corresponding CDF values (F_{KM}) to construct censored probability plots. The other is to use the Kaplan-Meier CDF to estimate the population mean and standard deviation.

REQUIREMENTS AND ASSUMPTIONS

The Kaplan-Meier estimator is a non-parametric procedure originally devised to estimate *survival probabilities* for right-censored samples (Kaplan and Meier, 1958), such as in medical studies of cancer treatments. Because it is non-parametric, there is no requirement that the underlying population be normal or transformable to normality. However, in adapting the technique to left-censored data (*i.e.*, samples containing non-detects), the Unified Guidance recommends that the Kaplan-Meier procedure be utilized to estimate the mean and variance of a normal or normalized distribution for use in *parametric* statistical tests.

The Kaplan-Meier assumes that all detected and non-detect data arise from the same population, but that non-detect values have been 'censored' at their RLs. This implies that the contaminant of

concern is *actually present* in non-detect samples, but that the analytical method cannot accurately measure, or is not sufficiently sensitive to, concentrations lower than the RL.

To construct a censored probability plot, a normal quantile or *z*-score needs to be computed for each value of the Kaplan-Meier CDF (F_{KM}). Doing so is straightforward except for the CDF value of the sample maximum, which is assigned a value of one. The *z*-score associated with a cumulative probability of one is infinite. To surmount this difficulty, the Unified Guidance recommends temporarily setting the CDF value for the sample maximum equal to $(n - .375)/(n + .25)$. This value is the Blom plotting position often utilized in standard probability plots (Helsel, 2005). It is close to one for large n, but allows for a finite *z*-score.

Estimation of the Kaplan-Meier mean and standard deviation using equations [15.4] and [15.5] below will tend to be slightly biased, typically with the mean on the high side and the standard deviation on the low side. This occurs because the Kaplan-Meier CDF levels corresponding to distinct RLs are treated as if they were known measurements rather than the upper bounds on possible values. As long as the total proportion of censored measurements is not too high, the degree of bias will tend to be small. Larger biases are more likely whenever the detection rate is less than 50%.

PROCEDURE

Step 1. Given a sample of size n containing left-censored measurements, identify and sort the $m < n$ distinct values, including distinct RLs. Label these as $x_{(1)}, x_{(2)}, \ldots, x_{(m)}$.

Step 2. For each $i = 1$ to m, calculate the *risk set* (n_i) as the total number of detects and non-detects no greater than $x_{(i)}$. Also compute d_i as the number of *detected* values exactly equal to $x_{(i)}$.

Step 3. Using equation [15.3], compute the Kaplan-Meier CDF estimate $F_{KM}\left(x_{(i)}\right)$ for $i = 1, \ldots, m-1$. Also let $F_{KM}\left(x_{(m)}\right) = 1$.

Step 4. Construct censored probability plots using the estimated CDF. First temporarily set $F_{KM}\left(x_{(m)}\right) = (n - .375)/(n + .25)$ so that a finite normal quantile (or *z*-score; see **Chapter 9**) can be associated with $x_{(m)}$. Then compute normal quantiles (*i.e.*, *z*-scores) for each value of F_{KM} from **Step 3** as $z_{(i)} = \Phi^{-1}\left[F_{KM}\left(x_{(i)}\right)\right]$, where $\Phi^{-1}[\cdot]$ is the inverse of the standard normal distribution function as discussed in the construction of probability plots in **Chapter 9**. Plot the values $z_{(i)}$ against the unique detected concentrations $x_{(i)}$ to form a *normal* censored probability plot. Plot the $z_{(i)}$'s against a transformation of the $x_{(i)}$'s (*e.g.*, log, square root, inverse, *etc.*) to form a *normalized* censored probability plot.

Step 5. For each attempted transformation $f(\cdot)$ including the unchanged observations as one option, compute the *correlation coefficient* between the pairs $[f(x_{(i)}), z_{(i)}]$ (**Chapter 3**). The transformation with the highest correlation coefficient and also a linear appearance on the censored probability plot, is one that optimally normalizes the left-censored sample. Estimate the mean and standard deviation in Step 6 on the transformed scale and use these estimates in subsequent statistical analysis.

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If no transformation results in an adequately linear censored probability plot, conclude that the sample cannot be normalized. Mean and standard deviation estimates of the original concentrations can still be computed, but they will not correspond to a known probability distribution.

Step 6. If the raw concentration data are approximately normal, compute mean and standard deviation estimates adjusted for censoring using the equations:

$$\hat{\mu}_{KM} = \sum_{i=1}^{m} x_{(i)} \cdot \left[F_{KM}\left(x_{(i)}\right) - F_{KM}\left(x_{(i-1)}\right)\right] \quad [15.4]$$

$$\hat{\sigma}_{KM} = \sqrt{\sum_{i=1}^{m} \left(x_{(i)} - \hat{\mu}_{KM}\right)^2 \cdot \left[F_{KM}\left(x_{(i)}\right) - F_{KM}\left(x_{(i-1)}\right)\right]} \quad [15.5]$$

where $x_{(0)} = 0$ and $F_{\mathrm{KM}}\left(x_{(0)}\right) = F_{\mathrm{KM}}\left(0\right) = 0$ by definition. Otherwise, compute the adjusted mean and standard deviation after applying the normalizing transformation $f(\cdot)$ with the equations:

$$\hat{\mu}_{KM} = \sum_{i=1}^{m} f\left(x_{(i)}\right) \cdot \left[F_{KM}\left(x_{(i)}\right) - F_{KM}\left(x_{(i-1)}\right)\right] \quad [15.6]$$

$$\hat{\sigma}_{KM} = \sqrt{\sum_{i=1}^{m} \left(f\left(x_i\right) - \hat{\mu}_{KM}\right)^2 \cdot \left[F_{KM}\left(x_{(i)}\right) - F_{KM}\left(x_{(i-1)}\right)\right]} \quad [15.7]$$

Estimates from equations [15.4] and [15.5] can then be used in place of the sample mean ($\bar{x}$) and standard deviation (s) in parametric equations for prediction and control limits, and for confidence intervals. If a normalizing transformation is required, equations [15.6] and [15.7] can be used to construct similar statistical limits and intervals on the ***transformed*** scale.

►EXAMPLE 15-1

Use the Kaplan-Meier technique on the following manganese concentration data to construct estimates of the population mean and standard deviation that are adjusted for censoring.

	Manganese Concentrations (ppb) in Background				
Sample	Well 1	Well 2	Well 3	Well 4	Well 5
1	<5.0	<5.0	<5.0	6.3	17.9
2	12.1	7.7	5.3	11.9	22.7
3	16.9	53.6	12.6	10.0	3.3
4	21.6	9.5	106.3	<2.0	8.4
5	<2.0	45.9	34.5	77.2	<2.0

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SOLUTION

Step 1. From the combined sample of n = 25 measurements, identify and sort the 21 distinct values including distinct RLs as in the table below. Compute the risk set (n_i) for each distinct level ($x_{(i)}$) as the total number of detects and non-detects no greater than $x_{(i)}$. Also calculate the exact number of detects (d_i) equal to each level.

Step 2. Compute the Kaplan-Meier estimate of the CDF using equations [15.1] and [15.3], shown in column 5 of the table below. Two example calculations are given by:

$$F_{KM}(22.7) = \left(1-\frac{1}{21}\right)\left(1-\frac{1}{22}\right)\left(1-\frac{1}{23}\right)\left(1-\frac{1}{24}\right)\left(1-\frac{1}{25}\right) = 0.8$$

$$F_{KM}(3.3) = \left(1-\frac{0}{7}\right)\cdot\left(1-\frac{1}{8}\right)\cdot\left(1-\frac{1}{9}\right)\cdot\ldots\cdot\left(1-\frac{1}{24}\right)\cdot\left(1-\frac{1}{25}\right) = 0.28$$

i	$x_{(i)}$	At Risk (n_i)	d_i	CDF
1	<2.0	3	0	0.21
2	3.3	4	1	0.28
3	<5.0	7	0	0.28
4	5.3	8	1	0.32
5	6.3	9	1	0.36
6	7.7	10	1	0.40
7	8.4	11	1	0.44
8	9.5	12	1	0.48
9	10.0	13	1	0.52
10	11.9	14	1	0.56
11	12.1	15	1	0.60
12	12.6	16	1	0.64
13	16.9	17	1	0.68
14	17.9	18	1	0.72
15	21.6	19	1	0.76
16	22.7	20	1	0.80
17	34.5	21	1	0.84
18	45.9	22	1	0.88
19	53.6	23	1	0.92
20	77.2	24	1	0.96
21	106.3	25	1	1.00

Step 3. Compute normal quantiles or z-scores for each value of F_{KM} in the above table. First re-set the last entry to $(n - .375)/(n + .25) = 0.9752$ so that a finite quantile can be associated with the sample maximum.

Step 4. Plot the *z*-scores against the distinct manganese levels to form a normal censored probability plot (**Figure 15-3**). The probability plot correlation coefficient is $r = 0.902$. The plot itself shows substantial curvature, suggesting that the sample is non-normal.

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Step 5. Plot the *z*-scores against one or more transformations of the manganese levels. First attempt a log transformation, as shown in **Figure 15-4**. In this case, the correlation coefficient improves to $r = 0.989$ and the normalized censored probability plot looks fairly linear. Conclude that the sample is approximately normal on the log-scale, that is, the manganese concentrations are lognormal in distribution.

Step 6. Compute Kaplan-Meier log-mean ($\hat{\mu}_{y,KM}$) and log-standard deviation ($\hat{\sigma}_{y,KM}$) estimates for the manganese data using equations [15.6] and [15.7], taking $f(\cdot)$ as the natural logarithm. This gives for the log-mean:

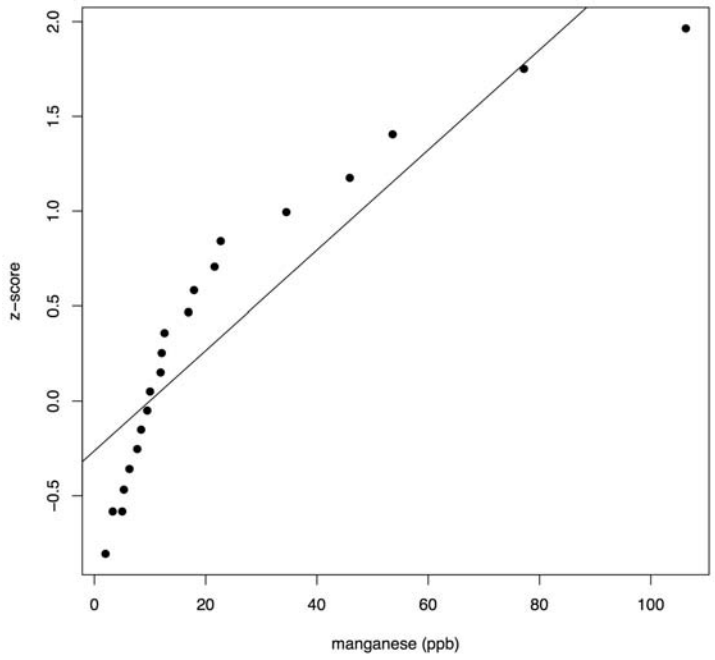
$$\hat{\mu}_{y,KM} = \log(2)\cdot[.21-0] + \log(3.3)\cdot[.28-.21] + \ldots + \log(106.3)\cdot[1-.96] = 2.31\log(ppb)$$

and for the log-standard deviation:

$$\hat{\sigma}_{y,KM} = \sqrt{(\log(2)-2.31)^2\cdot[.21-0] + \ldots + (\log(106.3)-2.31)^2\cdot[1-.96]} = 1.18\ \log(ppb)$$

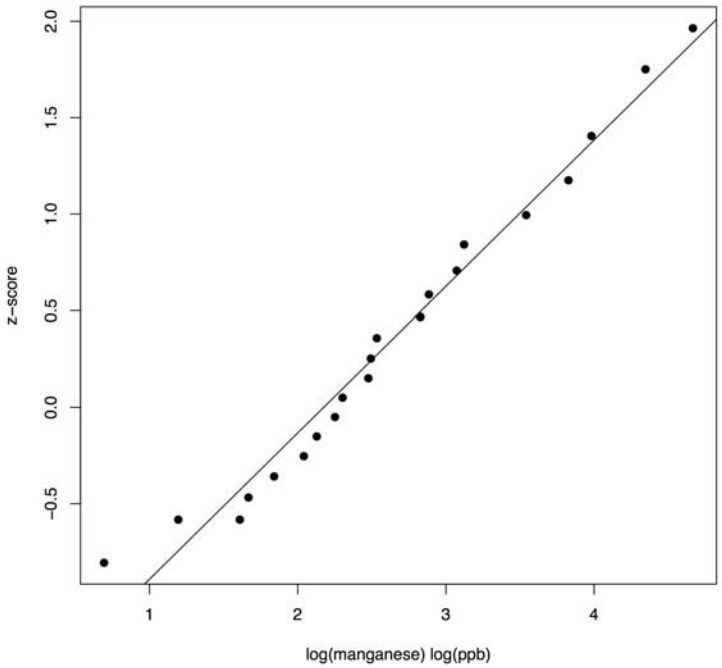
These adjusted mean and standard deviation estimates can then be used in place of the sample log-mean and log-standard deviation in parametric prediction and control limits, or in parametric confidence intervals. ◄

Figure 15-3. Censored Probability Plot of Manganese Concentrations



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Figure 15-4. Censored Probability Plot of Logged Manganese Sample



15.4 ROBUST REGRESSION ON ORDER STATISTICS

BACKGROUND AND PURPOSE

Robust regression on order statistics [ROS] differs from Kaplan-Meier in that it uses the fitted model to construct a ***model-based imputation*** for each non-detect. Once the imputations are made, the adjusted mean and standard deviation are estimated using standard equations for the sample mean ($\bar{x}$) and standard deviation (*s*).

The first step in using Robust ROS is to find a single distributional model that adequately fits the joint sample of detects and non-detects. Standard probability plots (**Chapter 9**) and normality tests (**Chapter 10**) rely on a full ranking or ordering of the sample in order to fit candidate distributions. With left-censored data, the true concentrations of non-detects are unknown, so only a *partial ranking* is possible. Like Kaplan-Meier, the Robust ROS technique constructs a partial ranking of the data, accounting for the non-detects and assigning explicit ranks to each of the detected values. These detected values can be graphed on a *censored probability plot* to check the fit of possible distributional models.

Once an adequate distribution is found, Robust ROS determines the approximate cumulative probability associated with each distinct RL. The method then arbitrarily distributes non-detects with a common RL so that each one accounts for an equal share of the estimated cumulative probability

assigned to that RL. Once non-detects are ranked in this manner, the fitted distributional model is used to impute a value for each non-detect. This last task is accomplished by conducting a linear regression (Chapter 17) between the detected values and the z-scores from the censored probability plot. The parameters of the regression line (i.e., intercept and slope) can be used to estimate the mean and standard deviation of the distributional model, which in turn will generate imputed values for the non-detects.

The mathematics behind Robust ROS can be expressed as follows. First suppose there are k distinct RLs in the sample. Order these from least to greatest. Define A_i as the number of detected values between the ith and (i+1)th RLs for $i = 1$ to k–1. Let A_k = number of detects above the highest RL, and take A_0 = number of detects below the lowest RL. Also define B_i as the total number of observations, both detects and non-detects, with values below the ith RL. Define $B_0 = 0$. Then the number of non-detects below the ith RL can be written as:

$$C_i = B_i - B_{i-1} - A_{i-1} \qquad for\ i = 1\ to\ k \qquad [15.8]$$

With these definitions in place, exceedance probabilities can be assigned to each of the k RLs, representing the proportion of the sample greater than or equal to each distinct RL. These probabilities can be written as:

$$pe_i = pe_{i+1} + \frac{A_i}{A_i + B_i}\left(1 - pe_{i+1}\right) \qquad [15.9]$$

where pe_j denotes the proportion of the sample exceeding the ith RL. Equation [15.9] can be interpreted in the following manner. The exceedance probability associated with a given RL is equal to the exceedance probability assigned to the next highest RL combined with a fraction of the remaining, non-exceedance probability (*i.e.*, $1 - pe_{i+1}$). The specific fraction depends on the relative occurrence of detects between the ith and (i+1)th RLs. When $i = k$, define $pe_{i+1} = 0$; when $i = 0$, define $pe_0 = 1$.

Once the exceedance probabilities are computed, plotting positions for the detects — *i.e.*, cumulative probabilities on a probability plot — can be calculated with the equation

$$pd_{ij} = \left(1 - pe_i\right) + \left(\frac{j}{A_i + 1}\right) \cdot \left(pe_i - pe_{i+1}\right) \qquad for\ j = 1\ to\ A_i;\quad and\ i = 0\ to\ k \qquad [15.10]$$

for each set of detected values falling between the ith and (i+1)th RLs. Note that this equation also applies to any detects below the lowest RL [$i = 0$] or above the highest RL [$i = k$]). Similarly, plotting positions for each group of non-detects can be written as:

$$pc_{ij} = \left(\frac{j}{C_i + 1}\right) \cdot \left(1 - pe_i\right) \qquad for\ j = 1\ to\ C_i;\ and\ i = 1\ to\ k \qquad [15.11]$$

With plotting positions for the detects, a normal quantile or z-score can be computed for each value of pd_{ij}. Then censored probability plots can be constructed using either the detected concentrations (x_{ij}) or some normalizing transformation of the detected values, say $f(x_{ij})$. If a linear probability plot can be identified, a linear regression (**Chapter 17**) can be calculated for the pairs (z_{ij}, $f(x_{ij})$) and used to impute values for the non-detects in the sample.

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REQUIREMENTS AND ASSUMPTIONS

Robust ROS was originally devised to account for non-detects in water quality data (Helsel, 2005). Robust ROS is an extension of a technique termed *regression on order statistics [ROS]* (Gilliom and Helsel, 1986), described in **Section 15.5.** That procedure assumes the joint sample of detects and non-detects follows an underlying lognormal distribution. The fitted lognormal is used to estimate the population mean and standard deviation as a parametric technique. Robust ROS by contrast only relies on a parametric model to impute values for the non-detects. It can be applied to any normal or normalized distribution, rather than just the lognormal distribution. It may also be regarded as quasi-non-parametric since estimates for the sample are computed from the combined group of observed detects and imputed non-detects, rather than from the mean and standard deviation of the underlying distributional model, as in the original formulation.

In practice, because Robust ROS is not fully non-parametric, a known distribution must be fitted to the entire sample in order to construct imputed values for the non-detects. Closely related to this, Robust ROS assumes that both detected and non-detect data arise from the same population, with non-detect values censored at their respective RLs. Like Kaplan-Meier, this implies that the contaminant of concern is *present* in non-detect samples, but that the analytical method cannot accurately measure concentrations lower than the RL.

PROCEDURE

Step 1. Given a left-censored sample with a total of n measurements, identify and sort the k distinct RLs. Following the discussion above, count the number of detected values below the lowest RL (A_0), the number of detected values at least as great as the highest RL (A_k), and the number of detects between the ith and (i+1)th RLs (A_i for i = 1 to k–1). Also let $B_0 = 0$ and count the total number of detects and non-detects below the ith RL (B_i for i = 1 to k). Then use equation [15.8] to calculate the number of non-detects (C_i for i = 1 to k) below the ith RL.

Step 2. Let $pe_0 = 1$ and $pe_{k+1} = 0$. For i = 1 to k, compute the probability of exceeding the ith distinct RL (pe_i) using equation [15.9].

Step 3. With the exceedance probabilities from Step 2, sort each group of detects associated with A_i and then compute plotting positions (*i.e.*, cumulative probabilities) for these detects — pd_{ij} — using equation [15.10].

Step 4. Form normal quantiles (*i.e.*, z-scores) associated with the detected measurements and plotting positions pd_{ij} by computing $z_{ij}^{d} = \Phi^{-1}\left(pd_{ij}\right)$, where $\Phi^{-1}(\cdot)$ is the inverse standard normal CDF.

Step 5. Construct censored probability plots using the z-scores from Step 4. Plot the values z_{ij}^{d} against the detected concentrations x_{ij}^{d} to form a *normal* censored probability plot. Plot the z_{ij}^{d}'s against a transformation of the x_{ij}^{d}'s (*e.g.*, log, square root, inverse, *etc.*) to form a *normalized* censored probability plot.

Step 6. For each attempted transformation $f(\cdot)$ including the unchanged observations as one option, compute the *correlation coefficient* between the pairs $\left[f\left(x_{ij}^{d}\right), z_{ij}^{d} \right]$ (**Chapter 3**). The transformation with the highest correlation coefficient and also a linear appearance on the censored probability plot, is the one that optimally normalizes the left-censored sample. If no transformation results in an adequately linear censored probability plot, conclude that the sample cannot be normalized and that the Robust ROS may not provide reasonable imputations for the non-detects.

Step 7. If a normalizing transformation can be identified, compute a linear regression (**Chapter 17**) of the values $f\left(x_{ij}^{d}\right)$ on the *z*-scores, z_{ij}^{d}, to form the regression equation $f(X) = \hat{a} + \hat{b} \cdot Z$. The slope and intercept can be estimated using the equations

$$\hat{b} = \sum_{i=0}^{k} \sum_{j=1}^{A_i} \left(z_{ij}^{d} - \bar{z}_{d}\right) \cdot f\left(x_{ij}^{d}\right) \Big/ \left(n_{d} - 1\right) \cdot s_{z_d}^{2} \qquad [15.12]$$

$$\hat{a} = \bar{x}_{d} - \hat{b} \cdot \bar{z}_{d} \qquad [15.13]$$

where $\bar{z}_{d}$ is the mean of the *z*-scores associated with the detected values, n_{d} = number of detects, $s_{z_d}^{2}$ is the sample variance of the detected *z*-scores, and $\bar{x}_{d}$ is the mean of the detected measurements. The regression intercept ($\hat{a}$) is an estimate of the population mean of the normalized distribution, while the slope ($\hat{b}$) is an estimate of the population standard deviation.

Step 8. Compute plotting positions (pc_{ij}) for the non-detects (*i.e.*, censored observations) associated with each distinct RL using equation [15.11]. Then form a second set of *z*-scores, this time associated with the non-detects, by computing $z_{ij}^{c} = \Phi^{-1}\left(pc_{ij}\right)$ for j = 1 to C_{i}; and i = 1 to k.

Step 9. Form imputed values $f\left(\hat{x}_{ij}^{c}\right) = \hat{a} + \hat{b} \cdot z_{ij}^{c}$ using the slope and intercept from **Step 7** and the censored z-scores from **Step 8**. Combine these (transformed) imputed values for the non-detects with the (transformed) detected measurements $f\left(x_{ij}^{d}\right)$ to get censored estimates of the population mean and standard deviation by computing the overall sample mean ($\hat{\mu} = \bar{x}$) and sample standard deviation ($\hat{\sigma} = s$).

These censored estimates can be used in place of the unadjusted sample mean ($\bar{x}$) and standard deviation (s) in parametric equations for prediction and control limits, and for confidence intervals. If a normalizing transformation $f(\cdot)$ is needed, the censored estimates should be used to construct statistical limits and intervals on the *transformed* scale.

►EXAMPLE 15-2

In **Example 15-1**, the Kaplan-Meier technique was used on a sample of background manganese concentrations to compute the log-mean and log-standard deviation, adjusted for the presence of non-detects. Apply Robust ROS to these same data to compare the estimates.

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SOLUTION

Step 1. The n = 25 manganese observations include 2 distinct RLs (<2 and <5). Count the number of detected measurements below the lowest RL, above the highest RL, and between the two RLs, denoted by A_i in the table below. Also count the total number of measurements — both detected and non-detect — below each RL, denoted below by B_i. Use equation [15.8] to count the number of non-detects associated with each RL, denoted below by C_i.

i	RL	A_i	B_i	C_i
0		0	0	0
1	<2	1	3	3
2	<5	18	7	3

Step 2. Compute the probability of exceeding each RL using equation [15.9] and noting that $pe_3 = 0$:

$$pe_2 = pe_3 + \frac{A_2}{A_2 + B_2}\left(1 - pe_3\right) = \frac{18}{18+7} = 0.72$$

$$pe_1 = pe_2 + \frac{A_1}{A_1 + B_1}\left(1 - pe_2\right) = 0.72 + \frac{1}{1+3}\left(1 - 0.72\right) = 0.79$$

Step 3. Sort the detects associated with each A_i and compute plotting positions for these detects using equation [15.10], as listed in the table below. For instance, $A_1 = 1$, corresponding to the detected value 3.3. The plotting position for this observation equals

$$pd_{11} = \left(1 - pe_1\right) + \left(\frac{1}{A_1 + 1}\right)\left(pe_1 - pe_2\right) = 0.21 + 0.5\left(0.79 - 0.72\right) = 0.245$$

Also form the normal quantiles (i.e., z-scores) associated with the detected observations, as listed below:

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Detected Value (ppb)	Plotting Position	z-score
3.3	0.245	−0.690
5.3	0.318	−0.474
6.3	0.356	−0.370
7.7	0.394	−0.270
8.4	0.432	−0.172
9.5	0.469	−0.077
10.0	0.507	0.018
11.9	0.545	0.114
12.1	0.583	0.210
12.6	0.621	0.308
16.9	0.659	0.410
17.9	0.697	0.515
21.6	0.735	0.627
22.7	0.773	0.748
34.5	0.811	0.880
45.9	0.848	1.030
53.6	0.886	1.207
77.2	0.924	1.434
106.3	0.962	1.776

Step 4. Plot the *z*-scores against the detected manganese levels to form a normal censored probability plot (**Figure 15-5)**. The probability plot correlation coefficient is $r = 0.901$, almost identical to the Kaplan-Meier censored probability plot constructed in **Example 15-1**. The plot also shows substantial curvature, suggesting that the sample is non-normal. Also plot the *z*-scores against a log transformation of the detected manganese values (**Figure 15-6**). Not only does the normalized probability plot appear linear, but the correlation coefficient increases to $r = 0.994$. Conclude as in **Example 15-1** that the sample is approximately normal on the log-scale, so that the manganese concentrations are lognormal in distribution.

Step 5. Compute a linear regression of the $n_d = 19$ logged manganese detects against their corresponding *z*-scores using equations [15.12] and [15.13]. The sample mean and variance of the detected *z*-scores are $\bar{z}_d = 0.3802$ and $s^2_{z_d} = 0.4577$. Also, the log-mean of the detected observations equals $\overline{\log(x_d)} = 2.80$. The slope and intercept of the resulting line are:

$$\hat{b} = \frac{1}{18 \times .4577}\left[1.194 \cdot (-.690 - .3802) + \ldots + 4.666(1.776 - .3802)\right] = 1.372$$

$$\hat{a} = \bar{x}_d - \hat{b} \cdot \bar{z}_d = 2.80 - 1.372 \times .3802 = 2.278$$

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Figure 15-5. Robust ROS Censored Probability Plot of Manganese Concentrations

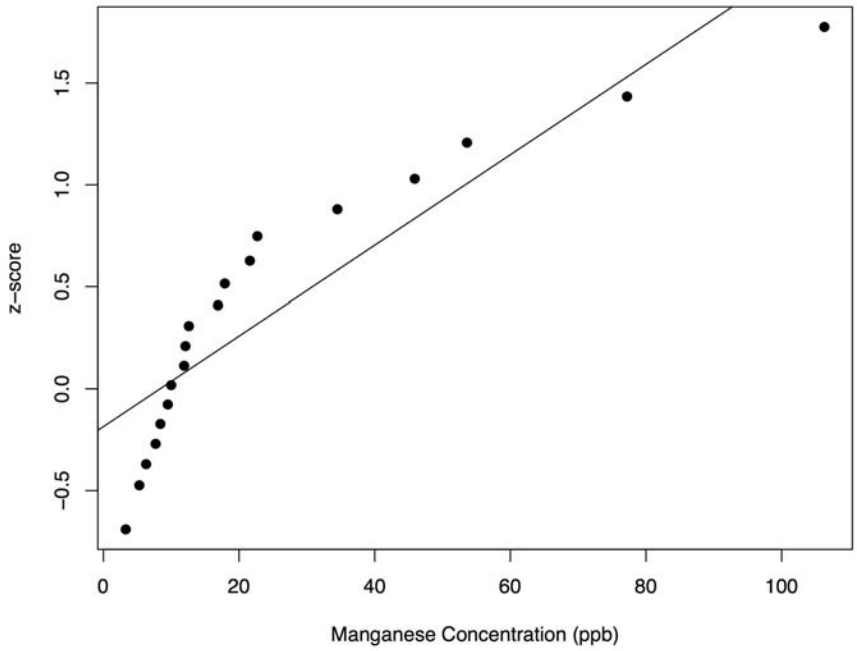
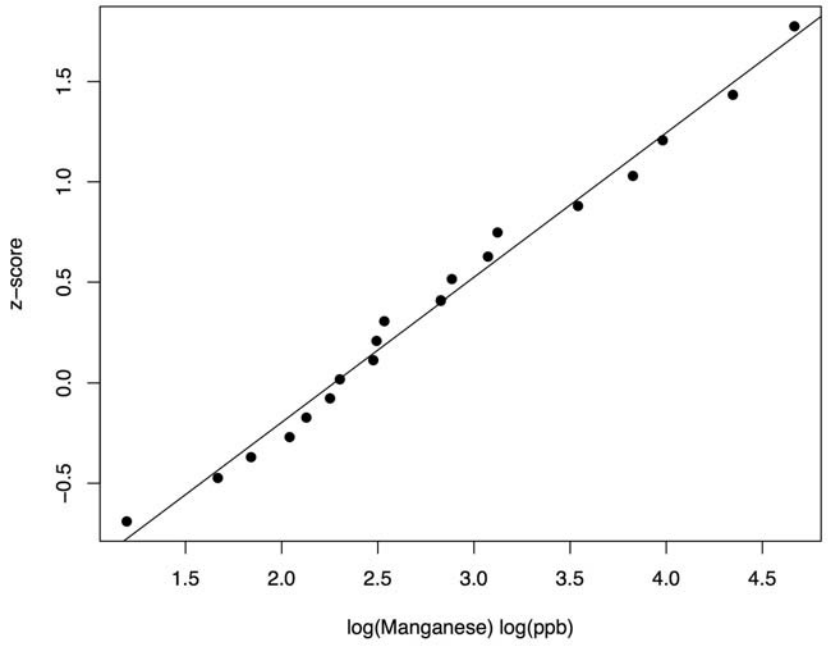


Figure 15-6. Robust ROS Censored Probability Plot of Logged Manganese



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Step 6. Compute plotting positions for the non-detects (*i.e.*, censored observations) associated with each distinct RL using equation [15.11], listed in the table below. Form a second set of *z*-scores, this time associated with the non-detects, also listed below. Note that each non-detect is given a distinct plotting position, even though they cannot be ordered. This is done to 'fill in' the unknown portion of the underlying distribution, but should *not* be interpreted as a legitimate 'estimate' for any particular non-detect observation. The positions for the first pair of the 3 non-detects with RLs of 2 (*i.e.*, <2) are

$$pc_{11} = \left(\frac{1}{C_1 + 1}\right)\left(1 - pe_1\right) = \left(\frac{1}{3+1}\right)\left(1 - 0.79\right) = 0.0525$$

$$pc_{12} = \left(\frac{2}{C_1 + 1}\right)\left(1 - pe_1\right) = \left(\frac{2}{3+1}\right)\left(1 - 0.79\right) = 0.105$$

RL	Plotting Position	z-score	Imputed Value
<2	0.0525	−1.621	0.054
<2	0.1050	−1.254	0.558
<2	0.1575	−1.005	0.899
<5	0.0700	−1.476	0.253
<5	0.1400	−1.080	0.796
<5	0.2100	−0.806	1.172

Step 7. Form a second set of z-scores associated with the censored plotting positions from **Step 6**. These are listed in the table above. Then, using the regression parameters from **Step 5**, form a prediction for each non-detect using the equation $\log\left(x_{ij}^{c}\right) = \hat{\alpha} + \hat{\beta} \cdot z_{ij}^{c}$. Take these predictions as the imputed values for the set of non-detects, as listed above. The first two imputed values are computed as:

$$\log\left(x_{11}^{c}\right) = 2.278 + 1.372 \cdot \left(-1.621\right) = 0.054$$

$$\log\left(x_{12}^{c}\right) = 2.278 + 1.372 \cdot \left(-1.254\right) = 0.558$$

Step 8. Combine the logged detected manganese values with the imputed values from Step 7. Then compute the sample mean and standard deviation using the adjusted sample. These calculations give $\hat{\mu} = 2.28 \log(ppb)$ and $\hat{\sigma} = 1.26 \log(ppb)$. By comparison, the Kaplan-Meier method in **Example 15-1** gives very similar corresponding estimates of 2.31 log(ppb) and 1.18 log(ppb). ◄

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SECTION 15.5 OTHER METHODS FOR A SINGLE CENSORING LIMIT

The two preferred methods using Kaplan-Meier or Robust ROS provided above for multiple detection limits are computationally intensive. Helsel (2005) indicates that public software is available for the Robust ROS method. Although the more common situation encountered in evaluating data sets is the presence of multiple detection limits (hence the UG recommendations), two older techniques are still applicable in some situations. The Cohen method and the parametric ROS techniques are both simpler to apply, but depend on the use of a single censoring limit. One needs to evaluate the prospects before applying them. If detectable data sets are large enough (e.g., $n > 50$) and detection percentages near or greater than 50%, most of these methods will work comparably.

15.5.1 COHEN'S ADJUSTMENT

Cohen's adjustment (Cohen, 1959) can be useful when a significant fraction (up to 50%) of the observed measurements in a data set are reported as non-detects. The technique assumes that all the measurements, detects and non-detects alike, arise from a common population, but that the lowest valued observations have been *censored* at the QL. Using the censoring point (*i.e.*, QL) and the pattern in the detected values, Cohen's method attempts to reconstruct the key features of the original population, providing explicit estimates of the population mean and standard deviation. These in turn can be used in certain statistical interval estimates, where Cohen's adjusted estimates are used as replacements for the sample mean and sample standard deviation.

REQUIREMENTS AND ASSUMPTIONS

Cohen's adjustment assumes that the common underlying population has a normal distribution. The technique should only be used when the observed sample data approximately fit a normal model including transformations to normality. Because the presence of a large fraction of non-detects will make explicit normality testing difficult, if not impossible, the most helpful diagnostic aid may be to construct a censored probability plot on the detected measurements. If the censored probability plot is clearly linear on the original measurement scale but not on the log-scale, assume normality for purposes of computing Cohen's adjustment. If, however, the censored probability plot is clearly linear on the log-scale, but not on the original scale, assume instead that the common underlying population is lognormal. Then compute Cohen's adjustment to the estimated mean and standard deviation on the log-scale measurements and construct the desired statistical interval using the algorithm for lognormally-distributed observations.

When the detection rate is less than 50%, the accuracy of Cohen's method worsens as the percentage of non-detects increases. The guidance does not generally recommend the use of Cohen's adjustment when more than half the data are non-detect. In such circumstances, one should consider an alternate statistical method, for instance a non-parametric interval or perhaps the Wilcoxon rank-sum test for small samples.

One other requirement of Cohen's original method is that there should be just a single censoring point. Data sets with multiple RLs will usually require a more sophisticated treatment such as Kaplan-Meier or Robust ROS methods or via maximum likelihood techniques (Cohen, 1963) or perhaps a multiply-censored probability plot technique (Helsel and Cohn, 1988). If only 2 or 3 RLs do not substantially differ and few detected intermingled data are lost, the censoring point (*QL*) can be set to

the highest RL. Cohen's method requires explicit definition of the censoring limit, and is somewhat sensitive to variation in this parameter.

PROCEDURE

Step 1. Divide the data set into two groups, detects and non-detects. If the total sample size equals *n*, let *m* represent the number of detects and (*n*–*m*) represent the number of non-detects. Denote the *i*th detected measurement by x_i. Then compute the mean and sample variance of the set of detects using the equations:

$$\bar{x}_d = \frac{1}{m}\sum_{i=1}^{m} x_i \quad \text{and} \quad s_d^2 = \frac{1}{m-1}\left[\sum_{i=1}^{m} x_i^2 - m\bar{x}_d^2\right]$$

Step 2. Denote the single censoring point by *QL*. Then compute the two intermediate quantities, *h* and γ, necessary to derive Cohen's adjustment via the following equations:

$$h = 100 \cdot (n-m)/n = ND\% \quad \text{and} \quad \gamma = s_d^2 \Big/ \left(\bar{x}_d - QL\right)^2$$

Step 3. Use the intermediate quantities *h* and γ to determine Cohen's adjustment parameter λ from the table below.

Values of Lamba (λ) for Cohen's Adjustment

γ\ND%	1	5	10	15	20	25	30	35	40	45	50
.01	.0102	.0530	.1111	.1747	.2443	.3205	.4043	.4967	.5989	.7128	.8403
.05	.0105	.0547	.1143	.1793	.2503	.3279	.4130	.5066	.6101	.7252	.8540
.10	.0110	.0566	.1180	.1848	.2574	.3366	.4233	.5184	.6234	.7400	.8703
.20	.0116	.0600	.1247	.1946	.2703	.3525	.4422	.5403	.6483	.7678	.9012
.30	.0122	.0630	.1306	.2034	.2819	.3670	.4595	.5604	.6713	.7937	.9300
.40	.0128	.0657	.1360	.2114	.2926	.3803	.4755	.5791	.6927	.8179	.9570
.50	.0133	.0681	.1409	.2188	.3025	.3928	.4904	.5967	.7129	.8408	.9826
.60	.0137	.0704	.1455	.2258	.3118	.4045	.5046	.6133	.7320	.8625	1.0070
.70	.0142	.0726	.1499	.2323	.3206	.4156	.5180	.6291	.7502	.8832	1.0303
.80	.0146	.0747	.1540	.2386	.3290	.4261	.5308	.6441	.7676	.9031	1.0527
.90	.0150	.0766	.1579	.2445	.3370	.4362	.5430	.6586	.7844	.9222	1.0743
1.00	.0153	.0785	.1617	.2502	.3447	.4459	.5548	.6725	.8005	.9406	1.0951
1.25	.0162	.0828	.1705	.2636	.3627	.4687	.5825	.7053	.8385	.9841	1.1443
1.50	.0170	.0868	.1786	.2758	.3793	.4897	.6081	.7357	.8738	1.0245	1.1901
1.75	.0177	.0905	.1861	.2873	.3948	.5094	.6321	.7641	.9069	1.0625	1.2332
2.00	.0184	.0940	.1932	.2981	.4093	.5279	.6547	.7909	.9382	1.0984	1.2739
2.25	.0191	.0973	.1999	.3082	.4231	.5454	.6761	.8164	.9679	1.1325	1.3127
2.50	.0197	.1005	.2062	.3179	.4363	.5621	.6965	.8407	.9962	1.1651	1.3498
2.75	.0203	.1035	.2123	.3272	.4489	.5781	.7161	.8639	1.0234	1.1963	1.3854
3.00	.0209	.1063	.2182	.3361	.4609	.5935	.7348	.8863	1.0495	1.2264	1.4197
3.50	.0219	.1118	.2292	.3529	.4838	.6226	.7704	.9287	1.0990	1.2835	1.4847
4.00	.0229	.1168	.2395	.3687	.5052	.6498	.8038	.9685	1.1455	1.3371	1.5458
4.50	.0239	.1216	.2492	.3836	.5253	.6755	.8353	1.0060	1.1895	1.3878	1.6037
5.00	.0248	.1262	.2585	.3977	.5445	.7000	.8653	1.0418	1.2312	1.4359	1.6587
5.50	.0256	.1305	.2673	.4111	.5628	.7233	.8938	1.0758	1.2711	1.4820	1.7113
6.00	.0264	.1346	.2757	.4240	.5803	.7456	.9212	1.1085	1.3094	1.5262	1.7617

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Step 4. Using the adjustment parameter λ found in Step 3, compute adjusted estimates of the population mean and standard deviation with the equations:

$$\hat{\mu} = \bar{x}_d - \lambda(\bar{x}_d - QL) \quad \text{and} \quad \hat{\sigma} = \sqrt{s_d^2 + \lambda \cdot (\bar{x}_d - QL)^2}$$

Step 5. Once the adjusted estimates for the population mean and standard deviation are derived, these values can be substituted for the sample mean and standard deviation in equations for the statistical intervals.

15.5.2 PARAMETRIC REGRESSION ON ORDER STATISTICS (ROS)

A second useful method (EPA, 2004) for estimating mean and standard deviation parameters for data sets with non-detect values censored at a single limit is a parametric Regression on Order Statistics (ROS). The same assumptions apply as with Cohen's method. Both the detected and non-detect portions of the data are presumed to arise from a single population. That population should either be normal or transformable to a normal distribution. The parametric ROS method performs similarly to Cohen's method, and offers two principal advantages. The procedure can easily be implemented on almost any statistical software, and the method is not sensitive to the exact censoring limit.

If variable X originates from a normal distribution with mean μ and standard deviation σ $[X \succ N(\mu,\sigma)]$ and Z is the standard normal distribution $[Z \succ N(0,1)]$, statistical theory indicates that $X = \mu + \sigma \cdot Z$ when X and Z are at the same percentiles in their respective distributions. For a given observation or sample x above a detection limit, the order statistic (i.e., the proportion of observations less than x) can be estimated. This order statistic is an estimate of the percentile. The corresponding Z-value can be obtained from reference tables or a computer algorithm. For a list of ordered observations above the detection limit $(x_1, x_2, \ldots \text{ to } x_m)$ of m detectable samples out of a total n and a corresponding set of Z-values $(Z_1, Z_2, \ldots \text{ to } Z_m)$ at the same percentiles, regression analysis of X against Z will provide estimates of the mean and standard deviation of distribution X. The intercept is the mean estimate and the slope of the regression is the standard deviation estimate.

When sample data better fit a lognormal or other normal transformable distribution, the regression is performed on the transformed data. The mean and standard deviation estimates are also for the transformed data (e.g., logarithmic mean and standard deviation). One may also use the regression results to "fill in" or quantify the values below the detection limit. When the Z-distribution is developed for the full set of total n sample values, the Z-values for the detectable portion are separated from those for the remaining $n - m$ non-detect percentiles. Estimates for the non-detect values are obtained from the equation $X = \hat{\mu} + \hat{\sigma} \cdot Z$, using $\hat{\mu}$ the intercept mean estimate, $\hat{\sigma}$ the slope standard deviation estimate and the non-detect Z-values. These can then be aggregated with the sample detectable values to obtain the overall mean and standard deviation estimate.

PROCEDURE

Step 1. Determine the appropriate normal transformation and convert the data if necessary. Divide the data set into two groups, detects and non-detects. If the total sample size equals n, let m represent the number of detects and $(n - m)$ represent the number of non-detects. Denote the ith detected measurement by x_i. Order the m detected data from smallest to largest.

Step 2. Define the normal percentiles for the total n sample set as follows. For a set of *i* values from 1 to *n*, $p_i = (i - .375)/(n + .25)$. Then convert to Z-values using the inverse normal distribution $Z_i = \Phi^{-1}(p_i)$. Separate the Z_i values into two groups: the larger *m* detected and *n - m* non-detected portions.

Step 3. Use linear regression of the ordered *m* data values against the corresponding Z-values. Obtain the intercept and slope of the regression as the estimated mean and standard deviation estimates, $\hat{\mu}$ and $\hat{\sigma}$. These can be used directly as the distributional parameter estimates or Step 4 can be followed.

Step 4. Using equation $X_{n-m} = \hat{\mu} + \hat{\sigma} \cdot Z_{n-m}$ with $\hat{\mu}$ the intercept mean estimate, $\hat{\sigma}$ the slope standard deviation estimate and the non-detect Z_{n-m} values, calculate the remaining x_{n-m} values and combine with the x_m detected data. Use the combined direct sample mean and standard deviation calculations as the final parameter estimates:

$$\hat{\mu} = \frac{1}{n}\sum_{i=1}^{n} x_i \quad \text{and} \quad \hat{\sigma} = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n-1}}$$

►EXAMPLE 15-3

Use Cohen's and the parametric ROS methods for the data in **Example 15-1** and compare the results to the Kaplan-Meier and Robust ROS Methods. A single overall logarithmic distribution can be assumed. In the example, it is possible to utilize the higher detection limit (<5) as the censoring limit, with the loss of only a single detected point of information. The detection frequency is still 72%.

For Cohen's method, h = .28 and γ = .465 for the logarithmic data. The adjustment parameter from the above table is interpolated as λ = .445. The resulting mean and standard deviation estimates for the full data set are $\hat{\mu}$ = 2.32 log(ppb) and $\hat{\sigma}$ = 1.22 log(ppb).

Mean and standard deviation estimates for the parametric ROS method are $\hat{\mu}$ = 2.33 log(ppb) and $\hat{\sigma}$ = 1.21 log(ppb) following regression of the ordered detectable log values against the corresponding Z- values of the standard normal distribution. With such few non-detects near the lowest end of the sample distribution, the results are quite similar to the Robust ROS and Kaplan-Meier methods. For higher non-detect percentages and more heavily intermingled non-detect data, the results using these methods can differ considerably. ◄

15.6 USE OF THE 15% AND 50% NON-DETECT RULE

In this chapter and elsewhere in the Unified Guidance, it is recommended that imputing arbitrary values be limited to data sets with 10-15% or fewer non-detects and that parametric procedures be applied when there are 50% or fewer non-detects. The guidance continues to suggest this basic non-detects rule for both historical and conservative reasons. The same approach was found in both the earlier RCRA 1989 and 1992 RCRA statistical guidance documents, although it was recognized in the

first as a guideline "based on judgment". It was also noted that "there is no general procedure that is applicable in all cases." The 10-15% rule using direct substitution of arbitrary values is believed adequate for many applications, but one of the censoring estimation techniques provided in this chapter can be used instead. For a skewed distribution like the lognormal, the latter approach would be preferable. We have cited studies above by Davis and others indicating that parameter estimation and test performance can suffer when more than 50% of the data are non-detects. Most of the common parameters (i.e., mean, median, standard deviation, etc.) can be estimated with tolerable bias and error when no more than 50% of the values are originally non-detect and the superior non-detect fitting techniques used. Statistical test performance using these limitations appears to be reasonable for most applications. However, it should be recognized that they are only "rules of thumb", not absolute criteria.

Other authors (e.g., Helsel 2005) have suggested that certain tests will perform adequately even with higher non-detect rates in data. The criterion of non-detect percentage is not the only factor. For example with very large data sets (e.g., 100-300), quite reasonable fits can be made to the detectable portion using techniques found in **Chapter 15** even with non-detect percentages greater than 50%. Having a sufficient number of detectable data is also an important consideration, applying equally to small data sets. One should have a fairly good idea that the detect data themselves follow one or another parametric distributions. To do so, one should have a sufficiently large number of detected data points for comparison.

A second factor is the potential application for fitted non-detect data. As an example, fits of high non-detect percentage larger data sets using the lognormal distribution can provide decent parameter estimates (log mean and log standard deviation) for use with upper prediction limit detection monitoring tests. Generally, the fits accurately describe the upper portions of the observed data sets. At the same time, these estimated logarithmic parameters may result in considerably larger errors when estimating the true arithmetic mean and standard deviation (the bias problem in transformations), such as with compliance level tests. In this case, the 50% rule is best followed.

The guidance generally recommends non-parametric options when non-detect data exceed 50%. However, even this suggestion comes with caveats. For example, if a number of wells to be compared using Kruskal-Wallis non-parametric ANOVA had mostly or all well data sets greater than 50% non-detects, the outcome would be ambiguous. This is because the test involves comparisons of medians, which would lie below the detection limit. At very high non-detect percentages, fewer options are available. Upper non-parametric prediction limits can work with very few detectable values, but the assumption of any distributional pattern is increasingly tenuous. In some cases, a binomial test of proportions (found in the 1989 guidance) may be the only realistic option. As a final suggestion, we recommend that users take these factors into account and consider recommendations of other statistical literature in the field as well, when considering non-detect limitations to specific test procedures.

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PART III. DETECTION MONITORING TESTS

This third part of the Unified Guidance presents core procedures recommended for formal detection monitoring at RCRA-regulated facilities. **Chapter 16** describes two-sample tests appropriate for some small facilities, facilities in interim status, or for periodic updating of background data. These tests include two varieties of the *t*-test and two non-parametric versions-- the Wilcoxon rank-sum and Tarone-Ware procedures. **Chapter 17** discusses one-way analysis of variance [ANOVA], tolerance limits, and the application of trend tests during detection monitoring. **Chapter 18** is a primer on several kinds of prediction limits, which are combined with retesting strategies in **Chapter 19** to address the statistical necessity of performing multiple comparisons during RCRA statistical evaluations. Retesting is also discussed in **Chapter 20**, which presents control charts as an alternative to prediction limits.

As discussed in **Section 7.5**, any of these detection-level tests may also be applied to compliance/assessment and corrective action monitoring, where a background groundwater protection standard [GWPS] is defined as a critical limit using *two- or multiple-sample* comparison tests. Caveats and limitations discussed for detection monitoring tests are also relevant to this situation. To maintain continuity of presentation, this additional application is presumed but not repeated in the following specific test and procedure discussions.

Although other users and programs may find these statistical tests of benefit due to their wider applicability to other environmental media and types of data, the methods described in **Parts III** and **IV** are primarily tailored to the RCRA setting and designed to address formal RCRA monitoring requirements. In particular, the series of prediction limit tests found in **Chapter 18** is designed to address the range of interpretations of the sampling rules in §264.97(g), §264.98(d) and §258.54. Further, *all* of the regulatory tests listed in §264.97(i) and §258.53(h) are discussed, as well as the Student's *t*-test requirements of §265.93(b).

Taken as a whole, the set of detection monitoring methods presented in the Unified Guidance should be appropriate for almost all the situations likely to be encountered in practice. Professional statistical consultation is recommended for the rest.

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CHAPTER 16. TWO-SAMPLE TESTS

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This chapter describes statistical tests between two groups of data, known as two-sample tests. These tests may be appropriate for the smallest of RCRA sites performing upgradient-to-downgradient comparisons on a very limited number of wells and constituents. They may also be required for certain facilities in interim status, and can be more generally used to compare older versus newer data when updating background.

Two versions of the classic Student's *t*-test are first discussed: the *pooled variance t-test* and *Welch's t-test*. Since both these tests expect approximately normally-distributed data as input, two non-parametric alternatives to the *t*-test are also described: the *Wilcoxon rank-sum test* (also known as the *Mann-Whitney*) and the *Tarone-Ware test*. The latter is particularly helpful when the sample data exhibit a moderate to larger fraction of non-detects and/or multiple detection/reporting limits.

16.1 PARAMETRIC T-TESTS

BACKGROUND AND PURPOSE

A statistical comparison between two sets of data is known as a two-sample test. While several varieties of two-sample tests exist, the most common is the parametric *t*-test. This test compares two distinct statistical populations. The goal of the two-sample *t*-test is to determine whether there is any statistically significant difference between the mean of the first population when compared against the mean of the second population, based on the results observed in the two respective *samples*.

In groundwater monitoring, the typical hypothesis at issue is whether the average concentration at a compliance point is the same as (or less than) the average concentration in background, or whether the compliance point mean is larger than the background mean, as represented in equation [16.1] below:

$$H_0 : \mu_C \le \mu_{BG} \quad vs. \quad H_A : \mu_C > \mu_{BG} \qquad [16.1]$$

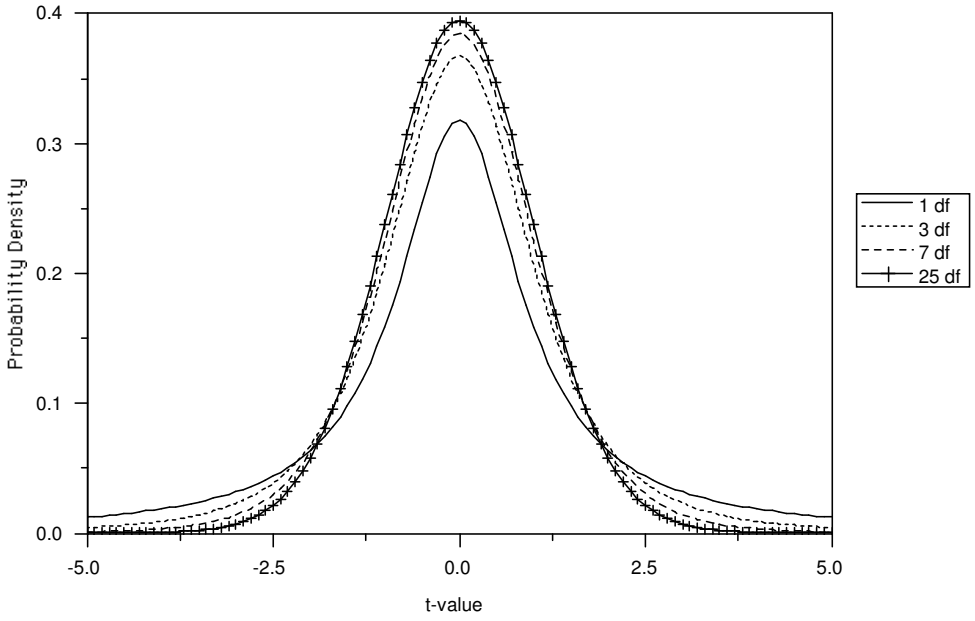
A natural statistic for comparing two population means is the difference between the sample means, $\left(\bar{x}_C - \bar{x}_{BG}\right)$. When this difference is small, a real difference between the respective population means is considered unlikely. However, when the sample mean difference is large, the null hypothesis is rejected, since in that case a real difference between the populations seems plausible. Note that an observed difference between the *sample* means does *not* automatically imply a true population difference. Sample means can vary for many reasons even if the two underlying parent populations are

identical. Indeed, the Student's *t*-test was invented precisely to determine when an observed sample difference should be considered significant (*i.e.*, more than a chance fluctuation), especially when the sizes of the two samples tend to be small, as is the usual case in groundwater monitoring.

Although the null hypothesis (H_0) represented in equation [16.1] allows for a true compliance point mean to be less than background, the behavior of the *t*-test statistic is assessed at the point where H_0 is most difficult to verify — that is, when H_0 is true and the two population means are identical. Under the assumption of equal population means, the test statistic in any *t*-test will tend to follow a Student's *t*-distribution. This fact allows the selection of critical points for the *t*-test based on a pre-specified Type I error or false positive rate (α). Unlike the similarly symmetric normal distribution, however, the Student's *t*-distribution also depends on the number of independent sample values used in the test, represented by the *degrees of freedom* [*df*].

The number of degrees of freedom impacts the shape of the *t*-distribution, and consequently the magnitude of the critical (percentage) points selected from the *t*-distribution to provide a basis of comparison against the *t*-statistic (see **Figure 16-1**). In general, the larger the sample sizes of the two groups being compared, the larger the corresponding degrees of freedom, and the smaller the critical points (in absolute value) drawn from the Student's *t*-distribution. In a one-sided hypothesis test of whether compliance point concentrations exceed background concentrations, a smaller critical point corresponds to a more powerful test. Therefore, all other things being equal, the larger the sample sizes used in the two-sample *t*-test, the more protective the test will be of human health and the environment.

Figure 16-1. Student's *t*-Distribution for Varying Degrees of Freedom



In groundwater monitoring, *t*-tests can be useful in at least two ways. First, a *t*-test can be employed to compare background data from one or more upgradient wells against a single compliance

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well. If more than one background well is involved, all the upgradient data would be pooled into a single group or sample before applying the test.

Second, a *t*-test can be used to assess whether updating of background data is appropriate (see **Chapter 5** for further discussion). Specifically, the two-sample *t*-test can be utilized to check whether the more recently collected data is consistent with the earlier data assigned initially as the background data pool. If the *t*-test is non-significant, both the initial background and more recent observations may be considered part of the same statistical population, allowing the overall background data set to grow and to provide more accurate information about the characteristics of the background population.

The Unified Guidance describes two versions of the parametric *t*-test, the pooled variance Student's *t*-test and a modification to the Student's *t*-test known as Welch's *t*-test. This guidance prefers the latter *t*-test to use of Cochran's Approximation to the Behrens-Fisher (CABF) Student's *t*-test. Initially codified in the 1982 RCRA regulations, the CABF *t*-test is no longer explicitly cited in the 1988 revision to those regulations. Both the pooled variance and Welch's *t*-tests are more standard in statistical usage than the CABF *t*-test. When the parametric assumptions of the two-sample *t*-test are violated, the Wilcoxon rank-sum or the Tarone-Ware tests are recommended as non-parametric alternatives.

REQUIREMENTS AND ASSUMPTIONS

The two-sample *t*-test has been widely used and carefully studied as a statistical procedure. Correct application of the Student's *t*-test depends on certain key assumptions. First, every *t*-test assumes that the observations in each data set or group are statistically independent. This assumption can be difficult to check in practice (see **Chapter 14** for further discussion of statistical independence), especially if only a handful of measurements are available for testing. As noted in **Chapter 5** in discussing data mixtures, lab replicates or field duplicates are not statistically independent and should not be treated as independent water quality samples. That section discussed the limited conditions under which certain replicate data might be applicable for *t*- testing. Incorrect usage of replicate data was one of the concerns that arose in the application of the CABF *t*-test.

Second, all *t*-tests assume that the underlying data are approximately normal in distribution. Checks of this assumption can be made using one of the tests of normality described in **Chapter 10**. The *t*-test is a reasonably robust statistical procedure, meaning that it will usually provide accurate results even if the assumption of normality is partially violated. This robustness of the *t*-test provides some insurance against incorrect test results if the underlying populations are non-normal. However, the robust assumption is dubious when the parent population is heavily skewed. For data that are lognormal and positively skewed, the two-sample *t*-test can give misleading results unless the data are first log-transformed. Similarly, a transformation may be needed to first normalize data from other non-normal distributions.

Another assumption particularly relevant to the use of *t*-tests in groundwater monitoring is that the population means need to be *stable* or *stationary* over the time of data collection and testing. As discussed in **Part II** of the guidance, many commonly monitored groundwater parameters exhibit mean changes in both space and time. Consequently, correct application of the *t*-test in groundwater requires an implicit assumption that the two populations being sampled (*e.g.*, a background well and a

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compliance point well) have average concentrations that are not trending with time. Time series plots and diagnostic trend tests (**Chapter 14**) can sometimes be used to check this assumption.

The *t*-test does an excellent job of identifying a stable mean level difference between two populations. However, if one or both populations have trends observable in the sample measurements, the *t*-test may have difficulty correctly identifying a difference between the two groups. For instance, if earlier samples in a compliance well were uncontaminated but later samples are increasing with time, the *t*-test may still provide a non-significant result. With compliance point concentrations increasing relative to background, the *t*-test may not be the appropriate method for identifying this change. Some form of trend testing will provide a better evaluation.

Another concern in applying the *t*-test to upgradient-downgradient interwell comparisons is that the null hypothesis is assumed to be true *unless* the downgradient well becomes contaminated. Absent such an impact, the population means are implicitly assumed to be identical. *Spatial variability* in background and compliance well groundwater concentrations for certain monitoring constituents do not allow clear conditions for comparisons intended to identify a release at a downgradient compliance well. Natural or pre-existing synthetic mean differences among background wells will be confused with a potential release. In such cases, neither the two-sample *t*-test nor *any* interwell procedure comparing upgradient against downgradient measurements is likely to give a correct conclusion.

One final requirement for running any *t*-test is that each group should have an adequate sample size. The *t*-test will have minimal statistical power to identify any but the largest of concentration differences if the sample size in each group is less than four. Four measurements per group should be considered a *minimum* requirement, and much greater power will accrue from larger sample sizes. Of course, the attractiveness of larger data sets must be weighed against the need to have statistically independent samples and the practical limitation of semi-annual or annual statistical evaluations. These latter requirements often constrain the frequency of sampling so that it may be impractical to secure more than 4 to 6 or possibly 8 samples during any annual period.

16.1.1 POOLED VARIANCE T-TEST

BACKGROUND AND PURPOSE

In the case of two independent samples from normal populations with common variance, the Student's *t*-test statistic is expressed by the following equation:

$$t = \left(\bar{x}_C - \bar{x}_{BG}\right) \Bigg/ \sqrt{\left[\frac{\left(n_{BG}-1\right)s_{BG}^2 + \left(n_C-1\right)s_C^2}{\left(n_{BG}+n_C-2\right)}\right]\left(\frac{1}{n_{BG}}+\frac{1}{n_C}\right)} \qquad [16.2]$$

The first bracketed quantity in the denominator is known as the *pooled variance*, a weighted average of the two sample variances. The entire denominator of equation [16.2] is labeled the *standard error of the difference* (SE_{diff}). It represents the probable chance fluctuation likely to be observed between the background and compliance point sample means when the null hypothesis in equation [16.1] is true. Note that the formula for SE_{diff} depends on both the pooled variance and the sample size of each group.

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When the null hypothesis (H_0) is satisfied and the two populations are truly identical, the test statistic in equation [16.2] behaves according to an exact Student's *t*-distribution. This fact enables critical points for the *t*-test to be selected based on a pre-specified Type I error rate (α) and an appropriate degrees of freedom. In equation [16.2], the joint degrees of freedom is equal to $\left(n_{BG} + n_C - 2\right)$, the sum of the background and compliance point sample sizes less two degrees of freedom (one for each mean estimate).

REQUIREMENTS AND ASSUMPTIONS

Along with the general requirements for *t*-tests, the pooled variance version of the test assumes that the population variances are equal in both groups. Since only the sample variances will be known, this assumption requires a formal statistical test of its own such as Levene's test described in **Chapter 11**. An easier, descriptive method is to construct side-by-side box plots of both data sets. If the population variances are equal, the interquartile ranges represented by the box lengths should also be comparable. If the population variances are distinctly different, on the other hand, the box lengths should also tend to be different, with one box much shorter than the other.

When variances are unequal, the Unified Guidance recommends Welch's *t*-test be run instead. Welch's *t*-test does not require the assumption of equal variances across population groups. Furthermore, the performance of Welch's *t*-test is almost always equal or superior to that of the usual Student's *t*-test. Therefore, one may be able to skip the test of equal variances altogether before running Welch's *t*-test.

All t-tests require approximately normally-distributed data. If a common variance (σ^2) exists between the background and compliance point data sets, normality in the pooled variance *t*-test can be assessed by examining the combined set of background and compliance point *residuals.* A residual can be defined as the difference between any individual value and its sample group mean (*e.g.*, $x_i - \bar{x}_{BG}$ for background values x_i). Not only will the combined set of residuals allow for a more powerful test of normality than if the two samples are checked separately, but it also avoids a difficulty that can occur if the sample measurements are naively evaluated with the *Shapiro-Wilk multiple group test*. The multiple group normality test allows for populations with different means *and* different variances. If an equal variance check has not already been made, the multiple group test could register both populations as being normal even though the two population variances are distinctly different. The latter would violate a key assumption of the pooled variance t-test. To avoid this potential problem, either always check explicitly for equal variances before running the pooled variance *t*-test, or consider running Welch's *t*-test instead.

PROCEDURE

Step 1. To conduct the two-sample Student's *t*-test at an α-level of significance, first compute the sample mean ($\bar{x}$) and standard deviation (s) of each group. Check for equal variances using a test from **Chapter 11**. If there is no evidence of heteroscedasticity, check normality in both samples, perhaps by calculating the residuals from each group and running a normality test on the combined data set.

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Step 2. Once the key assumptions have been checked, calculate the two-sample *t*-statistic in equation [16.2], making use of the sample mean, sample standard deviation, and sample size of each group.

Step 3. Set the degrees of freedom to $df = n_{BG} + n_C - 2$, and look up the $(1-\alpha) \times 100$th percentage point from the *t*-distribution in **Table 16-1** in **Appendix D**. Compare this α-level critical point against the *t*-statistic. If the *t*-statistic does not exceed the critical point, conclude there is insufficient evidence of a significant difference between the two population means. If, however, the *t*-statistic is greater than the critical point, conclude that the compliance point population mean is significantly greater than the background mean.

►EXAMPLE 16-1

Consider the quarterly sulfate data in the table below collected from one upgradient and one downgradient well during 1995-96. Use the Student's *t*-test to determine if the downgradient sulfate measurements are significantly higher than the background values at an $\alpha = 0.01$ significance level.

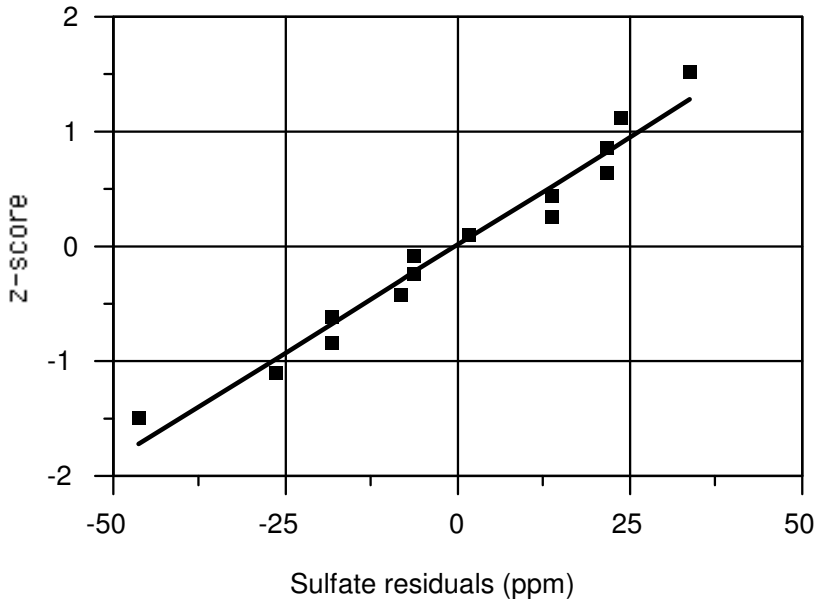
	Sulfate Concentrations (ppm)			
Quarter	Background	Downgradient	Background Residuals	Downgradient Residuals
1/95	560		23.75	
4/95	530		−6.25	
7/95	570	600	33.75	−8.33
10/95	490	590	−46.25	−18.33
1/96	510	590	−26.25	−18.33
4/96	550	630	13.75	21.67
7/96	550	610	13.75	1.67
10/96	530	630	−6.25	21.67
Mean	536.25	608.33		
SD	26.6927	18.3485		

SOLUTION

Step 1. Compute the sample mean and standard deviation in each well, as listed in the table above. Then compute the sulfate residuals by subtracting the well mean from each individual value. These differences are also listed above. Comparison of the sample variances shows no evidence that the population variances are unequal. Further, a probability plot of the combined set of residuals (**Figure 16-2**) indicates that the normal distribution appears to provide a reasonable fit to these data.

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Figure 16-2. Probability Plot of Combined Sulfate Residuals



Step 2. Compute the two-sample *t*-statistic on the raw sulfate measurements using equation [16.2]. Note that the background sample size is $n_{BG} = 8$ and the downgradient sample size is $n_C = 6$.

$$t = \left(608.33 - 536.25\right) \Bigg/ \sqrt{\left[\frac{7\left(26.6927\right)^2 + 5\left(18.3485\right)^2}{8+6-2}\right]\left(\frac{1}{8}+\frac{1}{6}\right)} = 5.66$$

Step 3. Compute the degrees of freedom as $df = 8 + 6 - 2 = 12$. Since $\alpha = .01$, the critical point for the test is the upper 99th percentile of the *t*-distribution with 12 *df*. **Table 16-1** in **Appendix D** then gives the value for $t_{cp} = 2.681$. Since the *t*-statistic is clearly larger than the critical point, conclude the downgradient sulfate population mean is significantly larger than the background population mean at the 0.01 level. ◄

16.1.2 WELCH'S T-TEST

BACKGROUND AND PURPOSE

The pooled variance Student's *t*-test in **Section 16.1.1** makes the explicit assumption that both populations have a common variance, σ^2. For many wells and monitoring constituents, local geochemical conditions can result in both different well means and variances. A contamination pattern at a compliance well can have very different variability than its background counterpart.

Welch's *t*-test was designed as a modification to the Student's *t*-test when the population variances might differ between the two groups. The Welch's *t*-test statistic is defined by the following equation:

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$$t = \left(\bar{x}_C - \bar{x}_{BG}\right) \Big/ \sqrt{\frac{s_{BG}^2}{n_{BG}} + \frac{s_C^2}{n_C}} \qquad [16.3]$$

The denominator of equation [16.3] is also called the *standard error of the difference* (SE_{diff}), similar to the pooled variance *t*-test. But it is a different weighted estimate based on the respective sample variances and sample sizes, reflecting the fact that the two population variances may not be the same.

The most difficult part of Welch's *t*-test is deriving the correct degrees of freedom. Under the assumption of a common variance, the pooled variance estimate incorporated into the usual Student's *t*-test has $df = \left(n_{BG} + n_C - 2\right)$ degrees of freedom, representing the number of independent "bits" of sample information included in the variance estimate. In Welch's *t*-test, the derivation of the degrees of freedom is more complicated, but can be approximately computed with the following equation:

$$\hat{df} = \left[\frac{s_{BG}^2}{n_{BG}} + \frac{s_C^2}{n_C}\right]^2 \Big/ \left[\frac{\left(s_{BG}^2/n_{BG}\right)^2}{n_{BG}-1} + \frac{\left(s_C^2/n_C\right)^2}{n_C-1}\right] \qquad [16.4]$$

Despite its lengthier calculations, Welch's *t*-test has several practical advantages. Best and Rayner (1987) found that among statistical tests specifically designed to compare two populations with different variances, Welch's *t*-test exhibited comparable statistical power (for $df \geq 5$) and was much easier to implement in practice than other tests they examined. Moser and Stevens (1992) compared Welch's *t*-test against the usual pooled variance *t*-test and determined that Welch's procedure was the more appropriate in almost every case. The only advantage registered by the usual Student's *t*-test in their study was in the case where the sample sizes in the two groups were unequal *and* the population variances were *known* to be essentially the same. In practice, the population variances will almost never be known in advance, so it appears reasonable to use Welch's *t*-test in the majority of cases where a two-sample *t*-test is warranted.

REQUIREMENTS AND ASSUMPTIONS

Welch's *t*-test is also a reasonably robust statistical procedure, and will usually provide accurate results even if the assumption of normality is partially violated. This robustness of the *t*-test provides some insurance against incorrect test results if the underlying populations are non-normal. But heavily skewed distributions do require normalizing transformations. Certain limitations apply when using transformed data, discussed in the following section.

Unlike the pooled variance *t*-test, Welch's procedure does not require that the population variances be equal in both groups. Other general requirements of *t*-tests, however, such as statistical independence of the sample data, lack of spatial variability when conducting an interwell test, and stationarity over time, are applicable to Welch's t-test and needs to be checked prior to running the procedure.

Because the variances of the tested populations may not be equal, an assessment of normality cannot be made under Welch's t-test by combining the residuals (as with the pooled variance t-test), unless an explicit check for equal variances is first conducted. The reason is that the combined residuals from normal populations with different variances may not test as normal, precisely because of the

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heteroscedasticity. Since this latter variance check is not required for Welch's test, it may be easier to input the sample data directly into the *multiple group test of normality* described in **Chapter 10**.

PROCEDURE

Step 1. To run the two-sample Welch's *t*-test, first compute the sample mean $(\bar{x})$, standard deviation (s), and variance (s^2) in each of the background (BG) and compliance point (C) data sets.

Step 2. Compute Welch's *t*-statistic with equation [16.3].

Step 3. Compute the approximate degrees of freedom in equation [16.4] using the sample variance and sample size from each group. Since this quantity often results in a fractional amount, round the approximate $\hat{df}$ to the nearest integer.

Step 4. Depending on the α significance level of the test, look up an appropriate critical point (t_{cp}) in **Table 16-1** in **Appendix D**. This entails finding the upper $(1-\alpha)\times 100th$ percentage point of the Student's *t*-distribution with *df* degrees of freedom.

Step 5. Compare the *t*-statistic against the critical point. If $t \le t_{cp}$, conclude there is no statistically significant difference between the background and compliance point population means. If, however, $t > t_{cp}$, conclude that the compliance point population mean is significantly greater than the background mean at the α level of significance.

►EXAMPLE 16-2

Consider the following series of monthly benzene measurements (in ppb) collected over 8 months from one upgradient and one downgradient well. What significant difference, if any, does Welch's *t*-test find between these populations at the α = .05 significance level?

	Benzene (ppb)	
Month	BG	DG
Jan	0.5	0.5
Feb	0.8	0.7
Mar	1.6	4.6
Apr	1.8	2.0
May	1.1	16.7
Jun	16.1	12.5
Jul	1.6	26.3
Aug	0.6	186.0
N	8	8
Mean	3.0	31.2
SD	5.31	63.22
Variance	28.204	3997.131

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Step 1. Compute the sample mean, standard deviation, and variance of each group as in the table above.

Step 2. Use equation [16.3] to compute Welch's *t*-statistic:

$$t = \left(31.2 - 3.0\right) \Big/ \sqrt{\frac{28.204}{8} + \frac{3997.131}{8}} = 1.257$$

Step 3. Compute the approximate degrees of freedom using equation [16.4]:

$$\hat{df} = \left[\frac{28.204}{8} + \frac{3997.131}{8}\right]^2 \Big/ \left[\frac{(28.204/8)^2}{7} + \frac{(3997.131/8)^2}{7}\right] = 7.1 \quad \approx 7$$

Step 4. Using **Table 16-1** in **Appendix D** and given $\alpha = .05$, the upper 95% critical point of the Student's *t*-distribution with 7 *df* is equal to 1.895.

Step 5. Compare the *t*-statistic against the critical point, t_{cp}. Since $t < t_{cp}$, the test on the raw concentrations provides insufficient evidence of a true difference in the population means. However, given the order of magnitude difference in the sample means and the fact that several of the downgradient measurements are substantially larger than almost all the background values, we might suspect that one or more of the *t*-test assumptions was violated, possibly invalidating the result. ◄

16.1.3 WELCH'S T-TEST AND LOGNORMAL DATA

Users should recall that if the underlying populations are *lognormal* instead of normal and Welch's *t*-test is run on the logged data, the procedure is not a comparison of arithmetic means but rather between the population *geometric means.* In the case of a lognormal distribution, the geometric means are equivalent to the population *medians*. In effect, a test of the log-means is equivalent to a test of the medians in terms of the raw concentrations. Both the population geometric mean and the lognormal median can be estimated from the logged measurements as $\exp(\bar{y})$, where $y = \log x$ represents a logged value and $\bar{y}$ is the log-mean. On the other hand, the (arithmetic) lognormal mean on the concentration scale would be estimated as $\exp\left(\bar{y} + s_y^2/2\right)$, a quantity larger than the geometric mean or median due to the presence of the term involving s_y^2, the log-variance.

Although a *t*-test conducted in the logarithmic domain is not a direct comparison of the arithmetic means, there are situations where that comparison can be *inferred* from the test results. For instance, consider using the pooled variance two-sample Student's *t*-test on logged data with a common (*i.e.*, equal) population log-variance (σ_y^2) in each group. In that case, finding a larger geometric mean or median in a compliance well population when compared to background also implies that the compliance point *arithmetic mean* is larger than the background *arithmetic mean*. However, when using Welch's *t*-test, the assumption of equal variances is not required. Because of this, on rare occasions one might find

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a larger compliance point geometric mean or median when testing the log-transformed data, even though the compliance point population arithmetic mean is *smaller* than the background arithmetic mean.

Fortunately, such a reversal can only occur in the unlikely situation that the background population log-variance is distinctly larger than the compliance point log-variance. Factors contributing to an increase in the log-mean concentration level in lognormal populations often serve, if anything, to also increase the log-variance, and almost never to *decrease* it. Consequently, *t*-test results indicating a compliance point geometric mean higher than background should very rarely imply a less-than-background compliance point log-variance. This in turn will generally ensure that the compliance point arithmetic mean is also larger than the background arithmetic mean, so that a test of the log-transformed measurements can be used to infer whether a difference exists in the population *concentration means*.

One caution in this discussion is for cases where the Welch's *t*-test is *not significant* on the log-transformed measurements. Because the log-variances (σ_y^2) are not required to be equal in the two populations when running Welch's *t*-test, yet the arithmetic lognormal mean depends on both the population log-mean (μ_y) and the log-variance through the quantity $\exp\left(\mu_y + \sigma_y^2/2\right)$, it should *not* be inferred that a non-significant comparison on the log-scale between a compliance point and background is equivalent to finding *no difference* between the lognormal arithmetic *means*. If the log-variances differ but the log-means do not, the lognormal arithmetic *means* will still be different even though the lognormal *medians* might be identical.

Therefore, if a comparison of arithmetic means is required, but the statistical populations are lognormal, care must be taken in interpreting the results of Welch's *t*-test. Two possible remedies would include: 1) only running a *t*-test on lognormal data if the log-variances can be shown to be approximately equivalent (this would allow use of the pooled variance *t*-test); and 2) using a non-parametric two-sample bootstrap procedure on the original (non-logged) measurements to compare the arithmetic means directly. Consultation with a professional statistician may be required in this second case.

►EXAMPLE 16-3

The benzene data from **Example 16-2** indicated no significant upgradient-to-downgradient difference in population means when tested on the raw measurement scale. Check to see whether the same data more closely approximate a lognormal distribution and conduct Welch's *t*-test under that assumption.

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	Benzene (ppb)		Log(Benzene) log(ppb)	
Month	BG	DG	BG	DG
Jan	0.5	0.5	−0.693	−0.693
Feb	0.8	0.7	−0.223	−0.357
Mar	1.6	4.6	0.470	1.526
Apr	1.8	2.0	0.588	0.693
May	1.1	16.7	0.095	2.815
Jun	16.1	12.5	2.779	2.526
Jul	1.6	26.3	0.470	3.270
Aug	0.6	186.0	−0.511	5.226
N	8	8	8	8
Mean	3.0	31.2	0.372	1.876
SD	5.31	63.22	1.0825	1.9847
Variance	28.204	3997.131	1.1719	3.9392

SOLUTION

Step 1. First check normality of the original measurements. To do this, compute the Shapiro-Wilk statistic (*SW*) separately for each well. *SW* = 0.505 for the background data, and *SW* = 0.544 for the downgradient well. Combining these two values using the equations in **Section 10.7**, the multiple group Shapiro-Wilk statistic becomes *G* = –6.671, which is significantly less than the 5% critical point of –1.645 from the standard normal distribution.[1] Thus, the assumption of normality was violated in **Example 16-2**.

Step 2. Compute the log-mean, log-standard deviation, and log-variance of each group, as listed above. Then compute the multiple group Shapiro-Wilk test to check for (joint) normality on the log-scale. The respective *SW* statistics now increase to 0.818 for the background data and 0.964 for the downgradient well. Combining these into an overall test, the multiple group Shapiro-Wilk statistic becomes –0.512 which now exceeds the $\alpha = 0.05$ standard normal critical point. A log transformation adequately normalizes the benzene data — suggesting that the underlying populations are lognormal in distribution — so that Welch's *t*-test can be run on the logged data.

Step 2. Using the logged measurements and equation [16.3], the *t*-statistic becomes:

$$t = \left(1.876 - 0.372\right) \Big/ \sqrt{\frac{1.1719}{8} + \frac{3.9392}{8}} = 1.88$$

[1] Note that $\alpha = 5\%$ is used in this example because the total sample size (BG and DG) is $n = 16$. Nevertheless, the test would also fail at $\alpha = 1\%$ or just about any significance level one might choose.

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Step 3. Again using the log-variances and equation [16.4], the approximate *df* works out to:

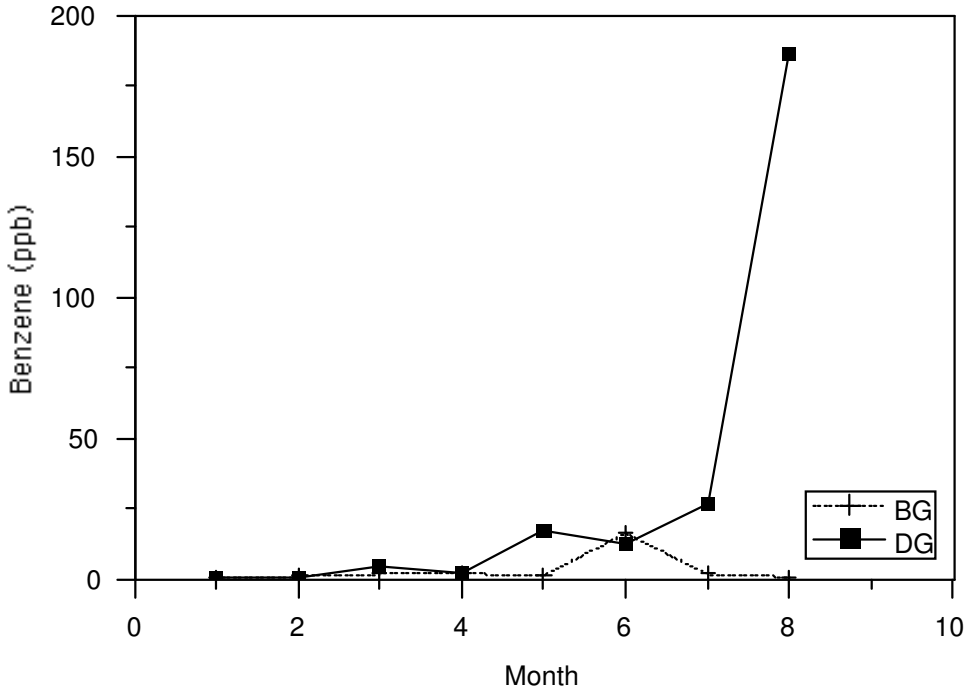
$$df = \left[\frac{1.1719}{8} + \frac{3.9392}{8}\right]^2 \Bigg/ \left[\frac{\left[1.1719/8\right]^2}{7} + \frac{\left[3.9392/8\right]^2}{7}\right] = 10.8 \approx 11$$

Note that the approximate *df* in Welch's *t*-test is somewhat less than the value that would be computed for the two-sample pooled variance Student's *t*-test. In that case, with 8 samples per data set, the *df* would have been 14 instead of 11. The reduction in degrees of freedom is due primarily to the apparent difference in variance between the two groups.

Step 4. Using **Table 16-1** in **Appendix D** and given $\alpha = .05$, the upper 95% critical point of the Student's *t*-distribution with 11 *df* is equal to 1.796.

Step 5. Comparing *t* against t_{cp}, we find that 1.88 exceeds 1.796, suggesting a statistically significant difference between the background and downgradient population log-means, at least at the 5% level of significance. This means that the downgradient geometric mean concentration — and equivalently for lognormal populations, the median concentration — is statistically greater than the same statistical measure in background. Further, since the downgradient sample log-variance is over three times the magnitude of the background log-variance, it is also probable that the downgradient arithmetic mean is larger than the background arithmetic mean.

Figure 16-3. Benzene Time Series Plot



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A note of caution in this example is that the same test run at the $\alpha = 0.01$ level would yield a *non-significant* result, since the upper 99% Student's *t* critical point in that case would be 2.718. The fact that the conclusion differs based on a small change to the significance level ought to prompt review of other *t*-test assumptions. A check of the downgradient sample measurements indicates an upward (non-stationary) trend over the sample collection period (**Figure 16-3**). This reinforces the fact that the *t*-test can be ill-suited for measuring differences between populations when trends over time cause instability in the underlying population means. It might be necessary to either perform a formal test of trend at the downgradient well or to limit the compliance data included in the evaluation only to those most representative of current conditions at the downgradient well (*e.g.*, the last four measurements). ◄

16.2 WILCOXON RANK-SUM TEST

BACKGROUND AND PURPOSE

When the underlying distribution of a data set is unknown and cannot be readily identified as normal or normalized via a transformation, a non-parametric alternative to the two-sample *t*-test is recommended. Probably the best and most practical substitute is the *Wilcoxon rank-sum test* (Lehmann, 1975; also known as the two-sample *Mann-Whitney U test*), which can be used to compare a single compliance well or data group against background. Like many non-parametric methods, the Wilcoxon rank-sum test is based on the ranks of the sample measurements rather than the actual concentrations. Some statistical information contained in the original data is lost when switching to the Wilcoxon test, since it only uses the relative magnitudes of data values.

The benefit is that the ranks can be used to conduct a statistical test even when the underlying population has an unusual form and is non-normal. The parametric *t*-test depends on the population being at least approximately normal; when this is not the case, the critical points of the *t*-test can be highly inaccurate. The Wilcoxon rank-sum test is also a statistically *efficient* procedure. That is, when compared to the *t*-test using normally-distributed data especially for larger sample sizes, it performs nearly as well as the *t*-test. Because of this fact, some authors (*e.g.*, Helsel and Hirsch, 2002) have recommended routine use of the Wilcoxon rank-sum even when the parametric *t*-test might be appropriate.

Although a reasonable strategy for larger data sets, one should be careful about automatically preferring the Wilcoxon over the *t*-test on samples as small as those often available in groundwater monitoring. For instance, a Wilcoxon rank-sum test of four samples in each of a background and compliance well and an $\alpha = 0.01$ level of significance can *never* identify a significant difference between the two populations. This is true no matter what the sample concentrations are, even if *all* four compliance measurements are larger than any of the background measurements. This Wilcoxon test will require at least five samples in at least one of the groups, or a higher level of significance (say $\alpha = 0.05$ or 0.10) is needed.

The Wilcoxon test statistic (*W*) consists of the sum of the *ranks* of the compliance well measurements. The rationale of the test is that if the ranks of the compliance data are quite large relative to the background ranks, then the hypothesis that the compliance and background values came from the

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same population ought to be rejected. Large values of the *W* statistic give evidence of possible contamination in the compliance well. Small values of *W*, on the other hand, suggest there is little difference between the background and compliance well measurements.

REQUIREMENTS AND ASSUMPTIONS

The Wilcoxon rank-sum test assumes that both populations being compared follow a common, though unknown, parent distribution under the null hypothesis (Hollander and Wolfe, 1999). Such an assumption is akin to that used in the two-sample pooled variance Student's *t*-test, although the form of the common distribution need not be normal. The Wilcoxon test assumes that both population variances are equal, unlike Welch's *t*-test. Side-by-side box plots of the two data groups can be compared (**Chapter 9**) to examine whether or not the level of variability appears to be approximately equal in both samples. Levene's test (**Chapter 11**) can also be applied as a formal test of heteroscedasticity given its relative robustness to non-normality. If there is a substantial difference in variance between the background and compliance point populations, one remedy is the *Fligner-Policello test* (Hollander and Wolfe, 1999), a more complicated rank-based procedure.

The Wilcoxon procedure as described in the Unified Guidance is generally used as an *interwell* test, meaning that it should be avoided under conditions of significant natural spatial variability. Otherwise, differences between background and compliance point wells identified by the test may be mistakenly attributed to possible contamination, instead of natural differences in geochemistry, *etc.* At small sites, the Wilcoxon procedure can be adapted for use as an *intrawell* test, involving a comparison between intrawell background and more recent measurements from the same well. However, the per-comparison false positive rate in this case should be raised to either $\alpha = 0.05$ or $\alpha = 0.10$. More generally, a significance level of at least 0.05 should be adopted whenever the sample size of either group is no greater than $n = 4$.

In addition to spatial stationarity (*i.e.*, lack of natural spatial variability), the Wilcoxon rank-sum test assumes that the tested populations are stationary *over time*, so that mean levels are not trending upward or downward. As with the *t*-test, if trends are evident in time series plots of the sample data, a formal trend test might need to be employed instead of the Wilcoxon rank-sum, or the scope of the sample may need to be limited to only include data representative of current groundwater conditions.

HANDLING TIES

When ties are present in a combined data set, adjustments need to be made to the usual Wilcoxon test statistic. Ties will occur in two situations: 1) detected measurements reported with the same numerical value and 2) non-detect measurements with a common RL. Non-detects are considered ties because the actual concentrations are unknown; presumably, every non-detect has a concentration somewhere between zero and the quantitation limit [QL]. Since these measurements cannot be ordered and ranked explicitly, the approximate remedy in the Wilcoxon rank-sum procedure is to treat such values as ties.

One may be able to partially rank the set of non-detects by making use of laboratory-supplied analytical qualifiers. As discussed in **Section 6.3**, there are probable concentration differences between measurements labeled as undetected (*i.e.*, given a "U" qualifier), non-detect (usually reported without a qualifier), or as estimated concentrations (usually labeled with "J" or "E"). One reasonable strategy is to

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group all U values as the lowest set of ties, other non-detects as a higher set of ties, and to rank all J and/or E values according to their estimated concentrations. In situations where estimated values for J and E samples are not provided, treat these measurements as the highest group of tied non-detects. Always give the highest ranks to explicitly quantified or estimated concentration measurements. In this way, a more detailed partial ranking of the data will be possible.

Tied observations in the Wilcoxon rank-sum test are handled as follows. All tied observations in a particular group should receive the same rank. This rank called the *midrank* (Lehmann, 1975) is computed as the average of the ranks that would be assigned to a group of ties if the tied values actually differed by a tiny amount and could be ranked uniquely. For example, if the first four ordered observations are all the same, the midrank given to each of these samples would be equal to (1 + 2 + 3 + 4)/4 = 2.5. If the next highest measurement is a unique value, its rank would be 5, and so on until all observations are appropriately ranked. A more detailed example is illustrated in **Figure 16-4**.

Figure 16-4. Computation of Midranks for Groups of Tied Values

Order	Concentration	Mid-Rank	
1	<1	1.5	$\Rightarrow \frac{1}{2}(1+2)$
2	<1	1.5	
3	1.2	3	
4	1.3	5	$\Rightarrow \frac{1}{3}(4+5+6)$
5	1.3	5	
6	1.3	5	
7	1.5	7.5	$\Rightarrow \frac{1}{2}(7+8)$
8	1.5	7.5	
9	1.6	9	

HANDLING NON-DETECTS

If either of the samples contains a substantial fraction of non-detect measurements (say more than 20-30%), identification of an appropriate distributional model (*e.g.*, normality) may be difficult, effectively ruling out the use of parametric tests like the *t*-test. Even when a normal or other parametric model can be fit to such left-censored data, a *t*-test cannot be run without imputing estimated values for each non-detect. Past guidance has recommended the Wilcoxon rank-sum test as an alternative to the *t*-test in the presence of non-detects, with all non-detects at a common RL being treated as tied values.

If the combined data set contains a single, common RL, that limit is smaller than any of the detected/quantified values, and the proportion of censored data is small (say no more than 10-15% of the total), it may be reasonable to treat the non-detects as a set of tied values and to apply the Wilcoxon rank-sum test adjusted for ties (described below). More generally, however, the statistical behavior of the Wilcoxon statistic depends on a full and accurate ranking of all the measurements. Groups of left-censored values cannot be ranked with certainty, even if each such measurement possesses a common

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RL. The problem is compounded in the presence of multiple RLs and/or quantified values less than the RL(s). What is the relative ranking, for instance, of the pair of measurements (<1, <5)? A higher RL does not guarantee that the second observation is larger in magnitude than the first. A similar uncertainty plagues the pair of values (4, <10). And there is no guarantee either that the pair (<2, <2) is actually tied. One may be able to partially rank the set of non-detects by making use of laboratory-supplied analytical qualifiers as described in the previous section.

Because non-detects generally prevent a complete ranking of the measurements, the Wilcoxon rank-sum test is not recommended for most censored data sets. Instead, a modified version of the Tarone-Ware test (Hollander and Wolfe, 1999) is presented in **Section 16.3**. The Tarone-Ware test is essentially a generalization of the Wilcoxon test specifically designed to accommodate censored values.

PROCEDURE

Step 1. To conduct the Wilcoxon rank-sum test, first combine the compliance and background data into a single data set. Sort the combined values from smallest to largest, and — if there are no tied values or non-detects with a common RL — rank the ordered values from 1 to N. Assume there are n compliance well samples and m background samples so that $N = m + n$. Denote the ranks of the compliance samples by C_i and the ranks of the background samples by B_i.

Step 2. If there are groups of tied values (including non-detects with a common RL), form the midranks of the combined data set by assigning to each set of ties the average of the potential ranks the tied members would have been given if they could be uniquely ranked.

Step 3. Sum the ranks of the compliance samples to get the Wilcoxon statistic W:

$$W = \Sigma_{i=1}^{n} C_i \qquad [16.5]$$

Step 4. Find the α-level critical point of the Wilcoxon test, making use of the fact that the sampling distribution of W under the null hypothesis, H_0, can be approximated by a normal curve. By standardizing the statistic W (*i.e.*, subtracting off its mean or expected value and dividing by its standard deviation), the standardized statistic or z-score, Z, can be approximated by a standard normal distribution. Then an appropriate critical point (z_{cp}) can be determined as the upper $(1-\alpha) \times 100$th percentage point of the standard normal distribution, listed in **Table 10-1** in **Appendix D**.

Step 5. To compute Z when there are no ties, first compute the expected value and standard deviation of W, given respectively by the following equations:

$$E(W) = \frac{1}{2} n(N+1) \qquad [16.6]$$

$$SD(W) = \sqrt{\frac{1}{12} mn(N+1)} \qquad [16.7]$$

Then compute the approximate z-score for the Wilcoxon rank-sum test as:

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$$Z = \frac{W - E(W) - 1/2}{SD(W)} \quad [16.8]$$

The factor of 1/2 in the numerator serves as a continuity correction since the discrete distribution of the Wilcoxon statistic W is being approximated by a continuous normal distribution.

Step 6. If there are tied values, compute the expected value of W using [16.6] and the standard deviation of W adjusted for the presence of ties with the equation:

$$SD^*(W) = \sqrt{\frac{mn(N+1)}{12}\left(1 - \Sigma_{i=1}^{g}\frac{t_i^3 - t_i}{N^3 - N}\right)} \quad [16.9]$$

where g equals the number of different groups of tied observations and t_i represents the number of tied values in the ith group.

Then compute the approximate z-score for the Wilcoxon rank-sum test as:

$$Z = \frac{W - E(W) - 1/2}{SD^*(W)} \quad (16.10)$$

Step 7. Compare the approximate z-score against the critical point, z_{cp}. If Z exceeds z_{cp}, conclude that the compliance well concentrations are significantly greater than background at the α level of significance. If not, conclude that the null hypothesis of equivalent background and compliance point distributions cannot be rejected.

►EXAMPLE 16-4

The table below contains copper concentrations (ppb) found in groundwater samples at a Western monitoring facility. Wells 1 and 2 denote background wells while Well 3 is a single downgradient well suspected of being contaminated. Calculate the Wilcoxon rank-sum test on these data at the $\alpha = .01$ level of significance.

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	Copper Concentration (ppb)		
	Background		Compliance
Month	Well 1	Well 2	Well 3
1	4.2	5.2	9.4
2	5.8	6.4	10.1
3	11.3	11.3	14.5
4	7.0	11.5	16.1
5	7.0	10.1	21.5
6	8.2	9.7	17.6

SOLUTION

Step 1. Sort the $N = 18$ observations from least to greatest. Since there are 3 pairs of tied values, compute the midranks as in the table below. Note that $m = 12$ and $n = 6$.

Step 2. Compute the Wilcoxon statistic by summing the compliance well ranks, so that $W = 84.5$.

Step 3. Using $\alpha = .01$, find the upper 99th percentage point of the standard normal distribution in **Table 10-1** of **Appendix D**. This gives a critical value of $z_{cp} = 2.326$.

	Midranks of Copper Concentrations		
	Background		Compliance
Month	Well 1	Well 2	Well 3
1	1	2	8
2	3	4	10.5
3	12.5	12.5	15
4	5.5	14	16
5	5.5	10.5	18
6	7	9	17

Step 4. Compute the expected value and adjusted standard deviation of W using equations [16.6] and (16.10), recognizing there are 3 groups of ties with $t_i = 2$ measurements in each group:

$$E(W) = \frac{1}{2} \cdot 6 \cdot 19 = 57$$

$$SD(W) = \sqrt{\frac{1}{12} \cdot 12 \cdot 6 \cdot (18+1)\left[1 - 3 \cdot \left(\frac{2^3 - 2}{18^3 - 18}\right)\right]} = \sqrt{113.647} = 10.661$$

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Then compute the standardized statistic or z-score, Z, using equation (16.10):

$$Z = \frac{84.5 - 57 - 0.5}{10.661} = 2.533$$

Step 5. Compare the observed z-score against the critical point z_{cp}. Since $Z = 2.533 > 2.326 = z_{.99}$, there is statistically significant evidence of possible contamination in the compliance well at the $\alpha = .01$ significance level. ◄

16.3 TARONE-WARE TWO-SAMPLE TEST FOR CENSORED DATA

BACKGROUND

In statistical terms, non-detect measurements represent left-censored values, in which the 'true' magnitude is known only to exist somewhere between zero and the RL, i.e., within the concentration interval [0, RL). The uncertainty introduced by non-detects impacts the applicability of other two-sample comparisons like the t-test and Wilcoxon rank-sum test. Because the Student's t-test cannot be run unless a specific magnitude is assigned to each observation, estimated or imputed values need to be assigned to the non-detects. The Wilcoxon procedure requires that every observation be ranked in relation to other values in the combined sample, even though non-detects allow at best only a partial ranking, as discussed in **Section 16.2**.

The Tarone-Ware two-sample test can be utilized to overcome these limitations for many groundwater data with substantial fractions of non-detects along with multiple RLs. Tarone and Ware (1977) actually proposed a family of tests to analyze censored data. One variant of this family is the logrank test, frequently used in survival analysis for right-censored data. Another variant is known as Gehan's generalized Wilcoxon test (Gehan, 1965). The Unified Guidance presents the variant recommended by Tarone and Ware, slightly modified to account for left-censored measurements.

The key benefit of the Tarone-Ware procedure is that it is designed to provide a valid statistical test, even with a large fraction of censored data. As a non-parametric test, it does not require normally-distributed observations. In addition, non-detects do not have to be imputed or even fully ranked. Instead, for each detected concentration (c), a simple count needs to be made within each sample of the number of detects and non-detects no greater in magnitude than c. These counts are then combined to form the Tarone-Ware statistic.

REQUIREMENTS AND ASSUMPTIONS

The null hypothesis (H_0) under the Tarone-Ware procedure assumes that the populations in background and the compliance well being tested are identical. This implies that the variances in the two distributions are the same, thus necessitating a check of equal variances. With many non-detect data sets, it can be very difficult to formally test for heteroscedasticity. Often the best remedy is to make an informal, visual check of variability using side-by-side box plots (**Chapter 9**), setting each non-detect to half its RL.

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The Tarone-Ware test will typically be used as an *interwell* test, meaning that it should be avoided under conditions of significant natural spatial variability. In addition, the tested populations should be stationary *over time*, so that mean levels are not trending upward or downward. Both assumptions can be more difficult to verify with censored data. Spatial variation can sometimes be checked with a non-parametric Kruskal-Wallis analysis of variance (**Chapter 17**). Trends with censored data can be identified with the Mann-Kendall test (**Chapter 14**).

As with other two-sample tests, if a trend is identified in one or both samples, a formal trend test may be needed instead of the Tarone-Ware, or the scope of the sample may need to be limited to only include data representative of current groundwater conditions.

Because the Tarone-Ware test presented in the Unified Guidance depends on counts of observations with magnitudes no greater than each detected concentration, and in that sense generalizes the ranking process used by the Wilcoxon rank-sum procedure, it is recommended that estimated concentrations (*i.e.*, sample measurements assigned unique magnitudes but labeled with qualifiers "J" or "E") be treated as detections for the purpose of computing the Tarone-Ware statistic. Such observations provide valuable statistical information about the relative ranking of each censored sample, even if estimated concentrations possess larger measurement uncertainty than fully quantified values.

PROCEDURE

Step 1. To compare a background data set against a compliance well using the Tarone-Ware test, first combine the two samples. Locate and sort the k distinct detected values and label these as:

$$w_{(1)} \langle w_{(2)} \langle \ldots \langle w_{(k-1)} \langle w_{(k)}$$

Note that the set of w's will not include any RLs from non-detects. Also, if two or more detects are tied, k will be less than the total number of detected measurements.

Step 2. For the combined sample, count the number of observations (described by Tarone & Ware as 'at risk') for each distinct detected concentration. That is, for $i = 1,\ldots,k$, let n_i = the number of detected values no greater than $w_{(i)}$ plus the number of non-detects with RLs no greater than $w_{(i)}$. Also let d_i = the number of detects with concentration equal to $w_{(i)}$. This value will equal 1 unless there are multiple detected values with the same reported concentration.

Step 3. For the compliance sample, count the observations 'at risk', much as in Step 2. For $i = 1$ to k, let n_{i2} = the number of detected compliance values no greater than $w_{(i)}$ plus the number of compliance point non-detects with RLs no greater than $w_{(i)}$. Also let d_{i2} = the number of compliance point detects with concentration equal to $w_{(i)}$. Note that $d_{i2} = 0$ if $w_{(i)}$ represents a detected value from background. Also compute n_{i1}, the number 'at risk' in the background sample.

Step 4. For $i = 1$ to k, compute the expected number of compliance point detections using the formula:

$$E_{i2} = d_i n_{i2} / n_i \qquad (16.11)$$

Also compute the variance of the number of compliance point detections, using the equation:

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$$V_{i2} = \frac{d_i\left(n_i - d_i\right)n_{i1}n_{i2}}{n_i^2\left(n_i - 1\right)} \tag{16.12}$$

Note in equation (16.12) that if $n_i = 1$ for the smallest detected value, the numerator of V_{i2} will necessarily equal zero (since $d_i = 1$ in that case), so compute $V_{i2} = 0$.

Step 5. Construct the Tarone-Ware statistic (*TW*) with the equation:

$$TW = \frac{\sum_{i=1}^{k}\sqrt{n_i}\left(d_{i2} - E_{i2}\right)}{\sqrt{\sum_{i=1}^{k} n_i V_{i2}}} \tag{16.13}$$

Step 6. Find the α-level critical point of the Tarone-Ware test, making use of the fact that the sampling distribution of *TW* under the null hypothesis, H_0, is designed to approximately follow a standard normal distribution. An appropriate critical point (z_{cp}) can be determined as the upper $(1-\alpha) \times 100$th percentage point of the standard normal distribution, listed in **Table 10-1** of **Appendix D**.

Step 7. Compare *TW* against the critical point, z_{cp}. If *TW* exceeds z_{cp}, conclude that the compliance well concentrations are significantly greater than background at the α level of significance. If not, conclude that the null hypothesis of equivalent background and compliance point distributions cannot be rejected.

►EXAMPLE 16-5

A heavily industrial site has been historically contaminated with tetrachloroethylene [PCE]. Using the Tarone-Ware procedure at an α = .05 significance level, test the following PCE measurements collected from one background and one compliance well.

PCE (ppb)	
Background	Compliance
<4	6.4
1.5	10.9
<2	7
8.7	14.3
5.1	1.9
<5	10.0
	6.8
	<5

SOLUTION

Step 1. Combine the background and compliance point samples. List and sort the distinct detected values (as in the table below), giving $k = 10$. Note that the 4 non-detects comprise 28% of the combined data.

Step 2. Compute the number of measurements (n_i) in the combined sample 'at risk' for each distinct detected value ($w_{(i)}$), indexed from $i = 1,\ldots, 10$, by adding the number of detects and non-

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detects no greater than $w_{(i)}$, as listed in column 6 of the table below. Also list in column 3 the number of detected values (d_i) exactly equal to $w_{(i)}$.

Step 3. For the compliance point sample, compute the number (n_{i2}) 'at risk' for each distinct detected value, as listed in column 5 below. Also compute the number (n_{i1}) 'at risk' for the background sample (column 4) and the number of compliance point measurements exactly equal to $w_{(i)}$ (column 2).

Step 4. Use equations (16.11) and (16.12) to compute the expected value (E_{i2}) and variance (V_{i2}) of the number of compliance point detections at each $w_{(i)}$ (columns 7 and 8 below).

$w_{(i)}$	d_{i2}	d_i	n_{i1}	n_{i2}	n_i	E_{i2}	V_{i2}
1.5	0	1	1	0	1	0	0
1.9	1	1	1	1	2	0.5	0.25
5.1	0	1	5	2	7	0.2857	0.2041
6.4	1	1	5	3	8	0.375	0.2344
6.8	1	1	5	4	9	0.4444	0.2469
7.0	1	1	5	5	10	0.5	0.25
8.7	0	1	6	5	11	0.4545	0.2479
10.0	1	1	6	6	12	0.5	0.25
10.9	1	1	6	7	13	0.5385	0.2485
14.3	1	1	6	8	14	0.5714	0.2449

Step 5. Calculate the Tarone-Ware statistic (TW) using equation (16.13):

$$TW = \frac{\sqrt{1}\cdot(0-0)+\sqrt{2}\cdot(1-0.5)+\sqrt{7}\cdot(0-.2857)+\ldots+\sqrt{14}\cdot(1-.5714)}{\sqrt{1\cdot 0+2\cdot .25+7\cdot .2041+\ldots+14\cdot .2449}} = 1.85$$

Step 6. Determine the 0.05 level critical point from **Table 10-1** in **Appendix D** as the upper 95th percentage point from a standard normal distribution. This gives $z_{cp} = 1.645$.

Step 7. Compare the Tarone-Ware statistic against the critical point. Since $TW = 1.85 > 1.645 = z_{cp}$, conclude that the PCE concentrations are significantly greater at the compliance well than in background at the 5% significance level. ◄

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CHAPTER 17. ANOVA, TOLERANCE LIMITS, AND TREND TESTS

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This chapter describes two statistical procedures — analysis of variance [ANOVA] and tolerance limits — explicitly allowed within §264.97(h) and §258.53(g) for use in groundwater monitoring. The Unified Guidance does not generally recommend either technique for formally making regulatory decisions about compliance wells or regulated units, instead focusing on prediction limits, control charts, and confidence intervals. But both ANOVA and tolerance tests are standard statistical procedures that can be adapted for a variety of uses. ANOVA is particularly helpful in both identifying on-site spatial variation and in sometimes aiding the computation of more effective and statistically powerful intrawell prediction limits (see **Chapters 6** and **13** for further discussion).

This chapter also presents selected trend tests as an alternative statistical method that can be quite useful in groundwater detection monitoring, particularly when groundwater populations are not *stationary* over time. Although trend tests are not explicitly listed within the RCRA regulations, they possess advantages in certain situations and can meet the performance requirements of §264.97(i) and §258.53(h). They can also be helpful during diagnostic evaluation and establishment of historical background (**Chapter 5**) and in verifying key statistical assumptions (**Chapter 14**).

17.1 ANALYSIS OF VARIANCE [ANOVA]

17.1.1 ONE-WAY PARAMETRIC F-TEST

BACKGROUND AND PURPOSE

The parametric one-way ANOVA is a statistical procedure to determine whether there are statistically significant differences in mean concentrations among a set of wells. In groundwater applications, the question of interest is whether there is potential contamination at one or more compliance wells when compared to background. By finding a significant difference in means and specifically *higher* average concentrations at one or more compliance wells, ANOVA results can sometimes be used to identify unacceptably high contaminant levels in the absence of natural spatial variability.

Like the two-sample *t*-test, the one-way ANOVA is a comparison of population means. However, the one-way parametric ANOVA is a comparison of *several* populations, not just two: one set of

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background data versus at least two compliance wells. The *F*-statistic that forms the heart of the ANOVA procedure is actually an extension of the *t*-statistic; an *F*-statistic formed in a comparison of only two datasets reduces to the square of the usual pooled variance Student's *t*-statistic. Like the *t*-statistic, the *F*-statistic is a ratio of two quantities. The numerator is a measure of the average squared difference observed between the pairs of sample means, while the denominator represents the average variability found in each well group.

Under the null hypothesis that all the wells or groups have the same population mean, the *F*-statistic follows the *F*-distribution. Unlike the *t*-distribution with a single degrees of freedom *df*, there are two *df* quantities associated with *F*. One is for the numerator and the other for the denominator. When critical points are needed from the *F*-distribution, one must specify both degrees of freedom values.

Computation of the *F*-statistic is only the first step of the full ANOVA procedure, when used as a formal compliance test. It can only determine whether *any* significant mean difference exists between the possible pairs of wells or data groups, and not whether or what specific compliance wells differ from background. To accomplish this latter task when a significant *F*-test is registered, individual tests between each compliance well and background needs to be conducted, known as individual *post-hoc comparisons* or *contrasts*. These individual tests are a specially constructed series of *t*-tests, with critical points chosen to limit the *test-wise* or *experiment-wise* false positive rate.

REQUIREMENTS AND ASSUMPTIONS

The parametric ANOVA assumes that the data groups are normally-distributed with constant variance. This means that the group *residuals* should be tested for normality (**Chapter 10**) and that the groups have to be tested for equality of variance, perhaps with Levene's test (**Chapter 11**). Since the *F*-test used in the one-way ANOVA is reasonably robust to small departures from normality, the first of these assumptions turns out to be less critical than the second. Research (Milliken and Johnson, 1984) has shown that the statistical power of the *F*-test is strongly affected by inequality in the population variances. A noticeable drop in power is seen whenever the ratio of the largest to smallest group variance is at least 4. A severe drop in power is found whenever the ratio of the largest to smallest group variance is at least a factor of 10. These ratios imply that the *F*-test will lose some statistical power if any of the group population standard deviations is at least twice the size of any other group's standard deviation, and that the power will be greatly curtailed if any standard deviation is at least 3 times as large as any other group's.

If the hypothesis of equal variances is rejected or if the group residuals are found to violate an assumption of normality (especially at the .01 significance level or less), one should consider a transformation of the data, followed by testing of the ANOVA assumptions on the transformed scale. If the residuals from the transformed data still do not satisfy normality or if there are too many non-detect measurements to adequately test the assumptions, a non-parametric ANOVA (called the *Kruskal-Wallis test*) using the ranks of the observations is recommended instead (see **Section 17.1.2**).

Since ANOVA is inherently an interwell statistical method, a critical point in using ANOVA for compliance testing is that the well field should exhibit *minimal spatial variability*. Interwell tests also require the groundwater well populations to be spatially *stationary*, so that absent a release the population well means are stable over time. Because spatial variation is frequently observed in many

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groundwater constituents, especially for common inorganic constituents and some metals, ANOVA may not be usable as compliance testing tool. Yet it can be utilized on the same data sets to help *identify* the presence of spatial variability. In this capacity, the same procedure and formulas are utilized as described below (with the exception of the post-hoc contrasts, which are unnecessary for assessing spatial variation). The results are then employed to guide the appropriate choice of a compliance test (*e.g.*, intrawell or interwell prediction limits).

For formal ANOVA testing under §264.97(i) and §258.53(h), the *experiment-wise* or *test-wise* false positive rate (α) needs to be at least 5% during any statistical evaluation for each constituent tested. Furthermore, the individual *post-hoc contrasts* used to test single compliance wells against background need to be run at a significance level of at least $\alpha^* = 1\%$ per well. Combined, these regulatory constraints imply that if there are more than five post-hoc contrasts that need to be tested (*i.e.*, more than 5 compliance wells are included in the ANOVA test), the overall, maximal false positive rate of the procedure will tend to be greater, and perhaps substantially so, than 5%. Also, since $\alpha = 5\%$ is the minimum significance level per monitoring constituent, running multiple ANOVA procedures to accommodate a list of constituents will lead to a minimum *site-wide false positive rate* [SWFPR] greater than the Unified Guidance recommended target of 10% per statistical evaluation.

In addition, if a contaminated compliance well exists but too many uncontaminated wells are also included in the same ANOVA, the *F*-statistic may result in a non-significant outcome. Performing ANOVA with more than 10 to 15 well groups can "swamp" the procedure, causing it to lose substantial power. It therefore will be necessary to consider one of the retesting strategies described in **Chapters 18** and **20** as an alternative to ANOVA in the event that either the expected false positive rate is too large, or if more than a small number of wells need to be tested.

Another drawback to the one-way ANOVA is that the *F*-test accounts for *all possible paired comparisons* among the well groups. In some cases, the *F*-statistic may be *significant* even though all of the contrasts between compliance wells and background are *non-significant*. This does not mean that the *F*-test has necessarily registered a false positive. Rather, it may be that two of the compliance wells significantly differ from each other, but neither differs from background. This could happen, for instance, if a compliance well has a lower mean concentration than background while other compliance wells have near background means. The *F*-test looks for all possible differences between pairs of well groups, not just those comparisons against background.

In order to run a valid one-way *F*-test, a minimum number of observations are needed. Denoting the number of data groups by p, at least $p > 2$ groups must be compared (*e.g.*, two or more compliance wells versus background). Each group should have at least three to four statistically independent observations and the total sample size, N, should be large enough so that $N–p > 5$. As long as $p \geq 3$ and there are at least 3 observations per well, this last requirement will always be met. But the statistical power of an ANOVA to identify differences in population means tends to be minimal unless there are at least 4 or more observations per data group. It is also helpful to have at least 8 measurements in background for the test.

Similarly to the two-sample *t*-test, it may be very difficult to verify that the measurements are statistically independent with only a handful of observations per well. One should additionally ensure that the samples are collected far enough apart in time to avoid significant *autocorrelation* (see **Chapter 14** for further discussion). A periodic check of statistical independence in each may be possible after a

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few testing periods, when enough data has been collected to enable a statistical assessment of this assumption.

PROCEDURE

Step 1. Combine all the relevant background data collected from multiple wells into one group. These wells should have insignificant mean differences under prior ANOVA testing. If the regulated unit has (p–1) compliance wells, there will then be a total of p data groups. Because there may be different numbers of observations per well, denote the sample size of the ith group by n_i and the total number of data points across all groups by N.

Step 2. Denote the observations in the ith well group by x_{ij} for $i = 1$ to p and $j = 1$ to n_i. The first subscript designates the well, while the second denotes the jth value in the ith well. Then compute the mean of each well group along with the overall (grand) mean of the combined dataset using the following formulas:

$$\bar{x}_{i\bullet} = \frac{1}{n_i}\sum_{j=1}^{n_i} x_{ij} \qquad [17.1]$$

$$\bar{x}_{\bullet\bullet} = \frac{1}{N}\sum_{i=1}^{p}\sum_{j=1}^{n_i} x_{ij} \qquad [17.2]$$

Step 3. Compute the sum of squares of differences between the well group means and the grand mean, denoted SS_{wells}:

$$SS_{wells} = \sum_{i=1}^{p} n_i\left(\bar{x}_{i\bullet} - \bar{x}_{\bullet\bullet}\right)^2 = \sum_{i=1}^{p} n_i\bar{x}_{i\bullet}^2 - N\bar{x}_{\bullet\bullet}^2 \qquad [17.3]$$

The formula on the far right is usually the most convenient for calculation. This sum of squares has (p–1) degrees of freedom associated with it and is a measure of the variability *between* wells. It constitutes the numerator of the F-statistic.

Step 4. Compute the corrected total sum of squares, denoted by SS_{total}:

$$SS_{total} = \sum_{i=1}^{p}\sum_{j=1}^{n_i}\left(x_{ij} - \bar{x}_{\bullet\bullet}\right)^2 = \sum_{i=1}^{p}\sum_{j=1}^{n_i} x_{ij}^2 - N\bar{x}_{\bullet\bullet}^2 \qquad [17.4]$$

The far right equation is convenient for calculation. This sum of squares has (N–1) degrees of freedom associated with it and is a measure of the variability in the entire dataset. In fact, if SS_{total} is divided by (N–1), one gets the overall sample variance.

Step 5. Compute the sum of squares of differences between the observations and the well group means. This is known as the within-wells component of the total sum of squares or, equivalently, as the sum of squares due to error. It is easiest to obtain by subtraction using the far right side of equation [17.5] and is denoted SS_{error}:

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$$SS_{error} = \sum_{i=1}^{p}\sum_{j=1}^{n_i}\left(x_{ij} - \bar{x}_{i\bullet}\right)^2 = SS_{total} - SS_{wells} \quad [17.5]$$

SS_{error} is associated with (N–p) degrees of freedom and is a measure of the variability *within* well groups. This quantity goes into the denominator of the F-statistic.

Step 6. Compute the mean sum of squares for both the between-wells and within-wells components of the total sum of squares, denoted by MS_{wells} and MS_{error}. These quantities are simply obtained by dividing each sum of squares by its corresponding degrees of freedom:

$$MS_{wells} = SS_{wells} \Big/ \left(p - 1\right) \quad [17.6]$$

$$MS_{error} = SS_{error} \Big/ \left(N - p\right) \quad [17.7]$$

Step 7. Compute the F-statistic by forming the ratio between the mean sum of squares for wells and the mean sum of squares due to error, as in **Figure 17-1**. This layout is known as a one-way parametric ANOVA table and illustrates the sum of squares contribution to the total variability, along with the corresponding degrees of freedom, the mean squares components, and the final F-statistic calculated as $F = MS_{wells}/MS_{error}$. Note that the first two rows of the one-way table sum to the last row.

Figure 17-1. One-Way Parametric ANOVA Table

Source of Variation	Sums of Squares	Degrees of Freedom	Mean Squares	F-Statistic
Between Wells	SS_{wells}	p–1	$MS_{wells} = SS_{wells}/(p-1)$	$F = MS_{wells}/MS_{error}$
Error (within wells)	SS_{error}	N–p	$MS_{error} = SS_{error}/(N-p)$	
Total	SS_{total}	N–1		

Step 8. To test the hypothesis of equal means for all p wells, compare the F-statistic in **Figure 17-1** to the α-level critical point found from the F-distribution with (p–1) and (N–p) degrees of freedom in **Table 17-1** of **Appendix D**. α is usually set at 5%, so that the needed comparison value equals the upper 95th percentage point of the F-distribution. The numerator (p-1) and denominator (N-p) degrees of freedom for the F-statistic are obtained from the above table. If the observed F-statistic exceeds the critical point ($F_{.95,\ p-1,\ N-p}$), reject the hypothesis of equal well group population means. Otherwise, conclude that there is insufficient evidence of a significant difference between the concentrations at the p well groups and thus no evidence of potential contamination in any of the compliance wells.

Step 9. In the case of a significant F-statistic that exceeds the critical point in Step 8, determine which compliance wells have elevated concentrations compared to background. This is done by comparing each compliance well individually against the background measurements. Tests to assess concentration differences between a pair of well groups are called *contrasts* in a multiple comparisons ANOVA framework. Since the contrasts are a series of individual

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statistical tests, each run at a fixed significance level α^*, the Type I error accumulates across the tests as the number of contrasts increases.

To keep the overall false positive rate close to the targeted rate of 5%, the individual contrasts should be set up as follows: Given (p–1) separate background-compliance contrasts, if (p–1) ≤ 5, run each contrast at a significance level equal to $\alpha^* = .05/(p-1)$. However, if (p–1) > 5, run each contrast at a significance level equal to $\alpha^* = .01$. Note that when there are more than 5 compliance wells, this last provision will tend to raise the overall false positive rate above 5%.

Step 10. Denote the background data set as the first well group, so that the number of background samples is equal to n_b. Then for each of the remaining (p–1) well groups, compute the standard error of the difference between each compliance well and background:

$$SE_i = \sqrt{MS_{error} \cdot \left(\frac{1}{n_b} + \frac{1}{n_i}\right)} \qquad [17.8]$$

Note that MS_{error} is taken from the one-way ANOVA table in **Figure 17-1**. The standard error here is an extension of the standard error of the difference involving the pooled variance in the Student's t-test of **Chapter 16**.

Step 11. Treat the background data as the first well group with the average background concentration equal to $\bar{x}_b$. Compute the Bonferroni t-statistic for each of the (p–1) compliance wells from i = 2 to p, dividing the standard error in Step 10 into the difference between the average concentration at the compliance well and the background average, as shown below:

$$t_i = \left(\bar{x}_i - \bar{x}_b\right) / SE_i \qquad [17.9]$$

Step 12. The Bonferroni t-statistic in equation [17.9] is a type of t-test. Since the estimate of variability used in equation [17.8] has (N–p) degrees of freedom, the critical point can be determined from the Student's t-distribution in **Table 16-1** of **Appendix D**. Let the Bonferroni critical point (t_{cp}) be equal to the upper $(1-\alpha^*) \times 100$th percentage point of the t-distribution with (N–p) degrees of freedom.

Step 13. If any of the Bonferroni t-statistics (t_i) exceed the critical point t_{cp}, conclude that these compliance wells have population mean concentrations significantly greater than background and thus exhibit evidence of possible contamination. Compliance wells for which the Bonferroni t-statistic does not exceed t_{cp} should be regarded as similar to background in mean concentration level.

►EXAMPLE 17-1

Lead concentrations in ground water at two background and four compliance wells were tested for normality and homoscedasticity. These data were found to be best fit by a lognormal distribution with approximately equal variances. The two background wells also indicated insignificant log mean differences. The natural logarithms of these lead values are shown in the table below. Use the one-way parametric ANOVA to determine whether there are any significant concentration increases over background in any of the compliance wells.

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Log(Lead) log(ppb)						
	Background		Compliance			
Date	Well 1	Well 2	Well 3	Well 4	Well 5	Well 6
Jan 1995	4.06	3.83	4.61	3.53	4.11	4.42
Apr 1995	3.99	4.34	5.14	4.54	4.29	5.21
Jul 1995	3.40	3.47	3.67	4.26	5.50	5.29
Oct 1995	3.83	4.22	3.97	4.42	5.31	5.08
Well Mean	3.82	3.96	4.35	4.19	4.80	5.00
Well SD	0.296	0.395	0.658	0.453	0.704	0.143
	$\bar{x}_{BG}$ = 3.89	s_{BG} = 0.333	Grand Mean = 4.35			

SOLUTION

Step 1. Combine the two background wells into one group, so that the background average becomes 3.89 log(ppb). Then $n_b = 8$, while $n_i = 4$ for each of the other four well groups. Note that the total sample size is $N = 24$ and $p = 5$.

Step 2. Compute the (overall) grand mean and the sample mean concentrations in each of the well groups using equations [17.1] and [17.2]. These values are listed (along with each group's standard deviation) in the above table.

Step 3. Compute the sum of squares due to well-to-well differences using equation [17.3]:

$$SS_{wells} = \left[8 \cdot (3.89)^2 + 4 \cdot (4.35)^2 + \ldots + 4 \cdot (5.00)^2\right] - 24 \cdot (4.35)^2 = 4.289$$

This quantity has (5–1) = 4 degrees of freedom.

Step 4. Compute the corrected total sum of squares using equation [17.4] with (N–1) = 23 *df*:

$$SS_{total} = \left[(4.06)^2 + \ldots + (5.08)^2\right] - 24 \cdot (4.35)^2 = 8.934$$

Step 5. Obtain the within-well or error sum of squares by subtraction using equation [17.5]:

$$SS_{error} = 8.934 - 4.289 = 4.646$$

This quantity has (N–p) = 24–5 = 19 degrees of freedom.

Step 6. Compute the mean sums of squares using equations [17.6] and [17.7]:

$$MS_{wells} = 4.289/4 = 1.072$$

$$MS_{error} = 4.646/19 = 0.245$$

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Step 7. Construct the F-statistic and the one-way ANOVA table, using **Figure 17-1** in **Appendix D** as a guide:

Source of Variation	Sums of Squares	Degrees of Freedom	Mean Squares	*F*-Statistic
Between Wells	4.289	4	1.072	F = 1.072/0.245
Error (within wells)	4.646	19	0.245	= 4.39
Total	8.934	23		

Step 8. Compare the observed *F*-statistic of 4.39 against the critical point taken as the upper 95th percentage point from the *F*-distribution with 4 and 19 degrees of freedom. Using **Table 17-1**, this gives a value of $F_{.95,4,19}$ = 2.90. Since the *F*-statistic exceeds the critical point, the hypothesis of equal well means is rejected, and post-hoc Bonferroni *t*-test comparisons should be conducted.

Step 9. Determine the number of individual contrasts needed. With four compliance wells, (p–1) = 4 comparisons need to be made against background. Therefore, run each Bonferroni *t*-test at the α^* = .05/4 = .0125 level of significance.

Step 10. Compute the standard error of the difference between each compliance well average and the background mean using equation [17.8]. Since the number of observations is the same in each compliance well, the standard error in all four cases will be equal to:

$$SE_i = \sqrt{0.245\left(\frac{1}{8}+\frac{1}{4}\right)} = 0.303$$

Step 11. Compute the Bonferroni *t*-statistic for each compliance well using equation [17.9]:

$$\text{Well 3:}\quad t_2 = \left(4.35 - 3.89\right)\Big/0.303 = 1.52$$
$$\text{Well 4:}\quad t_3 = \left(4.19 - 3.89\right)\Big/0.303 = 0.99$$
$$\text{Well 5:}\quad t_4 = \left(4.80 - 3.89\right)\Big/0.303 = 3.00$$
$$\text{Well 6:}\quad t_5 = \left(5.00 - 3.89\right)\Big/0.303 = 3.66$$

Note that because Wells 1 and 2 jointly constitute background, the subscripts above correspond to the well groups and not the actual well numbers. Thus, subscript 2 in the Bonferroni *t*-statistic corresponds to Well 3, subscript 3 corresponds to Well 4, and so forth.

Step 12. Look up the critical point from the *t*-distribution in **Table 16-1** of **Appendix D** using a significance level of α^* = .0125 and (N–p) = 19 *df*. This gives t_{cp} = 2.433.

Step 13. Compare each Bonferroni *t*-statistic from Step 11 against the critical point from Step 12. Because the *t*-statistics at compliance wells 5 and 6 both exceed 2.433, while those at wells 3 and 4 do not, conclude that the population averages in compliance wells 5 and 6 are significantly higher than background. ◄

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17.1.2 KRUSKAL-WALLIS TEST

BACKGROUND AND PURPOSE

The parametric one-way ANOVA makes a key assumption that the data residuals are normally-distributed. If this assumption is inappropriate or cannot be tested because of a large fraction of non-detects, a non-parametric ANOVA can be conducted using the *ranks* of the observations rather than the original observations. In **Chapter 16**, the Wilcoxon rank-sum test is presented as a non-parametric alternative to the Student's *t*-test when comparing two groups. The Kruskal-Wallis test is offered as a non-parametric alternative to the one-way *F*-test when several groups need to be simultaneously compared, for instance when assessing patterns of spatial variability. Instead of a test of means, the Kruskal-Wallis tests differences among average population ranks equivalent to the *medians*.

The Kruskal-Wallis test statistic, *H*, does not have the intuitive form of the Student's *t*-test. Under the null hypothesis that all the sample measurements come from identical parent populations, the Kruskal-Wallis statistic follows the well-known *chi-square* statistical distribution. Critical points for the Kruskal-Wallis test can be found as upper percentage points of the chi-square ($\chi^2_{1-\alpha,df}$) distribution in **Table 17-2** of **Appendix D**.

If *H* indicates a significant difference between the populations, individual post-hoc comparisons between each compliance well and background need to be conducted if the Kruskal-Wallis is being used for formal compliance testing. Post-hoc contrasts are not generally necessary for identifying spatial variability. Rather than Bonferroni *t*-statistics, contrasts are based on the data ranks and approximately follow a standard normal distribution. The critical points for these contrasts can be obtained from the standard normal distribution in **Table 10-1** of **Appendix D**.

REQUIREMENTS AND ASSUMPTIONS

While the Kruskal-Wallis test does not require the underlying populations to be normally-distributed, statistical independence of the data is still assumed. Under the null hypothesis of no difference among the groups, the observations are assumed to arise from identical distributions with equal population variances (Hollander and Wolfe, 1999). However, the form of the distribution need not be specified.

A non-parametric ANOVA can be used in any situation that the parametric ANOVA can be used. The minimum data requirements are similar: the sample size for each group in the Kruskal-Wallis procedure should generally be at least four to five observations per group. Despite this similarity, it is often true that non-parametric tests require larger sample sizes than their parametric test counterparts to ensure a similar level of statistical power or *efficiency*. Non-parametric tests make fewer assumptions concerning the underlying data distribution and so more observations are often needed to make the same judgment that would be rendered by a parametric test. However, the greater efficiency of parametric tests is only achieved when the parent population follows certain known statistical distributions. When the distribution is unknown, non-parametric tests may have much greater power than their parametric counterparts.

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Even when a known statistical distribution is considered, rank-based non-parametric tests like the Wilcoxon rank-sum and Kruskal-Wallis often perform reasonably well compared to the t-test and ANOVA. The relative *efficiency* of two procedures is defined as the ratio of the sample sizes needed by each to achieve a certain level of power against a specified alternative hypothesis. As sample sizes get larger, the efficiency of the Kruskal-Wallis test relative to the parametric ANOVA approaches a limit that depends on the underlying distribution of the data, but is always at least 86 percent. This means roughly that, in the worst case, if 86 measurements are available for a parametric ANOVA, only 100 sample values are needed to have an equivalently powerful Kruskal-Wallis test. In many cases, the increase in sample size necessary to match the power of a parametric ANOVA is much smaller or not needed at all. The efficiency of the Kruskal-Wallis test is 95% if the underlying data are really normal, and can be much larger than 100% in other cases (*e.g.*, it is 150% if the data residuals follow a distribution called the *double exponential*). When the efficiency exceeds 100%, the Kruskal-Wallis actually needs fewer observations than the parametric ANOVA to achieve a certain power.

These results imply that the Kruskal-Wallis test is reasonably powerful for detecting concentration differences despite the fact that the original data have been replaced by their ranks. The test can be used with fair success even when the data are normally-distributed and the Kruskal-Wallis is not needed. When the data are not normal or a normalizing transformation cannot be found, the Kruskal-Wallis procedure tends to be more powerful for detecting differences than the usual parametric approach.

ADJUSTING FOR TIED OBSERVATIONS

The Kruskal-Wallis procedure will frequently be used when the sample data contain a significant fraction of non-detects. However, the presence of non-detects prevents a unique and complete ranking of the concentration values since the exact values of non-detects are unknown.

To address this problem, two steps are necessary. Since they cannot be uniquely ranked, all non-detects are to be treated statistically as 'tied' values. This is an imperfect remedy, since non-detects represent left-censored values and are not necessarily tied. Unfortunately, there is no straightforward, easily implemented alternative to the Kruskal-Wallis for comparing three or more groups containing left-censored observations, unlike the Tarone-Ware alternative to the Wilcoxon rank-sum test discussed in **Chapter 16**. So in the presence of ties (*e.g.*, non-detects or quantified concentrations rounded to the same value), all tied observations should receive the same midrank (discussed in **Section 16.3**). This rank is computed as the *average* of the ranks that would be given to each group of ties if the tied values actually differed by a tiny amount and could be ranked.

To account for multiple reporting limits, all non-detects should be treated as if censored at the highest reporting limit [RL] in the overall sample. Thus, a non-detect reported as <5 would be treated as 'tied' with a non-detect reported as <1, due to the impossibility of knowing which value is actually larger. The only exception to this strategy is when laboratory qualifiers can be used to rank some non-detects as probably greater in magnitude than others. A reasonable strategy discussed in **Section 16.3** is to group all "U" values as the lowest set of ties, other non-detects as a higher set of ties, and to rank all "J" and/or "E" values according to their estimated concentrations. In situations where estimated values for J and E samples are not provided, treat these measurements as the highest group of tied non-detects. Always give the highest ranks to explicitly quantified or estimated concentration measurements.

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The second step for handling ties is to compute the Kruskal-Wallis statistic as described below, using for each tied value its corresponding midrank. Then an adjustment to the Kruskal-Wallis statistic needs to be made to account for the presence of ties. This adjustment requires computation of the formula:

$$H^* = H \Bigg/ \left[1 - \left(\sum_{i=1}^{g} \frac{t_i^3 - t_i}{N^3 - N} \right) \right] \qquad [17.10]$$

where g equals the number of distinct groups of tied observations, N is the total sample size across all groups, and t_i is the number of observations in the ith tied group. Unless there are a substantial number of ties in the overall dataset, the adjustment in equation [17.10] will tend to be small. Still, it is important to properly account for the presence of tied values.

PROCEDURE

Step 1. To run the Kruskal-Wallis test, denote the total sample size across all well groups by N. Temporarily combine all the data into one group and rank the observations from smallest to largest. Treat all non-detects as tied at the lowest possible concentration value, unless using lab qualifiers to distinguish between 'undetected' and other non-detects. Combine all background wells into a single group where appropriate. Denote this set of background data as group 1. Then let R_{ij} denote the jth rank from the ith well group, and let k equal the total number of groups (*i.e.*, one group of background values and (k–1) groups of compliance wells).

Step 2. Compute the sum of the ranks and the average rank in each well group, letting n_i equal the sample size in the ith group and using the following formulas:

$$R_{i\bullet} = \sum_{j=1}^{n_i} R_{ij} \qquad [17.11]$$

$$\bar{R}_{i\bullet} = \frac{1}{n_i} R_{i\bullet} \qquad [17.12]$$

Step 3. Calculate the Kruskal-Wallis test statistic H and the adjustment for ties, if necessary, using equation [17.10], where H is given by:

$$H = \left[\frac{12}{N(N+1)} \sum_{i=1}^{k} \frac{R_{i\bullet}}{n_i} \right] - 3(N+1) \qquad [17.13]$$

Step 4. Given the level of significance (α), determine the Kruskal-Wallis critical point (χ^2_{cp}) as the upper (1–α) × 100th percentage point from the chi-square distribution with (k–1) degrees of freedom (**Table 17-2** in **Appendix D**). Usually α is set equal to 0.05, so that the upper 95th percentage point of the chi-square distribution is needed.

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Step 5. Compare the Kruskal-Wallis test statistic, H, against the critical point χ^2_{cp}. If H is no greater than the critical point, conclude there is insufficient evidence of significant differences between any of the well group populations. If $H > \chi^2_{cp}$, however, conclude there is a significant difference between at least one pair of the well groups. Post-hoc comparisons are then necessary to determine whether any of the compliance wells significantly exceeds background (note that post-hoc comparisons are not necessary if using the Kruskal-Wallis test to merely identify spatial variability).

Step 6. In the case of a significant H-statistic that exceeds the critical point in Step 5, determine which compliance wells have elevated concentrations compared to background. This is done by comparing each compliance well against background, using a set of *contrasts* (as described for the parametric one-way ANOVA in **Section 17.1.1**).

To keep the test-wise or experiment-wise false positive rate close to the targeted (*i.e.*, nominal) rate of 5%, the individual contrasts should be set up as follows: Given (k–1) separate background-compliance contrasts, if (k–1) ≤ 5, run each contrast at a significance level equal to $\alpha^* = .05/(k–1)$. However, if (k–1) > 5, run each contrast at a significance level equal to $\alpha^* = .01$. Note that when there are more than 5 downgradient wells, this last provision will tend to raise the overall false positive rate above 5%.

Step 7. Since the background data is the first well group, the number of background observations is equal to n_1. For each of the remaining (k–1) well groups, compute the approximate rank-based standard error of the difference between each compliance well and background using equation [17.14]:

$$SE_i = \sqrt{\frac{N(N+1)}{12}\left(\frac{1}{n_1}+\frac{1}{n_i}\right)} \qquad [17.14]$$

Step 8. Let the average background rank be identified as $\overline{R}_b$. Compute the post-hoc Z-statistic for each of the (k–1) compliance wells for i = 2 to k, dividing the standard error in step 7 into the difference between the average rank at the compliance well and the background rank average, as shown below:

$$Z_i = \left(\overline{R}_i - \overline{R}_b\right) / SE_i \qquad [17.15]$$

Step 9. The Z-statistic in equation [17.15] has an approximate standard normal distribution under the null hypothesis that the ith compliance well is identical in distribution to background. The critical point (z_{cp}) can be found as the upper (1–α) × 100th percentage point of the normal distribution in **Table 10-1** of **Appendix D**.

Step 10. Compare the post-hoc Z-statistics for each of the (k–1) compliance wells against the critical point (z_{cp}). Any Z-statistic that exceeds the critical point provides significant evidence of an elevation over background in that compliance well at the α level of significance.

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►EXAMPLE 17-2

Use the non-parametric Kruskal-Wallis test on the following data to determine whether there is evidence of possible toluene contamination at a significance level of $\alpha = 0.05$.

	Toluene Concentration (ppb)				
	Background Wells		Compliance Wells		
Month	Well 1	Well 2	Well 3	Well 4	Well 5
1	<5	<5	<5	<5	<5
2	7.5	<5	12.5	13.7	20.1
3	<5	<5	8.0	15.3	35.0
4	<5	<5	<5	20.2	28.2
5	6.4	<5	11.2	25.1	19.0

SOLUTION

Step 1. Since non-detects account for 48% of these data, it would be very difficult to verify the assumptions of normality and equal variance necessary for a parametric ANOVA. Use the Kruskal-Wallis test instead, pooling both background wells into one group and treating each compliance well as a separate group. Note that $N = 25$ and $k = 4$.

Compute ranks for all the data including tied observations (*e.g.*, non-detects) as in the following table. Note that each non-detect is given the same midrank, equal to the average of the first 12 unique ranks.

	Toluene Ranks				
	Background Wells		Compliance Wells		
Month	Well 1	Well 2	Well 3	Well 4	Well 5
1	6.5	6.5	6.5	6.5	6.5
2	14	6.5	17	18	21
3	6.5	6.5	15	19	25
4	6.5	6.5	6.5	22	24
5	13	6.5	16	23	20
Group Size	$n_1 = 10$		$n_2 = 5$	$n_3 = 5$	$n_4 = 5$
Rank Sum	$R_{1\bullet} = 79$		$R_{2\bullet} = 61$	$R_{3\bullet} = 88.5$	$R_{4\bullet} = 96.5$
Rank Mean	$\bar{R}_{1\bullet} = 7.9$		$\bar{R}_{2\bullet} = 12.2$	$\bar{R}_{3\bullet} = 17.7$	$\bar{R}_{4\bullet} = 19.3$

Step 2. Calculate the sum and average of the ranks in each group using equations [17.11] and [17.12]. These results are given in the above table.

Step 3. Compute the Kruskal-Wallis statistic H using equation [17.13]:

$$H = \frac{12}{25 \cdot 26}\left[\frac{79^2}{10} + \frac{61^2}{5} + \frac{88.5^2}{5} + \frac{96.5^2}{5}\right] - (3 \cdot 26) = 10.56$$

Also compute the adjustment for ties with equation [17.10]. There is only one group of distinct tied observations — the non-detects — containing 12 samples. Thus, the adjusted Kruskal-Wallis statistic is given by:

$$H^* = 10.56 \Big/ \left[1 - \left(\frac{12^3 - 12}{25^3 - 25}\right)\right] = 11.87$$

Step 4. Determine the critical point of the Kruskal-Wallis test: with $\alpha = .05$, the upper 95th percentage point of the chi-square distribution with $(k–1) = 4–1 = 3$ degrees of freedom [*df*] is needed. **Table 17-2** of **Appendix D** gives $\chi^2_{cp} = \chi^2_{.95,3} = 7.81$.

Step 5. Since the observed Kruskal-Wallis statistic of 11.87 is greater than the chi-square critical point, there is evidence of significant differences between the well groups. Therefore, post-hoc pairwise comparisons are necessary.

Step 6. To determine the significance level appropriate for post-hoc comparisons, note there are three compliance wells that need to be tested against background. Therefore, each of these contrasts should be run at the $\alpha^* = 0.05/3 = 0.0167$ significance level.

Step 7. Calculate the standard error of the difference for the three contrasts using equation [17.14]. Since the sample size at each compliance well is five, the *SE* will be identical for each comparison, namely,

$$SE_i = \sqrt{\frac{25 \cdot 26}{12}\left(\frac{1}{10} + \frac{1}{5}\right)} = 4.031$$

Step 8. Form the post-hoc Z-statistic for each contrast using equation [17.15]:

$$\text{Well 3: } Z_2 = \left(12.2 - 7.9\right) \Big/ 4.031 = 1.07$$
$$\text{Well 4: } Z_3 = \left(17.7 - 7.9\right) \Big/ 4.031 = 2.43$$
$$\text{Well 5: } Z_4 = \left(19.3 - 7.9\right) \Big/ 4.031 = 2.83$$

Step 9. Find the upper $(1–\alpha^*) \times 100$th percentage point from the standard normal distribution in **Table 10-1** in **Appendix D**. With $\alpha^* = .0167$, this gives a critical point (by linear interpolation) of $z_{cp} = z_{.9833} = 2.127$.

Step 10. Since the *Z*-statistics at wells 4 and 5 exceed the critical point, there is significant evidence of increased concentration levels at wells 4 and 5, but not at well 3. ◄

17.2 TOLERANCE LIMITS

A *tolerance interval* is a concentration range designed to contain a pre-specified proportion of the underlying population from which the statistical sample is drawn (*e.g.*, 95 percent of all possible population measurements). Since the interval is constructed from random sample data, a tolerance interval is expected to contain the specified population proportion only with a certain level of statistical

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confidence. Two coefficients are thus associated with any tolerance interval. One is the population proportion that the interval is supposed to contain, called the coverage (γ). The second is the degree of confidence with which the interval reaches the specified coverage. This is sometimes known as the tolerance coefficient or more simply, the confidence level (1–α). A tolerance interval with 95% coverage and a tolerance coefficient of 90 percent is constructed to contain, on average, 95% of the distribution of all possible population measurements with a confidence probability of 90%.

A *tolerance limit* is a one-sided tolerance interval. The upper limit is typically of most interest in groundwater monitoring. Tolerance limits are a standard statistical method that can be useful in groundwater data analysis, especially as an alternative to *t*-tests or ANOVA for interwell testing. The RCRA regulations allow greater flexibility in the choice of α when using tolerance and prediction limits and control charts, so a larger variety of data configurations may be amenable to one of these approaches. The Unified Guidance still recommends prediction limits or control charts over tolerance limits for formal compliance testing in detection monitoring, and confidence intervals over tolerance limits in compliance/assessment monitoring when a background standard is needed.

An interwell tolerance limit constructed on background data is designed to cover all but a small percentage of the background population measurements. Hence background observations should rarely exceed the upper tolerance limit. By the same token, when testing a null hypothesis (H_0) that the compliance point population is identical to background, *compliance point* measurements also should rarely exceed the upper tolerance limit, unless H_0 is false. The upper tolerance limit thus gauges whether or not concentration measurements sampled from compliance point wells are too extreme relative to background.

17.2.1 PARAMETRIC TOLERANCE LIMITS

BACKGROUND AND PURPOSE

To test the null hypothesis (H_0) that a compliance point population is identical to that of background, an upper tolerance limit with high coverage (γ) can be constructed on the sample background data. Coverage of 95% is usually recommended. In this case, random observations from a distribution identical to background should exceed the upper tolerance limit less than 5% of the time. Similarly, a tolerance coefficient or confidence level of at least 95% is recommended. This gives 95% confidence that the (upper) tolerance limit will contain at least 95% of the distribution of observations in background or in any distribution similar to background. Note that a tolerance coefficient of 95% corresponds to choosing a significance level (α) equal to 5%. Hence, as with a one-way ANOVA, the overall false positive rate for a tolerance interval is set to approximately 5%.

Once the limit is constructed on background, each compliance point observation (perhaps from several different wells) is compared to the upper tolerance limit. This is different from the comparison of sample means in an ANOVA test. If any compliance point measurement exceeds the limit, the well from which it was drawn is flagged as showing a significant increase over background. Note that the factors κ used to adjust the width of the tolerance interval (**Table 17-3** in **Appendix D**) are designed to provide *at least* 95% coverage of the parent population. Applied over many data sets, the *average* coverage of these intervals will often be close to 98% or more (see Guttman, 1970). Therefore, it would be unusual to find

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more than 2 or 3 samples out of every 100 exceeding the tolerance limit under the null hypothesis. This fits with the purpose behind the use of a tolerance interval, which is to establish an upper limit on background that will rarely be exceeded, unless some change in the groundwater causes concentration levels to rise significantly at one or more compliance points.

Testing a large number of compliance point samples against such a background tolerance limit even under conditions of no releases practically ensures a few measurements will occasionally exceed the limit. The Unified Guidance therefore recommends that tolerance limits be used in conjunction with verification resampling of those wells suspected of possible contamination, in order to either verify or disconfirm the initial round of sampling and to avoid false positive results.

REQUIREMENTS AND ASSUMPTIONS

Standard parametric tolerance limits assume normality of the sample background data used to construct the limit. This assumption is critical to the statistical validity of the method, since a tolerance limit with high coverage can be viewed as an estimate of a *quantile* or *percentile* associated with the *tail probability* of the underlying distribution. If the background sample is non-normal, a normalizing transformation should be sought. If a suitable transformation is found, the limit should be constructed on the transformed measurements and can then be *back-transformed* to the raw concentration scale prior to comparison against individual compliance point values.

If no transformation will work, a non-parametric tolerance limit should be considered instead. Unfortunately, non-parametric tolerance limits generally require a much larger number of observations to provide the same levels of coverage and confidence as a parametric limit. It is recommended that a parametric model be fit to the data if at all possible.

A tolerance limit can be computed with as few as three observations from background. However, doing so results in a high upper tolerance limit with limited statistical power for detecting increases over background. Usually, a background sample size of at least eight measurements will be needed to generate an adequate tolerance limit. If multiple background wells are screened in equivalent hydrostratigraphic positions and the data can reasonably be combined (**Chapter 5**), one should consider using pooled background data from multiple wells to increase the background sample size.

Like many tests described in the Unified Guidance, tolerance limits as applied to groundwater monitoring assume *stationarity* of the well field populations both temporally (*i.e.*, over time) and spatially. The data also needs to be statistically *independent*. Since an adequately-sized background sample will have to be amassed over time (in part to maintain enough temporal spacing between observations so that independence can be assumed), the background data should be checked for apparent *trends* or *seasonal effects*. As long the background mean is stable over time, the amassed data from a longer span of sampling will provide a better statistical description of the underlying background population.

As a primarily interwell technique, tolerance limits should only be utilized when there is minimal *spatial variability*. Explicit checks for spatial variation should be conducted using box plots and/or ANOVA.

In the usual test setting, one new compliance point observation from each distinct well is compared against the tolerance limit during each statistical evaluation. Under the null hypothesis of identical

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populations, the compliance point measurements are assumed to follow the same distribution as background. Further, the compliance data are assumed to be mutually statistically independent. Such assumptions are almost impossible to check with only one new value per compliance well. However, periodic checks of the key assumptions are recommended after accumulating several sampling rounds of compliance data.

PROCEDURE

Step 1. Calculate the mean $\bar{x}$, and the standard deviation s, from the background sample.

Step 2. Construct the one-sided upper tolerance limit as

$$TL = \bar{x} + \kappa\left(n, \gamma, 1-\alpha\right) \cdot s \qquad [17.16]$$

where $\kappa(n, \gamma, 1-\alpha)$ is the one-sided normal tolerance factor found in **Table 17-3** of **Appendix D** associated with a sample size of n, coverage coefficient of γ, and confidence level of $(1-\alpha)$.

Equation [17.16] applies to normal data. If a transformation is needed to normalize the sample, the tolerance limit needs to be constructed on the transformed measurements and the limit back-transformed to the original concentration scale. If the limit was constructed, for example, on the logarithms of the original observations, where $\bar{y}$ and s_y are the log-mean and log-standard deviation, the tolerance limit can be back-transformed to the concentration scale by exponentiating the limit. The tolerance limit is computed as:

$$TL = \exp\left[\bar{y} + \kappa(n, \gamma, 1-\alpha) \cdot s_y\right] \qquad [17.17]$$

Step 3. Compare each observation from the compliance well(s) to the upper tolerance limit found in Step 2. If any observation exceeds the tolerance limit, there is statistically significant evidence that the compliance well concentrations are elevated above background. Verification resampling should be conducted to verify or disconfirm the initial result.

►EXAMPLE 17-3

The table below consists of chrysene concentration data (ppb) found in water samples obtained from two background wells (Wells 1 and 2) and three compliance wells (Wells 3, 4, and 5). Compute the upper tolerance limit on background for coverage of 95% with 95% confidence and determine whether there is evidence of possible contamination at any of the compliance wells.

	Chrysene Concentration (ppb)				
Month	Well 1	Well 2	Well 3	Well 4	Well 5
1	19.7	10.2	68.0	26.8	47.0
2	39.2	7.2	48.9	17.7	30.5
3	7.8	16.1	30.1	31.9	15.0
4	12.8	5.7	38.1	22.2	23.4
Mean	19.88	9.80	46.28	24.65	28.98
SD	13.78	4.60	16.40	6.10	13.58

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SOLUTION

Step 1. A Shapiro-Wilk test of normality on the pooled set of eight background measurements gives $W = 0.7978$ on the original scale and $W = 0.9560$ after log-transforming the data, suggesting that the data are better fit by a lognormal distribution. Therefore, construct the tolerance limit on the logged observations, listed below along with the log-means and log-standard deviations.

	Log Chrysene log(ppb)				
Month	Well 1	Well 2	Well 3	Well 4	Well 5
1	2.981	2.322	4.220	3.288	3.850
2	3.669	1.974	3.890	2.874	3.418
3	2.054	2.779	3.405	3.463	2.708
4	2.549	1.740	3.640	3.100	3.153
Mean	2.813	2.204	3.789	3.181	3.282
SD	0.685	0.452	0.349	0.253	0.479
BG Mean	2.509				
BG SD	0.628				

Step 2. Compute the upper tolerance limit on the pooled background data using the logged chrysene concentration data. The tolerance factor for a one-sided upper normal tolerance limit with 95% coverage and 95% probability and $n = 8$ observations is equal to (from **Table 17-3** of **Appendix D**) $\kappa = 3.187$. Therefore, the upper tolerance limit is computed using equation [17.17] as:

$$TL = \exp\left[2.509 + 3.187 \times 0.628\right] = 90.96 \text{ ppb}$$

Step 3. Compare the measurements at each compliance well to the upper tolerance limit, that is TL = 90.96 ppb. Since none of the original chrysene concentrations exceeds the upper TL, there is insufficient evidence of chrysene contamination in these data. ◄

17.2.2 NON-PARAMETRIC TOLERANCE INTERVALS

BACKGROUND AND PURPOSE

When an assumption of normality cannot be justified especially with a significant portion of non-detect observations, the use of non-parametric tolerance intervals should be considered. The upper tolerance limit in a non-parametric setting is usually chosen as an order statistic of the sample data (Guttman, 1970), commonly the maximum value or maybe the second or third largest value observed.

Because the maximum observed background value is often taken as the upper tolerance limit, non-parametric tolerance intervals are easy to construct and use. The sample data needs to be ordered, but no

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ranks need be assigned to the concentration values other than to determine the largest measurements. This also means that non-detects do not have to be uniquely ordered or handled in any special manner.

One advantage to using a maximum concentration instead of assigning ranks to the data (Wilcoxon rank-sum or Kruskal-Wallis tests) is that non-parametric tolerance intervals are reflective of actual concentration magnitudes. Another advantage is that unless all the background data are non-detect, the maximum value will be a detected concentration leading to a well-defined upper tolerance limit. If all the sample data are non-detect, an RL (*e.g.*, the lowest achievable *quantitation limit* [QL]) may serve as an approximate upper tolerance limit.

REQUIREMENTS AND ASSUMPTIONS

Unlike parametric tolerance intervals, the desired coverage (γ) or confidence level ($1-\alpha$) cannot be pre-specified using a non-parametric limit. Instead, the *achieved* coverage and/or confidence level depends entirely on the background sample size (n) and the order statistic chosen as the upper tolerance limit (*e.g.*, the maximum value). Guttman (1970) has shown that the *coverage* of the limit follows a *beta probability density* with cumulative distribution:

$$I_t(n-m+1,m) = \int_{u=0}^{t} \frac{\Gamma(n+1)}{\Gamma(n-m+1)\Gamma(m)} u^{n-m}(1-u)^{m-1}\,du \qquad [17.18]$$

where n = sample size and m = [(n+1)−(rank of upper tolerance limit value)]. If the background maximum is selected as the tolerance limit, its rank is equal to n and so m = 1. If the second largest value is chosen as the limit, its rank would be equal to (n−1) giving m = 2.

As a non-parametric procedure, no distributional model must be fit to the background measurements. It is assumed, however, that the compliance point data follow the same distribution as background — even if unknown — under the null hypothesis. Even though no distributional model is assumed, order statistics of any random sample follow certain probability laws as noted above. Since the beta distribution is closely related to the more familiar *binomial distribution*, Guttman showed that in order to construct a non-parametric tolerance interval with at least γ coverage and ($1-\alpha$) confidence probability, the number of (background) samples should be chosen such that:

$$\sum_{t=m}^{n} \binom{n}{t} (1-\gamma)^t \gamma^{n-t} \geq 1-\alpha \qquad [17.19]$$

If the background maximum is selected as the upper tolerance limit, so that m = 1, this inequality reduces to the simpler form

$$1-\gamma^n \geq 1-\alpha\,. \qquad [17.20]$$

Table 17-4 in **Appendix D** provides minimum coverage levels with 95% confidence for various choices of n, using either the maximum sample value or the second largest measurement as the tolerance limit. As an example, with n = 16 background measurements, the minimum coverage is γ = 83% if the background maximum is designated as the upper tolerance limit and γ = 74% if the tolerance limit is

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taken as the second largest background value. In general, **Table 17-4** of **Appendix D** illustrates that if the underlying distribution is unknown, *more background samples are needed compared to the parametric setting in order to construct a tolerance interval with sufficiently high coverage*. Parametric tolerance intervals do not require as many background samples precisely because the form of the underlying distribution is assumed to be known.

An alternate way to construct an appropriate tolerance limit is to calculate the maximum confidence level for various choices of n guaranteeing at least 95% coverage. With $n = 8$ background measurements, the approximate confidence level is at most 34% when the largest value is taken as the tolerance limit and only 6% if the second largest value is taken as the tolerance limit. Clearly, it is advantageous to fit a parametric distributional model to the data if at all possible unless n is fairly large.

Although non-parametric tolerance limits do not require an assumption of normality, other assumptions of tolerance limits apply equally to the parametric and non-parametric versions. Specifically, the sample data should be statistically *independent* and show no evidence of *autocorrelation*, *trends*, or *seasonal effects* in background. Applied as an interwell test, there should also be minimal to no natural on-site *spatial variation*.

By construction, outliers in background can be a particular problem for non-parametric tolerance limits, especially if the background maximum is chosen as the upper limit. A limit based on a large, extreme outlier will result in a test having little power to detect increases in compliance wells. Consequently, the background sample should be screened ahead of time for possible *outliers* (**Chapter 12**). Confirmed outliers should be removed from the data set before setting the tolerance limit.

An important caveat to this advice is that almost all statistical outlier tests depend crucially on the ability to fit the remaining data (minus the suspected outlier(s)) to a known statistical distribution. In those cases where a non-parametric tolerance limit is selected because of a large fraction of non-detects, fitting the data to a distributional model may be difficult or impossible, negating formal outlier tests. As an alternative, the non-parametric upper tolerance limit could be set to a different order statistic in background (*i.e.*, other than the maximum), to provide some insurance against possible large outliers. This strategy will work provided there are enough background measurements to allow for adequately high coverage and confidence in the resulting limit.

PROCEDURE

Step 1. Sort the set of background data into ascending order and choose either the largest or second largest measurement as the upper *TL*. Use **Table 17-4** in **Appendix D** to determine the coverage γ associated with 95% or 99% confidence. Note also that if the largest or second largest measurement is a non-detect, the upper tolerance limit should be set to the RL most appropriate to the data (*e.g.*, the lowest achievable practicable quantification limit [PQL]).

Step 2. Compare each compliance point measurement against the upper tolerance limit. Identify significant evidence of possible contamination at any compliance well in which one or more measurements exceed the upper tolerance limit. If the upper tolerance limit equals the RL, a violation should be flagged anytime a detected value is quantified above the RL.

Step 3. Because the risk of false positive errors is greatly increased if either the confidence level or coverage drop substantially below 95%, both of these parameters should be routinely reported

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and noted as being below the target levels. One should also strongly consider comparing one or more verification resamples against the upper tolerance limit before identifying a clear violation.

►EXAMPLE 17-4

Use the following copper background data to establish a non-parametric upper tolerance limit and determine if either compliance well shows evidence of copper contamination.

	Copper Concentration (ppb)				
	Background Wells			Compliance Wells	
Month	Well 1	Well 2	Well 3	Well 4	Well 5
1	<5	9.2	<5		
2	<5	<5	5.4		
3	7.5	<5	6.7		
4	<5	6.1	<5		
5	<5	8.0	<5	6.2	<5
6	<5	5.9	<5	<5	<5
7	6.4	<5	<5	7.8	5.6
8	6.0	<5	<5	10.4	<5

SOLUTION

Step 1. The pooled background data in Wells 1, 2, and 3 have a maximum observed value of 9.2 ppb. Set the 95% confidence upper tolerance limit equal to this value. Because 24 background samples are available, **Table 17-4** in **Appendix D** indicates that the minimum coverage is equal to 88%. To increase either the coverage, more background samples would have to be collected.

Step 2. Compare each sample in compliance Wells 4 and 5 to the upper tolerance limit. Since none of the measurements at Well 5 is above 9.2 ppb, while one sample from Well 4 is above the limit, conclude that there may be significant evidence of copper contamination at Well 4 but not Well 5.

Step 3. Note that with only 88% coverage and 24 background samples, the risk of a false positive result is more than 10%. Well 4 should be resampled to determine whether the exceedance is replicated. ◄

17.3 TREND TESTS

The Unified Guidance recommends *trend testing* as an intrawell alternative to prediction limits or control charts when those methods are not suitable. Prediction limits and control charts (as well as *t*-tests and ANOVA) all involve a comparison of compliance and background populations under the key assumption that the underlying concentration distributions are *stationary over time*. That is, the populations are presumed to have stable (*i.e.*, roughly constant) means over the period of sampling prior to statistical evaluation.

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Unfortunately, there is no guarantee that groundwater populations will remain stable during long-term monitoring. Because sampling at many sites is generally done on a quarterly, semi-annual, or annual basis, it will generally take one to two years or more to collect enough background data to run the statistical tests discussed in the Unified Guidance. Over this length of time, the statistical characteristics of groundwater may or may not change in significant ways.

If background groundwater conditions are in a state of flux, trend tests provide a significant advantage over both intrawell prediction limits and control charts. Both of the latter methods involve a designation of some portion of the historical sampling record as the intrawell background for a given compliance well. Ideally, this intrawell background should consist of measurements known to be uncontaminated and which represent a random sample from a stable underlying population, just as with *t*-tests and ANOVA. If the mean and/or standard deviation of the underlying population *changes* while intrawell background is being compiled, results of either prediction limit or control chart tests against more recently collected data can be severely biased or altogether inaccurate.

One drawback to the Shewhart-CUSUM control charts presented in **Chapter 20** is that they are somewhat sensitive to the parametric assumption of underlying normality. If the measurements are lognormal rather than normal, for instance, the nominal performance characteristics (*i.e.*, Type I error rate and statistical power) of control charts are significantly affected. By the same token, control charts are impacted if the intrawell background contains a large fraction of non-detects. Non-detect adjustments can sometimes be made to the baseline data via methods discussed in **Chapter 15**, but if a normalizing transformation or adjustment is not successful, no straightforward non-parametric control chart exists.

Consequently, neither prediction limits nor control charts are appropriate for every circumstance where an intrawell comparison may be warranted or necessary. Thus, ***the Unified Guidance recommends that users consider trend testing as an alternative to prediction limits or control charts when those methods are not suitable as intrawell techniques***. Tests for trend are specifically designed to identify those groundwater populations whose mean concentrations are not stationary over time, but rather are increasing (or decreasing) by measurable amounts. Ultimately, the goal of any reasonable detection or compliance/assessment monitoring program is to determine whether or not the concentration levels of key contaminants or indicator parameters have significantly increased during the period of monitoring and, if so, whether the increase is attributable to facility waste management practices.

The detection of trends is a complex subject. Whole textbooks are devoted to the more general topic of *time series analysis*, including the identification and modeling of time trends — step functions, linear and quadratic trends, exponential growth, *etc.* The Unified Guidance only attempts to identify the simplest kind of linear increases, not the specification or testing of more complex models. The methods described below are all designed to effectively test for (increasing) linear trends, though they will also identify simple increases over time when a trend is present but does not follow a strictly linear pattern.

The Unified Guidance recommends using trend tests in detection monitoring to measure the extent and nature of an apparent concentration increase, especially to determine whether or not the increase occurs consistently over time. Two questions are of particular interest: 1) is there a statistically significant, (positive) trend over the period of monitoring? and 2) what is the nature (*i.e.*, slope and intercept) of the trend? By identifying a positive trend, one can show that contaminant levels have gotten worse compared to early measurements from the well being tested. Furthermore, by measuring the nature

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of the trend, including the average rate of increase per unit of time, one can estimate how rapidly concentration levels are increasing and the current mean- or median-level magnitude of contamination. Such information can provide an invaluable portrait of the changes occurring on-site and probably offers the most compelling evidence — under these conditions — for demonstrating that the basic null hypothesis of detection monitoring has been violated.

17.3.1 LINEAR REGRESSION

BACKGROUND AND PURPOSE

The most common way to measure a linear trend is to compute a *linear regression* of concentration data when plotted against the time or date of sample collection. By way of interpretation, each point along a linear regression trend line is an estimate of the true mean concentration *at that point in time*. Thus, a linear regression can be used to assess whether or not the population mean at a compliance well has significantly increased or decreased.

Linear regression is a standard technique in statistics textbooks and many data analysis software packages. It is more generally applicable to linear relationships between any pair of random variables and not simply to time trends. Good references for performing linear regression and for checking and verifying its assumptions include Draper and Smith (1998) and Cook and Weisberg (1999).

Unlike prediction limits or control charts which are constructed using only the background data, trend tests including linear regression are computed with all available earlier and more recent data at the compliance well of interest. One then might incorrectly assume that a comparison against intrawell background is not being conducted. But an intrawell comparison does occur with a trend test. Statistical identification of a structured pattern of increase from the first portion of the sampling record to more recent data indicates that concentration levels are no longer similar to intrawell background, but have risen more than expected by chance.

Statistical identification of a positive trend involves testing the estimated slope coefficient from the linear regression trend line. A specially constructed *t*-test is used to make this determination, as described below. If this test is significant, the slope is judged to be different from zero, indicating that a change in concentration levels has occurred over the period of sampling represented by the data set.

REQUIREMENTS AND ASSUMPTIONS

Linear regression as a parametric statistical technique makes a number of underlying assumptions. Among the most important of these are that the regression residuals (*i.e.*, the difference between each concentration measurement and its predicted value from the regression equation) are approximately normal in distribution, homoscedastic (*i.e.*, equal in variance at different times and for different mean concentration levels), and statistically independent. Significant skewness or the presence of outliers can bias or invalidate the results of a trend test based on linear regression. Furthermore, standard linear regression methods do not account for non-detects or missing data values at selected sampling events.

Because the key assumptions for linear regression depend not on the original measurements but rather on the regression residuals, a tentative trend line needs to first be constructed before its

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assumptions can be checked. Once a linear regression on time is fitted to the data, the residuals around the trend line need to be computed and then tested for normality, apparent skewness, and equal variance over time. This last assumption is particularly important to testing whether the slope of an apparent trend is statistically different from zero (a zero slope indicating that well concentrations have not changed over time).

Inferences around a linear regression are generally appropriate when three conditions hold: 1) the residuals from the regression are approximately normal or at least reasonably symmetric in distribution; 2) a scatter plot of residuals versus concentrations indicates a scatter cloud of essentially uniform *vertical thickness or width* (i.e., the scatter cloud does not tend to increase in width with the level of concentration which would suggest a proportional effect between the underlying population mean and variance); and 3) a scatter plot of residuals versus time also exhibits a uniformly thick scatter cloud. If the thickness or width is substantially different at distinct time points, the assumption of equal variances over time may not be true.

If any of these conditions is substantially violated, it may indicate that the basic trend is either non-linear or the magnitude of the variance is not independent of the mean concentration level and/or the time of sampling. One possible remedy is to try a transformation of the concentration data and re-estimate the linear regression. This will change the interpretation of the estimated regression from a linear trend of the form $y = a + bt$, where y and t represent concentration and time respectively, to a non-linear pattern. As an example, if the concentration data are log-transformed, the regression equation will have the form $\log y = a + bt$. Back-transformed to the original concentration scale, the trend function will then have the form $y = \exp\left(a + bt\right)$.

In transforming the regression data this way, the estimated trend in the concentration domain (after back-transforming) no longer represents the original mean. Rather, the transformation induces a *bias* when converted back to the raw-scale data. If a log transformation is used, for instance, the back-transformed trend line will represent the raw-scale *geometric mean* and not the *arithmetic mean*. As with Student's t-tests on lognormal data (**Chapter 16**), demonstrating that the *geometric* mean is increasing also implies that the *arithmetic* mean has risen so long as the regression residuals are homoscedastic.

A minimum of 8 to 10 measurements is generally necessary to compute a linear regression, especially to estimate the variance around the trend line (known as the *mean squared error* or MSE). The regression residuals should be statistically independent, an assumption that can be approximately verified via one of the autocorrelation tests of **Chapter 14**.

One last assumption is that there should be few if any non-detects when computing a linear regression. As a matter of common sense, a significant increasing or decreasing trend should be based on reliably quantified measurements. If this is not the case, the user should check to see whether the "trend" may be an artifact induced by changes in detection and/or quantitation limits over time. The concentration levels of a series of non-detects may appear to be decreasing, for instance, simply because analytical methods have improved over the years leading to lower RLs. Such artifacts of plotting and data reporting should not be considered real trends.

When the assumptions of linear regression cannot be verified at least approximately, a non-parametric trend method should be considered instead. **Sections 17.3.2** and **17.3.3** discuss the *Mann-*

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Kendall test for trend and the *Theil-Sen trend line*. These methods can be particularly valuable when constructing trends on data sets containing non-detects.

PROCEDURE

Step 1. Construct a time series plot of the compliance point measurements. If a discernible trend is evident, compute a linear regression of concentration against sampling date (time), letting x_i denote the ith concentration value and t_i denote the ith sampling date. Estimate the linear slope $\hat{b}$ with the formula:

$$\hat{b} = \sum_{i=1}^{n} (t_i - \bar{t}) \cdot x_i \Big/ (n-1) \cdot s_t^2 \qquad [17.21]$$

This estimate then leads to the regression equation, given by:

$$\hat{x}_t = \bar{x} + \hat{b} \cdot (t - \bar{t}) \qquad [17.22]$$

where $\bar{t}$ denotes the mean sampling date, s_t^2 is the variance of sampling dates, $\bar{x}$ is the mean concentration level, and $\hat{x}_t$ represents the estimated mean concentration at time t.

Note: though the variable t above represents time, it could just as easily signify another variable, perhaps a second constituent for which an association with x is estimated.

Step 2. Compute the regression residual at each sampling event i with equation [17.23]:

$$r_i = x_i - \hat{x}_i \qquad [17.23]$$

Check the set of residuals for lack of normality and significant skewness using the techniques in **Chapter 10**. Also, plot the residuals against the estimated regression values ($\hat{x}_i$) to check for non-uniform vertical thickness in the scatter cloud. Make a similar check by plotting the residuals against the sampling dates (t_i).

If the residuals are non-normal and substantially skewed and/or the scatter clouds appear to have a definite pattern (*e.g.*, funnel-shaped; "U"-shaped; or, residuals mostly positive on one end of graph and mostly negative on the other end, instead of randomly scattered around the horizontal line $r = 0$), repeat **Steps 1** and **2** after first attempting a normalizing transformation.

Step 3. Calculate the estimated variance around the regression line (also known as the *mean squared error* [MSE]) with equation [17.24]:

$$s_e^2 = \frac{1}{n-2} \sum_{i=1}^{n} r_i^2 \qquad [17.24]$$

Step 4. Compute the standard error of the linear regression slope coefficient using the s^2_e result from Step 3 in equation [17.25]:

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$$se(\hat{b}) = \sqrt{s^2{}_e \Big/ \sum_{i=1}^{n} (t - \bar{t})^2} \qquad [17.25]$$

Step 5. Test whether the trend is significantly different from zero by forming the *t*-statistic ratio in equation [17.26]:

$$t_b = \hat{b} / se(\hat{b}) \qquad [17.26]$$

This *t*-statistic (t_b) has n–2 degrees of freedom [*df*]. Given a level of significance (α), choose the critical point (t_{cp}) for the test as the (1– α) × 100th percentage point of the Student's *t*-distribution with (n–2) *df* or $t_{cp} = t_{1-\alpha,n-2}$. Compare t_b against the critical point. If $t_b > t_{cp}$, conclude that the slope of the trend is both positive and significantly different from zero at the α-level of significance. If $t_b < -t_{cp}$, conclude there is a significant decreasing trend. If neither exists, there is insufficient evidence of an increasing or decreasing trend.

►EXAMPLE 17-5

The following groundwater chloride measurements (n = 19) were collected over a five-year period at a solid waste landfill. Test for a significant trend at the α = 0.01 level using linear regression.

Sample Date	Chloride (ppm)	Elapsed Days	Residuals
2002-03-18	11.5	76	–0.25
2002-05-14	12.6	133	0.67
2002-08-22	13.8	233	1.56
2003-02-12	12.3	407	–0.48
2003-05-29	12.8	513	–0.30
2003-08-18	13.2	594	–0.15
2003-11-20	14.1	688	0.45
2004-02-19	13.3	779	–0.63
2004-04-26	13.1	846	–1.04
2004-07-29	13.2	940	–1.23
2004-11-09	15.3	1043	0.56
2005-02-24	15.0	1150	–0.08
2005-06-14	15.2	1260	–0.22
2005-08-23	15.8	1330	0.17
2005-10-17	16.1	1385	0.30
2006-02-08	15.1	1499	–1.06
2006-04-27	16.4	1577	0.00
2006-08-10	17.7	1682	0.98
2006-10-26	17.7	1759	0.74

SOLUTION

Step 1. Check for an apparent trend on a time series plot (**Figure 17-2**). Since the chloride values are increasing in reasonably linear fashion, compute the tentative regression line using equations [17.21] and [17.22]. To compute the slope estimate, first convert the sample dates to elapsed days using a starting date prior to the first event. In this case, choose an arbitrary starting date of 2002-01-01 as zero and compute the elapsed days as listed in the table above.

Using elapsed days as the time variable, compute the sample mean and variance to get:

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$$\bar{t} = 941.79 \text{ days}$$
$$s_t^2 = 279374.3 \text{ days}^2$$

Then compute the tentative slope as:

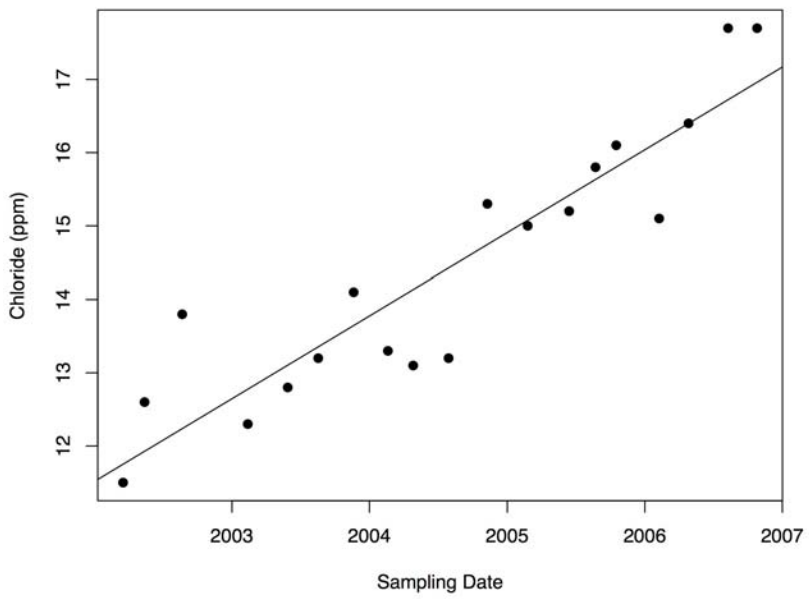
$$\hat{b} = \left[(76-941.79)\cdot 11.5 + \ldots + (1759-941.79)\cdot 17.7\right] / \left[(19-1)\cdot 279374.3\right] = .0031$$

and the regression line itself as:

$$\hat{x}_t = \bar{x} + \hat{b}\cdot(t-\bar{t}) = 14.432 + .0031\cdot(t-941.79)$$

where the mean chloride value is $\bar{x} = 14.432$ ppm. The regression line is overlaid on the scatter plot in **Figure 17-2**.

Figure 17-2. Time Series Plot of Chloride (ppm) Overlaid With Linear Regression



Step 2. Calculate the regression residual at each sampling event using equation [17.23]. This involves computing an estimated concentration along the regression line for each sampled time (t) and then subtracting from the observed concentration. For example, the residual at t = 407 is

$$x_t - \hat{x}_t = 12.3 - 12.78 = -0.48$$

All the residuals are listed in the table above. Then check the residuals for normality, homoscedasticity, and lack of association with the predicted values from the regression line.

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Figure 17-3 is a probability plot of the residuals, indicating good agreement with normality. **Figure 17-4** is a scatter plot of the residuals versus sampling date and **Figure 17-5** is a scatter plot of the residuals versus predicted values from the trend line. Both of these last plots do not exhibit any particular trends or patterns with sampling date or the trend line predicted values; the residuals are fairly randomly scattered.

Step 3. Compute the MSE of the regression using the squared residuals in equation [17.24] to get

$$s_e^2 = \frac{1}{n-2} \cdot \sum_{i=1}^{n} r_i^2 = \frac{1}{17} \cdot \left[(-.25)^2 + (.67)^2 + \ldots + (.74)^2 \right] = 0.5628$$

Step 4. Calculate the standard error of the regression slope coefficient using equation [17.25]:

$$se\left(\hat{b}\right) = \sqrt{s^2{}_e \Big/ \sum_{i=1}^{n} (t - \bar{t})^2} = \sqrt{.5628 \Big/ \left[(76 - 941.79)^2 + \ldots + (1759 - 941.79)^2 \right]} = .00033$$

Step 5. Form the *t*-statistic ratio with formula [17.26] to get:

$$t_b = \hat{b} \big/ se\left(\hat{b}\right) = 0.0031/0.00033 = 9.39$$

Since $\alpha = 0.01$, compare this value to a critical point equal to the 99th percentile of a Student's *t*-distribution with $(n-2) = 17$ degrees of freedom, that is, $t_{cp} = t_{.99,17} = 2.567$. Since the *t*-statistic is substantially larger than the critical point, conclude the upward trend is significant at the 1% α-level. ◄

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Figure 17-3. Probability Plot of Chloride Regression Residuals

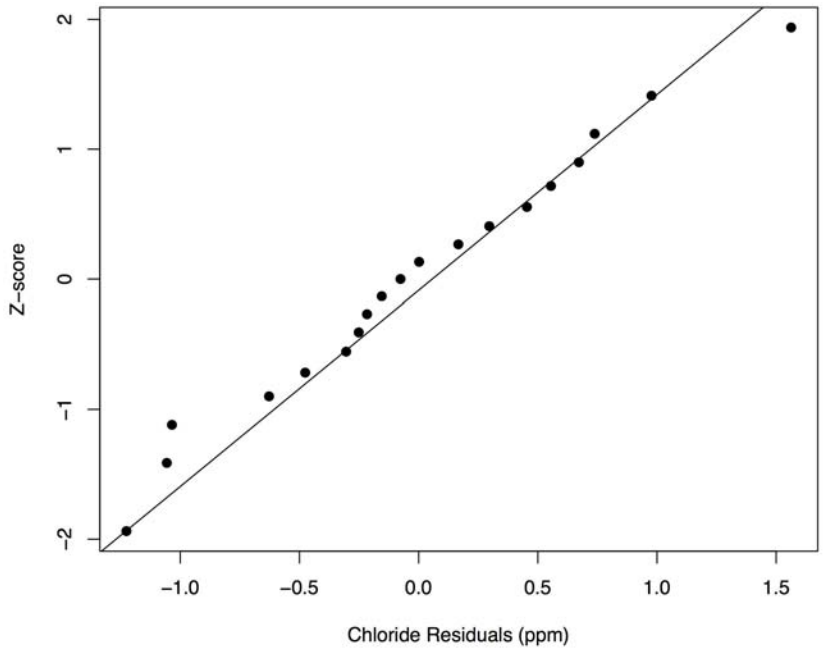
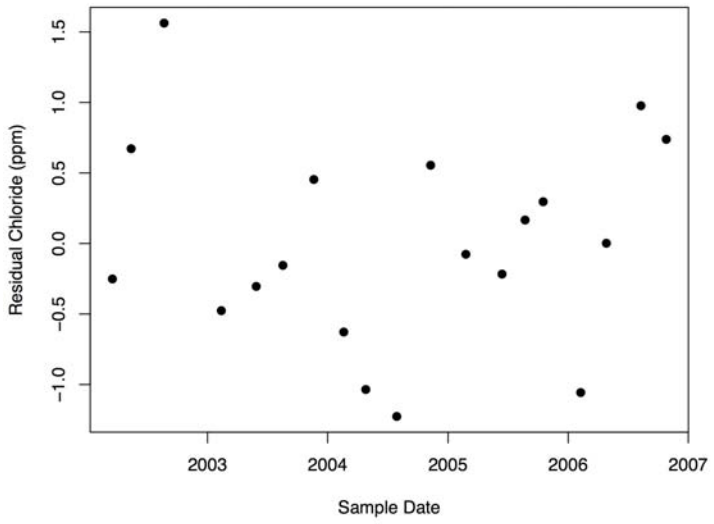
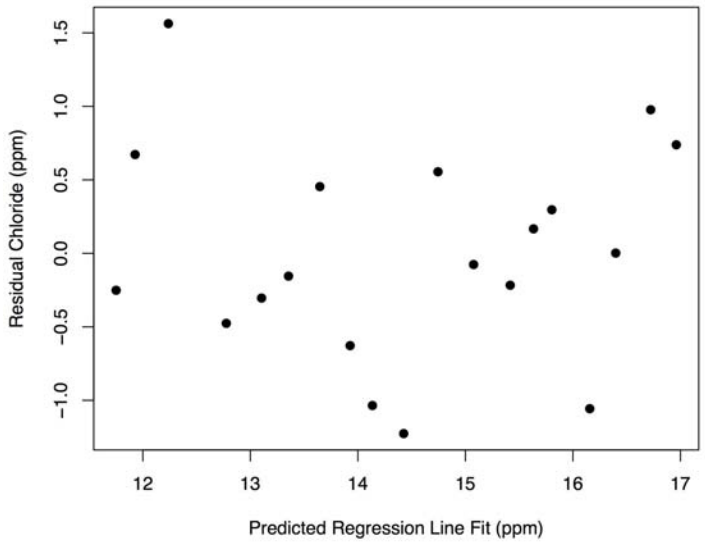


Figure 17-4. Scatter Plot of Chloride Residuals vs. Sampling Date



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Figure 17-5. Scatter Plot of Chloride Residuals vs. Predicted Regression Fits



17.3.2 MANN-KENDALL TREND TEST

BACKGROUND AND PURPOSE

The Mann-Kendall test (Gilbert, 1987) is a non-parametric test for linear trend, based on the idea that a lack of trend should correspond to a time series plot fluctuating randomly about a constant mean level, with no visually apparent upward or downward pattern. If an *increasing* trend really exists, the sample taken first from any randomly selected pair of measurements should on average have a *lower* concentration than the measurement collected at a later point. The Mann-Kendall statistic is computed by examining all possible pairs of measurements in the data set and scoring each pair as follows. An earlier measurement less in magnitude than a later one is assigned a value of 1. If an earlier value is greater in magnitude than a later sample, the pair is tallied as –1; two identical measurement values are assigned 0.

After scoring each pair in this way and adding up the total to get the Mann-Kendall statistic (*S*), a positive value of *S* implies that a majority of the differences between earlier and later measurements are positive, suggestive of an upward trend over time. Likewise, a negative value for *S* implies that a majority of the differences between earlier and later values are negative, suggestive of a decreasing trend. A value near zero indicates a roughly equal number of positive and negative differences. This would be expected if the measurements were randomly fluctuating about a constant mean with no apparent trend.

To account for randomness and inherent variability in the sample, the Mann-Kendall test is based on the critical ranges of the statistic *S* likely to occur under stationary conditions. The larger the absolute

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value of *S*, the stronger the evidence for a real increasing or decreasing trend. The critical points for identifying a trend get larger as the level of significance (α) drops. Only if the absolute value of the test statistic (*S*) is larger than the critical point is a statistically significant increasing or decreasing trend indicated.

REQUIREMENTS AND ASSUMPTIONS

As a non-parametric procedure, the Mann-Kendall test does not require the underlying data to follow a specific distribution. Ranks of the data are not explicitly used in forming the test statistic as with the Wilcoxon rank-sum. Only the relative magnitudes of the concentration values are needed to compute *S*, not the actual concentrations themselves. Non-detects can be treated by assigning them a common value lower than any of the detected measurements. Any pair of tied values or any pair of non-detects is simply given a score of 0 in the calculation of the Mann-Kendall statistic *S*.

This treatment of non-detects is an imperfect remedy since it is usually impossible to know whether censored values are actually tied in magnitude. Further complications are introduced when there are multiple RLs and/or an intermingling of detected values and RLs. Lab qualifiers may be used to aid the scoring of pairs that involve non-detects or estimated concentrations. Instead of treating all non-detects as tied, consider 'undetected or U' values as the lowest in magnitude, other non-detects as higher in magnitude than U's but lower than estimated concentrations ('J' or 'E' values). In this way, a richer scoring of the sample pairs may be possible.

When the sample size *n* becomes large, exact critical values for the statistic *S* are not readily available. However, as a sum of identically-distributed random quantities, the behavior of *S* for larger *n* tends to approximate the normal distribution by the Central Limit Theorem. Therefore a normal approximation to *S* can be used for $n > 10$[1]. In this case, a standardized *Z*-statistic is formed by first computing the expected mean value and standard deviation of *S*. From the discussion above, when no trend is present, positive differences in randomly selected pairs of measurements should balance negative differences, so the expected mean value of *S* under the null hypothesis of no trend is simply zero. The standard deviation of *S* can be computed using equation [17.27]:

$$SD\left[S\right] = \sqrt{\frac{1}{18}\left[n(n-1)(2n+5) - \sum_{j=1}^{g} t_j\left(t_j-1\right)\left(2t_j+5\right)\right]} \qquad [17.27]$$

where *n* is the sample size, *g* represents the number of groups of ties in the data set (if any), and t_j is the number of ties in the *j*th group of ties. If no ties or non-detects are present, equation [17.27] reduces to the simpler form:

$$SD\left[S\right] = \sqrt{\frac{1}{18}n(n-1)(2n+5)} \qquad [17.28]$$

[1] Guidance **Table 17-5** contains exact confidence levels up to $n = 10$. Exact confidence levels for $n \leq 20$ have been developed in (Hollander & Wolfe, 1999), Table A.30. These might be preferentially used if sample sizes are fairly small and the data contain non-detect values.

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Once the standard deviation of *S* has been derived, the standardized *Z*-statistic for an increasing (or decreasing) trend is formed using the equation:

$$Z = \left(\left|S\right| - 1\right) \Big/ SD\left[S\right] \qquad [17.29]$$

Note that although the expected mean value of *S* is zero, applying the continuous normal to the discrete *S* distribution is an approximation. Therefore, a *continuity correction* is made to *Z* by first subtracting 1 from the absolute value of *S*. The final *Z*-statistic can then be compared to an α-level critical point taken from **Table 10-1** in **Appendix D** to complete the test.

PROCEDURE

Step 1. Order the data set by sampling event or time of collection, x_1, x_2, to x_n. Then consider all possible differences between distinct pairs of measurements, $(x_j - x_i)$ for $j > i$. For each pair, compute the *sign* of the difference, defined by:

$$\operatorname{sgn}\left(x_j - x_i\right) = \begin{cases} 1 & \text{if } \left(x_j - x_i\right) > 0 \\ 0 & \text{if } \left(x_j - x_i\right) = 0 \\ -1 & \text{if } \left(x_j - x_i\right) < 0 \end{cases} \qquad [17.30]$$

Pairs of tied values including non-detects, will receive scores of zero using equation [17.30].

Step 2. Compute the Mann-Kendall statistic *S* using equation [17.31]:

$$S = \sum_{i=1}^{n} \sum_{j=i+1}^{n} \operatorname{sgn}\left(x_j - x_i\right) \qquad [17.31]$$

In equation [17.31] the summation starts with a comparison of the very first sampling event against each of the subsequent measurements. Then the second event is compared with each of the samples taken after it (*i.e.*, the third, fourth, fifth, *etc.*). Following this pattern is probably the most convenient way to ensure that all distinct pairs are tallied in forming *S*. For a sample of size *n*, there will be $n \cdot (n\text{-}1)/2$ distinct pairs.

Step 3. If $n \leq 10$, and given the level of significance (α), determine the critical point s_{cp} from **Table 17-5 of Appendix D.** If $S > 0$ and $\left|S\right| > s_{cp}$, conclude there is statistically significant evidence of an increasing trend at the α significance level. If $S < 0$ and $\left|S\right| > s_{cp}$, conclude there is statistically significant evidence of a decreasing trend. If $\left|S\right| \leq s_{cp}$, conclude there is insufficient evidence to identify a significant trend.

Step 4. If $n > 10$, determine the number of groups of ties (*g*) and the number of tied values in each group of ties (t_j). Then use equation [17.27] to compute the standard deviation of *S* and equation [17.29] in turn to compute the standardized *Z*-statistic.

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Step 5. Given the significance level (α), determine the critical point z_{cp} from the standard normal distribution in **Table 10-1** in **Appendix D**. Compare Z against this critical point. If $Z > z_{cp}$, conclude there is statistically significant evidence at the α-level of an increasing trend. If $Z < -z_{cp}$, conclude there is statistically significant evidence of a decreasing trend. If neither exists, conclude that the sample evidence is insufficient to identify a trend.

►EXAMPLE 17-6

Test for a significant upward trend using the Mann-Kendall procedure in the following set of sulfate measurements (ppm) collected over several years.

Sample No.	Sampling Date (yr.mon)	Sulfate Conc. (ppm)	Sample No.	Sampling Date (yr.mon)	Sulfate Conc. (ppm)
1	89.6	480	13	93.1	590
2	89.8	450	14	93.6	550
3	90.1	490	15	94.1	600
4	90.3	520	16	94.6	700
5	90.6	485	17	95.1	570
6	90.8	510	18	95.6	610
7	91.1	510	19	95.8	650
8	91.3	530	20	96.1	620
9	91.6	510	21	96.3	830
10	91.8	560	22	96.6	720
11	92.1	560	23	96.8	590
12	92.6	540			

SOLUTION

Step 1. Construct a time series plot of the sulfate observations to check for a possible trend as in **Figure 17-6**. A clearly rising concentration pattern is seen, although the variability in the measurements appears greater toward the end of the sampling record than at the beginning.

Step 2. Compute the difference between each distinct pair of measurements and determine the sign of the difference, using equation [17.30]. Then sum up the signs with equation [17.31]. Note that to make sure all the distinct pairs have been summed, begin with the first listed observation and compare it to each of values below it. Then take the second listed value and compare it to each of the remaining ones below it, *etc*. The Mann-Kendall statistic becomes:

$$S = \text{sgn}(450-480) + \text{sgn}(490-480) + \ldots + \text{sgn}(590-720) = 194$$

Step 3. Since the sample size $n = 23 > 10$, form the normal approximation to the Mann-Kendall statistic. Because there are some ties in the data, use equation [17.27] to compute the approximate standard deviation. Among the sulfate measurements, there are three groups of ties with 3, 2, and 2 tied values in each set respectively (at values 510, 560, and 590). The adjusted standard deviation is then:

$$SD[S] = \sqrt{\frac{1}{18}\cdot\left[23\cdot(23-1)(2\cdot 23+5) - \left\{3\cdot(3-1)(2\cdot 3+5)+\ldots+2\cdot(2-1)(2\cdot 2+5)\right\}\right]} = 37.79$$

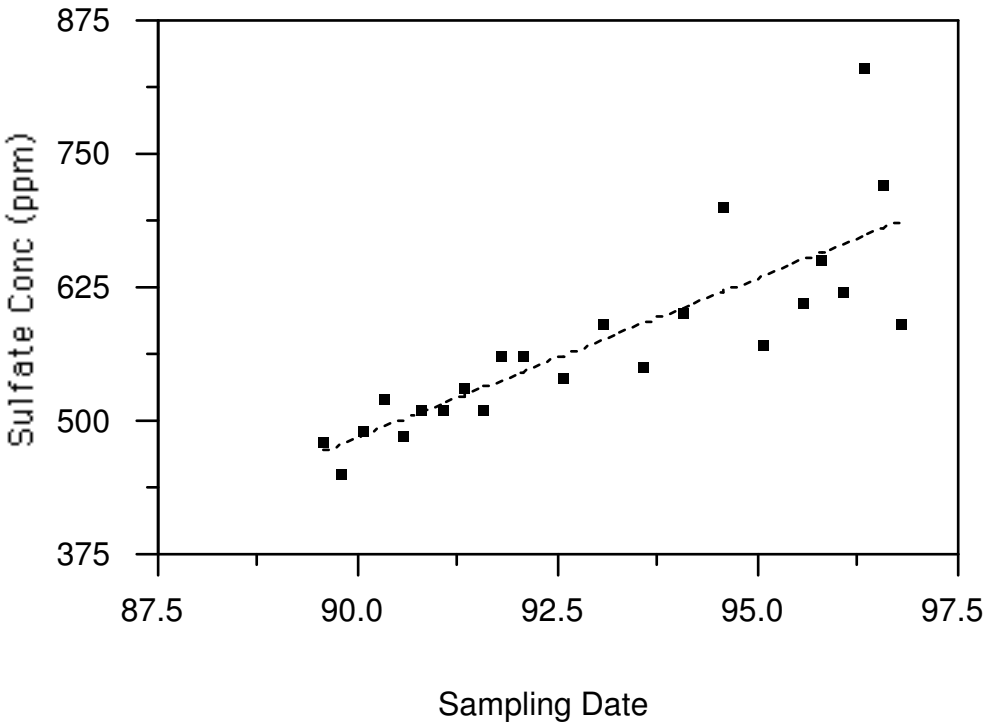
Finally, using equation [17.29], the normalized Mann-Kendall statistic is:

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$$Z = (|194| - 1)/37.79 = 5.11$$

Step 4. The Z statistic can be compared to a critical point from the standard normal distribution in **Table 10-1** in **Appendix D**. As large as it is, the test statistic is bigger than the critical point for any usual significance level, suggesting that the trend appears to be real and not just a chance artifact of the sample. ◄

Figure 17-6. Time Series Plot of Sulfate Concentrations (ppm)



17.3.3 THEIL-SEN TREND LINE

BACKGROUND AND PURPOSE

The Mann-Kendall procedure is a non-parametric test for a significant slope in a linear regression of the concentration values plotted against time of sampling. But the Mann-Kendall statistic S does not indicate the *magnitude* of the slope or estimate the trend line itself even when a trend is present. This is slightly different from parametric linear regression, where a test for a significant slope follows naturally from the estimate of the trend line. Even a relatively modest slope can be statistically distinguished from zero with a large enough sample. It is best to first identify whether or not a trend exists, and then determine how steeply the concentration levels are increasing over time for a significant trend. The *Theil-Sen trend line* (Helsel, 2005) is a non-parametric alternative to linear regression which can be used in conjunction with the Mann-Kendall test.

The Theil-Sen method handles non-detects in almost exactly the same manner as the Mann-Kendall test. It assigns each non-detect a common value less than any other detected measurement (*e.g.*,

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half the RL). Unlike the Mann-Kendall test, however, the actual concentration values are important in computing the slope estimate in the Theil-Sen procedure. The essential idea is that if a *simple slope estimate* is computed for every pair of distinct measurements in the sample (known as the set of *pairwise slopes*), the average of this series of slope values should approximate the true slope. The Theil-Sen method is non-parametric because instead of taking an *arithmetic average* of the pairwise slopes, the *median* slope value is determined. By taking the median pairwise slope instead of the mean, extreme pairwise slopes — perhaps due to one or more outliers or other errors — are ignored and have little if any impact on the final slope estimator.

The Theil-Sen trend line is also non-parametric because the median pairwise slope is combined with the median concentration value and the median sample date to construct the final trend line. As a consequence of this construction, the Theil-Sen line estimates the change in *median* concentration over time and not the *mean* as in linear regression.

REQUIREMENTS AND ASSUMPTIONS

The Theil-Sen procedure does not require normally-distributed trend residuals as in a linear regression. It is also not critical that the residuals be homoscedastic (*i.e.*, having equal variance over time and with increasing average concentration level). It *is* important to have at least 4 and preferably at least 8 or more observation on which to construct the trend. But trend residuals are assumed to be statistically independent. Approximate checks of this assumption can be made using the techniques of **Chapter 14**, once the estimated trend has been removed and the number of non-detect data is limited. Sampling events should also be spaced far enough apart relative to the site-specific groundwater velocity so that an assumption of *physical* independence of consecutive sample volumes is reasonable.

A more difficult problem is encountered when a large fraction of the data is non-detect. As long as less than half the measurements are non-detects occurring in the lower part of the observed concentration range, the median concentration value will be quantified and the median pairwise slope will generally be associated with a pair of detects. Larger proportions of non-detect data make computation of the Theil-Sen trend line more difficult and uncertain. The reason is that each time a non-detect is paired with a quantified measurement, the pairwise slope is known only within a range of values. One end of the range results from supposing the true non-detect concentration is equal to zero; the other when the non-detect concentration is equal to the RL.

PROCEDURE

Step 1. Order the data set by sampling event or time of collection, x_1, x_2, to x_n. Then consider all possible distinct pairs of measurements, (x_i, x_j) for $j > i$. For each pair, compute the simple pairwise slope estimate:

$$m_{ij} = \left(x_j - x_i\right) \Big/ \left(j - i\right) \qquad [17.32]$$

With a sample size of n, there should be a total of $N = n(n–1)/2$ such pairwise estimates m_{ij}. If a given observation is a non-detect, use half the RL as its estimated concentration.

Step 2. Order the N pairwise slope estimates (m_{ij}) from least to greatest and rename them as $m_{(1)}$, $m_{(2)}$, …, $m_{(N)}$. Then determine the Theil-Sen estimate of slope (Q) as the median value of this list.

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Finding this value will depend on whether N is even or odd, but the following equation can be used:

$$Q = \begin{cases} m_{(\lceil N+1 \rceil/2)} & \text{if } N \text{ is odd} \\ \left(m_{(N/2)} + m_{(\lceil N+2 \rceil/2)}\right)/2 & \text{if } N \text{ is even} \end{cases} \quad [17.33]$$

Step 3. Order the sample by concentration magnitude from least to greatest, $x_{(1)}$, $x_{(2)}$, to $x_{(n)}$. Determine the median concentration with the formula:

$$\tilde{x} = \begin{cases} x_{(n+1)/2} \ \textit{if n is odd} \\ \left(x_{n/2} + x_{(n+2)/2}\right)/2 \quad \textit{if n is even} \end{cases} \quad [17.34]$$

Again replace each non-detect by half its RL during this calculation. Also find the median sampling date ($\tilde{t}$) using the ordered times t_1, t_2, to t_n by a similar computation.

Step 4. Compute the Theil-Sen trend line with the equation:

$$x = \tilde{x} + Q \cdot \left(t - \tilde{t}\right) = \left(\tilde{x} - Q \cdot \tilde{t}\right) + Q \cdot t \quad [17.35]$$

Using equation [17.35], an estimate can be made at any time (t) of the expected median concentration (x).

►EXAMPLE 17-7

Use the following sodium measurements to compute a Theil-Sen trend line. Note that the sample dates are recorded as the year of collection (2-digit format) plus a fractional part indicating when during the year the sample was collected. This allows an annual slope estimate, since 1 unit = 1 year.

Sample Date (yr)	Sodium Conc. (ppm)
89.6	56
90.1	53
90.8	51
91.1	55
92.1	52
93.1	60
94.1	62
95.6	59
96.1	61
96.3	63

SOLUTION

Step 1. Compute the pairwise slopes for each distinct pair of measurements using equation [17.32]. With n = 10 observations, there will be a total of 10(9)/2 = 45 such pairs. The first few are listed below:

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$$m_{12} = (53-56)/(90.1-89.6) = -6$$
$$m_{13} = (51-56)/(90.8-89.6) = -4.17$$
$$m_{14} = (55-56)/(91.1-89.6) = -.667$$

Step 2. Since the total number of distinct pairs is odd, sort the list of pairwise slopes as in the table below and let Sen's estimated slope equal the middle or 23rd largest value in this list. This gives an estimate of Q = 1.33 ppm increase *per year*, an estimate in line with the time series plot of **Figure 17-7**.

Step 3. Compute the median concentration value $\tilde{x} = 57.5$ and the median sample date $\tilde{t} = 92.6$ from the table above. Then calculate the Theil-Sen trend line using the slope estimate from Step 2:

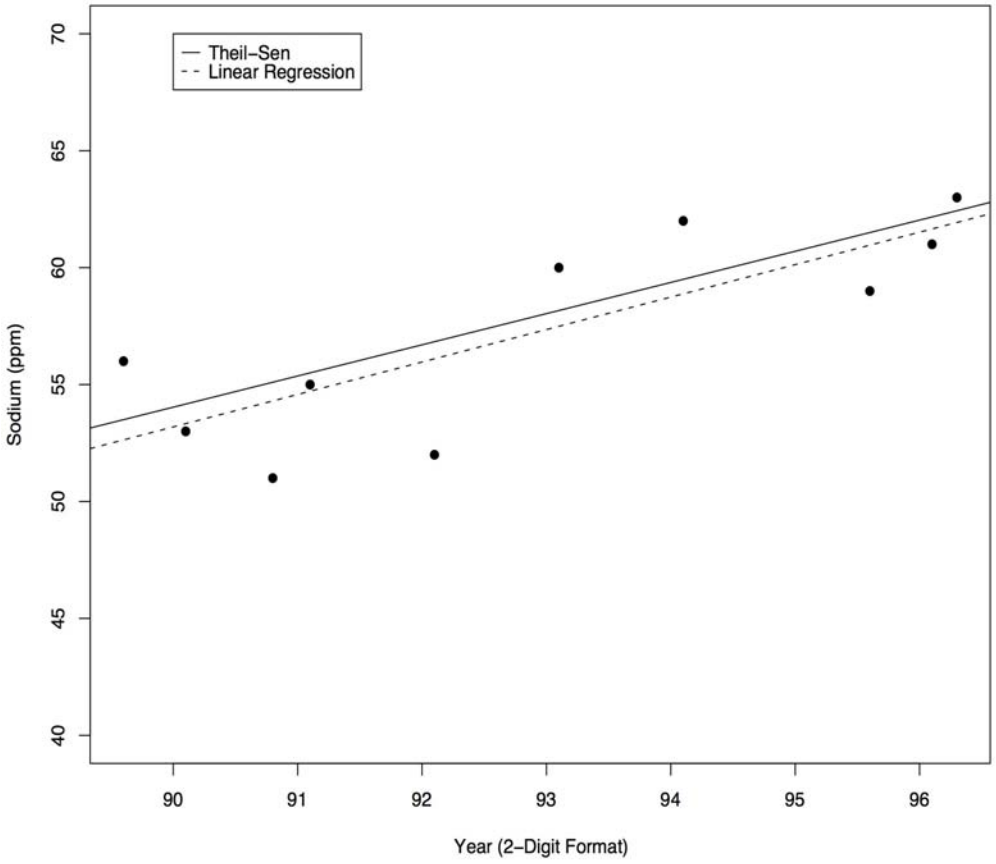
$$x = 57.5 + 1.333(t - 92.6) = -65.97 + 1.333t$$

This trend line can be used to estimate the predicted median concentration (x) at any desired time in years (t). For example, at the beginning of 1998 (t = 98), the trend line would predict a median sodium concentration of approximately x = 64.7 ppm. ◄

Rank	Pairwise Slope	Rank	Pairwise Slope
1	-6	24	1.538
2	-4.167	25	1.613
3	-3	26	1.667
4	-2.857	27	1.887
5	-2	28	2
6	-1.6	29	2
7	-0.667	30	2
8	-0.5	31	2.182
9	-0.5	32	2.25
10	-0.4	33	2.25
11	0.333	34	2.333
12	0.455	35	2.333
13	0.5	36	2.5
14	0.769	37	2.619
15	0.769	38	3.333
16	0.889	39	3.913
17	0.938	40	4
18	1.045	41	5
19	1.091	42	5.714
20	1.143	43	8
21	1.2	44	10
22	1.333	45	13.333
23	1.333		

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Figure 17-7. Time Series Plot of Sodium Concentrations (ppm)



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CHAPTER 18. PREDICTION LIMIT PRIMER

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This chapter introduces the concept of statistical intervals and focuses on several types of prediction limits useful for detection monitoring. The requirements and common assumptions of such limits are explained, as well as specific descriptions of:

- Prediction limits for *m* future values (**Section 18.2.1**)
- Prediction limits for future means (**Section 18.2.2**)
- Non-parametric prediction limits for *m* future values (**Section 18.3.1**)
- Non-parametric prediction limits for a future median (**Section 18.3.2**)

18.1 INTRODUCTION TO PREDICTION LIMITS

First discussed in **Chapter 6,** *prediction limits* belong to a class of methods known as *statistical intervals*. Statistical intervals represent concentration or measurement ranges computed from a sample that are designed to estimate one or more characteristics of the parent population. In groundwater monitoring, statistical intervals offer a convenient and statistically valid way to test for significant differences between background versus compliance point groundwater measurements.

The statistical interval accounts for variability inherent not only in future measurements, but also additional uncertainty in the prediction limit itself. The latter is derived from a relatively small background sample with an associated level of variability in estimating the true characteristics of the underlying groundwater population.

Prediction limits are generally easy to construct and have a straightforward interpretation. Background data are used to construct a concentration limit *PL*, which is then compared to one or more observations from a compliance point population. The acceptable range of concentrations includes all values no greater than the prediction limit. The appropriate *prediction interval* will generally have the form [0, *PL*], with the upper limit *PL* as the comparison of importance. Unless pH or a similar parameter is being monitored, a one-sided upper prediction limit is used in detection monitoring.

A significant advantage to prediction limits is their *flexibility*, which can accommodate a wide variety of groundwater monitoring networks. Prediction limits can be constructed so that as few as *one*

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new measurement per compliance well may suffice for a test. Prediction limits may be based on a comparison of means, medians, or individual compliance point measurements, depending on the characteristics of the monitoring network and the constituents being tested.

Prediction limits can also be designed to accommodate a wide range of *multiple statistical comparisons* or *tests*. Each periodic statistical evaluation (*e.g.*, semi-annually) under RCRA and other regulations involves separate tests at all compliance well locations for each monitoring constituent. Often, the number of separate statistical tests can be quite sizeable. Prediction limits can be constructed to precisely account for the number of tests to be conducted, so as to limit the *site-wide false positive rate* [SWFPR] and ensure an adequate level of *statistical power* (see discussion in **Chapter 6**).

This and the following chapter present basic concepts and procedures for using prediction limits as detection monitoring tests. The intent is to provide a relatively simple framework for using prediction limits in RCRA or CERCLA groundwater monitoring. **Chapter 18** describes the construction of prediction limits for tests involving a single constituent at one well. It describes the basic mechanics of each type of prediction limit and how they differ from one another.

Chapter 19 expands this discussion to cover multiple *simultaneous* prediction limit tests (*i.e.*, all occurring during a single statistical evaluation or during a single year of monitoring). Cumulative SWFPRs and statistical power are considered, including how these criteria impact the expected performance of a given prediction limit strategy. Examples are provided to illustrate these procedures, as well as explanations of associated tables and software.

Specific strategies in **Chapter 19** apply the concept of *retesting*. Generally speaking, ***almost any prediction limit procedure in detection monitoring should be combined with an appropriate retesting strategy***. The reason is that when testing a large number of compliance point samples, it is almost guaranteed that one or more measurements will exceed an upper prediction limit. *Resampling* of those wells where an exceedance has occurred can either verify the initial evidence of a release or disconfirm it, while avoiding unnecessary false positives.

Chapter 6 introduced a number of key terms used in the Unified Guidance, especially for prediction limit and control chart tests. The guidance applies the term *comparison* to individual future measurements or sample statistics evaluated against a prediction limit (or *control chart limit*), and the term *test* to represent a series of future data comparisons that ultimately result in a statistical decision. A 1-of-*m* retesting procedure (described below), for instance, might involve comparison of up to *m* distinct sample measurements against the prediction limit. Each of these individual samples involves a *comparison*, but only after all the necessary individual comparisons have been made is the *test* complete. This distinction becomes particularly important when properly determining SWFPRs, a subject discussed both in **Chapter 6** and **Chapter 19**.

One or more *future* observations are collected for purposes of testing compliance well data, as distinct from the *background* sample from which the prediction limit is constructed. Background data can be obtained from upgradient wells or in combination with historical, uncontaminated compliance well data. In intrawell testing, data from an individual compliance well constitute both the background and future samples. The two data sets need to be distinct and may not overlap, even if the historical

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background data is periodically updated with previously evaluated future samples. The key idea is that at any given point in time, background and future data sets are clearly distinguished.

Formally, prediction limits are constructed to contain one or more future observations or sample statistics generated from the background population with a specified probability equal to (1–α). The probability (1–α) is known as the confidence level of the limit. It represents the chance — over repeated applications of the limit to many similar data sets — that the prediction limit will contain future observations or statistics drawn from its background population.

A sample of *n* background measurements is used to construct the prediction limit. Under the null hypothesis that the compliance point population is identical to background, a set of *m* independent compliance point observations or a statistic like the mean based on those observations (*i.e.*, the future data) is then compared against the prediction limit. For the prediction limit to serve as a valid statistical test, the future observations are initially presumed to follow the same distribution as background.

Only background values are used to construct the prediction limit. But the probability that the limit contains all *m* future observations or sample statistics derived from those future data does not depend solely on the observed background. It is also based on the number of future measurements or sample statistics used in the comparison and *how* the individual comparisons are conducted. To underscore this point, consider the general equation for a prediction limit based on normal or transformably normal populations, given by

$$PL = \bar{x} + \kappa s \qquad [18.1]$$

where $\bar{x}$ is the sample mean in background, s is the background standard deviation, and κ is a multiplier depending on the type of prediction limit under construction. The simplest type of prediction limit test compares a specific number of individual future observations to the limit (*PL*). For example, do all three compliance measurements collected during a 6-month period fall within the prediction interval? The multiplier κ and hence the prediction limit itself, changes depending on whether one, two or three compliance observations will be compared against *PL*. More generally, the κ-multiplier is selected to account not only for the number of future comparisons, but also for the *rules of the comparison strategy* and the number of simultaneous tests to be conducted (*e.g.*, the number of monitoring constituents times the number of compliance wells).

In the simplest case of a successive comparison of *m* individual future measurements against *PL*, the test is labeled as an *m*-of-*m* prediction limit. All *m* of the future observations need to fall within the prediction interval for the test to 'pass' — that is, be no greater than *PL*. If any one or more of the future values exceed the PL, the test fails and the well is deemed to have a *statistically significant increase* [SSI] or constitute an exceedance.

The κ-multiplier appropriate for an *m*-of-*m* prediction limit test is different from the multipliers that would be computed for other kinds of comparison rules. Another simple type is a comparison of a single future *mean of order p*. Here, *p* future measurements are collected and *averaged* before comparing against *PL*. If the order-*p* mean is no greater than *PL*, the test passes; otherwise, it fails. A test following this rule is labeled a *1-of-1 prediction limit on a future mean*. The important thing to remember is that the κ-multiplier and thus the prediction limit will differ depending on whether or not the *p* future values are first averaged or simply compared against *PL* one-by-one. The choice to use one rule versus the other

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impacts the magnitude of the prediction limit and ultimately its expected statistical power and false positive rate.

Other comparison rules of substantial benefit in groundwater monitoring are 1-of-*m* prediction limit on future observations or a statistic like the mean or median. This test requires at least one of *m* successive observations or statistic to fall within the prediction interval in order to pass. Operationally this means that if an initial compliance well measurement is no greater than *PL*, the test is complete and no further sampling need be done. If the initial value exceeds *PL,* one or more of (*m*–1) *resamples* need to be obtained. Since these additional measurements are collected sequentially over sufficiently long time periods to maintain approximate statistical independence (**Chapter 3**), the first resample to fall within the prediction interval also ends the test as 'inbounds' or passing, frequently obviating the need to gather all *m* measurements.

Another comparison rule of some use is known as the California strategy, first developed for the State of California RCRA program. The California strategy can be construed as a *conditional* rule: if an initial future observation is no greater than *PL*, further comparisons are not needed and the test passes. However, if the initial observation exceeds the *PL*, 2-of-2 or 3-of-3 resamples *all need to not exceed the PL* in order for the well to remain in compliance. A slight modification to this rule termed the *modified California* approach has better statistical power and false positive rate characteristics than the original California strategies, and is therefore included as a potential prediction limit test.

18.1.1 BASIC REQUIREMENTS FOR PREDICTION LIMITS

All prediction limits share certain basic assumptions when applied as tests of groundwater. Further, *parametric* prediction limits as presented in the Unified Guidance require the sample data to be either normally-distributed or normalized via a transformation. The key points can be summarized as follows:

1. background and future sample measurements need to be identically and independently distributed (the *i.i.d.* presumption; see **Chapter 3**);
2. sample data do not exhibit temporal non-stationarity in the form of trends, autocorrelation, or other seasonal or cyclic variation;
3. for interwell tests (*e.g.*, upgradient-to-downgradient comparisons), sample data do not exhibit non-stationary distributions in the form of significant natural spatial variability;
4. background data do not include statistical outliers (a form of non-identical distributions);
5. for parametric prediction limits, background data are normal or can be normalized using a transformation; and
6. a minimum of 8 background measurements is available; more for non-parametric limits or when accounting for multiple, simultaneous prediction limit tests.

The first assumption implies that background data are randomly drawn from a single common parent population, especially if aggregated from more than one source well. As discussed in **Chapter 5**, analysis of variance [ANOVA] can be used to determine the appropriateness of pooling data from

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different background wells. There is also a presumption that the compliance point measurements follow the same distribution as background in the absence of a release.

The second assumption is corollary to the first, and requires that the background data are *stationary over time* (**Chapter 3**). This can be evaluated with one or more techniques described in **Chapter 14** on temporal variability. These account for trends, autocorrelation, or other variation, perhaps by utilizing *data residuals* instead of the raw measurements. If the background residuals meet the basic points above, they can be used to construct an adjusted prediction limit. Residuals of the future observations would also need to be computed and compared against the adjusted prediction limit to ensure a valid and consistent test.

The second assumption also requires that there be only a single source of variation in the data, when using the usual sample standard deviation (s) to compute the prediction limit. If there are other sources of variation such as seasonal patterns or temporal variation in lab analytical performance, these should be included in the estimate of variability. Otherwise s is likely to be *biased*. One method to accomplish this is by use of an appropriate ANOVA model to include temporal factors affecting the variability (**Chapter 14**). Determination of the components of variance in more complicated models is beyond the scope of this guidance and may require consultation with a professional statistician.

The third assumption requires that background and compliance point populations be identical in distribution, absent a release, for interwell tests. Spatial variation violates this assumption since the well population means (μ) will be different, making it impossible to know whether an apparent upgradient-to-downgradient difference is attributable to a release or simply variations in natural groundwater concentration levels. The assumption also requires that each population share a common variance (σ^2). Tests of equal variance (*i.e.*, homoscedasticity) when using prediction limits may be possible either by examining groups of historical background and compliance point data or by performing periodic tests when enough compliance point measurements have been accumulated to make a diagnostic test possible.

The fourth assumption implies that background data should be screened for outliers using the techniques in **Chapter 12**. Statistical outliers can potentially inflate a prediction limit and severely limit its statistical power and accuracy by over-inflating both the sample background mean ($\bar{x}$) and especially the background standard deviation (s). The Unified Guidance discourages automated removal of outliers from background samples, but all possible outliers should be examined to determine whether a cause can be identified (see discussion in **Chapter 6**). In some cases, an apparent outlier may represent a valid portion of the underlying background population that has not yet been sampled or observed. It also could represent evidence that conditions in background have changed or are changing.

The fifth assumption of normality for parametric prediction limits can be evaluated using the diagnostic techniques described in **Part II** of the guidance. If skewed background data can be normalized via a transformation (*e.g.*, the natural logarithm), the prediction limit should be constructed on the transformed background values. The resulting limit should either be: 1) back-transformed to the concentration domain (*e.g.*, by exponentiation) when comparing future individual compliance observations; or 2) left in the transformed scale when compared to future mean compliance data also based on *the same transformation*. In the latter case, use of a logarithmic transformation results in evaluating population medians or geometric means and *not* the arithmetic means.

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When normality cannot be justified, a non-parametric prediction limit should be considered instead. A non-parametric limit assumes only that all the data come from the same, usually unknown, continuous population. Non-parametric prediction limits generally require a much larger number of background observations in order to provide the same level of confidence (1–α) as a comparable parametric limit. Consequently, the Unified Guidance recommends that a parametric model be fit to the data if at all possible.

The last assumption concerns sufficient background sample sizes. A prediction interval can be computed with as few as three observations from background. However, this can result in an unacceptably large upper prediction limit and a test with very limited statistical power. A sample size of eight or more is generally needed to derive an adequate parametric prediction limit, especially if a retesting strategy is not employed. The exact requirements depend on the number of simultaneous tests (*i.e.*, number of wells times number of constituents per well) to be made against the prediction limit and the type of retesting strategy adopted (see **Chapter 19** for more discussion of retesting strategies).

If a minimum schedule of quarterly sampling is being followed and there is only one background well, at least two years of data will be needed before constructing the prediction limit.[1] If data from multiple background wells screened in comparable hydrologic conditions can reasonably be combined (see **Chapter 5**), pooling background data to increase background sample sizes is encouraged.

18.1.2 PREDICTION LIMITS WITH CENSORED DATA

When a sample contains a substantial fraction of non-detects or left-censored measurements, it may be impossible to even approximately normalize the data A sample data set may originate from a normal or transformable-to-normal population, but the uncertainty surrounding both the censored values and the consequent shape of the lower tail of the distribution prevents a clear identification. If the apparent underlying distribution is not normal or transformable to normality, a non-parametric prediction limit (**Section 18.3**) should be used.

Given that non-parametric prediction limits typically have much steeper background data requirements than their parametric counterparts, one remedy is to attempt a fit to normality by using censored probability plots (**Chapter 15**) in conjunction with either the *Kaplan-Meier* or *robust regression on order statistics* [ROS] techniques (**Chapter 15**) for left-censored data. Censored observations prevent a full and complete ordering of the sample, making it difficult to assess normality with standard probability plots (**Chapter 9**). Censored probability plots, on the other hand, only graph the detected values, but do so based on a *partial ordering and ranking* of the sample. Data that appear distinctly non-normal on a standard probability plot (where non-detects are perhaps replaced by half their reporting limits [RLs] to allow plotting) can sometimes appear reasonably normal on a censored probability plot. Transformations can also be applied and the censored probability plot reconstructed to see if the data can be normalized in that fashion.

[1] The Unified Guidance does not recommend that only one background well be used in any kind of interwell or upgradient-to-downgradient comparison. Multiple background wells are always preferred so that tests for spatial variability may be made and the exact nature of background better understood.

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If the censored probability plot is close to linear and the sample approximately normalized, an estimated mean and standard deviation should be computed. These estimates will not be the same if each non-detect were replaced by half its RL, and the sample mean calculated from the resulting imputed sample. To properly account for the censoring, the estimated mean (denoted as $\hat{\mu}$) and the estimated standard deviation ($\hat{\sigma}$) needs to be derived as parameters from the normal distribution providing the closest fit to a partial ordering of the sample (as on a censored probability plot). The Unified Guidance describes two slightly different techniques for accomplishing this task.

Once $\hat{\mu}$ and $\hat{\sigma}$ estimates have been computed, an adjusted parametric prediction limit is constructed by substituting $\hat{\mu}$ for $\bar{x}$ and $\hat{\sigma}$ for s in the equations of **Section 18.2** or **Chapter 19**. For example, the adjusted equation for a general parametric prediction limit would become:

$$PL = \hat{\mu} + \kappa \cdot \hat{\sigma} \qquad [18.2]$$

Another potential difference between the adjusted prediction limit in equation [18.2] and the unadjusted prediction limit in equation [18.1] is the number of *degrees of freedom* [*df*] used in selecting the κ-multiplier. Absent any censored measurements, a background sample of size n would normally have (n–1) *df*. With censoring, there is greater statistical uncertainty surrounding each non-detect than surrounding the detected values. Because of this, the actual degrees of freedom is somewhere between d (the number of detects) and (n–1) (the total sample minus one). Unfortunately, there is no straightforward, general method to determine the true *df*. To be conservative, the *df* should be set equal to d, since the value of each detect is known with reasonable certainty. Setting a lower *df* tends to raise the κ-multiplier and thus the prediction limit over what would be selected with an uncensored sample of the same size. This is consistent with the greater uncertainty associated with non-detect measurements. However, it is at best an approximate remedy. Further consultation with a professional statistician may be warranted to arrive at a better choice of the degrees of freedom.

18.2 PARAMETRIC PREDICTION LIMITS

18.2.1 PREDICTION LIMIT FOR M FUTURE VALUES

BACKGROUND AND PURPOSE

A prediction limit test for m future values is constructed so that m compliance point observations are evaluated by determining whether or not they fall within a prediction interval derived from background. As mentioned in **Chapter 2**, some State programs may require up to 4 successive sampling events per evaluation period for testing, which can be addressed by the prediction limit approach described below.

If the distributions of background and compliance point data are identical as assumed under the null hypothesis H_0, *all m of the compliance point observations* should be no greater than the upper prediction limit [*PL*]. If any of the future observations exceeds *PL*, there is statistical evidence that the

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compliance data do not come from the same distribution as background, but instead are elevated above background.[2]

With intrawell comparisons, a prediction limit can be computed on historical data or intrawell background to contain a specified number (*m*) of future (*i.e.*, more recent) observations from the same well. If any of the future values exceeds the upper prediction limit, there is evidence of recent contamination at the well.

REQUIREMENTS AND ASSUMPTIONS

As noted in **Section 18.1**, the prediction limit test on *m* future values is designated as an *m*-of-*m* test. *Each* of the *m* individual future observations need to be compared to the prediction limit [*PL*]. All should be no greater than *PL* for the test to pass. The number of future observations to be collected (*m*) need to be specified *in advance* in order to correctly compute the κ-multiplier from equation [18.1]. Consequently, if compliance data are collected on a regular schedule, the prediction interval can be constructed to cover a specified *time period* of future sampling. Usually this period will coincide with the time between statistical evaluations specified in the site permit (*e.g.*, on a semi-annual or annual basis). Keep in mind also that *m* denotes the number of consecutive sampling events being compared to the prediction limit at a given well for a given constituent.

As discussed in more detail in **Chapter 6**, a new prediction limit should be constructed prior to each statistical evaluation for *interwell* tests, when additional background data have been collected along with the new compliance point measurements. Unless there is evidence of characteristic changes within background groundwater quality (*e.g.*, as demonstrated by observable trends in background), background data should be amassed or accumulated over time. Earlier background measurements need not be discarded, both to maintain an adequate background sample size and also because a larger span of sampling results will provide a better statistical description of the underlying background population. The revised prediction limit will then reflect a larger background sample size, *n*, but possibly the same number, *m*, of future values to be predicted at the next statistical evaluation.

For *intrawell* tests, the prediction limits should be revised only after intrawell background has been updated (**Chapter 5**). Such updating may not coincide with the regular schedule of statistical evaluations if done, for instance, every two years or so. In that case, the same intrawell prediction limit might be used for multiple evaluations before being revised.

PROCEDURE

Step 1. Calculate the sample mean $\bar{x}$, and standard deviation *s*, from the set of *n* background measurements.

Step 2. Specify the number of individual future observations (*m*) from the compliance well to be included in the prediction interval for an *m*-of-*m* test. For an upper prediction limit with an overall $(1-\alpha)$ confidence test level for the *m* comparisons, use the equation:

[2] In the context of the Unified Guidance, *m* represents the number of consecutive samples being compared in the prediction limit test for a given well and constituent.

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$$PL = \bar{x} + t_{1-\alpha/m,n-1} s \sqrt{1+\frac{1}{n}} \quad [18.3]$$

It is assumed that exactly *m* consecutive sample values from the compliance point will be compared against the upper *PL*. Note that the quantile from a Student's *t*-distribution used in equation [18.3] has two parameters: the degrees of freedom (*n*–1) and a joint comparison confidence level $(1-\alpha/m)$. Most Student's *t*-quantiles can be found directly or approximated through interpolation by looking in **Table 16-1** of **Appendix D**.

Note: equation [18.3] assumes the prediction limit is applied to only one constituent at a single well. If multiple tests need to be performed (e.g., on multiple wells and/or multiple constituents), the prediction limit takes the form:

$$PL = \bar{x} + \kappa s \quad [18.4]$$

where the κ-multiplier is determined using one of the strategies described in **Chapter 19**.

If a log transformation is applied to the data to bring about approximate normality, the upper *PL* should be constructed using the log-mean ($\bar{y}$) and log-standard deviation (s_y), using the equation:

$$PL = \exp\left(\bar{y} + t_{1-\alpha/m,n-1} s_y \sqrt{1+\frac{1}{n}} \right) \quad [18.5]$$

If multiple tests must be conducted and a log transformation has been applied to the data, the upper *PL* will have the form:

$$PL = \exp\left(\bar{y} + \kappa s_y\right) \quad [18.6]$$

Note: other transformations besides the natural logarithm are handled in a similar manner; compute the prediction limit on the transformed data, then back-transform the limit to the original concentration scale prior to comparison with any future observations.

Step 3. Once the prediction limit (*PL*) has been calculated, compare each of *m* compliance point future values against *PL*. If all of these measurements are no greater than *PL*, the test passes and the well is deemed to be in compliance. If, however, any compliance point concentration exceeds *PL*, there is statistically significant evidence of an increase over background.

►EXAMPLE 18-1

The data in the table below represent quarterly arsenic concentrations measured in a single well at a solid waste landfill. Calculate an intrawell upper prediction limit for 4 future samples with 95% confidence and determine whether there is evidence at the annual statistical evaluation of a possible release during Year 4 of monitoring.

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Intrawell Background		Compliance Data	
Sampling Period	Arsenic (ppb)	Sampling Period	Arsenic (ppb)
Year 1	12.6	Year 4	48.0
	30.8		30.3
	52.0		42.5
	28.1		15.0
Year 2	33.3		
	44.0		
	3.0		
	12.8		
Year 3	58.1		
	12.6		
	17.6		
	25.3		
	n = 12		
	Mean = 27.52		
	SD = 17.10		

SOLUTION

Step 1. First check the sample data for the key points identified in **Section 18.1.1**. As an example, a Shapiro-Wilk test on the background data gives a test statistic of $SW = 0.947$. The critical point at the $\alpha = .05$ level for the Shapiro-Wilk test on $n = 12$ observations is 0.859. Since the test statistic exceeds the critical point, there is insufficient evidence to reject an assumption of normality.

Step 2. Compute the prediction interval using the raw background data. The sample mean and standard deviation of the 12 background samples are 27.52 ppb and 17.10 ppb, respectively.

Step 3. A single future year of compliance data then is compared to the prediction limit, leading to a test of $m = 4$ individual measurements. Setting the overall confidence level to $(1-\alpha) = 95\%$, the probability used to determine an appropriate Student's t-quantile needs to be set to $(1-\alpha/m) = 1-.05/4 = .9875$. The t-distribution with probability .9875 and (n–1) = 11 degrees of freedom in **Table 16-1** of **Appendix D** results in a t-quantile of 2.593. Using equation [18.3], the upper prediction limit can be computed as:

$$PL = 27.52 + t_{.9875,11}(17.10)\sqrt{1+\frac{1}{12}} = 27.52 + 2.593(17.10)\sqrt{1.0833} = 73.67 \text{ ppb}$$

Step 4. Compare the upper PL to each compliance measurement in Year 4. None of the four observations exceeds 73.67 ppb. Consequently, there is no statistically significant evidence of arsenic contamination during that year. ◄

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18.2.2 PREDICTION LIMIT FOR A FUTURE MEAN

BACKGROUND AND PURPOSE

Although prediction limits are often constructed as bounds on extreme individual measurements, they can also be formulated to predict an acceptable range of concentrations for the *mean* of *p* future values. The comparison rule for the test is then different: instead of requiring all of a set of m individual values to fall within the prediction interval for the test to pass, only the *average* of the (*p*) future values should not exceed the prediction limit.

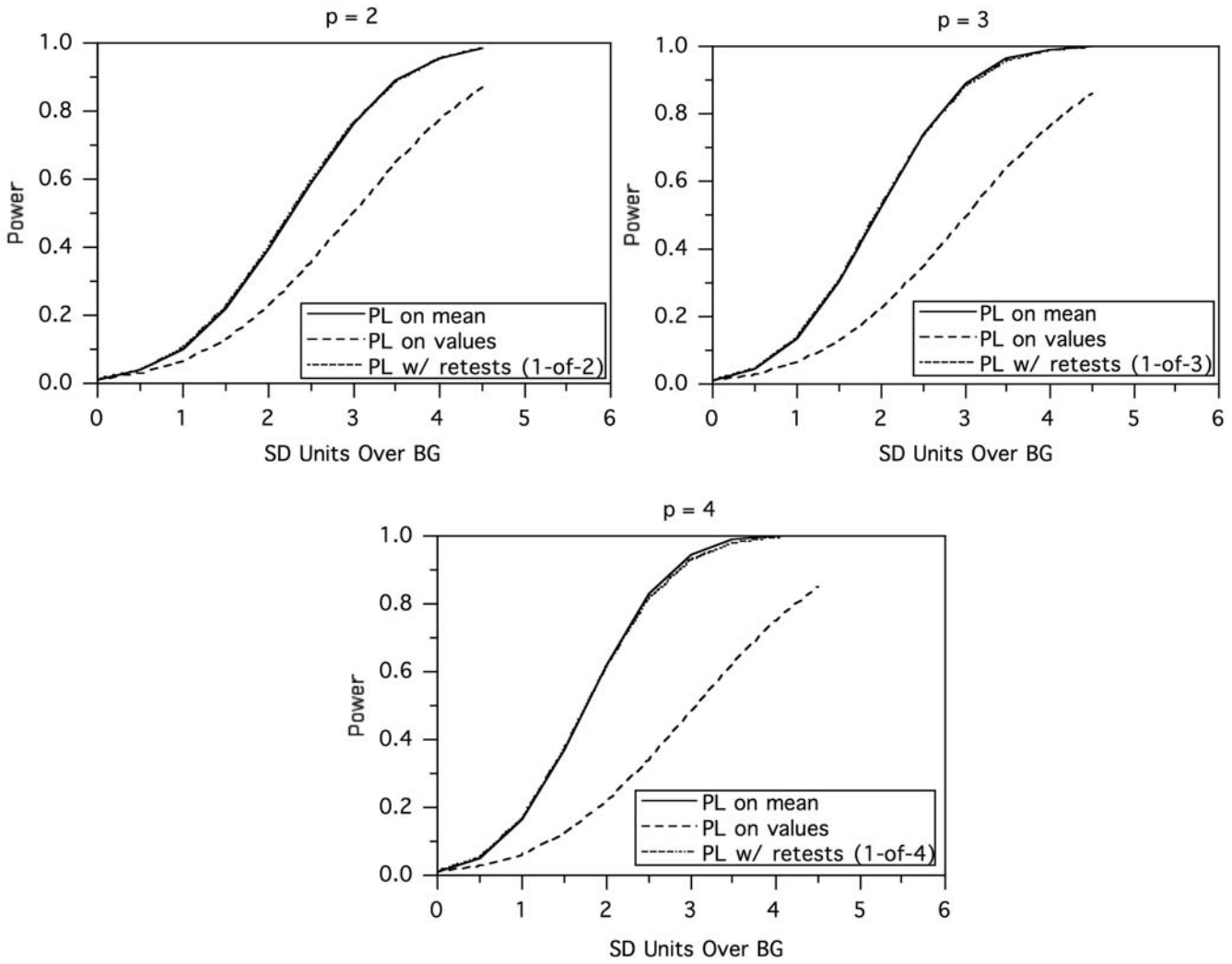
In this setting, the prediction limit for a future mean is more nearly akin to a *t*-test or parametric ANOVA, since the mean of the compliance point well is compared to a limit based on the background mean. The principal differences in using a prediction limit as opposed to those tests are: first that the variability of the compliance point population is *assumed* to be identical to that in background. With a *t*-test or ANOVA, each distinct well group contributes to the overall estimate of variability, not merely the background values. Secondly, t-tests and especially ANOVA are typically utilized as interwell tests, whereas prediction limits for a future mean can be constructed for either interwell or intrawell testing.

The hypothesis being tested when using a prediction limit for a future mean in detection monitoring is exactly the same as that posited for a prediction limit for *m* future values, namely, H_0: background population is identical to compliance population (implying $\mu_C \leq \mu_{BG}$) *vs*. H_A: compliance mean is greater than background mean (*i.e.*, $\mu_{DG} > \mu_{BG}$). However, the statistical properties of the two prediction interval formulations are somewhat different.

For the same background sample size (*n*), false positive rate (α), and number of future samples where $p = m$, the power of the prediction limit for a future mean of order *p* with normally-distributed data is generally higher than for a prediction limit of the next *m* individual future observations. *This suggests that* ***when feasible and appropriately implemented,*** *a prediction limit strategy based on future means may be more environmentally protective than a strategy based on predicting individual future measurements*. A few examples of the power differences are presented in **Figures 18-1** and **18-2**.

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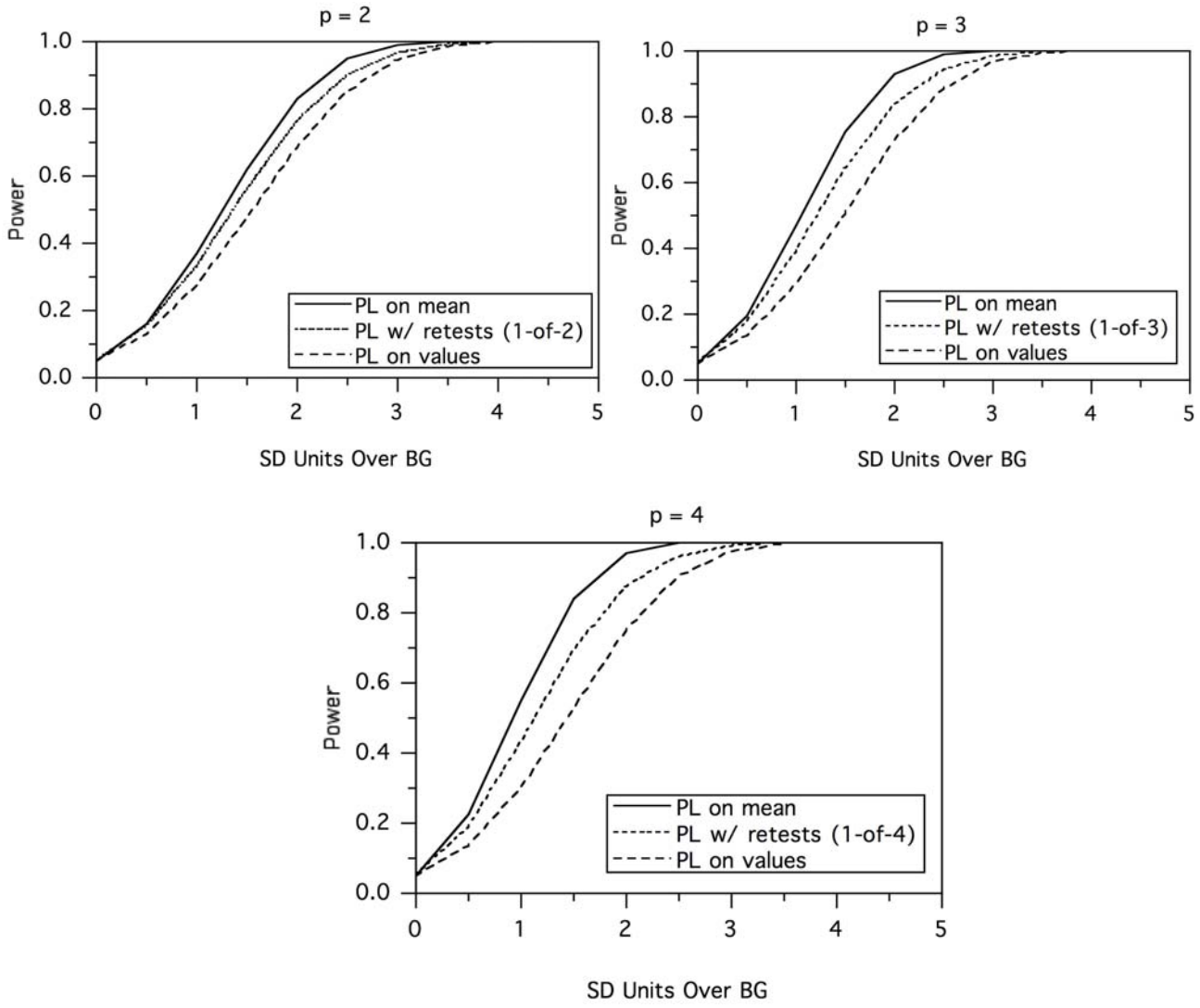
Figure 18-1. Comparison of Prediction limits (BG = 8, α = .01, 1 test)



Even when a retesting strategy is employed, such as the 1-of-*m* schemes for prediction limits on individual values described in **Chapter 19**, the statistical power at best *matches* that of a prediction limit on a single future mean with no retesting, when the same numbers of background and compliance point measurements are used. As **Figure 18-2** illustrates, for some cases the 1-of-*m* power is comparatively lower. Under background conditions, 1-of-*m* strategies provide an earlier indication of *uncontaminated* groundwater, since a single observation can indicate uncontaminated groundwater. By contrast, all $p = m$ individual samples need to be collected to form a mean of order $p = m$ when using a prediction limit test for a single future mean. With a groundwater release, no such potential time savings exists. In that case, *all p or m* samples need to be collected with either type of prediction limit.

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Figure 18-2. Comparison of Prediction limits (BG = 20, α = .05, 1 test)



REQUIREMENTS AND ASSUMPTIONS

Although a prediction limit for a future mean is generally preferable in terms of statistical power for identifying potential contamination, it is not always practical to implement. To accommodate the large number of statistical tests that all but the smallest sites must contend with, the Unified Guidance recommends that almost any prediction limit be implemented in conjunction with a retesting strategy (**Chapter 19**). Otherwise, the prediction limit formulations provided in this chapter will likely fall short of providing an adequate balance between false negative and positive decision errors. Retesting with a prediction limit for a future mean will necessitate the collection of *p* additional measurements to form the resampled mean, whenever the initial future mean exceeds the prediction limit. Since all prediction limit tests assume that both the background and compliance data are statistically independent, there needs to generally be enough temporal spacing between sampling events to avoid introducing significant autocorrelation in the series of compliance point values.

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If semi-annual evaluation of groundwater quality is required, and depending on data characteristics (see **Chapter 14** discussions on temporal variability), there may not be sufficient time for collecting at least 4 independent groundwater measurements from a given well over a six-month period. This would be the minimum needed to form an initial mean and potentially a resample mean of order 2. To avoid this dilemma, the guidance discusses an alternate approach in **Chapter 19** for using 1-of-1 prediction limit tests on means.

Like the parametric prediction limit for *m* future values, the prediction limit on a future mean assumes that the background data used to construct the limit are either normally-distributed or can be normalized. If a transformation is used (*e.g.*, the natural logarithm) and the limit built on the transformed values, the prediction limit should *not* be back-transformed before comparing to the compliance point data. Rather, because of transformation bias in the mean, the compliance point data should also be transformed, and the future mean computed from the *transformed* compliance measurements. Then the *mean of the transformed values* (*e.g.*, log-mean) should be compared to the prediction limit in the transformed domain. As previously mentioned, the prediction limit in the logarithmic domain is not a test of the arithmetic mean, but rather of the *geometric mean* or *median* (also see **Chapter 16**). In most situations, a decision that the lognormal median at the compliance point exceeds background will also imply that the lognormal arithmetic mean exceeds background.

PROCEDURE

Step 1. Calculate the sample mean, $\overline{x}$, and the standard deviation, *s*, from the set of *n* background measurements.

Step 2. Specify the order (*p*) of the mean to be predicted (*i.e.*, the number of individual compliance observations to be averaged). If the background data are approximately normal and an upper prediction limit with confidence level (1−α) is desired, use the equation:

$$PL = \overline{x} + t_{1-\alpha,n-1} s \sqrt{\frac{1}{p} + \frac{1}{n}} \qquad [18.7]$$

where it is assumed that an average of *p* consecutive sample values from the compliance point will be compared against *PL*. Note that the Student's *t*-quantile used in the equation has two parameters: the degrees of freedom (*n*–1) and the cumulative probability (1−α). Most Student's *t*-quantile values can be found directly or approximated through interpolation by using **Table 16-1** in **Appendix D**.

Note also that equation [18.7] assumes that the prediction limit is applied to only one constituent at a single well. If multiple tests are to be conducted and a retesting procedure is employed, the prediction limit will take the form of equation [18.4] where the κ-multiplier is determined using the tables described in **Chapter 19**.

Step 3. If a log transformation is applied to normalize the background sample, the upper *PL* on the log-scale should be constructed using the log-mean ($\overline{y}$) and log-standard deviation (s_y), using equation [18.8]:

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$$PL = \bar{y} + t_{1-\alpha,n-1} s_y \sqrt{\frac{1}{p} + \frac{1}{n}} \quad [18.8]$$

Note that unlike the lognormal prediction limit for future values, the limit in equation [18.8] is not exponentiated back to the concentration domain. Also, equation [18.8] only applies to a single test (*i.e.*, one constituent at a single well). If multiple tests are to be performed, the prediction limit will have the form:

$$PL = \bar{y} + \kappa s_y \quad [18.9]$$

where the κ-multiplier is again determined from the tables described in **Chapter 19**.

Other transformations are handled similarly: construct the prediction limit on the transformed background, but do *not* back-transform the limit.

Step 4. Once the limit has been computed, compare the compliance point mean against the prediction limit. If the compliance point mean is below the upper *PL*, the test passes. If the mean exceeds the *PL*, there is statistically significant evidence of an increase over background.

►EXAMPLE 18-2

The table below contains chrysene concentration data found in water samples obtained from two background wells (Wells 1 and 2) and a compliance well (Well 3). Compute the upper prediction limit for a future mean of order 4 with 99% confidence and determine whether there is evidence of possible chrysene contamination.

	Chrysene (ppb)			
	Background			Compliance
Month	Well 1	Well 2	Joint	Well 3
1	6.9	15.1		68.0
2	27.3	7.2		48.9
3	10.8	48.4		30.1
4	8.9	7.8		38.1
Mean	13.47	19.62	16.55	46.28
SD	9.35	19.52	14.54	16.40
Log-mean	2.451	2.656	2.553	3.789
Log-SD	0.599	.881	.706	0.349

SOLUTION

Step 1. Before constructing the prediction limit, check the key assumptions. Assuming there is no substantial natural spatial variability and it is appropriate to combine the background wells into a single data pool, the algorithm for a parametric prediction limit presumes that the background data jointly originate from a single normal population. Running the Shapiro-Wilk test on the pooled set of eight background measurements gives $SW = 0.7289$ on the original

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scale and $SW = 0.8544$ after log-transforming the data. Since the critical point for the test at the $\alpha = .10$ level of significance is $sw_{.10,8} = 0.851$ (from **Table 10-3** of **Appendix D**), the results suggest that the data should be fit to a lognormal model. The log-transformed statistics for the joint background and compliance well are also found in the above table.

Step 2. Construct the prediction limit on the pooled and logged background observations. Then $n = 8$, the log-mean is 2.553, and the log-standard deviation is 0.706. Since there are 4 observations in the compliance well, take $p = 4$ as the order of the mean to be predicted. Then setting $(1-\alpha) = .99$, the Student's t-quantile with $(n-1) = 7$ degrees of freedom and cumulative probability of .99 is found from **Table 16-1** in **Appendix D** to be 2.998. Using equation [18.8], the upper prediction limit on the log-scale is computed as:

$$PL = 2.553 + (2.998)(.706)\sqrt{\frac{1}{4}+\frac{1}{8}} = 3.85 \log(ppb)$$

Step 3. Compare the log-mean of the chrysene measurements at Well 3 against the upper prediction limit. Since it is less than the limit, there is insufficient evidence of chrysene contamination at this well at the $\alpha = 0.01$ significance level. ◄

18.3 NON-PARAMETRIC PREDICTION LIMITS

Two basic remedies are available when a data set cannot be even approximately normalized, often due to the presence of a significant fraction of non-detects. If the sample includes left-censored data (*e.g.*, non-detects), a fit to normality can be attempted using censored probability plots (**Chapter 15**) in conjunction with either the *Kaplan-Meier* or *Robust Regression on Order Statistics* [Robust ROS] techniques (**Chapter 15**). If a reasonable normality fit can be found, a parametric prediction limit can be applied. Otherwise, a non-parametric prediction limit can be considered. A non-parametric upper prediction limit is constructed by setting the limit as a large *order statistic* selected from background (*e.g.*, the maximum or second-largest background value).

As with their parametric counterparts, non-parametric prediction limits have an associated *confidence level* $(1-\alpha)$ which indicates the probability that the prediction interval $[0, PL]$ will accurately contain all m of a set of m future values over repeated application on many similar data sets. Unlike parametric limits, the confidence level for non-parametric limits is not *adjustable*. Despite being easily constructed for a fixed background sample size and the number of comparisons, the confidence level associated with the any maximal value used as the prediction limit is also fixed. To increase the confidence level, the primary choices are to *decrease* the number of future values to be predicted, or *increase* the number of background observations.

If existing background can be supplemented with data collected from other background wells (e.g., in interwell testing), a non-parametric test confidence level can be increased. Larger samples also provide a better characterization of site spatial variability. Unfortunately, it may always not be possible to supplement background. In these cases, another option to achieve a desired confidence level and

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correspondingly control the false positive rate is to incorporate a retesting strategy as outlined in **Chapter 19**.

Although non-parametric prediction limits do not require a presumption of normality, other assumptions apply equally to both parametric and non-parametric limits. Checks should be made of statistical independence, identical distributions (under the null hypothesis), and stationarity over time and space as discussed in **Chapter 3** and **Part II** of the guidance. One particular caution for non-parametric limits is that background should ideally be screened ahead of time for possible outliers, since the upper prediction limit may be set to the background maximum or second highest observed value. Unfortunately, this often cannot be accomplished with a formal statistical test. Outlier tests are rather sensitive to the underlying distribution of the data. If this distribution cannot be adequately determined due to the presence of non-detects, an outlier test is not likely to give reliable results.

Instead of a formal test, it may be possible to screen for outliers using box plots (**Chapter 12**). Even with non-detects, the box plot 'whiskers' delineating the concentration range associated with possible outliers are computed from the sample lower and upper quartiles (*i.e.*, the 25th and 75th percentiles), which may or may not be impacted by data censoring, or perhaps mildly so when computing the lower quartile. For large fractions of non-detects, the best that can usually be done is to identify a suspected outlier through close examination of laboratory results and chain-of-custody reports.

One of two steps can be taken in the event a possible outlier is flagged. If an error has occurred, it should be corrected before constructing the prediction limit. If an error is merely suspected but cannot be proven, the prediction limit can be constructed as another order statistic from background instead of the maximum (*e.g.*, the second largest value). This will prevent the suspected outlier from being adopted as the upper prediction limit without ignoring the possibility that it may be a real measurement.

18.3.1 PREDICTION LIMIT FOR M FUTURE VALUES

BACKGROUND AND PURPOSE

Given n background measurements and a desired confidence level $(1-\alpha)$, a non-parametric prediction limit test for m future values is an m-of-m comparison rule. *All m* future samples need to not exceed the upper prediction limit for the test to pass. Thus the procedure is an exact parallel to the parametric prediction limit for future values. Because the method is non-parametric, no distributional model needs to be fit to the background measurements. It is assumed that the compliance point data follow the same distribution as background under the null hypothesis — even if this distribution is unknown. Although no distributional model is assumed, order statistics of any random sample follow certain probability laws which allow the statistical properties of the non-parametric prediction limit to be determined.

Once an order statistic of the sample data (*e.g.*, the maximum value) is selected as the upper prediction limit, Guttman (1970) has shown that the statistical *coverage* of the interval — that is, the fraction of the background population actually contained within the prediction interval — when constructed repeatedly over many data sets, has a *beta probability density* with cumulative distribution equal to

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$$I_t\left(j, n-j+1\right) = \int_{u=0}^{t} \frac{\Gamma\left(n+1\right)}{\Gamma\left(n-j+1\right)\Gamma\left(j\right)} u^{j-1}\left(1-u\right)^{n-j}\, du \qquad [18.10]$$

where n = sample size, j = (rank of prediction limit value), and $\Gamma(n) = (n-1)! = (n-1)\times(n-2)\ldots\times 2\times 1$ denotes the gamma function. If the maximum is selected as the prediction limit, its rank is equal to n and so $j = n$. If the second largest value is chosen as the limit, its rank would be equal to $(n-1)$ and so $j = (n-1)$. The confidence probability for predicting that one future observation (*i.e.*, $m = 1$) from a compliance well does not exceed the prediction limit is equal to the *expected or average coverage* of the non-parametric prediction limit.

Because of these properties, the confidence probability for a prediction limit on one future measurement can be shown to equal $(1-\alpha) = j/(n+1)$. If the background maximum is taken as the upper prediction limit, the confidence level thus becomes n/(n+1). Gibbons (1991a) has shown that the probability of having m future samples all not exceed such a limit is $(1-\alpha) = n/(n+m)$. More generally, the same probability when the jth order statistic is taken as the upper prediction limit becomes (Davis and McNichols, 1999):

$$1-\alpha = \frac{(j+m-1)\cdot(j+m-2)\ldots\cdot(j+1)\cdot j}{(n+m)\cdot(n+m-1)\ldots\cdot(n+2)\cdot(n+1)} \qquad [18.11]$$

Table 18-1 in **Appendix D** lists these confidence levels for various choices of j, n, and m. The false positive rate (α) associated with a given prediction limit can be computed as one minus the confidence level. As this table illustrates, the penalty for not knowing the form of the underlying distribution can be severe. If a non-parametric prediction limit is to be used, *more background observations are needed compared to the parametric setting in order to construct a prediction interval with sufficiently high confidence*. As an example, to predict $m = 2$ future samples with 95% confidence, at least 38 background samples are needed. Parametric prediction intervals do not require as many background measurements precisely because the form of the underlying distribution is assumed to be known.

It is possible to create an approximate non-parametric limit with background data containing all non-detects, by using the RL (often a quantitation limit) as the PL. A quantified value above the PL would constitute an exceedance. A superior procedure is recommended in this guidance, using the Double Quantification Rule described in **Chapter 6**.

PROCEDURE

Step 1. Sort the background data into ascending order and set the prediction limit equal to the maximum, the second-largest observed value or another large background order statistic. Then use **Table 18-1** of **Appendix D** to determine the confidence level $(1-\alpha)$ associated with predicting the next m future samples.

Step 2. Compare each of the m compliance point measurements to the upper prediction limit [*PL*]. Identify significant evidence of possible contamination at the compliance well if one or more measurements exceed the *PL*.

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Step 3. Because the risk of false positive decision errors is greatly increased if the confidence level drops substantially below a target rate of at least 90% to 95%, the actual confidence level (as identified by equation [18.11]) needs to be routinely reported and noted whenever it is below the target level.

Note that equation [18.11] assumes the prediction limit is applied to only one constituent at a single well. If multiple tests must be conducted and a retesting procedure is employed, the confidence level of the prediction limit must be determined using the tables described in **Chapter 19**.

►EXAMPLE 18-3

Use the following trichloroethylene data to compute a non-parametric upper prediction limit for the next $m = 4$ monthly measurements from a downgradient well and determine the level of confidence associated with the prediction limit.

	Trichloroethylene Concentrations (ppb)			
	Background Wells			Compliance
Month	BW-1	BW-2	BW-3	CW-4
1	<5	7	<5	
2	<5	6.5	<5	
3	8	<5	10.5	7.5
4	<5	6	<5	<5
5	9	12	<5	8
6	10	<5	9	14

SOLUTION

Step 1. Determine the background maximum and use this value to estimate the non-parametric prediction limit. In this case, the maximum value of the $n = 18$ pooled background observations is 12 ppb. Set $PL = 12$ ppb.

Step 2. Compare each of the downgradient measurements against the prediction limit. Since the value of 14 ppb for Month 6 exceeds PL, conclude that there is statistically significant evidence of an increase over background at CW-4.

Step 3. Compute the confidence level and false positive rate associated with the prediction limit. Since four future samples are being predicted and $n = 18$, the confidence level equals $n/(n + m) = 18/22 = 82\%$. Consequently, the Type I error or false positive rate is at most $(1 - 0.82) = 18\%$ and the test is significant at the $\alpha = 0.18$ level. This means there is nearly a one in five chance that the test has been falsely triggered. Only additional background data and/or use of a retesting strategy would lower the false positive rate. ◄

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18.3.2 PREDICTION LIMIT FOR A FUTURE MEDIAN

BACKGROUND AND PURPOSE

A prediction limit for a future median is a non-parametric alternative to a parametric prediction limit for a future mean (**Section 18.2.2**) when the sample cannot be normalized. In groundwater monitoring, the most practical application for this kind of limit is for medians of order 3 (*i.e.*, the median of three consecutive measurement values), although the same procedure could theoretically be employed for medians of any odd order (*e.g.*, 5, 7, *etc.*). The comparison rule in this case is that the test passes only if the *median* of a set of 3 compliance point measurements does not exceed the upper prediction limit. Note that this is also the same as a 2-of-3 test, whereby the well is deemed in compliance if at least 2 of 3 consecutive observations fall within the prediction interval. Therefore, only 2 independent observations will generally be needed to complete the test at uncontaminated wells. The third measurement will be irrelevant if the first two pass and so will not need to be collected.

Given n background measurements and a desired confidence level $(1-\alpha)$, a non-parametric prediction limit for a future median involves a confidence probability that the median of the next p future observations will not exceed the limit. As noted in **Section 18.3.1**, order statistics of any random sample follow certain probability laws. In particular, the statistical coverage (C) of a prediction limit estimated by the jth order statistic (that is, the jth largest value) in background will follow a *beta distribution* with parameters j and $(n+1-j)$. Following the notation of Davis and McNichols (1987), the *conditional probability* that the median of 3 independent future values will not exceed the non-parametric prediction limit can be shown to equal

$$\Pr\left\{\text{Future median inbounds} \,\middle|\, X_{j:n}\right\} = 3C^2 - 2C^3 \qquad [18.12]$$

where $X_{j:n}$ denotes that the prediction limit equals the jth largest order statistic in a sample of n observations and a conditional probability denotes the chance that an event will occur given the observance of another event (in this case, after having observed $X_{j:n}$). The (unconditional) confidence probability $(1-\alpha)$ can then be derived by taking the *expected value* of equation [18.12] with respect to the random variable C. Using standard properties of the beta distribution, this probability becomes:

$$1-\alpha = \frac{(3n-2j+5)(j+1)j}{(n+3)(n+2)(n+1)} \qquad [18.13]$$

Thus the confidence level associated with a prediction limit for a future median of order 3 depends simply on the sample size of background (n) and the order statistic selected as the upper prediction limit (j). **Table 18-2** in **Appendix D** provides values of the confidence level for various n and choices of the order statistic. Like the non-parametric prediction limit for m future values, ease of construction comes with a price. More background measurements are required to achieve the same levels of confidence attainable via a parametric prediction limit for a future mean. For instance, to achieve 99% confidence in predicting a median of order 3 in a single test, at least 22 background observations are needed if the maximum is selected as the upper prediction limit, and at least 40 background observations are needed if the prediction limit is set to the second largest measurement. Parametric prediction intervals do not

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require as many background samples precisely because the form of the underlying distribution is assumed to be known.

REQUIREMENTS AND ASSUMPTIONS

Once an order statistic (of rank *j*) is selected as the upper prediction limit, the confidence level is fixed by the number of background samples (*n*). The confidence level can only be increased by enlarging background. However, equation [18.13] is only applicable for the case of predicting a future median of *a single constituent at a single well*. To account for multiple tests and to incorporate a retesting strategy (both of which are usually needed), the specific strategies and tables of confidence levels presented in **Chapter 19** should be consulted.

PROCEDURE

Step 1. Sort the background data into ascending order and set the upper prediction limit [*PL*] equal to one of the following: the background maximum, the second largest value, or another large order statistic in background. If the largest background measurement is a non-detect, set an approximate upper prediction limit as the RL most appropriate to the data (usually the lowest achievable quantitation limit [QL]).

Step 2. Compute the median of the next three consecutive compliance point measurements. Compare this statistic to the upper prediction limit. Identify significant evidence of possible contamination at the compliance well if the median exceeds *PL*. If *PL* equals the RL, identify an exceedance, if the median is quantified above the reporting limit.

Step 3. Based on the background sample size (*n*), use **Table 18-2** of **Appendix D** to determine the confidence level $(1-\alpha)$ associated with predicting the median of the next $p = 3$ future measurements. Because the risk of false positive errors is greatly increased if the confidence level drops much below a targeted rate of at least 90% to 95%, the actual confidence level (as identified in equation [18.13]) should be routinely reported and noted whenever it is below the target level.

Note that equation [18.13] assumes the prediction limit is applied to only one constituent at a single well. If multiple tests are conducted and a retesting procedure is employed, the confidence level of the prediction limit needs to be determined using the tables described in **Chapter 19**.

►EXAMPLE 18-4

Use the following xylene background data to establish a non-parametric upper prediction limit for a future median of order 3. Then determine if the compliance well shows evidence of excessive xylene contamination.

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	Xylene Concentrations (ppb)			
		Background		Compliance
Month	Well 1	Well 2	Well 3	Well 4
1	<5	9.2	<5	
2	<5	<5	5.4	
3	7.5	<5	6.7	
4	<5	6.1	<5	
5	<5	8.0	<5	
6	<5	5.9	<5	<5
7	6.4	<5	<5	7.8
8	6.0	<5	<5	10.4

SOLUTION

Step 1. The maximum value in the set of pooled background measurements is 9.2. Assign this value as the non-parametric upper prediction limit, $PL = 9.2$.

Step 2. Compute the median of the three compliance measurements. This statistic equals 7.8 ppb. Since the median does not exceed PL, there is insufficient evidence of xylene contamination at Well 4, despite the fact that the *maximum* at Well 4 is larger than the maximum observed in background.

Step 3. Compute the confidence level and false positive rate associated with this prediction limit. Given that $n = 24$ and the order statistic selected is the maximum (*i.e.*, $j = n$), use **Table 18-2** in **Appendix D** to determine that the confidence level for predicting a future median of order 3 equals 99.1% and therefore the Type I error or false positive rate is at most 0.9%. ◄

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CHAPTER 19. PREDICTION LIMIT STRATEGIES WITH RETESTING

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This chapter is a core part of the recommended statistical approach to detection monitoring. Even the smallest of facilities will perform enough statistical tests on an annual basis to justify use of a retesting strategy. Such strategies are described in detail in this chapter in conjunction with prediction limits. First, the Unified Guidance considers the concept and computation of site-wide false positive rates [SWFPR]. Then different retesting strategies useful for groundwater monitoring are presented, including:

- Parametric prediction limits with retesting (**Section 19.3**), and
- Non-parametric prediction limits with retesting (**Section 19.4**)

19.1 RETESTING STRATEGIES

Retesting is a statistical strategy designed to efficiently solve the problem of *multiple comparisons* (*i.e.*, multiple, simultaneous statistical tests). An introduction to multiple comparisons is presented in **Chapter 6**. At first glance, formal retesting seems little different than a repackaged form of *verification resampling*, a practical technique used for years to double-check or verify the results of initial groundwater sampling. Indeed, all retesting schemes are predicated on the idea that when the initial groundwater results indicate the presence of potentially contaminated groundwater, one or more additional groundwater samples should be collected and tested to determine whether or not the first results were accurate.

The difference between formal retesting schemes and verification resampling found in the regulations is that the former *explicitly incorporates the resample(s) into the calculation of the statistical properties of the overall test*. A statistical "test" then needs to be redefined to include not only the statistical manipulation of the initial groundwater sampling results, but also that for any further resamples. Both the initial samples and the resamples are integral components of any retesting method.

The principal advantage of retesting is that very large monitoring networks can be statistically tested without necessarily sacrificing either an acceptable false positive rate or adequately high *effective power*. Data requirements for a typical retesting scheme are often less onerous than those required for an analysis of variance (ANOVA). Instead of having to sample each well perhaps four times during any

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given evaluation period, many of the retesting strategies discussed below involve a minimum of one new sample at each compliance well. Resamples are collected only at wells where the initial results exceed a limit, and no explicit *post-hoc* testing of individual wells is necessary as with ANOVA in order to identify a contaminated well.

Since a statistical test utilizing retesting is not complete until all necessary resamples have been evaluated, it is important to outline the formal *decision rules* or *scheme* associated with each retesting strategy. Retesting schemes presented in the Unified Guidance fall into two types: 1-of-*m* and the modified California approach. The 1-of-*m* approach was initially suggested by Davis and McNichols (1987) as part of a broader method termed "*p*-of-*m*." The 1-of-*m* scheme assumes that as many as *m* samples might be collected for a particular constituent at a given well, including the initial groundwater sample and up to (*m*–1) resamples.

1-of-*m* schemes are particularly attractive as retesting strategies. If the initial groundwater observation is in-bounds, the test is complete and no resamples need to be collected. Only when the first value exceeds the background prediction limit, does additional sampling come into play. For practical reasons, only 1-of-*m* schemes with *m* no greater than 4 are considered in the Unified Guidance. A 1-of-4 retesting plan implies that *up to* 4 groundwater measurements may have to be collected at each compliance well, including the initial observation and 3 possible resamples. For the test to be valid, all of these sample measurements need to be statistically independent. This generally requires that sufficient time elapses *between resample collection* so that the assumption of statistical independence or lack of autocorrelation is reasonable (see the discussion in **Chapter 14**). Because many groundwater evaluations are conducted on a semi-annual basis, three will generally be a practical upper bound on the number of independent resamples that might be collected. Thus the 1-of-2, 1-of-3, and 1-of-4 retesting schemes are included below.

The second type of retesting scheme is known as the modified California approach. The decision rules for this test are slightly different from the 1-of-*m* schemes, although the test passes as before if the initial groundwater measurement is inbounds. If it exceeds the background limit, two of the three resample need to be inbounds for the test to pass. The modified California strategy thus requires a *majority* of the resamples to be inbounds for a compliance well test to be deemed 'in bounds'. A 1-of-4 scheme could have both the initial value and the first two resamples be out-of-bounds, yet pass the test with an inbounds result from the third resample. Although the modified California test appears to be more stringent, the prediction limit for a 1-of-4 test under the same input conditions will be lower and hence be more likely to trigger single comparison exceedances. With the prediction limits correctly defined, both will have identical false positive errors for any specific monitoring design. The guidance also provides the same four non-parametric versions of the 1-of-*m* and modified California tests for future values.

A useful variation on the 1-of-*m* retesting scheme for individual measurements is the 1-of-*m* strategy for *means or medians*. Instead of testing a series of individual values, a series of means or medians of order *p* is tested. The *order* of the mean or median refers to the number of individual measurements used to compute the statistic. For example, 1-of-2 retesting with means of order 2 requires that a pair of initial observations be averaged and the resulting mean compared against the background limit. If that initial mean is out-of-bounds, a second pair of observations (*i.e.*, two resamples) would be

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collected and averaged to form the resample mean. The test would fail only if both the initial mean and the resample mean exceeded the background limit.

Retesting schemes for means or medians have steeper data requirements than retesting strategies for individual measurements and may not be practical at many sites. Nevertheless, the statistical properties (*e.g.*, power and false positive rate) associated with the testing of means and medians are superior to comparable plans on individual observations. The Unified Guidance provides five mean retesting plans: 1-of-1, 1-of-2, or 1-of-3 for means of order 2; and 1-of-1 and 1-of-2 for means of order 3. The guidance also provides 1-of-1 and 1-of-2 tests of medians of size 3 as non-parametric options.

These plans were chosen to limit the maximum possible number of distinct and independent sampling measurements per compliance well during a single evaluation period to six. In fact, the data requirements vary substantially by scheme. With means of order 2, the 1-of-1 plan requires a maximum of two new sample measurements; the 1-of-2 plan requires as many as four; while only the 1-of-3 plan might need a total of six. For means of order 3, the 1-of-1 plan requires three new measurements to form the single mean; the 1-of-2 plan might require up to six. But for higher order 1-of-*m* mean or median tests, only the initial samples may be needed to identify a 'passing' test outcome under most background conditions.

The three 1-of-1 mean and median plans provided in the guidance are technically not retesting schemes. The decision rule for these plans merely requires a comparison of a single mean or median against the background limit. If the initial mean or median comparison is inbounds, the test passes. If not, the test fails. The fact that each average is computed from multiple individual measurements implies that an implicit retest or verification resampling is built into these strategies. The statistical properties of the 1-of-1 plans can often be better than comparable 1-of-*m* schemes for individual values, with fairly similar sampling requirements.

The Unified Guidance provides 1-of-1 and 1-of-2 non-parametric prediction limit tests for future medians of order 3. By 'median of order 3', it means that the median or 'middle value' of a set of three consecutive sampling events. In the 1-of-2 case, the test passes if either the initial median is inbounds or, if not, when the resample median is inbounds. The 1-of-1 scheme does not involve any resampling, but does require at least two distinct sampling measurements to determine whether the initial median is inbounds.[1]

As discussed in **Chapter 6**, proper design of a groundwater detection monitoring program will generally require an initial choice of a retesting scheme *before* future or compliance sampling data have been collected. As a practical matter, sample collection should be spaced far enough apart in time to ensure that any potentially needed resamples are statistically independent. Thus, the maximum number of resamples need to be known in advance in order to structure a feasible sampling plan for a particular retesting strategy. Each retesting scheme also involves a different set of decision rules for evaluating the status of any given compliance well. The rules will determine how the background limit will be computed. Given the same background sample and group of compliance wells, different retesting schemes lead to *different* background limits on the *same* data.

[1] As noted in **Chapter 18**, the 1-of-1 retesting scheme for medians of order 3 is equivalent as a decision rule to a 2-of-3 scheme for individual measurements.

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If parametric prediction limits are used, the general formula for the limit introduced in **Chapter 18** is $\bar{x} + \kappa s$. The κ-multiplier and thus the prediction limit will vary depending on which 1-of-*m* or modified California plan is chosen. The κ-multipliers also depend on the monitoring evaluation schedule in place at the facility. In typical applications, it is expected that the background sample used in statistical evaluations from any given year will either be *static* or substantially overlap from one evaluation to the next. The same background observations are likely to be utilized or will substantially overlap if newer background data are added to the existing pool. Since at least a subset of the background measurements will be commonly employed in all the evaluations, there will be a *statistical dependence* exhibited between distinct evaluations (see **Section 19.2** below). The number of evaluations per year against a common background will affect the correct identification of prediction limits. Consequently, the evaluation schedule (*i.e.*, annual, semi-annual, quarterly) also needs to be known or specified in advance.[2]

19.2 COMPUTING SITE-WIDE FALSE POSITIVE RATES [SWFPR]

As discussed in **Chapter 6**, the fundamental purpose of detection monitoring is to accurately identify a significant change in groundwater relative to background conditions. To meet this objective, statistical monitoring programs should be designed with the twin goals of ensuring adequate statistical power to flag well-constituent pairs elevated above background levels and limiting the risk of *falsely* flagging uncontaminated wells across an entire facility. The latter is accomplished by addressing the *site-wide false positive rate* [SWFPR]. Both goals contribute to accurate evaluation of groundwater and to the validity of statistical groundwater monitoring programs.

Retesting significantly aids this process of meeting *both* criteria. However, it can be much easier to design and implement an appropriate retesting scheme if one understands how the SWFPR is derived. The SWFPR is based on the assumptions that no contamination is actually present at on-site monitoring wells, and that each well-constituent pair in the network behaves independently of other constituents and wells from a statistical standpoint. If Q denotes the probability that a particular well-constituent pair will be falsely declared an exceedance (a *false positive* error), the probability of at least one such false positive error among r independent tests is given by:

$$\alpha = SWFPR = 1 - \left(1 - Q\right)^r \qquad [19.1]$$

$(1–Q)$ equals the chance that the test will correctly identify the well-constituent pair as 'inbounds.' The value of Q itself will depend on the type of retesting scheme being used.

[2] The Unified Guidance distinguishes between the statistical *evaluation* (or testing) schedule and the *sampling* schedule. Regularly scheduled sampling events might occur quarterly, even though a statistical evaluation of the data only occurs semi-annually or annually. Further, resamples do not constitute regular sampling events, since they are only collected at wells with initial exceedances, but they *are* associated with the data for a particular evaluation. By separately identifying the evaluation schedule, there is 1) less confusion about the role of resamples in the testing process, and 2) opportunity to design monitoring programs, so as to allow for multiple individual observations to be collected prior to each evaluation.

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Consider a 1-of-3 retesting plan for future observations. A false positive at a given well-constituent pair will be registered only if all three observations — the initial groundwater measurement and two resamples — exceed the background prediction or control limit. If ω represents the probability that one of these observations exceeds the background limit, Q can be calculated as $\omega \times \omega \times \omega$ (since the initial measurement and resamples are statistically independent) and the SWFPR as:

$$\alpha = SWFPR = 1 - \left(1 - \omega^3\right) \qquad [19.2]$$

By setting the target site-wide α equal to 0.10 and solving for ω, one could potentially compute the individual comparison false positive rate ($\alpha_{comp} = \omega$) associated with any single comparison against the background limit. This would identify the individual *per-comparison* confidence level ($1 - \alpha_{comp}$) necessary to compute the background limit in the first place.[3] If the background limit is computed as a prediction limit for the next single future measurement (*i.e.*, $m = 1$ in a 1-of-m scheme), then ω equals the probability that a single new observation (independent of background) exceeds the prediction limit, and (1–ω) equals the confidence level of that prediction limit. Further, since ω can be obtained from equation [19.2] as:

$$\omega = \sqrt[3]{1 - \left(1 - \alpha\right)^{1/r}} \qquad [19.3]$$

the upper prediction limit for a site involving 500 tests (for instance, 50 wells and 10 constituents per well) and 20 background samples could be computed using an individual, per-comparison confidence level of

$$1 - \omega = 1 - \sqrt[3]{1 - \left(1 - .10\right)^{1/500}} = 1 - .0595 = 94.0\%$$

leading to a final prediction limit of

$$PL = \bar{x} + t_{.94,19} s \sqrt{1 + \frac{1}{20}}$$

where $\bar{x}$ and s are the background sample mean and standard deviation.

Unfortunately, certain statistical dependencies render the foregoing calculations somewhat inaccurate. Whether or not a resample exceeds the background limit for any constituent depends partly on whether the initial observation for that test *also* eclipsed the limit. This is because the *same background data* are used in the comparison of both the initial groundwater measurement and the resamples. This creates a statistical dependence between the *comparisons,* even when the compliance point observations themselves are statistically *independent*. If the background data sample mean happens to be low relative to the true population mean, the background limit will tend to be low. Each of the compliance point observations (whether the first measurement or subsequent resamples) will have a

[3] Note that α_{comp} does not represent the false positive rate for the complete 1-of-3 test, but is being treated for the sake of argument as a one of a series of 3 individual and independent tests.

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greater than expected chance of exceeding it. Likewise, if the background sample mean is substantially higher than the population mean, the background limit will tend to be high, resulting in a lower-than-expected chance of exceedance for each of the compliance measurements.

A similar dependence occurs for each well-constituent pair tested against a single background across evaluation periods (see discussions in **Chapter 5** and **Section 19.1**). A further dependence occurs when well-constituent pairs from many compliance wells are compared to a common interwell background. The tests during each statistical evaluation again share a common (or nearly common) background, thus impacting the individual test false positive rate (α_{test}) and the SWFPR (α) in turn. Three common evaluation strategies are considered in the Unified Guidance: quarterly, semi-annual, and annual. The SWFPR is computed on a cumulative, annual basis, with the assumption that background and the associated background limit will not be updated or recomputed (especially for intrawell tests) more often than every one to two years.[4]

These dependencies between successive comparisons and tests against the background limit during retesting means that the derivation above will generally *not* result in a background limit with the targeted annual SWFPR of 10%. The actual false positive rate (α) will be somewhat higher and can be substantially higher if the background sample size (n) is small to moderate (say less than 50 samples). In part, this is because the correlation between successive comparisons against a common background limit is on the order of $1/(1+n)$. That is, the smaller the background size, the greater the correlation between the resamples and test comparisons. The impact on the SWFPR is also greater if this dependence is ignored.

Fortunately, as Gibbons (1994) has noted, the solution suggested in the previous example will be approximately valid for large background data sets (say $n > 50$), since then the correlation between successive resamples and/or tests is minimal. In fact, an approximate solution for the modified California and more general 1-of-m retesting schemes can also be derived. In the case of 1-of-m schemes, the probability Q of a false positive (for $m = 1$ to 4) is ω^m, leading to a SWFPR of :

$$\alpha = SWFPR = 1 - \left(1 - \omega^m\right)^Y \qquad [19.4]$$

Solving for ω in equation [19.4] leads to an approximate individual comparison false positive rate ($\alpha_{comp} = \omega$) of:

$$\omega = \sqrt[m]{1 - \left(1 - \alpha\right)^{1/r}} \qquad [19.5]$$

For the modified California plan, a false positive for a given well-constituent pair during a single evaluation will be registered only if both the initial measurement and at least two of three resamples are

[4] Even with these assumptions, not all the statistical dependence will be accounted for at every site or for all constituents. Even when background is updated with new measurements, some of the already existing background values are likely to be used in re-computing the background limit. Some well-constituent pairs may be correlated, contradicting the assumption of independence between tests at the same well or for the same constituent at different wells. The Unified Guidance also does not presume to compute the SWFPR for other multi-year periods or for the life of the facility.

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out-of-bounds (*i.e.*, exceed the background limit). Consequently, the probability Q of a false positive for that pair may be expressed as:

$$Q = \omega\left[3\omega^2\left(1-\omega\right)+\omega^3\right] = \omega^3\left(4-3\omega\right) \quad [19.6]$$

As before, ω represents the probability of any single observation exceeding the background limit. Both the initial and any resample comparisons against the limit are assumed to be statistically independent. Given Q, the approximate overall false positive rate then becomes:

$$\alpha = SWFPR = 1-\left[1-\omega^3\left(4-3\omega\right)\right]^r \quad [19.7]$$

Since ω will always be small in practice, one can usually ignore the term ω^4 when expanding the right-hand side of equation [19.7]. Then the approximate SWFPR becomes:

$$\alpha \approx 1-\left[1-4\omega^3\right]^r \quad [19.8]$$

Leading to a solution for ω:

$$\omega \approx \sqrt[3]{1-\left(1-\alpha\right)^{1/r}}\sqrt[3]{\frac{1}{4}} \quad [19.9]$$

which can again be used to construct a background limit for a single new observation.

As an example, if the target SWFPR is 10% and one must test r = 200 comparisons using the modified California plan, ω would become:

$$\omega \approx \sqrt[3]{1-.90^{1/200}}\sqrt[3]{\frac{1}{4}} = .0508 = 5.1\%$$

If the background limit is a prediction limit for the next future value, a confidence level of approximately 94.9% would be needed to achieve the desired overall false positive rate of 10%. This assumes that the background sample size is sufficiently large (say n > 50) to make the correlation between retests negligible. In similar fashion, the respective single comparison error rates for the 1-of-2 through 1-of-4 tests of future observations in this example would respectively be: ω = .0229, .0808, and .1515.

19.2.1 BASIC SUBDIVISION PRINCIPLE

The previous section highlighted certain dependencies in statistical tests due to comparisons of one or more samples or sample sets against a common background. In the sitewide design of a facility detection monitoring system, the overall target design SWFPR is proportionately divided among all relevant tests conducted in an annual period. Depending on the type of testing (e.g., interwell versus

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intrawell, or a parametric versus non-parametric), the target error rates for a portion of the total set of potential tests may need to be calculated.

Identifying false positive target rates is important when considering non-parametric prediction limit tests. The cumulative target error rate for a group of annual tests against a single constituent is needed to compare with the achievable levels in **Tables 19-19 through 19-24** in **Appendix D**. The latter achievable rates take into account the dependencies previously discussed. ***κ*-**multiple **Tables 19-1 to 19-18** in **Appendix D** for parametric prediction limit tests have already made use of target false positive rate calculations which are generally not needed for identifying the appropriate multipliers. The various dependencies against a common background are accounted for in the ***κ*-**multiple tables to meet the nominal target rates. **R-**script software for certain parametric prediction limit tests discussed in a following section and in **Appendix C** also makes use of a target per-test false positive error rate as input.

In assigning target rates, the Unified Guidance uses a basic *subdivision principle* which makes certain assumptions. First and foremost, it is assumed that the total suite of tests can be subdivided into mutually exclusive, independent[5] tests. Each relevant annual statistical test is assigned the same single test error rate (α_{test}). Using the properties of the Binomial distribution, the target single test error rate can be obtained using equation [19.10] for r total annual tests. The total number of annual tests r is the product of the number of compliance wells (w), the number of valid constituents (c), and the number of evaluations per year (n_E) or $r = w \times c \times n_E$, with α = SWFPR:

$$\alpha_{test} = 1 - (1-\alpha)^{1/r} \qquad [19.10]$$

Then a cumulative false positive rate can be assessed for any appropriate subset of tests. This principle would apply, for instance, if there is more than one regulated unit at a site and each regulated unit can be treated independently. A consistent portion of the overall targeted false positive rate α would be assigned to each regulated unit (α_{unit}), using a rearrangement of equation [19.10]. If a facility with three units B, C, and D had 120 total annual tests ($b + c + d = 120 = r$), the cumulative target error rate for Unit B would be: $a_{UnitB} = 1 - (1-\alpha_{test})^b$ and similarly for Units C and D. These three cumulative error rates will *approximately* (but not exactly) sum to a total sitewide value close to the SWFPR. However, as joint independent tests taken together, the annual SWFPR is in fact exactly 10%. The Bonferroni assumption makes use of the approximately linearity of such error rates for SWFPR calculations (discussed below).

The ways in which the overall SWFPR might be partitioned will vary with each site, considering units, types of tests, number of wells, constituents and evaluations per year. If unit-specific cumulative false positive rates were established, the group of tests associated with each monitoring constituent within each unit might be separately considered. Each group might potentially be further subdivided into intrawell versus interwell tests, or prediction limits versus control charts, *etc*., assuming a mixture of statistical methods is employed. By using the subdivision principle in a consistent way, the targeted SWFPR can be accurately maintained.

[5] The Unified Guidance does not presume that every statistical test is in fact independent. Tests or groups are treated as if independent, however, to allow the computation of nominal target false positive rates and/or to be consistent with regulatory constraints (*e.g.*, all constituents must be tested separately).

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One important use when calculating SWFPR rates is to account for multiple constituents. In particular, non-parametric test theory is applied to only a single constituent at a time. Since each constituent has its own set of background data and presuming the constituents behave independently of one another, the dependence caused by using a common background pertains only to those comparisons made against the background for that constituent. To clarify this concept, suppose a total set of *r* tests consists of *c* separate chemicals each monitored at *w* wells annually (*i.e.*, $r = c \times w \times n_E$ and $n_E = 1$). For each constituent, the dependence caused by a common background only applies to the *w* comparisons (one for each well) made for that monitoring parameter. This means that the overall target α = SWFPR needs to be apportioned into a fraction for each constituent, called the per-constituent false positive rate or α_c. This can be done using the Binomial formula based on the single test error rate for *w* wells as: $a_c = 1 - (1-\alpha_{test})^{w \cdot n_E}$ or by partitioning the overall α to each constituent *c*:

$$\alpha_c = 1 - (1-\alpha)^{1/c}$$

The two calculations are equivalent under these conditions, with the latter equation somewhat easier to use.

A similar situation occurs at sites requiring a combination of interwell and intrawell tests. Computation of the SWFPR can be appropriately handled using the basic subdivision principle. For interwell tests, measurements collected at each compliance well are compared against a common interwell background, creating a degree of statistical dependence not only between successive individual test comparisons (*i.e.*, initial sample and any resamples) at a given well, but also between tests at different compliance wells. With intrawell tests, each well supplies its own background. This implies that the component of between-well test dependence is eliminated, changing the way κ-multipliers for intrawell background limits with retesting are computed.

For a given set of *r* well-constituent pairs, *l* tests to be conducted on an interwell basis, and the remaining (*r* – *l*) tests conducted as intrawell, two cumulative false positive rates need to be computed. The single test false positive error rate α_{test} approach can be used: $a_{\text{int } er} = 1 - (1-\alpha_{test})^{l}$ for the subset of *l* interwell tests, and $a_{\text{int } ra} = 1 - (1-\alpha_{test})^{r-l}$ for the subset of $r - l$ intrawell tests, in order to correctly maintain the SWFPR equal to α. A somewhat more direct approach can also be used: $\alpha_{\text{int } er} = 1 - (1-\alpha)^{l/r}$ for the interwell tests and $\alpha_{\text{int } ra} = 1 - (1-\alpha)^{(r-l)/r}$ for the intrawell tests. The two sets of equations are consistent.

In general, the subdivision principle works as follows. If a group of *r* tests with targeted false positive rate, α, is divided into *s* distinct and mutually exclusive independent subsets, the false positive rate for each subset (α_{sub}) can be computed as:

$$\alpha_{sub} = 1 - (1-\alpha)^{1/s} \qquad [19.11]$$

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The basic subdivision principle does not guarantee that the resulting detection monitoring program will have sufficient effective power to match the EPA reference power curve (ERPC). The foregoing calculations merely point to the correct overall false positive rate.

As discussed in Section 6.2.2 of **Chapter 6**, a simpler approach would be to partition the overall SWFPR among a facility's annual number of tests, and can make use of the Bonferroni approximation. With low false positive rates characteristic of detection monitoring design, the total SWFPR can be divided by the number of annual tests for any of the various combinations of constituents, separate units, or interwell versus intrawell tests. The Bonferroni approach results in slightly different false positive values than by directly using the Binomial formula, as described above.

As an overall example, assume a facility with $w = 20$ wells monitored twice per year ($n_E = 2$) for $c = 8$ constituents Further, assume that 5 of the constituents can be monitored interwell and 3 need to be handled as intrawell comparisons. Non-parametric prediction limits will be considered for all tests. Calculate the target cumulative false positive error rates for interwell and intrawell comparisons, with the SWFPR = $\alpha = .1$.

This site has a total of $r = w \times c \times n_E = 20 \times 8 \times 2 = 320$ tests per year. For the five interwell constituents, there are $20 \times 2 \times 5 = 200$ tests, with $20 \times 2 \times 3 = 120$ intrawell tests. Each of the 5 interwell constituents will have $20 \times 2 = 40$ tests against a common background, while 2 semi-annual sample tests will be made against each of the $20 \times 3 = 60$ intrawell backgrounds.

From equation [19.10], the single test false positive error rate is: $\alpha_{test} = 1 - (1-\alpha)^{1/r} = 1 - (1-.1)^{1/320} = .0003292$. Each set of interwell constituent tests will have a cumulative false positive error rate α_c for the 40 annual tests as: $\alpha_c = 1 - (1-\alpha)^{1/c} = 1 - (1-.1)^{1/8} = .01308$. Note that *all 8* constituents are used in the equation, since the same false positive error rate is uniformly applied to all distinct subgroup tests. The result can be obtained using the single test error rate equation: $a_c = 1 - (1-\alpha_{test})^{w \cdot n_E} = 1 - (1-.0003292)^{40} = .01308$. This target value would be used to compare with achievable non-parametric test error rates for the same input conditions. The cumulative interwell error rate for all five constituents can be calculated as: $a_{\text{int } er} = 1 - (1-\alpha_c)^c = 1 - (1-.01308)^5 = .06371$.

For the intrawell tests, the simplest approach uses the single test error rate for two tests: $a_{2-\text{int } ra} = 1 - (1-\alpha_{test})^{w \cdot n_E} = 1 - (1-.0003292)^{1 \cdot 2} = .0006583$. This would be the cumulative error rate to consider with non-parametric intrawell tests. The overall intrawell cumulative error rate for the sixty tests would then be: $a_{60-\text{int } ra} = 1 - (1-\alpha_{2-\text{int } ra})^{w \cdot c} = 1 - (1-.0006583)^{60} = .03873$.

If the two overall interwell and intrawell cumulative error rates were added, the sum is .1024, quite close to the nominal 10% SWFPR. It is exactly that value when considered jointly. By comparison the single test error rate using the Bonferroni approximation would be .1/320 = .0003125, while the exact Binomial value is .0003292. The estimated interwell cumulative error for a single constituent would be 40 times the single test value or .0125 (versus the calculated .01308). For many non-parametric test considerations, these differences are relatively minor.

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19.3 PARAMETRIC PREDICTION LIMITS WITH RETESTING

BACKGROUND AND PURPOSE

Upper prediction limits for *m* future observations and for future means were described in **Chapter 18**. Applied to a network of statistical comparisons in detection monitoring, these procedures can be considered an extension to Dunnett's *multiple comparison with control* [MCC] procedure (Dunnett, 1955). These procedures explicitly incorporate retesting that is applicable to a wider variety of cases than addressed by Dunnett.

Retesting can be incorporated with either interwell or intrawell prediction limits. Depending on which approach is adopted, there is a distinct difference in the κ-multipliers of the general prediction limit formula. In an interwell retesting strategy, there are at least two forms of statistical dependence that impact the SWFPR. One is that each initial measurement or resample at a given compliance well is compared against the same background. A second is the dependence among compliance wells and number of annual evaluations, all of which are compared against a common upgradient background. In intrawell retesting, this second form of dependence is either essentially eliminated if there is only one annual statistical evaluation or else substantially reduced in the event of multiple evaluations.[6] The remaining dependence is among successive resamples at each well.

To account for the basic differences between interwell and intrawell prediction limit tests, an extensive series of tables is provided in **Appendix D** listing a wide combination of background sample sizes, numbers of wells, numbers of constituents, and distinctions between interwell and intrawell tests. In conjunction with an evaluation schedule (*i.e.*, annual, semi-annual, or quarterly), these tables can be used to design and implement specific parametric retesting strategies in this chapter. All of the κ-multiplier tables for parametric prediction limits are structured to meet an annual SWFPR of 10% per year and to accommodate groundwater networks ranging in size from one to 8,000 total statistical tests per year. The Unified Guidance tables are more extensive than similar tables in Gibbons (1994b). Further, each table is designed to indicate the effective power of the κ-multiplier entries.

If a particular network configuration is not directly covered in the **Appendix D** tables, two basic options are available. First, bilinear interpolation can be used to derive an approximate κ-multiplier (see below for guidance on table interpolation). Second, the free-of-charge, open source, and widely available **R** statistical programming package (www.r-project.org) can be employed to compute an exact κ-multiplier. Further instructions and the two template codes used to compute the Unified Guidance κ-multiplier tables are provided in **Appendix C**. After installing the **R** package, these template codes can be run by supplying specific parameters for the network of interest (*e.g.*, number of wells, constituents, background sample size, *etc*.). Some familiarity with properly installing a program like **R** is helpful. **Appendix C** explains how to execute a pre-batched set of commands. No other technical programming experience is needed.

[6] If multiple evaluations occur each year, new compliance samples each evaluation period are tested against the common intrawell background.

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REQUIREMENTS AND ASSUMPTIONS

The basic assumptions of parametric prediction limits were described in **Chapter 18**. These include data that are normal or can be normalized (via a transformation), lack of outliers, homogeneity of variance between the background and compliance point populations, absence of trends over time, stationarity, and statistical independence of the observations.

The Unified Guidance provides *separate* κ-tables for interwell and intrawell limits. One of these approaches should be justified before computing prediction limits. To use *interwell* prediction limits, there should be no significant natural spatial variation among the mean concentrations at different well locations. Otherwise, a prediction limit test could give meaningless results, since average downgradient levels might naturally be higher than background even in the absence of a contaminant release. The assumption of spatial variability should therefore be checked using the methods in **Chapter 13**.

While *intrawell* testing eliminates the problem of natural spatial variability, intrawell background often is developed using the first n samples from each compliance point well. Since historical data from compliance wells need to be utilized to do this, these groundwater measurements should be uncontaminated. The number of intrawell background samples available may also be rather limited. n will tend to be initially small prior to any updating of background. Such constraints will limit the intrawell retesting schemes that can both minimize the SWFPR yet maintain effective power similar to the ERPCs.

One possible way to overcome this limitation is to estimate a *pooled standard deviation* across many wells along the lines suggested by Davis (1998). Such a calculation is no more difficult than a one-way ANOVA (**Chapter 13**) for identifying on-site spatial variability. The *mean squared error* [MSE] component of the F-statistic in ANOVA gives an estimate of the average per-well variability. To the extent that mean levels vary by well location *but the population standard deviation does not*, a one-way ANOVA can be run on a collection of wells (both background and compliance) to estimate the average within-well variance, and hence, the common *intrawell* standard deviation (see **Chapter 13** for further details and examples).

Instead of a standard deviation estimate based solely on intrawell background at a single well with its attendant limits in size and degrees of freedom, the *mean* concentration level can be estimated on a well-specific basis, while the *standard deviation* is estimated utilizing a collection of wells leading to much larger degrees of freedom. Although the intrawell background size for a given well might be small (*e.g.*, n = 4 or 8), the κ-multiplier used to construct the prediction limit is based on both the *effective sample size* (*i.e.*, degrees of freedom plus one) *and* the intrawell sample size (n).

The pooled standard deviation for intrawell comparisons can be utilized if the population standard deviation is *approximately constant across wells*. Many data sets may not appear so initially; however, any transformation to normality must first be taken into account. The standard deviation is only assumed to be constant *on the transformed scale*. Furthermore, once any transformation is applied, the collection of wells should explicitly be tested for homogeneity of variance using the tools in **Chapter 11**. *Only if the assumption of equal variances across wells seems reasonable should the pooled standard deviation estimate be used.*

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With little or no spatial variability among well locations, an interwell test might be considered. However, the sample standard deviation (s) computed from background may not adequately estimate true background variability. This can happen when there is a temporal component to the variability affecting all wells at a site or regulated unit in parallel fashion, or when there is a significant degree of autocorrelation between successive samples.

A random, temporal component to the variability can result from changes to the laboratory analytical method or field sampling methodology, periodic re-calibration of lab instruments, or other sample handling or preparation artifacts that tend to impact all observations collected during a given sampling event. Such a temporal component can sometimes be identified through the use of parallel time series plots (**Section 14.2.1**) or through a one-way ANOVA using time-of-sampling as the factor (**Section 14.2.2**). Results of the ANOVA can be used to derive a better estimate of the background population standard deviation (σ), along with adjusted degrees of freedom for use in constructing the upper prediction limit (see **Chapter 14** for further details and an example).

When autocorrelation is present, methods to adjust the standard deviation estimate and degrees of freedom entail possibly modeling the autocorrelation function. This issue is beyond the scope of the Unified Guidance and consultation with a professional statistician is recommended. The most practical way to avoid significant autocorrelation between samples is to allow enough time to lapse between sampling events. Precisely how much time will vary from site to site, but Gibbons (1994a) and others (for instance, American Society for Testing and Materials, 2005) recommend that the frequency of sampling be no more frequent than quarterly. Alternatively, a pilot study can be run on two or three wells with the sample autocorrelation function estimated from the results (**Sections 14.3.1** and **14.2.3**). The minimum lag (*i.e.*, time) between sampling events at which the autocorrelation is effectively zero can be used as an appropriate sampling interval.

APPENDIX TABLES FOR PARAMETRIC RETESTING PLANS

The Unified Guidance provides tables of κ-multipliers for both interwell and intrawell prediction limits with retesting. It also provides separate tables for predicting individual future values versus future means. Four distinct retesting schemes are presented in the case of prediction limits for individual values: 1-of-2, 1-of-3, 1-of-4, and the modified California plan schemes. Five distinct schemes are presented for the case of future means: 1-of-1, 1-of-2, and 1-of-3 for means of order 2, and 1-of-1 and 1-of-2 for means of order 3.

Both the **Appendix D** interwell retesting tables (**Tables 19-1** through **19-9**) and the intrawell retesting tables (**Tables 19-10** through **19-18**) are similarly structured. Separate sub-tables are provided for a range of possible monitoring constituents (c = 1 to 40) and for each of the retesting schemes mentioned above. Each table is divided into three parallel sections, one section applicable to annual statistical evaluations, one to semi-annual evaluations, and one to quarterly evaluations. Within each section, κ-multipliers are listed for all combinations of background sample size (from n = 4 to 150) and number of wells (from w = 1 to 200). These κ-multipliers are computed to meet a target annual SWFPR of 10%, as discussed in **Chapter 6**.

The **Appendix** tables also list those κ-multipliers which achieve adequate effective power compared to the ERPCs. The κ-multipliers are **bolded** when the effective power consistently exceeds the appropriate ERPC for mean level increases above background of 3 or more standard deviations

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(designated as 'good' power). The multipliers are *italicized and shaded* when the effective power is somewhat less, but still consistently exceeds the ERPC at mean level increases of 4 or more standard deviations above background (designated as 'acceptable' power). Non-bolded, non-italicized entries achieve the target SWFPR, but have *low power*.

To use the tables, certain key statistical parameters should be known or identified. These include whether the prediction limit tests are interwell or intrawell, the evaluation schedule (annual, semi-annual, or quarterly), the number of constituents (c), the size of the background sample (n), and the number of compliance wells to be tested (w). In the interwell case, it is presumed that there are n (upgradient) background measurements for each constituent (c). The listed κ-multiplier would then be applied to each of c prediction limits, one for each monitoring constituent. The intrawell case presumes that there are n well-specific background measurements designated at each well-constituent pair, thus giving $w \times c$ separate sets of intrawell background. Here, the κ-multiplier would be applied to each of $w \times c$ distinct prediction limits.

In situations where a mixture of test types is needed (*e.g.*, intrawell testing for some constituents, interwell for others), the Unified Guidance tables can still be employed. The κ-multipliers are computed to apportion an *equal share* of the overall cumulative SWFPR to each of the $w \times c$ tests that need to be run during a given statistical evaluation. Because of this fact, if r of the constituents are analyzed using interwell tests, but $(c - r)$ of the constituents are handled using intrawell limits, correct prediction limits can be developed by first selecting an interwell κ-multiplier based on all c constituents, and then selecting an intrawell κ-multiplier *also* based on c constituents. This will ensure that the target SWFPR is met, although each multiplier is respectively applied only to a subset of the monitoring list.

Some background samples might be of different sizes, either for different constituents or at distinct wells (*e.g.*, when using intrawell background). Again the Unified Guidance tables can be inspected to select a different κ-multiplier for each distinct n. However, each multiplier should be chosen as if the background sample sizes were equal for all $w \times c$ tests. Thus, while a multiplier based on n_1 background observations is applied only to those tests involving that sample size, it should be selected from the **Appendix D** tables as if it will be applied to *all* the tests.

For network configurations not listed in **Tables 19-1** to **19-18** in **Appendix D**, an appropriate κ-multiplier can be estimated using bilinear interpolation. Such interpolation will be fairly accurate as long as adjacent table entries are used, representing the closest values to the desired combination of number of wells (w) and background sample size (n).

In general, to calculate a $\kappa_{w^*,\,n^*}$, where w^* and n^* are the desired input points that lie between the closest table entries as: $w_1 < w^* < w_2$ and $n_1 < n^* < n_2$, first calculate the fractional terms:

$$f_w = \frac{(w^* - w_1)}{(w_2 - w_1)} \quad \text{and} \quad f_n = \frac{(n^* - n_1)}{(n_2 - n_1)}$$

The interpolated κ-multiplier can then be computed as:

$$\kappa_{w^*,n^*} = (1-f_w)(1-f_n)\cdot\kappa_{w_1,n_1} + f_w(1-f_n)\cdot\kappa_{w_2,n_1} + (1-f_w)\cdot f_n\cdot\kappa_{w_1,n_2} + f_w\cdot f_n\cdot\kappa_{w_2,n_2} \qquad [19.12]$$

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For example, suppose a κ-multiplier is needed for a 1-of-3 interwell prediction limit test for individual values using an annual evaluation schedule. Assume the monitoring network consists of $c = 5$ constituents monitored at $w = 28$ compliance wells, using $n = 17$ upgradient background measurements on which to base the prediction limit. From **Table 19-2** in **Appendix D**, the closest table entries, $\kappa_{,w,n}$ to the desired combination are $\kappa_{20,16} = 1.59$, $\kappa_{30,16} = 1.70$, $\kappa_{20,20} = 1.52$, and $\kappa_{30,20} = 1.62$. The interpolated value, $\kappa_{25,18}$, can then be found using the equations in [19.12]:

$$f_w = \frac{(28-20)}{(30-20)} = .8 \qquad f_n = \frac{(17-16)}{(20-16)} = .25$$

$$\kappa_{25,18} = (1-.8)(1-.25)\cdot\kappa_{20,16} + .8(1-.25)\cdot\kappa_{30,16} + (1-.8)\cdot.25\cdot\kappa_{20,20} + .8\cdot.25\cdot\kappa_{30,20}$$

$$= .15\cdot1.59 + .60\cdot1.70 + .05\cdot1.52 + .20\cdot1.62 \quad = 1.659$$

Important considerations in designing a reasonable retesting scheme for detection monitoring are discussed in **Chapter 6**. Given a background sample and a particular network configuration and size, parametric 1-of-m plans tend to increase in statistical power as the order of m increases. All of the schemes have greater power with larger background sample sizes (n). Furthermore, plans involving prediction limits for future means tend to be more powerful than similar plans using prediction limits for individual observations. So if the κ-multiplier for a particular plan is not **bolded** or *italicized*, another plan can be sought to achieve sufficient effective power using more resamples or perhaps changing to a mean prediction limit. Alternatively, the background sample size might need to be augmented if feasible, prior to implementing the retesting procedure.

19.3.1 TESTING INDIVIDUAL FUTURE VALUES

The advantages to using a prediction limit for future individual values include: 1) the ability to explicitly control the SWFPR across a series of well-constituent pairs; and 2) greater flexibility than that provided by prediction limits for future means (**Section 19.3.2**) to handle temporal autocorrelation. In those cases when the sampling frequency needs to be reduced to maximize statistical independence of the observations, the method can be applied to evaluations of a single new measurement (plus possible resamples) at each compliance point well.

To properly implement a prediction limit strategy for future values with retesting, it needs to be feasible to collect 2 to 4 independent measurements at each compliance well during a given evaluation period. All initial and any resamples are assumed to be statistically independent and thus should exhibit no autocorrelation.

If statistical evaluations are done annually, it may be possible to collect data on a quarterly basis and meet the minimal sampling requirements of any of the resampling schemes discussed in the Unified Guidance. However, more frequent evaluations (say semi-annual or quarterly) will require that new samples be collected perhaps monthly or every six weeks. In these cases, explicit tests for autocorrelation may need to be conducted before adopting a 1-of-m retesting scheme with $m > 2$ or a

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modified California plan. If significant autocorrelation is identified, the sampling frequency may need to be reduced and/or an alternate strategy utilizing fewer resamples may need to be adopted instead.

PROCEDURE

Step 1. Identify the overall targeted annual false positive rate (SWFPR = α = 0.10). Determine the number of wells (w) to be monitored and the number of constituents (c) to be sampled at each well. Also determine whether the evaluation schedule at the unit or facility is *annual, semi-annual or quarterly*.

Step 2. Decide on the number of observations (m) to be predicted. To incorporate retesting, a maximum of two independent measurements should be collected from every compliance well during each evaluation period to use a 1-of-2 retesting scheme, three independent measurements if a 1-of-3 plan is desired, and four independent measurements if either a 1-of-4 plan or a modified California plan is employed.

Step 3. For interwell prediction limits given a background sample of n measurements, compute the background sample mean ($\bar{x}$) and standard deviation (s) for each constituent. Then, based on the evaluation schedule (annual, semi-annual or quarterly), c, n, w, and the specific retesting scheme chosen, use **Tables 19-1** to **19-4** in **Appendix D** to determine a κ-multiplier possessing acceptable statistical power. Interpolate within the tables to find the closest multiplier if an exact value is not available.

For intrawell prediction limits, designate n early measurements as intrawell background for each well-constituent pair; compute the intrawell background mean ($\bar{x}$) and standard deviation (s) for each case. Given the evaluation schedule, c, n, w, and the chosen retesting scheme, use **Tables 19-10** to **19-13** in **Appendix D** to determine an acceptably powerful κ-multiplier. Note: if the intrawell background sample size varies by well, a series of κ-multipliers should be computed, one for each distinct n.

For each κ-multiplier, calculate the upper prediction limit with (1– α) confidence as:

$$PL_{1-\alpha} = \bar{x} + \kappa s \qquad [19.13]$$

If data were transformed prior to constructing the prediction interval, *back-transform* the prediction limit *before* making comparisons against the compliance point data. Unlike a prediction limit for future means, the formula for predicting m future values *does not involve any transformation bias* if the comparison is made in the original measurement domain.

Step 4. Collect an initial measurement from each well-constituent pair being tested. Compare each value against either 1) the upper prediction limit based on upgradient background in the interwell case or 2) the intrawell prediction limit specific to that well-constituent pair. Depending on the retesting scheme chosen, if any initial compliance point concentration exceeds the limit, collect 1 to 3 additional resamples at that well. If feasible, analyze only for those constituents which exhibited initial exceedances. Compare these values sequentially against the upper prediction limit. If the test 'passes' prior to collection of all the scheduled resamples, the remaining resamples do not need to be gathered or compared against *PL*.

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Step 5. Decide that the test at a given well passes (*i.e.*, the well is in-compliance) if any one or more of the resamples does not exceed *PL* when using a 1-of-*m* scheme or when at least 2 resamples do not exceed PL when using the modified California scheme. Identify the well as failing when either (1) *all* resamples using a 1-of-*m* plan also exceed the prediction limit, or (2) at least two of three resamples using a modified California plan exceed *PL*.

►EXAMPLE 19-1

A large hazardous waste facility with 50 compliance wells is to monitor 10 naturally-occurring inorganic parameters in addition to 30 non-naturally occurring volatile organic compounds that have never been detected on-site. Groundwater evaluations are performed on a semi-annual basis. If the regulating authority will allow up to two resamples per exceedence of the background concentration limit, construct an interwell prediction limit with adequate statistical power and false positive rate control on the following pooled set (n = 25) of background sulfate measurements.

BG Well	Sampling Date	Sulfate (mg/l)	Log (Sulfate) log(mg/l)
GW-01	07-08-99	63	4.143
	09-12-99	51	3.932
	10-16-99	60	4.094
	11-02-99	86	4.454
GW-04	07-09-99	104	4.644
	09-14-99	102	4.625
	10-12-99	84	4.431
	11-15-99	72	4.277
GW-08	10-12-97	31	3.434
	11-16-97	84	4.431
	01-28-98	65	4.174
	04-20-99	41	3.714
	06-04-02	51.8	3.947
	09-16-02	57.5	4.052
	12-02-02	66.8	4.202
	03-24-03	87.1	4.467
GW-09	10-16-97	59	4.078
	01-28-98	85	4.443
	04-12-98	75	4.317
	07-12-98	99	4.595
	01-30-00	75.8	4.328
	04-24-00	82.5	4.413
	10-24-00	85.5	4.449
	12-01-02	188	5.236
	03-24-03	150	5.011

SOLUTION

Step 1. Assume for purposes of the example that there are no significant spatial differences among the well locations, either upgradient or downgradient. A check of normality of the pooled background sulfate measurements indicates that the interwell prediction limit should be constructed on the logged sulfate measurements rather than the raw concentrations.

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Step 2. Groundwater evaluations must be conducted semi-annually (S). By excluding never-detected organic chemicals from the SWFPR calculation, the number of constituents that are to be considered is $c = 10$ at each of $w = 50$ wells.

Step 3. Since a maximum of two resamples will be allowed during any given evaluation period, neither the 1-of-4 nor the modified California retesting plan are an option. Consequently, only a 1-of-2 or 1-of-3 retesting strategy is appropriate. With $n = 25$ background measurements, **Tables 19-1** and **19-2** in **Appendix D** should be examined for a semi-annual evaluation schedule to determine κ-multipliers with adequate power. The multiplier of $\kappa = 2.75$ for a 1-of-2 plan has 'acceptable' power compared to the semi-annual ERPC, but the multiplier of $\kappa = 2.00$ for a 1-of-3 plan has 'good' power. Use the latter value to construct the interwell prediction limit.

Step 4. The sample log-mean and log-standard deviation of the sulfate background measurements are $\bar{y} = 4.32$ and $s_y = 0.376$, respectively. Use these values and the κ-multiplier to compute the prediction limit on the log-scale as

$$PL = \bar{y} + \kappa s_y = 4.32 + 2.00 \times 0.376 = 5.072$$

Then exponentiate the limit to back-transform it to the original measurement domain, for a final sulfate prediction limit of $PL = e^{5.072} = 159.5$ mg/l.

Step 5. Compare the final prediction limit against one new sulfate measurement from each of the 50 compliance point wells. For any exceedence, compare the first of two resamples to the prediction limit. If the limit is still exceeded, test the second resample. If all three measurements (initial plus two resamples) are above the prediction limit at any specific well, declare that a statistically significant exceedence for sulfate has been identified. If, however, neither of the resamples exceeds the limit, judge the evidence to be insufficient to declare the well to be out-of-compliance. ◄

►EXAMPLE 19-2

Due to significant natural spatial variability, an intrawell testing scheme needs to be adopted at a solid waste landfill that monitors for 5 inorganic constituents at each of 10 compliance wells. If only one year's worth of quarterly sampling data is available at each well, but no recent contamination is suspected, develop an appropriate modified California intrawell retesting plan for the following chloride measurements. Assume that one statistical evaluation must be conducted each year.

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Well ID	Chloride (mg/l)	Well Mean ± SD (mg/l)	Well ID	Chloride (mg/l)	Well Mean ± SD (mg/l)
GW-09	22	28.5 ± 10.021	GW-16	31	43.6 ± 13.392
	18.4			34.6	
	39.9			60.1	
	33.7			48.7	
GW-12	78	68.7 ± 7.208	GW-24	23.4	33.98 ± 9.083
	70			36.4	
	61			31.1	
	65.8			45	
GW-13	75.1	65.75 ± 8.128	GW-25	33.5	31.38 ± 6.533
	65.6			30.2	
	67			23.1	
	55.3			38.7	
GW-14	59.2	51.28 ± 8.427	GW-26	79.8	60.92 ± 14.447
	57.1			61.3	
	41.1			57.8	
	47.7			44.8	
GW-15	35	50.72 ± 15.672	GW-28	37.7	38.0 ± 8.273
	56.8			26.6	
	69.8			45.7	
	41.3			42	

SOLUTION

Step 1. With $c = 5$ constituents, $w = 10$ wells, one annual evaluation, and an intrawell background size for each well of only $n = 4$, **Table 19-13** in **Appendix D** can be examined to locate a possible κ-multiplier, leading to an interpolated $\kappa = 4.33$. Although this multiplier will adequately control the annual SWFPR to 10% or less, it yields low power for identifying contamination. As an alternative, try computing a pooled standard deviation across the compliance wells for chloride.

Step 2. Side-by-side box plots (**Section 11.1**) of the chloride values exhibit no obvious differences in spread or variation. The *F*-statistic for Levene's test (**Section 11.2**) is also non-significant ($F = 1.0673$) at the $\alpha = 5\%$ level, suggesting that the variances are not unequal and that a pooled standard deviation can be appropriately formed.

Step 3. Conduct a one-way ANOVA on all chloride measurements from the 10 compliance wells, using Wells as the main factor (**Section 13.2.2**). The ANOVA table is presented below.

Source of Variation	Sums of Squares	Degrees of Freedom	Mean Squares	*F*-Statistic
Between Wells	7585.25	9	842.81	7.55
Error (within wells)	3350.37	30	111.68	
Total	10935.62	39		

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Step 4. Compute the square root of the Error Mean Squares (also called the *root mean squared error* or RMSE) component in the ANOVA table to derive an estimate of the pooled intrawell standard deviation of s_p = 10.568. This estimate of the average intrawell variation has 30 degrees of freedom [*df*], computed by multiplying (4–1) = 3 degrees of freedom per well times the number of wells, or $df = 3 \times 10 = 30$.

Step 5. The **Appendix D** tables are not used to derive κ-multipliers when a pooled standard deviation estimate is used for intrawell prediction limits. **R** script listed in **Appendix C** is used (see **Section 13.3**). For a modified California retesting strategy with n = 4 and *df* = 30, the κ-multiplier becomes $\kappa = 1.98$.[7] This value not only controls the SWFPR but also has good statistical power. So use this multiplier along with the pooled intrawell standard deviation to compute an intrawell prediction limit for each compliance well. As an example, since the mean for chloride at well GW-09 is 28.5, the intrawell prediction limit would be:

$$PL = 28.5 + 1.98 \times 10.568 = 49.4 \text{ mg/l}$$

Prediction limits for the other compliance wells would be computed similarly. ◄

19.3.2 TESTING FUTURE MEANS

BACKGROUND AND REQUIREMENTS

The background, requirements, and assumptions for a prediction limit on future means of order *p* are essentially identical to those for prediction limits for future values (**Section 19.3**). For a comparable level of sampling effort, predicting a future mean offers *increased effective power* compared to a strategy that uses prediction limits for individual future values. To properly implement a prediction limit strategy for future means with retesting, *it must be feasible to collect 2 to 6 independent measurements at each compliance well during a given evaluation period*. All initial and resample measurements are assumed to be statistically independent.

To include explicit retesting, it should be feasible to collect either 2*p* or 3*p* independent measurements per well during each evaluation. The initial *p* observations are used to form the initial mean, while the remaining values are used to form either one or two resample means. If statistical evaluations are done annually, it may be possible to collect quarterly data and meet the minimal sampling requirements for *p* = 2 and a 1-of-2 retesting scheme. For more frequent semi-annual or quarterly evaluations, a larger order *p* or a retesting scheme entailing two resample means will require that new samples be collected perhaps monthly or every six weeks. An explicit test for autocorrelation should be made before adopting the strategy presented here. If significant autocorrelation exists, the frequency of sampling may need to be reduced and alternate prediction limit strategies considered such as a 1-of-1 plan for a future mean (see **Section 19.1**) or individual future values (**Section 19.3.1**).

[7] The EPA Region 8 approximation equation described in **Chapter 13, Section 13.3** provides a κ-multiple estimate of 1.99 for individual wells at *n* = 4. The annual κ-factor for *w* = 10 and *c* =5 and *n* = 31 in **Table 19-13** of **Appendix D** is interpolated as $\kappa = 1.508$. Using the appropriate *A, b* & *c* coefficients from Chapter 13, Note 2 for the modified California plan, results are quite close to that generated from **R**-script.

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An important difference between testing means versus individual values is that in some cases it may not be necessary to implement a retest at all. As noted above, for the same degree of sampling effort, a prediction limit for a mean of two or more observations can provide greater effective power than a prediction limit for the same number of individual values, *even if a resampled mean is not collected*. In other words, when a 1-of-2 retesting plan for individual observations is compared to a 1-of-1 plan for means of order 2, the 1-of-1 mean-based scheme generally has greater power for identifying real concentration increases if background samples sizes are $n > 10$ (compare κ-multiple power ratings at higher *n, c,* and *w* in **Tables 19-1** and **19-5 *of* Appendix D**) A similar comparison holds between a 1-of-3 retesting plan for individual observations and a 1-of-1 plan for a mean of order 3 (**Table 19-2** versus **Table 19-8** in **Appendix D**).

Even more powerful prediction limits for future means are possible when explicit retesting is added to the procedure. However, the minimum sampling increases substantially. With a 1-of-2 retesting plan for means of order 2, as many as four independent groundwater measurements needs to be collected and analyzed per evaluation period. With a 1-of-3 plan for means of order 2 or a 1-of-2 plan for means of order 3, the sampling increases to as many as six independent observations per period. The latter plans may only be feasible for a single annual evaluation.

A problem common to all future mean prediction limits arises if the data have to be normalized via a transformation. In this case, all comparisons need to be made on the transformed data in order to avoid a transformation bias. As a consequence, the procedure is not a direct test of the background and compliance point *arithmetic* means. The test is still valid as a measure of significant mean differences in the transformed domain (*e.g.*, a test of geometric mean differences for logarithmic data). To the extent that the populations being compared share a common variance in the transformed domain, it may also indicate that a significant difference on the transformed scale also corresponds to a significant difference in the arithmetic means of the original populations.

A final potential drawback is that although a 1-of-*m* plan for future observations and a 1-of-1 plan for means of order $p = m$ seem to require the same total sampling effort, a prediction limit for observations can actually entail *less* sampling. For a future mean test of order $p = m$, m individual measurements will always need to be collected and analyzed. With a prediction limit for individual observations, the first sample is analyzed and compared to the limit. If it passes (*i.e.*, does not exceed the limit) there is no need to test the second or subsequent observations. Any subsequent resample that passes, also indicates that no further resample comparisons are needed for that test.

Under typical conditions at a site where most or all tested well-constituent pairs are likely to be at background conditions, there is a substantial savings in the number of samples for future observations versus means of the same size. It can also be noted that the same principle is true for a 1-of-2 test of a mean of order 2. Under background conditions, the two initial mean samples may be all that is required. When groundwater is contaminated, both the 1-of-*m* retesting plan for observations and the 1-of-1 plan for a mean of order $p = m$ require exactly the same amount of sampling and analysis to identify a significant exceedance.

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PROCEDURE

Step 1. Identify the number of wells (w) to be monitored and the number of constituents (c) to be sampled at each well. Also identify the evaluation schedule as annual (A), semi-annual (S), or quarterly (Q).

Step 2. Decide on the order (p) of the future mean to be predicted. To incorporate retesting, it needs to be possible to collect $2p$ independent samples during each evaluation period to use a 1-of-2 retesting scheme, or $3p$ independent samples if a 1-of-3 plan is desired.

Step 3. If an *interwell* prediction limit is needed, use the common sample of n (upgradient) background measurements to compute the background sample mean ($\bar{x}$) and standard deviation (s). Given the n background measurements, w, c, p, and the evaluation schedule (annual, semi-annual or quarterly), use **Tables 19-5 to 19-9** in **Appendix D** to determine a κ-multiplier possessing acceptable statistical power. Calculate the upper prediction limit on background as:

$$PL = \bar{x} + \kappa s \qquad [19.14]$$

If *intrawell* prediction limits are needed, designate n early measurements at each compliance well as intrawell background. Compute the background sample mean ($\bar{x}$) and standard deviation (s) for each well. Then, based on n, w, c, p, and the number of evaluations per year, use **Tables 19-14** to **19-18** in **Appendix D** to determine an adequately powerful κ-multiplier. Compute an intrawell prediction limit for each compliance well using equation [19.14]. Note: if the intrawell background sample sizes vary by well, a series of κ-multipliers will need to be identified in these **Appendix D** tables, one for each distinct n.

If the background data were transformed prior to constructing the prediction limit, *also transform any compliance point data before making comparisons against the prediction limit*. In particular, compute the comparison mean of order p using the *transformed values*, rather than transforming the sample mean of the raw concentrations.

Step 6. Collect p initial measurements from each compliance well. Compute the mean of order p for each well, *first transforming the data if necessary using the same function applied to background*. Then compare each mean against the upper prediction limit. If retesting is desired, for any compliance point mean that exceeds the limit, collect either p or $2p$ additional resamples at that well, depending on the retesting scheme chosen. Form either one or two resample means of order p from these data; compare these means sequentially to the upper prediction limit.

Step 7. Identify the well as potentially contaminated when either 1) the initial mean of order p exceeds the limit in a 1-of-1 plan, or 2) the initial mean and *all* resample means using a 1-of-2 or 1-of-3 plan also exceed the prediction limit. Deem the well to be in-compliance if either 1) the initial mean does not exceed the prediction limit, or 2) *any* of the resample means do not exceed the limit.

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►EXAMPLE 19-3

Suppose a large facility with minimal natural spatial variation is to monitor for 20 separate naturally-occurring inorganic chemicals along with a number of other never detected organic constituents. If 100 compliance wells are to be tested every six months and 25 background sample measurements are available, which resampling plans can control the SWFPR, providing acceptable statistical power? Assume that the data for each inorganic compound can be normalized and that the temporal autocorrelation between successive samples at the same well is minimal, *provided* that no more than four samples are collected during any semi-annual period.

SOLUTION

Step 1. The frequency of statistical evaluations is semi-annual (S). Excluding never-detected compounds from the SWFPR calculation leaves $c = 20$ constituents that need to be explicitly tested at each of $w = 100$ wells. For each of these constituents, since the data can be normalized, assume that an interwell prediction limit can be constructed using $n = 25$ background measurements.

Step 2. Determine κ-multipliers and power ratings for seven possible prediction limit retesting plans excluding the 1-of-3 mean order 2 and the 1-of-2 mean order 3 tests. Use the sub-tables identified as "*20 COCs, Semi-Annual*" for n =25 and w = 100 in interwell **Tables 19-1** through **10-9** in **Appendix D**, to obtain the following:

Prediction Limit Plan	κ-Multiplier	Power	Total Samples
1-of-2, observations	3.13	Low	2
1-of-3, observations	2.31	Good	3
1-of-4, observations	1.81	Good	4
Mod. California, observations	2.54	Good	4
1-of-1, mean order 2	3.56	Acceptable	2
1-of-2, mean order 2	2.29	Good	4
1-of-1, mean order 3	2.95	Good	3

Step 3. Compare the various plans in terms of statistical power and typical sampling effort. The only plan with low power is the 1-of-2 scheme for observations. The 1-of-1 mean order 2 has acceptable power. The other plans all have good power (*i.e.*, ones consistently meeting or bettering the ERPC for mean-level increases above background of 3 or more standard deviations), but potentially require either 2 or 3 resamples.

Restricting attention to those with good power, the least potential sampling effort is required by the 1-of-1 plan for a mean of order 3 or a 1-of-3 plan for observations. These two plans would requires *less total* sampling than the 1-of-4 plan for observations, the 1-of-2 mean order 2 plan and the *same or less* sampling than the modified California plan for observations in identifying a contaminant release.

If groundwater is not contaminated, the 1-of-m plans for observations require a minimum of 1 measurement to demonstrate that the well is in-bounds (*i.e.*, when the initial measurement does not exceed the background limit) as does the modified California plan. The 1-of-2 plan for a mean of order 2 requires a minimum of 2 measurements, and the 1-of-1 plan for a mean of order 3 requires a minimum of 3 measurements. On balance, the 1-of-3 plan for individual observations or the 1-of-2 plan for a mean of order 2 may provide the best compromise

between minimizing sampling effort and offering a higher probability of identifying contaminated groundwater. ◄

►EXAMPLE 19-4

Use the chloride data of **Example 19-2** to compute and contrast prediction limits for a future mean of order 2, with and without explicit retesting. Assume as before that 10 wells are monitored for 5 inorganic constituents, and evaluated on an annual basis.

SOLUTION

Step 1. The chloride data in **Example 19-2** showed significant spatial variability, suggesting the use of intrawell prediction limits. Furthermore, a one-way ANOVA evaluation of the $w = 10$ compliance wells indicated that a pooled standard deviation estimate of $s_p = 10.568$ with 30 degrees of freedom could be used to build intrawell prediction limits, instead of using individual variance estimates from each compliance well.

Step 2. With $c = 5$ constituents, $w = 10$ wells to be monitored, one annual evaluation (A), and a pooled degrees of freedom of $df = 30$, the **R** script in **Appendix C** can be repeatedly run to determine κ-multipliers for each retesting scheme for prediction limits on means of order 2. Since the sample size for each of the 10 wells is the same $n = 4$, the following multiples were generated from the **R**-script for the 1-of-1 to 1-of-3 tests of mean order 2: $\kappa = 2.68$, 1.88 and 1.51, respectively.[8] The prediction limits can then be constructed using equation [19.15], as shown for the first five compliance wells in the table below.

$$PL = \bar{x} + \kappa s_p \qquad [19.15]$$

Step 3. While the power of each retesting plan is rated 'good' compared to the annual-evaluation ERPC, the prediction limits are obviously higher when less (or no) explicit retesting is conducted. Depending on conditions at the site, the range of approximately 13 mg/l of chloride in the well-specific prediction limits may or may not be important in deciding which strategy to use. The 1-of-1 plan for a mean of order 2 requires fewer total samples than the other plans. In some situations, the higher initial limits may be outweighed by the savings in sampling cost.

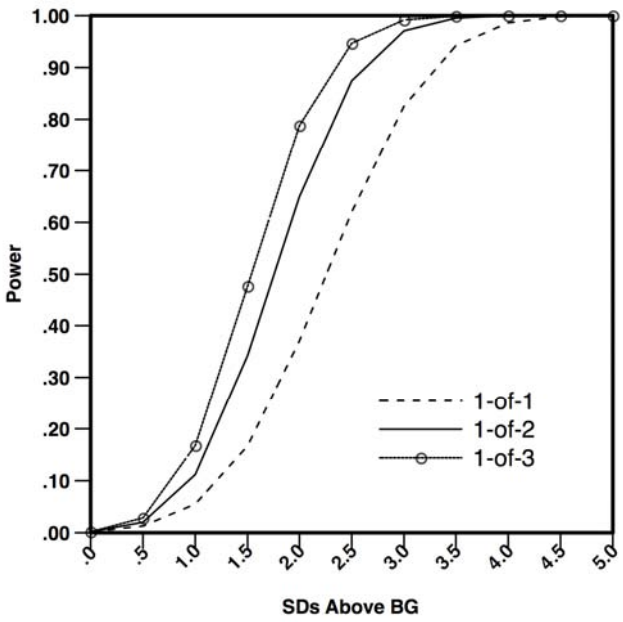
On the other hand, the ERPC provides a minimal standard for assessing statistical power. There can be a range of power curves even among plans all rated as 'good' seen in **Figure 19-1** below, where the full effective power curves for these three strategies are presented. Clearly, the 1-of-2 and 1-of-3 plans for means of order 2 have visibly higher power than the 1-of-1 retesting scheme. If site conditions permit, it may be beneficial to incorporate the 1-of-2 plan as a reasonable compromise between the gain in statistical power versus the increase in sampling requirements (for contaminated wells). ◄

[8] Using the Region 8 approximation equation in **Chapter 13**, the corresponding κ-multiples were 2.69, 1.89 and 1.52, respectively, based on tabular values at $n = 31$ of 2.258, 1.364 & .946 and using the appropriate A, b & c coefficients for each test. Results are very comparable to the R-script values.

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Well ID	Retesting Plan	κ Multiplier	Power Rating	Well Mean (mg/l)	Prediction Limit
GW-09	1-of-1	2.68	Good	28.50	56.82
	1-of-2	1.88	Good	28.50	48.37
	1-of-3	1.51	Good	28.50	44.46
GW-12	1-of-1	2.68	Good	68.70	97.02
	1-of-2	1.88	Good	68.70	88.57
	1-of-3	1.51	Good	68.70	84.66
GW-13	1-of-1	2.68	Good	65.75	94.07
	1-of-2	1.88	Good	65.75	85.62
	1-of-3	1.51	Good	65.75	81.71
GW-14	1-of-1	2.68	Good	51.28	79.60
	1-of-2	1.88	Good	51.28	71.15
	1-of-3	1.51	Good	51.28	67.24
GW-15	1-of-1	2.68	Good	50.72	79.04
	1-of-2	1.88	Good	50.72	70.59
	1-of-3	1.51	Good	50.72	66.68

Figure 19-1. Comparison of Power Curves for 1-of-m Plans for Mean of Order 2



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19.4 NON-PARAMETRIC PREDICTION LIMITS WITH RETESTING

BACKGROUND AND PURPOSE

When parametric prediction limits are not appropriate, either due to a large fraction of non-detects or data that cannot be normalized, retesting can be conducted using *non-parametric* prediction limits. The Unified Guidance discusses retesting schemes for both individual future values and for future medians (in parallel to the parametric options discussed in **Section 19.3**). Tests on individual observations include the three 1-of-*m* plans and modified California plan approaches. Tests on future medians include the 1-of-1 and 1-of-2 plans for medians of order 3. The basic strategy is to establish a non-parametric prediction limit for each monitoring constituent based on background measurements so that it accounts for the number of well-constituent tests in the overall network. Instead of determining a κ-multiplier, a non-parametric limit is computed as an *order statistic* from the background sample. The term order statistic refers to one of the values in a sorted (or *ordered*) data set.

In order to maintain adequate statistical power while minimizing the overall false positive rate, retesting will almost always be needed as part of the detection monitoring system design. As in the parametric case, a specific number of additional, *independent* resamples will potentially need to be collected for each compliance well test. The initial and subsequent resamples are then compared against the non-parametric prediction limit.

The largest or second-largest value in background is often selected as a non-parametric limit, representing the nth or $(n-1)$th order statistics. With higher level 1-of-*m* tests of observations, an even lower order statistic may be more appropriate in achieving an optimal balance between the desired SWFPR and adequate statistical power. This can be particularly true if the background sample size is large, but depends on the overall network design requirements. Although the Unified Guidance provides tables of non-parametric limits only for the largest and second-largest order statistics, EPA Region 8 has released software written in Visual Basic® labeled the *Optimal Rank Values Calculator* that computes the optimal choice of order statistic for 1-of-*m* retesting plans for $m = 1$ to 4. The program also provides approximate statistical power estimates based on user inputs of a target cumulative false positive rate, background sample size, and number of simultaneous tests to be conducted. The software and explanatory narrative will be provided on the EPA website.[9]

REQUIREMENTS AND ASSUMPTIONS

When more independent data are added to the testing procedure, retesting with non-parametric prediction limits leads to more powerful and more accurate assessments of possible contamination. As with parametric retesting schemes, a balance must be struck between 1) quick identification and confirmation of contaminated groundwater and 2) statistical independence of successive resamples. All retesting strategies depend on the assumption of statistical independence between successive resamples. This trade-off is typically resolved by allowing enough time between resamples to allow both the well to

[9] The calculator, an accompanying narrative, fact sheet and this guidance will be located on the EPA website: http://www.epa.gov/hazard/correctiveaction/resources/guidance/sitechar/gwstats/index.htm. If the calculator cannot be accessed, contact Mike Gansecki for assistance (e:mail: gansecki.mike@epa.gov; or phone: 303- 312-6150.)

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recharge and additional groundwater to flow past the well screen, and by limiting the number of possible resamples to 2 or 3.

Non-parametric retesting schemes offer somewhat less flexibility than their parametric counterparts. As with other non-parametric statistical intervals, the same SWFPR control afforded by a parametric interval based on a small *n* cannot usually be attained in a non-parametric interval; larger sample sizes are almost always necessary. κ-multipliers for parametric prediction limits are continuous statistical parameters that can be adjusted to match a desired false positive rate for even the smallest sample sizes. By contrast, the bounds of non-parametric intervals are restricted to values in the observed background sample. For a given sample size and number of tests to be run, any order statistic selected from background as the non-parametric prediction limit results in a *discrete probability* of false positive error. Altering the prediction limit by selecting a different order statistic changes the false positive rate only in discrete probability steps, providing a less efficient means of controlling the SWFPR.

The non-parametric prediction limit tests provided in the Unified Guidance do not require the underlying distribution to be normal. One potentially attractive application is for background data sets containing higher percentages of non-detects which cannot be normalized. For some constituent data sets, it may be possible to pool data from several upgradient and historical compliance wells to generate much larger total background sizes. A non-parametric Kruskal-Wallis test of medians can establish that these data are appropriate for pooling.

Since larger background sample sizes are needed because no distributional model is posited, the non-parametric testing schemes are *most applicable to interwell* comparisons. Small *intrawell* background sample sizes make it difficult for any of the non-parametric test options to be applied which can meet the SWFPR cumulative false positive design objective. Unlike parametric intrawell tests, effective sample sizes cannot be expanded by estimating a common pooled standard deviation across a number of wells. This conclusion is generally true no matter what order statistic is used to estimate the non-parametric prediction limit. But there are other considerations which might allow intrawell testing using non-parametric alternatives. For a given sample size, target false positive, a fixed maximum and number of total tests, the higher 1-of-*m* tests of future observations will have lower achievable false positive errors, with the 1-of-4 test the lowest. If the background sample size is increased through periodic additions, this false positive will continue to drop. The power of these tests using the maximum with small sample sizes is almost always greater than the EPA reference levels. A temporary strategy might be to utilize the highest order 1-of-*m* test for intrawell purposes until larger sample sizes are available. However, the target cumulative false positive rate may not initially be met. With larger sample sizes, it may also be possible to decrease the *m* of the test and still achieve the target false positive rate.

Even interwell comparisons between upgradient and downgradient wells are acceptable only if the degree of spatial variability is insignificant. Fortunately, spatial variability may be less of a problem in those cases where a non-parametric retesting scheme might be implemented, *i.e.*, when the detection rate of the chemical being monitored is fairly low. High constituent non-detect rates tend to result in more uniform spatial distribution across site wells, allowing for similar median concentrations.

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APPENDIX TABLES FOR NON-PARAMETRIC PREDICTION LIMITS

To design appropriate non-parametric prediction limits with retesting, the Unified Guidance provides separate tables for predicting individual future values versus future medians. Four distinct retesting schemes are presented in the case of prediction limits for individual values: 1-of-2, 1-of-3, 1-of-4, and modified California plan schemes. Two distinct schemes are presented for the case of future medians: 1-of-1 and 1-of-2 for medians of order 3.

Unlike the tables for parametric prediction limits discussed in **Section 19.3**, non-parametric prediction limits do not involve κ-multipliers. Instead, the entries in **Tables 19-19** to **19-24** of **Appendix D** consist of *per-constituent significance levels*. These levels represent the *achievable* false positive rate (α_{const}) associated with each tested constituent for a given retesting scheme, choice of non-parametric prediction limit, and network configuration (*i.e.*, number of wells [w] and background sample size [n]).[10] The non-parametric prediction limit can be estimated via any order statistic from the background sample. However, the most practical limits are usually either the maximum observed background value or the second-highest value. Consequently, the Unified Guidance provides tables for these two options.

Each table for the six specific non-parametric tests contains two sub-tables. One uses a limit based on the background maximum and the other the second-highest background value. All the tables are otherwise similarly structured. Within each table and sub-tables, per-constituent significance levels are given for all combinations of background sample size (n = 4 to 200) and number of wells (w = 1 to 200). These significance levels can be used to meet a target annual SWFPR of 10%, discussed in **Chapter 6**.

Correct use of these tables involves a few important considerations. First, if an *interwell* prediction limit is desired, the *target per-constituent* false positive rate (α_{const}) needs to be computed. Any prediction limit strategy selected should have a table entry no greater than α_{const} in order to ensure that the annual SWFPR is no greater than 10%. To compute this target rate, use the formula:

$$\alpha_{const} = 1 - \left(1 - \alpha\right)^{1/c} \qquad [19.16]$$

where c equals the number of monitoring constituents and α is the SWFPR = 0.10.

Unlike the tables for parametric prediction limits, separate tables are not provided for each of the three most common evaluation schedules (*i.e.*, annual, semi-annual, and quarterly). The number of 'wells' in each non-parametric table must be regarded as the actual number of compliance wells (w) times the number of annual statistical evaluations (n_E = 1, 2, or 4). For using these tables, let $w^* = w \times n_E$. This adjustment is necessary because on each evaluation, w wells should be compared against a prediction limit computed from a common interwell background. A site with w^* wells tested annually is statistically equivalent to a site having w distinct well locations tested n_E times per year ($w \times n_E$ tests).

[10] Per-constituent rates instead of network-wide false positive rates are given in these tables and those of Davis and McNichols (1994; 1999) for computational reasons. Although the mathematical algorithm is exact, it is difficult to compute with accuracy for a large number of tests (r). Hence the decomposition of r into constituents (c) times wells (w). By calculating the per-constituent false positive rate, only the number of wells (w) need be varied.

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Once w^* is computed in this way, the table entry corresponding to w^* and n represents the *achievable* annual false positive rate per constituent. As noted, this rate should not exceed the target rate (α_{const}) in order to meet the overall SWFPR. If α_{const} is exceeded for a given choice of retesting scheme and choice of non-parametric prediction limit, a different limit or scheme should be considered. In general, selecting a 1-of-m retesting scheme with larger m will lead to a lower achieved false positive rate. Also, per-constituent significance levels for the modified California approach are generally larger than those for the 1-of-m plans.

If *intrawell* prediction limits are needed, a somewhat different method needs to be employed to correctly use the per-constituent significance levels in **Tables 19-19** through **19-24** of **Appendix D**. In this case, a target *per well-constituent pair* false positive rate ($\alpha_{w\cdot c}$) needs to be first computed using the equation:

$$\alpha_{w\cdot c} = 1 - (1-\alpha)^{1/(w\cdot c)} \qquad [19.17]$$

where α is the SWFPR, w equals the actual number of compliance wells and c is the number of monitoring constituents. Then the placeholder w^* for the non-parametric tables is to be equated with the number of annual statistical evaluations ($w^* = n_E = 1$, 2, or 4). w^* represents the number of times per year that the common intrawell background at any given well-constituent pair will be compared against new compliance measurements from that well. The table entry corresponding to w^* and the intrawell background sample size n may be regarded as the achievable false positive rate per well-constituent pair. This rate should not exceed the target rate, $\alpha_{w\text{-}c}$, if the overall SWFPR is to be met.

The same approach presented in **Section 19.3** is used if a mixture of test methods is needed (*e.g.*, parametric prediction limits for some constituents, and non-parametric limits for other constituents). By construction, the target SWFPR is evenly proportioned across the list of monitored constituents. As long as the significance level per constituent (interwell case) or per well-constituent pair (intrawell case) is computed using all c constituents and not just those for which a non-parametric prediction limit test will be applied, the SWFPR will not exceed $\alpha = 0.10$ on an annual basis.

Tables 19-19 through **19-24** in **Appendix D** provide the same **bold**, *italicized* or plain text used to identify 'good', 'acceptable' and 'low' power ratings following the ERPC 3 and 4 standard deviation reference criteria as in the parametric prediction limit tables.

As final technical notes about these tables, the significance levels listed as table entries are presented using a short-hand notation in order to compactly present a wide range of false positive rates. In this notation, the first four non-zero digits of the significance level are given, followed if necessary, by the symbol *–d*. The value *d* represents the number of leading zeros to the right of the decimal point. This is equivalent to taking the non-zero portion of the entry and multiplying it by 10^{-d} to get the actual significance level. As an example, if the entry is .4251–4, the equivalent significance level is .00004251. Entries without the *–d* symbol are the actual fractional significance levels where no adjustment is needed.

For network configurations (number of wells [w] and background sample size [n]) not listed in **Tables 19-19** through **19-24** in **Appendix D**, bilinear interpolation can be used to approximate the significance level associated with the desired configuration. As discussed in **Section 19.3**, interpolation

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should be restricted to the closest four adjacent table entries. The shorthand significance level notations in the tables should first be converted to actual fractions before interpolating.

19.4.1 TESTING INDIVIDUAL FUTURE VALUES

BACKGROUND AND REQUIREMENTS

The Unified Guidance recommends two variations of non-parametric prediction limits for use in groundwater detection monitoring. The first is the prediction limit for individual future values, introduced in **Section 18.3.1**. The other is the prediction limit for future medians, detailed in **Section 18.3.2**. Basic requirements for non-parametric prediction limits are outlined in those sections.

The main advantage to a prediction limit for future values is its overall flexibility and ease of implementation. Fewer data from each compliance well are needed to implement the test compared to a prediction limit for a future median. Only an initial observation from each compliance point may be needed to identify a well-constituent pair 'in-bounds'; initial exceedances can be followed by up to a maximum of three additional individual resamples. Once the non-parametric upper prediction limit has been selected from background as a large order statistic (often the maximum or second-largest value), each compliance point measurement is compared directly against this upper limit.

The user should decide which retesting scheme to use and how many resamples per well are feasible, given that the measurements from any well during a given evaluation period need to be statistically independent. **Tables 19-19** through **19-22** in **Appendix D** can be employed to compare the *achievable false positive rates* of different schemes and to determine whether they exhibit adequate effective power. The user can also explore EPA Region VIII's *Optimal Rank Values Calculator* software to consider order statistics other than the maximum or second-largest.

PROCEDURE

Step 1. For an *interwell* test, use the number of monitoring constituents (c) in equation [19.16] to determine the target per-constituent false positive rate (α_{const}). Also multiply the number of yearly statistical evaluations (n_E) by the actual number of compliance wells (w) to determine the look-up table entry, w^*. Then depending on the background sample size n and w, choose a type of non-parametric prediction limit (*i.e.*, maximum or 2nd highest value in background) and a retesting scheme for individual observations using **Tables 19-19** through **19-22** in **Appendix D**. The final plan should have an achieved significance level no greater than α_{const} and also should be labeled with 'acceptable' or 'good' power in the **Appendix** tables.

Step 2. For an *intrawell* test, use the number of constituents (c) and the actual number of compliance wells (w) in equation [19.17] to compute the target significance level per well-constituent pair ($\alpha_{w\text{-}c}$). Set w^* in the look-up table equal to the number of yearly evaluations, n_E. Based on $w^* = n_E$ and the intrawell background sample size n, choose a non-parametric prediction limit and retesting scheme so that the achieved well-constituent pair significance level (*i.e.*, the selected table entry) does not exceed the target significance level, $\alpha_{w\text{-}c}$, and also is labeled with 'acceptable' or 'good' statistical power.

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Step 3. Sort the background data into ascending order and set the upper prediction limit equal to an appropriate order statistic of the data (*e.g.*, the maximum or the second-largest observed value). If all constituent measurements in a background sample are non-detect, use the Double Quantification rule in **Chapter 6**. The constituent should not be included in calculations for identifying the target false positive.

Step 4. Collect one initial measurement per compliance well. Then compare each initial measurement against the upper prediction limit. Depending on the retesting scheme chosen, for any compliance point value that exceeds the limit, collect one to three additional resamples from that well. Again compare the resamples against the upper prediction limit.

Step 5. Identify any well with an initial exceedance as potentially contaminated when either (1) *all* resamples using a 1-of-2, 1-of-3, or 1-of-4 plan also exceed the prediction limit, or (2) at least two resamples exceed the limit using a modified California retesting scheme. Conversely, declare a well to have 'passed' the test if either 1) the initial measurement does not exceed the prediction limit, 2) *any* resamples from a 1-of-*m* scheme do not exceed the limit, or 3) at least 2 of 3 resamples from a modified California approach do not exceed the limit.

19.4.2 TESTING FUTURE MEDIANS

BACKGROUND AND REQUIREMENTS

Prediction limits for a future median based on either a single or with one repeat (1of-1 or 1-of-2 tests) are two non-parametric procedures recommended as retesting methods in the Unified Guidance. Compared to a prediction limit for future individual values, the prediction of a median (**Chapter 18**) often requires more data to be collected from each compliance well particularly if resampling is included. Slightly greater statistical manipulation is also needed once the data are in hand. For the 1-of-1 test, the initial median to be predicted requires at least two initial observations from each compliance point, and any resample medians will require additional sets of up to three measurements, all of which needs to be statistically independent.

Given equal amounts of data and the same input conditions, a prediction limit for a future median tends to be more statistically powerful than a prediction limit for individual values. This is true whether one uses a fixed order statistic or selects across a range of order statistics to form the prediction limit. Because of this and the fact that both spatial variability and autocorrelation may be less of a problem (or at least less easily assessed) when the detection rate is low and a non-parametric strategy is needed, the Unified Guidance includes **Appendix D** tables for both a 1-of-1 scheme and a 1-of-2 scheme to predict medians of order 3. The 1-of-2 median test will have a lower achievable false positive rate than the 1-of-1 version, with all other conditions equal.

Depending on the number of annual evaluations and the test configuration, care needs to be taken that potentially needed samples are far enough apart in time. The series of observations from any well is assumed to be uncorrelated. If autocorrelation is a problem, a prediction limit for future values (**Section 19.4.1**) should be considered in which the per-well sampling requirements with explicit retesting are more modest.

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PROCEDURE

Step 1. For an *interwell* test, use the number of monitoring constituents (c) in equation [19.16] to determine the target per-constituent false positive rate (α_{const}). Also multiply the number of yearly statistical evaluations (n_E) by the actual number of compliance wells (w) to determine the look-up table margin value, w^*. Then, depending on the background sample size n and w^*, choose a type of non-parametric prediction limit (*i.e.*, maximum or 2nd highest value in background) and a retesting scheme for future medians using **Tables 19-23** to **19-24** in **Appendix D**. The final plan should have an achieved significance level no greater than α_{const}, and also should be labeled with 'acceptable' or 'good' power in the **Appendix** tables.

Step 2. For an *intrawell* test, use the number of constituents (c) and the actual number of compliance wells (w) in equation [19.17] to compute the target significance level per well-constituent pair ($\alpha_{w\text{-}c}$). Set w^* in the look-up table margin equal to the number of yearly evaluations, n_E. Based on $w^* = n_E$ and the intrawell background sample size (n), choose a non-parametric prediction limit and retesting scheme for future medians so that the achieved well-constituent pair significance level (*i.e.*, the selected table entry) does not exceed the target significance level, $\alpha_{w\text{-}c}$, and also is labeled with 'acceptable' or 'good' statistical power.

Step 3. Sort background into ascending order and set the upper prediction limit equal to a large background order statistic (*e.g.*, the maximum or second largest value). If all constituent measurements in a background sample are non-detect, use the Double Quantification rule in **Chapter 6**. The constituent should not be included in calculations identifying the target false positive rate.

Step 4. Collect two initial measurements per compliance well. If both do not exceed the upper prediction limit, the test passes since the median of order 3 will also not exceed the limit. There is no need to collect the third initial observation or any resamples. If both exceed the prediction limit, the median will also exceed the limit. There is no need to collect the third initial measurement. If using a 1-of-1 plan, move to Step 5. Otherwise, collect up to three resamples in order to assess the resample median.

If one initial measurement is above and one below the limit, collect a third observation to determine the position of the median relative to the prediction limit. In all cases, if two or more of the compliance point observations are non-detect, set the median equal to the quantification level (QL).

Step 5. Compare the median value for each compliance well against the upper prediction limit. If a 1-of-2 retesting scheme is selected and any compliance point median exceeds the limit, collect up to three additional resamples from that well. Compute the resample median and compare this value to the upper prediction limit.

Identify a compliance well as potentially contaminated when either the initial median exceeds the upper prediction limit for a 1-of-1 plan, or both the initial median and the resample median exceed the prediction limit in a 1-of-2 plan. Conversely, declare a well to have passed the test if the initial median does not exceed the prediction limit, or the resample median in a 1-of-2 scheme does not exceed it.

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►EXAMPLE 19-5

The following trace mercury data have been collected in the past year from a site with four background wells and 10 compliance wells (two of which are shown below). The facility must monitor for five constituents, including mercury. Assuming that the percentage of non-detects in background is too high to make a parametric analysis appropriate or feasible, compare interwell non-parametric prediction limits for both observations and medians at the annual statistical evaluation, and determine whether either compliance well indicates significant evidence of mercury contamination. Further assume that the sequentially reported compliance well data below are obtained as needed for the different test comparisons.

	Mercury Concentrations (ppb)					
Event	BG-1	BG-2	BG-3	BG-4	CW-1	CW-2
1	.21	<.2	<.2	<.2	.22	.36
2	<.2	<.2	.23	.25	.20	.41
3	<.2	<.2	<.2	.28	<.2	.28
4	<.2	.21	.23	<.2	.25	.45
5	<.2	<.2	.24	<.2	.24	.43
6					<.2	.54

SOLUTION

Step 1. Using a target SWFPR of 10%, compute the target per-constituent false positive rate, noting that the monitoring list consists of five parameters. This implies that $\alpha_{const} = 1-(1-.1)^{1/5} = .021$ using equation [19.16]. Since the detection rate in background is only 35%, it is reasonable to consider non-parametric prediction limits with retesting. The background sample size of $n = 20$ is to be used to construct an interwell prediction limit for all $w = 10$ compliance wells. Since there is only one annual evaluation ($n_E = 1$), the look-up table margin value of w^* equals $w \times n_E = 10$.

Step 2. Determine potentially applicable retesting plans. First consider non-parametric prediction limits for individual observations with $n = 20$ and $w = 10$. Consulting **Tables 19-19** through **19-22** in **Appendix D**, only the 1-of-3, 1-of-4, and modified California plans meet (*i.e.*, do not exceed) the target false positive rate of 2.1%. To use the 1-of-3 or modified California plans, the prediction limit needs to be set to the maximum background measurement. In the 1-of-4 plan, the prediction limit can be set to either the maximum or second-highest value in background using the **Appendix D** tables. A final 1-of-4 plan determined with the *Optimal Rank Values Calculator* allows the use of the 3rd highest value. All of these plans boast good power compared to the annual ERPC. Both the 1-of-4 and modified California schemes may require as many as 3 separate and independent resamples in addition to the initial observation.

Consider tests for future medians of order 3 in **Tables 19-23** and **19-24** in **Appendix D**. Only the 1-of-2 plan using the maximum background value as the prediction limit meets the α_{const} target. It also has good power, but requires 3 initial measurements and up to 3 additional individual resamples.

Step 3. Sort the combined background data and compute the possible prediction limits as $PL_{(n)}$ = .28 ppb, $PL_{(n-1)}$ = .25 ppb, and $PL_{(n-2)}$ = .24 ppb, respectively representing the maximum, second-largest, and third-largest background values.

Step 4. Determine the test outcomes at each compliance well using the various retesting plans, as shown in the table below. For the prediction limits on individual observations, the first sample collected during Event 1 is used as the initial screen to determine if any resampling is necessary. The first 3 measurements at each compliance well are used to form the initial comparison. The median at CW-1 is .20 ppb, while that at CW-2 is .36 ppb.

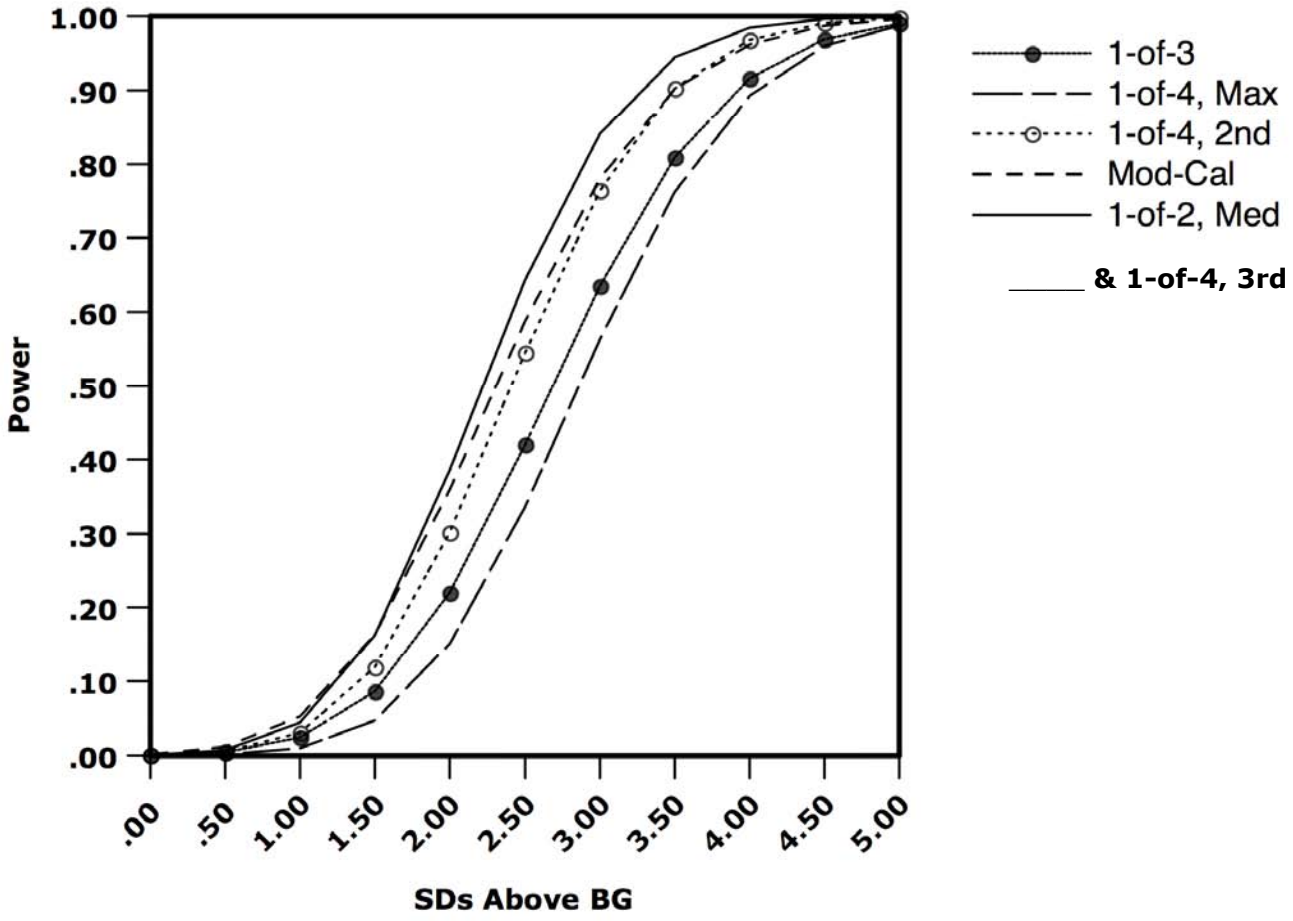
Compliance Well	Retesting Plan	Achieved α	# Initial Samples	Resamples Required	BG Limit	Result
CW-1	1-of-3	.0055	1	0	.28	Pass
	1-of-4, Max	.0009	1	0	.28	Pass
	1-of-4, 2nd	.0046	1	0	.25	Pass
	1-of-4, 3rd	.0135	1	0	.24	Pass
	Mod-Cal	.0140	1	0	.28	Pass
	1-of-2, Med	.0060	3	0	.28	Pass
CW-2	1-of-3	.0055	1	2	.28	Pass
	1-of-4, Max	.0009	1	2	.28	Pass
	1-of-4, 2nd	.0046	1	3	.25	Fail
	1-of-4, 3rd	.0135	1	3	.24	Fail
	Mod-Cal	.0140	1	3	.28	Fail
	1-of-2, Med	.0060	3	3	.28	Fail

All of the acceptable plans indicate that CW-1 is not statistically different from background, although more initial sampling is required for the 1-of-2 retesting plan with medians. For CW-2, the results are more problematic. The 1-of-3 and 1-of-4 plans based on the maximum background value allow the well to pass, while the other four plans indicate a significant difference from background. The least degree of sampling is required by the 1-of-3 plan; at some facilities, greater sampling efforts may not be feasible. When a well is likely to be contaminated, the number of samples required to actually make a decision about the well is similar across the plans with the exception of the 1-of-2 prediction limit on a median.

A further consideration is that although the power of each plan exceeds the annual ERPC when additional resampling is possible, it is helpful to compare the full power curves of multiple plans to determine whether a particular plan offers greater power than the rest. **Figure 19-2** displays an overlay of the six power curves associated with the retesting plans in this example. For these inputs, the 1-of-2 retesting plan for a median of order 3 using the background maximum and the 1-of-4 plan on individual observations using the 3rd highest background value achieve the best overall power (shown as a single curve on **Figure 19-2**).

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Figure 19-2. Comparison of Full Power Curves



As seen in **Figure 19-2**, the two plans that pass the second compliance well have visibly lower power — especially in the range of 2 to 3.5 standard deviations above background — than the four plans that failed CW-2. In such a situation, the user needs to carefully balance the risks and benefits of each acceptable resampling plan. In some cases, the cost of greater amounts of resampling may be outweighed by the added sensitivity of the test to evidence of groundwater contamination. ◄

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CHAPTER 20. MULTIPLE COMPARISONS USING CONTROL CHARTS

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This chapter describes control charts, a second recommended core strategy for detection monitoring. Control charts are a useful and powerful alternative to prediction limits. The Unified Guidance is the first EPA document to discuss retesting and simultaneous testing of multiple wells and/or constituents as they relate to control charts. Research of these topics is still ongoing.

20.1 INTRODUCTION TO CONTROL CHARTS

Control charts are a viable alternative to parametric prediction limits for testing groundwater in detection monitoring. They are similar to prediction limits for future observations in that a control chart limit is estimated from background and then compared to a sequence of compliance point measurements. If any of these values exceeds the control limit, there is initial evidence that the compliance point concentrations exceed background.

Control charts can be constructed as either interwell or intrawell tests. The main difference is how background is defined and what measurements are utilized to build the control limit. Interwell control charts establish the control limit from designated upgradient and potentially other background wells. Intrawell control charts, on the other hand, employ historical measurements from a compliance point well as background. Intrawell tests can only be appropriately applied if the historical compliance well background is uncontaminated.

An advantage of control charts over prediction limits is that a control chart graphs the compliance data over time. Certain varieties can also evaluate gradual increases above background over the period of monitoring. Trends and changes in concentration levels can be easily seen since the sample observations are consecutively plotted on the chart. This provides the analyst an historical overview of the pattern of measurement levels. Prediction limits are typically constructed to allow only ***point-in-time comparisons*** between the most recent compliance data and background, making long-term trends more difficult to identify.[1]

[1] Long-term results from repeated application of a prediction limit can be plotted over time, creating a graph similar in nature to a control chart. But this has been infrequently done in practice.

As a well-established statistical methodology, there are many kinds of control charts. Historically, control charts have been put to great use in quality engineering and manufacturing, but have more recently been adapted for use in groundwater monitoring. The specific control chart recommended in the Unified Guidance is known as a combined Shewhart-CUSUM control chart (Lucas, 1982). It is a 'combined' chart because it simultaneously utilizes two separate control chart evaluation procedures. The Shewhart portion is almost identical to a prediction limit in that compliance measurements are individually compared against a background limit. The cumulative sum [CUSUM] portion sequentially analyzes each new measurement with prior compliance data. Both portions are used to assess the similarity of compliance data to background in detection monitoring.

The Shewhart-CUSUM control chart works as follows. Appropriate background data are first collected from the specific compliance well for intrawell comparisons or from separate background wells for interwell tests. The baseline parameters for the chart, estimates of the mean and standard deviation, are obtained from these background data. These baseline measurements characterize the expected background concentrations at compliance wells.

As future compliance observations are collected, the baseline parameters are used to standardize the newly gathered data. After these measurements are standardized and plotted, a control chart is declared *out-of-control* if future concentrations exceed the baseline control limit. This is indicated on the control chart when either the Shewhart or CUSUM plot traces begins to exceed a control limit. The limit is based on the rationale that if the well remains uncontaminated as it was during the baseline period, new standardized observations should not deviate substantially from the baseline mean. If a release occurs, the standardized values will deviate significantly from baseline and tend to exceed the control limit. The historical baseline parameters then no longer accurately represent current well concentration levels.

Combined Shewhart-CUSUM control charts initially featured two control limits, one for testing the Shewhart portion of the chart, one for testing the CUSUM portion of the chart. Later research on control charts (Davis, 1999; Gibbons, 1999) indicated that having separate control limits for the Shewhart and CUSUM procedures is generally not important. Both control chart traces can instead be compared to a *single* control limit. This modification not only makes the control chart method slightly easier to apply, but also aids in measuring the statistical performance of control charts over a variety of monitoring networks.

20.2 BASIC PROCEDURE

The basic procedure for constructing a control chart is presented below. Requirements and assumptions for control charts are discussed in later sections:

Step 1. Given n background measurements (x_{jB}), estimate the baseline parameters by computing the sample mean ($\bar{x}_B$) and standard deviation (s_B).

Step 2. For a compliance point measurement (x_i) collected on sampling event T_i, compute the standardized concentration Z_i:

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$$Z_i = \left(x_i - \bar{x}_B\right) / s_B \quad [20.1]$$

Step 3. For each sampling event T_i, use the standardized concentrations from **Step 2** to compute the standardized CUSUM S_i. Set $S_0 = 0$ when computing the first CUSUM S_1.

$$S_i = \max[0,\ (Z_i - k) + S_{i-1}] \quad [20.2]$$

The notation max[*A*, *B*] in equation [20.2] refers to picking the maximum of quantities *A* and *B*. Furthermore, the parameter *k* designates half the ***displacement*** or shift in standard deviations that should be quickly detected on a control chart. Often *k* is set equal to 1, meaning that the control chart will be designed to rapidly detect upward concentration shifts of at least two standard deviations. Since Z_i is standardized by the estimated baseline standard deviation, an increase of *r* units in Z_i corresponds to an increase of *r* standard deviations above the baseline mean in the domain of concentrations x_i.

Step 4. To plot the control chart in concentration units, compute the ***non-standardized*** CUSUMs S_i^c with the equation:

$$S_i^c = \bar{x}_B + S_i \cdot s_B \quad [20.3]$$

Step 5. Calculate the non-standardized control limit used to assess compliance of both future measurements (x_i) and non-standardized CUSUMs (U_i). Traditionally, two parameters were used to compute standardized limits: the decision internal value (*h*) and the Shewhart Control Limit (*SCL*). The Unified Guidance instead recommends only one standardized control limit (*h*). Compute the non-standardized control limit (h_c) as:

$$h_c = \bar{x}_B + h \cdot s_B \quad [20.4]$$

Step 6. Construct the control chart by plotting both the compliance measurements (x_i) and the non-standardized CUSUMs (S_i^c) on the *y*-axis against the sampling events T_i along the *x*-axis. Also draw a horizontal line at the concentration value equal to the control limit, h_c.

Step 7. Moving forward in time from the first plotted sampling event T_1, declare the control chart to be potentially out-of-control if either of two situations occurs: 1) the trace of non-standardized concentrations exceeds h_c; or 2) the CUSUMs become too large, exceeding h_c.

The first case signifies a rapid increase in concentration level among the most recent sample data. The second can represent either a sudden rise in concentration levels or a gradual increase over time. A gradual increase or trend is particularly indicated if the CUSUM exceeds the control limit but the compliance concentrations do not. The reason for this is that several consecutive, small, increases in x_i will not trigger the control limit, but may cause a large enough increase in the CUSUM. As such, a control chart can indicate the onset of either sudden or gradual contamination at the compliance point.

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►EXAMPLE 20-1

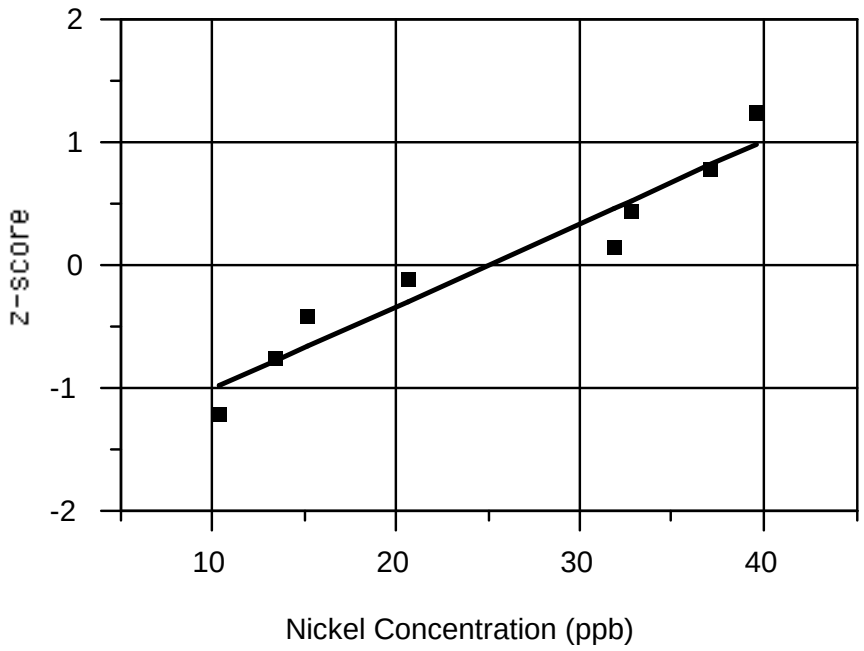
For background nickel data collected during 8 months in 1995 shown below, construct an intrawell control chart and compare it with the first 8 months of the compliance period (1996):

Month	Nickel Concentration (ppb)	
	Baseline Period (1995)	Compliance Period (1996)
1	32.8	19.0
2	15.2	34.5
3	13.5	17.8
4	39.6	23.6
5	37.1	34.8
6	10.4	28.8
7	31.9	23.7
8	20.6	81.8

SOLUTION

Step 1. As discussed in **Section 20.3.3**, control charts are a parametric procedure requiring normal or normalized data. Test the n = 8 baseline measurements for normality. A probability plot of these data provided in **Figure 20-1** exhibits a mostly linear trend. The Shapiro-Wilk test statistic computed for these data is $W = 0.896$. Compared to the $\alpha = .10$ level critical point of $w_{.10,8} = 0.851$ (**Table 10-3** of **Appendix D**), the Shapiro-Wilk test indicates that the baseline data are approximately normal. Construct the control chart using the original nickel measurements.

Figure 20-1. Probability Plot of Baseline Nickel Data



Step 2. Use the 1995 baseline nickel data to compute the sample mean and standard deviation: $\bar{x}_B$ = 25.14 ppb and s_B = 11.518 ppb. Then compute the standardized concentration Z_i for each 1996 compliance period sampling event using equation [20.1]. These values are listed in the fourth column of the table below.

Month	T_i	Nickel (ppb)	Z_i	$Z_i - k$	S_i	S_i^c
1	1	19.0	−0.53	−1.53	0.00	25.14
2	2	34.5	0.81	−0.19	0.00	25.14
3	3	17.8	−0.64	−1.64	0.00	25.14
4	4	23.6	−0.13	−1.13	0.00	25.14
5	5	34.8	0.84	−0.16	0.00	25.14
6	6	28.8	0.32	−0.68	0.00	25.14
7	7	43.7	1.61	0.61	0.61	32.16
8	8	81.8	4.92	3.92	4.53	77.31

Step 3. Compute the standardized CUSUMs as follows. First let the shift displacement parameter k = 1 and set $S_0 = 0$. After subtracting k from each Z_i, calculate the CUSUM using equation [20.2] . Note that none of the CUSUMs are positive until the first occurrence of a positive quantity ($Z_i - k$). As shown in the sixth column above, the standardized CUSUMs for the 6th, 7th and 8th events are calculated as:

$$S_6 = \max\left[0, \left(0.32 - 1\right) + 0\right] = 0$$
$$S_7 = \max\left[0, \left(1.61 - 1\right) + 0\right] = 0.61$$
$$S_8 = \max\left[0, \left(4.92 - 1\right) + 0.61\right] = 4.53$$

Step 4. Calculate the non-standardized CUSUMs (S_i^c) using the individual Z_i, baseline mean and standard deviation parameters in equation [20.3]. These values are listed in the last column of the table above. For the 8th sampling event, this calculation gives:

$$S_8^c = 25.14 + 11.518\left(4.53\right) = 77.31$$

Step 5. Compute the non-standardized control limit using equation [20.4]. For purposes of this example, set h = 5; the non-standardized limit becomes:

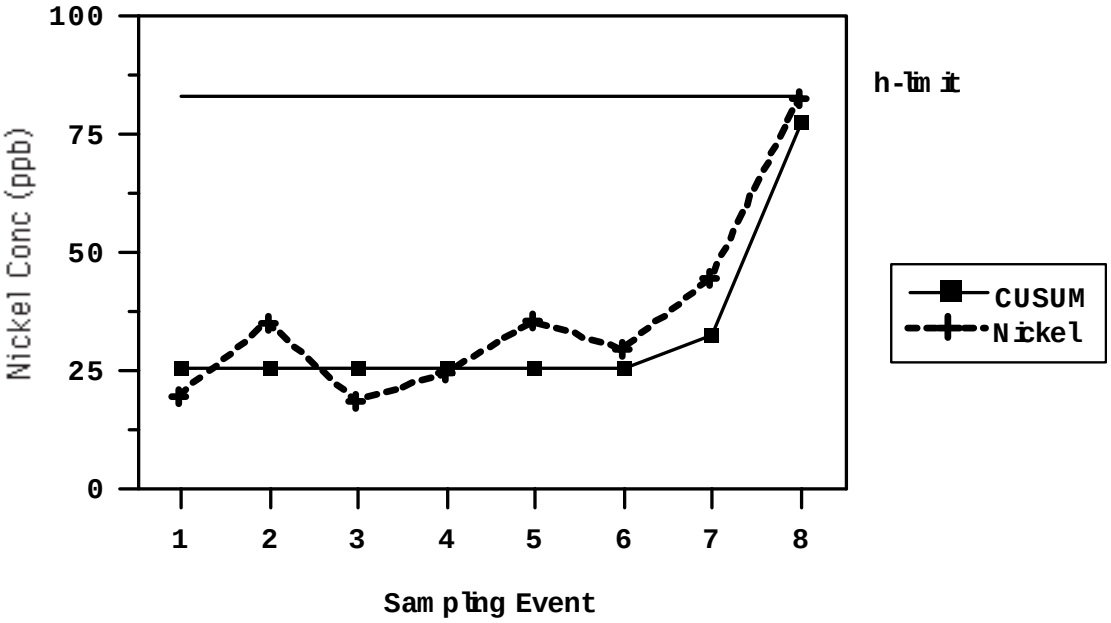
$$h_c = 25.14 + 11.518\left(5\right) = 82.73 \text{ ppb}$$

Step 6. Using the compliance period nickel concentrations and the non-standardized CUSUMs, plot the control chart as in **Figure 20-2**. The combined chart indicates there is insufficient evidence of groundwater contamination in 1996 because neither the nickel concentrations nor the CUSUM statistics exceed the control limit for the months examined. However, both traces nearly exceed h_c, and conceivably might do so in future sampling events if the apparent trend continues. If that were to happen, retesting can be performed to better determine whether the

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increase was one or a series of chance fluctuations or an actual mean-level change in nickel concentrations. ◄

Figure 20-2. Shewhart-CUSUM Control Chart for Nickel Measurements



20.3 CONTROL CHART REQUIREMENTS AND ASSUMPTIONS

As with other statistical methods, control charts are based on certain assumptions about the sample data. There are also some minimum requirements for constructing them. None of the assumptions or requirements are unique to control charts, although there are some special issues.

20.3.1 STATISTICAL INDEPENDENCE AND STATIONARITY

The methodology for control charts assumes that the sample data are statistically independent. A control chart can give misleading results if consecutive sample measurements are serially correlated (*i.e.*, autocorrelated). For this reason, it is important to design a sampling plan so that distinct volumes of groundwater are analyzed at each sampling event (**Section 14.3.1**). Duplicate laboratory analyses (*i.e.*, aliquot or field splits) should also not be treated as independent observations when constructing a control chart. Gibbons (1999) recommends that control chart observations be collected no more frequently than quarterly. Since physical independence does generally not guarantee statistical independence (**Section 14.1**), a test of autocorrelation using the sample autocorrelation function or rank von Neumann ratio tests (**Section 14.2**) should be performed to determine whether the current sampling interval affords uncorrelated measurements.

If the background data exhibit a clear seasonal cyclical pattern, the values should be deseasonalized before computing the control chart baseline parameters. For a seasonal pattern at a single well, the

method of **Section 14.3.3.1** can be used to create adjusted measurements having a stable mean. At several or a group of wells indicating a common seasonal pattern, the adjusted values can be computed using a one-way analysis of variance [ANOVA] for temporal effects (**Section 14.3.3.2**). When baseline data are deseasonalized, it is essential that newly collected compliance measurements also be deseasonalized in the same manner. It is presumed that the same pattern or physical cause will impact future data in the same manner as for the baseline measurements.

To deseasonalize compliance point measurements, simply use the seasonal and grand means estimated from background in computing the adjusted compliance point values. If the control chart remains in control following deseasonalizing, the existing background can be updated with the newer measurements. However, the revised background set should be checked again for seasonality and the seasonal and grand means re-computed, in order to more accurately adjust future measurements.

Control charts also assume that the background mean is *stationary over time*. This means there should be no apparent upward or downward trend in the background measurements. A trend imparts greater-than-expected variation to the background data, increasing the baseline standard deviation and ultimately the control limit. The net result is a control chart that has less power to identify groundwater contamination. Tests for trend described in **Chapter 17** can be used to check the assumption of no background trends. Should an upward or downward trend be verified, *the background data should not be de-trended*. While it is possible to construct and use a control chart with de-trended background and future data, the assumption that the trend will continue indefinitely is very problematic. The trend should first be investigated to ensure that background has been properly designated. Other monitoring wells should be checked to see if the same trend is occurring, indicating either evidence of an earlier release or possibly a sitewide change in the aquifer. In any case, a switch should be made to a trend test rather than a control chart.

As noted, control charts can be employed as either interwell or intrawell tests. However, interwell control charts require a spatially stationary mean across the monitoring network. If spatial variability exists among background wells for certain constituents, interwell control charts will be no more interpretable than prediction limits. A related problem can plague intrawell control charts if there is *prior* spatial variability (*i.e.*, some compliance wells are already contaminated prior to selection of intrawell backgrounds). *Historical observations should be used as baseline data in intrawell tests only if the compliance wells are known to be unaffected by a release from the monitored unit.* Otherwise, the control limit based on the greater-than-expected background values may be set too high to identify current contamination.

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20.3.2 SAMPLE SIZES AND UPDATING BACKGROUND

Both background mean and standard deviation estimates are needed to construct a control chart limit. The Unified Guidance recommends at least n = 8 measurements for the defining the baseline, particularly to ensure an accurate standard deviation estimate. *Baseline* observations are traditionally not plotted on the chart, although it may be visually helpful to include background values on the plot using a distinct symbol (*e.g.*, hollow instead of filled symbol).

Whether baseline observations are obtained from upgradient background wells for interwell testing or from individual compliance well historical data for intrawell use, these data are only small random samples used to estimate the true background population characteristics. Any particular sample set may not be adequately representative. Because of this likelihood, the background sample size requirements suggested above for constructing a control chart should be regarded as a minimum. More background observations should preferably be added to the initial set to improve the characterization of the background distribution.

For interwell control charts, periodic updating of background (**Chapter 5**) poses no difficulty. New observations should be collected at background wells on each sampling event. Then, every 1-2 years, the newly collected background should be added to the existing background pool after testing/checking for statistical similarity. The revised background can be used to re-compute the baseline parameters and, in turn, the control limit.

Updating background for intrawell control charts depends on the control chart remaining 'in-control' for several consecutive sampling events. As long as a confirmed exceedance does not occur, the in-control compliance measurements collected since the last background update can be tested against the existing background for statistical similarity using a Student's *t*- or Wilcoxon rank-sum test (**Section 5.3**). ASTM Standard D6312-98 (1999) recommends testing the newly revised background set for trends, using trend tests including those in **Chapter 17**. The ASTM methodology is intended to avoid incorporating a subtle trend into the control chart background, which influences the re-computed baseline parameters and weakens the statistical power of the control chart to identify contaminant releases.

If the comparison of recent in-control measurements against existing background indicates a statistically significant difference, it may reflect changes in natural groundwater conditions unrelated to contamination events. In these circumstances, it is possible to update background by creating a 'moving window.' The background sample size n remains fixed, with only the most recent n measurements included as background for computing baseline parameters. Earlier sampling events are excluded. The overriding goal is to ensure that background reflects the most current and representative groundwater conditions (**Chapter 3**).

Despite the apparent benefits, the statistical performance of control charts is only partially known when background is periodically updated. Davis (1999) has performed the most extensive simulations of this question. He suggests that substantially different simulation results occur with the CUSUM portion when background is periodically updated (especially early on) and combined with either a small maximum *run length* or a 'warm-up' period or both (see **Section 20.4.1**).

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Two other issues affect both control charts and prediction limits when updating intrawell background. First, if background is periodically augmented by adding new measurements (either from upgradient background wells or from recent in-control compliance measurements), the overall background sample size is increased. This in turn should cause the prediction or control chart limit to decrease.

For instance, prediction limit tables in **Chapter 19** demonstrate that as the background sample size increases, lower prediction limit κ–multipliers are appropriate. The expanded background sample is used to re-compute the prediction limit, provided that the measurements added to background do not indicate an adverse change in groundwater quality. New compliance measurements are then tested against the revised prediction limit. But the same cannot be done with control charts unless the CUSUM is *reset to zero*. The reason is that the CUSUM will have *already been affected* by those compliance measurements now being added to intrawell background. An independent comparison between compliance point values and background is thus precluded. Consequently, the Unified Guidance recommends that the CUSUM portion of the control chart be reset after each periodic update of intrawell background.[2]

The second issue is how to update intrawell background when an initial measurement has exceeded the control or prediction limit, but one or more resamples disconfirm the exceedance. Routine detection monitoring continues in this situation. No confirmed exceedance is registered for a prediction limit test and the control chart remains in-control. Should the initial exceedance be included or excluded when later updating intrawell background?

The Unified Guidance recommends a strategy parallel to the handling of outliers (**Chapter 12**). If the exceedance can be shown to be a measurement in error or a confirmed outlier, it should be excluded from the revised background. Otherwise, any disconfirmed exceedances (including any resamples that exceed the background limit but are disconfirmed by other resamples) should probably be included when updating the background. The reason is that background limits designed to incorporate retesting are computed as low as possible to ensure adequate statistical power. The trade-off is that compliance measurements legitimately similar to background but drawn from the upper tail of the distribution, sometimes exceed the limit and have to be disconfirmed with a resample. Any exceedance not documented as an error or outlier is most likely representative of some portion of the background population that previously had gone unsampled or unobserved.

20.3.3 NORMALITY AND NON-DETECT DATA

The combined Shewhart-CUSUM control chart is a parametric procedure. This implies that background used to estimate the baseline parameters should either be normal or normalized via a transformation. Normality can be tested on either the raw measurement or transformed scale using one of the goodness-of-fit techniques described in **Chapter 10**. If the hypothesis of normality is accepted,

[2] The same 'overlapping' dependence between the CUSUM and revised background will also be true when background is updated using a 'moving window' approach. The CUSUM should therefore be reset in these cases too. However, since the background sample size is kept fixed, the standardized control limit (h) will not decrease as it does when background is augmented.

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construct the control chart on the raw measurements. If it is rejected, try a transformation and retest the transformed data for normality. If the transformation works to normalize background, construct the control chart on the transformed measurements, being sure to use the same transformation on both background and the compliance values to be plotted.

Unlike prediction limits, no non-parametric version of the combined Shewhart-CUSUM control chart exists. If the background sample cannot be normalized perhaps due to a large fraction of non-detects, a non-parametric prediction limit should be considered (**Section 19.4**). Control charts will be most appropriate for those constituents with a reasonably high detection frequency. These include many inorganic constituents (***e.g.***, certain trace elements, indicators and geochemical monitoring parameters) that occur naturally in groundwater, or for other persistently detected, site-specific organic chemicals.

If no more than 10-15% of the data are non-detect, it may be possible to normalize the data via simple substitution (**Section 15.2**) of half the reporting limit [RL] for each background non-detect. A normalizing transformation can sometimes be found using a *censored probability plot* (**Chapter 15**) for background data containing a substantial fraction of non-detects up to 50%. A censored estimation technique such as Kaplan-Meier or Robust Regression on Order Statistics [Robust ROS] (**Chapter 15**) can then be used to compute estimates of the baseline mean ($\hat{\mu}_B$) and standard deviation ($\hat{\sigma}_B$) that account for the left-censored measurements. These adjusted estimates should replace the background sample mean ($\overline{x}_B$) and standard deviation (s_B) in the control chart equations of **Section 20.2**. The Unified Guidance differs somewhat from the recommended approach in ASTM Standard D6312-98 (ASTM, 1999), which is to set all non-detects identically to zero.

No matter how background non-detects are treated, control charts require an additional step for future observations that isn't needed with prediction limits. Each new compliance point measurement statistic must be added to the CUSUM associated with previous sampling events. If the new observation is a non-detect, some value (typically a fraction of the RL) needs to be imputed for the censored measurement in order to update the CUSUM. The Unified Guidance recommends that half the RL be substituted for these measurements.[3]

[3] If an intrawell control chart is constructed and it remains 'in-control' until the next background update, any non-detects observed in the meantime should be treated as left-censored measurements for purposes of updating the baseline mean and standard deviation estimates. In other words, the simple substitution of RL/2 should only apply temporarily to compute an updated CUSUM.

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20.4 CONTROL CHART PERFORMANCE CRITERIA

A significant difference exists between control charts and prediction limits in setting statistical performance criteria. Standard equations described in previous chapters allow the user to generate an exact confidence level (1–α) for prediction limits. Obtaining similar confidence levels for the Shewhart-CUSUM control charts needs to be done experimentally through varying the two background control chart limits (h) and the displacement parameter (k), as well as the retesting options. The control chart parameter limits in the two previous EPA RCRA statistical guidance documents were based on work by Lucas (1982), Hockman & Lucas (1987), and Starks (1988). Monte Carlo simulations for various combinations of control chart parameters (without retests) were used to develop the overall recommendations in their papers.

The specific parameter choices were not fixed, but appeared to work best in simulations at a single well. Starks (1988) recommended setting $h = 5$ and $k = 1$ for standardized measurements, especially in the early stages of monitoring. He further suggested that after 12 consecutive in-control measurements, the baseline mean and standard deviation be updated to include more recent sampling measurements. The values of k and *SCL* (the separate Shewhart control limit) could then be reduced to $k = 0.75$ and *SCL* = 4.0. In effect, this tightens the control chart limits to reflect that additional data are available to better characterize the baseline population.

More recent research (notably Gibbons, 1999) has demonstrated that control charts from the quality control literature do not account for several important characteristics of groundwater monitoring networks. The most important is the problem of multiple comparisons (*i.e.*, the need to simultaneously conduct testing of many well-constituent pairs during an evaluation period described in **Chapter 6**). Control chart performance is typically assessed on an individual well basis, rather than over a network of simultaneous tests. The recommended control limits have no obvious connection to the expected false positive rate (α), nor is the traditional control limit adjustable like the κ-factor in prediction limits. There is a need to account for differences in background sample sizes, a desired false positive rate, and the number of monitoring network tests in similar fashion to prediction limits. Moreover, early research and guidance did not address the issue of retesting in control charts. Retesting provides substantial improvements in prediction limit performance, and its potential needs to be evaluated for control charts.

It is standard practice to discuss the performance of prediction limits in terms of statistical power and false positive rates. However, statistical performance of control charts is usually measured via the *average run length* [ARL]. The ARL is the average number of sampling events before the control limit is first exceeded, identifying an 'out-of-control' process. Ideally, the ARL should be large when the mean concentration of the tested constituent is at or near the baseline average, but increasingly smaller as the true mean is gradually shifted above baseline.

Put in standard statistical terms, the control chart should not easily or quickly signal false evidence of a release when a release has *not* occurred. To have a low false positive rate when the null hypothesis of no contamination is true, the chart should stay 'in-control' for a long time indicated by a large ARL. The statistical power for detecting a release when it occurs should be as high as possible. A short ARL will indicate that a control chart is quickly determined to be out-of-control.

False positive rates (α) for CUSUM control charts cannot be equated precisely with ARLs. But it has been found that the ARLs closely follow a geometric distribution pattern with a mean equal to ($1/\alpha$). Thus, a control chart with an ARL of 100 would have an associated false positive rate of roughly 1%. The relationship is not exact, especially for combined Shewhart-CUSUM control charts. It is also affected by the randomness in the background data used to establish the control chart baseline.

Thus, the Unified Guidance offers a new framework for measuring control chart statistical performance. It is suggested that measuring false positive rates in control charts be conducted by establishing a time frame or run length of interest, specifically, a period of one year. A false positive is counted if the chart has a confirmed exceedance sometime during the year, under the assumption of no contaminant release. Statistical power is similarly evaluated for a fixed time interval (***e.g.***, one year) by measuring the proportion of run lengths with confirmed exceedances ***during that interval***. In this way, both the false positive rate and power are tied to a specific one-year time frame.

This framework is consistent with the guidance recommendations that prediction limit performance be measured according to an annual, cumulative 10% site-wide false positive rate [SWFPR] and that cumulative, annual effective power be comparable to the EPA reference power curves [ERPC]. The suggested framework for control charts allows a direct comparison with prediction limits when designing alternate statistical approaches.

20.4.1 CONTROL CHARTS WITH MULTIPLE COMPARISONS

Until recently, control charts were not designed to address the SWFPR when testing multiple well-constituent pairs. Furthermore, it was not clear to a user how to adjust for multiple tests using fixed control limits (SCL, k and h). Because of these problems, Gibbons (1999) performed a series of Monte Carlo simulations to gauge intrawell control chart performance for up to 500 simultaneous tests. Gibbons also examined the outcomes when the single Shewhart and CUSUM decision limit was allowed to vary between h = {4.5, 5.0, 5.5, and 6.0}. He found that control charts could be designed with both high power and a low SWFPR, as long as retesting was incorporated into the methodology.

Additional Monte Carlo simulation work was performed by Davis (1999). He found that control charts perform similarly to prediction limits when both use retests. But he also noted that certain favorable outcomes in Gibbons (1999) were the result of combining frequent updating of background and a 'warm-up' period for the chart. In the latter period, any control limit exceedances were ignored. The simulations were based on small ***maximum run lengths.***

Other researchers have noted (for instance, Luceño and Puig-Pey, 2000) that the run length distribution of CUSUM control charts is often close to geometric. This implies that even when the ARL is large, there can be significant probability of an early failure. The difficulty in a real-life setting is that one will not know whether an early exceedance of the control limit is due to contaminated groundwater or simply a false positive exceedance for an otherwise in-control chart. This guidance recommends against the use of 'warm-up' periods when implementing or assessing the performance of Shewhart-CUSUM control charts.

Gibbons (1999) provides results for a number of control chart limit options, but does not determine limits which can provide exact false positive rate control. A number of potential commonly applied retesting strategies are also not evaluated. In contrast, both Gibbons (1994) and the Unified Guidance (**Chapter 19**) do provide such control for prediction limits using a wider array of retesting strategies.

Facilities may need to conduct theirown specific Monte Carlo simulations if the published literature options cannot be applied at their site. Simulations might be needed for either intrawell or interwell control charts or both. Overall methodologies for Monte Carlo simulations are provided below. The first step for either type test is a simulation of the cumulative annual false positive rate. Then a second simulation measures the cumulative, annual statistical power.

To perform an *intrawell* simulation, repeat the following steps for a large number of simulations (*e.g.*, N_{sim} = 10,000):

1. Determine the total number of well-constituent pairs for which statistical testing is required, as well as the number of pairs at which intrawell control charts will be constructed. Use the basic subdivision principle (**Section 19.2.1**) to determine the per-test false positive rate (α_{test}) associated with each control chart that meets the target SWFPR.

2. Determine the intrawell background sample size (n). Generate n standard normal measurements. Then form baseline estimates by computing the sample mean ($\bar{x}_B$) and standard deviation (s_B).

3. Pick a set of possible standardized control limits (h). Choose a maximum run length (M), based on the number of sampling events conducted each year (*e.g.*, M = 4 for quarterly sampling).

4. For each potential control limit (h), compute the non-standardized control limit using equation [20.4]. Then simulate the behavior of the control chart from sampling event 1 to sampling event M by generating standard normal compliance measurements for each event. Generate enough random measurements to account for resamples potentially needed with a selected retesting strategy.

5. Test the initial measurement associated with each sampling event against the non-standardized control limit. Also form the CUSUM for events 1 to M using equations [20.2] and [20.3]. Compare the non-standardized CUSUM against the control limit.

6. If either the initial measurement or the CUSUM exceeds h_c, use the resample(s) for that sampling event to perform a retest (see below). If the retest confirms the initial exceedance, record a false positive for that particular simulation (out of N_{sim}).

7. After all N_{sim} runs have been conducted, compute the observed false positive rate (α_h) associated with each possible *standardized* control limit (h) by dividing N_{sim} into the number of observed false positives. Set the final control limit equal to that value of h for which α_h is closest to α_{test}.

The simulation for an *interwell* control chart is similar to the intrawell case, with a few key differences. First, instead of a per-test false positive rate, the basic subdivision principle must be used to compute a *per-constituent* false positive rate (α_{const}). The reason is that the same background measurements for a given constituent are used to test each of the compliance wells in the network.

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Secondly, when generating standard normal compliance point measurements in **Step 4** of the intrawell simulation, a set of such random observations needs to be generated for *each* of the *w* wells in the network. The behavior of *w* control charts must be simulated using a common set of background data and single control limit for each one.

Once a control limit meeting the target SWFPR has been established, a second Monte Carlo simulation is run to determine the statistical power of the control chart. Since effective power is defined as the ability to flag a single contaminated well-constituent pair, the basic steps are the same for either interwell or intrawell control charts. Repeat the following over a large number of simulations (N_{sim}).

1. Determine the background sample size (n). Generate n standard normal measurements. From these, form baseline estimates by computing the sample mean ($\bar{x}_B$) and standard deviation (s_B).

2. Using the standardized control limit (h) chosen in the first Monte Carlo simulation, compute a non-standardized control limit using equation [20.4]. Then simulate the behavior of the control chart from sampling event 1 to sampling event M by generating sets of normal N(Δ,1) compliance measurements for each event, where Δ varies from 1 to 5 by unit steps. Generate enough random measurements in each set to account for resamples potentially needed with a selected retesting strategy.

3. For each set of successively higher-valued compliance measurements, test the initial measurement associated with each sampling event against the non-standardized control limit. Also form the CUSUM for events 1 to M using equations [20.2] and [20.3]. Compare the non-standardized CUSUM against the control limit.

4. If either the initial measurement or the CUSUM exceeds h_c, use the resample(s) for that sampling event to perform a retest (see below). If the retest confirms the initial exceedance, record a true detection for that particular mean-level Δ and simulation (out of N_{sim}).

5. After all N_{sim} runs have been conducted, compute the observed power (1–β) associated with each true mean level (Δ) by dividing N_{sim} into the number of observed detections. The simulated effective power curve for standardized control limit (h) is a plot of (1–β) versus Δ for Δ = 1 to 5.

If the standardized control limit identified during Monte Carlo simulation has effective power comparable to the appropriate ERPC (matching the site-specific sampling frequency to one of the three curves in **Chapter 6**: quarterly, semi-annual, or annual), h can be used to form site-specific control limits. For interwell limits, compute the (upgradient) background mean and standard deviation for each monitoring constituent and use equation [20.4] to form the final, non-standardized control limits. For intrawell limits, use the same equation only with intrawell background at each well-constituent pair.

20.4.2 RETESTING IN CONTROL CHARTS

Control chart and prediction limit tests are only practical for most monitoring networks if retesting is part of the procedure, demonstrated both by Gibbons (1999) and Davis (1999). A key issue is to decide how control chart retesting should be conducted. Practical retesting strategies for prediction

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limits on future observations are described in **Section 19.1**, including both 1-of-*m* (for *m* = 2, 3, 4) and modified California plans.

ASTM Standard D6312-98 (1999) recommends a 1-of-2 retesting strategy: whenever an exceedance of the control limit occurs on a given sampling event, the next quarterly sampling event is used as the resample. Furthermore, if the exceedance is not confirmed by the resample, the ASTM standard recommends that the initial exceedance be *replaced* in the CUSUM by the follow-up sampling event, thus implicitly assuming that the initial observation was an error.

Gibbons (1999) considers the performance of other retesting plans, including 1-of-2, 1-of-3, and the original Cal-3 plan (see **Section 19.1** and **Appendix B**). For each plan, resampling is triggered when the most recent observation either by itself exceeds or causes the CUSUM to exceed the limit. Then, each resample (if more than one) is compared against *h*. The initial exceedance measurement is removed from the CUSUM computation, replaced by the resample, and then re-compared to the control limit. A statistically significant increase [SSI] is declared only if the resample verifies the initial exceedance (or both resamples for a 1-of-3 plan).

Gibbon's study and ASTM Standard D6312-98 raises an important concern as to the most statistically powerful treatment of the CUSUM when an initial exceedance is *not* confirmed by retesting. A second concern addresses when resamples should be collected.

The Unified Guidance suggests two practical possibilities to address the first concern. The initial exceedance can be removed from the CUSUM altogether, re-setting the CUSUM to its value from the previous sampling event. As noted above, this is essentially assuming the first sampling event was in error. Another option is to replace the initial exceedance by the first resample which disconfirms the exceedance, and then re-compute the CUSUM with that resample.

In either strategy, the effects on statistical power and accuracy should be simulated when constructing site-specific control limits as in the procedure outlined above. Both the false positive rate and power depend on a faithful simulation of *all* aspects of the control chart testing procedure. This includes background sample size, the number of well-constituent pairs evaluated, the retesting strategy and how the CUSUM is adjusted for resampling.

The second issue concerns when resamples should be collected. The Unified Guidance does not recommend using the next scheduled sampling event as a resample. If the exceedance were due to a laboratory analytical error or calculation mistake, a more quickly retrieved resample can resolve the discrepancy without waiting until the next quarterly or semi-annual monitoring event.

Where multiple resamples are used (a 1-of-3 plan, for instance), one would have to wait two additional sampling rounds simply to collect the resamples. These in turn could not be plotted on the control chart as regular sampling events without intermingling the roles of resamples and non-resamples, thereby complicating the interpretation and assessment of control chart performance. The common guidance recommendation is to identify an intermediate period or periods for resampling between regularly scheduled evaluations for both control charts and prediction limits.

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PART IV: COMPLIANCE/ASSESSMENT AND CORRECTIVE ACTION TESTS

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This last part of the Unified Guidance addresses statistical methods useful in compliance/assessment and corrective action monitoring, where single-sample testing is required against a fixed groundwater protection standard [GWPS]. These standards include not only health- or risk-based limits, but also those derived from background as a fixed standard. The full subject of background GWPS testing is treated in **Section 7.5,** but any of the procedures in the following chapters might be applied to single-sample background tests.

The primary tool for both stages of monitoring is the confidence interval. Several varieties of confidence intervals are presented in **Chapter 21**, including confidence intervals around means, medians, and upper percentiles for stationary populations, and confidence bands around a trend for cases where groundwater concentrations are actively changing.

Strategies to implement confidence interval tests are discussed in **Chapter 22**. In particular, the focus is on designing tests with reasonable statistical performance in terms of power and per-test false positive rates.

Chapter 7 of **Part I** provides a discussion of the overall compliance/assessment and corrective action monitoring network design. Program elements such as the appropriate hypothesis structure, selecting the appropriate parameter for comparison to a fixed limit GWPS, sampling frequency, statistical power, and confidence levels are covered. These final two chapters present the tests in greater detail.

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CHAPTER 21. CONFIDENCE INTERVALS

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Confidence intervals are the recommended general statistical strategy in compliance/assessment or corrective action monitoring. Groundwater monitoring data must typically be compared to a fixed numerical limit set as a GWPS. In compliance/assessment, the comparison is made to determine whether groundwater concentrations have increased above the compliance standard. In corrective action, the test determines whether concentrations have decreased below a clean-up criterion or compliance level. In compliance/assessment monitoring, the lower confidence limit [LCL] is of primary interest, while the upper confidence limit [UCL] is most important in corrective action. For single-sample background GWPS testing, the hypothesis structures are the same as for fixed-limit health-based standards. Where a GWPS is based on two- or multiple sample testing, a somewhat different hypothesis structure is used (**Section 7.5**) and detection monitoring test procedures in **Part III** are applicable.

General strategies for using confidence intervals in compliance/assessment or corrective action monitoring are presented in **Chapter 7**, including discussion of how regulatory standards should be matched to particular statistical parameters (*e.g.*, mean or upper percentile). More specific strategies and examples are detailed in **Chapter 22**. In this chapter, basic algorithms and equations for each type of confidence interval are described, along with an example of the calculations involved.

21.1 PARAMETRIC CONFIDENCE INTERVALS

Confidence intervals are designed to estimate statistical characteristics of some parameter of a sampled population. *Parametric* confidence intervals do this for known distributional models, *e.g.*, normal, lognormal, gamma, Weibull, *etc*. Given a statistical parameter of interest such as the population mean (μ), the lower and upper limits of a confidence interval define the most probable concentration range in which the true parameter ought to lie.

Like any estimate, the true parameter may not be located within the confidence interval. The frequency with which this error tends to occur (based on repeated confidence intervals on different samples of the same sample size and from the same population) is denoted α, while its complement ($1-\alpha$) is known as the *confidence level*. The confidence level represents the percentage of cases where a confidence interval constructed according to a fixed algorithm or equation will actually contain its

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intended target, *e.g.*, the population mean. **Section 7.2** discusses the difference between one- and two-sided confidence intervals and how the α error is assigned.

A point worth clarifying is the distinction between α as the complement of the confidence level when constructing a confidence interval and the significance level (α) used in hypothesis testing. Confidence intervals are often used strictly for estimation of population quantities. In that case, no test is performed, so α does not represent a false positive rate. Rather, it is simply the fraction of similar intervals that do not contain their intended target.

The Unified Guidance focuses on confidence interval limits compared to a fixed standard as a formal test procedure. In this case, the complement (α) of the confidence level used to generate the confidence interval is equivalent to the significance level (α) of the test. This assumes that the true population parameter under the null hypothesis is no greater than the standard in compliance/assessment monitoring or not less than the standard in corrective action.[1]

The parametric confidence intervals presented in the Unified Guidance share some common statistical assumptions. The most basic is that measurements used to construct a confidence interval be independent and identically distributed [*i.i.d.*]. Meeting this assumption requires that there be no outliers (**Chapter 12**), a stationary mean and variance over the period during which observations are collected (**Chapters 3** and **14**), and no autocorrelation between successive sampling events (**Chapter 14**). In particular, sampling events should be spaced far enough apart so that approximate statistical independence can be assumed (at many sites, observations should not be sampled more often than quarterly). Sample data should also be examined for trends. The mean is not stationary under a significant trend, as assumed in applying the other methods of this section. An apparent trend may need to be handled by computing a confidence band around the trend line (**Section 21.3**).

Another common assumption is that the sample data are either normal in distribution or can be normalized via a transformation (**Chapter 10**). Normality can be difficult to check if the sample contains a significant number of left-censored measurements (i.e., non-detects). The basic options for censored samples are presented in **Chapter 15**. If the non-detect percentage is no more than 10-15%, it may be possible to assess normality by first substituting one-half of the reporting limit [RL] for each non-detect. For higher non-detect percentages up to 50%, the Unified Guidance recommends computing a censored probability plot using either the Kaplan-Meier or Robust Regression on Order Statistics [Robust ROS] techniques (both in **Chapter 15**).

If a censored probability plot suggests that the sample (or some transformation of the sample) is normal, either Kaplan-Meier or Robust ROS can be used to construct estimates of the mean ($\hat{\mu}$) and standard deviation ($\hat{\sigma}$) adjusted for the presence of non-detects. These estimates should be used *in place of* the sample mean ($\bar{x}$) and standard deviation (s) in the parametric equations below.

[1] Technically, α represents the *maximum* possible false positive rate associated with the composite null hypothesis H_0: $\mu \leq$ GWPS or H_0: $\mu \geq$ GWPS.

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21.1.1 CONFIDENCE INTERVAL AROUND NORMAL MEAN

BACKGROUND AND PURPOSE

When compliance point data is to be compared to a fixed standard (*e.g.*, a maximum concentration limit [MCL]) and the standard in question is interpreted to represent an average or true mean concentration, a confidence interval around the mean is the method of statistical choice. A confidence interval around the mean is designed to estimate the true average of the underlying population, while at the same time accounting for variability in the sample data.

REQUIREMENTS AND ASSUMPTIONS

Confidence intervals around the mean of a normal distribution should only be constructed if the data are approximately normal or at least are reasonably symmetric (*i.e.*, the skewness coefficient is close to zero). An inaccurate confidence interval is likely to result if the sample data are highly non-normal, particularly for right-skewed distributions. If the observations are better fit by a lognormal distribution, special equations or methods need to be used to construct an accurate confidence interval on the arithmetic mean with a specified level of confidence (**Section 21.1.3**). *Therefore, checking for normality is an important first step*.

A confidence interval should not be constructed with less than 4 measurements per compliance well, and preferably 8 or more. The equation for a normal-based confidence interval around the mean involves estimating the population standard deviation via the sample standard deviation (s). This estimate can often be imprecise using a small sample size (*e.g.*, $n \leq 4$). The equation also involves a Student's t-quantile based on n–1 degrees of freedom [df], where n equals the sample size. The t-quantile is large for small n, leading to a much wider confidence interval than would occur with a larger sample size. For a 99% confidence level, the appropriate t-quantile would be $t = 31.82$ for $n = 2$, $t = 4.54$ for $n = 4$, and $t = 3.00$ for $n = 8$.

This last consideration is important since statistically significant evidence of a violation during compliance/assessment or success during corrective action is indicated only when the entire confidence interval is to one side of the standard (*i.e.*, it does not *straddle* the fixed standard; see **Chapter 7**). For a small sample size, the confidence interval may be so wide that a statistical difference is unlikely to be identified. This can happen *even if* the true mean groundwater concentration *is* different from the compliance or clean-up standard, due to the statistical uncertainty associated with the small number of observations. More specific recommendations on appropriate sample sizes are presented in **Chapter 22**, where the *statistical power* of the confidence interval tests is explored.

PROCEDURE

Step 1. Check the basic statistical assumptions of the sample as discussed above. Assuming a normal distributional model is acceptable, calculate the sample mean ($\bar{x}$) and standard deviation (s).

Step 2. Given a sample of size n and the desired level of confidence ($1-\alpha$), for each compliance well calculate either the lower confidence limit (for compliance/assessment monitoring) with the equation:

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$$LCL_{1-\alpha} = \bar{x} - t_{1-\alpha,n-1}\frac{s}{\sqrt{n}} \quad [21.1]$$

or the upper confidence limit (for corrective action) with the equation:

$$UCL_{1-\alpha} = \bar{x} + t_{1-\alpha,n-1}\frac{s}{\sqrt{n}} \quad [21.2]$$

where $t_{1-\alpha,n-1}$ is obtained from a Student's *t*-table with (n–1) degrees of freedom (**Table 16-1** in **Appendix D**). To construct a two-sided interval with overall confidence level equal to (1–α), substitute α/2 for α in the above equations.

Step 3. Compare the limit calculated in **Step 2** to the fixed compliance or clean-up standard (*e.g.*, the MCL or alternate concentration limit [ACL]. For compliance/assessment monitoring, the LCL in equation [21.1] should be used to compute the test. For corrective action, the UCL in equation [21.2] should be used instead.

►EXAMPLE 21-1

The table below lists concentrations of the pesticide Aldicarb in three compliance wells. For illustrative purposes, the health-based standard in compliance monitoring for Aldicarb has been set to 7 ppb. Determine at the α = 5% significance level whether or not any of the wells should be flagged as being out of compliance.

	Aldicarb Concentration (ppb)		
Sampling Date	Well 1	Well 2	Well 3
January	19.9	23.7	5.6
February	29.6	21.9	3.3
March	18.7	26.9	2.3
April	24.2	26.1	6.9
Mean	23.10	24.65	4.52
SD	4.93	2.28	2.10
Skewness (γ_1)	0.506	–0.234	0.074
Shapiro-Wilk (W)	0.923	0.943	0.950

SOLUTION

Step 1. First test the data for non-normality and/or significant skewness. Based on four samples per well, the skewness coefficients and Shapiro-Wilk statistics have been computed and are listed above. None of the skewness coefficients are significantly different from zero. In addition, the α = .10 critical point for the Shapiro-Wilk test with n = 4 (as presented in **Chapter 10**) is 0.792, less than each of the Shapiro-Wilk statistics; consequently, there is no significant evidence of non-normality. Construct a normal-based confidence interval around the mean.

Step 2. Calculate the sample mean and standard deviation of the Aldicarb concentrations for each compliance well. These statistics are listed above.

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Step 3. Since $\alpha = 0.05$, the confidence level must be set to $(1-\alpha) = 0.95$. Obtain the upper 95th percentile of the *t*-distribution with $(n-1) = 3$ degrees of freedom from **Table 16-1** in **Appendix D**, namely $t_{.95,3} = 2.353$. Then calculate the lower confidence limit [LCL] for each well's mean concentration, using equation [21.1]:

$$\text{Well 1: } LCL_{.95} = 23.10 - \left(2.353 \times 4.93\right)\Big/\sqrt{4} = 17.30 \text{ ppb}$$

$$\text{Well 2: } LCL_{.95} = 24.65 - \left(2.353 \times 2.28\right)\Big/\sqrt{4} = 21.97 \text{ ppb}$$

$$\text{Well 3: } LCL_{.95} = 4.52 - \left(2.353 \times 2.10\right)\Big/\sqrt{4} = 2.05 \text{ ppb}$$

Step 4. Compare each LCL to the compliance standard of 7 ppb. The LCLs for Well 1 and Well 2 lie above 7 ppb, indicating that the mean concentration of Aldicarb in both of these wells significantly exceeds the compliance standard. However, the LCL for Well 3 is below 7 ppb. providing insufficient evidence at the $\alpha = 0.05$ level that the mean in Well 3 is out of compliance. ◄

21.1.2 CONFIDENCE INTERVAL AROUND LOGNORMAL GEOMETRIC MEAN

PURPOSE AND BACKGROUND

For many groundwater monitoring constituents, neither the assumption of normality nor approximate symmetry holds for the original concentration data. Often the underlying population is heavily right-skewed, characterized by a majority of lower level concentrations combined with a long right-hand tail of infrequent but extreme values. A model such as the lognormal distribution is commonly used to analyze such data.

The lognormal is traditionally designated by the notation $\Lambda(\mu, \sigma)$ (Aitchison and Brown, 1976), where μ and σ denote parameters controlling the *location* and *scale* of the population. Typically designated as $N(\mu, \sigma)$, a normal distribution also has parameters μ and σ which denote the true mean and standard deviation. These two parameters play different roles in lognormal distributions. The key distinction is between the *arithmetic* domain (or the original measurement scale of the data) and the *logarithmic* domain. The latter denotes the mathematical space following a logarithmic transformation. Transformed lognormal data are *normally-distributed* in the logarithmic domain. In this new domain, μ represents the true mean of the log-transformed measurements--- that is, the *log-mean*. Likewise, σ represents the true standard deviation of the log-transformed values or the *log-standard deviation*.

A common misperception is to assume that a standard equation for a normal-based confidence interval can be applied to log-transformed data, with the interval endpoints then back-transformed (*i.e.*, exponentiated) to the arithmetic domain to get a confidence interval around the lognormal *arithmetic* mean. Invariably, such an interval will underestimate the true mean. The Student t- confidence interval applies to a *geometric* mean of the lognormal population when back-transformed, rather than the higher-valued *arithmetic* mean. The reason is that the sample log-mean gives an estimate of the lognormal parameter μ. When this estimate is back-transformed to the arithmetic domain, one has an estimate of

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$\exp(\mu)$ — the lognormal geometric mean — not an estimate of the lognormal arithmetic mean, which is expressed as $\exp(\mu + .5\sigma^2)$.

Although a confidence interval around the lognormal geometric mean is *not* an accurate estimate of the arithmetic mean, there are instances where such an interval may be helpful. While many GWPSs are interpreted to represent long-term arithmetic averages, some (as detailed in **Chapter 7**) can better represent medians or percentiles of the underlying distribution. Because the lognormal geometric mean is equivalent to the median, a geometric mean may in some cases be a better statistical parameter of comparison than the lognormal arithmetic mean. Furthermore, when the lognormal coefficient of variation is large, the arithmetic mean is substantially larger than the geometric mean, mostly due to infrequent but extreme individual measurements. The bulk of individual observations are located much closer to the geometric mean. It may be that a comparison of the GWPS to the geometric mean rather than to the arithmetic mean will provide a more reasonable test of long-term concentration levels.

Special equations or computational methods are used to construct an accurate confidence interval with a specified level of confidence (**Section 21.1.3**) when an estimate of the *arithmetic* mean is needed and the observations are approximately normal. There is another factor to consider when estimating an *upper* confidence limit on the lognormal arithmetic mean using Land's procedure (described in **Section 21.1.3**) or other possible procedures (see for instance Singh et al., 1997). When used with highly variable data, it can lead to severely-biased, high estimates of the confidence limit. This can make it very difficult to evaluate the success of corrective action measures.

In these cases, precise parametric estimation of the arithmetic mean may have to be foregone in favor of an alternate statistical procedure. One such alternative is a non-parametric confidence interval around the median (**Section 21.2**). Another alternative when the sample is approximately lognormal is an estimate around the geometric mean which is equivalent to the population median. A third more computationally intensive option is a *bootstrap confidence interval* around the lognormal arithmetic mean (see discussion in **Section 21.1.3**). Unlike the first two options, this last alternative allows a direct estimate of the arithmetic mean.

REQUIREMENTS AND ASSUMPTIONS

Confidence intervals around the geometric mean of a lognormal distribution should only be constructed if the log-transformed data are approximately normal or at least reasonably symmetric (*i.e.*, the skewness coefficient in the logarithmic domain is close to zero). The methods of **Chapter 10** can be used to test normality of the log-transformed values. If the log-transformed sample contains non-detects, normality *on the log-scale* should be assessed using a censored probability plot. Adjusted estimates of the mean and standard deviation on the log-scale can then be substituted for the log-mean ($\overline{y}$) and log-standard deviation (s_y) in the equations below. Like a normal arithmetic mean, a confidence interval around the lognormal geometric mean should not be constructed without a minimum of 4 measurements per compliance well, and preferably with 8 or more.

PROCEDURE

Step 1. Take the logarithm of each measurement, denoted as y_i, and check the n log-transformed values for normality. If the log-transformed measurements are approximately normal, calculate

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the log-mean ($\overline{y}$) and log-standard deviation (s_y). If the normal model is rejected, consider instead a non-parametric confidence interval (**Section 21.2**).

Step 2. Given the desired level of confidence (1–α), calculate either the LCL (for compliance/assessment monitoring) with the equation:

$$LCL_{1-\alpha} = \exp\left(\overline{y} - t_{1-\alpha,n-1} \frac{s_y}{\sqrt{n}} \right) \quad [21.3]$$

or the UCL (for corrective action) with the equation:

$$UCL_{1-\alpha} = \exp\left(\overline{y} + t_{1-\alpha,n-1} \frac{s_y}{\sqrt{n}} \right) \quad [21.4]$$

where $t_{1-\alpha,n-1}$ is obtained from a Student's *t*-table with (n–1) degrees of freedom (**Table 16-1** in **Appendix D**). In order to construct a two-sided interval with the overall confidence level equal to (1–α), substitute α/2 for α in the above equations.

Step 3. Compare the limits calculated in **Step 2** to the fixed compliance or clean-up standard (*e.g.*, the MCL or ACL). For compliance/assessment, use the LCL in equation [21.3]. For corrective action, use the UCL in equation [21.4].

Note in either case that the regulatory authority will have to approve the use of the geometric mean as a reasonable basis of comparison against the compliance standard. In some cases, there may be few other statistical options. However, stakeholders should understand that the geometric and arithmetic means estimate two distinct statistical characteristics of the underlying lognormal population.

►EXAMPLE 21-2

Suppose the following 8 sample measurements of benzene (ppb) have been collected at a landfill that previously handled smelter waste and is now undergoing remediation efforts. Determine whether or not there is statistically significant evidence at the α = 0.05 significance level that the true geometric mean benzene concentration has fallen below the permitted MCL of 5 ppb.

Sample Month	Benzene (ppb)	Log Benzene log(ppb)
1	0.5	–0.693
2	0.5	–0.693
3	1.6	0.470
4	1.8	0.588
5	1.1	0.095
6	16.1	2.779
7	1.6	0.470
8	<0.5	–1.386

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SOLUTION

Step 1. To estimate an upper confidence bound on the geometric mean benzene concentration with 95% confidence, first test the skewness and normality of the data set. Since the one non-detect concentration is unknown but presumably between 0 ppb and the RL of 0.5 ppb, a reasonable compromise is to impute this value at 0.25 ppb, half the RL. The skewness is computed as γ_1 = 2.21, a value too high to suggest the data are normal. In addition, a Shapiro-Wilk test statistic on the raw measurements works out to SW = 0.521, failing an assumption of normality at far below a significance level of α = 0.01.

On the other hand, transforming the data via natural logarithms gives a smaller skewness coefficient of γ_1 = 0.90 and a Shapiro-Wilk statistic of W = 0.896. Because these values are consistent with normality on the log-scale (the critical point for the Shapiro-Wilk test with n = 8 and α = 0.10 is 0.818), the data set should be treated as lognormal for estimation purposes. As a consequence, equation [21.4] can be used to construct a one-sided UCL on the geometric mean.

Step 2. Compute the sample log-mean and log-standard deviation. This gives $\bar{y}$ = 0.2037 log(ppb) and s_y = 1.2575 log(ppb).

Step 3. Apply the log-mean and log-standard deviation into equation [21.4] for a UCL with α = .05, n = 8, and 7 degrees of freedom. This gives an estimated limit of:

$$UCL_{.95} = \exp\left(\bar{y} + t_{.95,7} \frac{s_y}{\sqrt{8}} \right) = \exp\left(.2037 + 1.895 \times .4446\right) = 2.847 \text{ ppb}$$

Step 4. Compare the UCL to the MCL of 5 ppb. Since the limit is less than the fixed standard, there is statistically significant evidence that the benzene geometric mean, and consequently, the median benzene concentration, is less than 5 ppb. However, this calculation does *not* show that the benzene *arithmetic* mean is less than the MCL. Extreme individual benzene measurements could show up with enough regularity to cause the arithmetic mean to be higher than 5 ppb. ◄

21.1.3 CONFIDENCE INTERVAL AROUND LOGNORMAL ARITHMETIC MEAN

PURPOSE AND BACKGROUND

Estimation of a lognormal arithmetic mean is not completely straightforward. As discussed in **Section 21.1.2**, applying standard equations for normal-based confidence limits around the mean to log-transformed measurements and then exponentiating the limits, results in confidence intervals that are invariably underestimate the arithmetic mean.

Inferences on arithmetic means for certain kinds of skewed populations can be made either exactly or approximately through the use of special techniques. In particular, if a confidence interval on the arithmetic mean is desired, Land (1971; 1975) developed an exact technique along with extensive tables

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for implementing it when the underlying population is lognormal. Land also developed a more complicated approximate technique (for a full description and examples see EPA, 1997) when the population can be transformed to normality via any other increasing, 1-1, and twice differentiable transformation (*e.g.*, square, square root, cube root, *etc*.).

Although the core of Land's procedure is a correction for the so-called 'transformation bias' that occurs when making back-transforming estimates from the logarithmic domain to the raw concentration domain, it can produce unacceptable results, particularly with UCLs. The Unified Guidance advises caution when applying Land's procedure, particularly when the lognormal population has a high coefficient of variation. In those cases, the user may want to consider alternate techniques, such as those discussed in Singh, *et al* (1997 and 1999). One option is to use EPA's free-of-charge **Pro-UCL** software Version 4.0 (www.epa.gov/esd/tsc/software.htm). It computes a variety of upper confidence limits, including a bootstrap confidence interval around the arithmetic mean. This technique can be applied to lognormal data to get a direct, non-parametric UCL that tends to be less biased and to give less extreme results than Land's procedure.

For cases or sample sizes not covered by **Tables 21-1** through **21-8** in **Appendix D** when using Land's procedure, Gibbons and Coleman (2001) describe a method of approximating the necessary *H*-factors. The same authors review other alternate parametric methods for computing UCLs.

REQUIREMENTS AND ASSUMPTIONS

Confidence intervals around the arithmetic mean of a lognormal distribution should be constructed only if the data pass a test of approximate normality *on the log-scale*. While many groundwater and water quality populations tend to follow the lognormal distribution, the data should first be tested for normality on the original concentration scale. If such a test fails, the sample can be log-transformed and re-tested. If the log-transformed sample contains non-detects, normality *on the log-scale* should be assessed using a censored probability plot (**Chapter 15**). If a lognormal model is tenable, adjusted estimates of the mean and standard deviation on the log-scale can be substituted for the log-mean ($\overline{y}$) and log-standard deviation (s_y) in the equations below.

As with normal-based confidence intervals, the confidence interval here should not be constructed with fewer than 4 measurements per compliance well, and preferably with 8 or more. The reasons are similar: the equation for a lognormal-based confidence interval around the arithmetic mean depends on the sample log-standard deviation (s_y), used as an estimate of the underlying log-scale population standard deviation. This estimate can be quite imprecise when fewer than 4 to 8 observations are used. A special factor (H) was developed by Land to account for variability in a skewed population. These factors are larger for smaller samples sizes, and need to be exponentiated to estimate the final confidence limits (see below). Consequently there is a significant penalty associated with estimating the arithmetic mean using a small sample size, occasionally seen in remarkably wide confidence limits. The effect is especially noticeable when computing an UCL for corrective action monitoring.

PROCEDURE

Step 1. Test the log-tranformed sample for normality. If the lognormal model provides a reasonable fit, denote the log-transformed measurements by y_i and move to Step 2.

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Step 2. Compute the sample log-mean ($\overline{y}$) and log-standard deviation (s_y).

Step 3. Obtain the correct bias-correction factor(s) (H_α) from Land's (1975) tables (**Tables 21-1 through 21-8** in **Appendix D**), where the correct factor depends on the sample size (n), the sample log-standard deviation (s_y), and the desired confidence level ($1-\alpha$).

Step 4. Plug these factors into one of the equations given below for the LCL or UCL (depending on whether the comparison applies to compliance/assessment monitoring or to corrective action). Note that to construct a two-sided interval with an overall confidence level of ($1-\alpha$), the equations should be applied by substituting $\alpha/2$ for α.

$$LCL_{1-\alpha} = \exp\left(\overline{y} + .5s_y^2 + \frac{s_y H_\alpha}{\sqrt{n-1}} \right) \quad [21.5]$$

$$UCL_{1-\alpha} = \exp\left(\overline{y} + .5s_y^2 + \frac{s_y H_{1-\alpha}}{\sqrt{n-1}} \right) \quad [21.6]$$

Step 5. Compare the confidence limit computed in **Step 4** to the fixed compliance or clean-up standard. In compliance/assessment monitoring, use the LCL of equation [21.5]. In corrective action, use equation [21.6] for the UCL.

►EXAMPLE 21-3

Determine whether the benzene concentrations of **Example 21-2** indicate that the benzene arithmetic mean is below the permitted MCL of 5 ppb at the $\alpha = 0.05$ significance level.

SOLUTION

Step 1. From **Example 21-2**, the benzene data were found to fail a test of normality, but passed a test of lognormality (*i.e.*, they were approximately normal on the log-scale). As a consequence, Land's equation in [21.6] should be used to construct a one-sided UCL on the arithmetic mean.

Step 2. Compute the log-mean and log-standard deviation from the log-scale data. This gives $\overline{y}$ = 0.2037 log(ppb) and s_y = 1.2575 log(ppb).

Step 3. Using **Table 21-6** in **Appendix D**, pick the appropriate H-factor for estimating confidence limits around a lognormal arithmetic mean, noting that to achieve 95% confidence for a one-sided UCL, one must use ($1-\alpha$) = 0.95. With a sample size of n = 8 and a standard deviation on the log-scale of 1.2575 log(ppb), $H_{.95}$ = 4.069.

Step 4. Plug these values along with the log-mean of 0.2037 log(ppb) into equation [21.6] for the UCL. This leads to a 95% one-sided confidence limit equal to:

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$$UCL_{.95} = \exp\left(.2037 + .5\left(1.5813\right) + \frac{\left(1.2575\right)\left(4.069\right)}{\sqrt{7}} \right) = 18.7 \text{ ppb}$$

Step 5. Compare the UCL against the MCL of 5 ppb. Since the UCL is greater than the MCL, evidence is not sufficient at the 5% significance level to conclude that the true benzene arithmetic mean concentration is now below the MCL. This conclusion holds despite the fact that all but one of the benzene measurements is less than than 5 ppb. In lognormal populations, it is not uncommon to see one or two seemingly extreme measurements coupled with a majority of much lower concentrations. Since these extreme measurements help determine the location of the arithmetic mean, it is not unreasonable to expect that the true mean might be larger than 5 ppb.

The contrast in this result to **Example 21-2** is noteworthy. In that case, the UCL on the geometric mean was only 2.85 ppb. The estimated lognormal coefficient of variation with these data (**Chapters 3** and **10**) is $CV = 1.965$, somewhat on the high side. It is no surprise that results for the arithmetic and geometric means on the same sample are rather different. Neither estimator is necessarily invalid, but a decision needs to be made as to whether the MCL for benzene in this setting should be better compared to an arithmetic mean or to a geometric mean/ median for lognormal distributions. ◄

21.1.4 CONFIDENCE INTERVAL AROUND UPPER PERCENTILE

BACKGROUND AND PURPOSE

Although most MCLs and ACLs appear to represent arithmetic or long-term averages (**Chapter 7**), they can also be interpreted as standards not to be exceeded with any regularity. Other fixed standards like nitrate/nitrite attempt to limit short-term risks and thus represent upper percentiles instead of means. In these cases, the appropriate confidence interval is one built around a specific upper percentile.

The particular upper percentile chosen will depend on what the fixed compliance standard represents or is intended to represent. If the standard is a concentration that represents the 90th percentile, the confidence interval should be built around the upper 90th percentile. If the standard is meant to be a *maximum*, 'not to be exceeded,' concentration, a slightly different strategy should be used. Since there is no maximum value associated with continuous distributions like normal and lognormal, it is not possible to construct a confidence interval around the population maximum. Instead, one must settle for a confidence interval around a sufficiently high percentile, one that will exceed nearly all of the population measurements. Possible choices are the upper 90th to 95th percentile. By estimating the location of these percentiles, one needs to determine whether a sufficiently small fraction (*e.g.*, at most 1 in 10 or 1 in 20) of the possible measurements will ever exceed the standard. For even greater protection against exceedances, the upper 99th percentile could be selected, implying that at most 1 in 100 measurements would ever exceed the standard. But as noted in **Chapter 7**, selection of very high percentiles using non-parametric tests can make it extremely difficult to demonstrate corrective action success.

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REQUIREMENTS AND ASSUMPTIONS

The equations for constructing parametric confidence intervals around an upper percentile assume that the data are normally distributed, at least approximately. If the data can be normalized via a transformation, the observations should first be transformed before computing the confidence interval. Unlike confidence intervals around an arithmetic mean for transformed data, no special equations are required to construct similar intervals around an upper percentile. The same equations used for normal data can be applied to data in the transformed domain. The only additional step is that the confidence interval limits must be back-transformed prior to comparing them against the fixed standard.

The confidence interval presented here should not be constructed with fewer than 4 measurements per compliance well, and preferably with 8 or more. Too small a sample size leads to imprecise estimates of the sample standard deviation (s). Another reason is that the confidence interval equation involves a special multiplier τ, which depends on both the desired confidence level ($1-\alpha$) and the sample size (n). When n is quite small, the τ multiplier is much greater. This leads to a much wider confidence interval than that obtained with a larger n, and therefore much greater statistical uncertainty. For example, at a confidence level of 95%, the appropriate τ multiplier for an upper one-sided limit on the 95th percentile is $\tau = 26.260$ when $n = 2$, $\tau = 5.144$ when $n = 4$, and $\tau = 3.187$ when $n = 8$.

When determining the τ factor(s) needed for a confidence interval around an upper percentile, it should be noted that unlike the symmetric Student's t-distribution, separate τ factors need to be determined for the LCL and UCL. Since an upper percentile like the 95th is generally larger than the population mean, the equations for *both* the lower (*i.e.*, LCL) and upper (*i.e.*, UCL) limits involve *adding* a multiple of the standard deviation to the sample mean. The only difference is that a smaller multiple τ_{LCL} is used for the LCL, while a larger τ_{UCL} is used for the upper confidence limit. For certain choices of n, P and 1-α, the multiple τ_{LCL} can even be negative.

PROCEDURE

Step 1. Test the raw data for normality. If approximately normal, construct the interval on the original measurements. If the data can be normalized via a transformation, construct the interval on the transformed values.

Step 2. For a normal sample, compute the sample mean ($\bar{x}$) and standard deviation (s). If the data have been transformed, compute the mean and standard deviation of the transformed measurements.

Step 3. Given the percentile (P) to be estimated, sample size (n), and the desired confidence level ($1-\alpha$), use **Tables 21-9** and **21-10** in **Appendix D** to determine the τ factor(s) needed to construct the appropriate one-sided or two-sided interval. A one-sided LCL is then computed with the equation:

$$LCL_{1-\alpha} = \bar{x} + s \cdot \tau\left(P; n, \alpha\right) \qquad [21.7]$$

where $\tau(P; n, \alpha)$ is the lower α factor for the Pth percentile given n sample measurements. A one-sided UCL is given similarly by the equation:

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$$UCL_{1-\alpha} = \bar{x} + s \cdot \tau\left(P; n, 1-\alpha\right) \quad [21.8]$$

Finally, a two-sided confidence interval is computed by the pair of equations for the LCL and UCL:

$$LCL_{1-\alpha/2} = \bar{x} + s \cdot \tau\left(P; n, \alpha/2\right) \quad [21.9]$$

$$UCL_{1-\alpha/2} = \bar{x} + s \cdot \tau\left(P; n, 1-\alpha/2\right) \quad [21.10]$$

Step 4. If the data have been transformed, the equations of Step 3 would be used but with two changes: 1) the mean and standard deviation of the transformed values are substituted for $\bar{x}$ and s; and 2) the resulting limits back-transformed to get final confidence limits in the concentration domain. If a logarithmic transformation has been employed, the log-mean and log-standard deviation would be substituted for the sample mean and standard deviation. The resulting limit(s) must be exponentiated to get the final confidence limits, as in the equations below:

$$LCL_{1-\alpha} = \exp\left[\bar{y} + s_y \cdot \tau\left(P; n, \alpha\right)\right] \quad [21.11]$$

$$UCL_{1-\alpha} = \exp\left[\bar{y} + s_y \cdot \tau\left(P; n, 1-\alpha\right)\right] \quad [21.12]$$

Step 5. Compare the confidence limit(s) computed in Step 3 (or Step 4) versus the fixed compliance or clean-up standard. In compliance/assessment, use the LCL of equation [21.7]. In corrective action, use equation [21.8] for the UCL.

Note that although the above equations differentiate between the α-error used with the LCL and 1-α for the UCL, **Tables 21-9** and **21-10** in **Appendix D** are constructed identically. The α-error is represented by its confidence complement 1-α in **Table 21-10** of **Appendix D**.

►EXAMPLE 21-4

Assume that a facility permit has established an ACL of 30 ppb that should not be exceeded more than 5% of the time. Use the Aldicarb concentrations and diagnostic statistical information from **Example 21-1** to evaluate data from the three compliance wells. Determine whether any of the wells should be flagged as being out of compliance.

SOLUTION

Step 1. From **Example 21-1**, all of the wells pass a normality test. Use the sample mean and standard deviation for each compliance well, from the tabular information in **Example 21-1**.

Step 2. Select the correct τ factor from **Table 21-10** of **Appendix D** to construct a 99% LCL on the upper 95th percentile. The upper 95th percentile is needed because the permitted ACL cannot be exceeded more than 5% of the time, implying that 95% of all the Aldicarb measurements should fall below the fixed standard. With $n = 4$ observations per well, this leads to $\tau\ (P;\ n,\ \alpha) = \tau\ (.95;\ 4,\ .01) = 0.443$.

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Step 3. Compute the LCL for each well as follows using equation [21.7]:

$$Well1: LCL_{.99} = 23.10 + (0.443)(4.93) = 25.28\, ppb$$
$$Well2: LCL_{.99} = 24.65 + (0.443)(2.28) = 25.66\, ppb$$
$$Well3: LCL_{.99} = 4.52 + (0.443)(2.10) = 5.45\ ppb$$

Step 4. Compare each LCL against the ACL of 30 ppm. Since each well LCL is less than the ACL, there is insufficient statistical evidence that the upper 95th percentile of the Aldicarb distribution exceeds the fixed standard. Consequently, there is no conclusive evidence that more than 5% of the Aldicarb concentrations will exceed the ACL.

If the site were in corrective action instead of compliance/assessment monitoring, UCLs around the 95th percentile would be needed instead of LCLs. In that case, with n = 4 observations per well, τ (P; n, 1–α) = τ (.95; 4, .99) = 9.083 from **Table 21-9** of **Appendix D**. Then, the respective well UCLs would be:

$$Well1: UCL_{.99} = 23.10 + (9.083)(4.93) = 67.88\, ppb$$
$$Well2: UCL_{.99} = 24.65 + (9.083)(2.28) = 45.36\, ppb$$
$$Well3: UCL_{.99} = 4.52 + (9.083)(2.10) = 23.59\ ppb$$

In this case, two of the three wells would not meet the corrective action limit of 30 ppb. ◄

21.2 NON-PARAMETRIC CONFIDENCE INTERVALS

BACKGROUND AND PURPOSE

A non-parametric confidence interval should be considered when a sample is non-normal and cannot be normalized, perhaps due to a significant fraction of non-detects. Non-parametric confidence interval endpoints are generally chosen as *order statistics* of the sample data. The specific order statistics selected will depend on the sample size (n), the desired confidence level (1–α), and the population characteristic being estimated.

Since the data are not assumed to follow a particular distribution, it is generally not possible to construct a confidence interval around the population mean. One fairly rare exception would be if it were already known that the distribution is symmetric (where the mean is also the median). Sample order statistics represent, by definition, concentration levels exceeded by a certain number and hence a *fraction* of the sample values. They are excellent estimators of the *percentiles* of a distribution, but *not* of quantities like the arithmetic mean. The latter entails summing the data values and averaging the result. In positively-skewed populations, not only is the arithmetic mean greater than the median, it also may not correspond to any particular percentile.

Non-parametric confidence intervals can be developed either around a measure of the center of the population (*i.e.*, the population median or 50th percentile) or around an upper or lower percentile (*e.g.*, the upper 90th). The choice of percentile affects which order statistics are selected as interval endpoints.

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The sample median is generally estimated using a smaller order statistic than that used for an upper 95th percentile.

Despite the distinction between non-parametric confidence intervals around the median and similar intervals around an upper or lower percentile, the mathematical algorithm used to construct both types is essentially identical. Given an unknown $P \times 100$th percentile of interest (where P is between 0 and 1) and a sample of n concentration measurements, the probability that any randomly selected measurement will be less than the $P \times 100$th percentile is simply P. Then the probability that the measurement will exceed the $P \times 100$th percentile is $(1–P)$. Hence the number of sample values falling below the $P \times 100$th percentile out of a set of n should follow a *binomial distribution* with parameters n and *success probability* P, where 'success' is defined as the event that a sample measurement is below the $P \times 100$th percentile.

Because of this connection, the binomial distribution can be used to determine the probability that the interval formed by a given pair of order statistics will contain the percentile of interest. This kind of probability calculation makes repeated use of the cumulative binomial distribution, often denoted $Bin(x;n,p)$. It represents the probability of x or fewer successes occurring in n trials with success probability p. The computational equation for this expression[2] can be written as:

$$Bin\left(x;n,p\right)=\sum_{i=0}^{x}\binom{n}{i}p^{i}\left(1-p\right)^{n-i} \qquad [21.13]$$

To make statistical inferences about the $P \times 100$th percentile, P (expressed as a fraction) would be substituted for p in equation [21.13]. It can be seen why the same basic algorithm applies both to confidence intervals around the median and around upper percentiles like the 95th. If an interval around the median is desired, one would set $P = 0.50$. For an interval needed around the upper 95th percentile, one would set $P = 0.95$ and perform similar calculations.

When constructing non-parametric confidence intervals, the type of confidence interval needs to be matched against the kind of fixed standard to which it will be compared. Since the arithmetic mean cannot be estimated directly, a confidence interval around the *median* should be used for those cases where the compliance standard represents an average. Some fixed standards can, of course, be directly interpreted as *median* concentration levels, but even for those standards representing arithmetic averages, the confidence interval on the median will give the 'next best' comparison when a non-parametric method is used.

The interpretation of a confidence interval on the median is similar to that of a parametric confidence interval around the mean. In compliance/assessment monitoring, if the LCL with confidence level $(1–\alpha)$ exceeds the compliance standard, there is statistically significant evidence that the true

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[2] The mathematical expression $\binom{n}{i}$ refers to the combination of n events taken i at a time. It can be calculated as: $n!/(i!\times[n-i]!)$, where $n! = \{n \times (n-1) \times \ldots \times 2 \times 1\}$. By convention, $0! = 1$.

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population *median* is higher than the standard. In corrective action monitoring, if the UCL is *below* the clean-up standard, one can conclude that the true population median is less than the standard with α-level significance.

REQUIREMENTS AND ASSUMPTIONS

Because a non-parametric confidence interval does not assume a specific distributional form for the underlying population, there is no need to fit a probability model to the data. If a significant portion of the data are non-detect, it may be impossible to adequately fit such a model.. The non-parametric confidence interval method only requires the ability to rank the sample data values and pick out selected order statistics as the interval endpoints. Unfortunately, this ease of construction comes with a price. As opposed to parametric intervals, non-parametric confidence intervals tend to be wider and generally require larger sample sizes to achieve comparably high confidence levels. To compute the LCL around the median with 99% confidence, at least 7 compliance point measurements are needed in the non-parametric case. Therefore, sample data should be fit to a specific probability distribution whenever possible.

The general method for constructing non-parametric confidence intervals involves an *iterative testing procedure*, where potential endpoints are selected from the sorted data values (*i.e.*, order statistics) and then tested to determine what confidence level is associated with those endpoints. If the initial choice of order statistics gives an interval with insufficient confidence, the interval needs to be widened and tested again. Clearly, the greatest confidence will be associated with an interval defined by the minimum and maximum observed sample values. But if the sample size n is small, even the largest possible confidence level may be less than the desired target confidence (*e.g.*, $(1-\alpha) = 0.99$). As such, the *actual* or *achieved* confidence level needs to be listed when reporting results of a non-parametric confidence interval test.

It may be especially difficult to achieve target confidence levels around upper percentiles even when the sample size is fairly large. An instructive example is when estimating an upper 95th percentile with a sample size of $n = 20$. In that case, the highest possible two-sided confidence level is approximately 64%, achieved when the minimum and maximum data values are taken as the interval endpoints. The confidence level is substantially less than the usual targets of 90% or more, and has very limited value as a decision basis.

The *width* of a confidence interval (which expands as the level of confidence increases) should be balanced against the desire to construct an interval *narrow enough* to provide useful information about the probable location of the underlying population characteristic (*e.g.*, the P = 95th percentile in the above example). A reasonable goal is to construct the shortest interval possible that still approaches the highest confidence level. In the example, a confidence level of almost 63% could be achieved by setting the 17th and 20th ordered sample values as the confidence interval endpoints. The 20th ordered value is obviously the maximum observation and cannot be changed. However, if any ranked value less than the 17th is taken as the lower endpoint, the confidence level will increase only slightly, but the overall interval will be unnecessarily widened.

An iterative process is used to construct non-parametric confidence limits. It is recommended that a *stopping rule* be used to decide when the improvement in the confidence level brought about by picking more extreme order statistics is outweighed by the loss of information from making the interval

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too wide. A reasonable stopping rule might be to end the iterative computations if the confidence level changes by less than 1 or 2 percent when a new set of candidate ranks is selected.

Repeated calculation of cumulative binomial distribution probabilities $Bin(x;n,p)$ are quite tedious when performed manually. One can make use of either an extensive table of binomial probabilities or a software package that computes them. Almost all commercial statistical packages will compute binomial probabilities. For small sample sizes up to $n \leq 20$, **Table 21-11** in **Appendix D** provides achievable confidence levels for various choices of the sample order statistic endpoints such as the median and common upper percentiles.

Tied values do not affect the procedure for constructing non-parametric confidence intervals. All tied values (including any non-detects treated as ties) should be regarded as distinct measurements. Because of this, ties can be arbitrarily broken when ranking the data. For example, a list of 6 values including 3 non-detects would be ordered as [<5, <5, <5, 8, 12, 20] and given the set of ranks [1, 2, 3, 4, 5, 6]. Note that it is possible for the LCL to be set equal to the RL used for non-detects.

PROCEDURE FOR A CONFIDENCE INTERVAL AROUND THE MEDIAN

Step 1. Given a sample of size n, order the measurements from least to greatest. Denote the ordered values by $x_{(1)}, x_{(2)},\ldots, x_{(n)}$, where $x_{(i)}$ is the ith concentration value in the ordered list and numbers 1 through n represent the data ranks.

Step 2. Given $P = .50$, pick candidate interval endpoints by choosing ordered data values with ranks as close to and as symmetrical as possible around the product of $(n+1) \times 0.50$. If this last quantity is a fraction (an even-numbered sample size), the ranks immediately above and below it can be selected as candidate endpoints. If the product $(n+1) \times 0.50$ is an integer (an odd-numbered sample size), add 1 and subtract 1 to get the upper and lower candidate endpoints. Once the candidate endpoints have been selected, denote the ranks of these endpoints by L^* and U^*.

Step 3. For a two-sided confidence interval, compute the confidence level associated with the tentative endpoints L^* and U^* by taking the difference in the cumulative binomial probabilities given by the equation:

$$1-\alpha = Bin\left(U^*-1;\ n,.50\right) - Bin\left(L^*-1;\ n,.50\right) = \sum_{x=L^*}^{U^*-1}\binom{n}{x}\left(\frac{1}{2}\right)^n \qquad [21.14]$$

For a one-sided LCL, compute the confidence level associated with endpoint L^* using the equation:

$$1-\alpha = 1 - Bin\left(L^*-1;\ n,.50\right) = \sum_{x=L^*}^{n}\binom{n}{x}\left(\frac{1}{2}\right)^n \qquad [21.15]$$

For a one-sided UCL, compute the confidence level associated with endpoint U^* using the equation:

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$$1-\alpha = Bin\left(U^* - 1;\ n,.50\right) = \sum_{x=0}^{U^*-1}\binom{n}{x}\left(\frac{1}{2}\right)^n \qquad [21.16]$$

To minimize the amount of direct computation needed, these equations have been used to compute selected cases over a range of sample sizes for the median in **Table 21-11** of **Appendix D**.

Step 4. If the candidate endpoint(s) do not achieve the desired confidence level, compute new candidate endpoints (L^*-1) and (U^*+1) and re-calculate the achieved confidence level. Repeat this process until the target confidence level is achieved. If one candidate endpoint already equals the data minimum or maximum, only change the rank of the other endpoint. If neither endpoint rank can be changed, set either: 1) the minimum concentration value as a one-sided LCL; 2) the maximum concentration value as a one-sided UCL; or 3) the interval spanned by the range of the sample as a two-sided confidence interval around the median. In each case, report the achieved confidence level associated with the chosen confidence limit(s).

Step 5. Compare the confidence limit(s) computed in **Step 4** versus the fixed compliance or clean-up standard. In compliance/assessment monitoring, use the LCL derived as the order statistic with rank L^*. In corrective action monitoring, use the UCL derived as the order statistic with rank U^*.

►EXAMPLE 21-5

Use the following four years of well beryllium concentrations, collected quarterly for a total of n = 16 measurements, to compute a non-parametric LCL on the median concentration with (1–α) = 99% confidence.

SAMPLE DATA		ORDERED DATA	
Date	**Beryllium (ppb)**	**Be**	**Rank**
2002, 1st Q	3.17	2.32	(1)
2002, 2nd Q	2.32	3.17	(2)
2002, 3rd Q	7.37	3.39	(3)
2002, 4th Q	4.44	3.65	(4)
2003, 1st Q	9.50	3.74	(5)
2003, 2nd Q	21.36	4.44	(6)
2003, 3rd Q	5.15	5.15	(7)
2003, 4th Q	15.70	5.58	(8)
2004, 1st Q	5.58	6.15	(9)
2004, 2nd Q	3.39	6.94	(10)
2004, 3rd Q	8.44	7.37	(11)
2004, 4th Q	10.25	8.44	(12)
2005, 1st Q	3.65	9.50	(13)
2005, 2nd Q	6.15	10.25	(14)
2005, 3rd Q	6.94	15.70	(15)
2005, 4th Q	3.74	21.36	(16)

SOLUTION

Step 1. Order the 16 measurements from least to greatest and determine the rank associated with each value (listed above in the last two columns). The smallest observation, 2.32 ppb, receives the smallest rank, while the largest value, 21.36 ppb, receives a rank of 16.

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Step 2. Since a confidence interval on the median must be constructed, the desired percentile is the 50th (*i.e.*, $P = 0.50$). Therefore the quantity $(n+1) \times P = 17 \times 0.50 = 8.5$. The data ranks closest to this value are $L^* = 8$ and $U^* = 9$, so these are used as initial candidate endpoints.

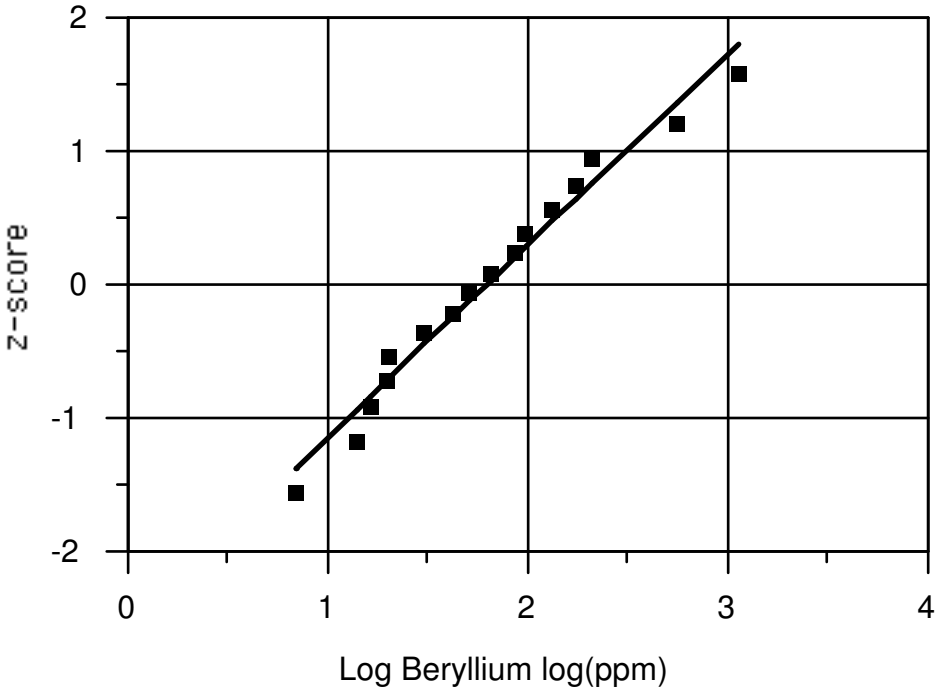
Step 3. Using the cumulative binomial distribution, and recognizing that only a lower confidence limit is needed, use equation [21.15] to calculate the actual confidence level associated with the order statistic $x_{(8)}$:

$$1-\alpha = 1 - Bin\left(L^* - 1;\ \text{n,P}\right) = 1 - Bin\left(7;\ 16,.50\right) = 1 - \sum_{x=0}^{7}\binom{16}{x}(.50)^{16} = 0.4018$$

Since the achieved confidence level is much less than 99%, subtract 1 from L^* and recompute the confidence level. Repeat this process until the confidence level is at least 99%. Since the achieved confidence when $L^* = 4$ is equal to .9894 or approximately 99%, the LCL should be selected as $x_{(4)}$ (*i.e.*, the 4th order statistic in the data set, also equal to the fourth smallest measurement), which equals 3.65 ppm. With statistical confidence of 98.94%, one can assert that the true median beryllium concentration in the underlying population is no less than 3.65 ppm.

Step 4. In this example, a lognormal model could also have been fit to the sample. Indeed the probability plot in **Figure 21-2** below indicates good agreement with a lognormal fit, enabling a comparison between the non-parametric LCL with that derived from assuming a parametric model for the same data.

Figure 21-2. Probability Plot on Logged Beryllium Data



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Step 5. Since the non-parametric LCL was constructed around the population median, the fairest comparison is to construct a lognormal-based confidence interval around the *median* and not the arithmetic mean. As discussed in **Section 21.1.2**, this is equivalent to constructing a confidence interval around the lognormal *geometric mean*. This can be built via a normal-based confidence interval around the mean using the log-transformed measurements and then exponentiating the interval limits. Thus, using equation [21.3] with the log-mean and log-standard deviation given by $\overline{y}$ = 1.8098 log(ppm) and s_y = 0.60202 log(ppm) respectively, one can compute the 99% LCL as:

$$LCL_{.99} = \exp\left(\overline{y} - t_{.99,n-1}\frac{s_y}{\sqrt{n}} \right) = \exp\left[1.8098 - (2.602)(.60202)/\sqrt{16} \right] = 4.13 \text{ ppm}$$

The non-parametric LCL around the median is slightly lower than the limit computed by assuming an underlying lognormal distribution. Given the apparent lognormal fit, the parametric LCL is probably a slightly better estimate, but the non-parametric method performs well nonetheless.

The chief virtue of using a parametric confidence interval is the ability to generate estimates at any confidence level even with small sample sizes. On the other hand, if the data are lognormally-distributed, a confidence interval on the arithmetic mean may be preferred for comparisons to a fixed standard, depending on the type of standard. The advantage of a non-parametric interval around the median is its greater flexibility to define confidence intervals on non-normal data sets. ◄

PROCEDURE FOR A CONFIDENCE INTERVAL AROUND A PERCENTILE

Step 1. Given a sample of size n, order the measurements from least to greatest. Denote the ordered values by $x_{(1)}$, $x_{(2)}$, …, $x_{(n)}$, where $x_{(i)}$ is the ith concentration value in the ordered list and numbers 1 through n represent the data ranks.

Step 2. Given the desired percentile P, pick candidate interval endpoints by choosing ordered data values with ranks as close to and as symmetrical as possible around the product $(n+1) \times P$, where n is the sample size and P is expressed as a fraction. If this last quantity is a fraction (even-numbered sample size), the ranks immediately above and below it can be selected as candidate endpoints (unless the fraction is larger than n, in which case the maximum rank n would be chosen as the upper endpoint). If the product $(n+1) \times P$ is an integer (odd-numbered sample size), add 1 and subtract 1 to get the upper and lower candidate endpoints. Once the candidate endpoints have been selected, denote these by L^* and U^*.

Step 3. For a two-sided confidence interval, compute the confidence level associated with the tentative endpoints L^* and U^* by taking the difference in the cumulative binomial probabilities given by the equation:

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$$1-\alpha = Bin\left(U^{*}-1;\ n,P\right) - Bin\left(L^{*}-1;\ n,P\right) = \sum_{x=L^{*}}^{U^{*}-1}\binom{n}{x}P^{x}\left(1-P\right)^{n-x} \qquad [21.17]$$

For a one-sided LCL, compute the confidence level associated with the endpoint L^* using the equation:

$$1-\alpha = 1 - Bin\left(L^{*}-1;\ n,P\right) = \sum_{x=L^{*}}^{n}\binom{n}{x}P^{x}\left(1-P\right)^{n-x} \qquad [21.18]$$

For a one-sided UCL, compute the confidence level associated with the endpoint U^* using the equation:

$$1-\alpha = Bin\left(U^{*}-1;\ n,P\right) = \sum_{x=0}^{U^{*}-1}\binom{n}{x}P^{x}\left(1-P\right)^{n-x} \qquad [21.19]$$

To minimize the amount of direct computation, these equations have been used to compute selected cases over a range of sample sizes and for certain percentiles in **Table 21-11** of **Appendix D**.

Step 4. If the candidate endpoint(s) do not achieve the desired or target confidence level, compute new candidate endpoints, (L^*–1) and (U^*+1), and re-calculate the achieved confidence level. Repeat this process until the target confidence level is achieved. If one candidate endpoint already equals the data minimum or maximum, only change the rank of the other endpoint. If neither endpoint rank can be changed, set either: 1) the minimum concentration value as a one-sided LCL; 2) the maximum concentration value as a one-sided UCL; or 3) the interval spanned by the range of the sample data as a two-sided confidence interval around the *P*th percentile. In each case, report the achieved confidence level associated with the chosen confidence limit(s).

Step 5. Compare the confidence limit(s) computed in **Step 4** versus the fixed compliance or clean-up standard. In compliance/assessment monitoring, use the LCL derived as the order statistic with rank L^*. In corrective action monitoring, use the UCL derived as the order statistic with rank U^*.

►EXAMPLE 21-6

Use the following 12 measurements of nitrate at a well used for drinking water to determine with 95% confidence whether or not the infant-based, acute risk standard of 10 mg/L has been violated. Assume that the risk standard represents an upper 95th percentile limit on nitrate concentrations.

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Sampling Date	Nitrate (mg/L)	Rank
7/28/99	<5.0	(1)
9/3/99	12.3	(11)
11/24/99	<5.0	(2)
5/3/00	<5.0	(3)
7/14/00	8.1	(7)
10/31/00	<5.0	(4)
12/14/00	11.0	(10)
3/27/01	35.1	(12)
6/13/01	<5.0	(5)
9/16/01	<5.0	(6)
11/26/01	9.3	(8)
3/2/02	10.3	(9)

SOLUTION

Step 1. Half of the sample concentrations are non-detects, making a test of normality extremely difficult. One could attempt to fit these data via the *Kaplan-Meier* or *Robust ROS* adjustments (see **Chapter 15**), but here a non-parametric confidence interval around the upper 95th percentile will be constructed.

Step 2. Order the data values from least to greatest and assign ranks as in the last column of the table above. Note that the apparent ties among the non-detects have been arbitrarily broken in order to give a unique rank to each measurement.

Step 3. Using **Table 21-11** in **Appendix D** for n = 12, there is approximately 88% confidence associated with using L^* = 11 as the rank of the lower confidence bound and approximately 98% confidence associated with using L^* = 10. Since the target confidence level is 95%, it can only be achieved by using a rank of 10 or less. Thus the non-parametric LCL needs to be set to the 10th smallest observation or $x_{(10)}$. Scanning the list of nitrate measurements, the LCL = 11.0 ppm.

Step 4. Since the order statistic $x_{(10)}$ achieves a confidence level of 98%, one can conclude that the true upper 95th percentile nitrate concentration is no smaller than 11.0 ppm with 98% confidence. Even by this more stringent confidence level, the acute risk standard for nitrate is violated and there is statistically significant evidence that at least 1 of every 20 nitrate measurements from the well will exceed 10 mg/L.

Step 5. If the well was being remediated under corrective action monitorign, the fixed standard would be compared against a one-way UCL around the upper 95th percentile. In that case, for n = 12, **Table 21-11** of **Appendix D** indicates that the maximum observed value of 35.1 mg/L taken as the UCL achieves a confidence level of only 46%. 95% confidence could not be achieved unless at least 59 sample measurements were available and the UCL was set to the maximum of those values. The remedial action would be considered successful only if *all* 59 measurements were below the fixed standard of 10 mg/L. ◄

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21.3 CONFIDENCE INTERVALS AROUND TREND LINES

It was assumed that the underlying population is stable, (*i.e.*, characteristics like the mean, median, or upper percentiles are stationary over the period of sampling) for the confidence intervals so far presented in this chapter. In some cases, however, the concentration data will exhibit a trend. Examples might include successful remediation efforts that serve to gradually drive down a well's concentration levels, or interception of an intensifying plume of contaminated groundwater.[3]

The problem with ignoring a discernible trend when building a confidence interval is that the interval will incorporate not only the natural variability in the underlying population, but also additional variation induced by the trend itself. The net result is a confidence interval that can be much wider than expected for a given confidence level and sample size (n). A wider confidence interval makes it more difficult to demonstrate an exceedance or return to compliance versus a fixed standard in compliance/assessment or corrective action monitoring. The confidence interval will have less statistical power to identify compliance violations, or to judge the success of remedial efforts.

When a linear trend is present, it is possible to construct an appropriate confidence interval built around the estimated trend. A continuous series of confidence intervals is estimated at each point along the trend, termed a *simultaneous confidence band*. An upper or lower confidence band will tend to follow the estimated trend line whether the trend is increasing or decreasing. It is computed once the trend line has been estimated.

Construction of a confidence interval around a trend line presumes that a trend actually exists. The algorithms presented in this section *assume* that a trend is readily discernible on a time series plot of the measurements and that it is essentially linear. Otherwise, the results may be less than credible.

21.3.1 PARAMETRIC CONFIDENCE BAND AROUND LINEAR REGRESSION

BACKGROUND AND PURPOSE

A standard method for estimating a linear trend is *linear regression*, introduced in **Chapter 17**. In this section, equations for constructing a linear regression are extended to form a *confidence band* around the trend. Although a parametric technique, there is no requirement that the concentration measurements be normal or transformable to normality. Instead, the *residual concentrations* after subtracting out the estimated trend line should be roughly normal in distribution or at least symmetric.

By way of interpretation, each point along the trend line is an estimate of the true mean concentration *at that point in time*. As the underlying population mean either increases or decreases, the confidence band similarly increases or decreases to reflect this change.

Although the equations presented below can be used to simultaneously construct a confidence interval around each point on the trend line, in practice, the user will want to compute a confidence

[3] This might occur if the well screen first intercepts the leading edge of the plume, followed by the more heavily contaminated core.

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interval for a few or several of the most recent sampling events. Because the individual confidence intervals comprising the simultaneous confidence band have a joint confidence level of (1–α), no matter how many confidence intervals are constructed, the overall false positive rate associated with the entire set of tests against the fixed standard will be no greater than a pre-specified α.

REQUIREMENTS AND ASSUMPTIONS

To accurately estimate a confidence band, the sample variance should be stationary or constant as a function of time. Although the mean level may be increasing or decreasing with time, the level of variation about the mean should be essentially the same.

Once a linear regression is fitted to the data, the residuals around the trend line should be tested for normality and apparent skewness. Inferences concerning a linear regression are generally appropriate when two conditions hold: 1) the residuals from the regression are approximately normal or at least reasonably symmetric in distribution; and 2) a plot of residuals versus concentrations indicates a scatter cloud of essentially uniform *vertical thickness or width*. That is, the scatter cloud does not tend to increase in width with the level of concentration or exhibit any kind of regular pattern other than looking like a random scatter of points.

If one or both of these conditions is seriously violated, it may indicate that the basic trend is either non-linear, or the size of the variance is not independent of the mean level. If the variance is roughly proportional to mean concentrations, one possible remedy is to try a transformation of the measurements and re-estimate the linear regression. This will change the interpretation of the estimated regression from a linear trend of the form $y = a + bt$, where y and t represent concentration and time respectively, to a non-linear pattern. As an example, if the concentration data are transformed via logarithms, the regression equation will have the form $\log y = a + bt$. On the original concentration scale, the trend function will then have the form $y = \exp\left(a + bt\right)$.

When the regression data are transformed in this way, the estimated trend in the concentration domain (after back-transforming) no longer represents the original mean. The transformation induces a *bias* in the confidence intervals comprising the confidence band when converted back to the original scale as in the case of samples with no trend. If a log transformation is used, for instance, the back-transformed confidence band around the trend line represents confidence intervals around the original-scale *geometric means* and not the *arithmetic means*. If a comparison of an estimated geometric mean or similar quantity to the fixed standard makes sense, computing a trend line on the transformed data should be acceptable. However, if a confidence interval around an arithmetic mean is required, consultation with a professional statistician may be necessary.

The technique presented here produces a confidence interval around the *mean* as a function of time and not an *upper percentile*. Thus, we recommend that the use of this method be restricted to cases where the fixed standard represents a mean concentration and not an explicit upper percentile or a 'not-to-exceed' limit.

At least 8 to 10 measurements should be available when computing a confidence band around a linear regression. There must be enough data to not only estimate the trend function but also to compute the variance around the trend line. In the simplest case when no trend is present, there are (n–1) *degrees*

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of freedom [*df*] in a sample of size *n* with which to estimate the population variance. With a linear trend, however, the available degrees of freedom *df* is reduced to (*n*–2). For moderate to large samples, loss of one or two degrees of freedom makes little difference. But for the smallest samples, the impact on the resulting confidence limits can be substantial.

One last assumption is that there should be few if any non-detects when computing the regression line and its associated confidence band. As a matter of common sense, a readily discernible trend in a data set (either increasing or decreasing) should be based on quantified measurements. Changes in detection and/or RLs over time can appear as a declining trend, but may actually be an artifact of improved analytical methods. Such artifacts of plotting and data reporting should generally *not* be considered real trends.

PROCEDURE

Step 1. Construct a time series plot of the measurements. If a discernible trend is evident, compute a linear regression of concentration against sampling date (time), letting x_i denote the *i*th concentration value and t_i denote the *i*th sampling date. Estimate the linear slope with the equation:

$$\hat{b} = \sum_{i=1}^{n} (t_i - \bar{t}) \cdot x_i / (n-1) \cdot s_t^2 \qquad [21.20]$$

This estimate leads to the regression equation, given by:

$$\hat{x} = \bar{x} + \hat{b} \cdot (t - \bar{t}) \qquad [21.21]$$

where $\bar{t}$ denotes the mean sampling date, s_t^2 is the variance of the sampling dates, $\bar{x}$ is the mean concentration level, and $\hat{x}$ represents the estimated mean concentration at time *t*.

Step 2. Compute the regression residual at each sampling event with the equation:

$$r_i = x_i - \hat{x}_i \qquad [21.22]$$

Check the set of residuals for lack of normality and significant skewness using the techniques in **Chapter 10**. Also, plot the residuals against the estimated regression values ($\hat{x}_i$) to check for non-uniform vertical thickness in the scatter cloud. If the residuals are non-normal and substantially skewed and/or the scatter cloud appears to have a definite pattern (*e.g.*, funnel-shaped; 'U'-shaped; or, residuals mostly positive on one end of the graph and mostly negative on the other end, instead of randomly scattered around the horizontal line $r = 0$), repeat Steps 1 and 2 after first transforming the concentration data.

Step 3. Calculate the estimated variance around the regression line (also known as the *mean squared error* [MSE]) with the equation:

$$s_e^2 = \frac{1}{n-2} \sum_{i=1}^{n} r_i^2 \qquad [21.23]$$

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Step 4. Given confidence level (1–α) and a point in time (t_0) at which a confidence interval around the trend line is desired, compute the lower and upper confidence limits with the respective equations:

$$LCL_{1-\alpha} = \hat{x}_0 - \sqrt{2s_e^2 \cdot F_{1-2\alpha,\,2,\,n-2} \cdot \left[\frac{1}{n} + \frac{(t_0 - \bar{t})^2}{(n-1)\cdot s_t^2}\right]} \quad [21.24]$$

$$UCL_{1-\alpha} = \hat{x}_0 + \sqrt{2s_e^2 \cdot F_{1-2\alpha,\,2,\,n-2} \cdot \left[\frac{1}{n} + \frac{(t_0 - \bar{t})^2}{(n-1)\cdot s_t^2}\right]} \quad [21.25]$$

where $\hat{x}_0$ is the estimated mean concentration at time t_0 from the regression using equation [21.21], and $F_{1-2\alpha,\,2,\,n-2}$ is the upper (1–2α)th percentage point from an *F*-distribution with 2 and (*n*–2) degrees of freedom. Values for *F* can be found in **Table 17-1** of **Appendix D**.

Step 5. Depending on whether the regulated unit is in compliance/assessment or corrective action monitoring, compare the appropriate confidence limit against the GWPS. Multiple confidence limits can be computed at a single compliance point well without increasing the significance level (α) of the comparison. It is possible to estimate at what point in time (if ever) the confidence limit first lies completely to one side of the fixed comparison standard, without risking an unacceptable false positive rate increase for that well.

►EXAMPLE 21-7

Trichloroethylene [TCE] concentrations are being monitored at a site undergoing remediation. If the GWPS for TCE has been set at 20 ppb, test the following 10 measurements collected at a compliance point well over the last two and a half years to determine if the clean-up goal has been reached at the α = 0.05 level of significance.

Month Sampled	TCE Concentration (ppb)	Regression Estimates	Residuals
2	54.2	51.735	2.465
4	44.3	48.530	-4.230
8	45.4	42.119	3.281
11	38.3	37.311	0.989
13	27.1	34.106	-7.006
16	30.2	29.298	0.902
20	28.3	22.888	5.412
23	17.6	18.080	-0.480
26	14.7	13.272	1.428
30	4.1	6.861	-2.761

SOLUTION

Step 1. Construct a time series plot of the TCE measurements as in the graph below (see **Figure 21-3**). A general downward, linear trend is evident. Then compute the estimated regression line

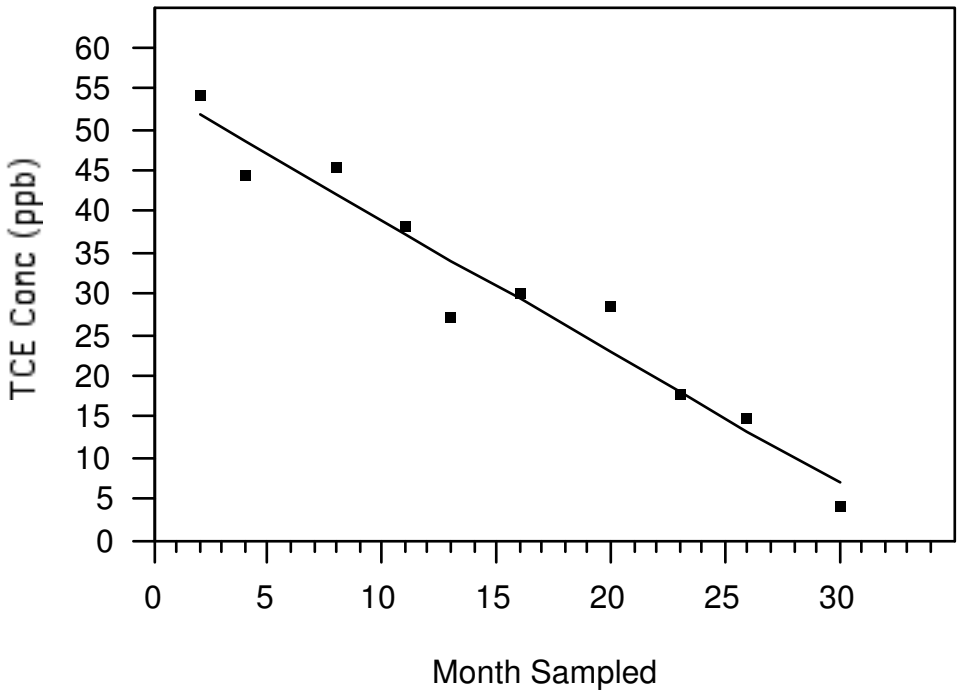
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using equations [21.20] and [21.21], first determining that the mean time value is $\bar{t} = 15.3$, the variance of time values is $s_t^2 = 88.2333$, and the mean TCE measurement is $\bar{x} = 30.42$ ppb:

$$\hat{b} = \left[(2-15.3)\cdot 54.2 + (4-15.3)\cdot 44.3 + \ldots + (30-15.3)\cdot 4.1\right]/(9\times 88.2333) = -1.603\ ppp/month$$

$$\hat{y} = 30.42 - 1.603\cdot(t-15.3)$$

Figure 21-3. Time Series Plot and Regression Line of TCE Measurements



Step 2. Compute the regression residuals using equation [21.22] (listed in the table above). Note that the residuals are found by first computing the regression line estimate for each sampled month (*i.e.*, t = 2, 4, 8, *etc.*) and then subtracting these estimates from the actual TCE concentrations. A probability plot of the regression residuals appears reasonably linear (**Figure 21-4**) and the Shapiro-Wilk statistic computed from these data yields $SW = 0.962$, well above the $\alpha = 0.05$ critical point for $n = 10$ of $sw_{.05,10} = 0.842$. Thus, normality of the residuals cannot be rejected.

In addition, a plot of the residuals versus the regression line estimates (**Figure 21-5**) exhibits no unusual pattern, merely random variation about the residual mean of zero. Therefore, proceed to compute a confidence interval around the trend line.

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Figure 21-4. Probability Plot of TCE Residuals

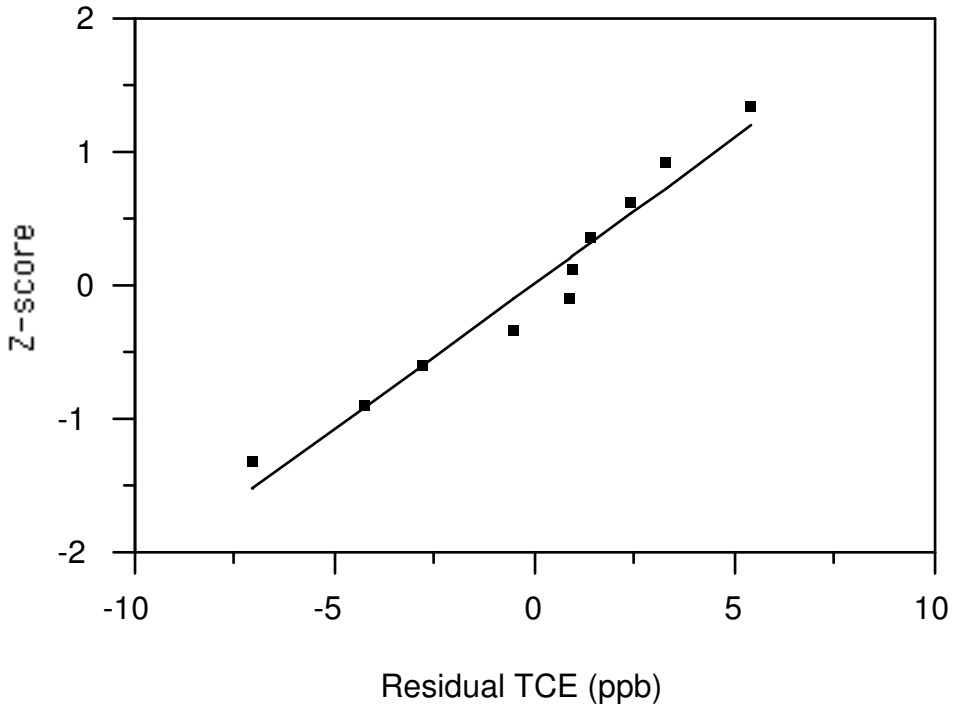
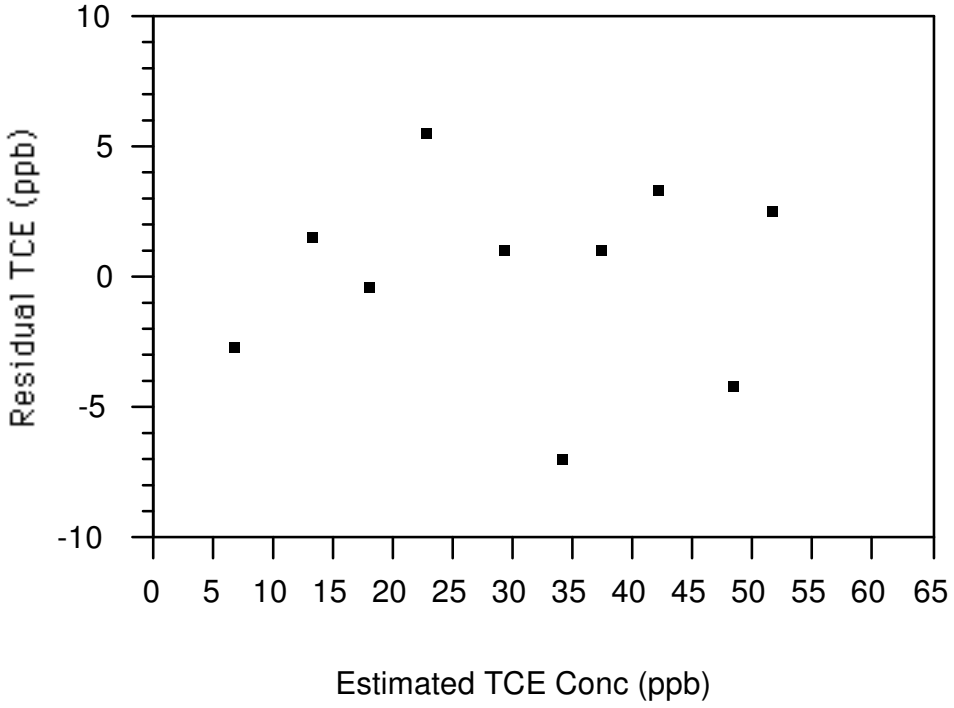


Figure 21-5. Scatterplot of TCE Residuals vs. Regression Line Estimates



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Step 3. Compute the variance around the estimated trend line using equation [21.23]:

$$s_e^2 = \frac{1}{8} \cdot \left[(2.465)^2 + (-4.230)^2 + \ldots + (-2.761)^2 \right] = 15.60$$

Step 4. Since the comparison to the GWPS of 20 ppb is to be made at the $\alpha = 0.05$ significance level, the confidence limit is $(1-\alpha) = 95\%$ confidence. Since the remediation effort aims to demonstrate that the true mean TCE level has dropped below 20 ppb, a one-way UCL needs to be determined using equation [21.25]. A logical point along the trend to examine is the last sampling event at $t_0 = 30$. Using the estimated regression value at $t_0 = 30$, and the fact that $F_{.90,2,8} = 3.1131$, the UCL on the mean TCE concentration at this point becomes:

$$UCL_{95} = 6.861 + \sqrt{2 \times 15.60 \times 3.1131 \times \left[\frac{1}{10} + \frac{(30-15.3)^2}{9 \times 88.2333} \right]} = 12.87 \; ppb$$

Since this upper limit is less than the GWPS for TCE, conclude that the remediation goal has been achieved by $t_0 = 30$. In fact, other times can also be tested using the same equation. At the next to last sampling event ($t_0 = 26$), the UCL is:

$$UCL_{95} = 13.272 + \sqrt{2 \times 15.60 \times 3.1131 \times \left[\frac{1}{10} + \frac{(26-15.3)^2}{9 \times 88.2333} \right]} = 18.14 \; ppb$$

which also meets the remediation target at the $\alpha = 0.05$ level of significance.

Step 5. If the linear trend is ignored, a one-way UCL of the mean might have been used. The overall TCE sample mean $\bar{x} = 30.42$, the TCE standard deviation s = 15.508, and the upper 95th percentage point of the t-distribution with 9 degrees of freedom is $t_{.95,9}$ = 1.8331. Using equation [21.2] with the same data yields the following:

$$UCL_{.95} = 30.42 + (1.8331)(15.508) / \sqrt{10} = 39.41 \text{ ppb}$$

Had the linear trend been ignored when computing the UCL, the remediation target would not have been achieved. The downward trend induces the largest part of the variation observed over the two and a half years of sampling and needs to be taken into account. ◄

21.3.2 NON-PARAMETRIC CONFIDENCE BAND AROUND THEIL-SEN LINE

BACKGROUND AND PURPOSE

The Theil-Sen trend line is introduced in **Section 17.3.3** as a non-parametric alternative to linear regression. Whether due to the presence of non-detects or trend residuals that cannot be normalized, the

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Theil-Sen method can usually construct a trend estimate without some of the assumptions needed by linear regression.

The Theil-Sen trend line is non-parametric because it combines the median pairwise slope (**Section 17.3.3**) with the median concentration value and the median sample date to construct the trend. Because of this construction, the Theil-Sen line estimates the change in *median* concentration over time and not the *mean* as in linear regression.

There are no simple formulas to construct a confidence band around the Theil-Sen line. However, a more computationally-intensive technique — bootstrapping — can be employed instead. The conceptual algorithm is fairly simple. First consider the set of n pairs of measurements used to construct the Theil-Sen trend. Each pair consists of a sample date (t_i) and the concentration value measured on that date (x_i) as a statistical sample. Next, repeatedly draw samples of size n *with replacement* from the original sample of pairs. These artificially constructed samples are known as *bootstrap samples*. At least 500 to 2,000 bootstrap samples are generated in order to improve the accuracy of the final confidence band. Note that a bootstrap sample is not precisely the same as the original because pairs are sampled with replacement. This means that a given pair might show up multiple times in any particular bootstrap sample.

For each bootstrap sample, use the Theil-Sen algorithm to construct an associated trend line (**Section 17.3.3**). Each of these trend lines is known as a *bootstrap replicate*. Finally, determine the distribution of the bootstrap replicates and select certain percentiles of this distribution to form lower and upper confidence limits. These limits can be constructed to represent a non-parametric simultaneous confidence band around the Theil-Sen trend line with $(1-\alpha)$ confidence.

REQUIREMENTS AND ASSUMPTIONS

The key requirements for constructing a confidence band around a Theil-Sen trend are the same as for the Theil-Sen procedure itself (**Section 17.3.3**). As a non-parametric procedure, the trend residuals do not have to be normal or have equal variance across the data range. But the residuals are assumed to be statistically independent. Approximate checks of this assumption can be made using the techniques of **Chapter 14**, after removing the estimated Theil-Sen trend and as long as there aren't too many non-detects. It is also important to have at least 8-10 observations from which to construct the bootstrap samples.

Non-detects can be accommodated by the Theil-Sen method as long as the detection frequency is at least 50%, and the censored values occur in the lower part of the observed concentration range. Then the median concentration value and the median pairwise slope used to compute the Theil-Sen trend will be based on clearly quantified values.

Since there are no simple mathematical equations which can construct the Theil-Sen confidence band, a computer software program is essential for performing the calculations. Perhaps the best current solution is to use the open-source, free-of-charge, statistical computing package **R** (www.r-project.org). A template program (or script) written in **R** to compute a Theil-Sen confidence band is listed in **Appendix C**. This script can be adapted to any site-specific data set and used as many times as necessary, once the **R** computing environment has been installed.

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PROCEDURE

Step 1. Given the original sample of n measurements, form a sample of n pairs (t_i, x_i), where each pair consists of a sample date (t_i) and the concentration measurement from that date (x_i).

Step 2. Form B bootstrap samples by repeatedly sampling n pairs at random with replacement from the original sample of pairs in Step 1. Typically, set $B \geq 500$.

Step 3. For each bootstrap sample, construct a Theil-Sen trend line using the algorithm in **Section 17.3.3**. Denote each of these B trend lines as a bootstrap replicate.

Step 4. Determine a series of equally spaced time points (t_j) along the range of sampling dates represented in the original sample, $j = 1$ to m. At each time point, use the Theil-Sen trend line associated with each bootstrap replicate to compute an estimated concentration ($\hat{x}_j^B$). There will be B such estimates at each of the m equally-spaced time points when this step is complete.

Step 5. Given a confidence level (1–α) to construct a two-sided confidence band, determine the lower (α/2)th and the upper (1–α/2)th percentiles, denoted $\hat{x}_j^{[\alpha/2]}$ and $\hat{x}_j^{[1-\alpha/2]}$ from the distribution of estimated concentrations at each time point (t_j). The collection of these lower and upper percentiles along the range of sampling dates (t_j, $j = 1$ to m) forms the bootstrapped confidence band. To construct a lower confidence band, follow the same strategy. But determine the lower αth percentile $\hat{x}_j^{[\alpha]}$ from the distribution of estimated concentrations at each time point (t_j). For an upper confidence band, compute the upper (1–α)th percentile, $\hat{x}_j^{[1-\alpha]}$ at each time point (t_j).

Step 6. Depending on whether the regulated unit is in compliance/assessment or corrective action monitoring, compare the appropriate confidence band against the GWPS. Estimate at what point in time (if ever) the confidence band first sits completely to one side of the fixed comparison standard.

►EXAMPLE 21-8

In **Example 17-7**, a Theil-Sen trend line was estimated for the following sodium measurements. Note that the sample dates are recorded as the year of collection (2-digit format), plus a fractional part indicating when during the year the sample was collected. Construct a two-sided 95% confidence band around the trend line.

Sample Date (yr)	Sodium Conc. (ppm)
89.6	56
90.1	53
90.8	51
91.1	55
92.1	52
93.1	60
94.1	62
95.6	59
96.1	61
96.3	63

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SOLUTION

Step 1. Designate the $n = 10$ (sample date, concentration) pairs as the original sample for purposes of bootstrapping. Set the number of bootstrap samples to $N_B = 500$.

Step 2. Sample at random and with replacement $N_B = 500$ times from the original sample to form the bootstrap samples. Compute a bootstrap replicate Theil-Sen trend line for each bootstrap sample. This gives 500 distinct linear trend lines.

Step 3. Divide the observed range of sampling dates from 89.6 to 96.3 into $m = 101$ equally-spaced time points, t_j (note: choice of m is arbitrary, depending on how often along the time range an estimate of the confidence band is needed). At each time point, compute the Theil-Sen concentration estimate using each bootstrap replicate trend. This leads to 500 estimates of the form:

$$\hat{x}_j^B = \tilde{x}^B + Q^B \cdot \left(t_j - \tilde{t}^B\right)$$

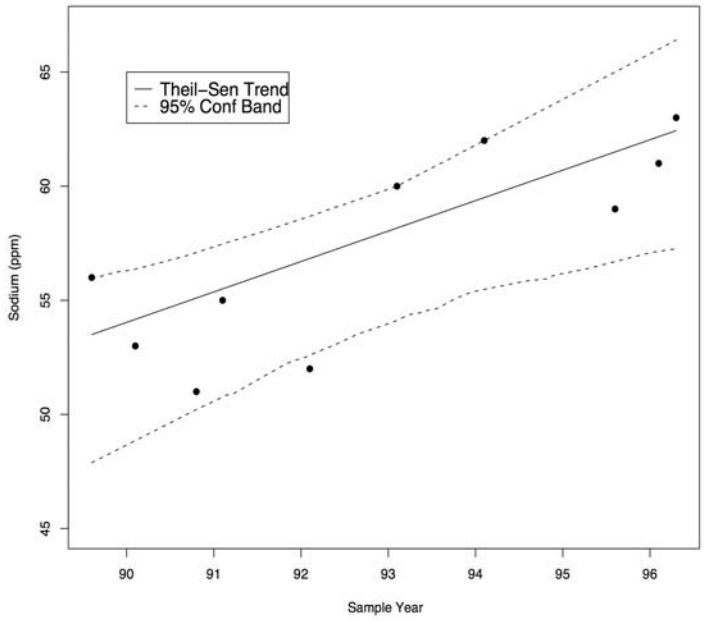
where $\tilde{x}^B$ is the median concentration of the Bth bootstrap sample, Q^B is the Theil-Sen slope of the Bth bootstrap sample, and $\tilde{t}^B$ is the median sampling date of the Bth bootstrap sample.

Step 4. Given a two-way confidence level of 95%, compute the lower $\alpha/2 = 0.05/2 = 0.025$ and upper $(1-\alpha/2) = (1-0.05/2) = 0.975$ sample percentiles (**Chapter 3**) for the set of 500 concentration estimates associated with each time point (t_j). This entails sorting each set and finding the value closest to rank $(n+1) \times p$, where p = desired percentile. In a list of $n = 500$, find the sorted values closest to the ranks $501 \times 0.025 = 12.525$ for the lower percentile and $501 \times 0.975 = 488.475$ for the upper percentile. Collectively, the lower and upper percentiles plotted by the time points give an approximation to the 95% two-sided confidence band.

Step 5. Plot the lower and upper confidence bands as well as the original Theil-Sen trend line and the raw sodium measurements, as in **Figure 21-6**. The fact that the trend is increasing over time is confirmed by the rising confidence band. ◄

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Figure 21-6. 95% Theil-Sen Confidence Band on Sodium Measurements



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CHAPTER 22. COMPLIANCE/ASSESSMENT AND CORRECTIVE ACTION TESTS

22.1 CONFIDENCE INTERVAL TESTS FOR MEANS 22-1
22.1.1 Pre-Specifying Power In Compliance/Assessment 22-2
22.1.2 Pre-Specifying False Positive Rates in Corrective Action 22-9
22.2 CONFIDENCE INTERVAL TESTS FOR UPPER PERCENTILES 22-18
22.2.1 Upper Percentile Tests in Compliance/Assessment 22-19
22.2.2 Upper Percentile Tests in Corrective Action 22-20

Chapter 7 lays out general strategies for statistical testing in compliance/assessment and corrective action monitoring via the use of confidence intervals. Procedures for constructing confidence intervals are described in **Chapter 21**. This chapter discusses potential methods for developing confidence interval tests so that adequate statistical power is maintained in compliance/assessment monitoring and false positive rates are minimized in corrective action monitoring.

22.1 CONFIDENCE INTERVAL TESTS FOR MEANS

As discussed in **Chapter 7**, EPA's primary concern in compliance/assessment and corrective action monitoring is the identification and remediation of contaminated groundwater. The basic statistical hypotheses are reversed in these two phases of monitoring as described in **Chapter 21** and earlier. The lower confidence limit [LCL] is of most interest in compliance/assessment, while the upper confidence limit [UCL] is used in corrective action. Statistical power is also of greater concern to the regulatory agency in compliance/assessment— representing the probability that contamination above a fixed standard will be identified. A sufficiently conservative false positive rate during corrective action is important from a regulatory standpoint, since a false positive implies that contaminated groundwater has been falsely declared to meet a compliance standard. The reverse of these risks is generally true for a regulated entity.

To ensure that contaminated groundwater is treated in ways that are statistically sound, the two specific strategies which follow separately address compliance/assessment monitoring and formal testing in corrective action. The latter occurs after the completion of remedial activities or when potential compliance can be anticipated. Each strategy is designed to allow stakeholders on both sides of the regulator/regulated divide to understand the expected statistical performance of a given confidence interval test.

The two strategies which follow are based on the behavior of the *normal mean* confidence interval. They especially assume that the monitoring data are stationary over the period of record. Other important assumptions were discussed in **Chapter 21**. In the discussion which follows, consideration is given to data that is normal following a logarithmic transformation and the possible tests which can be applied.

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22.1.1 PRE-SPECIFYING POWER IN COMPLIANCE/ASSESSMENT

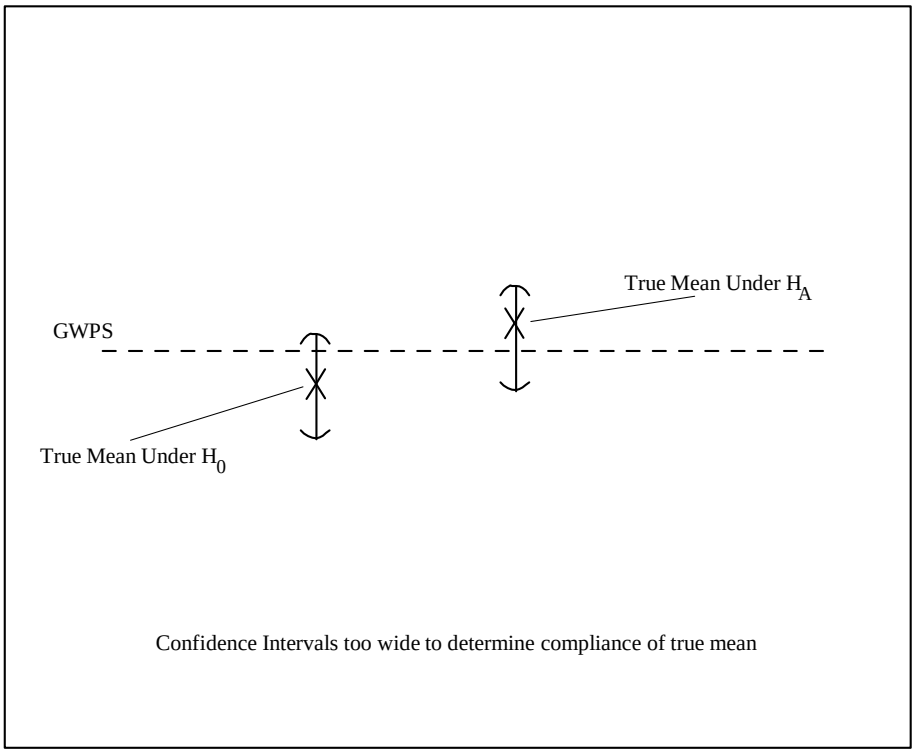
In most statistical literature including Gibbons & Coleman (2001) comparing a confidence interval against a fixed standard, a low false positive error rate (α) is chosen or recommended without respect to the power of the test. However, the power to detect increases above a fixed standard using a lower confidence limit around the mean can be negligible when contaminant variability is high and the sample size is small (**Chapter 7**). To remedy this problem, the Unified Guidance suggests an alternate strategy. That is, instead of pre-specifying the false positive rate α prior to computing confidence interval limits, a desired level of power ($1-\beta$) should be set as an initial target.

Ideally one would like to simultaneously minimize α and maximize power by also minimizing β (*i.e.*, the false negative rate). However, this is generally impossible given a fixed sample size (**Chapter 3**), since there is a trade-off between power and the false positive rate. Especially for small sample sizes, fixing a low α often leads to less than desirable power. Conversely, pre-specifying a high power necessitates a higher than typical false positive rate. Larger sample sizes are needed if both power and α are pre-specified. High variability at a fixed sample size both lowers power and/or increases the need for a larger false positive error rate.

A number of considerations are relevant when constructing mean confidence limits to achieve adequate statistical power. In most Agency risk assessment evaluations, chronic risk levels are generally *proportional* to the average concentration. Development of MCLs followed similar proportional risk methodologies. Fixed health-based limits which can serve as groundwater protection standards [GWPS] also cover an enormous concentration range when both carcinogenic and non-carcinogenic constituents are included.

Another relevant factor pertains to those situations where the true mean concentrations lie quite close to either side of a compliance standard. The difference between complying and not complying with the GWPS in terms of the true mean concentration level may be so small as to make a clear determination of compliance very difficult (**Figure 22-1**). Only sufficiently large differences relative to a standard are likely to be determined with a high level of certainty (*i.e.*, statistical power).

Figure 22-1. True Means Too Close to Standard to Clearly Identify Violation



With the wide range of GWPS in place and recognizing that risk factors are proportional or multiplicative rather than additive (***e.g.***, a 10^{-6} cancer risk), it would be appropriate to use a consistent measure of increased risk that is ***independent*** of the actual GWPS concentration level. While ultimately the decision of the regulatory authority, the Unified Guidance suggests a proportional increase (***i.e.***, a ratio) above the GWPS, which is identified at some predetermined level of statistical power to judge the appropriateness of any specific mean confidence interval test.

For compliance/assessment monitoring purposes, increases in the true concentration mean of 1.5 and 2 times a fixed standard are evaluated at a range of confidence levels. While this is not quite the same as evaluating an ***absolute*** mean increase for a given constituent, the use of a risk ratio (***R***) does in fact define a specific increase in concentration level. For example, a risk ratio of 1.5 would identify a critical increase above the 15 µg/l MCL standard for lead of 22.5 – 15 = 7.5 µg/l, while for chromium with an MCL = 100 ug/l, the absolute increase would be 50 ug/l. Each represents a 50% increase in risk relative to the GWPS.

Two approaches for assessing statistical power in compliance/assessment monitoring are provided using these critical risk ratios, based on different assumptions regarding sample variability. In the first approach, a constant population variance is assumed, equal to the standard (***i.e.***, GWPS) being tested. Under the null hypothesis that the true population mean is no greater than the GWPS, this assumption corresponds to having a coefficient of variation [***CV***] of 1 when the true mean equals the standard. Although observed sample variability is ignored, this case can be considered a relatively conservative approach.

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Assuming *CV* = 1, the relationship between the risk ratio (*R*), statistical power (1–β), sample size (*n*), and the false positive rate (α) can be obtained using the following equation:

$$1-\beta = G_{T,n-1}\left(t_{1-\alpha,n-1}\middle|\Delta=\sqrt{n}\left(R-1\right)\right) \qquad [22.1]$$

where $t_{1-\alpha,n-1}$ is the (1–α)th Student's *t*-quantile with (*n*–1) degrees of freedom and $G_{T,n-1}(\bullet|\Delta)$ represents the cumulative *non-central t*-distribution with (*n*–1) degrees of freedom and non-centrality parameter Δ. By fixing a desired or target power level, equation [22.1] can be used to choose the necessary α based on the available sample size *n*. Alternatively, the equation can be used to determine the sample size (*n*) needed to allow for a pre-determined choice of α.

Numerical tabulations of equation [22.1] are found in **Tables 22-1** and **22-2** in **Appendix D**. These tables cover a practical range of *n* = 3 to 40 and α = .001 to .20, and offer combinations of the minimum false positive rate (α) and sample size (*n*) for several fixed levels of power. These can be used to construct lower confidence limits having a pre-specified level of power. It is important to note that the listed combinations are the ***smallest*** α-values resulting in the targeted power. For a fixed *n*, use of an α-value ***larger*** than that listed in the tables will provide even greater power than the target. Similarly, for given α, use of a larger sample size than that listed in the tables will also result in greater power than the target.

Minimum parameter values are presented in **Tables 22-1** and **22-2** of **Appendix D** to document how the desired power level can be achieved with as few observations and as small a false positive error rate as possible. It is also true that an assumption of *CV* = 1 should be somewhat conservative at many sites. Actual power will be higher than that listed in these tables if the coefficient of variation is smaller. Not every power level is achievable in every combination of *n* and α, so some of the entries in these two tables are left blank.

The second approach requires an estimate of the population coefficient of variation. In this case, the required (but approximate) false positive rate of the test can be directly obtained from equation [22.2], where *R* is the desired risk ratio, *n* is the sample size, $\hat{CV}$ is the estimated sample coefficient of variation, $t_{1-\beta,n-1}$ is the (1–β)th Student's *t*-quantile with (*n*–1) degrees of freedom, and $F_{T,n-1}(\bullet)$ is the cumulative (central) Student's *t*-distribution function:

$$a \cong 1 - F_{T,n-1}\left(\frac{(R-1)\cdot\sqrt{n}}{R\cdot\hat{CV}} - t_{1-\beta,n-1}\right) \qquad [22.2]$$

Equation [22.2] was evaluated for sample sizes varying from n = 4 to 12 and for *CV*s ranging from 0.1 to 3.0 at two target combinations of power and risk ratio — *R* = 1.5 at 50% power and *R* = 2 at 80% power. Results of these calculations are provided in **Table 22-3** of **Appendix D**. Similar to the critical power targets recommended by the Unified Guidance in detection monitoring (*i.e.*, 55-60% power at 3σ above background, and 80-85% power at 4σ over background), two high power targets at proportionally increasing risk ratios were also chosen for this setting.

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Table 22-3 in **Appendix D** provides the approximate minimum false positive rate (α) necessary to achieve each power target in a single confidence interval test. The shaded and italicized entries in the table represent those cases where the minimum α is below the RCRA regulatory limitation of $\alpha = .01$ from §264.97(i)(2) for an individual test false positive error rate. For these situations, the user would need to set $\alpha = 0.01$, which in turn would provide even greater statistical power than the target.

For higher estimated *CV*s, many of the entries in this table exceed $\alpha = .5$ (bolded entries). These cases illustrate the difficulty of simultaneously attaining the recommended level of power while controlling the false positive rate, especially for small sample sizes and highly variable data. Setting a lower α, results in insufficient statistical power. On the other hand, setting $\alpha \geq .5$ amounts to a simple comparison of the sample mean against the fixed standard, with essentially no adjustment for sample variability or uncertainty. Similar to the first approach, a maximum false positive rate of $\alpha = .2$ is a reasonable upper bound which implies at most a 1-in-5 chance of an error.

Generally speaking, setting 80% power at a risk ratio of $R = 2$ in **Table 22-3** of **Appendix D** is more constraining (requiring higher α's) than 50% power at a risk ratio of $R = 1.5$, although the effect can be reversed for low *CV*s and sample sizes. To meet both targets simultaneously for a given *n*, the larger of the corresponding significance levels (α) should be selected. Guidance users may choose either of the two approaches described above. Other ratio and power options not covered in **Tables 22-1** through **22-3** of **Appendix D** can be handled by direct computation using either equation [22.1] or equation [22.2]. The first method makes an *a priori* assumption about the *CV*. The second method is approximate, depending on a sample *CV* estimate which might be erratic at small sample sizes and larger true population *CV*s especially if the compliance data are non-normal.

Both approaches are directly applicable to the normal mean LCL test in **Section 21.1.1**. While the *CV* can be directly estimated using $s/\bar{x}$ on the original concentration data, this statistic will underestimate the likely variability when data are lognormal. In that case, the logarithmic CV estimate in **Chapter 10**, **Section 10.4** should be used. If the data best fit a lognormal distribution, a number of considerations follow:

- It is possible to misapply the normal mean confidence interval test using the original concentration data, even when the data stem from a lognormal distribution. The mean is relatively robust with respect to departures from normality as long as the CV variability is not too great. If the predetermined false positive error α is selected based on the normal power criteria above, the resulting LCL test will be at least as powerful as the normal test. The actual false positive error rate will also differ.

- If a geometric mean test in **Section 21.1.2** is used, the LCL should be computed from the logarithmically transformed data. **Tables 22-1** to **22-3** in **Appendix D** are based on normal distribution assumptions and the error rates are very conservative with respect to the achievable power. As an example, given a data set from a lognormal distribution with n = 10, and an estimated CV = .8, an alpha value of .151 can be identified from **Table 22-3** in **Appendix D**. The actual power to detect a doubling above a GWPS at 80% confidence

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would result in a power level of 94.5%. The false positive needed to detect a geometric mean doubling for this example to meet the above criteria would be α = .026.[1]

- The Land lower confidence interval test from **Section 21.1.3** can also be used. But since there are limited α-choices in the tables, the guidance option is to select a fixed limit of .01, .05, or .1. If data are truly lognormal, the power of this test is at least as great as would be predicted by equations [22.1] and [22.2]. Otherwise, professional statistical assistance may be necessary.

Since compliance data will often be pooled over time to increase the eventual sample size (**Chapter 7**), the two approaches can be combined by determining the false positive rate for a given risk ratio and power level during the first year with **Tables 22-1** and **22-2** of **Appendix D**. Tests in subsequent years might use the second power approach when a better *CV* estimate (using more data) can be derived. Overall, each approach should provide a reasonable manner of adjusting the individual test false positive rate (α) to ensure adequate power to detect real contaminant increases. As a general guide, the Unified Guidance suggest formulating power in terms of risk ratios no higher than $R = 2$. There should be at least 70-80% statistical power for detecting increases of that magnitude during compliance/assessment monitoring.

►EXAMPLE 22-1

Compliance monitoring recently began at a solid waste landfill. Measurements for vinyl chloride during detection monitoring are listed below for two compliance wells. If a value of 5 ppb vinyl chloride is used as the GWPS and a confidence interval test must have 80% power for detecting an increase in mean vinyl chloride levels of twice the GWPS, how should the confidence interval bounds be constructed and what do they indicate? Assume that compliance monitoring began with Year 2 of the sampling record and that annual groundwater evaluations are required.

Vinyl Chloride Concentrations (ppb)

Sample	GW-1	GW-2	Sample	GW-1	GW-2
Q1, Yr1	6.3	5.9	Q1, Yr3	8.4	13.8
Q2, Yr1	9.5	3.0	Q2, Yr3	6.4	5.6
Q3, Yr1	8.1	8.8	Q3, Yr3	8.9	11.0
Q4, Yr1	11.9	12.0	Q4, Yr3	4.9	9.8
Q1, Yr2	7.3	11.2	Q1, Yr4	9.6	6.3
Q2, Yr2	11.2	8.6	Q2, Yr4	9.7	10.4
Q3, Yr2	6.0	12.6	Q3, Yr4	8.7	7.5
Q4, Yr2	7.5	7.2	Q4, Yr4	8.7	9.7

SOLUTION

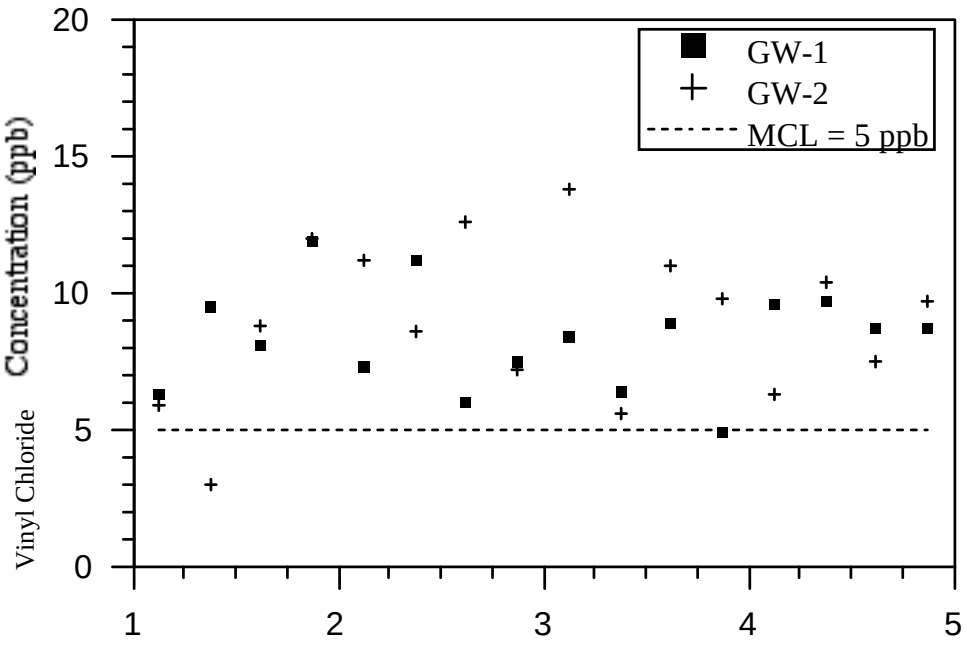
Step 1. Assume for purposes of this example that the vinyl chloride data are approximately normal. In practice, this should be explicitly checked. Also evaluate potential trends in the vinyl chloride

[1] For users with access to statistical software containing the cumulative non-central t-distribution, the inverse non-central t CDF can be used to identify the appropriate false positive level. For sample size df =n -1= 9, and a non-central t parameter = $\delta = \sqrt{n} \cdot \log(R) / s_y$, the appropriate central t-value can be obtained from $F^{-1}(df, \beta, \delta)$. The confidence level of this t-value is 1 - α. For the example, df = 9, β= .2, δ = 3.115, and the central t-value is 2.23 with α = .0264.

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measurements over time, as in the time series plot of **Figure 22-2**. Despite apparent fluctuations, no obvious trend is observed. So treat these data as if the population has a stable mean at least for the time frame indicated in the sampling record.

Figure 22-2. Vinyl Chloride Time Series Plot



Step 2. Given that compliance monitoring began in Year 2, use the four measurements available from each well to construct lower confidence limits. Since 80% power is desired for detecting vinyl chloride increases of two times the 5 ppb GWPS, **Table 22-2** in **Appendix D** indicates that for n = 4, a false positive rate of α = 0.163 must be used to guarantee the desired power. This corresponds to a Student's t-quantile of $t_{1-\alpha,n-1} = t_{.837,3} = 1.1714$. Then using the sample means and standard deviations of the Year 2 vinyl chloride measurements, the lower confidence limits can be computed as:

$$LCL_{GW-1} = \bar{x} - t_{1-\alpha,n-1}\frac{s}{\sqrt{n}} = 8.0 - 1.1714\left(2.2346/\sqrt{4}\right) = 6.7 \text{ ppb}$$

$$LCL_{GW-2} = \bar{x} - t_{1-\alpha,n-1}\frac{s}{\sqrt{n}} = 9.9 - 1.1714\left(2.4468/\sqrt{4}\right) = 8.5 \text{ ppb}$$

Step 3. Since both lower confidence limits exceed the GWPS, there is statistically significant evidence of an increase in vinyl chloride at these wells above the compliance limit. Such a conclusion also seems reasonable from **Figure 22-2**. However, the chance is better than 15% (*i.e.*, α =

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16.3%) that the apparent exceedance is merely a statistical artifact. If power criteria are ignored and a fixed minimum rate of $\alpha = .01$ is used, the lower confidence limits would be:

$$LCL_{GW-1} = \bar{x} - t_{\alpha,n-1}\frac{s}{\sqrt{n}} = 8.0 - 4.541\left(2.2346/\sqrt{4}\right) = 2.9 \text{ ppb}$$

$$LCL_{GW-2} = \bar{x} - t_{\alpha,n-1}\frac{s}{\sqrt{n}} = 9.9 - 4.541\left(2.4468/\sqrt{4}\right) = 4.3 \text{ ppb}$$

Neither limit now exceeds the GWPS, so the vinyl chloride concentrations would be judged in compliance with this test, illustrating the lack of power in lowering the false positive rate (α).

Step 4. To increase the confidence level (*i.e.*, by lowering α) of the tests at the end of the first year of compliance monitoring (*i.e.*, Year 2 in the preceding table of vinyl chloride values) ***without*** losing statistical power, combine the measurements from Years 1 and 2, where Year 1 samples represent the final measurements from detection monitoring prior to the start of compliance monitoring. In this case, $n = 8$, and the minimum false positive rate from **Table 22-2** of **Appendix D** can be lowered to $\alpha = .046$ or approximately 4.5%. Then the re-computed lower confidence limits $LCL_{GW-1} = 7.0\ ppb$ and $LCL_{GW-2} = 6.4\ ppb$ again both exceed the GWPS, indicating significant evidence of a compliance violation.

Step 5. If the strategy presented in **Step 4** of combining measurements from detection monitoring and compliance monitoring is considered untenable, additional confirmation of the results can be made at the end of Year 3 by combining the first two years of compliance monitoring samples and ignoring the measurements from Year 1. Again with $n = 8$, the minimum false positive rate guaranteeing at least 80% power will be $\alpha = .046$. The lower confidence limits are then:

$$LCL_{GW-1} = \bar{x} - t_{1-\alpha,n-1}\frac{s}{\sqrt{n}} = 7.575 - 1.9512\left(1.9521/\sqrt{8}\right) = 6.2 \text{ ppb}$$

$$LCL_{GW-2} = \bar{x} - t_{1-\alpha,n-1}\frac{s}{\sqrt{n}} = 9.975 - 1.9512\left(2.7473/\sqrt{8}\right) = 8.1 \text{ ppb}$$

Step 6. An even lower false positive rate can be achieved after the first three years of compliance monitoring. Pooling these measurements gives $n = 12$. Then **Table 22-2** in **Appendix D** identifies a minimum false positive rate of $\alpha = .013$ or less than 1.5%. In this case, the lower confidence limits $LCL_{GW-1} = 6.8\ ppb$ and $LCL_{GW-2} = 7.6\ ppb$ again exceed the GWPS, confirming the previous vinyl chloride exceedances from either Year 2, Years 1 and 2 combined, or Years 2 and 3 combined. Furthermore, not only is the false positive rate quite low, but the power of the test still meets the pre-specified target. ◄

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22.1.2 PRE-SPECIFYING FALSE POSITIVE RATES IN CORRECTIVE ACTION

As noted earlier, the primary regulatory concern in formal corrective action testing is false declarations of remedial success. If groundwater is truly contaminated above a regulatory standard yet a statistical test result indicates the concentrations are no longer so elevated, then on-going contamination has been missed and the remedial process should not be exited. Statistically, this idea translates into a desire to minimize the corrective action false positive rate (α). False positives in corrective action are precisely those decisions where the true concentration mean is falsely identified to be below the regulatory standard, when in fact it still exceeds the standard.

Constructing confidence interval tests by fixing a low target false positive rate is straightforward. All of the confidence interval tests presented in **Chapter 21** can be calibrated for choice of α. What is not straightforward is how best to incorporate statistical power in corrective action. As with any confidence interval test, selecting a low α when the sample size is small typically results in a confidence limit with low power. Power under corrective action monitoring represents the probability that the upper confidence limit [UCL] will fall below the fixed standard when in fact the true population mean is also less than the standard. Facilities undergoing remediation clearly have an interest in demonstrating the success of those clean-up efforts. They therefore may want to maximize the power of the confidence interval tests during corrective action, under the constraint that α must be kept low.

What statistical power criteria might a facility reasonably define in corrective action testing? Because of the orders of magnitude range found among various GWPS, a risk ratio approach similar to what is suggested in **Section 22.1.1;** only in this case, the target ratios (*R*) are *less than one*. While a true mean at a level of $R = 0.9$ times a given standard might be declared in compliance very infrequently, one at $R = 0.5$ times or $R = 0.25$ times the standard should meet the compliance requirements much more often. By using a consistent risk ratio across a variety of constituents, absolute decreases in the mean concentration are consistent with an assumed level of risk.

Unlike the risk ratio method detailed for compliance/assessment monitoring, where power was pre-specified but a combination of the false positive rate (α) and sample size (*n*) might be varied to meet that power level, in corrective action both power and α are likely to be pre-specified (power by the facility and α by the regulatory authority). The remaining component is how large a sample size is needed to attain the desired level of power, given a pre-specified false positive rate (α).

The normal distribution can be used to estimate sample size requirements for such risk ratios, given a specific false positive rate (α) and desired level of power (1–β). There is likely to be uncertainty, however, in the degree of sample variation, as expressed by the *CV*. Since the constituents in a contaminated aquifer may be modified by remedial actions, it can be difficult to estimate *future* variability (and the *CV*) from pre-treatment data. In some situations, a decrease in the mean over time might be paralleled by a decrease in total variation. If proportional, the *CV* would remain relatively constant. However, the *CV* could decrease or increase depending on aquifer conditions, constituent behavior, *etc*. The best that can be recommended is to develop an estimate of the expected future *CV* under conditions of aquifer stability.

As with compliance/assessment testing, future year estimates of the *CV* could be developed from the accumulated previous years' data. Sample sizes necessary to meet specific power targets (1–β) can

then be generated from the following approximate equation, where R = fractional risk ratio (less than 1.0), (1–α) is the desired confidence level, and $\tilde{CV}$ = estimated coefficient of variation:

$$n = \left[R \cdot \left(t_{1-\alpha,n-1} + t_{1-\beta,n-1}\right) \cdot \hat{CV} / (1-R)\right]^2 \qquad [22.3]$$

Since n appears on both sides of equation [22.3], it has to be solved iteratively for trial-and-error choices of n, making it difficult to calculate without a proper computing environment. **Tables 22-4** to **22-6** in **Appendix D** provide requisite sample sizes (n) based on equation [22.3] for three specific risk ratios (R = .75, .50, and .25) over a variety of inputs of α, β, and CV.

These tables can be consulted when designing a remedial program, especially when determining a sampling frequency adequate for generating the minimally needed sample size over a specific period of time. For example, to detect a drop in the true mean down to 0.75 × GWPS (*i.e.*, R = 0.75) with 80% power when CV = 0.6, **Table 22-4** in **Appendix D** indicates that a minimum of n = 16 observations are needed to have a false positive rate (α) no greater than 10%. Demonstrating such a reduction over the next two years might then require the collection of 8 measurements per year (or two per quarter) from the compliance well involved.[2]

While **Tables 22-4** to **22-6** in **Appendix D** identify the sampling requirements needed to simultaneously meet pre-specified targets for power (1–β) and the false positive rate (α), they come with some limitations. First, many of the minimum sample sizes are prohibitively large when sample variation as measured by the CV is substantial. Proving the success of any remedial program will be difficult when the compliance data exhibit significant relative variability. Less sampling is required to demonstrate a more substantial concentration drop below the compliance standard than to demonstrate a slight decrease (*e.g.*, compare the sample sizes for R = 0.75 to R = 0.25). This fact mirrors the statistical truth in both detection and compliance/assessment monitoring that highly contaminated wells are more easily identified (and require fewer observations to do so) than are only mildly contaminated wells.

Another limitation of equation [22.3] is that it assumes all n measurements are statistically independent. This assumption puts practical limits on the amount of sampling at a compliance well that can reasonably be achieved over a specific time period. Samples obtained too frequently may be autocorrelated and thus violate statistical independence. Minimum sample sizes do not apply to data exhibiting an obvious trend, and are appropriate only when the aquifer is in a relatively steady-state. Alternate methods to construct confidence bands around trends are presented in **Chapter 21**. However, equation [22.3] cannot be used to plan sample sizes in this setting. Finally, **Tables 22-4** to **22-6** in **Appendix D** are based on an assumption of normally-distributed data. Although non-normal data sets might be approximated to some degree by the range of CVs considered, more sophisticated methods might be needed to compute sample size requirements for such data. This might entail consultation with a professional statistician.

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[2] A slightly more approximate direct calculation using the standard normal distribution instead of Student t-values will also provide the needed sample size estimate as: $n = \left[R \cdot \left(z_{1-\alpha} + z_{1-\beta}\right) \cdot \hat{CV} / (1-R)\right]^2$. The recommended sample size in the example above is rounded to n = 15 using the z-normal equation. The estimate can be improved and made more conservative by adding an additional sample.

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►EXAMPLE 22-2

Suppose elevated levels of specific conductance (μmho) shown in the table below must be remediated at a hazardous waste facility. If the clean-up standard has been set at L = 1000 μmho, at what point should remediation efforts be declared a success for the two compliance well data in the table below? Assume that the risk of false positive error needs to be no greater than $\alpha = 0.05$ at either well.

Well ID	Date	Spec. Cond.	Well ID	Date	Spec. Cond.
GW-12	10-16-87	2100	GW-13	10-16-87	2200
GW-12	01-28-88	2550	GW-13	01-27-88	1463
GW-12	04-13-88	2360	GW-13	04-13-88	935
GW-12	06-15-88	2405	GW-13	07-12-88	809
GW-12	10-12-88	2560	GW-13	10-12-88	469
GW-12	12-20-88	1163	GW-13	12-19-88	465
GW-12	04-19-89	1880	GW-13	01-31-89	374
GW-12	10-12-89	1650	GW-13	04-19-89	499
GW-12	04-25-90	2410	GW-13	07-10-89	503
GW-12	07-19-90	862	GW-13	10-10-89	590
GW-12	10-23-90	1114	GW-13	01-29-90	403
GW-12	02-13-91	1346	GW-13	04-25-90	527
GW-12	06-27-91	909	GW-13	07-23-90	513
GW-12	09-10-91	888	GW-13	10-24-90	451
GW-12	12-06-91	749	GW-13	02-13-91	622
GW-12	03-18-92	515	GW-13	06-27-91	495
GW-12	06-03-92	180	GW-13	09-12-91	420
GW-12	09-16-92	526	GW-13	12-04-91	634
GW-12	12-02-92	610	GW-13	03-20-92	526
GW-12	03-24-93	570	GW-13	06-04-92	472
			GW-13	09-17-92	442
			GW-13	12-01-92	530
			GW-13	03-24-93	625

SOLUTION

Step 1. First consider the data in well GW-12. A time series plot of the most recent 20 specific conductance values is shown in **Figure 22-3**. This plot indicates a fairly linear downward trend, suggesting that a trend line should be fit to the data, along with an upper confidence bound around the trend.

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Figure 22-3. Time Series Plot of Specific Conductance Measurements at GW-12

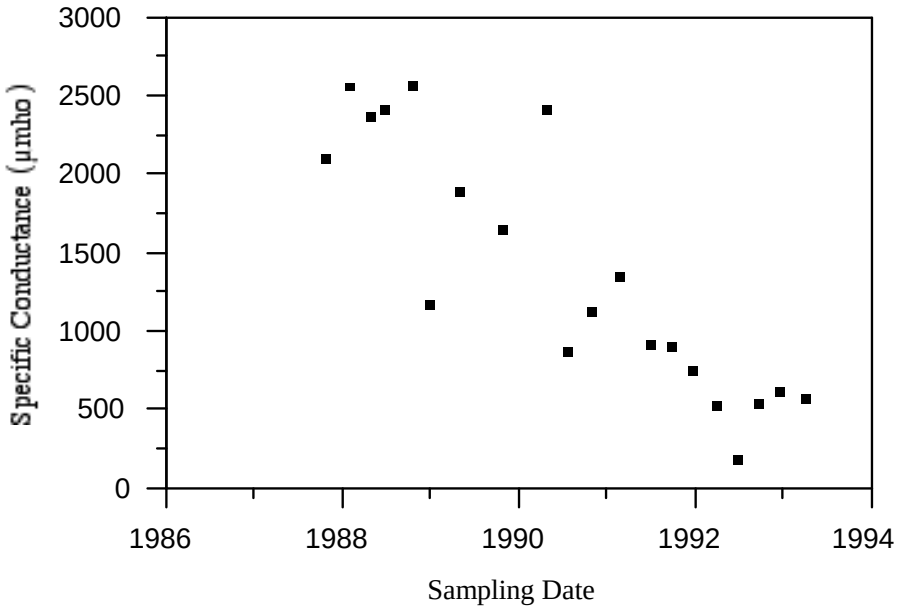
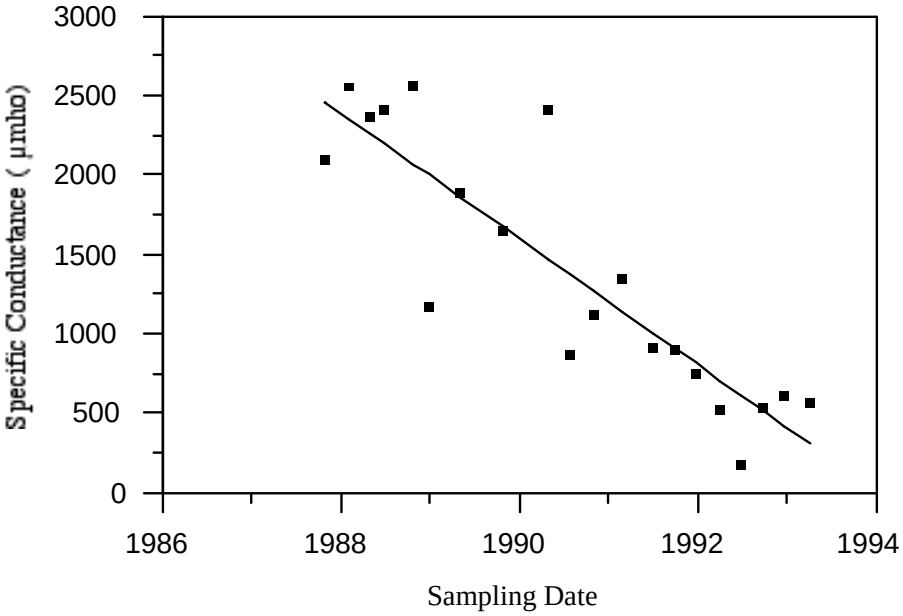


Figure 22-4. Regression of Specific Conductance *vs*. Sampling Date



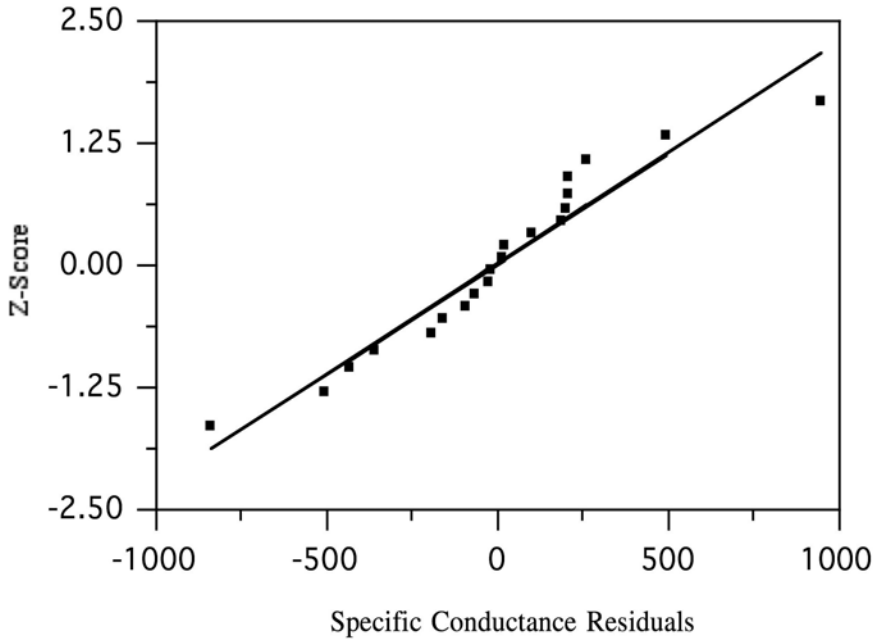
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Step 2. Fit a regression line of specific conductance versus sampling date using the formulas in **Section 21.3**. The equation of estimated trend line shown on **Figure 22-4** is:

$$\hat{y} = 790360 - 396.36 \cdot t$$

Step 3. Examine the trend residuals. A probability plot of the residuals is given in **Figure 22-5**. Since this plot is reasonably linear and the Shapiro-Wilk test statistic for these residuals (SW = .9622) is much larger than the 1% critical point for n = 20 ($sw_{.01,\ 20}$ = 0.868), there is no reason to reject the assumption of normality.

Figure 22-5. Probability Plot of Specific Conductance Residuals at GW-12



Also plot the residuals against sampling date (**Figure 22-6**). As no unusual pattern is evident on this scatter plot (*e.g.*, trend, funnel-shape, *etc.*) and the variability of the residuals is reasonably constant across the range of sampling dates, the key assumptions of the linear regression appear to be satisfied.

Step 4. Since the false positive error rate must be no greater than 5%, use α = .05 when constructing an upper confidence band around the regression line. Using the formulas in **Section 21.3** at each observed sampling date, both a 95% *upper* confidence band and a 95% *lower* confidence band are computed and shown in **Figure 22-7**. Only the upper confidence band is needed to measure the success of the remedial effort. Note that the formula uses an F-confidence level of 1-α or .95 for a one-sided confidence interval. The lower 95% confidence band is shown for illustrative purposes and the confidence level between the upper and lower bands is actually 90%.

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Figure 22-6. Plot of Specific Conductance Residuals *vs*. Sampling Date

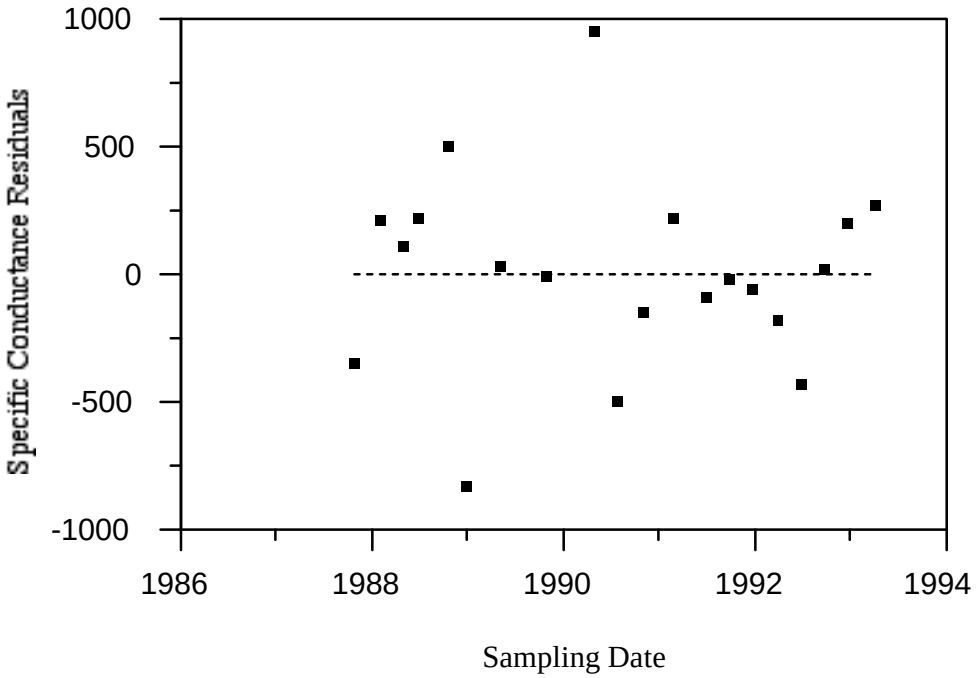
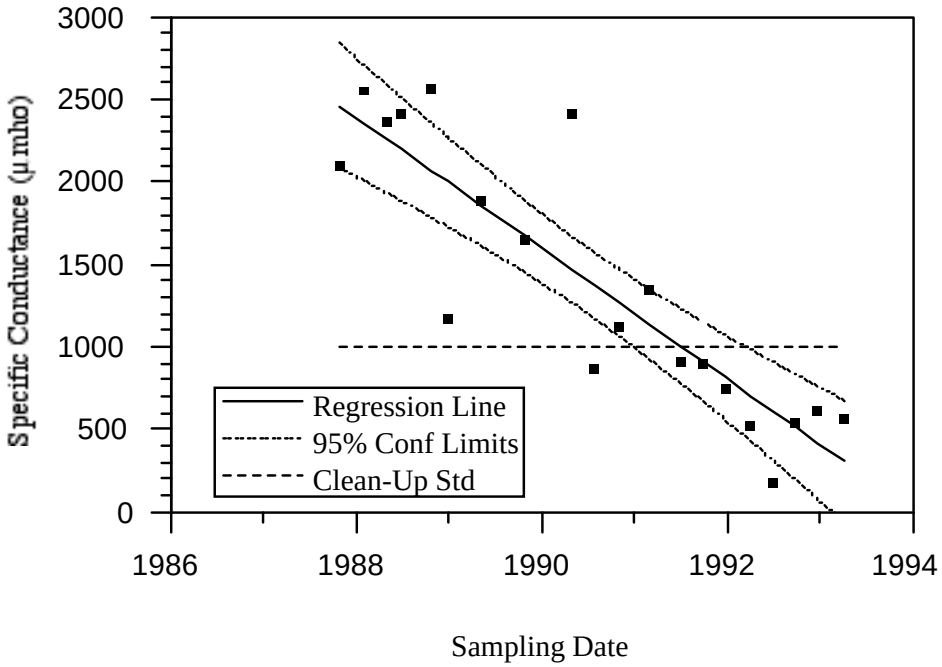


Figure 22-7. 95% Confidence Bounds Around Trend Line at GW-12

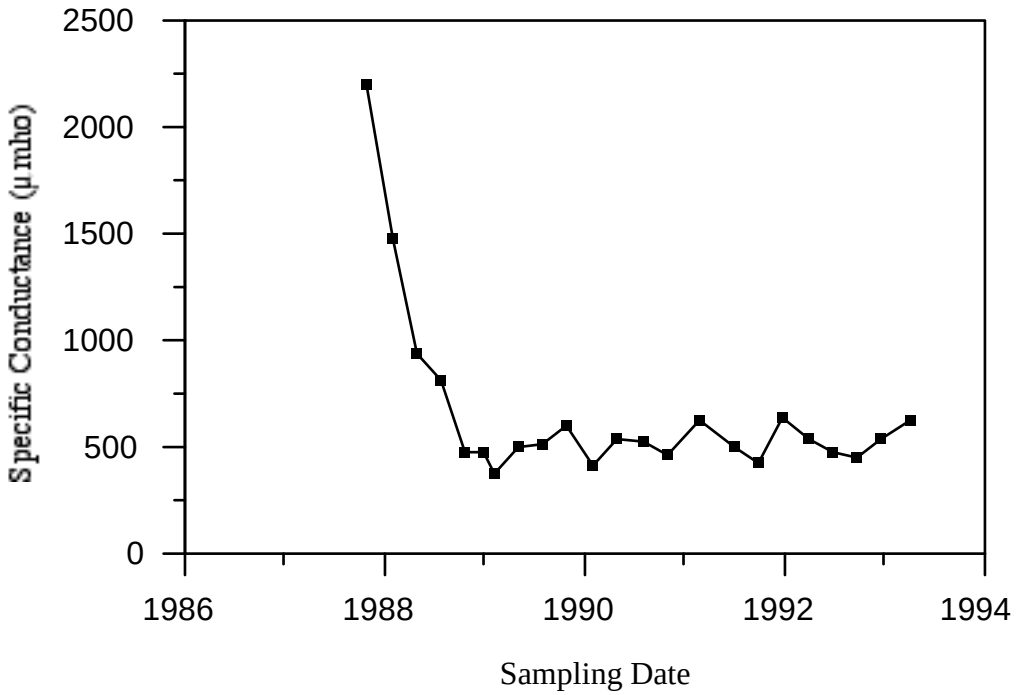


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Step 5. Determine the first time point at which the remediation effort should be judged successful. In **Figure 22-7**, the upper confidence band drops below the clean-up standard of L = 1000 μmho in the second quarter of 1992, so well GW-12 could be declared in compliance at this point.

Step 6. Now consider compliance well GW-13. A time series plot of the specific conductance measurements in this case (**Figure 22-8**) shows an initially steep drop in conductance level, followed by a more or less stable mean for the rest of the sampling record. The best strategy in this situation is to remove the four earliest measurements and then compute an upper confidence limit on the remaining values.

Figure 22-8. Time Series Plot of Specific Conductance Measurements at GW-13



Step 7. Before computing an upper confidence limit, test normality of the data. If the entire sampling record is included, the Shapiro-Wilk test statistic is only .5804, substantially below the 1% critical point with n = 23 of $sw_{.01,23}$ = 0.881, indicating a non-normal pattern. Certainly, a transformation of the data could be attempted. But simply removing the first four values (representing the steep drop in conductance levels) gives a Shapiro-Wilk statistic equal to .9536, passing the normality test easily. Further confirmation is found by comparing the probability plots in **Figures 22-9** and **22-10**. In the first plot, all the data from GW-13 are included, while in the second the first four values have been removed.

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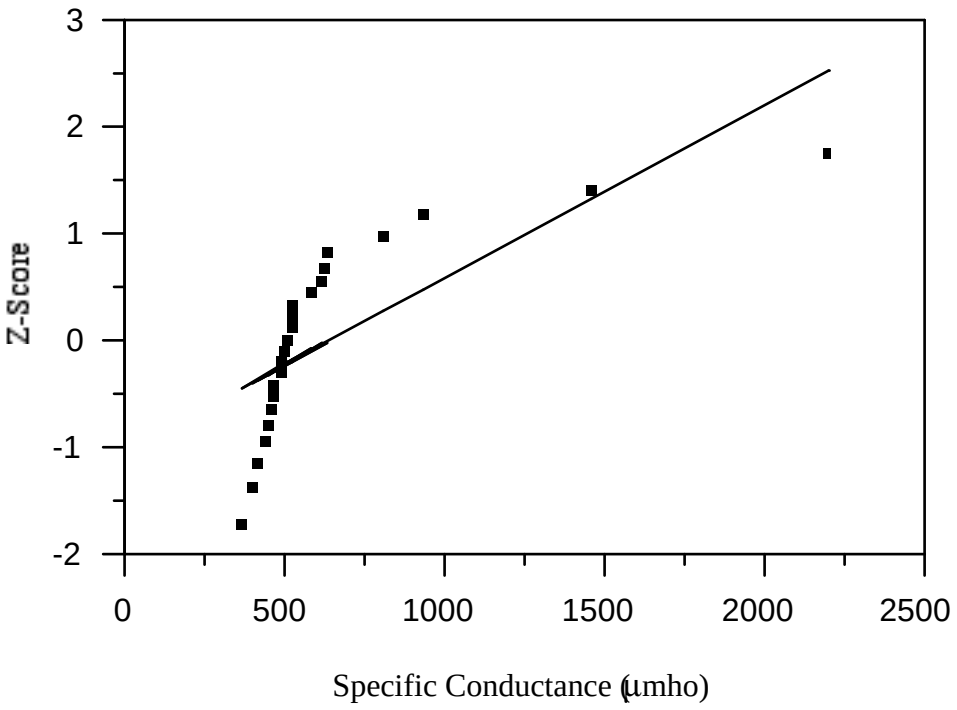
Step 8. Another instructive comparison is to compute the upper confidence limits on the same data with and without the first four values. Consider the initial 8 conductance measurements, representing the first two years of quarterly data under corrective action. If all 8 values are used to compute the upper 95% confidence bound (taking 95% so that $\alpha = .05$) and the formula for a confidence interval around a normal mean from **Section 21.1** is applied, the limit becomes:

$$UCL_{.95} = \bar{x} + t_{1-\alpha,n-1}\frac{s}{\sqrt{n}} = 901.75 + 1.8946 \times \frac{635.7126}{\sqrt{8}} = 1327.6\ \mu\text{mho}$$

While this limit exceeds the clean-up standard of L = 1000 µmho, the same limit excluding the first four measurements is easily below the compliance standard:

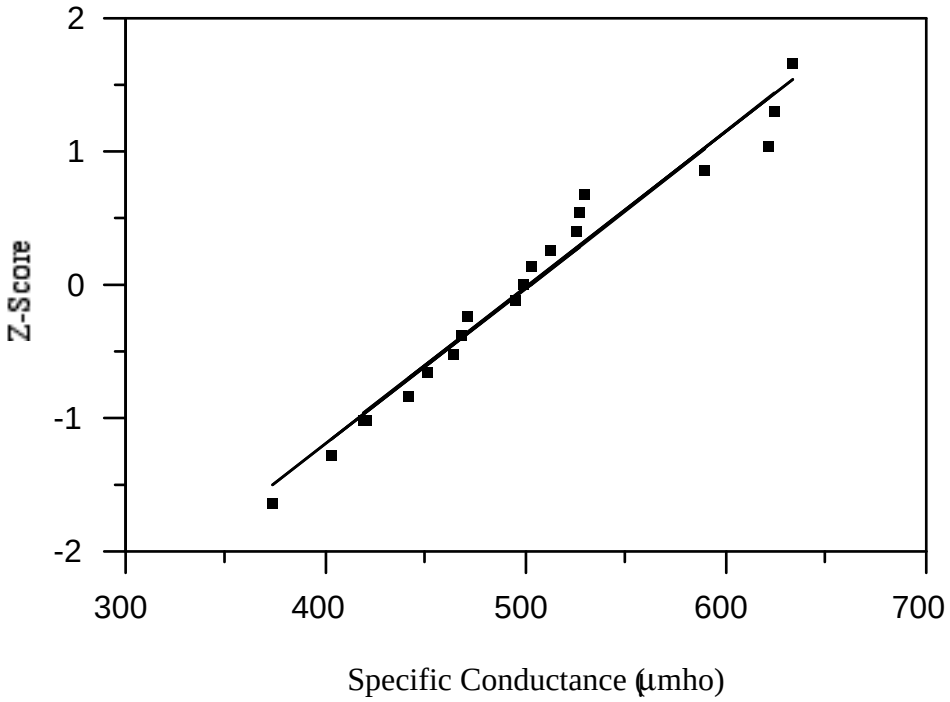
$$UCL_{.95} = 451.75 + 2.3534 \times \frac{54.0085}{\sqrt{4}} = 515.3\ \mu\text{mho}$$

Figure 22-9. Probability Plot at GW-13 Using Entire Sampling Record



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Figure 22-10. Probability Plot at GW-13 Excluding First Four Measurements



Step 9. Based on the calculation in **Step 8**, the clean-up standard is certainly met by early 1990 at GW-13. However, it is also instructive to examine the confidence bounds on larger sets of data from the stable portion of the sampling record. For instance, if the initial 4 measurements are excluded and then the next 8 values are used, the upper 95% confidence bound is:

$$UCL_{.95} = 478.75 + 1.8946 \times \frac{68.3452}{\sqrt{8}} = 524.5\ \mu\text{mho}$$

If all of the last 19 specific conductance values are used, a similar 95% confidence bound becomes:

$$UCL_{.95} = 503.158 + 1.7341 \times \frac{74.2760}{\sqrt{19}} = 532.7\ \mu\text{mho}$$

Step 10. Both of the limits in **Step 9** easily meet the clean-up standard of L = 1000 µmho. However, the amount of data used in the latter case is more than double than that of the former, which can impact the relative statistical power of the upper confidence limit for detecting decreases below the fixed standard. Given that the specific conductance seems to level off at close to 500 µmho, or one-half the clean-up standard, and given that the CV is approximately equal to .15, **Table 22-5** in **Appendix D** (looking under CV = 0.2) indicates that at least 6 measurements are needed to have a 95% chance of detecting a drop in conductance level to half the standard. So in this example, both UCLs are sufficiently powerful for detecting such a decrease. ◄

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22.2 CONFIDENCE INTERVAL TESTS FOR UPPER PERCENTILES

For fixed standards which represent an upper percentile or maximum, the proper comparison in compliance/assessment monitoring utilizes the *lower* confidence limit around an *upper* percentile tested against the GWPS. In formal corrective action testing, the appropriate comparison employs an *upper* confidence limit around an upper percentile. Parametric and non-parametric confidence intervals around percentiles are presented in **Chapter 21**.

While the basic comparison is similar to confidence intervals around a mean, two points should be noted. First, any numerical standard identified as a maximum concentration 'not to be exceeded' needs to be treated statistically as an upper percentile. The reason is that while every observed data set has a finite maximum, there is no way to estimate the confidence bounds around the maximum of a continuous population. The true 'maximum' is always positive infinity, illustrating a point of breakdown between mathematical models and physical reality. Nonetheless, confidence limits around an upper 90th to 99th percentile can be used as a close approximation to a maximum or some limit likely to only be infrequently exceeded.

Secondly, computing statistical power for an interval around an upper percentile is similar to but not quite the same as, statistical power for an interval around the mean. Statistical power for a compliance/assessment test of the upper 90th percentile is derived by considering whether more than 10% of all the population measurements exceed the GWPS. If so, the 90th percentile must also exceed the standard. In corrective action testing, the equivalent question is whether *less* than 10% of the measurements exceed the GWPS. In that case, the true 90th percentile must also be less than the standard.

Statistically, each observation is set equal to 0 or 1 depending on whether the measured concentration is less than or greater than the fixed standard. Then the percentage of measurements exceeding the GWPS is given by the *average* of the set of zeros and ones. In other words, the problem is similar to estimating an arithmetic *mean*.

The similarity ends, however, when it comes to setting power targets. For mean-based evaluations, power at true mean concentration levels is equivalent to a fixed multiple or fraction of the GWPS (*e.g.*, 1.5 or 2 times the standard; 0.25 or 0.5 times the standard). But for upper percentile power, the alternative hypothesis is defined in terms of the *actual percentage of measurements* either *exceeding the standard* in compliance/assessment monitoring (*e.g.*, 20% or 30% instead of the null hypothesis value of 10%) or *exceeding the clean-up level* in corrective action monitoring (*e.g.*, 2% or 5% instead of 10%). In both hypothesis frameworks, the actual fraction of measurements above the standard can be denoted by p. Furthermore, the power formulas rely on a normal approximation to the binomial distribution. If p is the probability that an individual observation exceeds the GWPS, and p_0 is the percentage of values exceeding the GWPS when the $(1–p_0)$th upper percentile concentration equals the standard, the quantity:

$$Z = \left(p - p_0\right) \Big/ \sqrt{p_0\left(1 - p_0\right)/n} \qquad [22.4]$$

has an approximately standard normal distribution under either the compliance/assessment null hypothesis $p \le p_0$ or the corrective action null hypothesis $p \ge p_0$.

Under the compliance/assessment alternative hypothesis (H_A), the true fraction exceeding the standard is greater than the null value ($p = p_1 > p_0$). With the corrective action alternative hypothesis, the true fraction is less than the null value ($p = p_1 < p_0$). p_1 can be specified as a multiple of p_0, say $p_1 = k \cdot p_0$, where k can either be greater or less than one. Then it is possible to compute the sample size (n) necessary to simultaneously achieve a pre-specified level of power (1–β) and false positive rate (α) with the equation:

$$n = \left[\frac{z_{1-\alpha}\sqrt{p_0\left(1-p_0\right)} + z_{1-\beta}\sqrt{kp_0\left(1-kp_0\right)}}{\left(k-1\right)p_0} \right]^2 \qquad [22.5]$$

where z_c represents the cth percentile from a standard normal distribution.

Equation [22.5] can be used for designing and constructing confidence interval tests around upper percentiles in both compliance/assessment and corrective action monitoring. However, the interpretation and practical approach to its use differ depending on the stage of monitoring.

22.2.1 UPPER PERCENTILE TESTS IN COMPLIANCE/ASSESSMENT

In compliance/assessment monitoring, the alternative hypothesis (*i.e.*, that the well is contaminated above the compliance standard) is expressed in terms of the relative percentage of concentration values that will exceed the GWPS compared to an uncontaminated well. To illustrate, if the compliance standard represents the 95th percentile so that no more than p_0 = 5% of the individual measurements exceed this level, the percentage exceeding under the alternative hypothesis might be taken as $p_1 = 2 \times p_0$ = 10%. Then a power level would be targeted so that exceedances of the standard occurring as frequently as p_1 would be identified with a probability equal to (1–β).

If n measurements are used to construct a lower confidence bound on the upper percentile ($1–p_0$) of interest (*e.g.*, the 95th), there will be a (1–β) × 100% chance of showing that the lower confidence limit exceeds the GWPS when in fact at least $kp_0 \times 100\%$ of the measurements actually exceed the standard. Furthermore, equation [22.5] also implies that the LCL will *falsely* exceed the GWPS with probability α. That is, when the true percentage of measurements exceeding the standard is actually p_0 or less, the test will identify a compliance violation $\alpha \times 100\%$ of the time.

Because EPA's primary concern in compliance/assessment monitoring is having adequate statistical power to detect groundwater contaminated above the regulatory standard, a high power level (1–β) should first be pre-specified. Then α can be varied in equation [22.5] until the resulting minimum sample size (n) matches the available sample or a feasible sample size for future sampling is found. In other words, power should always be kept high (*e.g.*, at least 70-75%), even at the expense of the false positive rate (α). However, there may be sites where a feasible sample size can be calculated such that *both* β and α are minimized.

Values of n for various choices of power level (1–β), Type I error rate (α), and upper percentile (1–p_0) are tabulated in **Table 22-7** in **Appendix D**. These can be used to maintain a specific level of power when employing a confidence interval around an upper percentile in compliance/assessment monitoring. The percentiles covered in this table include the 90th, 95th, 98th, and 99th. Levels of statistical power (1–β) provided include .50, .60, .70, .80, .90, .95, and .99, while the false positive rate (α) ranges from .20 down to .01. Specific cases not covered by **Table 22-7** in **Appendix D** can be computed directly with equation [22.5].

►EXAMPLE 22-3

Suppose a compliance limit for the pressure under which chlorine gas is stored in a moving container (for instance, a rail car) is designed to protect against acute, short-term exposures due to ruptures or leaks in the container. If the compliance limit represents an upper 90th percentile of the possible range of pressures that might be used to seal a series of such containers, how many containers should be sampled/tested to ensure that if in fact 30% or more of the container pressures exceed the limit, violation of the standard will be identified with 90% probability and exhibit only a 5% chance of false positive error?

SOLUTION

Step 1. Since the compliance limit on chlorine gas pressure represents the 90th percentile, at most 10% of the container pressures should exceed this limit under normal operations. In statistical notation, $p_0 = 0.10$ and $(1–p_0) = 0.90$. If there is a problem with the process used to seal the containers and 30% of the pressures instead exceed the limit, this amounts to considering a multiple of $k = 3$ times the nominal exceedance amount.

Step 2. Since a violation of the pressure standard by at least $3p_0$ or 30% needs to be identified with 90% probability, the target power is $(1–\beta) = 0.90$. Also, the chance of constructing a lower confidence limit on the true 90th percentile gas pressure that *falsely* identifies an exceedance of the standard must be kept to $\alpha = .05$.

Step 3. Looking in **Table 22-7** in **Appendix D** under the 90th percentile and $k = 3$, the necessary minimum sample size is $n = 30$. Thus, 30 similarly-sealed containers should be tested for gas pressure so that a confidence interval around the 90th percentile can be constructed on these 30 measurements using either the parametric or non-parametric formulas in **Chapter 21**. ◄

22.2.2 UPPER PERCENTILE TESTS IN CORRECTIVE ACTION

Equation [22.5] can also be used in formal corrective action testing. In this setting, an upper confidence limit [UCL] around an upper percentile is of interest and the false positive rate (α) needs to be minimized to ensure a low probability of falsely or prematurely declaring remedial success. In practice, α should be pre-specified to a low value. Then, different values for power (1–β) can be input into equation [22.5] until the resulting minimum sample size (n) either matches the available amount of sampling data or is feasible to collect in future sampling.

Once the minimum sample size is computed and these n measurements are used to construct a UCL on the upper percentile (1–p_0) of interest (*e.g.*, the 95th), there will be a $(1–\beta) \times 100\%$ chance that

the UCL will be less than the clean-up standard when in fact no more than $kp_0 \times 100\%$ of the measurements actually exceed the standard. For instance, if $k = 1/2$, $(1-\beta)$ will be the power of the test when in fact half as many of the measurements exceed the standard as are nominally allowed.

Equation [22.5] also implies that the UCL will *falsely* drop below the clean-up standard with probability α. That is, when the true percentage of measurements exceeding the standard is actually p_0 or greater — indicating that the clean-up standard has not been met — the test will still declare the remedial effort successful $\alpha \times 100\%$ of the time.

Values of n for various choices of power level $(1-\beta)$, Type I error rate (α), and upper percentile $(1-p_0)$ are tabulated in **Table 22-8** in **Appendix D**. This table can be used to determine or adjust the feasible power level based on a pre-specified α when employing a confidence interval around an upper percentile in corrective action. Note that the minimum sample sizes in **Table 22-8** of **Appendix D** are generally quite large, especially for small error rates (α). Because of the regulatory interest in minimizing the risk of prematurely exiting remediation, statistical comparisons in corrective action are likely to initially have fairly low power. As the clean-up process continues, enough additional data can be accumulated to adequately raise the odds of declaring the remediation a success when in fact it is.

►EXAMPLE 22-4

Suppose excessive nitrate levels must be remediated in a rural drinking water supply. If the clean-up standard for infant nitrate exposure represents an upper 95th percentile of the concentration distribution, what sample size (n) should be selected to ensure that if true nitrate levels drop below the clean-up standard, the remediation effort will be judged successful with at least 80% probability?

SOLUTION

Step 1. Examining **Table 22-8** in **Appendix D** under the 95th percentile and power = $(1-\beta) = .80$, a choice of n cannot be made until two other statistical parameters are fixed: the false positive rate (α) and the relative fraction of exceedances (p). The false positive rate governs the likelihood that the upper confidence limit on nitrate will be below the clean-up standard, even though *more* than 5% of all nitrate measurements are above the compliance standard (so that the *true* 95th percentile for nitrate still exceeds the clean-up criterion). The relative fraction of exceedances (p) sets the true percentage of individual nitrate concentrations that exceed the clean-up standard under the alternative hypothesis (H_A); that is, what fraction of nitrate values are exceedances when the clean-up standard is truly met.

Unfortunately, no matter what choices of α and p are selected in **Table 22-8** of **Appendix D**, the smallest required sample size is $n = 55$, when $\alpha = .20$ and $p = .25$. Even if it is practical and affordable to test 55 samples of groundwater for nitrate, the chance of falsely declaring the remediation effort a success will still be 20%. To cut that probability in half to $\alpha = .10$, $n = 99$ samples needs to be tested.

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Step 2. To lessen the required sampling effort, consider the alternatives. Lower sample sizes are needed if the percentile of interest is less extreme, for instance if the clean-up standard represents a 90th percentile instead of the 95th. In this case, only $n = 48$ samples are needed for 80% power and a 10% false positive rate with $p = .25$. Of course, more frequent exceedances of the compliance limit are then allowed (*i.e.*, 10% versus 5% of the largest nitrate concentrations).

Another less desirable option is to raise the α level of the test. This raises the risk of falsely declaring the remediation effort to be a success. One could also lower p. At $p = .25$ for the 95th percentile, 80% power is guaranteed only when the true nitrate exceedance frequency is one-fourth the maximum allowable rate--- i.e., when the true rate of exceedances is $.25 \times 5\% = 1.25\%$. Exceedance rates greater than this will be associated with *less* than 80% power. But while lowering p and keeping other parameters constant will indeed decrease n, it also has the effect of requiring a very low actual exceedance rate before the power of the test will be sufficiently high. At $p = .10$ for the 95th percentile, for instance, the true exceedance rate then needs to be only $.10 \times 5\% = 0.5\%$ to maintain the same level of power.

The final option is to lower the desired power. Power in this setting is the probability that the UCL on nitrate will be below the clean-up standard, when the groundwater is no longer contaminated above the standard. When the true nitrate levels are sufficiently low to meet the compliance standard, demonstrating this fact will only occur with high probability (*i.e.*, high power) when the sample size is fairly large. By taking a greater chance that the status of the remediation will be declared inconclusive (*i.e.*, when the UCL still exceeds the clean-up standard even though the true nitrate levels have dropped), power could be lowered to 70% or 60% for instance, with a corresponding reduction in the required n. To illustrate, if the power is set at 60% instead of 80% for the 95th percentile and the false positive rate is set at $\alpha = .10$, the required sample size would drop from $n = 99$ to $n = 68$.

Step 3. In many groundwater contexts, the minimum sample sizes of **Table 22-8** in **Appendix D** may seem excessive. Certainly, the sampling requirements associated with upper percentile clean-up standards are substantially greater than those needed to test mean-based standards. However, remediation efforts often last several years, so it may be possible to accumulate larger amounts of data for statistical use than is possible in, say, detection or compliance monitoring. In any event, it is important to recognize how the type of standard and the statistical parameters associated with a confidence interval test impact the amount of data necessary to run the comparison. Each parameter should be assessed and interpreted in the planning stages of an analysis, so that the pros and cons of each choice can be weighed.

Step 4. Once a sample size has been selected and the data collected, either a parametric or non-parametric upper confidence limit should be constructed on the nitrate measurements and compared to the clean-up standard. ◄

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STATISTICAL ANALYSIS OF GROUNDWATER MONITORING DATA AT RCRA FACILITIES

UNIFIED GUIDANCE APPENDICES MARCH 2009

EPA 530/R-09-007



Table 19-1 κ-Multipliers for 1-of-2 Interwell Prediction Limits

w/n	4	6	8	10
8	2.93	**2.35**	**2.12**	**2.00**
12	3.16	**2.52**	**2.28**	**2.15**
16	3.33	2.65	**2.39**	**2.24**
20	3.45	2.74	*2.47*	**2.32**
30	3.67	2.91	2.61	*2.46*
40	3.82	3.02	2.71	2.55
50	3.93	3.11	2.79	2.62
60	4.03	3.18	2.85	2.68
75	4.14	3.26	2.93	2.75

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A.2 GLOSSARY

Alpha (α) level	Decimal level of significance or false positive error of a statistical test
1-of-*m* Plan	Retesting plan consisting of an initial sample followed by up to (*m*–1) resamples; resamples are collected only if initial sample exhibits a statistical difference
Accuracy	Closeness of a measured or computed value to its "true" value, where the true value is obtained with perfect information.
ACL	Alternate Concentration Limit; a fixed standard or clean-up action level alternative to prescribed RCRA regulatory health- or background limits
Aliquot replicates	Physical splits of a single water quality sample for multiple analyses
ANOVA	Analysis of Variance; a statistical method for identifying differences among several population means or medians
Appendix I	40 CFR Part 258 chemical parameter list for Subtitle D detection monitoring programs
Appendix II	40 Part 258 CFR chemical parameter list for Subtitle D compliance or assessment monitoring programs
Autocorrelation	Correlation of values of a single variable data set over successive time intervals
Background	Natural or baseline groundwater quality at a site; can be characterized by upgradient, historical, or sometimes sidegradient water quality
Beta (β) level	Decimal value representing a false negative error rate in a statistical test
Bias	Systematic deviation between a measured (i.e., observed) or computed value and its true value. Bias is affected by faulty instrument calibration and other measurement errors, systematic errors during data collection, and sampling errors such as incomplete spatial randomization during the design of sampling programs.
Box Plot	Plot of selected descriptive statistics at a monitoring point (*e.g.*, mean, median, upper and lower quartiles)
Calibration	Comparison of a measurement standard, instrument, or item with a standard or instrument of higher precision and lower bias to detect and quantify inaccuracies and to report or eliminate those inaccuracies by adjustments. Also used to quantify instrument measurements of a given concentration in a given sample.
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act (or Superfund); statute for non-active hazardous waste site management and remediation
Confidence Interval	Statistical interval designed to bound the true value of a population parameter such as the mean or an upper percentile
Confidence Level	Degree of confidence associated with a statistical estimate or test, denoted as $(1 - \alpha)$

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Coverage	Fraction of a population expected to be contained within a tolerance interval
Critical value	Predetermined decision level for a test of statistical hypotheses
Degrees of freedom	The number of ways which members of a data set or sets can be independently varied
Descriptive Statistics	Statistics used to organize and summarize sample data
Effective Power	In a groundwater network of statistical tests, the power of the test method to identify a single well contaminated by a single constituent
EPA Reference Power Curves (ERPC)	Recommended standards for comparing performance of RCRA statistical methods in detection monitoring; based on individual prediction limit using n = 10 background samples and α = .01
False Negative	Finding of no statistically significant difference when there is, in fact, a physical difference in the underlying populations or between a single population and a fixed compliance standard; also known as beta (β) or Type II error
False Positive	Finding a statistically significant difference when there is, in fact, no physical difference in the underlying populations or between a single population and a fixed compliance standard; also known as alpha (α), significance level, or Type I error
GWPS	(Ground Water Protection Standards) Concentration limits set by the regulatory agency as a standard to be attained in groundwater monitoring. These may be fixed health- or risk-based limits (e.g. MCLs) or a background level.
Heterogeneous	Non-uniform in structure or composition throughout
Histogram	Graphical representation of frequency with data values grouped into specified numerical ranges
Homogeneous	Uniform in structure and composition throughout
Homoscedasticity	Equality of variance among sets of data
Hypothesis	One of two statements made about potential outcomes of a statistical test. The null and alternative hypothesis statements refer to the condition of a population parameter. The null hypothesis is favored, unless the statistical test demonstrates the greater likelihood of the alternative hypothesis.
Independent & Identically Distributed (i.i.d)	Groundwater measurements having the same statistical distribution and exhibiting no statistical dependence or correlation
Indicator Parameters	Chemical parameters whose presence or elevation is possibly indicative of a facility release
Interwell	Comparisons between distinct monitoring wells
Intrawell	Comparisons over time at a given monitoring well between early and later measurements
Mann-Kendall Test	Non-parametric test of trend

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MCL	Maximum Contaminant Level; a fixed water quality standard defined under the Safe Drinking Water Act and used in 40 CFR 258.40(e)(3)
MDL	Method Detection Limit—the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero in a specific matrix.
Modified California Plan	Retesting plan consisting of an initial sample followed by three resamples; if initial value exhibits a statistical difference, two of three resamples must *not* exhibit a difference for the test to 'pass'
Non-detects (NDs)	Observations below the MDL, RL, or QL
Non-parametric Test	Statistical test that does not depend on knowledge of the distribution of the sampled population
Normal distribution	A family of symmetric continuous probability distributions defined by two finite parameters, the mean and variance
Outlier	Value unusually discrepant from rest of a series of observations
Parametric Test	Statistical test that depends upon or assumes observations from a particular probability distribution or distributions
Percentile	The specific value of a distribution that divides the distribution such that p percent of the distribution is equal to or below that value. If the 95th percentile is X, it means that 95 percent of the values in the statistical sample are less than or equal to X.
Population	All possible measurements/values over a period of time at a given location, series of locations, or over a spatial or volumetric extent
PQL or QL	Practical Quantification Limit—lowest concentration level for an analytical method which can be reliably achieved within specified limits of precision and accuracy under routine laboratory operating conditions
Precision	A measure of mutual agreement among individual measurements of the same property, usually under prescribed similar conditions, expressed generally in terms of the sample standard deviation.
Prediction Interval	Statistical interval constructed from background data on the next 'future' sample or samples arising from the same population
Prediction Limit	Upper or lower limit of a prediction interval
Probability	Quantitative measure of uncertainty about the occurrence of a random or uncertain event
Probability Distribution	Numerical statistical pattern associated with a population of measurements; many common patterns can be described using mathematical formulas
Proportion	A population proportion (p) is the ratio of the number of units of a population that have the specified characteristic or attribute (M) to the total number of units in the population (N).
Random sample	Collected data which are based only on their probability of occurrence in random fashion

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Ranking	Assignment of numbers to an ordered data set indicating their relative position, generally integer values from 1 to *n* for the smallest to largest values in a sample of size *n* (unless specified in reverse rank order)
RCRA	Resource Conservation and Recovery Act; statutory provisions for active facility hazardous (Subtitle C) and non-hazardous waste (Subtitle D) definition, storage, treatment and disposal
Reporting Limit	Reporting Limit—lowest concentration level for an analytical method which can be reliably measured by a laboratory
Residual	Typically, the difference of a value in a data set from its mean
ROS	Regression on order statistics, either parametric or robust; techniques for fitting non-detect data to a single distribution
Sample	Set of measurements from a population (can be as few as one)
SDWA	Safe Drinking Water Act; statute under which drinking water standards are promulgated and water treatment sites regulated
Seasonality	The presence of seasonal effects on ground water quality observations; effects may be natural or man-made.
Sen's Slope Estimator	Non-parametric method to estimate the rate of change of concentration levels over time
SWFPR	Site Wide False Positive Rate; design probability of at least one statistically significant finding among a network of statistical test comparisons at a group of uncontaminated wells
Spearman's Test	Non-parametric test of trend using data ranks
Statistical Parameter	A numerical characteristic of a statistical population or probability distribution
Statistical Power	Strength of a test to identify an actual release of contaminated groundwater or difference from a compliance standard
Statistically Significant Difference (or Increase)	Statistical difference exceeding a test limit large enough to account for data variability and chance
Time Series Plot	Graphical plot of individual concentration values over time
Tolerance Interval	Statistical interval constructed to 'cover' a specified proportion of the underlying population of measurements
Tolerance Limit	The upper or lower limit of a tolerance interval
Trace Value	Measured value close to, but above the limit of detection; may lie between the MDL and the QL
Random Variable	A numerical value or characteristic that can assume different values on different sampling events or at different locations
Variance	A measure of spread or dispersion calculated as the average of squared differences from the mean in a set of data or a population
Verification Resampling or Retesting Plan	A plan to collect an additional resample or resamples to confirm or disconfirm an initial statistically significant finding

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APPENDIX B. HISTORICAL NOTES

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B.1 PAST GUIDANCE FOR CHECKING NORMALITY

The 1989 ***Interim Final Guidance*** [IFG] outlined three different methods for checking normality: the coefficient of variation [CV] test, probability plots, and the chi-square test. Of these three, only probability plots are recommended within the Unified Guidance. The coefficient-of-variation and chi-square tests each have potential problems or are inferior to alternate methods. These alternatives include the coefficient of skewness, the Shapiro-Wilk or Shapiro-Francía tests, and Filliben's probability plot correlation coefficient.

The coefficient of variation [CV] test in the original 1982 RCRA Part 264 groundwater monitoring regulations was recommended within the IFG because it is easy to calculate and amenable to small sample sizes. To ensure that a normal model with a significant fraction of negative concentration values was not fit to positive data, the IFG recommended that a sample CV be less than one to indicate 'normality.' The test was inexact since the distribution of sample CV's from a truly normal population itself is a function of both sample size and the true coefficient of variation. Truly normal populations of positive-valued data are likely to have a CV of 0.3 or lower, although individual sample CV's will occasionally exceed one, depending on the sample size. It was also possible to incorrectly reject normality using this criterion even when the population was really normal.

While the coefficient of variation indirectly offers an estimate of skewness and hence normality/non-normality, there are better formal tests to accomplish both goals. The Unified Guidance recommends estimating skewness of a data set using the coefficient of skewness (**Section 10.4**), along with other tests of normality in **Chapter 10**. Nevertheless, the coefficient of variation provides a measure of intrinsic variability in positive-valued data sets. Although approximate, the coefficient of variation can indicate the relative variability of certain data, especially with small sample sizes and in the absence of other formal tests.

The CV is also a valid measure of the multiplicative relationship between the mean and the standard deviation for positively-valued random variables. The estimator $\hat{CV} = s/\bar{x}$ reasonably approximates the true CV for non-negative normal populations. In lognormal populations, the coefficient of variation can also be used in evaluations of statistical power. For the lognormal distribution, the population coefficient of variation works out to be:

$$CV = \sqrt{\exp\left(\sigma_y^2\right) - 1}$$

where σ_y is the population log-standard deviation. Because of this, instead of a ratio between the standard deviation and the mean, the lognormal coefficient of variation is usually estimated by

$$CV = \sqrt{\exp\left(s_y^2\right) - 1}$$

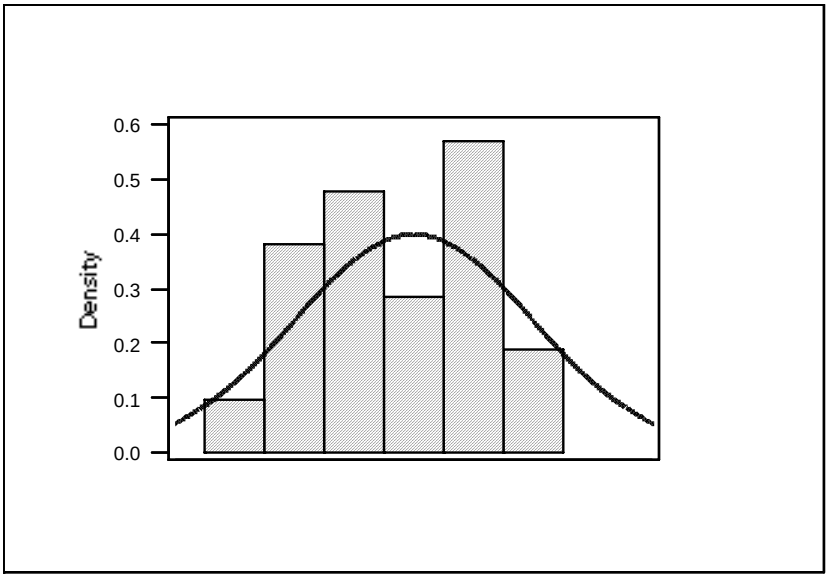
where s_y is the log-standard deviation. This last estimate is usually more accurate than the simple ratio of standard deviation-to-mean, especially when the underlying population coefficient of variation is high. However, neither coefficient of variation estimator is a satisfactory test as to whether a data set is truly normal or lognormal.

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The chi-square test was also recommended within the IFG. Though an acceptable goodness-of-fit test, it is not considered the most sensitive or powerful test of normality (Gan and Koehler, 1990). The downside to the chi-square test can be explained by considering the behavior of parametric tests based on the normal distribution. Most tests, like the *t*-test or parametric prediction limits, which assume that the underlying data are normal, give fairly robust results when the normality assumption fails over the middle ranges of the data distribution. That is, if the extreme tails are approximately normal in shape even if the middle part of the density is not, these parametric tests will still tend to produce valid results. However, if the extreme tails are non-normal in shape (*e.g.*, highly skewed), normal-based tests can lead to false conclusions, meaning that either a data transformation or a non-parametric technique should be used instead.

The chi-square test entails a division of the sample data into 'bins' or 'cells' representing distinct, non-overlapping ranges of the data (**Figure B-1**). In each bin, an expected value is computed based on the number of data points that would be found if the normal distribution provided an appropriate model. The squared difference between the expected number and observed number is then computed and summed over all the bins to calculate the chi-square test statistic.

Figure B-1. How the Chi-Square Goodness-of-Fit Test Works



If the chi-square test indicates that the data are not normal, it may not be clear what ranges of the data most violate the normality assumption. Departures from normality in the middle bins are given nearly the same weight as departures in bins representing the extreme tails, and all the departures are summed together to form the test statistic. As such, the chi-square test is not as powerful for detecting departures from normality in the extreme tails of the distribution, the areas most crucial to the validity of parametric tests like the *t*-test or ANOVA (Miller, 1986). This implies that if there are departures in the tails, but the middle portion of the data distribution is approximately normal, the chi-square test may not register as statistically significant even when better tests of normality would.

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The IFG also suggested that the original data should be presumed to be normal prior to testing the distributional assumption. If a statistical test rejected the model of normality, the data could be checked instead for lognormality by evaluating their natural logarithms. The 1992 ***Addendum to Interim Final Guidance*** [Addendum] noted that many data sets in environmental monitoring are better fit by a lognormal than by a normal distributional model. Primarily on that basis, it was recommended that the lognormal distribution replace the normal as the default model for groundwater analysis, especially since for small data sets, the available tests of normality have limited statistical power to reject the null hypothesis of normality, even if the data arise from a lognormal distribution. The Unified Guidance brings this argument around almost full circle by arguing that the normal model is a slightly better default for small samples, but that distributional testing is recommended in any case in order to establish the most appropriate model (**Section 10.3**).

B.2 THE CABF PROCEDURE

Facilities operating under a RCRA permit specifying Cochran's Approximation to the Behrens-Fisher Student's *t*-test [CABF] may change this method to a more appropriate procedure at the time of State or Regional permit review and update. Owners and operators may also apply for a permit modification under §270.41(a)(3). This change is considered a Class 1 permit modification, which must be made with prior approval from the Director.[1] Depending on the nature of the permit conditions, it may also be appropriate, on a facility-specific basis, for an oversight agency to approve a change of method without a formal permit modification.

Under appropriate circumstances, an owner or operator may wish to continue using a *t*-test type procedure. However, instead of the CABF method, it is recommended that either a pooled variance Student's *t*-test or a variant of this test due to Welch (1937) be employed (**Chapter 16**). Not only is Welch's test a more standard type of *t*-test than the CABF procedure, but research has shown it to be equivalent or preferable to other varieties of the *t*-test (Moser and Stevens, 1992).

Circumstances appropriate for the use of a *t*-test procedure might include facilities with very few monitoring wells (*e.g.*, three or less) and that monitor for a very limited number of constituents (*e.g.*, one or two). As long as no more than 5 to 10 statistical comparisons are being made each year, running a *t*-test at the 0.01 level of significance in each case should result in at most a 10% annual probability of any comparison registering as a false positive when there is no actual contamination.

One of the problems with the CABF procedure in practice was the use of aliquot replicate samples to bolster the total sample size (**Section 2.2.4**). Both the pooled variance *t*-test and Welch's *t*-test make the assumption that the sample observations are statistically independent. Though aliquot replicate sampling increases the number of available measurements, aliquot replicate samples mostly provide information about *analytical* variability and accuracy, and tend to be highly correlated. Since the goal of a RCRA groundwater statistical program is to provide data about hydro-geochemical variability in the (uppermost) aquifer below the facility, aliquot replicate sampling (like the CABF procedure itself) should be avoided unless a more sophisticated components of variance model is used to account for the separate effects of analytical variability and natural groundwater variance.

[1] See 53 FR 37912, September 28, 1988 for more details about the permit modification process.

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B.3 PAST GUIDANCE FOR NON-DETECTS

Guidance for handling non-detect measurements was first offered in the 1989 ***Interim Final Guidance*** [IFG]. There the basic recommendations included the following: 1) if less than 15% of all samples are non-detect, replace each non-detect by half its detection or quantitation limit [QL] and proceed with a parametric analysis, such as ANOVA, tolerance limits, or prediction limits; 2) if the percentage of non-detects is between 15 and 50, either use Cohen's adjustment to the sample mean and variance in order to proceed with a parametric analysis, or employ a non-parametric procedure by using the ranks of the observations and treating all non-detects as tied values; 3) if the percentage of non-detects is greater than 50, use the test of proportions.

In the 1992 ***Addendum to Interim Final Guidance*** [Addendum], the recommendation for data sets with small fractions of non-detects (*i.e.*, ≤ 15%) was left unchanged; however, for cases with moderate detection rates (*i.e.*, non-detects comprising 15% to 50% of the data), Cohen's adjustment was supplemented by Aitchison's method for data sets in which non-detects could be regarded as zero concentrations. In addition, the *test of proportions* was deleted from the Addendum. Instead, for large fractions of non-detects, three options were suggested: 1) for two sample comparisons, the Wilcoxon rank-sum test was recommended over the test of proportions; 2) for moderately large background samples, the Addendum recommended non-parametric prediction and tolerance limits; and 3) for extremely low detection rates (*e.g.*, ≥ 90% non-detects) and small background samples, the Addendum recommended the use of Poisson prediction and tolerance limits.

The test of proportions was not recommended in the Addendum, even for detection rates under 50%, for the following reason. Although acceptable as a statistical procedure, the test of proportions does not account for potentially different magnitudes among the concentrations of detected values. Rather, each sample is treated essentially as a '0' or '1' depending on whether the measured concentration is below or above the QL. The test of proportions ignores information about concentration magnitudes, and hence is often less powerful than a non-parametric rank-based test like the Wilcoxon rank-sum, even after adjusting for a large fraction of tied observations (*e.g.*, non-detects). In part, this is because the ranks of a data set preserve additional information about the relative magnitudes of the concentration values, information which is lost when all observations are scored as 0's and 1's.

Furthermore, small-scale Monte Carlo simulations comparing the test of proportions to the Wilcoxon rank-sum test showed that for small to moderately large proportions of non-detects (say 0% to 60%), the Wilcoxon rank-sum procedure adjusted for ties was more powerful in identifying real concentration differences than the test of proportions. When the percentage of non-detects was quite high (at least 70% to 75%), the test of proportions was occasionally more powerful than the Wilcoxon for extremely small group sample sizes (*e.g.*, no more than 4 to 6 measurements per group), but the results of the two tests usually led to the same conclusion. Consequently, the Wilcoxon rank-sum test was recommended in all cases where non-detects constituted more than 15 percent of the samples.

The revised Unified Guidance also places less emphasis on Cohen's method. The reason is that it could only accommodate a single censoring limit (*e.g.*, reporting limit [RL]) in its original formulation and assumed that all quantified values were necessarily greater than this limit. Because many environmental data sets include multiple reporting and/or detection limits and an intermixing of detects and non-detects, two other methods are now recommended that are designed to handle more complex data configurations (**Chapter 15**). Cohen's and the parametric ROS method may have limited

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applicability when both detect and non-detect data are expected to stem from a single parametric distribution and a single censoring limit can be used.

B.4 TREND TESTS

The Unified Guidance recommends trend testing as an alternative to prediction limits or control charts when those methods are not suitable. To understand the basis for this recommendation, it may help to consider how intrawell comparisons initially supplemented, and then came in many cases to supplant, interwell comparisons.

In the 1989 IFG and the 1992 Addendum, the recommended statistical methods closely followed the 1988 and 1991 Final Rules published in the Federal Register. Although these methods replaced historical use of the CABF Student's *t*-test, there was still an emphasis on interwell comparisons between background and downgradient wells through the use of *t*-tests and ANOVA. Indeed, where justified, interwell comparisons provide undeniable conceptual advantages over other kinds of tests. When (upgradient) background measurements can be used to establish a reasonable baseline concentration level, such data offer invaluable information about site-specific conditions at uncontaminated locations and the level of variability one should expect to encounter in the absence of events that precipitate groundwater contamination.

Unfortunately, ANOVA and *t*-tests all involve a comparison of population means under the key assumption that the populations *have not changed over time*. The underlying distributions in each group or well are assumed to be stable over the period of monitoring, so that concentration measurements fluctuate randomly around a constant mean level. Stability, of course, is not guaranteed. Several factors can impact the statistical characteristics of the underlying aquifer at either upgradient or downgradient wells, including natural fluctuations in aquifer parameters, migration of contaminants from off-site sources, changes in the mixture of deposited waste and its geochemical interaction with the subsurface environment, and alterations in geochemistry from 'percolation' effects due to past waste disposal practices or land usage.

EPA's hope in the 1989 IFG was that ANOVA-type comparisons would be done quickly enough (*e.g.*, every six months) that the underlying populations could be considered essentially static during each testing period. At some sites, this may be a reasonable assumption. However, in practice, sampling is now done on a quarterly, semi-annual, or annual basis. In order to gather the four to five samples needed— at a minimum — to run a *t*-test or ANOVA, at least one to four years of sampling is necessary. Over this length of time, the statistical characteristics of groundwater may or may not change.

Furthermore, interwell comparisons between upgradient and downgradient well locations are not always appropriate, either due to natural spatial variability, screening of background and downgradient wells in different hydrostratigraphic positions, effects of groundwater mounding, *etc.* In such cases, the appropriate statistical approach is to use an *intrawell* test at each compliance location. Intrawell tests involve a comparison only of data collected at that specific well location, thus eliminating spurious differences that might arise due to natural spatial variability or other background-to-downgradient differences not attributable to the presence of contaminated groundwater.

Two basic intrawell techniques are described in the Unified Guidance: intrawell prediction limits and control charts. Both designate some portion of the historical sampling record as intrawell 'background' for that well. Ideally, this intrawell background should consist of measurements known to

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be uncontaminated. Furthermore, both methods assume (unless special adjustments are made) that the intrawell background represents a random sample from a stable population, just as with the *t*-test and ANOVA. If the population mean and/or standard deviation *change* while intrawell background is being compiled, results of either prediction limit or control chart tests against more recent data from the well can be severely biased or altogether inaccurate.

For these reasons, neither prediction limits nor control charts are appropriate for every circumstance where an intrawell test is warranted. The Unified Guidance recommends trend testing as an alternative to prediction limits or control charts when those methods are not suitable as intrawell techniques (**Chapter 17**). Tests for trend are specifically designed to identify groundwater populations whose mean concentration levels are not stable over time, but rather are significantly increasing (or decreasing).

B.5 PREDICTION LIMITS AND RETESTING

B.5.1 RETESTING SCHEMES

Since roughly 1987, several different retesting schemes have been suggested in regulatory documents or published in scientific literature. Classification of these schemes shows that they fall into three basic types: 1-of-*m*, California, and tolerance screens. The 1-of-*m* approach was initially suggested by Davis and McNichols (1987) as part of a broader method termed '*p*-of-*m*.' Essentially the *p*-of-*m* approach assumed that as many as *m* observations would be collected for a particular constituent at a given well, including the initial groundwater measurement and up to (*m*–1) resamples. As long as at least *p* of these observations were below a predetermined upper prediction limit, the constituent would 'pass' the test at that well, allowing detection monitoring to continue.

Davis and McNichols determined how to calculate the necessary prediction limits so that the overall false positive rate would remain below a fixed value (say 5%, as targeted in the 1992 Addendum), even when the same testing procedure was applied over many different testing periods (*r* in their terminology). By applying the same technique to *r* different well-constituent pairs (and assuming mutual statistical independence among constituents and compliance wells) instead of to *r* different testing or evaluation periods, one then has a retesting scheme that can be applied at a large variety of monitoring networks while ensuring that the site-wide false positive rate [SWFPR] is kept to a minimum.

In practice, though the *p*-of-*m* strategy provides a great deal of flexibility in designing a retesting scheme, only those schemes known as 1-of-*m* are typically useful in the current regulatory context of groundwater monitoring. Consider, for example, a 2-of-3 strategy. By definition, if at least two of three groundwater samples are below the upper prediction limit (*i.e.*, are 'in-bounds'), the constituent passes and is not flagged as exceeding background. Since at least two samples must be 'in-bounds,' it is not enough to collect one initial groundwater measurement and show that it is below the prediction limit. At least one additional resample must *always* be collected and measured. 1-of-*m* strategies, by contrast, only require a single groundwater observation to pass. If the initial measurement is below the prediction limit, the constituent passes the overall test and no resamples need be collected.

The second retesting scheme, known as California-style plans, was suggested partly in response to perceived problems with the 1-of-*m* plans. California regulators noted, for instance, that a 1-of-3 retesting scheme would allow a constituent in a given well to pass even if *both* the initial groundwater

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measurement *and* one of the two retests exceeded the predetermined prediction limit. The only way for that well-constituent pair to fail would be if all three measurements — the initial and the two resamples — exceeded the prediction limit. To many regulators (and not just those in California) the 1-of-*m* scheme appeared to practically guarantee that contaminated wells would go unidentified, 'passing' the test each time and undermining protection of human health and the environment.

In 1991, California received explicit approval from EPA to use an alternate retesting scheme constructed as follows. For each well-constituent pair, collect an initial groundwater observation. If this initial measurement is in-bounds (*i.e.*, below the prediction limit), the test for that pair passes and no resamples need be collected. If the initial measurement exceeds the prediction limit, two or possibly three resamples must be collected and *each* must be in-bounds for the test to pass. If any of the resamples exceeds the prediction limit (*i.e.*, is 'out-of-bounds'), the test fails and possible groundwater contamination is indicated.

The California strategy was seen as a more environmentally 'conservative' approach to retesting. An initially high groundwater measurement would only be deemed 'spurious' if all the subsequent resamples were below the target prediction limit, providing at least double reconfirmation that the well was 'clean' for that constituent. Unfortunately, the more stringent requirements of the California plans came with unexpected consequences. A California retesting plan typically requires a *larger* target prediction limit (or 'trigger level') than a 1-of-*m* plan with a comparable number of resamples, in order to achieve the same overall SWFPR. Since a larger trigger level corresponds to a *less* statistically powerful test, a given California plan may or may not have adequate effective power even if a similar 1-of-*m* plan does.

The net result is that 1-of-*m* retesting schemes often provide greater statistical power for detecting real groundwater contamination, particularly in large networks, even though not every resample need be below the prediction limit. If the trigger level is low enough, at least one of the resamples may exceed the prediction limit even when there is no contamination. So these cases should not automatically be classified as verified contamination. Conversely, a lower prediction limit increase the odds (*i.e.*, power) that truly contaminated groundwater will be identified, since both the initial observation and any resamples will be more likely to exceed a lower trigger level than one set to a higher benchmark.

B.5.2 TOLERANCE SCREENS

A final type of retesting scheme might be termed the *tolerance screen* approach. First suggested by Gibbons (1991b), this approach was modified and recommended by EPA in the 1992 Addendum, but — for reasons discussed below — is *not* recommended within the Unified Guidance. In contrast to the 1-of-*m* and California-style plans, which make use of repeated *prediction* limits as the trigger levels, the tolerance screen involves a two-stage testing procedure as follows. An initial groundwater measurement is collected from each well in the network and compared to an upper *tolerance* limit with specified coverage and confidence levels. If any measurement exceeds the tolerance limit, one or more resamples are collected from that well and these measurements are compared against an upper *prediction* limit.

Other than the use of a tolerance limit instead of a prediction limit as the 'screen' for the initial groundwater measurement, the rules for passing the test are the same as a modified California approach described in **Section 19.1**. Either the first observation must be below the tolerance limit (*i.e.*, 'in-bounds') or q-of-$(m-1)$ resamples must be below the prediction limit. If both of these conditions are violated, possible groundwater contamination is indicated.

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The use of two separate trigger levels (*i.e.*, tolerance limit and prediction limit) for the initial observation versus the resamples may seem an unnecessary complication in developing a retesting procedure. However, there are two advantages to this approach. For one, the tolerance and prediction limits are computed on the same background data and both these calculations are done prior to any data comparisons. Secondly, by allowing two different trigger levels, greater flexibility is gained in designing — for a given sized network of comparisons — a retesting scheme that meets a target SWFPR.

Gibbons' (1991b) original tolerance screen approach advocated constructing a 95% confidence tolerance limit with a degree of coverage that would vary depending on the network size. For 100 tests, Gibbons reasoned that a tolerance limit with 95% coverage would result in as many as 5 exceedances of the initial trigger just by chance (*i.e.*, even when no contamination was present). Any such exceedance would then require that a resample be collected at that well and compared to a prediction limit with 95% confidence for the next 5 future samples ($m = 5$), in order to maintain an overall 5% SWFPR. The same type of false positive rate control could be achieved by setting the degree of coverage to 99%, so that only 1 exceedance would be expected in 100 tests against the tolerance limit. In this case, the prediction limit would be computed with 95% confidence but $m = 1$ instead. In all cases, the number of future measurements (m) being predicted would equal the number of measurements possibly expected to exceed the tolerance limit just by chance.

To offer even greater flexibility, EPA recommended a modification to Gibbons' tolerance screen within the 1992 Addendum. To understand why a modified version was adopted, note that the formula for an upper prediction limit on the next m future samples with $(1-\alpha)$ confidence may be expressed as follows:

$$PL_{1-\alpha} = \bar{x} + t_{n-1,1-\alpha/m} s \sqrt{1+\frac{1}{n}}$$

Careful examination of this formula shows that the effect of changing the number of future samples m for a given confidence level is equivalent to changing the *confidence level* associated with a prediction limit for a *single* future observation ($m = 1$).

Because of this, EPA suggested three alterations to Gibbons' original scheme: 1) instead of fixing the level of confidence and varying the number of future samples m, fix $m = 1$ and allow the confidence level of the prediction limit to vary; 2) allow more than one resample per comparison up to a practical maximum of three; and 3) use a tolerance limit with *average* coverage instead of *minimum* coverage. While Gibbons offered power comparisons with his scheme against either a single tolerance limit or a single prediction limit, the Addendum offered recommended choices of degrees of coverage and confidence levels that would simultaneously limit the SWFPR to approximately 5% and generate effective power at least as high as the EPA reference power curve.

Unfortunately, as Davis and McNichols (1994) noted, the Monte Carlo simulations used in the Addendum to generate recommended retesting plans based on the tolerance screen approach were partly flawed. Two criticisms were particularly relevant. First, Davis and McNichols noted that the Appendix to the Addendum spoke of networks in terms of number of *wells* rather than the number of *tests*. Since the total number of tests is a product of the number of wells and the number of constituents being

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monitored in each well, they suggested that the Addendum recommendations for retesting plans might elevate the SWFPR above 5% (the recommended per-evaluation rate in 1992).

The reason is that if a particular plan in the Addendum was only applicable to a single constituent (albeit across a large number of wells), a similar but separate plan would be needed for each constituent. This in turn would imply that the target overall false positive rate of 5% would only apply *per constituent*, meaning that tests for many constituents in the same network would lead to a sharply elevated SWFPR. Of course, the *text* of the Addendum clearly spoke of tests as a combination of wells and constituents. Still, Davis and McNichols were correct to note that some may have misunderstood the contextual meaning of the phrase 'wells' in the Appendix and also in the table on non-parametric retesting strategies, which was naively used as a simple shorthand for the more awkward 'well-constituent pairs.'

A second criticism related to the algorithm used to simulate the effective power of the tolerance screen plans. Davis and McNichols correctly observed that while effective power was defined in terms of a single well contaminated by a single constituent, the power curves illustrated in the Addendum Appendix mistakenly added those cases where the contaminated well failed the overall testing procedure to those where *uncontaminated* wells failed the procedure (*i.e.*, instances of false positives). The net effect was to slightly raise the stated power above the actual power, especially at lower standard deviation shifts in the mean level above background (*e.g.*, $0 < \Delta < 2$). As a result of this criticism, all calculations in the Unified Guidance with respect to retesting plans have been divided into two components: 1) computation of the SWFPR based on the total number of tests, taken as a product of wells times constituents, and 2) computation of the effective power based on a single contaminated well-constituent pair.

A third criticism can now be added to those offered by Davis and McNichols. Given a fixed background sample, one drawback to both 1-of-*m* and California-style plans is that they have limited flexibility when it comes to controlling the SWFPR below a target level (*e.g.*, 10%) over a variety of network sizes. In some cases, sufficient false positive rate control and adequate power can only be achieved by switching, say, from a 1-of-2 plan to a 1-of-3 plan, or from a California plan to a 1-of-*m* scheme, or by increasing the background sample size. The problem is that using the same trigger level — here a prediction limit — to test both the initial measurement and any resamples restricts the number of simultaneous tests that can be accommodated. The EPA tolerance screen approach uses different trigger levels at each stage, allowing greater manipulation of the statistical parameters used to construct the tolerance and prediction limits and ultimately more flexibility in designing a retesting scheme that can meet a target SWFPR for a fixed background size over a wide variety of networks.

Despite this advantage, new research done in preparing the Unified Guidance indicates that the effective power of any tolerance screen retesting procedure is always *less* than a comparable scheme based on a single repeated trigger value. The gain in flexibility in controlling false positive rates is real, but the most powerful retesting procedures will be of the 1-of-*m* or modified California-style varieties. Because of this loss in effective power, the Unified Guidance recommends an appropriate 1-of-*m* or modified California-style plan (**Chapter 19**).

B.5.3 NON-PARAMETRIC RETESTING SCHEMES

In the Addendum, two basic approaches to non-parametric retesting were described, each suggested by Gibbons (1990; 1991a). Both of these strategies defined the upper prediction limit as the

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maximum observed background value. Once in hand, one new observation was collected from each downgradient well and compared against the non-parametric prediction limit. Measurements that exceeded the prediction limit were then retested. In his 1990 article, Gibbons presented tables of approximate network-wide significance levels for the case of 1-of-*m* retesting plans. Gibbons' 1991 article detailed the more stringent non-parametric California plans, giving exact false positive rates, but only in the case where the prediction limit was defined as the maximum of background.

Both of these efforts were superseded by Davis and McNichols (1994), who give exact false positive rates are given for both 1-of-*m* and strict California retesting strategies. In addition, Davis and McNichols compute these false positive rates when the non-parametric prediction limit is taken as either the maximum background value or the second-largest background concentration. The latter calculation is helpful in two ways. First, if a particular background concentration is unusually high and possibly an outlier, one could choose to fix the non-parametric prediction limit as the second-highest (and presumably more representative) background concentration. The statistical characteristics of the retesting scheme would still be assured without having to 'throw out' the suspected background outlier. Secondly, the statistical power of prediction limits based on the second-largest background value is greater than for those prediction limits based on the maximum. For large background samples (*n*), use of this alternate prediction limit may be the only option at some sites to achieve both the targeted false positive rate and sufficient effective power.

While the tables in the Davis and McNichols article are extremely useful, they do not include results for the modified California retesting scheme with $m = 4$, in which either the initial measurement or two of three resamples must be in-bounds. To complete the tables needed for the Unified Guidance, a variation of the Davis and McNichols algorithm was initially used to calculate the significance levels of the modified California retesting scheme with $m = 4$. Since that time, Davis and McNichols (1999) published an exact algorithm not only for the 1-of-*m* and strict California plans, but also for the modified California plan first suggested in an earlier draft of the Unified Guidance. Following their algorithm with some minor computational adjustments, the Unified Guidance tables have been recomputed, covering first the non-parametric 1-of-*m* plans and then the non-parametric modified California plan (**Chapter 19**). In each case, results are provided for non-parametric prediction limits taken either as the maximum value in background or as the second-largest concentration.

To measure the statistical power of these non-parametric retesting strategies, Davis and McNichols estimated power using Monte Carlo simulation with normally-distributed random variates. They then offered a new measure of power labeled the *Modified Addendum Criterion* or MAC, which rated schemes against an EPA reference power curve with $n = 8$ background samples. Recognizing that a particular power curve might only exceed the EPA reference power curve at large mean concentration shifts (Δ) above background, the MAC evaluated at what percentage power a proposed scheme did in fact begin to exceed the EPA reference power curve (*e.g.*, starting at 30% power, or 50% power, *etc.*).

In the Unified Guidance, effective power of non-parametric retesting schemes is measured in a similar, though not identical, manner. One difference is that the recommended EPA reference power curves are based on 10 rather than 8 background samples. With $n = 8$, there is less than a 50% probability of identifying a mean concentration increase above background of 3 standard deviations and less than an 80% chance of identifying an increase of 4 standard deviations. Another mostly semantic difference is that the schemes in the Unified Guidance are evaluated on whether or not they exceed the EPA reference power curve for concentrations exceeding background by a given number of standard

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deviation units (*e.g.*, 3 or 4 standard deviations), instead of at a particular power percentage (*e.g.*, 30%, 70%, *etc.*).

To actually compute effective power, Monte Carlo simulations were not utilized in the Unified Guidance. Rather, since the underlying data were assumed to be normal, a simple modification to the numerical integration algorithms presented in Davis and McNichols (1987) was used to compute the power directly. Of course, if the data are normal in the first place, a parametric retesting scheme would be more appropriate. Non-parametric strategies should only be considered when the data appear to be distinctly non-normal or exhibit too many non-detects to judge normality. Nevertheless, since the true underlying distribution is unknown, the usual method of attack is to measure the statistical power that results when the underlying distribution is taken to be normal.

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APPENDIX C. TECHNICAL APPENDIX

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C.1 SPECIAL STUDY: NORMAL VS. LOGNORMAL PREDICTION LIMITS

Section 10.3 outlines the strategy for distributional testing in the Unified Guidance. Among these recommendations is that the normal distribution should be treated as a default model until specific testing indicates otherwise. To establish this recommendation, a special study was conducted for the Unified Guidance to answer two key questions: 1) what are the consequences of incorrectly applying statistical techniques based on one distributional assumption (normal or lognormal), when the underlying distribution is, in fact, the other? and 2) what is the impact on statistical power and accuracy of assuming the wrong underlying distribution? These questions were tested for prediction limit tests in detection monitoring (and, by extension, for control charts).

The general effects of violating test assumptions can be measured in terms of false positive and negative error rates (and therefore power). A series of Monte Carlo simulations was generated for the Unified Guidance to evaluate the impacts on prediction limit false positive error rates and statistical power of using normal and lognormal distributions when applied either correctly or incorrectly to the underlying 'true' distributions. For varying inputs of background sample size, population coefficients of variation and confidence levels, sample data sets were generated and prediction limits computed for a single future observation using either a normal prediction limit [*NorPL*] or a lognormal prediction limit [*LgnPL*], as given in the equations below. $\bar{x}$ and s_x are the mean and standard deviation respectively of the original measurements, while $\bar{y}$ and s_y represent the log-mean and log-standard deviation:

$$NorPL_{1-\alpha} = \bar{x} + t_{n-1,1-\alpha} s_x \sqrt{1+\frac{1}{n}}$$

$$LgnPL_{1-\alpha} = \exp\left[\bar{y} + t_{n-1,1-\alpha} s_y \sqrt{1+\frac{1}{n}}\right]$$

To evaluate prediction limit performance, for each choice of inputs and statistical parameters, one million (N = 1,000,000) simulated normal background data sets and one million lognormal background data sets were generated and tested against each limit. When the underlying distribution was normal, a fixed unit standard deviation was coupled with a series of increasing mean levels to vary the population coefficient of variation. Then, to measure power in each case, new measurements were generated from similar normal models with mean levels incremented by k standard deviation units above the background mean, for k ranging from 0 to 5. A parallel evaluation was also conducted when a retest was added to the procedure. In this case, the prediction limits were constructed using the κ multiples for a 1-of-2 retesting scheme as described in **Chapter 19**. A summary of these results is given in **Figure C-1**.

C.1.1 RESULTS FOR NORMAL DATA

If the underlying population is truly normal, *treating the sample data as lognormal* in constructing a prediction limit can have significant consequences. **Figure C-1** presents key results, either averaged over all the statistical input parameters or broken down by sample size, confidence level, and coefficient of variation. These statistics include the average ratio between the normal prediction limit [*NorPL*] and the lognormal prediction limit [*LgnPL*], the average difference between the *nominal* (*i.e.*, expected) false positive rate (α) of the test and the *observed* false positive rate, and the average percentage of cases

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where two statistical power targets were met, those being 50% power at 3 standard deviations above the background mean and 80% power at 4 standard deviations above the background mean.

With no retesting and truly normal data, the lognormal prediction limits were in every case considerably longer and thus less powerful than the normal prediction limits. The discrepancies in performance were smallest for larger sample sizes, lower confidence levels, and smaller coefficients of variation. However, in only one of the category breakdowns ($1–\alpha = 0.995$) did the normal prediction limits fail to meet *both* power targets at least half the time, while the lognormal limits jointly met both power targets less than half the time in all cases except one ($1–\alpha = 0.90$). As to false positives, the lognormal limits consistently exhibited *less* than the expected (nominal) false positive rate. The normal prediction limits tended to have slightly higher than nominal error rates.

When retesting was added to the procedure, the performance of both limits improved. The false positive rates of both were closer to the nominal rates, though the normal prediction limits were relatively closer to the expected rates. While power improved across the board compared to *not* using a retest, the normal limits were on average about 13% shorter than the lognormal limits, leading again to a measurable loss of statistical power for the lognormal prediction limits. Particularly noticeable was the significant difference in power at higher confidence levels, the very kinds of confidence levels needed when designing retesting strategies for multiple tests against a prediction limit.

On balance, *misapplication* of logarithmic prediction limits to normal data consistently resulted in lower power (often considerably) and false positive rates that were lower than expected, unless the population coefficient of variation was quite small, the background sample size was larger, and the confidence level more moderate. Since a lognormal prediction limit will be applied only if the underlying population is thought or assumed to be lognormal, it is helpful to gauge how these factors work in practice. On one hand, the higher confidence levels and consequently lower α values needed for retesting strategies with simultaneous tests (**Chapter 19**) would argue *against* presuming the underlying data to be lognormal without specific goodness-of-fit testing. In other words, if the data are actually normal but the lognormal prediction limit is misapplied, a high price in statistical power may be paid.

In terms of sample size, the greatest penalties from misapplying lognormal prediction limits occur for smaller background sizes. Since goodness-of-fit tests are least able to distinguish between normal and lognormal data with small samples, small background samples be not be presumed to be lognormal *as a default* unless other site-specific evidence suggests otherwise. For larger sample sizes, goodness-of-fit tests have much better discriminatory power, enabling a better indication of which model to use.

With regard to coefficient of variation [CV], the guidelines are less clear cut. Given that groundwater data are generally positive in value, truly normal populations are likely to have population coefficients of variation of 0.3 or lower. Larger coefficients of variation would result in a significant fraction of negative measurements. In addition, the probability of observing a large sample coefficient of variation from a normal population with population coefficient of variation of 0.3 or less is rather small.

However, the measurement and *censoring* of small concentration values complicates the picture. Such values are measured below a reporting limit [RL] and are generally listed as 'less thans.' A measurement process that is normal with high coefficient of variation and mean close to the RL can generate a mixture of left-censored and detected values with fairly high coefficient of variation yet not be lognormal. In fact, the cases in **Figure C-1** with higher coefficients of variation were analyzed in essentially this fashion, with negative values imputed to a small, positive reporting limit prior to

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calculation of the prediction limits. The results indicate a substantial loss of performance when lognormal limits are misapplied to these left-censored normal data sets, *with or without retesting*. Therefore, the observed CV should not be used as the sole criterion of whether to presume an underlying normal or lognormal data model. Rather, if large fractions of censored data are present, censored probability plots (**Chapter 15**) should be constructed to aid in choosing an appropriate distribution.

C.1.2 RESULTS FOR LOGNORMAL DATA

Do normal-based prediction limits suffer in a similar comparison when the underlying population it really lognormal? The results from applying normal and lognormal prediction limits to underlying lognormal data are presented in **Figure C-2**. There, the summaries are similar to **Figure C-1** with one important exception. As explained in **Chapter 10** and **Appendix Section C.2**, the lognormal distribution is not an additive model. Because of this fact, the distributional alternatives used in assessing the statistical power of a lognormal-based prediction limit usually involve setting the alternative mean to a *multiple* of the background mean while keeping a *constant* lognormal coefficient of variation.

The net effect is that the power of lognormal-based tests depends greatly on the actual level of the coefficient of variation. This is different from normal-based power analyses, where the coefficient of variation only plays a role in terms of the degree of censoring in the data (thus affecting power through the handling of left-censored values, *i.e.*, non-detects). Because the achievable power varies over such a large range — depending on the level of skewness of the specific lognormal distribution — reference statistical power for lognormal models must be tied to the observed background coefficient of variation. However, since a performance comparison *across* coefficient of variation levels was needed for the results of **Figure C-2**, a *single benchmark* was used to assess the comparative power of the normal and lognormal prediction limits. While imperfect for practical use, this benchmark was set at 25% power for alternatives of three times the background mean and 50% power at five times the background mean.

For an underlying lognormal model with no retesting, **Figure C-2** indicates that while the false positive rates of lognormal-based prediction limits are essentially as advertised (*i.e.*, a 95% confidence prediction limit has close to the nominal 5% false positive rate), the false positive rates of normal-based limits are higher than expected, often substantially, especially for higher confidence levels and higher coefficients of variation. The most significant drawback to *misapplying* normal prediction limits to lognormal data would then be an excessive site-wide false positive rate from using such limits on multiple well-constituent pairs.

However, the situation changes dramatically with the addition of even a single retest. In this case, the lognormal prediction limits are still more accurate than the normal limits, in terms of having false positive rates closer to the nominal targets. Nevertheless, with the added retest, the achieved false positive rates for the normal limits tend to be *less* than the expected rates, especially for moderate to larger sample sizes. In addition, except for very skewed lognormal distributions, the power of the normal limits is comparable or greater than the power of the lognormal limits.

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Figure C-1. Accuracy and Power of Normal vs. Lognormal Prediction Limits When Underlying Data Are Normal

No Retesting, 1-of-1 Scheme

Category		Assumed Model	Length Ratio	α-Error	Power-50%	Power-80%	Power-Both
ALL		normal	0.6599	0.00611	0.759	0.741	0.741
		lognormal		-0.01965	0.348	0.277	0.277
N	4	normal	0.5729	0.00643	0.500	0.500	0.500
		lognormal		-0.01590	0.286	0.107	0.107
	8	normal	0.6713	0.00607	0.679	0.607	0.607
		lognormal		-0.01962	0.357	0.321	0.321
	12	normal	0.6935	0.00599	0.857	0.857	0.857
		lognormal		-0.02107	0.357	0.321	0.321
	16	normal	0.7020	0.00596	1.000	1.000	1.000
		lognormal		-0.02201	0.393	0.357	0.357
(1−α)	0.900	normal	0.8437	0.00898	1.000	1.000	1.000
		lognormal		-0.03843	1.000	0.857	0.857
	0.950	normal	0.7436	0.00857	1.000	1.000	1.000
		lognormal		-0.02884	0.393	0.250	0.250
	0.990	normal	0.5583	0.00416	0.643	0.607	0.607
		lognormal		-0.00749	0.000	0.000	0.000
	0.995	normal	0.4940	0.00274	0.393	0.357	0.357
		lognormal		-0.00385	0.000	0.000	0.000
CV	0.125	normal	0.9504	-0.00005	0.688	0.688	0.688
		lognormal		-0.00740	0.500	0.438	0.438
	0.250	normal	0.8401	-0.00009	0.688	0.688	0.688
		lognormal		-0.01486	0.438	0.438	0.438
	0.333	normal	0.7439	0.00015	0.688	0.688	0.688
		lognormal		-0.01959	0.438	0.313	0.313
	0.500	normal	0.5794	0.00266	0.750	0.688	0.688
		lognormal		-0.02614	0.250	0.188	0.188
	0.667	normal	0.5112	0.00830	0.813	0.813	0.813
		lognormal		-0.02611	0.250	0.188	0.188
	0.752	normal	0.4989	0.01160	0.813	0.813	0.813
		lognormal		-0.02458	0.250	0.188	0.188
	1.000	normal	0.4954	0.02021	0.875	0.813	0.813
		lognormal		-0.01887	0.313	0.188	0.188

Legend. **Category**: N = Sample size; (1-α) = Nominal confidence level; CV = Coefficient of variation of underlying normal distribution. For each case, results for all simulations with that characteristic were averaged to derive that line of the figure.
Assumed Model: Whether normal or lognormal formulas were used to compute the prediction limits.
Length Ratio: Ratio of the normal prediction limit to the lognormal prediction limit.
α-error: Achieved false positive rate minus nominal false positive rate.
Power-50%: Fraction of simulations in which 50% power target at 3 standard deviations above background was met by the prediction limit.
Power-80%: Fraction of simulations in which 80% power target at 4 standard deviations above background was met by the prediction limit.
Power-Both: Fraction of simulations in which both the 50% and 80% power targets were met.

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Retesting, 1-of-2 Scheme

Category		Assumed Model	Length Ratio	α-Error	Power-50%	Power-80%	Power-Both
ALL		normal	0.8712	0.00134	0.911	0.884	0.884
		lognormal		0.00052	0.670	0.625	0.625
n	4	normal	0.7870	0.00254	0.643	0.536	0.536
		lognormal		-0.00302	0.500	0.500	0.500
	8	normal	0.8815	0.00130	1.000	1.000	1.000
		lognormal		0.00070	0.643	0.607	0.607
	12	normal	0.9034	0.00066	1.000	1.000	1.000
		lognormal		0.00157	0.714	0.679	0.679
	16	normal	0.9129	0.00087	1.000	1.000	1.000
		lognormal		0.00283	0.821	0.714	0.714
(1–α)	0.900	normal	1.0370	-0.00134	1.000	1.000	1.000
		lognormal		0.01496	1.000	1.000	1.000
	0.950	normal	0.9543	0.00235	1.000	1.000	1.000
		lognormal		-0.00485	1.000	1.000	1.000
	0.990	normal	0.7807	0.00252	0.893	0.786	0.786
		lognormal		-0.00510	0.500	0.321	0.321
	0.995	normal	0.7129	0.00185	0.750	0.750	0.750
		lognormal		-0.00295	0.179	0.179	0.179
CV	0.125	normal	0.9867	0.00009	0.875	0.875	0.875
		lognormal		0.00023	0.875	0.875	0.875
	0.250	normal	0.9486	0.00003	0.875	0.875	0.875
		lognormal		-0.00048	0.813	0.813	0.813
	0.333	normal	0.9065	0.00016	0.875	0.875	0.875
		lognormal		-0.00164	0.688	0.625	0.625
	0.500	normal	0.8289	0.00095	0.938	0.875	0.875
		lognormal		-0.00190	0.563	0.500	0.500
	0.667	normal	0.8051	0.00242	0.938	0.875	0.875
		lognormal		0.00132	0.563	0.500	0.500
	0.752	normal	0.8048	0.00270	0.938	0.875	0.875
		lognormal		0.00241	0.563	0.500	0.500
	1.000	normal	0.8178	0.00306	0.938	0.938	0.938
		lognormal		0.00371	0.625	0.563	0.563

Legend. **Category**: N = Sample size; (1-α) = Nominal confidence level; CV = Coefficient of variation of underlying normal distribution. For each case, results for all simulations with that characteristic were averaged to derive that line of the figure.
Assumed Model: Whether normal or lognormal formulas were used to compute the prediction limits.
Length Ratio: Ratio of the normal prediction limit to the lognormal prediction limit.
α-error: Achieved false positive rate minus nominal false positive rate.
Power-50%: Fraction of simulations in which 50% power target at 3 standard deviations above background was met by the prediction limit.
Power-80%: Fraction of simulations in which 80% power target at 4 standard deviations above background was met by the prediction limit.
Power-Both: Fraction of simulations in which both the 50% and 80% power targets were met.

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Figure C-2. Accuracy and Power of Normal vs. Lognormal Prediction Limits When Underlying Data Are Lognormal

No Retesting, 1-of-1 Scheme

Category		Assumed Model	Length Ratio	α-Error	Power-25%	Power-50%	Power-Both
ALL		normal	0.6082	0.03557	0.806	0.581	0.581
		lognormal		-0.00001	0.500	0.412	0.412
n	4	normal	0.4444	0.04682	0.775	0.550	0.550
		lognormal		0.00000	0.400	0.325	0.325
	8	normal	0.6006	0.03782	0.825	0.600	0.600
		lognormal		-0.00002	0.500	0.425	0.425
	12	normal	0.6723	0.03102	0.825	0.600	0.600
		lognormal		0.00001	0.550	0.450	0.450
	16	normal	0.7153	0.02660	0.800	0.575	0.575
		lognormal		-0.00003	0.550	0.450	0.450
(1–α)	0.900	normal	0.8985	0.02509	1.000	0.750	0.750
		lognormal		-0.00001	0.950	0.650	0.650
	0.950	normal	0.7108	0.04175	0.975	0.675	0.675
		lognormal		-0.00002	0.525	0.475	0.475
	0.990	normal	0.4472	0.04037	0.700	0.475	0.475
		lognormal		0.00000	0.275	0.275	0.275
	0.995	normal	0.3762	0.03505	0.550	0.425	0.425
		lognormal		0.00000	0.250	0.250	0.250
CV	0.125	normal	0.9549	0.00733	1.000	1.000	1.000
		lognormal		-0.00003	1.000	1.000	1.000
	0.250	normal	0.8749	0.01419	1.000	1.000	1.000
		lognormal		-0.00004	1.000	1.000	1.000
	0.500	normal	0.7282	0.02535	1.000	1.000	1.000
		lognormal		-0.00004	0.813	0.813	0.813
	0.750	normal	0.6278	0.03315	1.000	0.938	0.938
		lognormal		0.00006	0.500	0.500	0.500
	1.000	normal	0.5629	0.03829	0.938	0.813	0.813
		lognormal		-0.00008	0.438	0.438	0.438
	1.250	normal	0.5204	0.04216	0.938	0.500	0.500
		lognormal		0.00009	0.375	0.188	0.188
	1.500	normal	0.4915	0.04479	0.750	0.438	0.438
		lognormal		-0.00002	0.250	0.188	0.188
	2.000	normal	0.4566	0.04815	0.500	0.125	0.125
		lognormal		0.00003	0.250	0.000	0.000
	2.500	normal	0.4378	0.05037	0.500	0.000	0.000
		lognormal		-0.00004	0.188	0.000	0.000
	3.000	normal	0.4266	0.05189	0.438	0.000	0.000
		lognormal		-0.00002	0.188	0.000	0.000

Legend. **Category**: N = Sample size; (1-α) = Nominal confidence level; CV = Coefficient of variation of underlying lognormal distribution. For each case, results for all simulations with that characteristic were averaged to derive that line of the figure.
Assumed Model: Whether normal or lognormal formulas were used to compute the prediction limits.
Length Ratio: Ratio of the normal prediction limit to the lognormal prediction limit.
α-error: Achieved false positive rate minus nominal false positive rate.
Power-25%: Fraction of simulations in which 25% power target at 3 times the background mean was met by the prediction limit.
Power-50%: Fraction of simulations in which 50% power target at 5 times the background mean was met by the prediction limit.
Power-Both: Fraction of simulations where both 25% and 50% power targets were met.

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Retesting, 1-of-2 Scheme

Category		Assumed Model	Length Ratio	α-Error	Power-25%	Power-50%	Power-Both
ALL		normal	0.9920	-0.00405	0.587	0.544	0.537
		lognormal		0.00009	0.600	0.544	0.531
n	4	normal	0.7334	0.00804	0.625	0.525	0.500
		lognormal		0.00022	0.550	0.425	0.425
	8	normal	0.9830	-0.00354	0.600	0.550	0.550
		lognormal		0.00016	0.600	0.550	0.550
	12	normal	1.0931	-0.00897	0.575	0.550	0.550
		lognormal		-0.00020	0.625	0.600	0.575
	16	normal	1.1586	-0.01175	0.550	0.550	0.550
		lognormal		0.00018	0.625	0.600	0.575
(1–α)	0.900	normal	1.3532	-0.02895	0.800	0.700	0.700
		lognormal		0.00027	1.000	0.850	0.850
	0.950	normal	1.1500	-0.00478	0.700	0.600	0.600
		lognormal		0.00009	0.750	0.625	0.625
	0.990	normal	0.7890	0.00892	0.475	0.475	0.475
		lognormal		0.00000	0.375	0.375	0.375
	0.995	normal	0.6759	0.00860	0.375	0.400	0.375
		lognormal		0.00000	0.275	0.325	0.275
CV	0.125	normal	0.9889	-0.00035	1.000	1.000	1.000
		lognormal		0.00011	1.000	1.000	1.000
	0.250	normal	0.9684	-0.00099	1.000	1.000	1.000
		lognormal		0.00008	1.000	1.000	1.000
	0.500	normal	0.9332	-0.00214	1.000	1.000	1.000
		lognormal		0.00008	0.938	0.938	0.938
	0.750	normal	0.9199	-0.00317	0.938	1.000	0.938
		lognormal		0.00018	0.688	0.813	0.688
	1.000	normal	0.9253	-0.00416	0.688	0.688	0.688
		lognormal		0.00008	0.500	0.500	0.500
	1.250	normal	0.9428	-0.00481	0.500	0.500	0.500
		lognormal		0.00014	0.500	0.438	0.438
	1.500	normal	0.9673	-0.00527	0.438	0.250	0.250
		lognormal		0.00011	0.500	0.375	0.375
	2.000	normal	1.0266	-0.00606	0.188	0.000	0.000
		lognormal		0.00004	0.375	0.188	0.188
	2.500	normal	1.0913	-0.00662	0.063	0.000	0.000
		lognormal		0.00003	0.250	0.188	0.188
	3.000	normal	1.1566	-0.00696	0.063	0.000	0.000
		lognormal		0.00004	0.250	0.000	0.000

Legend. **Category**: N = Sample size; (1-α) = Nominal confidence level; CV = Coefficient of variation of underlying lognormal distribution. For each case, results for all simulations with that characteristic were averaged to derive that line of the figure.
Assumed Model: Whether normal or lognormal formulas were used to compute the prediction limits.
Length Ratio: Ratio of the normal prediction limit to the lognormal prediction limit.
α-error: Achieved false positive rate minus nominal false positive rate.
Power-25%: Fraction of simulations in which 25% power target at 3 times the background mean was met by the prediction limit.
Power-50%: Fraction of simulations in which 50% power target at 5 times the background mean was met by the prediction limit.
Power-Both: Fraction of simulations in which both the 25% and 50% power targets were met.

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On balance, adding a retest to the testing procedure significantly minimizes the penalty of misapplying normal prediction limits to lognormal data, as long one uses a sample size of at least 8 and the coefficient of variation is not too large. Consequently, for most situations, there is *less* penalty associated with making a default assumption of *normality* than in making a default assumption of *lognormality*. With highly skewed data, say with large coefficients of variation of 1.5 or more, goodness-of-fit tests tend to better discriminate between the normal and lognormal models. Again such diagnostic testing should be done *explicitly*, rather than simply assuming the data are normal or lognormal.

The most problematic cases occur for very small background sample sizes, where a misapplication of prediction limits in either direction can result in poorer statistical performance, even with retesting. In some situations, testing may have to done on an interim or ad-hoc basis until more data is collected. Still, the Unified Guidance does not recommend an automatic *default* assumption of lognormality.

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C.2 CALCULATING STATISTICAL POWER

C.2.1 STATISTICAL POWER OF WELCH'S T-TEST

The statistical power of any test represents the probability that the alternative hypothesis, H_A, will be accepted, given that the null hypothesis, H_0, is actually false. In groundwater monitoring, power usually represents the probability that the compliance point concentrations will be identified as significantly higher than background, when in fact they *are* higher. Of course, statistical power is not a single number, but rather a *function* of the increase in the compliance population mean above the background average. This fact makes the exact power of many tests difficult to calculate, especially since many test statistics have a complicated distributional behavior under the alternative hypothesis.

The critical points or percentage points of any test are computed under the assumption that the null hypothesis is true. In the case of Welch's *t*-test, the *t*-statistic approximately follows a Student's *t*-distribution under H_0. That is not the case, however, when the alternative hypothesis is true; then the *t*-statistic follows what is known as a *non-central t*-distribution with non-centrality parameter δ. Essentially, the non-centrality parameter δ governs the average or expected value of the *t*-statistic.

When the null hypothesis is true, so that the two population means are equal, the *t*-statistic should tend to be close to zero. The distribution of the *t*-statistic is in fact centered at zero in this case, meaning that the usual Student's *t*-distribution can be regarded as a non-central *t*-distribution with non-centrality parameter equal to zero.

When H_A is true instead, and the compliance point population mean is larger than the background mean, Welch's *t*-statistic will tend to be positive rather than centered at zero. The actual center of the distribution will depend on precisely how much larger the compliance point mean is compared to background. However, if σ_x represents the standard deviation of the first population and σ_y represents the standard deviation of the second population, it can be shown that the two-sample Welch's *t*-statistic approximately follows a non-central *t*-distribution with degrees of freedom equal to

$$df = \left[\frac{\sigma_x^2}{n_x} + \frac{\sigma_y^2}{n_y}\right]^2 \Bigg/ \left[\frac{\sigma_x^4}{n_x^2\left(n_x - 1\right)} + \frac{\sigma_y^4}{n_y^2\left(n_y - 1\right)}\right] \qquad [C.1]$$

and non-centrality parameter equal to

$$\delta = \Delta \Bigg/ \sqrt{\frac{\sigma_x^2}{n_x} + \frac{\sigma_y^2}{n_y}} \qquad [C.2]$$

where Δ is the concentration difference separating the background and compliance point population means.

Clearly, the distribution of the *t*-statistic under H_A depends in a complex manner not only on the sample sizes and the true difference between the population means, but also the respective population variances. Since statistical power is the probability that the Welch's *t*-statistic exceeds the original critical point, t_{cp}, yet the population variances are almost always unknown, computation of an exact

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power is essentially impossible. Instead, an *approximate power* can be computed by substituting the sample variances for their population counterparts into equations [C.1] and [C.2]. By letting $f = \sigma_y^2 / \sigma_x^2$, the non-centrality parameter becomes

$$\delta = \frac{\Delta}{\sigma_x}\sqrt{\frac{n_x n_y}{n_y + f n_x}} = k\sqrt{\frac{n_x n_y}{n_y + f n_x}} \qquad [C.3]$$

where *k* represents the increase in standard deviation units above the background mean. The non-centrality parameter can be approximated by substituting $\hat{f} = s_y^2 / s_x^2$ for *f* in [C.3].

Using this formulation, the approximate statistical power of Welch's *t*-test can be computed by repeatedly increasing *k* (*e.g.*, in half units starting with 0.5) and determining the probability of exceeding the original critical point, t_{cp}, under the non-central *t*-distribution. A concise summary of the non-central t-distribution can be found in Evans, Hastings, and Peacock (1993). Percentage points of this distribution can be computed in selected standard statistical packages, including the free, open-source statistical software **R** (www.r-project.org).

►EXAMPLE C-1

Determine the approximate power of the *t*-test on benzene data used in **Example 16-1**.

SOLUTION

Step 1. Since Welch's *t*-test was run on the logged benzene measurements, power should also be computed using the logged values. In that case, the degrees of freedom was approximated at *df* = 11 and the critical point at α = .05 was found to be t_{cp} = 1.796 from the Student's *t*-distribution in **Table 16-1**.

Step 2. Determine the non-centrality parameter δ from equation [C.3], substituting $\hat{f} = s_y^2 / s_x^2$ for *f*. Since $n_x = n_y = 8$, the sample downgradient log-standard deviation is s_y = 1.9849, and the sample background log-standard deviation is s_x = 1.0826. Plugging these values into $\hat{f}$ gives $\hat{f} = (1.9849)^2 / (1.0826)^2 = 3.362$. The approximate non-centrality parameter becomes

$$\delta = k\sqrt{\frac{8 \times 8}{8 + 3.362 \times 8}} = k(1.354)$$

where *k* represents the increase above the benzene background log-scale mean in log-standard deviation units.

Step 3. Systematically increase *k* from 0.5 to 5 in steps of 0.5 to determine the non-centrality parameter δ at each point to be computed on the power curve (presented in the table below). Then determine each power value by calculating from the non-central *t*-distribution, with non-centrality parameter δ and *df* = 11, the probability of exceeding the original critical point of t_{cp} = 1.796.

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k	δ	power
0.5	0.677	0.1565
1.0	1.354	0.3541
1.5	2.031	0.6022
2.0	2.708	0.8135
2.5	3.385	0.9360
3.0	4.062	0.9843
3.5	4.739	0.9973
4.0	5.416	0.9997
4.5	6.093	1.0000
5.0	6.770	1.0000

Step 4. Interpret the power results. The table in **Step 3** shows an approximate probability of 81% for detecting a two log-standard deviation increase above the background mean benzene level. If the data had been analyzed in the original units, a two standard deviation increase would translate into almost 11 ppb (using the sample background standard deviation of 5.31 ppb from **Example 16-1** as an estimate of the true standard deviation).

However, in the logarithmic domain, the interpretation is a bit different. As discussed in **Section C.2.3**, adding $k\sigma$ to the log-scale mean is equivalent to *multiplying* the arithmetic mean by $\exp(k\sigma)$. Therefore, a two log-standard deviation increase in the log-scale background mean is roughly equivalent to multiplying the *original* background mean by a factor of $\exp(2 \times 1.0826) = 8.7$, taking the sample log-scale background standard deviation of 1.0826 as an estimate for the true log-scale standard deviation.

Consequently, if the true background mean for benzene is close to the sample value of 3 ppb, the test will have more than 80% power for detecting a downgradient benzene mean of at least $3 \times 8.7 \approx 26$ ppb or larger. ◄

C.2.2 POWER OF PREDICTION LIMITS FOR FUTURE MEAN VS. OBSERVATIONS

The Unified Guidance discusses two basic kinds of parametric prediction limits: those for individual future observations and those for future means. Analytical expressions for the statistical power of each can be written and compared using the same sample size (n), the same false positive rate (α), and the same number of future measurements ($p = m$).

The power of a prediction limit for a future mean of order p (that is, a mean of p individual future values) with normally-distributed data can be expressed in the equation

$$1-\beta = \Pr\left\{T_{n-1}\left(\delta = \Delta\Big/\sqrt{\frac{1}{p}+\frac{1}{n}}\right) > t_{1-\alpha,n-1}\right\} \qquad [C.4]$$

where $(1-\beta)$ is a notation for power, Δ is the true difference (in standard deviation units) between the background and compliance point population means, and

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$$T_{n-1}\left(\delta = \Delta \Big/ \sqrt{\frac{1}{p}+\frac{1}{n}}\right) \qquad [C.5]$$

denotes a random variable distributed according to the non-central *t*-distribution with non-centrality parameter δ and (n–1) degrees of freedom.

By contrast, the power of a prediction limit for p individual future values can be derived using the formulation in Davis and McNichols (1987), leading to the expression

$$1-\beta = 1-\int_0^1 \Pr\left\{T_{n-1}\left(\delta = \sqrt{n}\left[\Phi^{-1}(u)+\Delta\right]\right) \le t_{1-\alpha/p,n-1}\sqrt{n+1}\right\} p u^{p-1} du \qquad [C.6]$$

where in this case $\Phi^{-1}(u)$ denotes the inverse standard normal transformation. The non-central *t*-distribution is required in each case, with further integration of the non-central *t* cumulative distribution function [CDF] needed for the case of p individual future measurements. These formulas are utilized in **Chapter 18** to provide graphical power comparisons between prediction limits for future means versus prediction limits for individual values.

C.2.3 COMPUTING POWER WITH LOGNORMAL DATA

The special Monte Carlo study presented in **Section C.1** involved a computation of statistical power when the underlying data are lognormal in distribution rather than normal. In the case of normal data, effective power is computed by adding an upward 'shift' in the mean of the baseline distribution, in order to simulate an increasing compliance point concentration. Adding such a shift does not increase the variance (σ^2) of the shifted distribution, only the mean (μ).

With lognormal data, both the mean and variance depend on the two distributional parameters, μ and σ. Adding a shift to the log-mean μ on the log-scale thus increases *both* the variance and the mean in the concentration domain, confusing the usual interpretation of power as the ability to detect upward changes in the mean level when all other factors (including the variance) are held constant.

In fact, if computations are conducted on the log-scale and a shift (Δ) is added to the log-mean parameter (μ), the effect is to *multiply* the lognormal mean in the arithmetic domain by a factor of $\exp(\Delta)$. To see this, note that the lognormal mean is written as

$$M = \exp\left(\mu + .5\sigma^2\right) \qquad [C.7]$$

An additive shift to the log-mean results in a change to the (arithmetic) lognormal mean of

$$M_A = \exp\left(\mu + \Delta + .5\sigma^2\right) = \exp(\Delta)\exp\left(\mu + .5\sigma^2\right) = \exp(\Delta)M \qquad [C.8]$$

To compute statistical power, one must assess test performance both under background conditions and under increasing levels of contamination. But the power that can be expected with lognormal data varies depending on the lognormal coefficient of variation [*CV*]. For a fixed coefficient of variation, as lognormal concentrations increase, the lognormal standard deviation increases proportionally to the

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lognormal mean. Because of this — and in contrast to the case of normal data — a different lognormal power curve could be associated with each unique value of the *CV*.

To sidestep this problem, the Unified Guidance assumes that if background is lognormal, the *same* coefficient of variation [*CV*] will apply to both the background and compliance point populations. This assumption has two important consequences: 1) compliance point data with mean levels higher than background will tend to also be more variable than the background measurements, a common empirical truth in environmental data sets; and 2) on the log-scale, the log-variance parameter (σ^2) will be the *same* in both populations. The reason that this second consequence holds is that the log-standard deviation parameter is solely a function of the coefficient of variation, as expressed in the following equation:

$$\sigma = \sqrt{\log\left(1 + CV^2\right)} \qquad [C.9]$$

Thus if the *CV* is held constant, to will the log-standard deviation parameter (σ).

The upshot of the second consequence is that all power computations for lognormal data can be done in the log-domain, using the fact that the transformed data will be normally distributed and that the background and compliance point populations will have a common standard deviation. Consequently, the computational framework for simulating statistical power of lognormal data is almost precisely the same as the framework for the normal case.

In particular, the power curve for a given test can always be generated — without loss of generality — by assuming that the background data follow (perhaps in the log-domain) a standard normal distribution, and that the compliance point data follow (again in the log-domain for lognormal populations) a normal distribution with unit variance and shifted mean equal to $k\sigma = k$, since σ is assumed for computational purposes equal to 1. Then the multiplier k is typically allowed to range from 0 to 5, as this adequately sketches out the normal power curve in most situations.

The only aspect of the lognormal case that differs from the normal is the scaling of the horizontal axis of the power curve. In the log-domain, the curve documents power at increasing multiples of k log-standard deviations (σ) above the background log-mean (μ). To interpret these values in terms of the original concentrations, the background mean has to be reconstructed using the formula

$$M_{BG} = \exp\left(\mu + 0.5\sigma^2\right) \qquad [C.10]$$

while the compliance point (arithmetic) mean corresponding to the $k\sigma$ log-scale increase becomes

$$M_{CW} = \exp\left(\mu + k\sigma + 0.5\sigma^2\right) = M_{BG}\exp\left(k\sigma\right) \qquad [C.11]$$

or equivalently, a multiple of $\exp(k\sigma)$ times the mean background level.

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►EXAMPLE C-2

Suppose that background data are fit best by a lognormal distribution with *CV* = 0.5. What steps must be taken to simulate the statistical performance of a lognormal prediction limit on observations with a single verification resample?

SOLUTION

Step 1. Compute the background log-standard deviation parameter as:

$$\sigma = \sqrt{\log\left(1 + CV^2\right)} = \sqrt{\log\left(1 + .25\right)} = 0.4724$$

taking multiplier $k = 0$ to represent the background population.

Step 2. Generate simulated random values from a standard normal distribution with zero mean and unit standard deviation. These values represent simulated and standardized log-domain background measurements.

Step 3. Compute the background prediction limit for lognormal data with a single resample using the formula:

$$PL = \exp\left(\bar{y} + \kappa s_y\right) \qquad [C.12]$$

where $\bar{y}$ and s_y are respectively the log-mean and log-standard deviation, and κ is taken from the **Chapter 19** tables in the **Appendix**, depending on the background sample size, the number of tests to be run, and the type of 1-of-2 retesting plan (interwell or intrawell). Note that the simulated background values do not need to be exponentiated prior to computing the background prediction limit, due to the construction of formula [C.12].

Step 4. For any specific *k* in the range from 0 to 5 (with increasing steps of 0.5), set the compliance point log-mean equal to $\mu_A = k$. Use this result to generate two normal measurements with shifted mean μ_A and unit standard deviation. The two simulated values represent an original sample and a possible resample from the contaminated compliance point. Exponentiate these two values to get simulated lognormal measurements from the desired (alternative) distribution.

Step 5. Compare the simulated values against the background prediction limit. If both exceed the limit, increment the count of cases associated with *k* in which a difference from background has been identified. If only one or none exceeds the limit, do not increment the count.

Step 6. Repeat **Steps 2** through **5** a large number of iterations (say 10,000 or more) and determine the fraction of cases for given *k* at which an exceedance of background is found. This fraction represents the estimated power of the lognormal prediction limit in the log-domain of a $k\sigma$ increase above the background log-mean. Equivalently, with a population *CV* = 0.5, this represents a compliance point mean level of $\exp\left(k\sigma\right) = \exp\left(k \times .4724\right)$ times the (arithmetic) background mean. Repeat this entire process for each *k* in the range of 0 to 5 to estimate the full lognormal power curve for that prediction limit. ◄

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C.3 R SCRIPTS

Certain calculations in the Unified Guidance cannot easily be done either by hand, with a spreadsheet, or even within many common statistical packages. In some cases, proprietary software tailored to groundwater statistics can be consulted. Barring that, an alternate solution is to download and install the free-of-charge, open source, statistical analysis and programming environment **R** software. It can be utilized to perform or program almost any kind of statistical test or calculation. However, with its power and flexibility comes a somewhat steeper learning curve for new programming language.

One of **R**'s advantages is the ability to run 'scripts,' short pre-written programs that can be run repeatedly to perform specific statistical calculations. Scripts can be easily tailored to data- or site-specific configurations using a simple text editor. Because users of the Unified Guidance may occasionally need calculations not covered in the **Appendix** tables or which are unavailable in standard statistical software, a small number of **R** scripts are listed below. These scripts can be modified as necessary and then run in **R**, once the **R** environment is installed on a personal computer. They are provided as a courtesy to users of the Unified Guidance and are provided without any guarantees or implied warranties.

The scripts provided in the Unified Guidance below cover two specific topics: 1) calculation of parametric intrawell prediction limit κ-multipliers used with retesting, especially in cases where a pooled standard deviation estimate might be used in place of the usual sample standard deviation (**Section 13.3**); and 2) computation of a bootstrapped non-parametric confidence band around a Theil-Sen trend line (**Section 21.3.2**).

It is first necessary to install the R-software. As of this date, the latest version is 2.7.2. The program can be downloaded from the website: http://cran.r-project.org. Versions are available for most current Windows operating systems, as well as other types. Once the program has been downloaded (approximately 30 mb), it can be accessed through a self-installed desktop icon.

The R-scripts should first be transferred to a working directory; copies are provided with the distribution CD. If copied directly from the guidance Acrobat pdf using a text editor such as Notepad, it will be necessary to copy each page of the script separately and combine (avoiding unnecessary margin, header and footer information). Each file should be named and saved with the extension changed to a *xxx.r* format. It may be necessary to add a number of additional comment codes (#) at the beginning of the scripts using the text editor, so that each line of narrative text is first identfied by a comment code. To run the scripts:

1) Open the R-software from the desktop icon; you will be in the R-console window;

2) Click File on the toolbar, select Change_dir and hit [Enter]; set the working directory to the one with your scripts; hit [Enter];

3) Then click File and select Open Script [Enter]; Click on the desired R-script file and hit Enter;

4) In the R-console window; change script inputs as desired; Click Edit on the toolbar and select Run All.

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5) The program will run behind the console window. Outputs can be read by minimizing the R-editor. Using the side scrollbar, check the R-script text run to determine if any errors occurred. As noted above, it may be necessary to add the comment code (#) where line length has been exceeded. To run additional inputs within a script, simply modify the inputs in the R-console window and then follow steps 4) and 5). To run other scripts, minimize R, select the new script, adjust as appropriate and follow steps 3) to 5).

6) If an effect size power level is desired for the two prediction limit scripts, change one of the two values in parentheses on the line *del = c(3,4)* and run again.

C.3.1 PARAMETRIC INTRAWELL PREDICTION LIMIT MULTIPLIERS

1-of-m Retesting Plans

```
# R Script for 1-of-m retesting plans
# Compute multiplier for intrawell prediction limit using either regular or pooled SD estimate
# and 1-of-m  retesting for either observations or means of order p
# Solve for kappa given an SWFPR adjusted for nbr of constituents and wells;
# then rate by effective power
# ne = number of yearly evaluations
# Note: ne=4 (quarterly eval), ne=2 (semi-annual), ne=1 (annual)
# n = intrawell BG sample size; w = # wells; coc = # constituents
# df = degrees of freedom associated with variance estimate of prediction limit formula
# Note: if the usual std deviation for a single well is used, set df = (n-1);
#       if using a pooled SD estimate across w equal sized wells, set df= w*(n-1) or
#       df = (sum of well n's) –  w, if  w pooled wells are of different sizes
# alph = per-test false positive rate
# m = type of 1-of-m retesting scheme (usually m= 1,2,3,or 4)
# ord = order of the mean to be predicted (for tests on observations, set ord=1)
# swfpr is the targeted network-wide false positive rate, by default set to 10%
# Rate power at 3 and 4 SD units above BG;
# use ERPC power values as the reference power
# user supplied values of n, w, coc, df, evaluation frequency, m, and ord
n= 4
w= 10
coc= 5
df= w*(n-1)
ne= 1
m= 3
ord= 2

swfpr= .1
alph= 1 - (1-swfpr)^(1/(coc*w))
ref= c()
if (ne==1) ref= c(.54,.81)
if (ne==2) ref= c(.59,.85)
if (ne==4) ref= c(.60,.86)

# default tolerance values for convergence
tol= .000001
tol2= .0001

# default lower and upper limits on range for desired multiplier
ll= 0
ul= 15

# recursive function to compute correct multiplier within limits (lo,hi)
```


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```
kfind= function(lo,hi,n,alph,ne,tol) {
        if (abs(hi-lo)<tol2) return(lo)
        nc= function(x) sqrt(n)*qnorm(x)/sqrt(ord)
        tt= sqrt(n)*lo
        g= function(x) ne*m*(1-(1-x)^m)^(ne-1)*(1-x)^(m-1)*pt(tt,df,nc(x))
        klo = 1 - alph - integrate(g,0,1)$value
        if (abs(klo)<=tol) return(lo)
        tt= sqrt(n)*hi
        khi = 1 - alph - integrate(g,0,1)$value
        if (abs(khi)<=tol) return(hi)
        tt= sqrt(n)*(mean(c(lo,hi)))
        kmid= 1 - alph - integrate(g,0,1)$value
        if (abs(kmid)<=tol) return(mean(c(lo,hi)))
        if (sign(klo)!=sign(khi)) {
                if (sign(klo)!=sign(kmid)) {
                        kfind(lo,mean(c(lo,hi)),n,alph,ne,tol) }
                else {
                        kfind(mean(c(lo,hi)),hi,n,alph,ne,tol) } }
        else {
                stop('bad limits') }
        }

del= c(3,4)
pow= c()
powrate= c()

kap= kfind(ll,ul,n,alph,ne,tol)

for (jj in 1:length(del)) {
        dc= del[jj]
        tt= sqrt(n)*kap
        nc= function(x) {sqrt(n)*(qnorm(x)/sqrt(ord) + del[jj])}
        h= function(x) {
                if (ne==1) {
                        m*((1-x)^(m-1))*pt(tt,df,nc(x))
                        }
                else {
                        ne*m*((1-(1-x)^m)^(ne-1))*((1-x)^(m-1))*pt(tt,df,nc(x))
                        }
                }
        pow[jj]= 1 - integrate(h,0,1,stop.on.error=F)$value
        }

if ((pow[1] >= ref[1]) && (pow[2] >= ref[2])) powrate= 'GOOD'
if ((pow[1] < ref[1]) && (pow[2] >= ref[2])) powrate= 'ACCEPTABLE'
if ((pow[1] >= ref[1]) && (pow[2] < ref[2])) powrate= 'ACCEPTABLE'
if ((pow[1] < ref[1]) && (pow[2] < ref[2])) powrate= 'LOW'

print(paste('intrawell 1ofm'),quote=F)
print(paste('n,w,coc,ne= ',n,w,coc,ne),quote=F)
print(paste('m,ord=',m,ord),quote=F)
print(paste('ref power from ERPC at 3 and 4 SDs'),quote=F)
print(ref)
print(paste('kappa=',round(kap,2)),quote=F)
print(paste('calculated power at 3 and 4 SDs'),quote=F)
print(round(pow,3))
print(paste('power rating=',powrate),quote=F)
```

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Modified California Retesting Plans

```
# R Script for modified California plan
# Compute multiplier for intrawell prediction limit using regular
# or pooled SD estimate and modified Calif retesting for observations
# Solve for kappa given an SWFPR adjusted for number of constituents and wells;
# then rate by effective power
# ne = number of yearly evaluations
# Note: ne=4 (quarterly eval), ne=2 (semi-annual), ne=1 (annual)
# n = intrawell BG sample size; w = # wells; coc = # constituents
# df = degrees of freedom associated with variance estimate of prediction limit formula
# Note: if the usual std deviation is used, set df = (n-1);
#       if using a pooled SD estimate across w wells, set df= w*(n-1)
# alph = per-test false positive rate
# swfpr is the targeted network-wide false positive rate, by default set to 10%
# Rate power at 3 and 4 SD units above BG; use ERPC power values as the reference power
# user supplied values of n, w, coc, df, and evaluation frequency
n= 4
w= 10
coc= 5
df= w*(n-1)
ne= 1

swfpr= .1
alph= 1 - (1-swfpr)^(1/(coc*w))

ref= c()

if (ne==1) ref= c(.54,.81)
if (ne==2) ref= c(.59,.85)
if (ne==4) ref= c(.60,.86)

# default tolerance values for convergence
tol= .000001
tol2= .0001

# default lower and upper limits on range for desired multiplier
ll= 0
ul= 15

# recursive function to compute correct multiplier within limits (lo,hi)
kfind= function(lo,hi,n,alph,ne,tol) {
        if (abs(hi-lo)<tol2) return(lo)
        nc= function(x) sqrt(n)*qnorm(x)
        tt= sqrt(n)*lo
        g= function(x) ne*(x*(1 + 3*x - 5*x^2 + 2*x^3))^(ne-1)*(1 + 6*x - 15*x^2 +
8*x^3)*pt(tt,df,nc(x))
        klo = 1 - alph - integrate(g,0,1)$value
        if (abs(klo)<=tol) return(lo)
        tt= sqrt(n)*hi
        khi = 1 - alph - integrate(g,0,1)$value
        if (abs(khi)<=tol) return(hi)
        tt= sqrt(n)*(mean(c(lo,hi)))
        kmid= 1 - alph - integrate(g,0,1)$value
        if (abs(kmid)<=tol) return(mean(c(lo,hi)))
        if (sign(klo)!=sign(khi)) {
                if (sign(klo)!=sign(kmid)) {
                        kfind(lo,mean(c(lo,hi)),n,alph,ne,tol) }
                else {
                        kfind(mean(c(lo,hi)),hi,n,alph,ne,tol) } }
```


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```
        else {
                stop('bad limits') }
        }

del= c(3,4)
pow= c()
powrate= c()

kap= kfind(ll,ul,n,alph,ne,tol)

for (jj in 1:length(del)) {
        dc= del[jj]
        tt= sqrt(n)*kap
        nc= function(x) {sqrt(n)*(qnorm(x) + del[jj])}
        h= function(x) {
                if (ne==1) {
                        (1 + 6*x - 15*x^2 + 8*x^3)*pt(tt,df,nc(x))
                        }
                else {
                        ne*(x*(1 + 3*x - 5*x^2 + 2*x^3))^(ne-1)*(1 + 6*x - 15*x^2 +
8*x^3)*pt(tt,df,nc(x))
                        }
                }
        pow[jj]= 1 - integrate(h,0,1,stop.on.error=F)$value
        }

if ((pow[1] >= ref[1]) && (pow[2] >= ref[2])) powrate= 'GOOD'
if ((pow[1] < ref[1]) && (pow[2] >= ref[2])) powrate= 'ACCEPTABLE'
if ((pow[1] >= ref[1]) && (pow[2] < ref[2])) powrate= 'ACCEPTABLE'
if ((pow[1] < ref[1]) && (pow[2] < ref[2])) powrate= 'LOW'

print(paste('intrawell modCal'),quote=F)
print(paste('n,w,coc,ne= ',n,w,coc,ne),quote=F)
print(paste('ref power from ERPC at 3 and 4 SDs'),quote=F)
print(ref)
print(paste('kappa=',round(kap,2)),quote=F)
print(paste('calculated power at 3 and 4 SDs'),quote=F)
print(round(pow,3))
print(paste('power rating=',powrate),quote=F)
```

C.3.2 THEIL-SEN CONFIDENCE BAND

```
# R script for Theil-Sen Confidence band
# Compute bootstrapped confidence band around Theil-Sen trend line
# user inputs: list of x-values, list of y-values, desired confidence level
# Note: replace numbers in parentheses below with specific x and y values
#       corresponding to data-specific ordered pairs
# x-values should be numeric values representing sampling dates or events
# y-values should be concentration values corresponding to these dates or events
# Script produces a plot of the Theil-Sen trend line, the confidence band around the trend,
# and an overlay of the actual data values

x= c(89.6,90.1,90.8,91.1,92.1,93.1,94.1,95.6,96.1,96.3)
y= c(56,53,51,55,52,60,62,59,61,63)
conf = .90

elimna= function(m){
#
# remove any rows of data having missing values
m= as.matrix(m)
```


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```
ikeep= c(1:nrow(m))
for(i in 1:nrow(m)) if (sum(is.na(m[i,])>=1)) ikeep[i]= 0
elimna= m[ikeep[ikeep>=1],]
elimna
}

theilsen2= function(x,y){
#
# Compute the Theil-Sen regression estimator
# Do not compute residuals in this version
# Assumes missing pairs already removed
#
ord= order(x)
xs= x[ord]
ys= y[ord]
vec1= outer(ys,ys,"-")
vec2= outer(xs,xs,"-")
v1= vec1[vec2>0]
v2= vec2[vec2>0]
slope= median(v1/v2)
coef= 0
coef[1]= median(y)-slope*median(x)
coef[2]= slope
list(coef=coef)
}

nb= 1000
temp= matrix(c(x,y),ncol=2)
temp= elimna(temp)                          #remove any pairs with missing values
x= temp[,1]
y= temp[,2]
n= length(x)
ord= order(x)
cut= min(x) + (0:100)*(max(x)-min(x))/100   #compute 101 cut pts
t0= theilsen2(x,y)                          #compute trend line on original data
tmp= matrix(nrow=nb,ncol=101)

for (i in 1:nb) {
        idx= sample(ord,n,rep=T)
        xboot= x[idx]
        yboot= y[idx]
        tboot= theilsen2(xboot,yboot)
        tmp[i,]= tboot$coef[1] + cut*tboot$coef[2]
        }

lb= 0; ub= 0
for (i in 1:101){
        lb[i]= quantile(tmp[,i],c((1-conf)/2))
        ub[i]= quantile(tmp[,i],c((1+conf)/2))
        }
tband= list(xcut=cut,lo=lb,hi=ub,ths0=t0)
yt= tband$ths0$coef[1] + tband$ths0$coef[2]*tband$xcut
plot(yt~tband$xcut,type='l',xlim=range(x),ylim=c(min(tband$lo),max(tband$hi)),xlab='Date',ylab='Conc')
points(x,y,pch=16)
lines(tband$hi~tband$xcut,type='l',lty=2)
lines(tband$lo~tband$xcut,type='l',lty=2)
```

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APPENDIX D: STATISTICAL TABLES

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D STATISTICAL TABLES

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Table 10-1. Percentiles of Standard Normal Distribution

P	0.000	0.001	0.002	0.003	0.004	0.005	0.006	0.007	0.008	0.009
0.50	0.0000	0.0025	0.0050	0.0075	0.0100	0.0125	0.0150	0.0175	0.0201	0.0226
0.51	0.0251	0.0276	0.0301	0.0326	0.0351	0.0376	0.0401	0.0426	0.0451	0.0476
0.52	0.0502	0.0527	0.0552	0.0577	0.0602	0.0627	0.0652	0.0677	0.0702	0.0728
0.53	0.0753	0.0778	0.0803	0.0828	0.0853	0.0878	0.0904	0.0929	0.0954	0.0979
0.54	0.1004	0.1030	0.1055	0.1080	0.1105	0.1130	0.1156	0.1181	0.1206	0.1231
0.55	0.1257	0.1282	0.1307	0.1332	0.1358	0.1383	0.1408	0.1434	0.1459	0.1484
0.56	0.1510	0.1535	0.1560	0.1586	0.1611	0.1637	0.1662	0.1687	0.1713	0.1738
0.57	0.1764	0.1789	0.1815	0.1840	0.1866	0.1891	0.1917	0.1942	0.1968	0.1993
0.58	0.2019	0.2045	0.2070	0.2096	0.2121	0.2147	0.2173	0.2198	0.2224	0.2250
0.59	0.2275	0.2301	0.2327	0.2353	0.2378	0.2404	0.2430	0.2456	0.2482	0.2508
0.60	0.2533	0.2559	0.2585	0.2611	0.2637	0.2663	0.2689	0.2715	0.2741	0.2767
0.61	0.2793	0.2819	0.2845	0.2871	0.2898	0.2924	0.2950	0.2976	0.3002	0.3029
0.62	0.3055	0.3081	0.3107	0.3134	0.3160	0.3186	0.3213	0.3239	0.3266	0.3292
0.63	0.3319	0.3345	0.3372	0.3398	0.3425	0.3451	0.3478	0.3505	0.3531	0.3558
0.64	0.3585	0.3611	0.3638	0.3665	0.3692	0.3719	0.3745	0.3772	0.3799	0.3826
0.65	0.3853	0.3880	0.3907	0.3934	0.3961	0.3989	0.4016	0.4043	0.4070	0.4097
0.66	0.4125	0.4152	0.4179	0.4207	0.4234	0.4261	0.4289	0.4316	0.4344	0.4372
0.67	0.4399	0.4427	0.4454	0.4482	0.4510	0.4538	0.4565	0.4593	0.4621	0.4649
0.68	0.4677	0.4705	0.4733	0.4761	0.4789	0.4817	0.4845	0.4874	0.4902	0.4930
0.69	0.4959	0.4987	0.5015	0.5044	0.5072	0.5101	0.5129	0.5158	0.5187	0.5215
0.70	0.5244	0.5273	0.5302	0.5330	0.5359	0.5388	0.5417	0.5446	0.5476	0.5505
0.71	0.5534	0.5563	0.5592	0.5622	0.5651	0.5681	0.5710	0.5740	0.5769	0.5799
0.72	0.5828	0.5858	0.5888	0.5918	0.5948	0.5978	0.6008	0.6038	0.6068	0.6098
0.73	0.6128	0.6158	0.6189	0.6219	0.6250	0.6280	0.6311	0.6341	0.6372	0.6403
0.74	0.6433	0.6464	0.6495	0.6526	0.6557	0.6588	0.6620	0.6651	0.6682	0.6713
0.75	0.6745	0.6776	0.6808	0.6840	0.6871	0.6903	0.6935	0.6967	0.6999	0.7031

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Table 10-1. Percentiles of Standard Normal Distribution

P	0.000	0.001	0.002	0.003	0.004	0.005	0.006	0.007	0.008	0.009
0.76	0.7063	0.7095	0.7128	0.7160	0.7192	0.7225	0.7257	0.7290	0.7323	0.7356
0.77	0.7388	0.7421	0.7454	0.7488	0.7521	0.7554	0.7588	0.7621	0.7655	0.7688
0.78	0.7722	0.7756	0.7790	0.7824	0.7858	0.7892	0.7926	0.7961	0.7995	0.8030
0.79	0.8064	0.8099	0.8134	0.8169	0.8204	0.8239	0.8274	0.8310	0.8345	0.8381
0.80	0.8416	0.8452	0.8488	0.8524	0.8560	0.8596	0.8633	0.8669	0.8705	0.8742
0.81	0.8779	0.8816	0.8853	0.8890	0.8927	0.8965	0.9002	0.9040	0.9078	0.9116
0.82	0.9154	0.9192	0.9230	0.9269	0.9307	0.9346	0.9385	0.9424	0.9463	0.9502
0.83	0.9542	0.9581	0.9621	0.9661	0.9701	0.9741	0.9782	0.9822	0.9863	0.9904
0.84	0.9945	0.9986	1.0027	1.0069	1.0110	1.0152	1.0194	1.0237	1.0279	1.0322
0.85	1.0364	1.0407	1.0450	1.0494	1.0537	1.0581	1.0625	1.0669	1.0714	1.0758
0.86	1.0803	1.0848	1.0893	1.0939	1.0985	1.1031	1.1077	1.1123	1.1170	1.1217
0.87	1.1264	1.1311	1.1359	1.1407	1.1455	1.1503	1.1552	1.1601	1.1650	1.1700
0.88	1.1750	1.1800	1.1850	1.1901	1.1952	1.2004	1.2055	1.2107	1.2160	1.2212
0.89	1.2265	1.2319	1.2372	1.2426	1.2481	1.2536	1.2591	1.2646	1.2702	1.2759
0.90	1.2816	1.2873	1.2930	1.2988	1.3047	1.3106	1.3165	1.3225	1.3285	1.3346
0.91	1.3408	1.3469	1.3532	1.3595	1.3658	1.3722	1.3787	1.3852	1.3917	1.3984
0.92	1.4051	1.4118	1.4187	1.4255	1.4325	1.4395	1.4466	1.4538	1.4611	1.4684
0.93	1.4758	1.4833	1.4909	1.4985	1.5063	1.5141	1.5220	1.5301	1.5382	1.5464
0.94	1.5548	1.5632	1.5718	1.5805	1.5893	1.5982	1.6072	1.6164	1.6258	1.6352
0.95	1.6449	1.6546	1.6646	1.6747	1.6849	1.6954	1.7060	1.7169	1.7279	1.7392
0.96	1.7507	1.7624	1.7744	1.7866	1.7991	1.8119	1.8250	1.8384	1.8522	1.8663
0.97	1.8808	1.8957	1.9110	1.9268	1.9431	1.9600	1.9774	1.9954	2.0141	2.0335
0.98	2.0537	2.0749	2.0969	2.1201	2.1444	2.1701	2.1973	2.2262	2.2571	2.2904
0.99	2.3263	2.3656	2.4089	2.4573	2.5121	2.5758	2.6521	2.7478	2.8782	3.0902

Table 10-2. Coefficients [a_{n-i+1}] for Shapiro-Wilk Test of Normality, n = 2(1)50

i/n	2	3	4	5	6	7	8	9	10	
1	0.7071	0.7071	0.6872	0.6646	0.6431	0.6233	0.6052	0.5888	0.5739	
2	----	.0000	.1677	.2413	.2806	.3031	.3164	.3244	.3291	
3	----	----	----	.0000	.0875	.1401	.1743	.1976	.2141	
4	----	----	----	----	----	.0000	.0561	.0947	.1224	
5	----	----	----	----	----	----	----	.0000	.0399	
i/n	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
1	0.5601	0.5475	0.5359	0.5251	0.5150	0.5056	0.4968	0.4886	0.4808	0.4734
2	.3315	.3325	.3325	.3318	.3306	.3290	.3273	.3253	.3232	.3211
3	.2260	.2347	.2412	.2460	.2495	.2521	.2540	.2553	.2561	.2565
4	.1429	.1586	.1707	.1802	.1878	.1939	.1988	.2027	.2059	.2085
5	.0695	.0922	.1099	.1240	.1353	.1447	.1524	.1587	.1641	.1686
6	0.0000	0.0303	0.0539	0.0727	0.0880	0.1005	0.1109	0.1197	0.1271	0.1334
7	----	----	.0000	.0240	.0433	.0593	.0725	.0837	.0932	.1013
8	----	----	----	----	.0000	.0196	.0359	.0496	.0612	.0711
9	----	----	----	----	----	----	.0000	.0163	.0303	.0422
10	----	----	----	----	----	----	----	----	.0000	.0140
i/n	**21**	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**
1	0.4643	0.4590	0.4542	0.4493	0.4450	0.4407	0.4366	0.4328	0.4291	0.4254
2	.3185	.3156	.3126	.3098	.3069	.3043	.3018	.2992	.2968	.2944
3	.2578	.2571	.2563	.2554	.2543	.2533	.2522	.2510	.2499	.2487
4	.2119	.2131	.2139	.2145	.2148	.2151	.2152	.2151	.2150	.2148
5	.1736	.1764	.1787	.1807	.1822	.1836	.1848	.1857	.1864	.1870
6	0.1399	0.1443	0.1480	0.1512	0.1539	0.1563	0.1584	0.1601	0.1616	0.1630
7	.1092	.1150	.1201	.1245	.1283	.1316	.1346	.1372	.1395	.1415
8	.0804	.0878	.0941	.0997	.1046	.1089	.1128	.1162	.1192	.1219
9	.0530	.0618	.0696	.0764	.0823	.0876	.0923	.0965	.1002	.1036
10	.0263	.0368	.0459	.0539	.0610	.0672	.0728	.0778	.0822	.0862
11	0.0000	0.0122	0.0228	0.0321	0.0403	0.0476	0.0540	0.0598	0.0650	0.0697
12	----	----	.0000	.0107	.0200	.0284	.0358	.0424	.0483	.0537
13	----	----	----	----	.0000	.0094	.0178	.0253	.0320	.0381
14	----	----	----	----	----	----	.0000	.0084	.0159	.0227
15	----	----	----	----	----	----	----	----	.0000	.0076
i/n	**31**	**32**	**33**	**34**	**35**	**36**	**37**	**38**	**39**	**40**
1	0.4220	0.4188	0.4156	0.4127	0.4096	0.4068	0.4040	0.4015	0.3989	0.3964
2	.2921	.2898	.2876	.2854	.2834	.2813	.2794	.2774	.2755	.2737
3	.2475	.2463	.2451	.2439	.2427	.2415	.2403	.2391	.2380	.2368
4	.2145	.2141	.2137	.2132	.2127	.2121	.2116	.2110	.2104	.2098
5	.1874	.1878	.1880	.1882	.1883	.1883	.1883	.1881	.1880	.1878
6	0.1641	0.1651	0.1660	0.1667	0.1673	0.1678	0.1683	0.1686	0.1689	0.1691
7	.1433	.1449	.1463	.1475	.1487	.1496	.1503	.1513	.1520	.1526
8	.1243	.1265	.1284	.1301	.1317	.1331	.1344	.1356	.1366	.1376
9	.1066	.1093	.1118	.1140	.1160	.1179	.1196	.1211	.1225	.1237
10	.0899	.0931	.0961	.0988	.1013	.1036	.1056	.1075	.1092	.1108

Source: Madansky (1988)
Footnote. The notation n = 2(1)50 is shorthand for n from 2 to 50 in unit steps

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Table 10-2. Coefficients [a_{n-i+1}] for Shapiro-Wilk Test of Normality, n = 2(1)50

i/n	31	32	33	34	35	36	37	38	39	40
11	0.0739	0.0777	0.0812	0.0844	0.0873	0.0900	0.0924	0.0947	0.0967	0.0986
12	.0585	.0629	.0669	.0706	.0739	.0770	.0798	.0824	.0848	.0870
13	.0435	.0485	.0530	.0572	.0610	.0645	.0677	.0706	.0733	.0759
14	.0289	.0344	.0395	.0441	.0484	.0523	.0559	.0592	.0622	.0651
15	.0144	.0206	.0262	.0314	.0361	.0404	.0444	.0481	.0515	.0546
16	0.0000	0.0068	0.0131	0.0187	0.0239	0.0287	0.0331	0.0372	0.0409	0.0444
17	----	----	.0000	.0062	.0119	.0172	.0220	.0264	.0305	.0343
18	----	----	----	----	.0000	.0057	.0110	.0158	.0203	.0244
19	----	----	----	----	----	----	.0000	.0053	.0101	.0146
20	----	----	----	----	----	----	----	----	.0000	.0049

i/n	41	42	43	44	45	46	47	48	49	50
1	0.3940	0.3917	0.3894	0.3872	0.3850	0.3830	0.3808	0.3789	0.3770	0.3751
2	.2719	.2701	.2684	.2667	.2651	.2635	.2620	.2604	.2589	.2574
3	.2357	.2345	.2334	.2323	.2313	.2302	.2291	.2281	.2271	.2260
4	.2091	.2085	.2078	.2072	.2065	.2058	.2052	.2045	.2038	.2032
5	.1876	.1874	.1871	.1868	.1865	.1862	.1859	.1855	.1851	.1847
6	0.1693	0.1694	0.1695	0.1695	0.1695	0.1695	0.1695	0.1693	0.1692	0.1691
7	.1531	.1535	.1539	.1542	.1545	.1548	.1550	.1551	.1553	.1554
8	.1384	.1392	.1398	.1405	.1410	.1415	.1420	.1423	.1427	.1430
9	.1249	.1259	.1269	.1278	.1286	.1293	.1300	.1306	.1312	.1317
10	.1123	.1136	.1149	.1160	.1170	.1180	.1189	.1197	.1205	.1212
11	0.1004	0.1020	0.1035	0.1049	0.1062	0.1073	0.1085	0.1095	0.1105	0.1113
12	.0891	.0909	.0927	.0943	.0959	.0972	.0986	.0998	.1010	.1020
13	.0782	.0804	.0824	.0842	.0860	.0876	.0892	.0906	.0919	.0932
14	.0677	.0701	.0724	.0745	.0775	.0785	.0801	.0817	.0832	.0846
15	.0575	.0602	.0628	.0651	.0673	.0694	.0713	.0731	.0748	.0764
16	0.0476	0.0506	0.0534	0.0560	0.0584	0.0607	0.0628	0.0648	0.0667	0.0685
17	.0379	.0411	.0442	.0471	.0497	.0522	.0546	.0568	.0588	.0608
18	.0283	.0318	.0352	.0383	.0412	.0439	.0465	.0489	.0511	.0532
19	.0188	.0227	.0263	.0296	.0328	.0357	.0385	.0411	.0436	.0459
20	.0094	.0136	.0175	.0211	.0245	.0277	.0307	.0335	.0361	.0386
21	0.0000	0.0045	0.0087	0.0126	0.0163	0.0197	0.0229	0.0259	0.0288	0.0314
22	----	----	.0000	.0042	.0081	.0118	.0153	.0185	.0215	.0244
23	----	----	----	----	.0000	.0039	.0076	.0111	.0143	.0174
24	----	----	----	----	----	----	.0000	.0037	.0071	.0104
25	----	----	----	----	----	----	----	----	.0000	.0035

Source: Madansky (1988)
Footnote. The notation n = 2(1)50 is shorthand for n from 2 to 50 in unit steps

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Table 10-3. α-Level Critical Points for Shapiro-Wilk Test, n = 3(1)50

n\α	0.01	0.05	0.10
3	0.753	0.767	0.789
4	0.687	0.748	0.792
5	0.686	0.762	0.806
6	0.713	0.788	0.826
7	0.730	0.803	0.838
8	0.749	0.818	0.851
9	0.764	0.829	0.859
10	0.781	0.842	0.869
11	0.792	0.850	0.876
12	0.805	0.859	0.883
13	0.814	0.866	0.889
14	0.825	0.874	0.895
15	0.835	0.881	0.901
16	0.844	0.887	0.906
17	0.851	0.892	0.910
18	0.858	0.897	0.914
19	0.863	0.901	0.917
20	0.868	0.905	0.920
21	0.873	0.908	0.923
22	0.878	0.911	0.926
23	0.881	0.914	0.928
24	0.884	0.916	0.930
25	0.888	0.918	0.931
26	0.891	0.920	0.933
27	0.894	0.923	0.935
28	0.896	0.924	0.936
29	0.898	0.926	0.937
30	0.900	0.927	0.939
31	0.902	0.929	0.940
32	0.904	0.930	0.941
33	0.906	0.931	0.942
34	0.908	0.933	0.943
35	0.910	0.934	0.944
36	0.912	0.935	0.945
37	0.914	0.936	0.946
38	0.916	0.938	0.947
39	0.917	0.939	0.948
40	0.919	0.940	0.949
41	0.920	0.941	0.950
42	0.922	0.942	0.951
43	0.923	0.943	0.951
44	0.924	0.944	0.952
45	0.926	0.945	0.953
46	0.927	0.945	0.953
47	0.928	0.946	0.954
48	0.929	0.947	0.954
49	0.929	0.947	0.955
50	0.930	0.947	0.955

Source: Madansky (1988)
Footnote. The notation n = 3(1)50 is shorthand for n from 3 to 50 in unit steps

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Table 10-4. α-Level Critical Points for Shapiro-Francía Test, n = 50(1)99

n\α	0.01	0.05	0.10
50	0.935	0.953	0.963
51	0.935	0.954	0.964
53	0.938	0.957	0.964
55	0.940	0.958	0.965
57	0.944	0.961	0.966
59	0.945	0.962	0.967
61	0.947	0.963	0.968
63	0.947	0.964	0.970
65	0.948	0.965	0.971
67	0.950	0.966	0.971
69	0.951	0.966	0.972
71	0.953	0.967	0.972
73	0.956	0.968	0.973
75	0.956	0.969	0.973
77	0.957	0.969	0.974
79	0.957	0.970	0.975
81	0.958	0.970	0.975
83	0.960	0.971	0.976
85	0.961	0.972	0.977
87	0.961	0.972	0.977
89	0.961	0.972	0.977
91	0.962	0.973	0.978
93	0.963	0.973	0.979
95	0.965	0.974	0.979
97	0.965	0.975	0.979
99	0.967	0.976	0.980

Source: Shapiro & Francía (1972)
Footnote. The notation n = 50(1)99 is shorthand for n from 50 to 99 in unit steps

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Table 10-5. α-Critical Pts., Prob. Plot Correlation Coeff. Test, n = 3(1)50(5)100

n\α	0.01	0.025	0.05	0.10
3	0.869	0.872	0.879	0.891
4	0.822	0.845	0.868	0.894
5	0.822	0.855	0.879	0.902
6	0.835	0.868	0.890	0.911
7	0.847	0.876	0.899	0.916
8	0.859	0.886	0.905	0.924
9	0.868	0.893	0.912	0.929
10	0.876	0.900	0.917	0.934
11	0.883	0.906	0.922	0.938
12	0.889	0.912	0.926	0.941
13	0.895	0.917	0.931	0.944
14	0.901	0.921	0.934	0.947
15	0.907	0.925	0.937	0.950
16	0.912	0.928	0.940	0.952
17	0.912	0.931	0.942	0.954
18	0.919	0.934	0.945	0.956
19	0.923	0.937	0.947	0.958
20	0.925	0.939	0.950	0.960
21	0.928	0.942	0.952	0.961
22	0.930	0.944	0.954	0.962
23	0.933	0.947	0.955	0.964
24	0.936	0.949	0.957	0.965
25	0.937	0.950	0.958	0.966
26	0.939	0.952	0.959	0.967
27	0.941	0.953	0.960	0.968
28	0.943	0.955	0.962	0.969
29	0.945	0.956	0.962	0.969
30	0.947	0.957	0.964	0.970
31	0.948	0.958	0.965	0.971
32	0.949	0.959	0.966	0.972
33	0.950	0.960	0.967	0.973
34	0.951	0.960	0.967	0.973
35	0.952	0.961	0.968	0.974
36	0.953	0.962	0.968	0.974
37	0.955	0.962	0.969	0.975
38	0.956	0.964	0.970	0.975
39	0.957	0.965	0.971	0.976
40	0.958	0.966	0.972	0.977
41	0.958	0.967	0.973	0.977
42	0.959	0.967	0.973	0.978
43	0.959	0.967	0.973	0.978
44	0.960	0.968	0.974	0.978
45	0.961	0.969	0.974	0.978
46	0.962	0.969	0.974	0.979
47	0.963	0.970	0.975	0.979
48	0.963	0.970	0.975	0.980
49	0.964	0.971	0.977	0.980
50	0.965	0.972	0.978	0.981
55	0.967	0.974	0.980	0.982
60	0.970	0.976	0.981	0.983
65	0.972	0.977	0.982	0.984
70	0.974	0.978	0.983	0.985
75	0.975	0.979	0.984	0.986
80	0.976	0.980	0.985	0.987
85	0.977	0.981	0.985	0.987
90	0.978	0.982	0.985	0.988
95	0.979	0.983	0.986	0.989
100	0.981	0.984	0.987	0.989

Source: Filliben (1975)

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Table 10-6. Shapiro-Wilk Multiple Group Test: Values to Compute G_i for n = 7(1)50

n	γ	δ	ε	n	γ	δ	ε
7	-2.356	1.245	.4533	**31**	-6.248	1.965	.1840
8	-2.696	1.333	.4186	**32**	-6.324	1.976	.1811
9	-2.968	1.400	.3900	**33**	-6.402	1.988	.1781
10	-3.262	1.471	.3660	**34**	-6.480	2.000	.1755
11	-3.485	1.515	.3451	**35**	-6.559	2.012	.1727
12	-3.731	1.571	.3270	**36**	-6.640	2.024	.1702
13	-3.936	1.613	.3111	**37**	-6.721	2.037	.1677
14	-4.155	1.655	.2969	**38**	-6.803	2.049	.1656
15	-4.373	1.695	.2842	**39**	-6.887	2.062	.1633
16	-4.567	1.724	.2727	**40**	-6.961	2.075	.1612
17	-4.713	1.739	.2622	**41**	-7.035	2.088	.1591
18	-4.885	1.770	.2528	**42**	-7.111	2.101	.1572
19	-5.018	1.786	.2440	**43**	-7.188	2.114	.1552
20	-5.153	1.802	.2359	**44**	-7.266	2.128	.1534
21	-5.291	1.818	.2264	**45**	-7.345	2.141	.1516
22	-5.413	1.835	.2207	**46**	-7.414	2.155	.1499
23	-5.508	1.848	.2157	**47**	-7.484	2.169	.1482
24	-5.605	1.862	.2106	**48**	-7.555	2.183	.1466
25	-5.704	1.876	.2063	**49**	-7.615	2.198	.1451
26	-5.803	1.890	.2020	**50**	-7.677	2.212	.1436
27	-5.905	1.905	.1980				
28	-5.988	1.919	.1943				
29	-6.074	1.934	.1907				
30	-6.150	1.949	.1872				

Source: Gibbons (1994)
Footnote. The notation n = 7(1)50 is shorthand for n from 7 to 50 in unit steps

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Table 10-7. Shapiro-Wilk Multiple Group Test: Values of G_i for n = 3(1)6

	n = 3 (ε = .7500)		n = 4 (ε = .6297)		n = 5 (ε = .5521)		n = 6 (ε = .4963)	
u	W	G_i	W	G_i	W	G_i	W	G_i
-7.0	.7502	-3.291						
-5.4	.7511	-2.810						
-5.0	.7517	-2.678						
-4.6	.7525	-2.543						
-4.2	.7537	-2.400						
-3.8	.7555	-2.254	.6378	-3.497				
-3.4	.7581	-2.099	.6417	-3.270				
-3.0	.7619	-1.937	.6473	-3.043	.5733	-4.013		
-2.6	.7673	-1.767	.6553	-2.839	.5831	-3.698		
-2.2	.7749	-1.589	.6666	-2.642	.5968	-3.383		
-1.8	.7855	-1.404	.6822	-2.441	.6156	-3.113		
-1.4	.7995	-1.210	.7030	-2.222	.6407	-2.874		
-1.0	.8172	-1.010	.7293	-1.964	.6726	-2.558	.6318	-3.719
-0.6	.8386	-0.805	.7609	-1.664	.7108	-2.181	.6748	-2.878
-0.2	.8625	-0.599	.7964	-1.309	.7537	-1.815	.7230	-2.273
0.0	.8750	-0.496	.8149	-1.122	.7761	-1.635	.7482	-2.068
0.2	.8875	-0.395	.8333	-0.944	.7984	-1.418	.7733	-1.858
0.4	.8997	-0.294	.8514	-0.766	.8203	-1.200	.7979	-1.614
0.6	.9114	-0.195	.8688	-0.573	.8413	-0.970	.8215	-1.383
1.0	.9328	-0.003	.9004	-0.192	.8795	-0.513	.8645	-0.842
1.4	.9505	0.181	.9267	0.148	.9114	-0.057	.9004	-0.349
1.6	.9580	0.268	.9378	0.298	.9248	0.174	.9154	-0.075
1.8	.9645	0.354	.9475	0.451	.9365	0.374	.9285	0.182
2.2	.9751	0.516	.9631	0.739	.9553	0.745	.9498	0.653
2.6	.9827	0.669	.9744	0.998	.9690	1.087	.9652	1.045
3.0	.9881	0.812	.9824	1.202	.9788	1.403	.9761	1.440
3.4	.9919	0.947	.9880	1.426	.9855	1.673	.9837	1.838
3.8	.9945	1.074	.9919	1.660	.9902	1.907	.9890	2.170
4.2	.9963	1.195	.9945	1.847	.9934	2.136	.9926	2.512
4.6	.9975	1.309	.9963	2.028	.9955	2.455	.9950	2.748
5.0	.9983	1.418	.9975	2.193	.9970	2.850	.9966	3.090
5.4	.9989	1.522	.9983	2.341	.9980	3.245	.9977	3.540
5.8	.99925	1.621	.9989	2.483	.9986	3.640		
6.2	.99949	1.717	.9993	2.628				
6.6	.99966	1.809	.9995	2.754				
7.0	.99977	1.899	.9997	2.869				
7.4	.99985	1.985	.9998	2.971				
7.8	.99990	2.068	.9998	3.084				
8.2	.99993	2.149	.9999	3.224				
8.6	.99995	2.226	.9999	3.359				

Source: Wilk & Shapiro (1968)
Footnote. The notation n = 3(1)6 is shorthand for n from 3 to 6 in unit steps

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Table 12-1. α-Level Critical Points for Dixon's Outlier Test, n = 3(1)25

n\α	.01	.05	.10
3	0.988	0.941	0.886
4	0.889	0.765	0.679
5	0.780	0.642	0.557
6	0.698	0.560	0.482
7	0.637	0.507	0.434
8	0.683	0.554	0.479
9	0.635	0.512	0.441
10	0.597	0.477	0.409
11	0.679	0.576	0.517
12	0.642	0.546	0.490
13	0.615	0.521	0.467
14	0.641	0.546	0.492
15	0.616	0.525	0.472
16	0.595	0.507	0.454
17	0.577	0.490	0.438
18	0.561	0.475	0.424
19	0.547	0.462	0.412
20	0.535	0.450	0.401
21	0.524	0.440	0.391
22	0.514	0.430	0.382
23	0.505	0.421	0.374
24	0.497	0.413	0.367
25	0.489	0.406	0.360

Source: USEPA (1998)
Footnote. The notation n = 3(1)25 is shorthand for n from 3 to 25 in unit steps

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Table 12-2. α-Level Critical Points for Rosner's Outlier Test

	k = 2		k = 3	
n \ α	**.05**	**.01**	**.05**	**.01**
20	2.83	3.09	2.88	3.13
	2.52	2.76	2.60	2.83
			2.45	2.68
30	3.05	3.35	3.12	3.41
	2.67	2.92	2.73	3.01
			2.56	2.75
40	3.17	3.52	3.22	3.58
	2.77	2.98	2.81	3.03
			2.62	2.82
50	3.27	3.61	3.34	3.68
	2.85	3.08	2.89	3.15
			2.68	2.89
60	3.34	3.70	3.42	3.75
	2.90	3.17	2.95	3.20
			2.73	2.95
80	3.45	3.80	3.49	3.85
	2.97	3.23	3.03	3.27
			2.81	3.01
100	3.52	3.87	3.60	3.97
	3.03	3.28	3.10	3.34
			2.86	3.06

Source: Barnett & Lewis (1994)
Footnote. *k* = number of suspected outliers. Since *k* critical points are needed for each test, there are 2 values under each *k* = 2 entry, 3 under each *k* = 3 entry, etc.

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Table 12-2. α-Level Critical Points for Rosner's Outlier Test (cont.)

	k = 4		k = 5	
n\α	**.05**	**.01**	**.05**	**.01**
20	2.95	3.20	2.97	3.18
	2.63	2.83	2.65	2.89
	2.49	2.68	2.51	2.69
	2.39	2.58	2.42	2.61
			2.37	2.57
30	3.16	3.48	3.19	3.48
	2.77	3.02	2.78	3.03
	2.59	2.79	2.60	2.80
	2.49	2.70	2.51	2.74
			2.45	2.62
40	3.32	3.64	3.31	3.63
	2.86	3.10	2.88	3.13
	2.67	2.87	2.69	2.89
	2.55	2.74	2.55	2.74
			2.47	2.65
50	3.40	3.74	3.45	3.77
	2.93	3.18	2.96	3.21
	2.72	2.92	2.74	2.94
	2.59	2.78	2.61	2.79
			2.52	2.70
60	3.48	3.82	3.51	3.81
	2.98	3.20	3.01	3.24
	2.77	2.97	2.77	2.96
	2.63	2.82	2.65	2.83
			2.56	2.72
80	3.57	3.91	3.61	3.93
	3.05	3.31	3.11	3.36
	2.84	3.04	2.86	3.08
	2.69	2.87	2.72	2.89
			2.62	2.76
100	3.64	3.96	3.70	4.01
	3.13	3.34	3.16	3.42
	2.89	3.06	2.91	3.10
	2.74	2.90	2.77	2.93
			2.67	2.84

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Table 14-1. Approximate α-Level Critical Points for Rank von Neumann Ratio Test for n = 4(1)30(2)50(5)100

n\α	.005	.01	.025	.05	.10
4	——	——	——	——	0.60
5	——	——	0.40	0.70	——
6	0.29	0.46	0.63	0.80	0.97
7	0.50	0.54	0.64	0.86	1.11
8	0.55	0.62	0.76	0.93	1.14
9	0.57	0.67	0.82	0.98	1.18
10	0.62	0.72	0.89	1.04	1.23
11	0.67	0.77	0.93	1.08	1.26
12	0.71	0.81	0.96	1.11	1.29
13	0.74	0.84	1.00	1.14	1.32
14	0.78	0.87	1.03	1.17	1.34
15	0.81	0.90	1.05	1.19	1.36
16	0.84	0.93	1.08	1.21	1.38
17	0.87	0.96	1.10	1.24	1.40
18	0.89	0.98	1.13	1.26	1.41
19	0.92	1.01	1.15	1.27	1.43
20	0.94	1.03	1.17	1.29	1.44
21	0.96	1.05	1.18	1.31	1.45
22	0.98	1.07	1.20	1.32	1.46
23	1.00	1.09	1.22	1.33	1.48
24	1.02	1.10	1.23	1.35	1.49
25	1.04	1.12	1.25	1.36	1.50
26	1.05	1.13	1.26	1.37	1.51
27	1.07	1.15	1.27	1.38	1.51
28	1.08	1.16	1.28	1.39	1.52
29	1.10	1.18	1.30	1.40	1.53
30	1.11	1.19	1.31	1.41	1.54
32	1.13	1.21	1.33	1.43	1.55
34	1.16	1.23	1.35	1.45	1.57
36	1.18	1.25	1.36	1.46	1.58
38	1.20	1.27	1.38	1.48	1.59
40	1.22	1.29	1.39	1.49	1.60
42	1.24	1.30	1.41	1.50	1.61
44	1.25	1.32	1.42	1.51	1.62
46	1.27	1.33	1.43	1.52	1.63
48	1.28	1.35	1.45	1.53	1.63
50	1.29	1.36	1.46	1.54	1.64
55	1.33	1.39	1.48	1.56	1.66
60	1.35	1.41	1.50	1.58	1.67
65	1.38	1.43	1.52	1.60	1.68
70	1.40	1.45	1.54	1.61	1.70
75	1.42	1.47	1.55	1.62	1.71
80	1.44	1.49	1.57	1.64	1.71
85	1.45	1.50	1.58	1.65	1.72
90	1.47	1.52	1.59	1.66	1.73
95	1.48	1.53	1.60	1.66	1.74
100	1.49	1.54	1.61	1.67	1.74

Sources: Bartels (1982), Madansky (1988)
Footnote. The notation *n* = 4(1)30(2)50(5)100 is shorthand for *n* from 4 to 30 in unit steps, then from 30 to 50 by 2's, then from 50 to 100 by 5's

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Table 16-1. Percentiles of Student's *t*-Distribution

df\P	.75	.80	.85	.90	.95	.96	.97	.975	.98	.9833	.9875	.99	.995	.999
1	1.000	1.376	1.963	3.078	6.314	7.916	10.579	12.706	15.895	19.043	25.452	31.821	63.657	318.309
2	0.816	1.061	1.386	1.886	2.920	3.320	3.896	4.303	4.849	5.334	6.205	6.965	9.925	22.327
3	0.765	0.978	1.250	1.638	2.353	2.605	2.951	3.182	3.482	3.738	4.177	4.541	5.841	10.215
4	0.741	0.941	1.190	1.533	2.132	2.333	2.601	2.776	2.999	3.184	3.495	3.747	4.604	7.173
5	0.727	0.920	1.156	1.476	2.015	2.191	2.422	2.571	2.757	2.910	3.163	3.365	4.032	5.893
6	0.718	0.906	1.134	1.440	1.943	2.104	2.313	2.447	2.612	2.748	2.969	3.143	3.707	5.208
7	0.711	0.896	1.119	1.415	1.895	2.046	2.241	2.365	2.517	2.640	2.841	2.998	3.499	4.785
8	0.706	0.889	1.108	1.397	1.860	2.004	2.189	2.306	2.449	2.565	2.752	2.896	3.355	4.501
9	0.703	0.883	1.100	1.383	1.833	1.973	2.150	2.262	2.398	2.508	2.685	2.821	3.250	4.297
10	0.700	0.879	1.093	1.372	1.812	1.948	2.120	2.228	2.359	2.465	2.634	2.764	3.169	4.144
11	0.697	0.876	1.088	1.363	1.796	1.928	2.096	2.201	2.328	2.430	2.593	2.718	3.106	4.025
12	0.695	0.873	1.083	1.356	1.782	1.912	2.076	2.179	2.303	2.402	2.560	2.681	3.055	3.930
13	0.694	0.870	1.079	1.350	1.771	1.899	2.060	2.160	2.282	2.379	2.533	2.650	3.012	3.852
14	0.692	0.868	1.076	1.345	1.761	1.887	2.046	2.145	2.264	2.359	2.510	2.624	2.977	3.787
15	0.691	0.866	1.074	1.341	1.753	1.878	2.034	2.131	2.249	2.342	2.490	2.602	2.947	3.733
16	0.690	0.865	1.071	1.337	1.746	1.869	2.024	2.120	2.235	2.327	2.473	2.583	2.921	3.686
17	0.689	0.863	1.069	1.333	1.740	1.862	2.015	2.110	2.224	2.315	2.458	2.567	2.898	3.646
18	0.688	0.862	1.067	1.330	1.734	1.855	2.007	2.101	2.214	2.303	2.445	2.552	2.878	3.610
19	0.688	0.861	1.066	1.328	1.729	1.850	2.000	2.093	2.205	2.293	2.433	2.539	2.861	3.579
20	0.687	0.860	1.064	1.325	1.725	1.844	1.994	2.086	2.197	2.285	2.423	2.528	2.845	3.552
21	0.686	0.859	1.063	1.323	1.721	1.840	1.988	2.080	2.189	2.277	2.414	2.518	2.831	3.527
22	0.686	0.858	1.061	1.321	1.717	1.835	1.983	2.074	2.183	2.269	2.405	2.508	2.819	3.505
23	0.685	0.858	1.060	1.319	1.714	1.832	1.978	2.069	2.177	2.263	2.398	2.500	2.807	3.485
24	0.685	0.857	1.059	1.318	1.711	1.828	1.974	2.064	2.172	2.257	2.391	2.492	2.797	3.467
25	0.684	0.856	1.058	1.316	1.708	1.825	1.970	2.060	2.167	2.251	2.385	2.485	2.787	3.450
26	0.684	0.856	1.058	1.315	1.706	1.822	1.967	2.056	2.162	2.246	2.379	2.479	2.779	3.435
27	0.684	0.855	1.057	1.314	1.703	1.819	1.963	2.052	2.158	2.242	2.373	2.473	2.771	3.421
28	0.683	0.855	1.056	1.313	1.701	1.817	1.960	2.048	2.154	2.237	2.368	2.467	2.763	3.408
29	0.683	0.854	1.055	1.311	1.699	1.814	1.957	2.045	2.150	2.233	2.364	2.462	2.756	3.396
30	0.683	0.854	1.055	1.310	1.697	1.812	1.955	2.042	2.147	2.230	2.360	2.457	2.750	3.385

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Table 16-1. Percentiles of Student's *t*-Distribution (cont.)

df\P	.75	.80	.85	.90	.95	.96	.97	.975	.98	.9833	.9875	.99	.995	.999
31	0.682	0.853	1.054	1.309	1.696	1.810	1.952	2.040	2.144	2.226	2.356	2.453	2.744	3.375
32	0.682	0.853	1.054	1.309	1.694	1.808	1.950	2.037	2.141	2.223	2.352	2.449	2.738	3.365
33	0.682	0.853	1.053	1.308	1.692	1.806	1.948	2.035	2.138	2.220	2.348	2.445	2.733	3.356
34	0.682	0.852	1.052	1.307	1.691	1.805	1.946	2.032	2.136	2.217	2.345	2.441	2.728	3.348
35	0.682	0.852	1.052	1.306	1.690	1.803	1.944	2.030	2.133	2.215	2.342	2.438	2.724	3.340
36	0.681	0.852	1.052	1.306	1.688	1.802	1.942	2.028	2.131	2.212	2.339	2.434	2.719	3.333
37	0.681	0.851	1.051	1.305	1.687	1.800	1.940	2.026	2.129	2.210	2.336	2.431	2.715	3.326
38	0.681	0.851	1.051	1.304	1.686	1.799	1.939	2.024	2.127	2.207	2.334	2.429	2.712	3.319
39	0.681	0.851	1.050	1.304	1.685	1.798	1.937	2.023	2.125	2.205	2.331	2.426	2.708	3.313
40	0.681	0.851	1.050	1.303	1.684	1.796	1.936	2.021	2.123	2.203	2.329	2.423	2.704	3.307
41	0.681	0.850	1.050	1.303	1.683	1.795	1.934	2.020	2.121	2.201	2.327	2.421	2.701	3.301
42	0.680	0.850	1.049	1.302	1.682	1.794	1.933	2.018	2.120	2.199	2.325	2.418	2.698	3.296
43	0.680	0.850	1.049	1.302	1.681	1.793	1.932	2.017	2.118	2.198	2.323	2.416	2.695	3.291
44	0.680	0.850	1.049	1.301	1.680	1.792	1.931	2.015	2.116	2.196	2.321	2.414	2.692	3.286
45	0.680	0.850	1.049	1.301	1.679	1.791	1.929	2.014	2.115	2.195	2.319	2.412	2.690	3.281
46	0.680	0.850	1.048	1.300	1.679	1.790	1.928	2.013	2.114	2.193	2.317	2.410	2.687	3.277
47	0.680	0.849	1.048	1.300	1.678	1.789	1.927	2.012	2.112	2.192	2.315	2.408	2.685	3.273
48	0.680	0.849	1.048	1.299	1.677	1.789	1.926	2.011	2.111	2.190	2.314	2.407	2.682	3.269
49	0.680	0.849	1.048	1.299	1.677	1.788	1.925	2.010	2.110	2.189	2.312	2.405	2.680	3.265
50	0.679	0.849	1.047	1.299	1.676	1.787	1.924	2.009	2.109	2.188	2.311	2.403	2.678	3.261
51	0.679	0.849	1.047	1.298	1.675	1.786	1.924	2.008	2.108	2.186	2.310	2.402	2.676	3.258
52	0.679	0.849	1.047	1.298	1.675	1.786	1.923	2.007	2.107	2.185	2.308	2.400	2.674	3.255
53	0.679	0.848	1.047	1.298	1.674	1.785	1.922	2.006	2.106	2.184	2.307	2.399	2.672	3.251
54	0.679	0.848	1.046	1.297	1.674	1.784	1.921	2.005	2.105	2.183	2.306	2.397	2.670	3.248
55	0.679	0.848	1.046	1.297	1.673	1.784	1.920	2.004	2.104	2.182	2.304	2.396	2.668	3.245
56	0.679	0.848	1.046	1.297	1.673	1.783	1.920	2.003	2.103	2.181	2.303	2.395	2.667	3.242
57	0.679	0.848	1.046	1.297	1.672	1.782	1.919	2.002	2.102	2.180	2.302	2.394	2.665	3.239
58	0.679	0.848	1.046	1.296	1.672	1.782	1.918	2.002	2.101	2.179	2.301	2.392	2.663	3.237
59	0.679	0.848	1.046	1.296	1.671	1.781	1.918	2.001	2.100	2.178	2.300	2.391	2.662	3.234
60	0.679	0.848	1.045	1.296	1.671	1.781	1.917	2.000	2.099	2.177	2.299	2.390	2.660	3.232
70	0.678	0.847	1.044	1.294	1.667	1.776	1.912	1.994	2.093	2.170	2.291	2.381	2.648	3.211
80	0.678	0.846	1.043	1.292	1.664	1.773	1.908	1.990	2.088	2.165	2.284	2.374	2.639	3.195
90	0.677	0.846	1.042	1.291	1.662	1.771	1.905	1.987	2.084	2.160	2.280	2.368	2.632	3.183
100	0.677	0.845	1.042	1.290	1.660	1.769	1.902	1.984	2.081	2.157	2.276	2.364	2.626	3.174
110	0.677	0.845	1.041	1.289	1.659	1.767	1.900	1.982	2.078	2.154	2.272	2.361	2.621	3.166
120	0.677	0.845	1.041	1.289	1.658	1.766	1.899	1.980	2.076	2.152	2.270	2.358	2.617	3.160

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Table 17-1. Percentiles of *F*-Distribution for $(1-\alpha) = .80$

$\nu_2 \backslash \nu_1$	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	9.47	12.00	13.06	13.64	14.01	14.26	14.44	14.58	14.68	14.77	14.84	14.90	14.95	15.00	15.04
2	3.56	4.00	4.16	4.24	4.28	4.32	4.34	4.36	4.37	4.38	4.39	4.40	4.40	4.41	4.42
3	2.68	2.89	2.94	2.96	2.97	2.97	2.97	2.98	2.98	2.98	2.98	2.98	2.98	2.98	2.98
4	2.35	2.47	2.48	2.48	2.48	2.47	2.47	2.47	2.46	2.46	2.46	2.46	2.45	2.45	2.45
5	2.18	2.26	2.25	2.24	2.23	2.22	2.21	2.20	2.20	2.19	2.19	2.18	2.18	2.18	2.18
6	2.07	2.13	2.11	2.09	2.08	2.06	2.05	2.04	2.03	2.03	2.02	2.02	2.01	2.01	2.01
7	2.00	2.04	2.02	1.99	1.97	1.96	1.94	1.93	1.93	1.92	1.91	1.91	1.90	1.90	1.89
8	1.95	1.98	1.95	1.92	1.90	1.88	1.87	1.86	1.85	1.84	1.83	1.83	1.82	1.82	1.81
9	1.91	1.93	1.90	1.87	1.85	1.83	1.81	1.80	1.79	1.78	1.77	1.76	1.76	1.75	1.75
10	1.88	1.90	1.86	1.83	1.80	1.78	1.77	1.75	1.74	1.73	1.72	1.72	1.71	1.70	1.70
11	1.86	1.87	1.83	1.80	1.77	1.75	1.73	1.72	1.70	1.69	1.69	1.68	1.67	1.67	1.66
12	1.84	1.85	1.80	1.77	1.74	1.72	1.70	1.69	1.67	1.66	1.65	1.65	1.64	1.63	1.63
13	1.82	1.83	1.78	1.75	1.72	1.69	1.68	1.66	1.65	1.64	1.63	1.62	1.61	1.61	1.60
14	1.81	1.81	1.76	1.73	1.70	1.67	1.65	1.64	1.63	1.62	1.61	1.60	1.59	1.58	1.58
15	1.80	1.80	1.75	1.71	1.68	1.66	1.64	1.62	1.61	1.60	1.59	1.58	1.57	1.56	1.56
16	1.79	1.78	1.74	1.70	1.67	1.64	1.62	1.61	1.59	1.58	1.57	1.56	1.55	1.55	1.54
17	1.78	1.77	1.72	1.68	1.65	1.63	1.61	1.59	1.58	1.57	1.56	1.55	1.54	1.53	1.53
18	1.77	1.76	1.71	1.67	1.64	1.62	1.60	1.58	1.56	1.55	1.54	1.53	1.53	1.52	1.51
19	1.76	1.75	1.70	1.66	1.63	1.61	1.58	1.57	1.55	1.54	1.53	1.52	1.51	1.51	1.50
20	1.76	1.75	1.70	1.65	1.62	1.60	1.58	1.56	1.54	1.53	1.52	1.51	1.50	1.50	1.49
21	1.75	1.74	1.69	1.65	1.61	1.59	1.57	1.55	1.53	1.52	1.51	1.50	1.49	1.49	1.48
22	1.75	1.73	1.68	1.64	1.61	1.58	1.56	1.54	1.53	1.51	1.50	1.49	1.49	1.48	1.47
23	1.74	1.73	1.68	1.63	1.60	1.57	1.55	1.53	1.52	1.51	1.50	1.49	1.48	1.47	1.46
24	1.74	1.72	1.67	1.63	1.59	1.57	1.55	1.53	1.51	1.50	1.49	1.48	1.47	1.46	1.46
25	1.73	1.72	1.66	1.62	1.59	1.56	1.54	1.52	1.51	1.49	1.48	1.47	1.46	1.46	1.45
26	1.73	1.71	1.66	1.62	1.58	1.56	1.53	1.52	1.50	1.49	1.48	1.47	1.46	1.45	1.44
27	1.73	1.71	1.66	1.61	1.58	1.55	1.53	1.51	1.49	1.48	1.47	1.46	1.45	1.44	1.44
28	1.72	1.71	1.65	1.61	1.57	1.55	1.52	1.51	1.49	1.48	1.47	1.46	1.45	1.44	1.43
29	1.72	1.70	1.65	1.60	1.57	1.54	1.52	1.50	1.49	1.47	1.46	1.45	1.44	1.43	1.43
30	1.72	1.70	1.64	1.60	1.57	1.54	1.52	1.50	1.48	1.47	1.46	1.45	1.44	1.43	1.42
35	1.71	1.69	1.63	1.58	1.55	1.52	1.50	1.48	1.46	1.45	1.44	1.43	1.42	1.41	1.40
40	1.70	1.68	1.62	1.57	1.54	1.51	1.49	1.47	1.45	1.44	1.42	1.41	1.40	1.40	1.39
45	1.69	1.67	1.61	1.57	1.53	1.50	1.48	1.46	1.44	1.43	1.41	1.40	1.39	1.38	1.38
50	1.69	1.66	1.60	1.56	1.52	1.49	1.47	1.45	1.43	1.42	1.41	1.39	1.38	1.38	1.37
55	1.68	1.66	1.60	1.55	1.52	1.49	1.46	1.44	1.43	1.41	1.40	1.39	1.38	1.37	1.36
60	1.68	1.65	1.60	1.55	1.51	1.48	1.46	1.44	1.42	1.41	1.39	1.38	1.37	1.36	1.35
70	1.67	1.65	1.59	1.54	1.50	1.47	1.45	1.43	1.41	1.40	1.38	1.37	1.36	1.35	1.35
80	1.67	1.64	1.58	1.53	1.50	1.47	1.44	1.42	1.41	1.39	1.38	1.37	1.36	1.35	1.34
90	1.67	1.64	1.58	1.53	1.49	1.46	1.44	1.42	1.40	1.38	1.37	1.36	1.35	1.34	1.33
100	1.66	1.64	1.58	1.53	1.49	1.46	1.43	1.41	1.40	1.38	1.37	1.36	1.35	1.34	1.33
110	1.66	1.63	1.57	1.52	1.49	1.46	1.43	1.41	1.39	1.38	1.36	1.35	1.34	1.33	1.32
120	1.66	1.63	1.57	1.52	1.48	1.45	1.43	1.41	1.39	1.37	1.36	1.35	1.34	1.33	1.32

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Table 17-1. Percentiles of *F*-Distribution for $(1-\alpha) = .90$

$\nu_2 \backslash \nu_1$	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	39.86	49.50	53.59	55.83	57.24	58.20	58.91	59.44	59.86	60.19	60.47	60.71	60.90	61.07	61.22
2	8.53	9.00	9.16	9.24	9.29	9.33	9.35	9.37	9.38	9.39	9.40	9.41	9.41	9.42	9.42
3	5.54	5.46	5.39	5.34	5.31	5.28	5.27	5.25	5.24	5.23	5.22	5.22	5.21	5.20	5.20
4	4.54	4.32	4.19	4.11	4.05	4.01	3.98	3.95	3.94	3.92	3.91	3.90	3.89	3.88	3.87
5	4.06	3.78	3.62	3.52	3.45	3.40	3.37	3.34	3.32	3.30	3.28	3.27	3.26	3.25	3.24
6	3.78	3.46	3.29	3.18	3.11	3.05	3.01	2.98	2.96	2.94	2.92	2.90	2.89	2.88	2.87
7	3.59	3.26	3.07	2.96	2.88	2.83	2.78	2.75	2.72	2.70	2.68	2.67	2.65	2.64	2.63
8	3.46	3.11	2.92	2.81	2.73	2.67	2.62	2.59	2.56	2.54	2.52	2.50	2.49	2.48	2.46
9	3.36	3.01	2.81	2.69	2.61	2.55	2.51	2.47	2.44	2.42	2.40	2.38	2.36	2.35	2.34
10	3.29	2.92	2.73	2.61	2.52	2.46	2.41	2.38	2.35	2.32	2.30	2.28	2.27	2.26	2.24
11	3.23	2.86	2.66	2.54	2.45	2.39	2.34	2.30	2.27	2.25	2.23	2.21	2.19	2.18	2.17
12	3.18	2.81	2.61	2.48	2.39	2.33	2.28	2.24	2.21	2.19	2.17	2.15	2.13	2.12	2.10
13	3.14	2.76	2.56	2.43	2.35	2.28	2.23	2.20	2.16	2.14	2.12	2.10	2.08	2.07	2.05
14	3.10	2.73	2.52	2.39	2.31	2.24	2.19	2.15	2.12	2.10	2.07	2.05	2.04	2.02	2.01
15	3.07	2.70	2.49	2.36	2.27	2.21	2.16	2.12	2.09	2.06	2.04	2.02	2.00	1.99	1.97
16	3.05	2.67	2.46	2.33	2.24	2.18	2.13	2.09	2.06	2.03	2.01	1.99	1.97	1.95	1.94
17	3.03	2.64	2.44	2.31	2.22	2.15	2.10	2.06	2.03	2.00	1.98	1.96	1.94	1.93	1.91
18	3.01	2.62	2.42	2.29	2.20	2.13	2.08	2.04	2.00	1.98	1.95	1.93	1.92	1.90	1.89
19	2.99	2.61	2.40	2.27	2.18	2.11	2.06	2.02	1.98	1.96	1.93	1.91	1.89	1.88	1.86
20	2.97	2.59	2.38	2.25	2.16	2.09	2.04	2.00	1.96	1.94	1.91	1.89	1.87	1.86	1.84
21	2.96	2.57	2.36	2.23	2.14	2.08	2.02	1.98	1.95	1.92	1.90	1.87	1.86	1.84	1.83
22	2.95	2.56	2.35	2.22	2.13	2.06	2.01	1.97	1.93	1.90	1.88	1.86	1.84	1.83	1.81
23	2.94	2.55	2.34	2.21	2.11	2.05	1.99	1.95	1.92	1.89	1.87	1.84	1.83	1.81	1.80
24	2.93	2.54	2.33	2.19	2.10	2.04	1.98	1.94	1.91	1.88	1.85	1.83	1.81	1.80	1.78
25	2.92	2.53	2.32	2.18	2.09	2.02	1.97	1.93	1.89	1.87	1.84	1.82	1.80	1.79	1.77
26	2.91	2.52	2.31	2.17	2.08	2.01	1.96	1.92	1.88	1.86	1.83	1.81	1.79	1.77	1.76
27	2.90	2.51	2.30	2.17	2.07	2.00	1.95	1.91	1.87	1.85	1.82	1.80	1.78	1.76	1.75
28	2.89	2.50	2.29	2.16	2.06	2.00	1.94	1.90	1.87	1.84	1.81	1.79	1.77	1.75	1.74
29	2.89	2.50	2.28	2.15	2.06	1.99	1.93	1.89	1.86	1.83	1.80	1.78	1.76	1.75	1.73
30	2.88	2.49	2.28	2.14	2.05	1.98	1.93	1.88	1.85	1.82	1.79	1.77	1.75	1.74	1.72
35	2.85	2.46	2.25	2.11	2.02	1.95	1.90	1.85	1.82	1.79	1.76	1.74	1.72	1.70	1.69
40	2.84	2.44	2.23	2.09	2.00	1.93	1.87	1.83	1.79	1.76	1.74	1.71	1.70	1.68	1.66
45	2.82	2.42	2.21	2.07	1.98	1.91	1.85	1.81	1.77	1.74	1.72	1.70	1.68	1.66	1.64
50	2.81	2.41	2.20	2.06	1.97	1.90	1.84	1.80	1.76	1.73	1.70	1.68	1.66	1.64	1.63
55	2.80	2.40	2.19	2.05	1.95	1.88	1.83	1.78	1.75	1.72	1.69	1.67	1.65	1.63	1.61
60	2.79	2.39	2.18	2.04	1.95	1.87	1.82	1.77	1.74	1.71	1.68	1.66	1.64	1.62	1.60
70	2.78	2.38	2.16	2.03	1.93	1.86	1.80	1.76	1.72	1.69	1.66	1.64	1.62	1.60	1.59
80	2.77	2.37	2.15	2.02	1.92	1.85	1.79	1.75	1.71	1.68	1.65	1.63	1.61	1.59	1.57
90	2.76	2.36	2.15	2.01	1.91	1.84	1.78	1.74	1.70	1.67	1.64	1.62	1.60	1.58	1.56
100	2.76	2.36	2.14	2.00	1.91	1.83	1.78	1.73	1.69	1.66	1.64	1.61	1.59	1.57	1.56
110	2.75	2.35	2.13	2.00	1.90	1.83	1.77	1.73	1.69	1.66	1.63	1.61	1.59	1.57	1.55
120	2.75	2.35	2.13	1.99	1.90	1.82	1.77	1.72	1.68	1.65	1.63	1.60	1.58	1.56	1.55

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Table 17-1. Percentiles of *F*-Distribution for $(1-\alpha) = .95$

$\nu_2 \backslash \nu_1$	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	161.45	199.50	215.71	224.58	230.16	233.99	236.77	238.88	240.54	241.88	242.98	243.91	244.69	245.36	245.95
2	18.51	19.00	19.16	19.25	19.30	19.33	19.35	19.37	19.38	19.40	19.40	19.41	19.42	19.42	19.43
3	10.13	9.55	9.28	9.12	9.01	8.94	8.89	8.85	8.81	8.79	8.76	8.74	8.73	8.71	8.70
4	7.71	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00	5.96	5.94	5.91	5.89	5.87	5.86
5	6.61	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.77	4.74	4.70	4.68	4.66	4.64	4.62
6	5.99	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10	4.06	4.03	4.00	3.98	3.96	3.94
7	5.59	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.68	3.64	3.60	3.57	3.55	3.53	3.51
8	5.32	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.39	3.35	3.31	3.28	3.26	3.24	3.22
9	5.12	4.26	3.86	3.63	3.48	3.37	3.29	3.23	3.18	3.14	3.10	3.07	3.05	3.03	3.01
10	4.96	4.10	3.71	3.48	3.33	3.22	3.14	3.07	3.02	2.98	2.94	2.91	2.89	2.86	2.85
11	4.84	3.98	3.59	3.36	3.20	3.09	3.01	2.95	2.90	2.85	2.82	2.79	2.76	2.74	2.72
12	4.75	3.89	3.49	3.26	3.11	3.00	2.91	2.85	2.80	2.75	2.72	2.69	2.66	2.64	2.62
13	4.67	3.81	3.41	3.18	3.03	2.92	2.83	2.77	2.71	2.67	2.63	2.60	2.58	2.55	2.53
14	4.60	3.74	3.34	3.11	2.96	2.85	2.76	2.70	2.65	2.60	2.57	2.53	2.51	2.48	2.46
15	4.54	3.68	3.29	3.06	2.90	2.79	2.71	2.64	2.59	2.54	2.51	2.48	2.45	2.42	2.40
16	4.49	3.63	3.24	3.01	2.85	2.74	2.66	2.59	2.54	2.49	2.46	2.42	2.40	2.37	2.35
17	4.45	3.59	3.20	2.96	2.81	2.70	2.61	2.55	2.49	2.45	2.41	2.38	2.35	2.33	2.31
18	4.41	3.55	3.16	2.93	2.77	2.66	2.58	2.51	2.46	2.41	2.37	2.34	2.31	2.29	2.27
19	4.38	3.52	3.13	2.90	2.74	2.63	2.54	2.48	2.42	2.38	2.34	2.31	2.28	2.26	2.23
20	4.35	3.49	3.10	2.87	2.71	2.60	2.51	2.45	2.39	2.35	2.31	2.28	2.25	2.22	2.20
21	4.32	3.47	3.07	2.84	2.68	2.57	2.49	2.42	2.37	2.32	2.28	2.25	2.22	2.20	2.18
22	4.30	3.44	3.05	2.82	2.66	2.55	2.46	2.40	2.34	2.30	2.26	2.23	2.20	2.17	2.15
23	4.28	3.42	3.03	2.80	2.64	2.53	2.44	2.37	2.32	2.27	2.24	2.20	2.18	2.15	2.13
24	4.26	3.40	3.01	2.78	2.62	2.51	2.42	2.36	2.30	2.25	2.22	2.18	2.15	2.13	2.11
25	4.24	3.39	2.99	2.76	2.60	2.49	2.40	2.34	2.28	2.24	2.20	2.16	2.14	2.11	2.09
26	4.23	3.37	2.98	2.74	2.59	2.47	2.39	2.32	2.27	2.22	2.18	2.15	2.12	2.09	2.07
27	4.21	3.35	2.96	2.73	2.57	2.46	2.37	2.31	2.25	2.20	2.17	2.13	2.10	2.08	2.06
28	4.20	3.34	2.95	2.71	2.56	2.45	2.36	2.29	2.24	2.19	2.15	2.12	2.09	2.06	2.04
29	4.18	3.33	2.93	2.70	2.55	2.43	2.35	2.28	2.22	2.18	2.14	2.10	2.08	2.05	2.03
30	4.17	3.32	2.92	2.69	2.53	2.42	2.33	2.27	2.21	2.16	2.13	2.09	2.06	2.04	2.01
35	4.12	3.27	2.87	2.64	2.49	2.37	2.29	2.22	2.16	2.11	2.07	2.04	2.01	1.99	1.96
40	4.08	3.23	2.84	2.61	2.45	2.34	2.25	2.18	2.12	2.08	2.04	2.00	1.97	1.95	1.92
45	4.06	3.20	2.81	2.58	2.42	2.31	2.22	2.15	2.10	2.05	2.01	1.97	1.94	1.92	1.89
50	4.03	3.18	2.79	2.56	2.40	2.29	2.20	2.13	2.07	2.03	1.99	1.95	1.92	1.89	1.87
55	4.02	3.16	2.77	2.54	2.38	2.27	2.18	2.11	2.06	2.01	1.97	1.93	1.90	1.88	1.85
60	4.00	3.15	2.76	2.53	2.37	2.25	2.17	2.10	2.04	1.99	1.95	1.92	1.89	1.86	1.84
70	3.98	3.13	2.74	2.50	2.35	2.23	2.14	2.07	2.02	1.97	1.93	1.89	1.86	1.84	1.81
80	3.96	3.11	2.72	2.49	2.33	2.21	2.13	2.06	2.00	1.95	1.91	1.88	1.84	1.82	1.79
90	3.95	3.10	2.71	2.47	2.32	2.20	2.11	2.04	1.99	1.94	1.90	1.86	1.83	1.80	1.78
100	3.94	3.09	2.70	2.46	2.31	2.19	2.10	2.03	1.97	1.93	1.89	1.85	1.82	1.79	1.77
110	3.93	3.08	2.69	2.45	2.30	2.18	2.09	2.02	1.97	1.92	1.88	1.84	1.81	1.78	1.76
120	3.92	3.07	2.68	2.45	2.29	2.18	2.09	2.02	1.96	1.91	1.87	1.83	1.80	1.78	1.75

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Table 17-1. Percentiles of *F*-Distribution for $(1-\alpha) = .98$

$\nu_2 \backslash \nu_1$	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	1012.55	1249.50	1350.50	1405.83	1440.61	1464.45	1481.80	1494.99	1505.34	1513.69	1520.56	1526.31	1531.20	1535.40	1539.05
2	48.51	49.00	49.17	49.25	49.30	49.33	49.36	49.37	49.39	49.40	49.41	49.42	49.42	49.43	49.43
3	20.62	18.86	18.11	17.69	17.43	17.25	17.11	17.01	16.93	16.86	16.81	16.76	16.72	16.69	16.66
4	14.04	12.14	11.34	10.90	10.62	10.42	10.27	10.16	10.07	10.00	9.94	9.89	9.85	9.81	9.78
5	11.32	9.45	8.67	8.23	7.95	7.76	7.61	7.50	7.42	7.34	7.28	7.23	7.19	7.16	7.12
6	9.88	8.05	7.29	6.86	6.58	6.39	6.25	6.14	6.05	5.98	5.93	5.88	5.83	5.80	5.76
7	8.99	7.20	6.45	6.03	5.76	5.58	5.44	5.33	5.24	5.17	5.11	5.06	5.02	4.98	4.95
8	8.39	6.64	5.90	5.49	5.22	5.04	4.90	4.79	4.70	4.63	4.58	4.53	4.49	4.45	4.42
9	7.96	6.23	5.51	5.10	4.84	4.65	4.52	4.41	4.33	4.26	4.20	4.15	4.11	4.07	4.04
10	7.64	5.93	5.22	4.82	4.55	4.37	4.23	4.13	4.04	3.97	3.92	3.87	3.83	3.79	3.76
11	7.39	5.70	4.99	4.59	4.34	4.15	4.02	3.91	3.83	3.76	3.70	3.65	3.61	3.57	3.54
12	7.19	5.52	4.81	4.42	4.16	3.98	3.85	3.74	3.66	3.59	3.53	3.48	3.44	3.40	3.37
13	7.02	5.37	4.67	4.28	4.02	3.84	3.71	3.60	3.52	3.45	3.39	3.34	3.30	3.26	3.23
14	6.89	5.24	4.55	4.16	3.90	3.72	3.59	3.48	3.40	3.33	3.27	3.23	3.18	3.15	3.11
15	6.77	5.14	4.45	4.06	3.81	3.63	3.49	3.39	3.30	3.23	3.18	3.13	3.09	3.05	3.02
16	6.67	5.05	4.36	3.97	3.72	3.54	3.41	3.30	3.22	3.15	3.09	3.05	3.00	2.97	2.93
17	6.59	4.97	4.29	3.90	3.65	3.47	3.34	3.23	3.15	3.08	3.02	2.97	2.93	2.89	2.86
18	6.51	4.90	4.22	3.84	3.59	3.41	3.27	3.17	3.09	3.02	2.96	2.91	2.87	2.83	2.80
19	6.45	4.84	4.16	3.78	3.53	3.35	3.22	3.12	3.03	2.96	2.91	2.86	2.81	2.78	2.74
20	6.39	4.79	4.11	3.73	3.48	3.30	3.17	3.07	2.98	2.91	2.86	2.81	2.77	2.73	2.70
21	6.34	4.74	4.07	3.69	3.44	3.26	3.13	3.02	2.94	2.87	2.81	2.76	2.72	2.68	2.65
22	6.29	4.70	4.03	3.65	3.40	3.22	3.09	2.99	2.90	2.83	2.77	2.73	2.68	2.65	2.61
23	6.25	4.66	3.99	3.61	3.36	3.19	3.05	2.95	2.87	2.80	2.74	2.69	2.65	2.61	2.58
24	6.21	4.63	3.96	3.58	3.33	3.15	3.02	2.92	2.83	2.77	2.71	2.66	2.62	2.58	2.55
25	6.18	4.59	3.93	3.55	3.30	3.13	2.99	2.89	2.81	2.74	2.68	2.63	2.59	2.55	2.52
26	6.14	4.56	3.90	3.52	3.28	3.10	2.97	2.86	2.78	2.71	2.65	2.60	2.56	2.52	2.49
27	6.11	4.54	3.87	3.50	3.25	3.07	2.94	2.84	2.76	2.69	2.63	2.58	2.54	2.50	2.46
28	6.09	4.51	3.85	3.47	3.23	3.05	2.92	2.82	2.73	2.66	2.61	2.56	2.51	2.48	2.44
29	6.06	4.49	3.83	3.45	3.21	3.03	2.90	2.80	2.71	2.64	2.58	2.54	2.49	2.45	2.42
30	6.04	4.47	3.81	3.43	3.19	3.01	2.88	2.78	2.69	2.62	2.57	2.52	2.47	2.44	2.40
35	5.94	4.38	3.73	3.35	3.11	2.93	2.80	2.70	2.61	2.55	2.49	2.44	2.39	2.36	2.32
40	5.87	4.32	3.67	3.30	3.05	2.88	2.74	2.64	2.56	2.49	2.43	2.38	2.34	2.30	2.26
45	5.82	4.27	3.62	3.25	3.01	2.83	2.70	2.60	2.51	2.44	2.39	2.34	2.29	2.25	2.22
50	5.78	4.23	3.59	3.22	2.97	2.80	2.67	2.56	2.48	2.41	2.35	2.30	2.26	2.22	2.18
55	5.74	4.20	3.56	3.19	2.94	2.77	2.64	2.54	2.45	2.38	2.32	2.27	2.23	2.19	2.16
60	5.71	4.18	3.53	3.16	2.92	2.75	2.62	2.51	2.43	2.36	2.30	2.25	2.21	2.17	2.13
70	5.67	4.14	3.49	3.13	2.88	2.71	2.58	2.48	2.39	2.32	2.26	2.21	2.17	2.13	2.10
80	5.64	4.11	3.47	3.10	2.86	2.68	2.55	2.45	2.37	2.30	2.24	2.19	2.14	2.10	2.07
90	5.61	4.09	3.45	3.08	2.84	2.66	2.53	2.43	2.35	2.28	2.22	2.17	2.12	2.08	2.05
100	5.59	4.07	3.43	3.06	2.82	2.65	2.52	2.41	2.33	2.26	2.20	2.15	2.10	2.07	2.03
110	5.57	4.05	3.41	3.05	2.81	2.63	2.50	2.40	2.32	2.25	2.19	2.14	2.09	2.05	2.02
120	5.56	4.04	3.40	3.04	2.80	2.62	2.49	2.39	2.30	2.23	2.18	2.12	2.08	2.04	2.01

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Table 17-1. Percentiles of *F*-Distribution for $(1-\alpha) = .99$

$\nu_2 \backslash \nu_1$	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	4052.18	4999.50	5403.35	5624.58	5763.65	5858.99	5928.36	5981.07	6022.47	6055.85	6083.32	6106.32	6125.86	6142.67	6157.28
2	98.50	99.00	99.17	99.25	99.30	99.33	99.36	99.37	99.39	99.40	99.41	99.42	99.42	99.43	99.43
3	34.12	30.82	29.46	28.71	28.24	27.91	27.67	27.49	27.35	27.23	27.13	27.05	26.98	26.92	26.87
4	21.20	18.00	16.69	15.98	15.52	15.21	14.98	14.80	14.66	14.55	14.45	14.37	14.31	14.25	14.20
5	16.26	13.27	12.06	11.39	10.97	10.67	10.46	10.29	10.16	10.05	9.96	9.89	9.82	9.77	9.72
6	13.75	10.92	9.78	9.15	8.75	8.47	8.26	8.10	7.98	7.87	7.79	7.72	7.66	7.60	7.56
7	12.25	9.55	8.45	7.85	7.46	7.19	6.99	6.84	6.72	6.62	6.54	6.47	6.41	6.36	6.31
8	11.26	8.65	7.59	7.01	6.63	6.37	6.18	6.03	5.91	5.81	5.73	5.67	5.61	5.56	5.52
9	10.56	8.02	6.99	6.42	6.06	5.80	5.61	5.47	5.35	5.26	5.18	5.11	5.05	5.01	4.96
10	10.04	7.56	6.55	5.99	5.64	5.39	5.20	5.06	4.94	4.85	4.77	4.71	4.65	4.60	4.56
11	9.65	7.21	6.22	5.67	5.32	5.07	4.89	4.74	4.63	4.54	4.46	4.40	4.34	4.29	4.25
12	9.33	6.93	5.95	5.41	5.06	4.82	4.64	4.50	4.39	4.30	4.22	4.16	4.10	4.05	4.01
13	9.07	6.70	5.74	5.21	4.86	4.62	4.44	4.30	4.19	4.10	4.02	3.96	3.91	3.86	3.82
14	8.86	6.51	5.56	5.04	4.69	4.46	4.28	4.14	4.03	3.94	3.86	3.80	3.75	3.70	3.66
15	8.68	6.36	5.42	4.89	4.56	4.32	4.14	4.00	3.89	3.80	3.73	3.67	3.61	3.56	3.52
16	8.53	6.23	5.29	4.77	4.44	4.20	4.03	3.89	3.78	3.69	3.62	3.55	3.50	3.45	3.41
17	8.40	6.11	5.18	4.67	4.34	4.10	3.93	3.79	3.68	3.59	3.52	3.46	3.40	3.35	3.31
18	8.29	6.01	5.09	4.58	4.25	4.01	3.84	3.71	3.60	3.51	3.43	3.37	3.32	3.27	3.23
19	8.18	5.93	5.01	4.50	4.17	3.94	3.77	3.63	3.52	3.43	3.36	3.30	3.24	3.19	3.15
20	8.10	5.85	4.94	4.43	4.10	3.87	3.70	3.56	3.46	3.37	3.29	3.23	3.18	3.13	3.09
21	8.02	5.78	4.87	4.37	4.04	3.81	3.64	3.51	3.40	3.31	3.24	3.17	3.12	3.07	3.03
22	7.95	5.72	4.82	4.31	3.99	3.76	3.59	3.45	3.35	3.26	3.18	3.12	3.07	3.02	2.98
23	7.88	5.66	4.76	4.26	3.94	3.71	3.54	3.41	3.30	3.21	3.14	3.07	3.02	2.97	2.93
24	7.82	5.61	4.72	4.22	3.90	3.67	3.50	3.36	3.26	3.17	3.09	3.03	2.98	2.93	2.89
25	7.77	5.57	4.68	4.18	3.85	3.63	3.46	3.32	3.22	3.13	3.06	2.99	2.94	2.89	2.85
26	7.72	5.53	4.64	4.14	3.82	3.59	3.42	3.29	3.18	3.09	3.02	2.96	2.90	2.86	2.81
27	7.68	5.49	4.60	4.11	3.78	3.56	3.39	3.26	3.15	3.06	2.99	2.93	2.87	2.82	2.78
28	7.64	5.45	4.57	4.07	3.75	3.53	3.36	3.23	3.12	3.03	2.96	2.90	2.84	2.79	2.75
29	7.60	5.42	4.54	4.04	3.73	3.50	3.33	3.20	3.09	3.00	2.93	2.87	2.81	2.77	2.73
30	7.56	5.39	4.51	4.02	3.70	3.47	3.30	3.17	3.07	2.98	2.91	2.84	2.79	2.74	2.70
35	7.42	5.27	4.40	3.91	3.59	3.37	3.20	3.07	2.96	2.88	2.80	2.74	2.69	2.64	2.60
40	7.31	5.18	4.31	3.83	3.51	3.29	3.12	2.99	2.89	2.80	2.73	2.66	2.61	2.56	2.52
45	7.23	5.11	4.25	3.77	3.45	3.23	3.07	2.94	2.83	2.74	2.67	2.61	2.55	2.51	2.46
50	7.17	5.06	4.20	3.72	3.41	3.19	3.02	2.89	2.78	2.70	2.63	2.56	2.51	2.46	2.42
55	7.12	5.01	4.16	3.68	3.37	3.15	2.98	2.85	2.75	2.66	2.59	2.53	2.47	2.42	2.38
60	7.08	4.98	4.13	3.65	3.34	3.12	2.95	2.82	2.72	2.63	2.56	2.50	2.44	2.39	2.35
70	7.01	4.92	4.07	3.60	3.29	3.07	2.91	2.78	2.67	2.59	2.51	2.45	2.40	2.35	2.31
80	6.96	4.88	4.04	3.56	3.26	3.04	2.87	2.74	2.64	2.55	2.48	2.42	2.36	2.31	2.27
90	6.93	4.85	4.01	3.53	3.23	3.01	2.84	2.72	2.61	2.52	2.45	2.39	2.33	2.29	2.24
100	6.90	4.82	3.98	3.51	3.21	2.99	2.82	2.69	2.59	2.50	2.43	2.37	2.31	2.27	2.22
110	6.87	4.80	3.96	3.49	3.19	2.97	2.81	2.68	2.57	2.49	2.41	2.35	2.30	2.25	2.21
120	6.85	4.79	3.95	3.48	3.17	2.96	2.79	2.66	2.56	2.47	2.40	2.34	2.28	2.23	2.19

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Table 17-2. Percentiles of Chi-Square Distribution for *df* = 1(1)30(5)100

df \ (1−α)	0.90	0.95	0.975	0.98	0.99
1	2.706	3.841	5.024	5.412	6.635
2	4.605	5.991	7.378	7.824	9.210
3	6.251	7.815	9.348	9.837	11.345
4	7.779	9.488	11.143	11.668	13.277
5	9.236	11.070	12.833	13.388	15.086
6	10.645	12.592	14.449	15.033	16.812
7	12.017	14.067	16.013	16.622	18.475
8	13.362	15.507	17.535	18.168	20.090
9	14.684	16.919	19.023	19.679	21.666
10	15.987	18.307	20.483	21.161	23.209
11	17.275	19.675	21.920	22.618	24.725
12	18.549	21.026	23.337	24.054	26.217
13	19.812	22.362	24.736	25.472	27.688
14	21.064	23.685	26.119	26.873	29.141
15	22.307	24.996	27.488	28.259	30.578
16	23.542	26.296	28.845	29.633	32.000
17	24.769	27.587	30.191	30.995	33.409
18	25.989	28.869	31.526	32.346	34.805
19	27.204	30.144	32.852	33.687	36.191
20	28.412	31.410	34.170	35.020	37.566
21	29.615	32.671	35.479	36.343	38.932
22	30.813	33.924	36.781	37.659	40.289
23	32.007	35.172	38.076	38.968	41.638
24	33.196	36.415	39.364	40.270	42.980
25	34.382	37.652	40.646	41.566	44.314
26	35.563	38.885	41.923	42.856	45.642
27	36.741	40.113	43.195	44.140	46.963
28	37.916	41.337	44.461	45.419	48.278
29	39.087	42.557	45.722	46.693	49.588
30	40.256	43.773	46.979	47.962	50.892
35	46.059	49.802	53.203	54.244	57.342
40	51.805	55.758	59.342	60.436	63.691
45	57.505	61.656	65.410	66.555	69.957
50	63.167	67.505	71.420	72.613	76.154
55	68.796	73.311	77.380	78.619	82.292
60	74.397	79.082	83.298	84.580	88.379
65	79.973	84.821	89.177	90.501	94.422
70	85.527	90.531	95.023	96.388	100.425
75	91.061	96.217	100.839	102.243	106.393
80	96.578	101.879	106.629	108.069	112.329
85	102.079	107.522	112.393	113.871	118.236
90	107.565	113.145	118.136	119.648	124.116
95	113.038	118.752	123.858	125.405	129.973
100	118.498	124.342	129.561	131.142	135.807

Footnote. The notation *df* = 1(1)30(5)100 is a shorthand for *df* from 1 to 30 by unit steps, then from 35 to 100 by 5's

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Table 17-3. Upper Tolerance Limit Factors With γ Coverage for n = 4(1)30(5)100

	95% Confidence			99% Confidence		
n \ γ	**0.90**	**0.95**	**0.99**	**0.90**	**0.95**	**0.99**
4	4.162	5.144	7.042	7.380	9.083	12.387
5	3.407	4.203	5.741	5.362	6.578	8.939
6	3.006	3.708	5.062	4.411	5.406	7.335
7	2.755	3.399	4.642	3.859	4.728	6.412
8	2.582	3.187	4.354	3.497	4.285	5.812
9	2.454	3.031	4.143	3.240	3.972	5.389
10	2.355	2.911	3.981	3.048	3.738	5.074
11	2.275	2.815	3.852	2.898	3.556	4.829
12	2.210	2.736	3.747	2.777	3.410	4.633
13	2.155	2.671	3.659	2.677	3.290	4.472
14	2.109	2.614	3.585	2.593	3.189	4.337
15	2.068	2.566	3.520	2.521	3.102	4.222
16	2.033	2.524	3.464	2.459	3.028	4.123
17	2.002	2.486	3.414	2.405	2.963	4.037
18	1.974	2.453	3.370	2.357	2.905	3.960
19	1.949	2.423	3.331	2.314	2.854	3.892
20	1.926	2.396	3.295	2.276	2.808	3.832
21	1.905	2.371	3.263	2.241	2.766	3.777
22	1.886	2.349	3.233	2.209	2.729	3.727
23	1.869	2.328	3.206	2.180	2.694	3.681
24	1.853	2.309	3.181	2.154	2.662	3.640
25	1.838	2.292	3.158	2.129	2.633	3.601
26	1.824	2.275	3.136	2.106	2.606	3.566
27	1.811	2.260	3.116	2.085	2.581	3.533
28	1.799	2.246	3.098	2.065	2.558	3.502
29	1.788	2.232	3.080	2.047	2.536	3.473
30	1.777	2.220	3.064	2.030	2.515	3.447
35	1.732	2.167	2.995	1.957	2.430	3.334
40	1.697	2.125	2.941	1.902	2.364	3.249
45	1.669	2.092	2.898	1.857	2.312	3.180
50	1.646	2.065	2.862	1.821	2.269	3.125
55	1.626	2.042	2.833	1.790	2.233	3.078
60	1.609	2.022	2.807	1.764	2.202	3.038
65	1.594	2.005	2.785	1.741	2.176	3.004
70	1.581	1.990	2.765	1.722	2.153	2.974
75	1.570	1.976	2.748	1.704	2.132	2.947
80	1.559	1.964	2.733	1.688	2.114	2.924
85	1.550	1.954	2.719	1.674	2.097	2.902
90	1.542	1.944	2.706	1.661	2.082	2.883
95	1.534	1.935	2.695	1.650	2.069	2.866
100	1.527	1.927	2.684	1.639	2.056	2.850

Source of algorithm used to compute table: Odeh & Owen (1980)
Footnote. The notation n = 4(1)30(5)100 is a shorthand for n from 4 to 30 by unit steps, then from 35 to 100 by 5's

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Table 17-4. Minimum Coverage of Non-Parametric Upper Tolerance Limit for n = 4(1)30(5)100

	Maximum		2nd Largest	
n\(1−α)	0.95	0.99	0.95	0.99
4	0.473	0.316	0.248	0.140
5	0.549	0.398	0.342	0.222
6	0.607	0.464	0.418	0.294
7	0.652	0.518	0.479	0.356
8	0.688	0.562	0.529	0.410
9	0.717	0.599	0.570	0.455
10	0.741	0.631	0.605	0.495
11	0.762	0.658	0.635	0.530
12	0.779	0.681	0.661	0.560
13	0.794	0.702	0.683	0.587
14	0.807	0.720	0.703	0.610
15	0.819	0.736	0.720	0.632
16	0.829	0.750	0.736	0.651
17	0.838	0.763	0.749	0.668
18	0.847	0.774	0.762	0.683
19	0.854	0.785	0.773	0.698
20	0.861	0.794	0.783	0.711
21	0.867	0.803	0.793	0.723
22	0.873	0.811	0.801	0.734
23	0.878	0.819	0.809	0.744
24	0.883	0.825	0.817	0.753
25	0.887	0.832	0.823	0.762
26	0.891	0.838	0.830	0.770
27	0.895	0.843	0.836	0.778
28	0.899	0.848	0.841	0.785
29	0.902	0.853	0.846	0.792
30	0.905	0.858	0.851	0.798
35	0.918	0.877	0.871	0.824
40	0.928	0.891	0.886	0.845
45	0.936	0.903	0.898	0.861
50	0.942	0.912	0.908	0.874
55	0.947	0.920	0.916	0.885
60	0.951	0.926	0.923	0.894
65	0.955	0.932	0.929	0.902
70	0.958	0.936	0.934	0.908
75	0.961	0.940	0.938	0.914
80	0.963	0.944	0.942	0.919
85	0.965	0.947	0.945	0.924
90	0.967	0.950	0.948	0.928
95	0.969	0.953	0.951	0.932
100	0.970	0.955	0.953	0.935

Footnotes. Maximum, 2nd Largest refer to Largest and next largest sample values
The notation *n* = 4(1)30(5)100 is a shorthand for *n* from 4 to 30 by unit steps, then from 35 to 100 by 5's

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Table 17-5. Significance Levels (α) for Mann-Kendall Trend Test for *n* = 4(1)10

n = 4		n = 5		n = 6		n = 7		n = 8		n = 9		n = 10	
S	α	S	α	S	α	S	α	S	α	S	α	S	α
0	0.6250	0	0.5920	1	0.5000	1	0.5000	0	0.5480	0	0.5400	1	0.5000
2	0.3750	2	0.4080	3	0.3600	3	0.3860	2	0.4520	2	0.4600	3	0.4310
4	0.1670	4	0.2420	5	0.2350	5	0.2810	4	0.3600	4	0.3810	5	0.3640
6	0.0420	6	0.1170	7	0.1360	7	0.1910	6	0.2740	6	0.3060	7	0.3000
		8	0.0420	9	0.0680	9	0.1190	8	0.1990	8	0.2380	9	0.2420
		10	0.0083	11	0.0280	11	0.0680	10	0.1380	10	0.1790	11	0.1900
				13	0.0083	13	0.0350	12	0.0890	12	0.1300	13	0.1460
				15	0.0014	15	0.0150	14	0.0540	14	0.0900	15	0.1080
						17	0.0054	16	0.0310	16	0.0600	17	0.0780
						19	0.0014	18	0.0160	18	0.0380	19	0.0540
						21	0.0002	20	0.0071	20	0.0220	21	0.0360
								22	0.0028	22	0.0120	23	0.0230
								24	0.0009	24	0.0063	25	0.0140
								26	0.0002	26	0.0029	27	0.0083
								28	0.0000	28	0.0012	29	0.0046
										30	0.0004	31	0.0023
										32	0.0001	33	0.0011
										34	0.0000	35	0.0005
										36	0.0000	37	0.0002
												39	0.0001
												41	0.0000
												43	0.0000
												45	0.0000

Source: Gilbert (1987)
Footnote: Notation *n* = 4(1)10 is shorthand for *n* from 4 to 10 by unit steps

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Table 18-1. Confidence Levels of Non-Parametric Prediction Limits for Next *m* Values (PL = *j*th Order Statistic) for *n* = 4(1)60

	j = n				j = n-1				j = n-2			
n	**m = 1**	**m = 2**	**m = 3**	**m = 4**	**m = 1**	**m = 2**	**m = 3**	**m = 4**	**m = 1**	**m = 2**	**m = 3**	**m = 4**
4	0.800	0.667	0.571	0.500	0.600	0.400	0.286	0.214	0.400	0.200	0.114	0.071
5	0.833	0.714	0.625	0.556	0.667	0.476	0.357	0.278	0.500	0.286	0.179	0.119
6	0.857	0.750	0.667	0.600	0.714	0.536	0.417	0.333	0.571	0.357	0.238	0.167
7	0.875	0.778	0.700	0.636	0.750	0.583	0.467	0.382	0.625	0.417	0.292	0.212
8	0.889	0.800	0.727	0.667	0.778	0.622	0.509	0.424	0.667	0.467	0.339	0.255
9	0.900	0.818	0.750	0.692	0.800	0.655	0.545	0.462	0.700	0.509	0.382	0.294
10	0.909	0.833	0.769	0.714	0.818	0.682	0.577	0.495	0.727	0.545	0.420	0.330
11	0.917	0.846	0.786	0.733	0.833	0.705	0.604	0.524	0.750	0.577	0.453	0.363
12	0.923	0.857	0.800	0.750	0.846	0.725	0.629	0.550	0.769	0.604	0.484	0.393
13	0.929	0.867	0.812	0.765	0.857	0.743	0.650	0.574	0.786	0.629	0.511	0.421
14	0.933	0.875	0.824	0.778	0.867	0.758	0.669	0.595	0.800	0.650	0.535	0.446
15	0.938	0.882	0.833	0.789	0.875	0.772	0.686	0.614	0.812	0.669	0.558	0.470
16	0.941	0.889	0.842	0.800	0.882	0.784	0.702	0.632	0.824	0.686	0.578	0.491
17	0.944	0.895	0.850	0.810	0.889	0.795	0.716	0.648	0.833	0.702	0.596	0.511
18	0.947	0.900	0.857	0.818	0.895	0.805	0.729	0.662	0.842	0.716	0.614	0.530
19	0.950	0.905	0.864	0.826	0.900	0.814	0.740	0.676	0.850	0.729	0.629	0.547
20	0.952	0.909	0.870	0.833	0.905	0.823	0.751	0.688	0.857	0.740	0.644	0.563
21	0.955	0.913	0.875	0.840	0.909	0.830	0.761	0.700	0.864	0.751	0.657	0.578
22	0.957	0.917	0.880	0.846	0.913	0.837	0.770	0.711	0.870	0.761	0.670	0.592
23	0.958	0.920	0.885	0.852	0.917	0.843	0.778	0.721	0.875	0.770	0.681	0.605
24	0.960	0.923	0.889	0.857	0.920	0.849	0.786	0.730	0.880	0.778	0.692	0.618
25	0.962	0.926	0.893	0.862	0.923	0.855	0.794	0.739	0.885	0.786	0.702	0.629
26	0.963	0.929	0.897	0.867	0.926	0.860	0.800	0.747	0.889	0.794	0.712	0.640
27	0.964	0.931	0.900	0.871	0.929	0.865	0.807	0.755	0.893	0.800	0.720	0.651
28	0.966	0.933	0.903	0.875	0.931	0.869	0.813	0.762	0.897	0.807	0.729	0.660
29	0.967	0.935	0.906	0.879	0.933	0.873	0.819	0.769	0.900	0.813	0.737	0.670

Footnotes: Notation *n* = 4(1)60 is shorthand for n from 4 to 60 by unit steps
PL = Prediction Limit

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Table 18-1. Confidence Levels of Non-Parametric Prediction Limits for Next *m* Values (PL = *j*th Order Statistic) for *n* = 4(1)60

	j = n				j = n-1				j = n-2			
n	**m = 1**	**m = 2**	**m = 3**	**m = 4**	**m = 1**	**m = 2**	**m = 3**	**m = 4**	**m = 1**	**m = 2**	**m = 3**	**m = 4**
30	0.968	0.938	0.909	0.882	0.935	0.877	0.824	0.775	0.903	0.819	0.744	0.678
31	0.969	0.939	0.912	0.886	0.938	0.881	0.829	0.782	0.906	0.824	0.751	0.687
32	0.970	0.941	0.914	0.889	0.939	0.884	0.834	0.787	0.909	0.829	0.758	0.695
33	0.971	0.943	0.917	0.892	0.941	0.887	0.838	0.793	0.912	0.834	0.764	0.702
34	0.971	0.944	0.919	0.895	0.943	0.890	0.842	0.798	0.914	0.838	0.770	0.709
35	0.972	0.946	0.921	0.897	0.944	0.893	0.846	0.803	0.917	0.842	0.776	0.716
36	0.973	0.947	0.923	0.900	0.946	0.896	0.850	0.808	0.919	0.846	0.781	0.723
37	0.974	0.949	0.925	0.902	0.947	0.899	0.854	0.812	0.921	0.850	0.786	0.729
38	0.974	0.950	0.927	0.905	0.949	0.901	0.857	0.816	0.923	0.854	0.791	0.735
39	0.975	0.951	0.929	0.907	0.950	0.904	0.861	0.821	0.925	0.857	0.796	0.741
40	0.976	0.952	0.930	0.909	0.951	0.906	0.864	0.825	0.927	0.861	0.801	0.746
41	0.976	0.953	0.932	0.911	0.952	0.908	0.867	0.828	0.929	0.864	0.805	0.751
42	0.977	0.955	0.933	0.913	0.953	0.910	0.870	0.832	0.930	0.867	0.809	0.756
43	0.977	0.956	0.935	0.915	0.955	0.912	0.872	0.835	0.932	0.870	0.813	0.761
44	0.978	0.957	0.936	0.917	0.956	0.914	0.875	0.839	0.933	0.872	0.817	0.766
45	0.978	0.957	0.938	0.918	0.957	0.916	0.878	0.842	0.935	0.875	0.820	0.770
46	0.979	0.958	0.939	0.920	0.957	0.918	0.880	0.845	0.936	0.878	0.824	0.774
47	0.979	0.959	0.940	0.922	0.958	0.919	0.882	0.848	0.938	0.880	0.827	0.779
48	0.980	0.960	0.941	0.923	0.959	0.921	0.885	0.851	0.939	0.882	0.831	0.783
49	0.980	0.961	0.942	0.925	0.960	0.922	0.887	0.853	0.940	0.885	0.834	0.786
50	0.980	0.962	0.943	0.926	0.961	0.924	0.889	0.856	0.941	0.887	0.837	0.790
51	0.981	0.962	0.944	0.927	0.962	0.925	0.891	0.859	0.942	0.889	0.840	0.794
52	0.981	0.963	0.945	0.929	0.962	0.927	0.893	0.861	0.943	0.891	0.842	0.797
53	0.981	0.964	0.946	0.930	0.963	0.928	0.895	0.863	0.944	0.893	0.845	0.801
54	0.982	0.964	0.947	0.931	0.964	0.929	0.897	0.866	0.945	0.895	0.848	0.804
55	0.982	0.965	0.948	0.932	0.964	0.930	0.898	0.868	0.946	0.897	0.850	0.807
56	0.982	0.966	0.949	0.933	0.965	0.932	0.900	0.870	0.947	0.898	0.853	0.810
57	0.983	0.966	0.950	0.934	0.966	0.933	0.902	0.872	0.948	0.900	0.855	0.813
58	0.983	0.967	0.951	0.935	0.966	0.934	0.903	0.874	0.949	0.902	0.857	0.816
59	0.983	0.967	0.952	0.937	0.967	0.935	0.905	0.876	0.950	0.903	0.860	0.819
60	0.984	0.968	0.952	0.938	0.967	0.936	0.906	0.878	0.951	0.905	0.862	0.821

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Table 18-2. Confidence Levels for Non-Parametric Prediction Limit on Future Median of Order 3 (PL = *j*th Order Statistic) for n = 4(1)60

n	j = n	j = n-1	j = n-2
4	0.857	0.629	0.371
5	0.893	0.714	0.500
6	0.917	0.774	0.595
7	0.933	0.817	0.667
8	0.945	0.848	0.721
9	0.955	0.873	0.764
10	0.962	0.892	0.797
11	0.967	0.907	0.824
12	0.971	0.919	0.846
13	0.975	0.929	0.864
14	0.978	0.937	0.879
15	0.980	0.944	0.892
16	0.982	0.949	0.903
17	0.984	0.954	0.912
18	0.986	0.959	0.920
19	0.987	0.962	0.927
20	0.988	0.966	0.933
21	0.989	0.968	0.939
22	0.990	0.971	0.943
23	0.991	0.973	0.948
24	0.991	0.975	0.951
25	0.992	0.977	0.955
26	0.993	0.978	0.958
27	0.993	0.980	0.961
28	0.994	0.981	0.963
29	0.994	0.982	0.965
30	0.994	0.983	0.967
31	0.995	0.984	0.969
32	0.995	0.985	0.971
33	0.995	0.986	0.973
34	0.995	0.987	0.974
35	0.996	0.987	0.975
36	0.996	0.988	0.977
37	0.996	0.989	0.978
38	0.996	0.989	0.979
39	0.997	0.990	0.980
40	0.997	0.990	0.981
41	0.997	0.991	0.982
42	0.997	0.991	0.982
43	0.997	0.991	0.983
44	0.997	0.992	0.984
45	0.997	0.992	0.985
46	0.997	0.992	0.985
47	0.998	0.993	0.986
48	0.998	0.993	0.986
49	0.998	0.993	0.987
50	0.998	0.994	0.987
51	0.998	0.994	0.988
52	0.998	0.994	0.988
53	0.998	0.994	0.989
54	0.998	0.994	0.989
55	0.998	0.995	0.989
56	0.998	0.995	0.990
57	0.998	0.995	0.990
58	0.998	0.995	0.990
59	0.998	0.995	0.991
60	0.998	0.995	0.991

Footnotes: Notation *n* = 4(1)60 is shorthand for n from 4 to 60 by unit steps;PL = Prediction Limit

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D STATISTICAL TABLES

D.2 TABLES FROM CHAPTER 19: INTERWELL PREDICTION LIMITS FOR FUTURE VALUES

TABLE 19-1 κ-Multipliers for 1-of-2 Interwell Prediction Limits on Observations.....D-34

TABLE 19-2 κ-Multipliers for 1-of-3 Interwell Prediction Limits on Observations.....D-43

TABLE 19-3 κ-Multipliers for 1-of-4 Interwell Prediction Limits on Observations.....D-52

TABLE 19-4 κ-Multipliers for Mod. Cal. Interwell Prediction Limits on Observations.....D-61

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Table 19-1. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Observations (1 COC, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**0.78**	**0.67**	**0.61**	**0.59**	**0.57**	**0.54**	**0.53**	**0.52**	**0.51**	**0.51**	**0.50**	**0.50**	**0.50**	**0.50**	**0.49**	**0.49**	**0.49**	**0.49**	**0.49**	**0.49**
2	**1.21**	**1.03**	**0.95**	**0.90**	**0.88**	**0.84**	**0.82**	**0.81**	**0.80**	**0.79**	**0.79**	**0.78**	**0.78**	**0.77**	**0.77**	**0.77**	**0.77**	**0.76**	**0.76**	**0.76**
3	**1.47**	**1.23**	**1.13**	**1.08**	**1.05**	**1.01**	**0.98**	**0.96**	**0.95**	**0.94**	**0.94**	**0.93**	**0.93**	**0.92**	**0.92**	**0.92**	**0.91**	**0.91**	**0.91**	**0.91**
4	**1.65**	**1.37**	**1.26**	**1.20**	**1.16**	**1.12**	**1.09**	**1.07**	**1.06**	**1.05**	**1.04**	**1.03**	**1.03**	**1.02**	**1.02**	**1.01**	**1.01**	**1.01**	**1.00**	**1.00**
5	**1.79**	**1.48**	**1.36**	**1.29**	**1.25**	**1.20**	**1.17**	**1.15**	**1.13**	**1.12**	**1.11**	**1.11**	**1.10**	**1.10**	**1.09**	**1.09**	**1.08**	**1.08**	**1.08**	**1.07**
8	**2.09**	**1.71**	**1.56**	**1.48**	**1.43**	**1.37**	**1.34**	**1.31**	**1.29**	**1.28**	**1.27**	**1.26**	**1.25**	**1.25**	**1.24**	**1.24**	**1.23**	**1.23**	**1.22**	**1.22**
12	**2.34**	**1.90**	**1.73**	**1.64**	**1.58**	**1.51**	**1.47**	**1.44**	**1.42**	**1.40**	**1.39**	**1.39**	**1.38**	**1.37**	**1.36**	**1.36**	**1.35**	**1.35**	**1.34**	**1.34**
16	2.52	**2.03**	**1.85**	**1.75**	**1.68**	**1.61**	**1.56**	**1.53**	**1.51**	**1.49**	**1.48**	**1.47**	**1.46**	**1.45**	**1.44**	**1.44**	**1.43**	**1.43**	**1.42**	**1.42**
20	2.65	**2.14**	**1.94**	**1.83**	**1.76**	**1.68**	**1.64**	**1.60**	**1.57**	**1.56**	**1.54**	**1.53**	**1.53**	**1.52**	**1.51**	**1.50**	**1.50**	**1.49**	**1.49**	**1.48**
30	2.89	**2.32**	**2.10**	**1.98**	**1.90**	**1.81**	**1.76**	**1.72**	**1.69**	**1.67**	**1.66**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**	**1.60**	**1.59**	**1.59**
40	3.06	**2.45**	**2.21**	**2.08**	**2.00**	**1.90**	**1.85**	**1.80**	**1.78**	**1.75**	**1.74**	**1.73**	**1.72**	**1.70**	**1.69**	**1.69**	**1.68**	**1.67**	**1.67**	**1.66**
50	3.19	2.54	**2.29**	**2.16**	**2.08**	**1.97**	**1.91**	**1.87**	**1.84**	**1.82**	**1.80**	**1.79**	**1.78**	**1.76**	**1.75**	**1.74**	**1.74**	**1.73**	**1.72**	**1.72**
60	3.29	2.62	**2.36**	**2.22**	**2.13**	**2.03**	**1.97**	**1.92**	**1.89**	**1.86**	**1.85**	**1.83**	**1.82**	**1.81**	**1.80**	**1.79**	**1.78**	**1.78**	**1.77**	**1.76**
75	3.41	2.71	*2.44*	**2.30**	**2.21**	**2.10**	**2.03**	**1.98**	**1.95**	**1.92**	**1.91**	**1.89**	**1.88**	**1.86**	**1.85**	**1.84**	**1.84**	**1.83**	**1.82**	**1.81**
100	3.57	2.83	2.55	**2.40**	**2.30**	**2.18**	**2.11**	**2.06**	**2.02**	**2.00**	**1.98**	**1.96**	**1.95**	**1.94**	**1.92**	**1.91**	**1.91**	**1.90**	**1.89**	**1.88**
125	3.69	2.92	2.63	*2.47*	**2.37**	**2.25**	**2.18**	**2.12**	**2.08**	**2.06**	**2.04**	**2.02**	**2.01**	**1.99**	**1.98**	**1.97**	**1.96**	**1.95**	**1.94**	**1.93**
150	3.79	3.00	2.69	*2.53*	*2.42*	**2.30**	**2.23**	**2.17**	**2.13**	**2.10**	**2.08**	**2.07**	**2.05**	**2.03**	**2.02**	**2.01**	**2.00**	**1.99**	**1.98**	**1.97**
175	3.87	3.06	2.75	2.58	*2.47*	**2.34**	**2.27**	**2.21**	**2.17**	**2.14**	**2.12**	**2.10**	**2.09**	**2.07**	**2.05**	**2.04**	**2.04**	**2.03**	**2.02**	**2.01**
200	3.93	3.11	2.79	2.62	*2.51*	**2.38**	**2.30**	**2.24**	**2.20**	**2.17**	**2.15**	**2.13**	**2.12**	**2.10**	**2.09**	**2.07**	**2.07**	**2.06**	**2.05**	**2.04**

Table 19-1. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Observations (1 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.21**	**1.03**	**0.95**	**0.90**	**0.88**	**0.84**	**0.82**	**0.81**	**0.80**	**0.79**	**0.79**	**0.78**	**0.78**	**0.77**	**0.77**	**0.77**	**0.77**	**0.76**	**0.76**	**0.76**
2	**1.65**	**1.37**	**1.26**	**1.20**	**1.16**	**1.12**	**1.09**	**1.07**	**1.06**	**1.05**	**1.04**	**1.03**	**1.03**	**1.02**	**1.02**	**1.01**	**1.01**	**1.01**	**1.00**	**1.00**
3	**1.91**	**1.57**	**1.44**	**1.37**	**1.32**	**1.27**	**1.24**	**1.21**	**1.19**	**1.18**	**1.18**	**1.17**	**1.16**	**1.16**	**1.15**	**1.15**	**1.14**	**1.14**	**1.14**	**1.13**
4	**2.09**	**1.71**	**1.56**	**1.48**	**1.43**	**1.37**	**1.34**	**1.31**	**1.29**	**1.28**	**1.27**	**1.26**	**1.25**	**1.25**	**1.24**	**1.24**	**1.23**	**1.23**	**1.22**	**1.22**
5	**2.23**	**1.82**	**1.65**	**1.57**	**1.51**	**1.45**	**1.41**	**1.38**	**1.36**	**1.35**	**1.34**	**1.33**	**1.32**	**1.31**	**1.31**	**1.30**	**1.30**	**1.30**	**1.29**	**1.29**
8	**2.52**	**2.03**	**1.85**	**1.75**	**1.68**	**1.61**	**1.56**	**1.53**	**1.51**	**1.49**	**1.48**	**1.47**	**1.46**	**1.45**	**1.44**	**1.44**	**1.43**	**1.43**	**1.42**	**1.42**
12	2.76	**2.22**	**2.01**	**1.90**	**1.83**	**1.74**	**1.69**	**1.65**	**1.63**	**1.61**	**1.60**	**1.59**	**1.58**	**1.57**	**1.56**	**1.55**	**1.55**	**1.54**	**1.53**	**1.53**
16	2.93	**2.35**	**2.12**	**2.00**	**1.93**	**1.83**	**1.78**	**1.74**	**1.71**	**1.69**	**1.68**	**1.67**	**1.66**	**1.64**	**1.63**	**1.63**	**1.62**	**1.62**	**1.61**	**1.60**
20	3.06	**2.45**	**2.21**	**2.08**	**2.00**	**1.90**	**1.85**	**1.80**	**1.78**	**1.75**	**1.74**	**1.73**	**1.72**	**1.70**	**1.69**	**1.69**	**1.68**	**1.67**	**1.67**	**1.66**
30	3.29	**2.62**	**2.36**	**2.22**	**2.13**	**2.03**	**1.97**	**1.92**	**1.89**	**1.86**	**1.85**	**1.83**	**1.82**	**1.81**	**1.80**	**1.79**	**1.78**	**1.78**	**1.77**	**1.76**
40	3.45	**2.74**	**2.47**	**2.32**	**2.23**	**2.12**	**2.05**	**2.00**	**1.97**	**1.94**	**1.92**	**1.91**	**1.90**	**1.88**	**1.87**	**1.86**	**1.85**	**1.85**	**1.84**	**1.83**
50	3.57	2.83	**2.55**	**2.40**	**2.30**	**2.18**	**2.11**	**2.06**	**2.02**	**2.00**	**1.98**	**1.96**	**1.95**	**1.94**	**1.92**	**1.91**	**1.91**	**1.90**	**1.89**	**1.88**
60	3.67	2.91	**2.61**	**2.46**	**2.36**	**2.24**	**2.16**	**2.11**	**2.07**	**2.05**	**2.03**	**2.01**	**2.00**	**1.98**	**1.97**	**1.96**	**1.95**	**1.94**	**1.93**	**1.92**
75	3.79	3.00	**2.69**	**2.53**	**2.42**	**2.30**	**2.23**	**2.17**	**2.13**	**2.10**	**2.08**	**2.07**	**2.05**	**2.03**	**2.02**	**2.01**	**2.00**	**1.99**	**1.98**	**1.97**
100	3.93	3.11	*2.79*	**2.62**	**2.51**	**2.38**	**2.30**	**2.24**	**2.20**	**2.17**	**2.15**	**2.13**	**2.12**	**2.10**	**2.09**	**2.07**	**2.07**	**2.06**	**2.05**	**2.04**
125	4.05	3.19	*2.87*	**2.69**	**2.58**	**2.44**	**2.36**	**2.30**	**2.26**	**2.23**	**2.21**	**2.19**	**2.17**	**2.15**	**2.14**	**2.12**	**2.12**	**2.11**	**2.10**	**2.09**
150	4.14	3.26	2.93	**2.75**	**2.63**	**2.49**	**2.41**	**2.35**	**2.30**	**2.27**	**2.25**	**2.23**	**2.22**	**2.19**	**2.18**	**2.17**	**2.16**	**2.15**	**2.14**	**2.13**
175	4.21	3.32	2.98	*2.79*	**2.68**	**2.54**	**2.45**	**2.39**	**2.34**	**2.31**	**2.28**	**2.27**	**2.25**	**2.23**	**2.21**	**2.20**	**2.19**	**2.18**	**2.17**	**2.16**
200	4.28	3.37	3.02	*2.84*	**2.72**	**2.57**	**2.49**	**2.42**	**2.37**	**2.34**	**2.32**	**2.30**	**2.28**	**2.26**	**2.24**	**2.23**	**2.22**	**2.21**	**2.20**	**2.19**

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Table 19-1. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Observations (1 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.65**	**1.37**	**1.26**	**1.20**	**1.16**	**1.12**	**1.09**	**1.07**	**1.06**	**1.05**	**1.04**	**1.03**	**1.03**	**1.02**	**1.02**	**1.01**	**1.01**	**1.01**	**1.00**	**1.00**
2	**2.09**	**1.71**	**1.56**	**1.48**	**1.43**	**1.37**	**1.34**	**1.31**	**1.29**	**1.28**	**1.27**	**1.26**	**1.25**	**1.25**	**1.24**	**1.24**	**1.23**	**1.23**	**1.22**	**1.22**
3	**2.34**	**1.90**	**1.73**	**1.64**	**1.58**	**1.51**	**1.47**	**1.44**	**1.42**	**1.40**	**1.39**	**1.39**	**1.38**	**1.37**	**1.36**	**1.36**	**1.35**	**1.35**	**1.34**	**1.34**
4	**2.52**	**2.03**	**1.85**	**1.75**	**1.68**	**1.61**	**1.56**	**1.53**	**1.51**	**1.49**	**1.48**	**1.47**	**1.46**	**1.45**	**1.44**	**1.44**	**1.43**	**1.43**	**1.42**	**1.42**
5	**2.65**	**2.14**	**1.94**	**1.83**	**1.76**	**1.68**	**1.64**	**1.60**	**1.57**	**1.56**	**1.54**	**1.53**	**1.53**	**1.52**	**1.51**	**1.50**	**1.50**	**1.49**	**1.49**	**1.48**
8	**2.93**	**2.35**	**2.12**	**2.00**	**1.93**	**1.83**	**1.78**	**1.74**	**1.71**	**1.69**	**1.68**	**1.67**	**1.66**	**1.64**	**1.63**	**1.63**	**1.62**	**1.62**	**1.61**	**1.60**
12	3.16	**2.52**	**2.28**	**2.15**	**2.06**	**1.96**	**1.90**	**1.86**	**1.83**	**1.80**	**1.79**	**1.78**	**1.77**	**1.75**	**1.74**	**1.73**	**1.73**	**1.72**	**1.71**	**1.71**
16	3.33	**2.65**	**2.39**	**2.24**	**2.16**	**2.05**	**1.99**	**1.94**	**1.90**	**1.88**	**1.86**	**1.85**	**1.84**	**1.82**	**1.81**	**1.80**	**1.80**	**1.79**	**1.78**	**1.78**
20	3.45	**2.74**	**2.47**	**2.32**	**2.23**	**2.12**	**2.05**	**2.00**	**1.97**	**1.94**	**1.92**	**1.91**	**1.90**	**1.88**	**1.87**	**1.86**	**1.85**	**1.85**	**1.84**	**1.83**
30	3.67	**2.91**	**2.61**	**2.46**	**2.36**	**2.24**	**2.16**	**2.11**	**2.07**	**2.05**	**2.03**	**2.01**	**2.00**	**1.98**	**1.97**	**1.96**	**1.95**	**1.94**	**1.93**	**1.92**
40	3.82	**3.02**	**2.71**	**2.55**	**2.44**	**2.32**	**2.24**	**2.19**	**2.15**	**2.12**	**2.10**	**2.08**	**2.07**	**2.05**	**2.03**	**2.02**	**2.02**	**2.01**	**2.00**	**1.99**
50	3.93	**3.11**	**2.79**	**2.62**	**2.51**	**2.38**	**2.30**	**2.24**	**2.20**	**2.17**	**2.15**	**2.13**	**2.12**	**2.10**	**2.09**	**2.07**	**2.07**	**2.06**	**2.05**	**2.04**
60	4.03	3.18	**2.85**	**2.68**	**2.57**	**2.43**	**2.35**	**2.29**	**2.25**	**2.22**	**2.20**	**2.18**	**2.16**	**2.14**	**2.13**	**2.12**	**2.11**	**2.10**	**2.09**	**2.08**
75	4.14	3.26	**2.93**	**2.75**	**2.63**	**2.49**	**2.41**	**2.35**	**2.30**	**2.27**	**2.25**	**2.23**	**2.22**	**2.19**	**2.18**	**2.17**	**2.16**	**2.15**	**2.14**	**2.13**
100	4.28	3.37	**3.02**	**2.84**	**2.72**	**2.57**	**2.49**	**2.42**	**2.37**	**2.34**	**2.32**	**2.30**	**2.28**	**2.26**	**2.24**	**2.23**	**2.22**	**2.21**	**2.20**	**2.19**
125	4.39	3.45	**3.10**	**2.90**	**2.78**	**2.63**	**2.54**	**2.47**	**2.43**	**2.39**	**2.37**	**2.35**	**2.33**	**2.31**	**2.29**	**2.28**	**2.27**	**2.26**	**2.24**	**2.23**
150	4.47	3.52	*3.15*	**2.96**	**2.83**	**2.68**	**2.59**	**2.52**	**2.47**	**2.44**	**2.41**	**2.39**	**2.37**	**2.35**	**2.33**	**2.32**	**2.31**	**2.30**	**2.28**	**2.27**
175	4.54	3.57	*3.20*	**3.00**	**2.87**	**2.72**	**2.63**	**2.56**	**2.51**	**2.47**	**2.44**	**2.42**	**2.41**	**2.38**	**2.36**	**2.35**	**2.34**	**2.33**	**2.31**	**2.30**
200	4.61	3.62	3.24	**3.04**	**2.91**	**2.75**	**2.66**	**2.59**	**2.54**	**2.50**	**2.47**	**2.45**	**2.44**	**2.41**	**2.39**	**2.38**	**2.37**	**2.36**	**2.34**	**2.33**

Table 19-1. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Observations (2 COCs, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.27**	**1.05**	**0.97**	**0.92**	**0.89**	**0.85**	**0.83**	**0.81**	**0.80**	**0.79**	**0.79**	**0.78**	**0.78**	**0.78**	**0.77**	**0.77**	**0.77**	**0.77**	**0.76**	**0.76**
2	**1.76**	**1.42**	**1.29**	**1.22**	**1.18**	**1.13**	**1.10**	**1.08**	**1.06**	**1.05**	**1.04**	**1.04**	**1.03**	**1.02**	**1.02**	**1.02**	**1.01**	**1.01**	**1.01**	**1.00**
3	**2.05**	**1.63**	**1.48**	**1.39**	**1.34**	**1.28**	**1.25**	**1.22**	**1.20**	**1.19**	**1.18**	**1.17**	**1.17**	**1.16**	**1.15**	**1.15**	**1.14**	**1.14**	**1.14**	**1.13**
4	**2.27**	**1.78**	**1.61**	**1.51**	**1.45**	**1.39**	**1.35**	**1.32**	**1.30**	**1.28**	**1.27**	**1.26**	**1.26**	**1.25**	**1.24**	**1.24**	**1.23**	**1.23**	**1.23**	**1.22**
5	**2.43**	**1.90**	**1.71**	**1.60**	**1.54**	**1.47**	**1.42**	**1.39**	**1.37**	**1.35**	**1.34**	**1.33**	**1.33**	**1.32**	**1.31**	**1.30**	**1.30**	**1.30**	**1.29**	**1.29**
8	2.79	**2.15**	**1.91**	**1.79**	**1.72**	**1.63**	**1.58**	**1.54**	**1.52**	**1.50**	**1.49**	**1.48**	**1.47**	**1.46**	**1.45**	**1.44**	**1.44**	**1.43**	**1.43**	**1.42**
12	3.10	**2.36**	**2.09**	**1.95**	**1.87**	**1.77**	**1.71**	**1.67**	**1.64**	**1.62**	**1.60**	**1.59**	**1.58**	**1.57**	**1.56**	**1.55**	**1.55**	**1.54**	**1.54**	**1.53**
16	3.32	*2.51*	**2.22**	**2.07**	**1.97**	**1.86**	**1.80**	**1.76**	**1.72**	**1.70**	**1.69**	**1.67**	**1.66**	**1.65**	**1.64**	**1.63**	**1.62**	**1.62**	**1.61**	**1.61**
20	3.48	2.62	**2.31**	**2.15**	**2.05**	**1.94**	**1.87**	**1.82**	**1.79**	**1.77**	**1.75**	**1.73**	**1.72**	**1.71**	**1.70**	**1.69**	**1.68**	**1.68**	**1.67**	**1.66**
30	3.78	2.83	*2.48*	**2.31**	**2.20**	**2.07**	**2.00**	**1.94**	**1.90**	**1.88**	**1.86**	**1.84**	**1.83**	**1.81**	**1.80**	**1.79**	**1.79**	**1.78**	**1.77**	**1.76**
40	3.99	2.97	2.60	**2.41**	**2.30**	**2.16**	**2.08**	**2.02**	**1.98**	**1.96**	**1.93**	**1.92**	**1.91**	**1.89**	**1.87**	**1.86**	**1.86**	**1.85**	**1.84**	**1.83**
50	4.15	3.08	2.70	*2.50*	**2.37**	**2.23**	**2.15**	**2.09**	**2.04**	**2.01**	**1.99**	**1.98**	**1.96**	**1.94**	**1.93**	**1.92**	**1.91**	**1.90**	**1.89**	**1.88**
60	4.28	3.17	2.77	*2.56*	*2.44*	**2.29**	**2.20**	**2.14**	**2.09**	**2.06**	**2.04**	**2.02**	**2.01**	**1.99**	**1.97**	**1.96**	**1.95**	**1.95**	**1.93**	**1.93**
75	4.43	3.27	2.86	2.65	*2.51*	**2.36**	**2.27**	**2.20**	**2.15**	**2.12**	**2.10**	**2.08**	**2.06**	**2.04**	**2.03**	**2.01**	**2.01**	**2.00**	**1.99**	**1.98**
100	4.63	3.41	2.97	2.75	2.61	*2.44*	**2.35**	**2.28**	**2.23**	**2.19**	**2.17**	**2.15**	**2.13**	**2.11**	**2.09**	**2.08**	**2.07**	**2.06**	**2.05**	**2.04**
125	4.78	3.51	3.06	2.83	2.68	*2.51*	*2.41*	**2.34**	**2.28**	**2.25**	**2.22**	**2.20**	**2.19**	**2.16**	**2.14**	**2.13**	**2.12**	**2.11**	**2.10**	**2.09**
150	4.90	3.60	3.13	2.89	2.74	*2.56*	*2.46*	**2.38**	**2.33**	**2.29**	**2.27**	**2.25**	**2.23**	**2.20**	**2.19**	**2.17**	**2.16**	**2.15**	**2.14**	**2.13**
175	5.00	3.67	3.19	2.94	2.79	*2.61*	*2.51*	*2.42*	**2.37**	**2.33**	**2.30**	**2.28**	**2.27**	**2.24**	**2.22**	**2.21**	**2.20**	**2.19**	**2.17**	**2.16**
200	5.08	3.73	3.24	2.99	2.83	2.65	*2.54*	*2.46*	*2.40*	**2.37**	**2.34**	**2.31**	**2.30**	**2.27**	**2.25**	**2.24**	**2.23**	**2.22**	**2.20**	**2.19**

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Table 19-1. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Observations (2 COCs, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.76**	**1.42**	**1.29**	**1.22**	**1.18**	**1.13**	**1.10**	**1.08**	**1.06**	**1.05**	**1.04**	**1.04**	**1.03**	**1.02**	**1.02**	**1.02**	**1.01**	**1.01**	**1.01**	**1.00**
2	**2.27**	**1.78**	**1.61**	**1.51**	**1.45**	**1.39**	**1.35**	**1.32**	**1.30**	**1.28**	**1.27**	**1.26**	**1.26**	**1.25**	**1.24**	**1.24**	**1.23**	**1.23**	**1.23**	**1.22**
3	**2.57**	**2.00**	**1.79**	**1.68**	**1.61**	**1.53**	**1.48**	**1.45**	**1.43**	**1.41**	**1.40**	**1.39**	**1.38**	**1.37**	**1.36**	**1.36**	**1.35**	**1.35**	**1.34**	**1.34**
4	2.79	**2.15**	**1.91**	**1.79**	**1.72**	**1.63**	**1.58**	**1.54**	**1.52**	**1.50**	**1.49**	**1.48**	**1.47**	**1.46**	**1.45**	**1.44**	**1.44**	**1.43**	**1.43**	**1.42**
5	2.96	**2.27**	**2.01**	**1.88**	**1.80**	**1.71**	**1.65**	**1.61**	**1.58**	**1.57**	**1.55**	**1.54**	**1.53**	**1.52**	**1.51**	**1.50**	**1.50**	**1.49**	**1.49**	**1.48**
8	3.32	**2.51**	**2.22**	**2.07**	**1.97**	**1.86**	**1.80**	**1.76**	**1.72**	**1.70**	**1.69**	**1.67**	**1.66**	**1.65**	**1.64**	**1.63**	**1.62**	**1.62**	**1.61**	**1.61**
12	3.62	**2.71**	**2.39**	**2.22**	**2.12**	**2.00**	**1.93**	**1.88**	**1.84**	**1.82**	**1.80**	**1.78**	**1.77**	**1.76**	**1.74**	**1.74**	**1.73**	**1.72**	**1.71**	**1.71**
16	3.83	2.86	**2.51**	**2.33**	**2.22**	**2.09**	**2.02**	**1.96**	**1.92**	**1.89**	**1.88**	**1.86**	**1.85**	**1.83**	**1.82**	**1.81**	**1.80**	**1.80**	**1.79**	**1.78**
20	3.99	2.97	**2.60**	**2.41**	**2.30**	**2.16**	**2.08**	**2.02**	**1.98**	**1.96**	**1.93**	**1.92**	**1.91**	**1.89**	**1.87**	**1.86**	**1.86**	**1.85**	**1.84**	**1.83**
30	4.28	3.17	**2.77**	**2.56**	**2.44**	**2.29**	**2.20**	**2.14**	**2.09**	**2.06**	**2.04**	**2.02**	**2.01**	**1.99**	**1.97**	**1.96**	**1.95**	**1.95**	**1.93**	**1.93**
40	4.48	3.30	*2.89*	**2.67**	**2.53**	**2.38**	**2.29**	**2.21**	**2.17**	**2.14**	**2.11**	**2.09**	**2.08**	**2.06**	**2.04**	**2.03**	**2.02**	**2.01**	**2.00**	**1.99**
50	4.63	3.41	2.97	**2.75**	**2.61**	**2.44**	**2.35**	**2.28**	**2.23**	**2.19**	**2.17**	**2.15**	**2.13**	**2.11**	**2.09**	**2.08**	**2.07**	**2.06**	**2.05**	**2.04**
60	4.75	3.49	3.05	*2.81*	**2.67**	**2.50**	**2.40**	**2.32**	**2.27**	**2.24**	**2.21**	**2.19**	**2.18**	**2.15**	**2.14**	**2.12**	**2.11**	**2.10**	**2.09**	**2.08**
75	4.90	3.60	3.13	*2.89*	**2.74**	**2.56**	**2.46**	**2.38**	**2.33**	**2.29**	**2.27**	**2.25**	**2.23**	**2.20**	**2.19**	**2.17**	**2.16**	**2.15**	**2.14**	**2.13**
100	5.08	3.73	3.24	2.99	*2.83*	**2.65**	**2.54**	**2.46**	**2.40**	**2.37**	**2.34**	**2.31**	**2.30**	**2.27**	**2.25**	**2.24**	**2.23**	**2.22**	**2.20**	**2.19**
125	5.23	3.82	3.33	3.06	*2.90*	**2.71**	**2.60**	**2.52**	**2.46**	**2.42**	**2.39**	**2.37**	**2.35**	**2.32**	**2.30**	**2.29**	**2.27**	**2.26**	**2.25**	**2.24**
150	5.34	3.90	3.39	3.13	*2.96*	*2.76*	**2.65**	**2.56**	**2.50**	**2.46**	**2.43**	**2.41**	**2.39**	**2.36**	**2.34**	**2.32**	**2.31**	**2.30**	**2.29**	**2.27**
175	5.43	3.97	3.45	3.18	3.01	*2.81*	**2.69**	**2.60**	**2.54**	**2.50**	**2.47**	**2.44**	**2.42**	**2.39**	**2.37**	**2.36**	**2.35**	**2.34**	**2.32**	**2.31**
200	5.52	4.03	3.50	3.22	3.05	*2.85*	**2.73**	**2.64**	**2.57**	**2.53**	**2.50**	**2.47**	**2.45**	**2.42**	**2.40**	**2.39**	**2.37**	**2.36**	**2.35**	**2.33**

Table 19-1. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Observations (2 COCs, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.27**	**1.79**	**1.61**	**1.51**	**1.45**	**1.39**	**1.35**	**1.32**	**1.30**	**1.28**	**1.27**	**1.26**	**1.26**	**1.25**	**1.24**	**1.24**	**1.23**	**1.23**	**1.23**	**1.22**
2	**2.79**	**2.15**	**1.91**	**1.79**	**1.72**	**1.63**	**1.58**	**1.54**	**1.52**	**1.50**	**1.49**	**1.48**	**1.47**	**1.46**	**1.45**	**1.44**	**1.44**	**1.43**	**1.43**	**1.42**
3	3.10	**2.36**	**2.09**	**1.95**	**1.87**	**1.77**	**1.71**	**1.67**	**1.64**	**1.62**	**1.60**	**1.59**	**1.58**	**1.57**	**1.56**	**1.55**	**1.55**	**1.54**	**1.54**	**1.53**
4	3.32	**2.51**	**2.22**	**2.07**	**1.97**	**1.86**	**1.80**	**1.75**	**1.72**	**1.70**	**1.69**	**1.67**	**1.66**	**1.65**	**1.64**	**1.63**	**1.62**	**1.62**	**1.61**	**1.61**
5	3.48	**2.62**	**2.31**	**2.15**	**2.05**	**1.94**	**1.87**	**1.82**	**1.79**	**1.77**	**1.75**	**1.73**	**1.72**	**1.71**	**1.70**	**1.69**	**1.68**	**1.68**	**1.67**	**1.66**
8	3.83	**2.86**	**2.51**	**2.33**	**2.22**	**2.09**	**2.02**	**1.96**	**1.92**	**1.89**	**1.88**	**1.86**	**1.85**	**1.83**	**1.82**	**1.81**	**1.80**	**1.80**	**1.79**	**1.78**
12	4.12	**3.06**	**2.68**	**2.48**	**2.36**	**2.22**	**2.14**	**2.07**	**2.03**	**2.00**	**1.98**	**1.97**	**1.95**	**1.93**	**1.92**	**1.91**	**1.90**	**1.89**	**1.88**	**1.87**
16	4.32	3.20	**2.80**	**2.59**	**2.46**	**2.31**	**2.22**	**2.15**	**2.11**	**2.08**	**2.06**	**2.04**	**2.02**	**2.00**	**1.99**	**1.98**	**1.97**	**1.96**	**1.95**	**1.94**
20	4.48	3.30	**2.89**	**2.67**	**2.53**	**2.38**	**2.29**	**2.22**	**2.17**	**2.14**	**2.11**	**2.09**	**2.08**	**2.06**	**2.04**	**2.03**	**2.02**	**2.01**	**2.00**	**1.99**
30	4.75	3.49	**3.05**	**2.81**	**2.67**	**2.50**	**2.40**	**2.32**	**2.27**	**2.24**	**2.21**	**2.19**	**2.18**	**2.15**	**2.14**	**2.12**	**2.11**	**2.10**	**2.09**	**2.08**
40	4.94	3.63	*3.16*	**2.91**	**2.76**	**2.58**	**2.48**	**2.40**	**2.35**	**2.31**	**2.28**	**2.26**	**2.24**	**2.22**	**2.20**	**2.19**	**2.18**	**2.17**	**2.15**	**2.14**
50	5.08	3.72	3.24	**2.99**	**2.83**	**2.65**	**2.54**	**2.46**	**2.40**	**2.37**	**2.34**	**2.31**	**2.30**	**2.27**	**2.25**	**2.24**	**2.23**	**2.22**	**2.20**	**2.19**
60	5.20	3.81	3.31	**3.05**	**2.89**	**2.70**	**2.59**	**2.51**	**2.45**	**2.41**	**2.38**	**2.36**	**2.34**	**2.31**	**2.29**	**2.28**	**2.26**	**2.26**	**2.24**	**2.23**
75	5.34	3.91	3.39	*3.13*	**2.96**	**2.76**	**2.65**	**2.56**	**2.50**	**2.46**	**2.43**	**2.41**	**2.39**	**2.36**	**2.34**	**2.32**	**2.31**	**2.30**	**2.29**	**2.28**
100	5.52	4.03	3.50	*3.22*	**3.05**	**2.85**	**2.73**	**2.64**	**2.57**	**2.53**	**2.50**	**2.47**	**2.45**	**2.42**	**2.40**	**2.39**	**2.37**	**2.36**	**2.35**	**2.33**
125	5.65	4.12	3.58	3.29	**3.12**	**2.91**	**2.79**	**2.69**	**2.63**	**2.58**	**2.55**	**2.52**	**2.50**	**2.47**	**2.45**	**2.43**	**2.42**	**2.41**	**2.39**	**2.38**
150	5.76	4.20	3.64	3.35	*3.17*	**2.96**	**2.83**	**2.74**	**2.67**	**2.63**	**2.59**	**2.56**	**2.54**	**2.51**	**2.49**	**2.47**	**2.46**	**2.45**	**2.43**	**2.41**
175	5.85	4.26	3.70	3.40	*3.22*	**3.00**	**2.87**	**2.77**	**2.71**	**2.66**	**2.63**	**2.60**	**2.58**	**2.54**	**2.52**	**2.50**	**2.49**	**2.48**	**2.46**	**2.45**
200	5.93	4.32	3.74	3.45	*3.26*	**3.04**	**2.91**	**2.81**	**2.74**	**2.69**	**2.66**	**2.63**	**2.61**	**2.57**	**2.55**	**2.53**	**2.52**	**2.50**	**2.48**	**2.47**

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Table 19-1. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Observations (5 COCs, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.02**	**1.58**	**1.42**	**1.33**	**1.28**	**1.22**	**1.18**	**1.16**	**1.14**	**1.13**	**1.12**	**1.11**	**1.11**	**1.10**	**1.09**	**1.09**	**1.09**	**1.08**	**1.08**	**1.08**
2	2.62	**1.97**	**1.74**	**1.63**	**1.56**	**1.48**	**1.43**	**1.40**	**1.37**	**1.36**	**1.35**	**1.34**	**1.33**	**1.32**	**1.31**	**1.31**	**1.30**	**1.30**	**1.29**	**1.29**
3	3.00	**2.20**	**1.93**	**1.80**	**1.72**	**1.62**	**1.57**	**1.53**	**1.50**	**1.48**	**1.47**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**	**1.42**	**1.42**	**1.41**	**1.40**
4	3.27	**2.37**	**2.07**	**1.92**	**1.83**	**1.72**	**1.66**	**1.62**	**1.59**	**1.57**	**1.56**	**1.54**	**1.54**	**1.52**	**1.51**	**1.51**	**1.50**	**1.50**	**1.49**	**1.48**
5	3.49	*2.51*	**2.18**	**2.01**	**1.91**	**1.80**	**1.74**	**1.69**	**1.66**	**1.64**	**1.62**	**1.61**	**1.60**	**1.59**	**1.57**	**1.57**	**1.56**	**1.56**	**1.55**	**1.54**
8	3.96	2.79	**2.40**	**2.21**	**2.09**	**1.96**	**1.89**	**1.83**	**1.80**	**1.77**	**1.75**	**1.74**	**1.73**	**1.71**	**1.70**	**1.69**	**1.69**	**1.68**	**1.67**	**1.66**
12	4.37	3.03	2.59	**2.38**	**2.25**	**2.10**	**2.02**	**1.95**	**1.91**	**1.89**	**1.86**	**1.85**	**1.84**	**1.82**	**1.80**	**1.80**	**1.79**	**1.78**	**1.77**	**1.76**
16	4.66	3.20	2.73	*2.49*	**2.35**	**2.19**	**2.11**	**2.04**	**1.99**	**1.96**	**1.94**	**1.92**	**1.91**	**1.89**	**1.88**	**1.87**	**1.86**	**1.85**	**1.84**	**1.83**
20	4.88	3.34	2.84	2.59	*2.44*	**2.27**	**2.17**	**2.10**	**2.06**	**2.02**	**2.00**	**1.98**	**1.97**	**1.95**	**1.93**	**1.92**	**1.91**	**1.91**	**1.89**	**1.89**
30	5.28	3.58	3.03	2.75	*2.59*	*2.40*	**2.30**	**2.22**	**2.17**	**2.13**	**2.11**	**2.09**	**2.07**	**2.05**	**2.03**	**2.02**	**2.01**	**2.00**	**1.99**	**1.98**
40	5.56	3.75	3.16	2.87	2.69	*2.49*	**2.38**	**2.30**	**2.24**	**2.21**	**2.18**	**2.16**	**2.14**	**2.12**	**2.10**	**2.09**	**2.08**	**2.07**	**2.05**	**2.04**
50	5.77	3.88	3.26	2.96	2.77	*2.57*	*2.45*	**2.36**	**2.30**	**2.26**	**2.23**	**2.21**	**2.19**	**2.17**	**2.15**	**2.14**	**2.13**	**2.12**	**2.10**	**2.09**
60	5.94	3.98	3.35	3.03	2.84	2.62	*2.50*	*2.41*	**2.35**	**2.31**	**2.28**	**2.26**	**2.24**	**2.21**	**2.19**	**2.18**	**2.17**	**2.16**	**2.14**	**2.13**
75	6.15	4.11	3.45	3.12	2.92	2.69	*2.57*	*2.47*	*2.41*	**2.37**	**2.34**	**2.31**	**2.29**	**2.26**	**2.24**	**2.23**	**2.22**	**2.21**	**2.19**	**2.18**
100	6.42	4.27	3.58	3.23	3.02	2.78	2.65	*2.55*	*2.48*	*2.44*	*2.40*	**2.38**	**2.36**	**2.33**	**2.31**	**2.29**	**2.28**	**2.27**	**2.25**	**2.24**
125	6.62	4.40	3.68	3.32	3.10	2.85	2.71	*2.61*	*2.54*	*2.49*	*2.46*	*2.43*	*2.41*	*2.38*	**2.36**	**2.34**	**2.33**	**2.32**	**2.30**	**2.29**
150	6.79	4.50	3.75	3.39	3.16	2.91	2.77	2.66	*2.59*	*2.54*	*2.50*	*2.47*	*2.45*	*2.42*	*2.40*	*2.38*	**2.37**	**2.35**	**2.34**	**2.32**
175	6.92	4.58	3.82	3.45	3.22	2.96	2.81	2.70	*2.63*	*2.58*	*2.54*	*2.51*	*2.49*	*2.45*	*2.43*	*2.41*	*2.40*	*2.39*	**2.37**	**2.35**
200	7.04	4.65	3.88	3.49	3.26	3.00	2.85	2.73	*2.66*	*2.61*	*2.57*	*2.54*	*2.52*	*2.48*	*2.46*	*2.44*	*2.43*	*2.41*	*2.39*	*2.38*

Table 19-1. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Observations (5 COCs, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.62**	**1.97**	**1.74**	**1.63**	**1.56**	**1.48**	**1.43**	**1.40**	**1.37**	**1.36**	**1.35**	**1.34**	**1.33**	**1.32**	**1.31**	**1.31**	**1.30**	**1.30**	**1.29**	**1.29**
2	3.27	**2.37**	**2.07**	**1.92**	**1.83**	**1.72**	**1.66**	**1.62**	**1.59**	**1.57**	**1.56**	**1.54**	**1.54**	**1.52**	**1.51**	**1.51**	**1.50**	**1.50**	**1.49**	**1.48**
3	3.67	**2.62**	**2.26**	**2.09**	**1.98**	**1.86**	**1.80**	**1.75**	**1.71**	**1.69**	**1.67**	**1.66**	**1.65**	**1.63**	**1.62**	**1.62**	**1.61**	**1.60**	**1.60**	**1.59**
4	3.96	**2.79**	**2.40**	**2.21**	**2.09**	**1.96**	**1.89**	**1.83**	**1.80**	**1.77**	**1.75**	**1.74**	**1.73**	**1.71**	**1.70**	**1.69**	**1.69**	**1.68**	**1.67**	**1.66**
5	4.18	2.92	**2.51**	**2.30**	**2.18**	**2.04**	**1.96**	**1.90**	**1.86**	**1.83**	**1.82**	**1.80**	**1.79**	**1.77**	**1.76**	**1.75**	**1.74**	**1.74**	**1.73**	**1.72**
8	4.66	3.20	**2.73**	**2.49**	**2.35**	**2.19**	**2.11**	**2.04**	**1.99**	**1.96**	**1.94**	**1.92**	**1.91**	**1.89**	**1.88**	**1.87**	**1.86**	**1.85**	**1.84**	**1.83**
12	5.06	3.45	2.92	**2.66**	**2.51**	**2.33**	**2.23**	**2.15**	**2.11**	**2.07**	**2.05**	**2.03**	**2.01**	**1.99**	**1.98**	**1.97**	**1.96**	**1.95**	**1.94**	**1.93**
16	5.34	3.62	3.06	*2.78*	**2.61**	**2.42**	**2.32**	**2.24**	**2.19**	**2.15**	**2.12**	**2.10**	**2.09**	**2.06**	**2.05**	**2.03**	**2.02**	**2.02**	**2.00**	**1.99**
20	5.56	3.75	3.16	*2.87*	**2.69**	**2.49**	**2.38**	**2.30**	**2.24**	**2.21**	**2.18**	**2.16**	**2.14**	**2.12**	**2.10**	**2.09**	**2.08**	**2.07**	**2.05**	**2.04**
30	5.94	3.98	3.35	3.03	*2.84*	**2.62**	**2.50**	**2.41**	**2.35**	**2.31**	**2.28**	**2.26**	**2.24**	**2.21**	**2.19**	**2.18**	**2.17**	**2.16**	**2.14**	**2.13**
40	6.21	4.15	3.48	3.14	*2.94*	**2.71**	**2.59**	**2.49**	**2.43**	**2.38**	**2.35**	**2.33**	**2.31**	**2.28**	**2.26**	**2.24**	**2.23**	**2.22**	**2.20**	**2.19**
50	6.42	4.27	3.58	3.23	3.02	*2.78*	**2.65**	**2.55**	**2.48**	**2.44**	**2.40**	**2.38**	**2.36**	**2.33**	**2.31**	**2.29**	**2.28**	**2.27**	**2.25**	**2.24**
60	6.59	4.37	3.66	3.30	3.09	*2.84*	**2.70**	**2.60**	**2.53**	**2.48**	**2.45**	**2.42**	**2.40**	**2.37**	**2.35**	**2.33**	**2.32**	**2.31**	**2.29**	**2.28**
75	6.79	4.50	3.75	3.39	3.16	*2.91*	*2.77*	**2.66**	**2.59**	**2.54**	**2.50**	**2.47**	**2.45**	**2.42**	**2.40**	**2.38**	**2.37**	**2.35**	**2.34**	**2.32**
100	7.04	4.65	3.88	3.49	3.26	*3.00*	*2.85*	**2.73**	**2.66**	**2.61**	**2.57**	**2.54**	**2.52**	**2.48**	**2.46**	**2.44**	**2.43**	**2.41**	**2.39**	**2.38**
125	7.23	4.77	3.98	3.58	3.34	3.06	*2.91*	*2.79*	**2.72**	**2.66**	**2.62**	**2.59**	**2.57**	**2.53**	**2.51**	**2.49**	**2.47**	**2.46**	**2.44**	**2.43**
150	7.38	4.87	4.05	3.65	3.40	3.12	*2.96*	*2.84*	*2.76*	**2.70**	**2.66**	**2.63**	**2.61**	**2.57**	**2.54**	**2.52**	**2.51**	**2.50**	**2.48**	**2.46**
175	7.52	4.95	4.12	3.70	3.45	3.17	*3.00*	*2.88*	*2.80*	**2.74**	**2.70**	**2.67**	**2.64**	**2.60**	**2.58**	**2.56**	**2.54**	**2.53**	**2.51**	**2.49**
200	7.62	5.02	4.17	3.75	3.50	3.20	*3.04*	*2.91*	*2.83*	*2.77*	**2.73**	**2.70**	**2.67**	**2.63**	**2.60**	**2.58**	**2.57**	**2.55**	**2.53**	**2.52**

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Table 19-1. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Observations (5 COCs, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.27	**2.37**	**2.07**	**1.92**	**1.83**	**1.72**	**1.66**	**1.62**	**1.59**	**1.57**	**1.56**	**1.54**	**1.54**	**1.52**	**1.51**	**1.51**	**1.50**	**1.50**	**1.49**	**1.48**
2	3.96	**2.79**	**2.40**	**2.21**	**2.09**	**1.96**	**1.89**	**1.83**	**1.80**	**1.77**	**1.75**	**1.74**	**1.73**	**1.71**	**1.70**	**1.69**	**1.69**	**1.68**	**1.67**	**1.66**
3	4.37	**3.03**	**2.59**	**2.38**	**2.25**	**2.10**	**2.02**	**1.95**	**1.91**	**1.89**	**1.86**	**1.85**	**1.84**	**1.82**	**1.80**	**1.80**	**1.79**	**1.78**	**1.77**	**1.76**
4	4.66	3.20	**2.73**	**2.49**	**2.35**	**2.19**	**2.11**	**2.04**	**1.99**	**1.96**	**1.94**	**1.92**	**1.91**	**1.89**	**1.88**	**1.87**	**1.86**	**1.85**	**1.84**	**1.83**
5	4.88	3.34	**2.84**	**2.59**	**2.44**	**2.27**	**2.17**	**2.10**	**2.06**	**2.02**	**2.00**	**1.98**	**1.97**	**1.95**	**1.93**	**1.92**	**1.91**	**1.91**	**1.89**	**1.89**
8	5.34	3.62	**3.06**	**2.78**	**2.61**	**2.42**	**2.32**	**2.24**	**2.19**	**2.15**	**2.12**	**2.10**	**2.09**	**2.06**	**2.05**	**2.03**	**2.02**	**2.02**	**2.00**	**1.99**
12	5.74	3.86	3.24	**2.94**	**2.76**	**2.55**	**2.44**	**2.35**	**2.29**	**2.25**	**2.22**	**2.20**	**2.19**	**2.16**	**2.14**	**2.13**	**2.12**	**2.11**	**2.09**	**2.08**
16	6.01	4.02	3.37	**3.06**	**2.86**	**2.64**	**2.52**	**2.43**	**2.37**	**2.33**	**2.30**	**2.27**	**2.25**	**2.23**	**2.21**	**2.19**	**2.18**	**2.17**	**2.16**	**2.15**
20	6.21	4.15	3.48	*3.14*	**2.94**	**2.71**	**2.59**	**2.49**	**2.43**	**2.38**	**2.35**	**2.33**	**2.31**	**2.28**	**2.26**	**2.24**	**2.23**	**2.22**	**2.20**	**2.19**
30	6.59	4.37	3.66	3.30	**3.09**	**2.84**	**2.70**	**2.60**	**2.53**	**2.48**	**2.45**	**2.42**	**2.40**	**2.37**	**2.35**	**2.33**	**2.32**	**2.31**	**2.29**	**2.28**
40	6.84	4.53	3.78	3.41	*3.19*	**2.93**	**2.79**	**2.68**	**2.60**	**2.55**	**2.52**	**2.49**	**2.47**	**2.43**	**2.41**	**2.39**	**2.38**	**2.37**	**2.35**	**2.34**
50	7.04	4.65	3.88	3.49	*3.26*	**3.00**	**2.85**	**2.73**	**2.66**	**2.61**	**2.57**	**2.54**	**2.52**	**2.48**	**2.46**	**2.44**	**2.43**	**2.41**	**2.39**	**2.38**
60	7.20	4.75	3.96	3.56	*3.32*	**3.05**	**2.90**	**2.78**	**2.71**	**2.65**	**2.61**	**2.58**	**2.56**	**2.52**	**2.50**	**2.48**	**2.46**	**2.45**	**2.43**	**2.42**
75	7.38	4.87	4.05	3.65	3.40	*3.12*	**2.96**	**2.84**	**2.76**	**2.70**	**2.66**	**2.63**	**2.61**	**2.57**	**2.54**	**2.52**	**2.51**	**2.50**	**2.48**	**2.46**
100	7.62	5.02	4.17	3.75	3.50	*3.20*	**3.04**	**2.91**	**2.83**	**2.77**	**2.73**	**2.70**	**2.67**	**2.63**	**2.60**	**2.58**	**2.57**	**2.55**	**2.53**	**2.52**
125	7.81	5.13	4.26	3.83	3.57	*3.27*	**3.10**	**2.97**	**2.88**	**2.82**	**2.78**	**2.75**	**2.72**	**2.68**	**2.65**	**2.63**	**2.61**	**2.60**	**2.58**	**2.56**
150	7.96	5.23	4.34	3.90	3.63	*3.32*	*3.15*	**3.02**	**2.93**	**2.87**	**2.82**	**2.79**	**2.76**	**2.72**	**2.69**	**2.67**	**2.65**	**2.63**	**2.61**	**2.59**
175	8.09	5.30	4.40	3.95	3.68	*3.37*	*3.19*	**3.05**	**2.96**	**2.90**	**2.86**	**2.82**	**2.79**	**2.75**	**2.72**	**2.70**	**2.68**	**2.66**	**2.64**	**2.62**
200	8.19	5.37	4.45	4.00	3.72	3.41	*3.23*	**3.09**	**3.00**	**2.93**	**2.89**	**2.85**	**2.82**	**2.78**	**2.75**	**2.72**	**2.70**	**2.69**	**2.67**	**2.65**

Table 19-1. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Observations (10 COCs, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	2.69	**1.99**	**1.76**	**1.64**	**1.56**	**1.48**	**1.43**	**1.40**	**1.37**	**1.36**	**1.35**	**1.34**	**1.33**	**1.32**	**1.31**	**1.31**	**1.30**	**1.30**	**1.29**	**1.29**
2	3.43	**2.42**	**2.09**	**1.93**	**1.84**	**1.73**	**1.67**	**1.62**	**1.59**	**1.57**	**1.56**	**1.55**	**1.54**	**1.52**	**1.51**	**1.51**	**1.50**	**1.50**	**1.49**	**1.48**
3	3.88	2.68	**2.29**	**2.11**	**2.00**	**1.87**	**1.80**	**1.75**	**1.71**	**1.69**	**1.68**	**1.66**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**	**1.60**	**1.59**
4	4.24	2.86	*2.44*	**2.23**	**2.11**	**1.97**	**1.89**	**1.84**	**1.80**	**1.77**	**1.76**	**1.74**	**1.73**	**1.71**	**1.70**	**1.69**	**1.69**	**1.68**	**1.67**	**1.66**
5	4.51	3.01	2.55	**2.33**	**2.20**	**2.05**	**1.97**	**1.91**	**1.86**	**1.84**	**1.82**	**1.80**	**1.79**	**1.77**	**1.76**	**1.75**	**1.74**	**1.74**	**1.73**	**1.72**
8	5.09	3.33	2.79	*2.53*	**2.38**	**2.21**	**2.11**	**2.04**	**2.00**	**1.97**	**1.94**	**1.93**	**1.91**	**1.89**	**1.88**	**1.87**	**1.86**	**1.85**	**1.84**	**1.83**
12	5.60	3.60	3.00	2.71	*2.54*	**2.34**	**2.24**	**2.16**	**2.11**	**2.08**	**2.05**	**2.03**	**2.02**	**1.99**	**1.98**	**1.97**	**1.96**	**1.95**	**1.94**	**1.93**
16	5.95	3.80	3.14	2.83	2.65	*2.44*	**2.33**	**2.25**	**2.19**	**2.15**	**2.12**	**2.11**	**2.09**	**2.06**	**2.05**	**2.03**	**2.02**	**2.02**	**2.00**	**1.99**
20	6.23	3.96	3.26	2.93	2.73	*2.51*	*2.40*	**2.31**	**2.25**	**2.21**	**2.18**	**2.16**	**2.14**	**2.12**	**2.10**	**2.09**	**2.08**	**2.07**	**2.05**	**2.04**
30	6.73	4.22	3.47	3.10	2.89	2.65	*2.52*	*2.42*	**2.36**	**2.32**	**2.28**	**2.26**	**2.24**	**2.21**	**2.19**	**2.18**	**2.17**	**2.16**	**2.14**	**2.13**
40	7.08	4.42	3.61	3.23	3.00	2.74	*2.61*	*2.50*	*2.44*	*2.39*	**2.35**	**2.33**	**2.31**	**2.28**	**2.26**	**2.24**	**2.23**	**2.22**	**2.20**	**2.19**
50	7.35	4.56	3.72	3.32	3.08	2.82	2.67	*2.56*	*2.49*	*2.45*	*2.41*	*2.38*	**2.36**	**2.33**	**2.31**	**2.29**	**2.28**	**2.27**	**2.25**	**2.24**
60	7.58	4.69	3.81	3.40	3.15	2.88	2.73	*2.61*	*2.54*	*2.49*	*2.45*	*2.43*	*2.40*	**2.37**	**2.35**	**2.33**	**2.32**	**2.31**	**2.29**	**2.28**
75	7.83	4.83	3.93	3.49	3.23	2.95	2.79	2.67	*2.60*	*2.55*	*2.51*	*2.48*	*2.46*	*2.42*	*2.40*	*2.38*	**2.37**	**2.36**	**2.34**	**2.32**
100	8.17	5.02	4.07	3.61	3.34	3.04	2.88	2.75	2.67	*2.62*	*2.58*	*2.55*	*2.52*	*2.49*	*2.46*	*2.44*	*2.43*	*2.42*	*2.40*	*2.38*
125	8.43	5.16	4.17	3.70	3.42	3.11	2.94	2.81	2.73	2.67	*2.63*	*2.60*	*2.57*	*2.54*	*2.51*	*2.49*	*2.47*	*2.46*	*2.44*	*2.43*
150	8.63	5.27	4.27	3.78	3.49	3.17	2.99	2.86	2.77	2.72	*2.67*	*2.64*	*2.61*	*2.57*	*2.55*	*2.53*	*2.51*	*2.50*	*2.48*	*2.46*
175	8.80	5.37	4.34	3.84	3.55	3.22	3.04	2.90	2.81	2.75	2.71	2.67	2.65	2.61	2.58	2.56	2.54	2.53	2.51	2.49
200	8.94	5.46	4.40	3.89	3.60	3.26	3.08	2.94	2.85	2.79	2.74	2.70	2.68	2.64	2.61	2.59	2.57	2.56	2.53	2.52

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Table 19-1. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Observations (10 COCs, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.43	**2.42**	**2.09**	**1.93**	**1.84**	**1.73**	**1.67**	**1.62**	**1.59**	**1.57**	**1.56**	**1.55**	**1.54**	**1.52**	**1.51**	**1.51**	**1.50**	**1.50**	**1.49**	**1.48**
2	4.24	2.86	**2.44**	**2.23**	**2.11**	**1.97**	**1.89**	**1.84**	**1.80**	**1.77**	**1.76**	**1.74**	**1.73**	**1.71**	**1.70**	**1.69**	**1.69**	**1.68**	**1.67**	**1.66**
3	4.72	3.13	**2.65**	**2.40**	**2.27**	**2.11**	**2.02**	**1.96**	**1.92**	**1.89**	**1.87**	**1.85**	**1.84**	**1.82**	**1.81**	**1.80**	**1.79**	**1.78**	**1.77**	**1.76**
4	5.09	3.33	*2.79*	**2.53**	**2.38**	**2.21**	**2.11**	**2.04**	**2.00**	**1.97**	**1.94**	**1.93**	**1.91**	**1.89**	**1.88**	**1.87**	**1.86**	**1.85**	**1.84**	**1.83**
5	5.37	3.48	2.90	**2.63**	**2.46**	**2.28**	**2.18**	**2.11**	**2.06**	**2.03**	**2.00**	**1.99**	**1.97**	**1.95**	**1.93**	**1.92**	**1.91**	**1.91**	**1.89**	**1.89**
8	5.95	3.80	3.14	*2.83*	**2.65**	**2.44**	**2.33**	**2.25**	**2.19**	**2.15**	**2.12**	**2.11**	**2.09**	**2.06**	**2.05**	**2.03**	**2.02**	**2.02**	**2.00**	**1.99**
12	6.46	4.08	3.35	3.01	*2.80*	**2.57**	**2.45**	**2.36**	**2.30**	**2.26**	**2.23**	**2.21**	**2.19**	**2.16**	**2.14**	**2.13**	**2.12**	**2.11**	**2.09**	**2.08**
16	6.82	4.27	3.49	3.13	*2.91*	**2.67**	**2.54**	**2.44**	**2.38**	**2.33**	**2.30**	**2.28**	**2.26**	**2.23**	**2.21**	**2.19**	**2.18**	**2.17**	**2.16**	**2.15**
20	7.08	4.42	3.61	3.23	3.00	**2.74**	**2.61**	**2.50**	**2.44**	**2.39**	**2.35**	**2.33**	**2.31**	**2.28**	**2.26**	**2.24**	**2.23**	**2.22**	**2.20**	**2.19**
30	7.58	4.69	3.81	3.40	3.15	*2.88*	**2.73**	**2.61**	**2.54**	**2.49**	**2.45**	**2.43**	**2.40**	**2.37**	**2.35**	**2.33**	**2.32**	**2.31**	**2.29**	**2.28**
40	7.92	4.88	3.96	3.52	3.26	*2.97*	*2.81*	**2.69**	**2.62**	**2.56**	**2.52**	**2.49**	**2.47**	**2.44**	**2.41**	**2.39**	**2.38**	**2.37**	**2.35**	**2.34**
50	8.17	5.02	4.07	3.61	3.34	3.04	*2.88*	*2.75*	**2.67**	**2.62**	**2.58**	**2.55**	**2.52**	**2.49**	**2.46**	**2.44**	**2.43**	**2.42**	**2.40**	**2.38**
60	8.37	5.13	4.15	3.69	3.41	3.10	*2.93*	*2.80*	**2.72**	**2.66**	**2.62**	**2.59**	**2.56**	**2.52**	**2.50**	**2.48**	**2.46**	**2.45**	**2.43**	**2.42**
75	8.63	5.27	4.27	3.78	3.49	3.17	*2.99*	*2.86*	*2.77*	**2.72**	**2.67**	**2.64**	**2.61**	**2.57**	**2.55**	**2.53**	**2.51**	**2.50**	**2.48**	**2.46**
100	8.94	5.46	4.40	3.89	3.60	3.26	3.08	*2.94*	*2.85*	*2.79*	**2.74**	**2.70**	**2.68**	**2.64**	**2.61**	**2.59**	**2.57**	**2.56**	**2.53**	**2.52**
125	9.19	5.60	4.51	3.98	3.68	3.33	3.14	*3.00*	*2.90*	*2.84*	*2.79*	*2.76*	**2.73**	**2.68**	**2.65**	**2.63**	**2.62**	**2.60**	**2.58**	**2.56**
150	9.39	5.70	4.59	4.06	3.74	3.39	3.19	*3.04*	*2.95*	*2.88*	*2.83*	*2.79*	*2.77*	**2.72**	**2.69**	**2.67**	**2.65**	**2.64**	**2.61**	**2.60**
175	9.56	5.80	4.66	4.12	3.80	3.43	3.24	*3.08*	*2.99*	*2.92*	*2.87*	*2.83*	*2.80*	*2.76*	**2.72**	**2.70**	**2.68**	**2.67**	**2.64**	**2.63**
200	9.70	5.88	4.73	4.17	3.85	3.48	3.27	3.12	*3.02*	*2.95*	*2.90*	*2.86*	*2.83*	*2.78*	*2.75*	**2.73**	**2.71**	**2.69**	**2.67**	**2.65**

Table 19-1. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Observations (10 COCs, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	4.24	**2.86**	**2.44**	**2.23**	**2.11**	**1.97**	**1.89**	**1.84**	**1.80**	**1.77**	**1.76**	**1.74**	**1.73**	**1.71**	**1.70**	**1.69**	**1.69**	**1.68**	**1.67**	**1.66**
2	5.09	3.33	**2.79**	**2.53**	**2.38**	**2.21**	**2.11**	**2.04**	**2.00**	**1.97**	**1.94**	**1.93**	**1.91**	**1.89**	**1.88**	**1.87**	**1.86**	**1.85**	**1.84**	**1.83**
3	5.60	3.60	**2.99**	**2.71**	**2.54**	**2.34**	**2.24**	**2.16**	**2.11**	**2.08**	**2.05**	**2.03**	**2.02**	**1.99**	**1.98**	**1.97**	**1.96**	**1.95**	**1.94**	**1.93**
4	5.94	3.80	*3.15*	**2.83**	**2.65**	**2.44**	**2.33**	**2.24**	**2.19**	**2.15**	**2.12**	**2.11**	**2.09**	**2.06**	**2.05**	**2.04**	**2.03**	**2.02**	**2.00**	**1.99**
5	6.22	3.96	3.26	**2.93**	**2.73**	**2.52**	**2.40**	**2.31**	**2.25**	**2.21**	**2.19**	**2.16**	**2.14**	**2.12**	**2.10**	**2.09**	**2.08**	**2.07**	**2.05**	**2.04**
8	6.82	4.27	3.50	*3.13*	**2.91**	**2.67**	**2.54**	**2.44**	**2.38**	**2.33**	**2.30**	**2.28**	**2.26**	**2.23**	**2.21**	**2.19**	**2.18**	**2.17**	**2.16**	**2.15**
12	7.30	4.55	3.70	3.30	**3.06**	**2.80**	**2.66**	**2.55**	**2.48**	**2.44**	**2.40**	**2.37**	**2.35**	**2.32**	**2.30**	**2.28**	**2.27**	**2.26**	**2.24**	**2.23**
16	7.64	4.72	3.84	3.42	*3.18*	**2.90**	**2.74**	**2.63**	**2.56**	**2.51**	**2.47**	**2.44**	**2.42**	**2.39**	**2.36**	**2.35**	**2.33**	**2.32**	**2.31**	**2.29**
20	7.92	4.88	3.96	3.52	*3.26*	**2.97**	**2.81**	**2.69**	**2.62**	**2.56**	**2.52**	**2.49**	**2.47**	**2.44**	**2.41**	**2.39**	**2.38**	**2.37**	**2.35**	**2.34**
30	8.37	5.14	4.15	3.69	3.41	**3.10**	**2.93**	**2.80**	**2.72**	**2.66**	**2.62**	**2.59**	**2.56**	**2.52**	**2.50**	**2.48**	**2.46**	**2.45**	**2.43**	**2.42**
40	8.71	5.31	4.29	3.80	3.52	*3.19*	**3.01**	**2.88**	**2.79**	**2.73**	**2.69**	**2.65**	**2.63**	**2.59**	**2.56**	**2.54**	**2.52**	**2.51**	**2.49**	**2.48**
50	8.94	5.46	4.41	3.90	3.60	*3.26*	**3.08**	**2.94**	**2.85**	**2.79**	**2.74**	**2.71**	**2.68**	**2.63**	**2.61**	**2.59**	**2.57**	**2.56**	**2.53**	**2.52**
60	9.17	5.57	4.49	3.97	3.66	*3.32*	*3.13*	**2.99**	**2.89**	**2.83**	**2.78**	**2.74**	**2.72**	**2.67**	**2.65**	**2.62**	**2.61**	**2.59**	**2.57**	**2.55**
75	9.39	5.71	4.59	4.05	3.74	*3.39*	*3.19*	**3.04**	**2.95**	**2.88**	**2.83**	**2.79**	**2.77**	**2.72**	**2.69**	**2.67**	**2.65**	**2.64**	**2.61**	**2.60**
100	9.68	5.88	4.72	4.17	3.84	3.47	*3.28*	*3.12*	**3.02**	**2.95**	**2.90**	**2.86**	**2.83**	**2.78**	**2.75**	**2.73**	**2.71**	**2.69**	**2.67**	**2.65**
125	9.90	6.01	4.83	4.26	3.93	3.54	*3.33*	*3.18*	**3.07**	**3.00**	**2.95**	**2.91**	**2.88**	**2.83**	**2.79**	**2.77**	**2.75**	**2.74**	**2.71**	**2.69**
150	10.13	6.11	4.92	4.33	3.98	3.60	*3.39*	*3.22*	*3.12*	**3.04**	**2.99**	**2.95**	**2.91**	**2.86**	**2.83**	**2.81**	**2.79**	**2.77**	**2.74**	**2.73**
175	10.24	6.19	4.97	4.39	4.04	3.64	*3.43*	*3.26*	*3.16*	**3.08**	**3.02**	**2.98**	**2.95**	**2.90**	**2.86**	**2.84**	**2.82**	**2.80**	**2.77**	**2.76**
200	10.41	6.28	5.03	4.44	4.08	3.69	3.47	*3.30*	*3.18*	**3.11**	**3.05**	**3.01**	**2.97**	**2.92**	**2.89**	**2.86**	**2.84**	**2.83**	**2.80**	**2.78**

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Table 19-1. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Observations (20 COCs, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.53	**2.44**	**2.11**	**1.94**	**1.85**	**1.73**	**1.67**	**1.63**	**1.59**	**1.58**	**1.56**	**1.55**	**1.54**	**1.52**	**1.51**	**1.51**	**1.50**	**1.50**	**1.49**	**1.48**
2	4.41	2.91	*2.46*	**2.24**	**2.11**	**1.97**	**1.89**	**1.84**	**1.80**	**1.77**	**1.76**	**1.74**	**1.73**	**1.71**	**1.70**	**1.69**	**1.69**	**1.68**	**1.67**	**1.66**
3	5.00	3.20	2.67	*2.43*	**2.28**	**2.11**	**2.03**	**1.96**	**1.92**	**1.89**	**1.87**	**1.85**	**1.84**	**1.82**	**1.81**	**1.80**	**1.79**	**1.78**	**1.77**	**1.76**
4	5.43	3.42	2.82	*2.55*	**2.39**	**2.21**	**2.12**	**2.05**	**2.00**	**1.97**	**1.94**	**1.93**	**1.92**	**1.89**	**1.88**	**1.87**	**1.86**	**1.85**	**1.84**	**1.83**
5	5.77	3.57	2.95	2.65	*2.48*	**2.29**	**2.19**	**2.11**	**2.06**	**2.03**	**2.00**	**1.99**	**1.97**	**1.95**	**1.93**	**1.92**	**1.92**	**1.91**	**1.89**	**1.89**
8	6.50	3.93	3.20	2.86	2.67	*2.45*	**2.33**	**2.25**	**2.19**	**2.16**	**2.13**	**2.11**	**2.09**	**2.06**	**2.05**	**2.04**	**2.03**	**2.02**	**2.00**	**1.99**
12	7.13	4.24	3.43	3.05	2.83	*2.59*	*2.46*	**2.36**	**2.31**	**2.26**	**2.23**	**2.21**	**2.19**	**2.16**	**2.14**	**2.13**	**2.12**	**2.11**	**2.09**	**2.09**
16	7.58	4.46	3.59	3.18	2.94	2.69	*2.55*	*2.45*	**2.38**	**2.33**	**2.31**	**2.28**	**2.26**	**2.23**	**2.21**	**2.20**	**2.18**	**2.17**	**2.16**	**2.15**
20	7.92	4.63	3.71	3.28	3.03	2.76	*2.62*	*2.51*	*2.44*	*2.39*	**2.36**	**2.33**	**2.31**	**2.28**	**2.26**	**2.25**	**2.23**	**2.22**	**2.21**	**2.19**
30	8.54	4.95	3.94	3.47	3.20	2.90	2.74	*2.62*	*2.55*	*2.50*	*2.46*	*2.43*	*2.41*	**2.37**	**2.35**	**2.33**	**2.32**	**2.31**	**2.29**	**2.28**
40	9.00	5.17	4.10	3.59	3.31	2.99	2.83	2.70	*2.62*	*2.57*	*2.53*	*2.50*	*2.48*	*2.44*	*2.41*	*2.40*	*2.38*	**2.37**	**2.35**	**2.34**
50	9.34	5.34	4.22	3.70	3.40	3.07	2.89	2.76	2.68	*2.62*	*2.58*	*2.55*	*2.52*	*2.49*	*2.46*	*2.44*	*2.43*	*2.42*	*2.40*	*2.38*
60	9.62	5.48	4.32	3.78	3.47	3.13	2.95	2.81	2.73	*2.67*	*2.62*	*2.59*	*2.57*	*2.53*	*2.50*	*2.48*	*2.47*	*2.45*	*2.43*	*2.42*
75	9.96	5.65	4.44	3.88	3.56	3.20	3.01	2.87	2.78	2.72	2.68	*2.64*	*2.62*	*2.57*	*2.55*	*2.53*	*2.51*	*2.50*	*2.48*	*2.46*
100	10.36	5.85	4.59	4.01	3.67	3.30	3.10	2.95	2.86	2.79	2.74	2.71	*2.68*	*2.64*	*2.61*	*2.59*	*2.57*	*2.56*	*2.54*	*2.52*
125	10.70	6.02	4.72	4.11	3.76	3.37	3.17	3.01	2.91	2.84	2.80	2.76	2.73	*2.69*	*2.66*	*2.63*	*2.62*	*2.60*	*2.58*	*2.56*
150	10.92	6.16	4.80	4.19	3.83	3.43	3.22	3.06	2.96	2.89	2.84	2.80	2.77	2.72	2.69	*2.67*	*2.65*	*2.64*	*2.61*	*2.60*
175	11.15	6.28	4.89	4.25	3.89	3.48	3.26	3.10	3.00	2.92	2.87	2.84	2.80	2.76	2.72	2.70	*2.68*	*2.67*	*2.64*	*2.62*
200	11.38	6.36	4.96	4.31	3.94	3.53	3.30	3.13	3.03	2.96	2.90	2.86	2.83	2.79	2.75	2.73	2.71	*2.69*	*2.67*	*2.65*

Table 19-1. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Observations (20 COCs, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	4.41	2.91	**2.46**	**2.24**	**2.11**	**1.97**	**1.89**	**1.84**	**1.80**	**1.77**	**1.76**	**1.74**	**1.73**	**1.71**	**1.70**	**1.69**	**1.69**	**1.68**	**1.67**	**1.66**
2	5.43	3.42	*2.82*	**2.55**	**2.39**	**2.21**	**2.12**	**2.05**	**2.00**	**1.97**	**1.94**	**1.93**	**1.92**	**1.89**	**1.88**	**1.87**	**1.86**	**1.85**	**1.84**	**1.83**
3	6.05	3.71	3.05	**2.73**	**2.55**	**2.35**	**2.25**	**2.16**	**2.11**	**2.08**	**2.05**	**2.03**	**2.02**	**1.99**	**1.98**	**1.97**	**1.96**	**1.95**	**1.94**	**1.93**
4	6.50	3.93	3.20	*2.86*	**2.67**	**2.45**	**2.33**	**2.25**	**2.19**	**2.16**	**2.13**	**2.11**	**2.09**	**2.06**	**2.05**	**2.04**	**2.03**	**2.02**	**2.00**	**1.99**
5	6.84	4.10	3.32	2.96	*2.76*	**2.52**	**2.40**	**2.31**	**2.26**	**2.21**	**2.19**	**2.16**	**2.14**	**2.12**	**2.10**	**2.09**	**2.08**	**2.07**	**2.05**	**2.04**
8	7.58	4.46	3.59	3.18	*2.94*	**2.69**	**2.55**	**2.45**	**2.38**	**2.33**	**2.31**	**2.28**	**2.26**	**2.23**	**2.21**	**2.20**	**2.18**	**2.17**	**2.16**	**2.15**
12	8.20	4.78	3.81	3.36	3.11	*2.82*	**2.67**	**2.56**	**2.49**	**2.44**	**2.40**	**2.38**	**2.35**	**2.32**	**2.30**	**2.28**	**2.27**	**2.26**	**2.25**	**2.23**
16	8.66	5.00	3.97	3.49	3.22	*2.92*	*2.76*	**2.64**	**2.56**	**2.51**	**2.48**	**2.44**	**2.42**	**2.39**	**2.37**	**2.35**	**2.33**	**2.32**	**2.31**	**2.29**
20	9.00	5.17	4.10	3.59	3.31	*2.99*	*2.83*	**2.70**	**2.62**	**2.57**	**2.53**	**2.50**	**2.48**	**2.44**	**2.41**	**2.40**	**2.38**	**2.37**	**2.35**	**2.34**
30	9.62	5.48	4.32	3.78	3.47	3.13	*2.95*	*2.81*	**2.73**	**2.67**	**2.62**	**2.59**	**2.57**	**2.53**	**2.50**	**2.48**	**2.47**	**2.45**	**2.43**	**2.42**
40	10.02	5.70	4.48	3.91	3.59	3.23	*3.03*	*2.89*	*2.80*	**2.74**	**2.69**	**2.66**	**2.63**	**2.59**	**2.56**	**2.54**	**2.52**	**2.51**	**2.49**	**2.48**
50	10.36	5.85	4.59	4.01	3.67	3.30	3.10	*2.95*	*2.86*	*2.79*	**2.74**	**2.71**	**2.68**	**2.64**	**2.61**	**2.59**	**2.57**	**2.56**	**2.54**	**2.52**
60	10.64	5.99	4.69	4.09	3.74	3.36	3.16	*3.00*	*2.90*	*2.84*	*2.79*	*2.75*	**2.72**	**2.68**	**2.65**	**2.62**	**2.61**	**2.60**	**2.57**	**2.55**
75	10.92	6.16	4.80	4.19	3.83	3.43	3.22	*3.06*	*2.96*	*2.89*	*2.84*	*2.80*	*2.77*	**2.72**	**2.69**	**2.67**	**2.65**	**2.64**	**2.61**	**2.60**
100	11.38	6.36	4.96	4.31	3.94	3.53	3.30	3.13	*3.03*	*2.96*	*2.90*	*2.86*	*2.83*	*2.79*	*2.75*	**2.73**	**2.71**	**2.69**	**2.67**	**2.65**
125	11.66	6.53	5.09	4.41	4.03	3.60	3.37	3.20	*3.08*	*3.01*	*2.96*	*2.91*	*2.88*	*2.83*	*2.80*	*2.77*	*2.75*	**2.74**	**2.71**	**2.69**
150	11.88	6.65	5.17	4.49	4.10	3.66	3.42	3.24	3.13	*3.05*	*3.00*	*2.95*	*2.92*	*2.87*	*2.83*	*2.81*	*2.79*	*2.77*	**2.74**	**2.73**
175	12.11	6.76	5.26	4.56	4.15	3.71	3.47	3.28	3.17	*3.09*	*3.03*	*2.99*	*2.95*	*2.90*	*2.86*	*2.84*	*2.82*	*2.80*	*2.77*	*2.76*
200	12.28	6.84	5.31	4.61	4.20	3.75	3.50	3.32	3.20	3.12	*3.06*	*3.02*	*2.98*	*2.93*	*2.89*	*2.86*	*2.84*	*2.83*	*2.80*	*2.78*

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Table 19-1. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Observations (20 COCs, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	5.43	3.42	**2.82**	**2.55**	**2.40**	**2.21**	**2.11**	**2.04**	**2.00**	**1.97**	**1.94**	**1.93**	**1.92**	**1.89**	**1.88**	**1.87**	**1.86**	**1.85**	**1.85**	**1.83**
2	6.50	3.93	*3.20*	**2.86**	**2.67**	**2.45**	**2.34**	**2.25**	**2.19**	**2.16**	**2.13**	**2.11**	**2.09**	**2.06**	**2.04**	**2.04**	**2.03**	**2.02**	**2.00**	**1.99**
3	7.13	4.24	3.42	**3.05**	**2.82**	**2.60**	**2.45**	**2.37**	**2.30**	**2.26**	**2.23**	**2.21**	**2.19**	**2.16**	**2.14**	**2.13**	**2.11**	**2.11**	**2.09**	**2.09**
4	7.58	4.46	3.59	*3.18*	**2.95**	**2.68**	**2.55**	**2.45**	**2.38**	**2.33**	**2.31**	**2.28**	**2.26**	**2.23**	**2.21**	**2.19**	**2.19**	**2.17**	**2.16**	**2.14**
5	7.92	4.63	3.70	*3.28*	**3.03**	**2.77**	**2.62**	**2.51**	**2.44**	**2.40**	**2.35**	**2.33**	**2.31**	**2.28**	**2.26**	**2.24**	**2.23**	**2.22**	**2.21**	**2.19**
8	8.66	5.00	3.98	3.50	*3.22*	**2.92**	**2.76**	**2.64**	**2.57**	**2.51**	**2.48**	**2.45**	**2.43**	**2.39**	**2.36**	**2.35**	**2.33**	**2.33**	**2.31**	**2.29**
12	9.22	5.31	4.18	3.67	3.39	**3.06**	**2.88**	**2.75**	**2.67**	**2.61**	**2.57**	**2.54**	**2.51**	**2.48**	**2.45**	**2.43**	**2.42**	**2.41**	**2.39**	**2.38**
16	9.68	5.54	4.35	3.81	3.50	*3.15*	**2.96**	**2.83**	**2.74**	**2.68**	**2.64**	**2.61**	**2.58**	**2.54**	**2.52**	**2.50**	**2.48**	**2.47**	**2.45**	**2.43**
20	10.02	5.71	4.46	3.90	3.59	*3.23*	**3.03**	**2.89**	**2.80**	**2.74**	**2.69**	**2.66**	**2.63**	**2.59**	**2.56**	**2.54**	**2.52**	**2.51**	**2.49**	**2.48**
30	10.58	5.99	4.69	4.10	3.74	*3.36*	*3.15*	**3.00**	**2.91**	**2.84**	**2.79**	**2.75**	**2.72**	**2.68**	**2.65**	**2.62**	**2.61**	**2.60**	**2.57**	**2.55**
40	11.04	6.22	4.86	4.21	3.86	3.46	*3.23*	**3.08**	**2.98**	**2.91**	**2.85**	**2.82**	**2.78**	**2.74**	**2.71**	**2.68**	**2.67**	**2.65**	**2.62**	**2.61**
50	11.38	6.36	4.97	4.32	3.94	3.53	*3.30*	*3.13*	**3.03**	**2.96**	**2.91**	**2.86**	**2.83**	**2.79**	**2.75**	**2.73**	**2.71**	**2.69**	**2.67**	**2.65**
60	11.60	6.50	5.06	4.39	4.01	3.59	*3.36*	*3.18*	**3.08**	**3.00**	**2.95**	**2.91**	**2.87**	**2.82**	**2.79**	**2.77**	**2.74**	**2.73**	**2.70**	**2.69**
75	11.83	6.67	5.17	4.49	4.10	3.66	*3.42*	*3.25*	*3.13*	**3.06**	**3.00**	**2.95**	**2.92**	**2.87**	**2.84**	**2.81**	**2.79**	**2.77**	**2.74**	**2.72**
100	12.28	6.84	5.31	4.61	4.21	3.76	3.50	*3.32*	*3.20*	*3.12*	**3.06**	**3.02**	**2.98**	**2.93**	**2.89**	**2.86**	**2.84**	**2.83**	**2.80**	**2.78**
125	12.51	7.01	5.43	4.72	4.29	3.83	3.57	*3.37*	*3.26*	*3.18*	**3.11**	**3.06**	**3.03**	**2.97**	**2.94**	**2.91**	**2.89**	**2.87**	**2.84**	**2.82**
150	12.73	7.13	5.54	4.78	4.35	3.88	3.62	*3.42*	*3.30*	*3.22*	*3.15*	**3.11**	**3.06**	**3.01**	**2.97**	**2.94**	**2.92**	**2.90**	**2.87**	**2.85**
175	12.96	7.24	5.60	4.86	4.41	3.93	3.66	*3.46*	*3.34*	*3.25*	*3.19*	*3.13*	**3.10**	**3.04**	**3.00**	**2.97**	**2.95**	**2.93**	**2.90**	**2.88**
200	13.19	7.30	5.65	4.90	4.46	3.97	3.70	3.50	*3.37*	*3.28*	*3.22*	*3.16*	*3.13*	**3.07**	**3.03**	**3.00**	**2.98**	**2.96**	**2.92**	**2.90**

Table 19-1. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Observations (40 COCs, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	4.56	2.92	*2.48*	**2.24**	**2.12**	**1.98**	**1.89**	**1.84**	**1.80**	**1.77**	**1.75**	**1.75**	**1.73**	**1.71**	**1.70**	**1.69**	**1.68**	**1.68**	**1.67**	**1.67**
2	5.69	3.48	2.85	*2.57*	*2.41*	**2.22**	**2.12**	**2.05**	**2.01**	**1.97**	**1.95**	**1.93**	**1.91**	**1.89**	**1.88**	**1.87**	**1.87**	**1.86**	**1.84**	**1.83**
3	6.34	3.81	3.06	2.73	*2.57*	**2.36**	**2.24**	**2.17**	**2.11**	**2.08**	**2.05**	**2.03**	**2.02**	**2.00**	**1.98**	**1.96**	**1.96**	**1.95**	**1.94**	**1.93**
4	6.91	4.00	3.25	2.88	2.69	*2.45*	**2.34**	**2.24**	**2.20**	**2.16**	**2.12**	**2.10**	**2.09**	**2.07**	**2.05**	**2.03**	**2.03**	**2.02**	**2.01**	**2.00**
5	7.38	4.19	3.37	2.99	2.78	*2.52*	*2.41*	**2.31**	**2.25**	**2.22**	**2.18**	**2.16**	**2.15**	**2.12**	**2.10**	**2.09**	**2.08**	**2.07**	**2.05**	**2.04**
8	8.31	4.61	3.62	3.20	2.97	2.69	*2.55*	*2.45*	**2.38**	**2.34**	**2.30**	**2.28**	**2.27**	**2.23**	**2.21**	**2.20**	**2.18**	**2.17**	**2.16**	**2.15**
12	9.06	4.94	3.91	3.39	3.13	2.83	2.69	*2.57*	*2.49*	*2.44*	*2.41*	*2.38*	**2.36**	**2.32**	**2.30**	**2.29**	**2.28**	**2.27**	**2.24**	**2.23**
16	9.62	5.22	4.05	3.53	3.25	2.93	2.76	*2.64*	*2.57*	*2.51*	*2.48*	*2.45*	*2.43*	*2.38*	**2.36**	**2.35**	**2.34**	**2.32**	**2.30**	**2.29**
20	10.00	5.41	4.19	3.65	3.34	3.02	2.83	2.71	*2.62*	*2.57*	*2.52*	*2.50*	*2.48*	*2.44*	*2.42*	*2.39*	*2.38*	2.37	2.35	2.34
30	10.75	5.78	4.42	3.86	3.51	3.16	2.96	2.82	2.73	*2.66*	*2.63*	*2.59*	*2.57*	*2.52*	*2.50*	*2.48*	*2.46*	*2.45*	*2.43*	*2.42*
40	11.50	6.06	4.61	4.00	3.62	3.25	3.04	2.90	2.80	2.73	2.69	*2.66*	*2.63*	*2.59*	*2.56*	*2.55*	*2.52*	*2.51*	*2.49*	*2.48*
50	11.88	6.25	4.75	4.09	3.72	3.32	3.11	2.96	2.86	2.79	2.75	2.71	2.69	*2.64*	*2.61*	*2.59*	*2.57*	*2.56*	*2.54*	*2.52*
60	12.25	6.34	4.84	4.19	3.81	3.39	3.17	3.02	2.91	2.84	2.79	2.76	2.72	*2.68*	*2.65*	*2.63*	*2.61*	*2.59*	*2.57*	*2.56*
75	12.62	6.53	4.98	4.28	3.91	3.46	3.24	3.06	2.97	2.90	2.84	2.80	2.77	2.72	2.70	*2.68*	*2.65*	*2.64*	*2.62*	*2.59*
100	13.00	6.81	5.17	4.42	4.00	3.55	3.32	3.16	3.04	2.97	2.91	2.86	2.83	2.78	2.76	2.73	2.71	*2.70*	*2.66*	*2.65*
125	13.38	7.00	5.31	4.54	4.09	3.65	3.39	3.20	3.10	3.02	2.96	2.92	2.89	2.83	2.80	2.77	2.76	2.73	2.71	*2.69*
150	13.75	7.19	5.41	4.61	4.19	3.70	3.44	3.25	3.13	3.06	3.00	2.96	2.92	2.88	2.84	2.80	2.79	2.77	2.75	2.72
175	14.12	7.28	5.50	4.70	4.23	3.74	3.48	3.30	3.18	3.10	3.04	2.99	2.96	2.90	2.86	2.84	2.82	2.80	2.77	2.76
200	14.31	7.38	5.59	4.75	4.30	3.79	3.53	3.34	3.21	3.13	3.06	3.02	2.98	2.93	2.90	2.86	2.84	2.82	2.79	2.78

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Table 19-1. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Observations (40 COCs, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	5.69	3.48	*2.85*	**2.57**	**2.41**	**2.22**	**2.12**	**2.05**	**2.01**	**1.97**	**1.95**	**1.93**	**1.91**	**1.89**	**1.88**	**1.87**	**1.87**	**1.86**	**1.84**	**1.83**
2	6.91	4.00	3.25	*2.88*	**2.69**	**2.45**	**2.34**	**2.24**	**2.20**	**2.16**	**2.12**	**2.10**	**2.09**	**2.07**	**2.05**	**2.03**	**2.03**	**2.02**	**2.01**	**2.00**
3	7.66	4.38	3.48	3.06	*2.85*	**2.59**	**2.46**	**2.36**	**2.31**	**2.27**	**2.23**	**2.21**	**2.20**	**2.16**	**2.15**	**2.12**	**2.12**	**2.11**	**2.09**	**2.08**
4	8.31	4.61	3.62	3.20	*2.97*	**2.69**	**2.55**	**2.45**	**2.38**	**2.34**	**2.30**	**2.28**	**2.27**	**2.23**	**2.21**	**2.20**	**2.18**	**2.17**	**2.16**	**2.15**
5	8.69	4.80	3.77	3.32	3.06	*2.78*	**2.62**	**2.51**	**2.44**	**2.39**	**2.36**	**2.34**	**2.31**	**2.29**	**2.27**	**2.24**	**2.23**	**2.22**	**2.21**	**2.20**
8	9.62	5.22	4.05	3.53	3.25	*2.93*	*2.76*	**2.64**	**2.57**	**2.51**	**2.48**	**2.45**	**2.43**	**2.38**	**2.36**	**2.35**	**2.34**	**2.32**	**2.30**	**2.29**
12	10.38	5.59	4.33	3.74	3.41	3.06	*2.90*	*2.76*	**2.68**	**2.62**	**2.57**	**2.55**	**2.51**	**2.48**	**2.45**	**2.43**	**2.42**	**2.41**	**2.38**	**2.37**
16	10.94	5.83	4.47	3.88	3.53	3.18	*2.98*	*2.83*	**2.75**	**2.69**	**2.64**	**2.61**	**2.58**	**2.55**	**2.51**	**2.50**	**2.48**	**2.46**	**2.44**	**2.43**
20	11.50	6.06	4.61	4.00	3.62	3.25	*3.04*	*2.90*	*2.80*	**2.73**	**2.69**	**2.66**	**2.63**	**2.59**	**2.56**	**2.55**	**2.52**	**2.51**	**2.49**	**2.48**
30	12.25	6.34	4.84	4.19	3.81	3.39	3.17	*3.02*	*2.91*	*2.84*	*2.79*	*2.76*	**2.72**	**2.68**	**2.65**	**2.63**	**2.61**	**2.59**	**2.57**	**2.56**
40	12.62	6.62	5.03	4.33	3.91	3.48	3.25	3.09	*2.98*	*2.91*	*2.85*	*2.82*	*2.78*	**2.73**	**2.71**	**2.69**	**2.66**	**2.65**	**2.63**	**2.61**
50	13.00	6.81	5.17	4.42	4.00	3.55	3.32	3.16	*3.04*	*2.97*	*2.91*	*2.86*	*2.83*	*2.78*	*2.76*	**2.73**	**2.71**	**2.70**	**2.66**	**2.65**
60	13.38	7.00	5.27	4.52	4.09	3.62	3.38	3.20	*3.09*	*3.00*	*2.95*	*2.91*	*2.88*	*2.83*	*2.79*	*2.77*	**2.75**	**2.73**	**2.70**	**2.69**
75	13.75	7.19	5.41	4.61	4.19	3.70	3.44	3.25	3.13	*3.06*	*3.00*	*2.96*	*2.92*	*2.88*	*2.84*	*2.80*	*2.79*	*2.77*	**2.75**	**2.72**
100	14.31	7.38	5.59	4.75	4.30	3.79	3.53	3.34	3.21	3.13	*3.06*	*3.02*	*2.98*	*2.93*	*2.90*	*2.86*	*2.84*	*2.82*	*2.79*	*2.78*
125	14.88	7.56	5.69	4.84	4.38	3.88	3.60	3.39	3.27	3.18	*3.12*	*3.06*	*3.03*	*2.98*	*2.93*	*2.91*	*2.89*	*2.88*	*2.84*	*2.82*
150	15.06	7.75	5.78	4.94	4.47	3.93	3.65	3.44	3.32	3.23	3.16	*3.11*	*3.07*	*3.02*	*2.97*	*2.95*	*2.92*	*2.90*	*2.87*	*2.85*
175	15.25	7.84	5.88	5.03	4.52	3.98	3.70	3.48	3.34	3.26	3.19	3.14	*3.10*	*3.04*	*3.00*	*2.97*	*2.95*	*2.93*	*2.90*	*2.88*
200	15.62	7.94	5.97	5.08	4.56	4.02	3.74	3.52	3.39	3.30	3.23	3.17	*3.13*	*3.07*	*3.03*	*3.00*	*2.98*	*2.96*	*2.92*	*2.90*

Table 19-1. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Observations (40 COCs, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	6.91	4.00	3.25	**2.88**	**2.69**	**2.45**	**2.34**	**2.24**	**2.20**	**2.16**	**2.12**	**2.10**	**2.09**	**2.07**	**2.05**	**2.03**	**2.03**	**2.02**	**2.01**	**2.00**
2	8.31	4.61	3.62	*3.20*	**2.97**	**2.69**	**2.55**	**2.45**	**2.38**	**2.34**	**2.30**	**2.28**	**2.27**	**2.23**	**2.21**	**2.20**	**2.18**	**2.17**	**2.16**	**2.15**
3	9.06	4.94	3.91	3.39	*3.13*	**2.83**	**2.69**	**2.57**	**2.49**	**2.44**	**2.41**	**2.38**	**2.36**	**2.32**	**2.30**	**2.29**	**2.28**	**2.27**	**2.24**	**2.23**
4	9.62	5.22	4.05	3.53	*3.25*	**2.93**	**2.76**	**2.64**	**2.57**	**2.51**	**2.48**	**2.45**	**2.43**	**2.38**	**2.36**	**2.35**	**2.34**	**2.32**	**2.30**	**2.29**
5	10.00	5.41	4.19	3.65	3.34	**3.02**	**2.83**	**2.71**	**2.62**	**2.57**	**2.52**	**2.50**	**2.48**	**2.44**	**2.42**	**2.39**	**2.38**	**2.37**	**2.35**	**2.34**
8	10.94	5.83	4.47	3.88	3.53	*3.18*	**2.98**	**2.83**	**2.75**	**2.69**	**2.64**	**2.61**	**2.58**	**2.55**	**2.51**	**2.50**	**2.48**	**2.46**	**2.44**	**2.43**
12	11.69	6.16	4.75	4.07	3.72	*3.32*	**3.11**	**2.95**	**2.85**	**2.78**	**2.73**	**2.70**	**2.68**	**2.63**	**2.61**	**2.58**	**2.56**	**2.55**	**2.50**	**2.51**
16	12.25	6.44	4.89	4.21	3.84	3.41	*3.18*	**3.03**	**2.92**	**2.85**	**2.80**	**2.77**	**2.73**	**2.69**	**2.66**	**2.64**	**2.62**	**2.61**	**2.58**	**2.57**
20	12.62	6.62	5.03	4.33	3.91	3.48	*3.25*	**3.09**	**2.98**	**2.91**	**2.85**	**2.82**	**2.78**	**2.73**	**2.71**	**2.69**	**2.66**	**2.65**	**2.63**	**2.61**
30	13.38	7.00	5.27	4.52	4.09	3.62	*3.38*	*3.20*	**3.09**	**3.00**	**2.95**	**2.91**	**2.88**	**2.83**	**2.79**	**2.77**	**2.75**	**2.73**	**2.70**	**2.69**
40	13.94	7.19	5.45	4.66	4.21	3.72	3.46	*3.27*	*3.16*	**3.07**	**3.02**	**2.97**	**2.93**	**2.89**	**2.85**	**2.83**	**2.80**	**2.78**	**2.76**	**2.73**
50	14.31	7.38	5.59	4.75	4.30	3.79	3.53	*3.34*	*3.21*	*3.13*	**3.06**	**3.02**	**2.98**	**2.93**	**2.90**	**2.86**	**2.84**	**2.82**	**2.79**	**2.78**
60	14.69	7.56	5.69	4.84	4.38	3.86	3.58	*3.39*	*3.25*	*3.18*	**3.11**	**3.06**	**3.03**	**2.97**	**2.92**	**2.90**	**2.88**	**2.86**	**2.83**	**2.82**
75	15.06	7.75	5.78	4.94	4.47	3.93	3.65	*3.44*	*3.32*	*3.23*	*3.16*	**3.11**	**3.07**	**3.02**	**2.97**	**2.95**	**2.92**	**2.90**	**2.87**	**2.85**
100	15.62	7.94	5.97	5.08	4.56	4.02	3.74	3.52	*3.39*	*3.30*	*3.23*	*3.17*	*3.13*	**3.07**	**3.03**	**3.00**	**2.98**	**2.96**	**2.92**	**2.90**
125	16.00	8.12	6.11	5.17	4.66	4.09	3.81	3.58	*3.44*	*3.34*	*3.27*	*3.21*	*3.18*	*3.12*	**3.07**	**3.04**	**3.02**	**3.00**	**2.97**	**2.95**
150	16.19	8.31	6.20	5.27	4.75	4.16	3.86	3.62	*3.48*	*3.39*	*3.31*	*3.26*	*3.21*	*3.16*	**3.11**	**3.07**	**3.05**	**3.03**	**2.99**	**2.97**
175	16.38	8.41	6.25	5.34	4.80	4.21	3.91	3.67	3.52	*3.41*	*3.34*	*3.30*	*3.25*	*3.18*	*3.13*	**3.11**	**3.07**	**3.06**	**3.03**	**3.00**
200	16.75	8.50	6.34	5.41	4.84	4.26	3.93	3.70	3.55	*3.45*	*3.38*	*3.32*	*3.27*	*3.21*	*3.17*	*3.13*	**3.11**	**3.09**	**3.05**	**3.03**

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Table 19-2. κ-Multipliers for 1-of-3 Interwell Prediction Limits on Observations (1 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	0.33	0.25	0.21	0.18	0.17	0.15	0.14	0.13	0.12	0.12	0.11	0.11	0.11	0.11	0.10	0.10	0.10	0.10	0.10	0.10
2	0.67	0.54	0.49	0.45	0.43	0.41	0.39	0.38	0.37	0.36	0.36	0.36	0.35	0.35	0.35	0.34	0.34	0.34	0.34	0.34
3	0.87	0.71	0.64	0.60	0.58	0.54	0.53	0.51	0.50	0.49	0.49	0.48	0.48	0.48	0.47	0.47	0.47	0.47	0.46	0.46
4	1.01	0.82	0.75	0.70	0.67	0.64	0.62	0.60	0.59	0.58	0.58	0.57	0.57	0.56	0.56	0.56	0.55	0.55	0.55	0.55
5	1.12	0.91	0.83	0.78	0.75	0.71	0.69	0.67	0.66	0.65	0.64	0.64	0.63	0.63	0.62	0.62	0.62	0.61	0.61	0.61
8	1.34	1.09	0.99	0.93	0.90	0.85	0.82	0.80	0.79	0.78	0.77	0.77	0.76	0.75	0.75	0.75	0.74	0.74	0.74	0.73
12	1.54	1.25	1.13	1.06	1.02	0.97	0.94	0.91	0.90	0.89	0.88	0.87	0.87	0.86	0.85	0.85	0.85	0.84	0.84	0.84
16	1.68	1.36	1.22	1.15	1.11	1.05	1.02	0.99	0.97	0.96	0.95	0.94	0.94	0.93	0.92	0.92	0.92	0.91	0.91	0.91
20	1.78	1.44	1.30	1.22	1.17	1.11	1.08	1.05	1.03	1.02	1.01	1.00	0.99	0.98	0.98	0.97	0.97	0.97	0.96	0.96
30	1.97	1.58	1.43	1.34	1.29	1.22	1.18	1.15	1.13	1.12	1.10	1.10	1.09	1.08	1.07	1.07	1.06	1.06	1.05	1.05
40	2.10	1.69	1.52	1.43	1.37	1.30	1.25	1.22	1.20	1.18	1.17	1.16	1.16	1.14	1.14	1.13	1.13	1.12	1.12	1.11
50	2.21	1.76	1.59	1.49	1.43	1.35	1.31	1.27	1.25	1.23	1.22	1.21	1.20	1.19	1.18	1.18	1.17	1.17	1.16	1.16
60	2.29	1.83	1.64	1.54	1.48	1.40	1.35	1.32	1.29	1.28	1.26	1.25	1.24	1.23	1.22	1.22	1.21	1.21	1.20	1.20
75	2.39	1.90	1.71	1.60	1.54	1.46	1.41	1.37	1.34	1.33	1.31	1.30	1.29	1.28	1.27	1.26	1.26	1.25	1.25	1.24
100	2.51	2.00	1.80	1.68	1.61	1.53	1.48	1.44	1.41	1.39	1.37	1.36	1.35	1.34	1.33	1.32	1.32	1.31	1.30	1.30
125	2.61	2.07	1.86	1.74	1.67	1.58	1.53	1.49	1.46	1.44	1.42	1.41	1.40	1.39	1.38	1.37	1.36	1.36	1.35	1.34
150	2.68	2.13	1.91	1.79	1.72	1.62	1.57	1.53	1.50	1.48	1.46	1.45	1.44	1.42	1.41	1.40	1.40	1.39	1.38	1.38
175	2.75	*2.18*	1.96	1.83	1.76	1.66	1.60	1.56	1.53	1.51	1.49	1.48	1.47	1.45	1.44	1.43	1.43	1.42	1.41	1.41
200	2.80	*2.22*	1.99	1.87	1.79	1.69	1.63	1.59	1.56	1.54	1.52	1.51	1.50	1.48	1.47	1.46	1.45	1.45	1.44	1.43

Table 19-2. κ-Multipliers for 1-of-3 Interwell Prediction Limits on Observations (1 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	0.67	0.54	0.49	0.45	0.43	0.41	0.39	0.38	0.37	0.36	0.36	0.36	0.35	0.35	0.35	0.34	0.34	0.34	0.34	0.34
2	1.01	0.82	0.75	0.70	0.67	0.64	0.62	0.60	0.59	0.58	0.58	0.57	0.57	0.56	0.56	0.56	0.55	0.55	0.55	0.55
3	1.21	0.98	0.89	0.84	0.80	0.76	0.74	0.72	0.71	0.70	0.69	0.69	0.68	0.68	0.67	0.67	0.67	0.66	0.66	0.66
4	1.34	1.09	0.99	0.93	0.90	0.85	0.82	0.80	0.79	0.78	0.77	0.77	0.76	0.75	0.75	0.75	0.74	0.74	0.74	0.73
5	1.45	1.18	1.07	1.00	0.96	0.92	0.89	0.87	0.85	0.84	0.83	0.83	0.82	0.81	0.81	0.80	0.80	0.80	0.79	0.79
8	1.68	1.36	1.22	1.15	1.11	1.05	1.02	0.99	0.97	0.96	0.95	0.94	0.94	0.93	0.92	0.92	0.92	0.91	0.91	0.91
12	1.87	1.50	1.36	1.28	1.22	1.16	1.12	1.09	1.08	1.06	1.05	1.04	1.04	1.03	1.02	1.02	1.01	1.01	1.00	1.00
16	2.00	1.61	1.45	1.36	1.31	1.24	1.20	1.17	1.15	1.13	1.12	1.11	1.10	1.09	1.09	1.08	1.08	1.07	1.07	1.06
20	2.10	1.69	1.52	1.43	1.37	1.30	1.25	1.22	1.20	1.18	1.17	1.16	1.16	1.14	1.14	1.13	1.13	1.12	1.12	1.11
30	2.29	1.83	1.64	1.54	1.48	1.40	1.35	1.32	1.29	1.28	1.26	1.25	1.24	1.23	1.22	1.22	1.21	1.21	1.20	1.20
40	2.41	1.92	1.73	1.62	1.55	1.47	1.42	1.38	1.36	1.34	1.33	1.32	1.31	1.29	1.28	1.28	1.27	1.27	1.26	1.25
50	2.51	2.00	1.80	1.68	1.61	1.53	1.48	1.44	1.41	1.39	1.37	1.36	1.35	1.34	1.33	1.32	1.32	1.31	1.30	1.30
60	2.59	2.06	1.85	1.73	1.66	1.57	1.52	1.48	1.45	1.43	1.41	1.40	1.39	1.38	1.37	1.36	1.35	1.35	1.34	1.33
75	2.68	2.13	1.91	1.79	1.72	1.62	1.57	1.53	1.50	1.48	1.46	1.45	1.44	1.42	1.41	1.40	1.40	1.39	1.38	1.38
100	2.80	2.22	1.99	1.87	1.79	1.69	1.63	1.59	1.56	1.54	1.52	1.51	1.50	1.48	1.47	1.46	1.45	1.45	1.44	1.43
125	2.90	2.29	2.06	1.93	1.84	1.74	1.68	1.64	1.60	1.58	1.56	1.55	1.54	1.52	1.51	1.50	1.50	1.49	1.48	1.47
150	2.97	2.35	2.11	1.97	1.89	1.79	1.72	1.67	1.64	1.62	1.60	1.59	1.57	1.56	1.55	1.54	1.53	1.52	1.51	1.51
175	3.03	2.40	2.15	2.01	1.93	1.82	1.76	1.71	1.67	1.65	1.63	1.62	1.60	1.59	1.57	1.57	1.56	1.55	1.54	1.53
200	3.08	2.44	2.18	2.05	1.96	1.85	1.79	1.73	1.70	1.68	1.66	1.64	1.63	1.61	1.60	1.59	1.58	1.58	1.57	1.56

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Table 19-2. κ-Multipliers for 1-of-3 Interwell Prediction Limits on Observations (1 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	1.01	0.82	0.75	0.70	0.67	0.64	0.62	0.60	0.59	0.58	0.58	0.57	0.57	0.56	0.56	0.56	0.55	0.55	0.55	0.55
2	1.34	1.09	0.99	0.93	0.90	0.85	0.82	0.80	0.79	0.78	0.77	0.77	0.76	0.75	0.75	0.75	0.74	0.74	0.74	0.73
3	1.54	1.25	1.13	1.06	1.02	0.97	0.94	0.91	0.90	0.89	0.88	0.87	0.87	0.86	0.85	0.85	0.85	0.84	0.84	0.84
4	1.68	1.36	1.22	1.15	1.11	1.05	1.02	0.99	0.97	0.96	0.95	0.94	0.94	0.93	0.92	0.92	0.92	0.91	0.91	0.91
5	1.78	1.44	1.30	1.22	1.17	1.11	1.08	1.05	1.03	1.02	1.01	1.00	0.99	0.98	0.98	0.97	0.97	0.97	0.96	0.96
8	2.00	1.61	1.45	1.36	1.31	1.24	1.20	1.17	1.15	1.13	1.12	1.11	1.10	1.09	1.09	1.08	1.08	1.07	1.07	1.06
12	2.19	1.75	1.57	1.48	1.42	1.34	1.30	1.26	1.24	1.23	1.21	1.20	1.20	1.18	1.18	1.17	1.17	1.16	1.15	1.15
16	2.32	1.85	1.66	1.56	1.50	1.42	1.37	1.33	1.31	1.29	1.28	1.27	1.26	1.25	1.24	1.23	1.23	1.22	1.21	1.21
20	2.41	1.92	1.73	1.62	1.55	1.47	1.42	1.38	1.36	1.34	1.33	1.32	1.31	1.29	1.28	1.28	1.27	1.27	1.26	1.25
30	2.59	2.06	1.85	1.73	1.66	1.57	1.52	1.48	1.45	1.43	1.41	1.40	1.39	1.38	1.37	1.36	1.35	1.35	1.34	1.33
40	2.71	2.15	1.93	1.81	1.73	1.64	1.58	1.54	1.51	1.49	1.47	1.46	1.45	1.44	1.42	1.42	1.41	1.41	1.40	1.39
50	2.80	2.22	1.99	1.87	1.79	1.69	1.63	1.59	1.56	1.54	1.52	1.51	1.50	1.48	1.47	1.46	1.45	1.45	1.44	1.43
60	2.88	2.28	2.04	1.92	1.83	1.73	1.67	1.63	1.60	1.57	1.56	1.54	1.53	1.52	1.50	1.49	1.49	1.48	1.47	1.47
75	2.97	2.35	2.11	1.97	1.89	1.79	1.72	1.67	1.64	1.62	1.60	1.59	1.57	1.56	1.55	1.54	1.53	1.52	1.51	1.51
100	3.08	2.44	2.18	2.05	1.96	1.85	1.79	1.73	1.70	1.68	1.66	1.64	1.63	1.61	1.60	1.59	1.58	1.58	1.57	1.56
125	3.17	2.50	2.24	2.10	2.01	1.90	1.83	1.78	1.74	1.72	1.70	1.68	1.67	1.65	1.64	1.63	1.62	1.62	1.61	1.60
150	3.24	2.56	2.29	2.15	2.05	1.94	1.87	1.82	1.78	1.75	1.73	1.72	1.71	1.69	1.67	1.66	1.66	1.65	1.64	1.63
175	3.30	2.60	2.33	2.18	2.09	1.97	1.90	1.85	1.81	1.78	1.76	1.75	1.73	1.72	1.70	1.69	1.68	1.68	1.66	1.66
200	3.35	2.64	2.37	2.22	2.12	2.00	1.93	1.87	1.84	1.81	1.79	1.77	1.76	1.74	1.73	1.71	1.71	1.70	1.69	1.68

Table 19-2. κ-Multipliers for 1-of-3 Interwell Prediction Limits on Observations (2 COCs, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	0.71	0.57	0.50	0.46	0.44	0.41	0.39	0.38	0.37	0.37	0.36	0.36	0.35	0.35	0.35	0.34	0.34	0.34	0.34	0.34
2	1.08	0.86	0.77	0.72	0.69	0.65	0.62	0.61	0.59	0.59	0.58	0.57	0.57	0.56	0.56	0.56	0.55	0.55	0.55	0.55
3	1.30	1.03	0.92	0.86	0.82	0.77	0.75	0.73	0.71	0.70	0.70	0.69	0.69	0.68	0.67	0.67	0.67	0.67	0.66	0.66
4	1.47	1.15	1.02	0.96	0.91	0.86	0.83	0.81	0.79	0.78	0.78	0.77	0.76	0.76	0.75	0.75	0.74	0.74	0.74	0.74
5	1.59	1.24	1.11	1.03	0.99	0.93	0.90	0.87	0.86	0.84	0.84	0.83	0.82	0.82	0.81	0.81	0.80	0.80	0.79	0.79
8	1.86	1.44	1.27	1.19	1.13	1.07	1.03	1.00	0.98	0.97	0.96	0.95	0.94	0.93	0.93	0.92	0.92	0.92	0.91	0.91
12	2.09	1.60	1.42	1.32	1.25	1.18	1.14	1.11	1.08	1.07	1.06	1.05	1.04	1.03	1.02	1.02	1.01	1.01	1.00	1.00
16	2.26	1.72	1.52	1.41	1.34	1.26	1.21	1.18	1.16	1.14	1.13	1.12	1.11	1.10	1.09	1.08	1.08	1.08	1.07	1.06
20	2.39	1.81	1.59	1.48	1.41	1.32	1.27	1.23	1.21	1.19	1.18	1.17	1.16	1.15	1.14	1.13	1.13	1.12	1.12	1.11
30	2.62	1.97	1.73	1.60	1.52	1.43	1.38	1.33	1.31	1.29	1.27	1.26	1.25	1.24	1.23	1.22	1.22	1.21	1.20	1.20
40	2.78	2.08	1.83	1.69	1.61	1.50	1.45	1.40	1.37	1.35	1.34	1.32	1.31	1.30	1.29	1.28	1.28	1.27	1.26	1.26
50	2.91	2.17	1.90	1.76	1.67	1.56	1.50	1.45	1.42	1.40	1.38	1.37	1.36	1.35	1.34	1.33	1.32	1.32	1.31	1.30
60	3.01	*2.24*	1.96	1.81	1.72	1.61	1.55	1.50	1.46	1.44	1.42	1.41	1.40	1.38	1.37	1.36	1.36	1.35	1.34	1.34
75	3.13	2.33	2.03	1.88	1.78	1.67	1.60	1.55	1.51	1.49	1.47	1.46	1.45	1.43	1.42	1.41	1.40	1.40	1.39	1.38
100	3.29	2.44	2.13	1.96	1.86	1.74	1.67	1.61	1.58	1.55	1.53	1.52	1.50	1.49	1.47	1.46	1.46	1.45	1.44	1.43
125	3.41	2.52	*2.20*	2.03	1.92	1.79	1.72	1.66	1.62	1.60	1.58	1.56	1.55	1.53	1.52	1.51	1.50	1.49	1.48	1.48
150	3.50	2.59	*2.25*	2.08	1.97	1.84	1.76	1.70	1.66	1.63	1.61	1.60	1.59	1.57	1.55	1.54	1.53	1.53	1.52	1.51
175	3.58	2.64	*2.30*	2.12	2.01	1.87	1.80	1.74	1.69	1.67	1.64	1.63	1.62	1.60	1.58	1.57	1.56	1.56	1.54	1.54
200	3.65	2.69	2.34	*2.16*	2.04	1.91	1.83	1.76	1.72	1.69	1.67	1.65	1.64	1.62	1.61	1.60	1.59	1.58	1.57	1.56

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Table 19-2. κ-Multipliers for 1-of-3 Interwell Prediction Limits on Observations (2 COCs, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	1.08	0.86	0.77	0.72	0.69	0.65	0.62	0.61	0.59	0.59	0.58	0.57	0.57	0.56	0.56	0.56	0.55	0.55	0.55	0.55
2	1.47	1.15	1.02	0.96	0.91	0.86	0.83	0.81	0.79	0.78	0.78	0.77	0.76	0.76	0.75	0.75	0.74	0.74	0.74	0.74
3	1.70	1.32	1.17	1.09	1.04	0.98	0.95	0.92	0.91	0.89	0.88	0.88	0.87	0.86	0.86	0.85	0.85	0.85	0.84	0.84
4	1.86	1.44	1.27	1.19	1.13	1.07	1.03	1.00	0.98	0.97	0.96	0.95	0.94	0.93	0.93	0.92	0.92	0.92	0.91	0.91
5	1.99	1.53	1.35	1.26	1.20	1.13	1.09	1.06	1.04	1.02	1.01	1.00	1.00	0.99	0.98	0.98	0.97	0.97	0.96	0.96
8	2.26	1.72	1.52	1.41	1.34	1.26	1.21	1.18	1.16	1.14	1.13	1.12	1.11	1.10	1.09	1.08	1.08	1.08	1.07	1.06
12	2.49	1.88	1.65	1.53	1.46	1.37	1.32	1.28	1.25	1.23	1.22	1.21	1.20	1.19	1.18	1.17	1.17	1.16	1.16	1.15
16	2.66	2.00	1.75	1.62	1.54	1.45	1.39	1.35	1.32	1.30	1.29	1.27	1.27	1.25	1.24	1.23	1.23	1.22	1.22	1.21
20	2.78	2.08	1.83	1.69	1.61	1.50	1.45	1.40	1.37	1.35	1.34	1.32	1.31	1.30	1.29	1.28	1.28	1.27	1.26	1.26
30	3.01	2.24	1.96	1.81	1.72	1.61	1.55	1.50	1.46	1.44	1.42	1.41	1.40	1.38	1.37	1.36	1.36	1.35	1.34	1.34
40	3.17	2.35	2.05	1.90	1.80	1.68	1.61	1.56	1.53	1.50	1.48	1.47	1.46	1.44	1.43	1.42	1.41	1.41	1.40	1.39
50	3.29	2.44	2.13	1.96	1.86	1.74	1.67	1.61	1.58	1.55	1.53	1.52	1.50	1.49	1.47	1.46	1.46	1.45	1.44	1.43
60	3.38	*2.50*	2.18	2.01	1.91	1.78	1.71	1.65	1.61	1.59	1.57	1.55	1.54	1.52	1.51	1.50	1.49	1.49	1.48	1.47
75	3.50	2.59	2.25	2.08	1.97	1.84	1.76	1.70	1.66	1.63	1.61	1.60	1.59	1.57	1.55	1.54	1.53	1.53	1.52	1.51
100	3.65	2.69	2.34	2.16	2.04	1.91	1.83	1.76	1.72	1.69	1.67	1.65	1.64	1.62	1.61	1.60	1.59	1.58	1.57	1.56
125	3.77	2.77	2.41	2.22	2.10	1.96	1.88	1.81	1.77	1.74	1.72	1.70	1.68	1.66	1.65	1.64	1.63	1.62	1.61	1.60
150	3.86	2.84	*2.47*	2.27	2.15	2.00	1.92	1.85	1.81	1.77	1.75	1.73	1.72	1.70	1.68	1.67	1.66	1.65	1.64	1.63
175	3.94	2.89	*2.51*	2.31	2.19	2.04	1.95	1.88	1.84	1.81	1.78	1.76	1.75	1.73	1.71	1.70	1.69	1.68	1.67	1.66
200	4.00	2.94	*2.55*	2.35	2.22	2.07	1.98	1.91	1.86	1.83	1.81	1.79	1.77	1.75	1.73	1.72	1.71	1.70	1.69	1.68

Table 19-2. κ-Multipliers for 1-of-3 Interwell Prediction Limits on Observations (2 COCs, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	1.47	1.15	1.02	0.96	0.91	0.86	0.83	0.81	0.79	0.78	0.78	0.77	0.76	0.76	0.75	0.75	0.74	0.74	0.74	0.74
2	1.86	1.44	1.27	1.19	1.13	1.07	1.03	1.00	0.98	0.97	0.96	0.95	0.94	0.93	0.93	0.92	0.92	0.92	0.91	0.91
3	2.09	1.60	1.42	1.32	1.25	1.18	1.14	1.11	1.08	1.07	1.06	1.05	1.04	1.03	1.02	1.02	1.01	1.01	1.00	1.00
4	2.26	1.72	1.52	1.41	1.34	1.26	1.21	1.18	1.16	1.14	1.13	1.12	1.11	1.10	1.09	1.08	1.08	1.08	1.07	1.06
5	2.39	1.81	1.59	1.48	1.41	1.32	1.27	1.23	1.21	1.19	1.18	1.17	1.16	1.15	1.14	1.13	1.13	1.12	1.12	1.11
8	2.66	2.00	1.75	1.62	1.54	1.45	1.39	1.35	1.32	1.30	1.29	1.27	1.27	1.25	1.24	1.23	1.23	1.22	1.22	1.21
12	2.88	2.16	1.89	1.75	1.66	1.55	1.49	1.44	1.41	1.39	1.38	1.36	1.35	1.34	1.33	1.32	1.31	1.31	1.30	1.29
16	3.04	2.27	1.98	1.83	1.74	1.63	1.56	1.51	1.48	1.45	1.44	1.42	1.41	1.40	1.39	1.38	1.37	1.37	1.36	1.35
20	3.17	2.35	2.05	1.90	1.80	1.68	1.61	1.56	1.53	1.50	1.48	1.47	1.46	1.44	1.43	1.42	1.41	1.41	1.40	1.39
30	3.38	2.50	2.18	2.01	1.91	1.78	1.71	1.65	1.61	1.59	1.57	1.55	1.54	1.52	1.51	1.50	1.49	1.49	1.48	1.47
40	3.54	2.61	2.27	2.10	1.98	1.85	1.78	1.72	1.68	1.65	1.63	1.61	1.60	1.58	1.56	1.55	1.55	1.54	1.53	1.52
50	3.65	2.69	2.34	2.16	2.04	1.91	1.83	1.76	1.72	1.69	1.67	1.65	1.64	1.62	1.61	1.60	1.59	1.58	1.57	1.56
60	3.75	2.76	2.40	2.21	2.09	1.95	1.87	1.80	1.76	1.73	1.71	1.69	1.68	1.66	1.64	1.63	1.62	1.61	1.60	1.59
75	3.86	*2.84*	2.47	2.27	2.15	2.00	1.92	1.85	1.81	1.77	1.75	1.73	1.72	1.70	1.68	1.67	1.66	1.65	1.64	1.63
100	4.00	2.94	2.55	2.35	2.22	2.07	1.98	1.91	1.86	1.83	1.81	1.79	1.77	1.75	1.73	1.72	1.71	1.70	1.69	1.68
125	4.11	3.02	2.62	2.41	2.28	2.12	2.03	1.96	1.91	1.88	1.85	1.83	1.81	1.79	1.77	1.76	1.75	1.74	1.73	1.72
150	4.20	3.08	2.67	2.46	2.32	2.16	2.07	1.99	1.95	1.91	1.88	1.86	1.85	1.82	1.81	1.79	1.78	1.77	1.76	1.75
175	4.28	3.13	2.71	2.50	2.36	2.20	2.10	2.03	1.98	1.94	1.91	1.89	1.88	1.85	1.83	1.82	1.81	1.80	1.79	1.78
200	4.34	3.17	2.75	2.53	2.39	2.23	2.13	2.05	2.00	1.97	1.94	1.92	1.90	1.87	1.86	1.84	1.83	1.82	1.81	1.80

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Table 19-2. κ-Multipliers for 1-of-3 Interwell Prediction Limits on Observations (5 COCs, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.27**	**0.98**	**0.87**	**0.81**	**0.77**	**0.72**	**0.70**	**0.68**	**0.66**	**0.65**	**0.65**	**0.64**	**0.64**	**0.63**	**0.62**	**0.62**	**0.62**	**0.62**	**0.61**	**0.61**
2	**1.71**	**1.29**	**1.13**	**1.05**	**1.00**	**0.94**	**0.90**	**0.88**	**0.86**	**0.85**	**0.84**	**0.83**	**0.83**	**0.82**	**0.81**	**0.81**	**0.80**	**0.80**	**0.80**	**0.79**
3	**1.99**	**1.47**	**1.28**	**1.19**	**1.13**	**1.06**	**1.02**	**0.99**	**0.97**	**0.95**	**0.94**	**0.94**	**0.93**	**0.92**	**0.91**	**0.91**	**0.90**	**0.90**	**0.90**	**0.89**
4	**2.19**	**1.60**	**1.39**	**1.29**	**1.22**	**1.14**	**1.10**	**1.07**	**1.04**	**1.03**	**1.02**	**1.01**	**1.00**	**0.99**	**0.98**	**0.98**	**0.97**	**0.97**	**0.96**	**0.96**
5	2.35	**1.70**	**1.48**	**1.36**	**1.29**	**1.21**	**1.16**	**1.12**	**1.10**	**1.08**	**1.07**	**1.06**	**1.05**	**1.04**	**1.04**	**1.03**	**1.02**	**1.02**	**1.01**	**1.01**
8	2.70	**1.92**	**1.65**	**1.52**	**1.43**	**1.34**	**1.28**	**1.24**	**1.22**	**1.20**	**1.18**	**1.17**	**1.16**	**1.15**	**1.14**	**1.14**	**1.13**	**1.13**	**1.12**	**1.11**
12	3.00	**2.11**	**1.81**	**1.65**	**1.56**	**1.45**	**1.39**	**1.34**	**1.31**	**1.29**	**1.28**	**1.26**	**1.25**	**1.24**	**1.23**	**1.22**	**1.22**	**1.21**	**1.20**	**1.20**
16	3.22	*2.24*	**1.91**	**1.75**	**1.65**	**1.53**	**1.46**	**1.41**	**1.38**	**1.36**	**1.34**	**1.33**	**1.32**	**1.30**	**1.29**	**1.28**	**1.28**	**1.27**	**1.26**	**1.26**
20	3.39	2.35	**2.00**	**1.82**	**1.71**	**1.59**	**1.52**	**1.47**	**1.43**	**1.41**	**1.39**	**1.38**	**1.37**	**1.35**	**1.34**	**1.33**	**1.32**	**1.32**	**1.31**	**1.30**
30	3.70	2.54	**2.15**	**1.95**	**1.83**	**1.70**	**1.62**	**1.56**	**1.52**	**1.50**	**1.48**	**1.46**	**1.45**	**1.43**	**1.42**	**1.41**	**1.40**	**1.40**	**1.39**	**1.38**
40	3.92	2.67	*2.25*	**2.05**	**1.92**	**1.77**	**1.69**	**1.63**	**1.59**	**1.56**	**1.54**	**1.52**	**1.51**	**1.49**	**1.48**	**1.47**	**1.46**	**1.45**	**1.44**	**1.44**
50	4.08	2.77	*2.34*	**2.12**	**1.98**	**1.83**	**1.75**	**1.68**	**1.64**	**1.61**	**1.59**	**1.57**	**1.56**	**1.54**	**1.52**	**1.51**	**1.50**	**1.50**	**1.48**	**1.48**
60	4.22	2.86	2.40	*2.18*	**2.04**	**1.88**	**1.79**	**1.72**	**1.68**	**1.65**	**1.62**	**1.61**	**1.59**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**	**1.51**
75	4.38	2.96	2.48	*2.25*	**2.10**	**1.94**	**1.84**	**1.77**	**1.73**	**1.69**	**1.67**	**1.65**	**1.64**	**1.61**	**1.60**	**1.59**	**1.58**	**1.57**	**1.56**	**1.55**
100	4.59	3.09	2.59	*2.34*	*2.18*	**2.01**	**1.91**	**1.84**	**1.79**	**1.75**	**1.73**	**1.71**	**1.69**	**1.67**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**
125	4.75	3.19	2.67	2.41	*2.25*	**2.07**	**1.96**	**1.88**	**1.83**	**1.80**	**1.77**	**1.75**	**1.73**	**1.71**	**1.69**	**1.68**	**1.67**	**1.66**	**1.65**	**1.64**
150	4.88	3.27	2.73	2.46	*2.30*	**2.11**	**2.01**	**1.92**	**1.87**	**1.83**	**1.81**	**1.79**	**1.77**	**1.74**	**1.73**	**1.71**	**1.70**	**1.70**	**1.68**	**1.67**
175	4.99	3.33	2.79	2.51	*2.34*	*2.15*	**2.04**	**1.96**	**1.90**	**1.87**	**1.84**	**1.82**	**1.80**	**1.77**	**1.76**	**1.74**	**1.73**	**1.72**	**1.71**	**1.70**
200	5.09	3.39	2.83	2.55	*2.38*	*2.18*	**2.07**	**1.99**	**1.93**	**1.89**	**1.86**	**1.84**	**1.82**	**1.80**	**1.78**	**1.77**	**1.76**	**1.75**	**1.73**	**1.72**

Table 19-2. κ-Multipliers for 1-of-3 Interwell Prediction Limits on Observations (5 COCs, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.71**	**1.29**	**1.13**	**1.05**	**1.00**	**0.94**	**0.90**	**0.88**	**0.86**	**0.85**	**0.84**	**0.83**	**0.83**	**0.82**	**0.81**	**0.81**	**0.80**	**0.80**	**0.80**	**0.79**
2	**2.19**	**1.60**	**1.39**	**1.29**	**1.22**	**1.14**	**1.10**	**1.06**	**1.04**	**1.03**	**1.02**	**1.01**	**1.00**	**0.99**	**0.98**	**0.98**	**0.97**	**0.97**	**0.96**	**0.96**
3	2.49	**1.79**	**1.55**	**1.42**	**1.35**	**1.26**	**1.21**	**1.17**	**1.15**	**1.13**	**1.11**	**1.10**	**1.10**	**1.09**	**1.08**	**1.07**	**1.07**	**1.06**	**1.06**	**1.05**
4	2.70	**1.92**	**1.65**	**1.52**	**1.43**	**1.34**	**1.28**	**1.24**	**1.22**	**1.20**	**1.18**	**1.17**	**1.16**	**1.15**	**1.14**	**1.14**	**1.13**	**1.13**	**1.12**	**1.11**
5	2.87	**2.03**	**1.74**	**1.59**	**1.50**	**1.40**	**1.34**	**1.30**	**1.27**	**1.25**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.18**	**1.17**	**1.17**	**1.16**
8	3.22	**2.25**	**1.91**	**1.75**	**1.65**	**1.53**	**1.46**	**1.41**	**1.38**	**1.36**	**1.34**	**1.33**	**1.32**	**1.30**	**1.29**	**1.28**	**1.28**	**1.27**	**1.26**	**1.26**
12	3.53	**2.43**	**2.07**	**1.88**	**1.77**	**1.64**	**1.56**	**1.51**	**1.47**	**1.45**	**1.43**	**1.42**	**1.40**	**1.39**	**1.38**	**1.37**	**1.36**	**1.35**	**1.34**	**1.34**
16	3.75	*2.57*	**2.17**	**1.97**	**1.85**	**1.71**	**1.64**	**1.58**	**1.54**	**1.51**	**1.49**	**1.48**	**1.46**	**1.45**	**1.43**	**1.42**	**1.42**	**1.41**	**1.40**	**1.39**
20	3.92	2.67	**2.25**	**2.05**	**1.92**	**1.77**	**1.69**	**1.63**	**1.59**	**1.56**	**1.54**	**1.52**	**1.51**	**1.49**	**1.48**	**1.47**	**1.46**	**1.45**	**1.44**	**1.44**
30	4.22	2.86	**2.40**	**2.18**	**2.04**	**1.88**	**1.79**	**1.72**	**1.68**	**1.65**	**1.62**	**1.61**	**1.59**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**	**1.51**
40	4.43	2.99	*2.51*	**2.27**	**2.12**	**1.95**	**1.86**	**1.79**	**1.74**	**1.71**	**1.68**	**1.66**	**1.65**	**1.63**	**1.61**	**1.60**	**1.59**	**1.58**	**1.57**	**1.56**
50	4.59	3.09	*2.59*	**2.34**	**2.19**	**2.01**	**1.91**	**1.84**	**1.79**	**1.75**	**1.73**	**1.71**	**1.69**	**1.67**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**
60	4.73	3.17	*2.65*	**2.39**	**2.24**	**2.06**	**1.95**	**1.88**	**1.82**	**1.79**	**1.76**	**1.74**	**1.73**	**1.70**	**1.69**	**1.67**	**1.66**	**1.66**	**1.64**	**1.63**
75	4.88	3.27	2.73	*2.46*	**2.30**	**2.11**	**2.01**	**1.92**	**1.87**	**1.83**	**1.81**	**1.79**	**1.77**	**1.74**	**1.73**	**1.71**	**1.70**	**1.70**	**1.68**	**1.67**
100	5.09	3.39	2.83	*2.55*	**2.38**	**2.18**	**2.07**	**1.99**	**1.93**	**1.89**	**1.86**	**1.84**	**1.82**	**1.80**	**1.78**	**1.77**	**1.76**	**1.75**	**1.73**	**1.72**
125	5.24	3.49	2.91	*2.62*	**2.44**	**2.24**	**2.12**	**2.03**	**1.98**	**1.94**	**1.91**	**1.88**	**1.87**	**1.84**	**1.82**	**1.80**	**1.79**	**1.79**	**1.77**	**1.76**
150	5.37	3.56	2.97	*2.67*	*2.49*	**2.28**	**2.16**	**2.07**	**2.01**	**1.97**	**1.94**	**1.92**	**1.90**	**1.87**	**1.85**	**1.84**	**1.82**	**1.82**	**1.80**	**1.79**
175	5.47	3.63	3.02	2.72	*2.53*	**2.32**	**2.20**	**2.11**	**2.05**	**2.00**	**1.97**	**1.95**	**1.93**	**1.90**	**1.88**	**1.86**	**1.85**	**1.84**	**1.83**	**1.81**
200	5.56	3.69	3.07	2.76	*2.57*	**2.35**	**2.23**	**2.13**	**2.07**	**2.03**	**2.00**	**1.97**	**1.95**	**1.92**	**1.90**	**1.89**	**1.87**	**1.86**	**1.85**	**1.84**

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Table 19-2. κ-Multipliers for 1-of-3 Interwell Prediction Limits on Observations (5 COCs, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.19**	**1.60**	**1.39**	**1.29**	**1.22**	**1.14**	**1.10**	**1.06**	**1.04**	**1.03**	**1.02**	**1.01**	**1.00**	**0.99**	**0.98**	**0.98**	**0.97**	**0.97**	**0.96**	**0.96**
2	**2.70**	**1.92**	**1.65**	**1.52**	**1.43**	**1.34**	**1.28**	**1.24**	**1.22**	**1.20**	**1.18**	**1.17**	**1.16**	**1.15**	**1.14**	**1.14**	**1.13**	**1.13**	**1.12**	**1.11**
3	3.00	**2.11**	**1.81**	**1.65**	**1.56**	**1.45**	**1.39**	**1.34**	**1.31**	**1.29**	**1.28**	**1.26**	**1.25**	**1.24**	**1.23**	**1.22**	**1.22**	**1.21**	**1.20**	**1.20**
4	3.22	**2.25**	**1.91**	**1.75**	**1.65**	**1.53**	**1.46**	**1.41**	**1.38**	**1.36**	**1.34**	**1.33**	**1.32**	**1.30**	**1.29**	**1.28**	**1.28**	**1.27**	**1.26**	**1.26**
5	3.39	**2.35**	**2.00**	**1.82**	**1.71**	**1.59**	**1.52**	**1.47**	**1.43**	**1.41**	**1.39**	**1.38**	**1.37**	**1.35**	**1.34**	**1.33**	**1.32**	**1.32**	**1.31**	**1.30**
8	3.75	**2.57**	**2.17**	**1.97**	**1.85**	**1.71**	**1.64**	**1.58**	**1.54**	**1.51**	**1.49**	**1.48**	**1.46**	**1.45**	**1.43**	**1.42**	**1.42**	**1.41**	**1.40**	**1.39**
12	4.05	**2.75**	**2.32**	**2.10**	**1.97**	**1.82**	**1.74**	**1.67**	**1.63**	**1.60**	**1.58**	**1.56**	**1.55**	**1.53**	**1.51**	**1.50**	**1.50**	**1.49**	**1.48**	**1.47**
16	4.27	2.89	**2.43**	**2.20**	**2.06**	**1.90**	**1.81**	**1.74**	**1.69**	**1.66**	**1.64**	**1.62**	**1.60**	**1.58**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**
20	4.43	2.99	**2.51**	**2.27**	**2.12**	**1.95**	**1.86**	**1.79**	**1.74**	**1.71**	**1.68**	**1.66**	**1.65**	**1.63**	**1.61**	**1.60**	**1.59**	**1.58**	**1.57**	**1.56**
30	4.73	3.17	**2.65**	**2.39**	**2.24**	**2.06**	**1.95**	**1.88**	**1.82**	**1.79**	**1.76**	**1.74**	**1.73**	**1.70**	**1.69**	**1.67**	**1.66**	**1.66**	**1.64**	**1.63**
40	4.93	3.30	**2.75**	**2.48**	**2.32**	**2.13**	**2.02**	**1.94**	**1.89**	**1.85**	**1.82**	**1.80**	**1.78**	**1.76**	**1.74**	**1.73**	**1.72**	**1.71**	**1.69**	**1.68**
50	5.09	3.39	*2.83*	**2.55**	**2.38**	**2.18**	**2.07**	**1.99**	**1.93**	**1.89**	**1.86**	**1.84**	**1.82**	**1.80**	**1.78**	**1.77**	**1.76**	**1.75**	**1.73**	**1.72**
60	5.21	3.47	*2.90*	**2.61**	**2.43**	**2.23**	**2.11**	**2.03**	**1.97**	**1.93**	**1.90**	**1.88**	**1.86**	**1.83**	**1.81**	**1.80**	**1.79**	**1.78**	**1.76**	**1.75**
75	5.37	3.56	2.97	**2.67**	**2.49**	**2.28**	**2.16**	**2.07**	**2.01**	**1.97**	**1.94**	**1.92**	**1.90**	**1.87**	**1.85**	**1.84**	**1.82**	**1.82**	**1.80**	**1.79**
100	5.56	3.69	3.07	**2.76**	**2.57**	**2.35**	**2.23**	**2.13**	**2.07**	**2.03**	**2.00**	**1.97**	**1.95**	**1.92**	**1.90**	**1.89**	**1.87**	**1.86**	**1.85**	**1.84**
125	5.71	3.78	3.14	*2.82*	**2.63**	**2.41**	**2.28**	**2.18**	**2.12**	**2.07**	**2.04**	**2.01**	**1.99**	**1.96**	**1.94**	**1.92**	**1.91**	**1.90**	**1.88**	**1.87**
150	5.83	3.85	3.20	*2.88*	**2.68**	**2.45**	**2.32**	**2.22**	**2.15**	**2.11**	**2.07**	**2.05**	**2.03**	**1.99**	**1.97**	**1.95**	**1.94**	**1.93**	**1.91**	**1.90**
175	5.93	3.92	3.25	*2.92*	**2.72**	**2.49**	**2.35**	**2.25**	**2.18**	**2.14**	**2.10**	**2.07**	**2.05**	**2.02**	**2.00**	**1.98**	**1.97**	**1.96**	**1.94**	**1.93**
200	6.02	3.97	3.30	*2.96*	**2.76**	**2.52**	**2.38**	**2.28**	**2.21**	**2.16**	**2.13**	**2.10**	**2.08**	**2.04**	**2.02**	**2.00**	**1.99**	**1.98**	**1.96**	**1.95**

Table 19-2. κ-Multipliers for 1-of-3 Interwell Prediction Limits on Observations (10 COCs, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.76**	**1.31**	**1.14**	**1.06**	**1.00**	**0.94**	**0.91**	**0.88**	**0.86**	**0.85**	**0.84**	**0.83**	**0.83**	**0.82**	**0.81**	**0.81**	**0.80**	**0.80**	**0.80**	**0.79**
2	2.29	**1.63**	**1.41**	**1.30**	**1.23**	**1.15**	**1.10**	**1.07**	**1.04**	**1.03**	**1.02**	**1.01**	**1.00**	**0.99**	**0.98**	**0.98**	**0.97**	**0.97**	**0.96**	**0.96**
3	2.62	**1.83**	**1.57**	**1.44**	**1.35**	**1.26**	**1.21**	**1.17**	**1.15**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**	**1.07**	**1.06**	**1.06**	**1.05**
4	2.87	**1.97**	**1.68**	**1.53**	**1.45**	**1.35**	**1.29**	**1.25**	**1.22**	**1.20**	**1.18**	**1.17**	**1.16**	**1.15**	**1.14**	**1.14**	**1.13**	**1.13**	**1.12**	**1.11**
5	3.07	**2.08**	**1.77**	**1.61**	**1.52**	**1.41**	**1.35**	**1.30**	**1.27**	**1.25**	**1.24**	**1.22**	**1.22**	**1.20**	**1.19**	**1.18**	**1.18**	**1.17**	**1.17**	**1.16**
8	3.50	2.33	**1.95**	**1.77**	**1.66**	**1.54**	**1.47**	**1.42**	**1.38**	**1.36**	**1.34**	**1.33**	**1.32**	**1.30**	**1.29**	**1.28**	**1.28**	**1.27**	**1.26**	**1.26**
12	3.88	2.54	**2.12**	**1.91**	**1.79**	**1.65**	**1.57**	**1.51**	**1.48**	**1.45**	**1.43**	**1.42**	**1.41**	**1.39**	**1.38**	**1.37**	**1.36**	**1.35**	**1.35**	**1.34**
16	4.15	2.69	*2.23*	**2.01**	**1.88**	**1.73**	**1.65**	**1.58**	**1.54**	**1.51**	**1.49**	**1.48**	**1.47**	**1.45**	**1.43**	**1.42**	**1.42**	**1.41**	**1.40**	**1.39**
20	4.36	2.81	*2.32*	**2.08**	**1.95**	**1.79**	**1.70**	**1.63**	**1.59**	**1.56**	**1.54**	**1.52**	**1.51**	**1.49**	**1.48**	**1.47**	**1.46**	**1.46**	**1.44**	**1.44**
30	4.75	3.02	2.49	*2.22*	**2.07**	**1.90**	**1.80**	**1.73**	**1.68**	**1.65**	**1.63**	**1.61**	**1.59**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**	**1.51**
40	5.02	3.17	2.60	*2.32*	*2.16*	**1.97**	**1.87**	**1.79**	**1.75**	**1.71**	**1.69**	**1.67**	**1.65**	**1.63**	**1.61**	**1.60**	**1.59**	**1.58**	**1.57**	**1.56**
50	5.22	3.29	2.69	2.40	*2.23*	**2.03**	**1.93**	**1.84**	**1.79**	**1.76**	**1.73**	**1.71**	**1.69**	**1.67**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**
60	5.39	3.38	2.76	2.46	*2.28*	**2.08**	**1.97**	**1.89**	**1.83**	**1.79**	**1.77**	**1.75**	**1.73**	**1.71**	**1.69**	**1.68**	**1.67**	**1.66**	**1.64**	**1.63**
75	5.61	3.50	2.85	2.53	*2.35*	*2.14*	**2.02**	**1.94**	**1.88**	**1.84**	**1.81**	**1.79**	**1.77**	**1.75**	**1.73**	**1.72**	**1.71**	**1.70**	**1.68**	**1.67**
100	5.86	3.64	2.96	2.63	2.44	*2.21*	**2.09**	**2.00**	**1.94**	**1.90**	**1.87**	**1.85**	**1.83**	**1.80**	**1.78**	**1.77**	**1.76**	**1.75**	**1.73**	**1.72**
125	6.06	3.76	3.05	2.71	2.50	*2.27*	*2.14*	**2.05**	**1.99**	**1.94**	**1.91**	**1.89**	**1.87**	**1.84**	**1.82**	**1.81**	**1.80**	**1.79**	**1.77**	**1.76**
150	6.23	3.85	3.12	2.77	2.56	*2.32*	*2.19*	**2.09**	**2.03**	**1.98**	**1.95**	**1.92**	**1.90**	**1.87**	**1.85**	**1.84**	**1.83**	**1.82**	**1.80**	**1.79**
175	6.37	3.93	3.18	2.82	2.60	*2.36*	*2.22*	*2.12*	**2.06**	**2.01**	**1.98**	**1.95**	**1.93**	**1.90**	**1.88**	**1.87**	**1.85**	**1.84**	**1.83**	**1.82**
200	6.48	3.99	3.23	2.86	2.64	*2.39*	*2.26*	*2.15*	**2.08**	**2.04**	**2.00**	**1.98**	**1.96**	**1.93**	**1.90**	**1.89**	**1.88**	**1.87**	**1.85**	**1.84**

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Table 19-2. κ-Multipliers for 1-of-3 Interwell Prediction Limits on Observations (10 COCs, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.29**	**1.63**	**1.41**	**1.29**	**1.23**	**1.15**	**1.10**	**1.07**	**1.04**	**1.03**	**1.02**	**1.01**	**1.00**	**0.99**	**0.98**	**0.98**	**0.97**	**0.97**	**0.96**	**0.96**
2	2.87	**1.97**	**1.68**	**1.53**	**1.45**	**1.35**	**1.29**	**1.25**	**1.22**	**1.20**	**1.18**	**1.17**	**1.16**	**1.15**	**1.14**	**1.14**	**1.13**	**1.13**	**1.12**	**1.11**
3	3.23	**2.18**	**1.84**	**1.67**	**1.57**	**1.46**	**1.39**	**1.35**	**1.32**	**1.29**	**1.28**	**1.27**	**1.26**	**1.24**	**1.23**	**1.22**	**1.22**	**1.21**	**1.20**	**1.20**
4	3.50	**2.32**	**1.95**	**1.77**	**1.66**	**1.54**	**1.47**	**1.42**	**1.38**	**1.36**	**1.34**	**1.33**	**1.32**	**1.30**	**1.29**	**1.28**	**1.28**	**1.27**	**1.26**	**1.26**
5	3.70	**2.44**	**2.04**	**1.85**	**1.73**	**1.60**	**1.53**	**1.47**	**1.44**	**1.41**	**1.39**	**1.38**	**1.37**	**1.35**	**1.34**	**1.33**	**1.32**	**1.32**	**1.31**	**1.30**
8	4.14	2.69	**2.23**	**2.01**	**1.88**	**1.73**	**1.65**	**1.58**	**1.54**	**1.51**	**1.49**	**1.48**	**1.47**	**1.45**	**1.44**	**1.43**	**1.42**	**1.41**	**1.40**	**1.39**
12	4.53	2.90	**2.39**	**2.15**	**2.00**	**1.84**	**1.75**	**1.68**	**1.63**	**1.60**	**1.58**	**1.56**	**1.55**	**1.53**	**1.51**	**1.50**	**1.50**	**1.49**	**1.48**	**1.47**
16	4.80	3.06	*2.51*	**2.25**	**2.09**	**1.91**	**1.82**	**1.74**	**1.70**	**1.66**	**1.64**	**1.62**	**1.61**	**1.58**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**
20	5.02	3.17	*2.60*	**2.32**	**2.16**	**1.97**	**1.87**	**1.79**	**1.75**	**1.71**	**1.69**	**1.67**	**1.65**	**1.63**	**1.61**	**1.60**	**1.59**	**1.58**	**1.57**	**1.56**
30	5.39	3.38	2.76	*2.46*	**2.28**	**2.08**	**1.97**	**1.88**	**1.83**	**1.79**	**1.77**	**1.75**	**1.73**	**1.71**	**1.69**	**1.67**	**1.67**	**1.66**	**1.64**	**1.63**
40	5.66	3.53	2.88	*2.56*	**2.37**	**2.16**	**2.04**	**1.95**	**1.89**	**1.85**	**1.82**	**1.80**	**1.78**	**1.76**	**1.74**	**1.73**	**1.72**	**1.71**	**1.69**	**1.68**
50	5.86	3.64	2.96	*2.63*	**2.44**	**2.21**	**2.09**	**2.00**	**1.94**	**1.90**	**1.87**	**1.85**	**1.83**	**1.80**	**1.78**	**1.77**	**1.76**	**1.75**	**1.73**	**1.72**
60	6.04	3.74	3.03	*2.69*	*2.49*	**2.26**	**2.14**	**2.04**	**1.98**	**1.94**	**1.90**	**1.88**	**1.86**	**1.83**	**1.81**	**1.80**	**1.79**	**1.78**	**1.76**	**1.75**
75	6.23	3.85	3.12	2.76	*2.56*	**2.32**	**2.19**	**2.09**	**2.02**	**1.98**	**1.95**	**1.92**	**1.90**	**1.88**	**1.85**	**1.84**	**1.83**	**1.82**	**1.80**	**1.79**
100	6.48	3.99	3.23	2.86	*2.64*	**2.39**	**2.26**	**2.15**	**2.08**	**2.04**	**2.00**	**1.98**	**1.96**	**1.93**	**1.90**	**1.89**	**1.88**	**1.87**	**1.85**	**1.84**
125	6.68	4.10	3.32	2.93	*2.71*	*2.45*	**2.31**	**2.20**	**2.13**	**2.08**	**2.05**	**2.02**	**2.00**	**1.97**	**1.94**	**1.93**	**1.91**	**1.90**	**1.88**	**1.87**
150	6.84	4.19	3.38	2.99	2.76	*2.50*	**2.35**	**2.24**	**2.17**	**2.12**	**2.08**	**2.05**	**2.03**	**2.00**	**1.97**	**1.96**	**1.94**	**1.93**	**1.91**	**1.90**
175	6.97	4.27	3.44	3.04	2.80	*2.53*	**2.39**	**2.27**	**2.20**	**2.15**	**2.11**	**2.08**	**2.06**	**2.02**	**2.00**	**1.98**	**1.97**	**1.96**	**1.94**	**1.93**
200	7.07	4.34	3.49	3.08	2.84	*2.57*	**2.41**	**2.30**	**2.22**	**2.17**	**2.13**	**2.10**	**2.08**	**2.05**	**2.02**	**2.00**	**1.99**	**1.98**	**1.96**	**1.95**

Table 19-2. κ-Multipliers for 1-of-3 Interwell Prediction Limits on Observations (10 COCs, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	2.87	**1.97**	**1.68**	**1.53**	**1.45**	**1.35**	**1.29**	**1.25**	**1.22**	**1.20**	**1.18**	**1.17**	**1.16**	**1.15**	**1.14**	**1.14**	**1.13**	**1.13**	**1.12**	**1.11**
2	3.50	**2.32**	**1.95**	**1.77**	**1.66**	**1.54**	**1.47**	**1.42**	**1.38**	**1.36**	**1.34**	**1.33**	**1.32**	**1.30**	**1.29**	**1.28**	**1.28**	**1.27**	**1.26**	**1.26**
3	3.88	**2.54**	**2.11**	**1.91**	**1.79**	**1.65**	**1.57**	**1.51**	**1.48**	**1.45**	**1.43**	**1.42**	**1.41**	**1.39**	**1.38**	**1.37**	**1.36**	**1.35**	**1.35**	**1.34**
4	4.14	**2.69**	**2.23**	**2.01**	**1.88**	**1.73**	**1.65**	**1.58**	**1.54**	**1.51**	**1.49**	**1.48**	**1.47**	**1.45**	**1.44**	**1.43**	**1.42**	**1.41**	**1.40**	**1.39**
5	4.36	*2.81*	**2.32**	**2.08**	**1.95**	**1.79**	**1.70**	**1.64**	**1.59**	**1.56**	**1.54**	**1.53**	**1.51**	**1.49**	**1.48**	**1.47**	**1.46**	**1.46**	**1.44**	**1.44**
8	4.80	3.06	**2.51**	**2.25**	**2.09**	**1.91**	**1.82**	**1.74**	**1.70**	**1.66**	**1.64**	**1.62**	**1.61**	**1.58**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**
12	5.19	3.27	**2.67**	**2.38**	**2.21**	**2.02**	**1.92**	**1.84**	**1.78**	**1.75**	**1.72**	**1.70**	**1.69**	**1.66**	**1.65**	**1.63**	**1.63**	**1.62**	**1.60**	**1.60**
16	5.45	3.42	*2.79*	**2.48**	**2.30**	**2.10**	**1.98**	**1.90**	**1.85**	**1.81**	**1.78**	**1.76**	**1.74**	**1.72**	**1.70**	**1.69**	**1.68**	**1.67**	**1.66**	**1.65**
20	5.66	3.53	*2.88*	**2.56**	**2.37**	**2.16**	**2.04**	**1.95**	**1.89**	**1.85**	**1.82**	**1.80**	**1.78**	**1.76**	**1.74**	**1.73**	**1.72**	**1.71**	**1.69**	**1.68**
30	6.04	3.74	3.03	**2.69**	**2.49**	**2.26**	**2.14**	**2.04**	**1.98**	**1.94**	**1.90**	**1.88**	**1.86**	**1.83**	**1.81**	**1.80**	**1.79**	**1.78**	**1.76**	**1.75**
40	6.29	3.88	3.14	*2.79*	**2.58**	**2.34**	**2.20**	**2.10**	**2.04**	**1.99**	**1.96**	**1.94**	**1.92**	**1.89**	**1.87**	**1.85**	**1.84**	**1.83**	**1.81**	**1.80**
50	6.48	3.99	3.23	*2.86*	**2.64**	**2.39**	**2.26**	**2.15**	**2.08**	**2.04**	**2.00**	**1.98**	**1.96**	**1.93**	**1.90**	**1.89**	**1.88**	**1.87**	**1.85**	**1.84**
60	6.64	4.08	3.30	*2.92*	**2.70**	**2.44**	**2.30**	**2.19**	**2.12**	**2.07**	**2.04**	**2.01**	**1.99**	**1.96**	**1.94**	**1.92**	**1.91**	**1.90**	**1.88**	**1.87**
75	6.84	4.19	3.38	*2.99*	**2.76**	**2.50**	**2.35**	**2.24**	**2.17**	**2.12**	**2.08**	**2.05**	**2.03**	**2.00**	**1.97**	**1.96**	**1.94**	**1.93**	**1.91**	**1.90**
100	7.07	4.34	3.49	3.08	*2.84*	**2.57**	**2.41**	**2.30**	**2.22**	**2.17**	**2.13**	**2.10**	**2.08**	**2.05**	**2.02**	**2.00**	**1.99**	**1.98**	**1.96**	**1.95**
125	7.27	4.44	3.57	3.15	*2.91*	**2.62**	**2.47**	**2.35**	**2.27**	**2.22**	**2.18**	**2.15**	**2.12**	**2.08**	**2.06**	**2.04**	**2.03**	**2.02**	**2.00**	**1.98**
150	7.42	4.52	3.64	3.21	*2.96*	**2.67**	**2.51**	**2.39**	**2.30**	**2.25**	**2.21**	**2.18**	**2.15**	**2.12**	**2.09**	**2.07**	**2.06**	**2.05**	**2.02**	**2.01**
175	7.54	4.60	3.70	3.26	*3.00*	**2.71**	**2.54**	**2.42**	**2.34**	**2.28**	**2.24**	**2.21**	**2.18**	**2.14**	**2.12**	**2.10**	**2.08**	**2.07**	**2.05**	**2.03**
200	7.66	4.66	3.75	3.30	*3.04*	**2.74**	**2.57**	**2.44**	**2.36**	**2.30**	**2.26**	**2.23**	**2.20**	**2.17**	**2.14**	**2.12**	**2.10**	**2.09**	**2.07**	**2.05**

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Table 19-2. κ-Multipliers for 1-of-3 Interwell Prediction Limits on Observations (20 COCs, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	2.34	**1.65**	**1.42**	**1.30**	**1.23**	**1.15**	**1.10**	**1.07**	**1.04**	**1.03**	**1.02**	**1.01**	**1.00**	**0.99**	**0.98**	**0.98**	**0.97**	**0.97**	**0.96**	**0.96**
2	2.99	**2.00**	**1.69**	**1.54**	**1.45**	**1.35**	**1.29**	**1.25**	**1.22**	**1.20**	**1.19**	**1.17**	**1.16**	**1.15**	**1.14**	**1.14**	**1.13**	**1.13**	**1.12**	**1.11**
3	3.40	*2.22*	**1.86**	**1.68**	**1.58**	**1.46**	**1.40**	**1.35**	**1.32**	**1.29**	**1.28**	**1.27**	**1.26**	**1.24**	**1.23**	**1.22**	**1.22**	**1.21**	**1.21**	**1.20**
4	3.71	2.38	**1.98**	**1.78**	**1.67**	**1.54**	**1.47**	**1.42**	**1.38**	**1.36**	**1.34**	**1.33**	**1.32**	**1.30**	**1.29**	**1.28**	**1.28**	**1.27**	**1.26**	**1.26**
5	3.95	2.50	**2.07**	**1.87**	**1.74**	**1.61**	**1.53**	**1.47**	**1.44**	**1.41**	**1.39**	**1.38**	**1.37**	**1.35**	**1.34**	**1.33**	**1.32**	**1.32**	**1.31**	**1.30**
8	4.48	2.77	*2.27*	**2.03**	**1.89**	**1.73**	**1.65**	**1.59**	**1.55**	**1.52**	**1.50**	**1.48**	**1.47**	**1.45**	**1.44**	**1.43**	**1.42**	**1.41**	**1.40**	**1.39**
12	4.96	3.01	2.44	*2.18*	**2.02**	**1.85**	**1.75**	**1.68**	**1.64**	**1.60**	**1.58**	**1.56**	**1.55**	**1.53**	**1.52**	**1.50**	**1.50**	**1.49**	**1.48**	**1.47**
16	5.29	3.18	2.57	*2.28*	**2.11**	**1.92**	**1.82**	**1.75**	**1.70**	**1.67**	**1.64**	**1.62**	**1.61**	**1.59**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**
20	5.57	3.32	2.67	*2.36*	*2.18*	**1.98**	**1.88**	**1.80**	**1.75**	**1.71**	**1.69**	**1.67**	**1.65**	**1.63**	**1.61**	**1.60**	**1.59**	**1.58**	**1.57**	**1.56**
30	6.04	3.55	2.84	2.50	*2.31*	**2.09**	**1.98**	**1.89**	**1.84**	**1.80**	**1.77**	**1.75**	**1.73**	**1.71**	**1.69**	**1.68**	**1.67**	**1.66**	**1.64**	**1.64**
40	6.39	3.73	2.97	2.61	2.40	*2.17*	**2.05**	**1.96**	**1.90**	**1.86**	**1.83**	**1.80**	**1.79**	**1.76**	**1.74**	**1.73**	**1.72**	**1.71**	**1.69**	**1.68**
50	6.64	3.87	3.07	2.69	2.47	*2.23*	**2.10**	**2.01**	**1.95**	**1.90**	**1.87**	**1.85**	**1.83**	**1.80**	**1.78**	**1.77**	**1.76**	**1.75**	**1.73**	**1.72**
60	6.86	3.97	3.14	2.75	2.53	*2.28*	*2.15*	**2.05**	**1.98**	**1.94**	**1.91**	**1.88**	**1.86**	**1.84**	**1.82**	**1.80**	**1.79**	**1.78**	**1.76**	**1.75**
75	7.11	4.10	3.24	2.84	2.60	*2.34*	*2.20*	**2.10**	**2.03**	**1.98**	**1.95**	**1.93**	**1.91**	**1.88**	**1.86**	**1.84**	**1.83**	**1.82**	**1.80**	**1.79**
100	7.46	4.27	3.36	2.94	2.69	2.42	*2.27*	*2.16*	**2.09**	**2.04**	**2.01**	**1.98**	**1.96**	**1.93**	**1.91**	**1.89**	**1.88**	**1.87**	**1.85**	**1.84**
125	7.70	4.40	3.46	3.02	2.76	2.48	*2.32*	*2.21*	*2.14*	**2.09**	**2.05**	**2.02**	**2.00**	**1.97**	**1.94**	**1.93**	**1.91**	**1.90**	**1.88**	**1.87**
150	7.91	4.51	3.54	3.08	2.82	2.53	*2.37*	*2.25*	*2.18*	*2.12*	**2.08**	**2.06**	**2.03**	**2.00**	**1.98**	**1.96**	**1.94**	**1.93**	**1.92**	**1.90**
175	8.09	4.59	3.60	3.13	2.87	2.57	*2.40*	*2.28*	*2.21*	*2.15*	*2.11*	**2.08**	**2.06**	**2.03**	**2.00**	**1.98**	**1.97**	**1.96**	**1.94**	**1.93**
200	8.24	4.67	3.66	3.18	2.91	2.60	2.44	*2.31*	*2.23*	*2.18*	*2.14*	**2.11**	**2.08**	**2.05**	**2.02**	**2.01**	**1.99**	**1.98**	**1.96**	**1.95**

Table 19-2. κ-Multipliers for 1-of-3 Interwell Prediction Limits on Observations (20 COCs, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	2.99	**2.00**	**1.69**	**1.54**	**1.45**	**1.35**	**1.29**	**1.25**	**1.22**	**1.20**	**1.19**	**1.17**	**1.16**	**1.15**	**1.14**	**1.14**	**1.13**	**1.13**	**1.12**	**1.11**
2	3.71	**2.38**	**1.98**	**1.78**	**1.67**	**1.54**	**1.47**	**1.42**	**1.38**	**1.36**	**1.34**	**1.33**	**1.32**	**1.30**	**1.29**	**1.28**	**1.28**	**1.27**	**1.26**	**1.26**
3	4.16	2.61	**2.15**	**1.93**	**1.80**	**1.66**	**1.58**	**1.52**	**1.48**	**1.45**	**1.43**	**1.42**	**1.41**	**1.39**	**1.38**	**1.37**	**1.36**	**1.35**	**1.35**	**1.34**
4	4.48	2.77	**2.27**	**2.03**	**1.89**	**1.73**	**1.65**	**1.59**	**1.55**	**1.52**	**1.50**	**1.48**	**1.47**	**1.45**	**1.44**	**1.43**	**1.42**	**1.41**	**1.40**	**1.39**
5	4.75	2.91	**2.36**	**2.11**	**1.96**	**1.80**	**1.71**	**1.64**	**1.59**	**1.56**	**1.54**	**1.53**	**1.51**	**1.49**	**1.48**	**1.47**	**1.46**	**1.46**	**1.44**	**1.44**
8	5.29	3.18	*2.57*	**2.28**	**2.11**	**1.92**	**1.82**	**1.75**	**1.70**	**1.67**	**1.64**	**1.62**	**1.61**	**1.59**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**
12	5.78	3.43	2.74	**2.43**	**2.24**	**2.04**	**1.92**	**1.84**	**1.79**	**1.75**	**1.72**	**1.70**	**1.69**	**1.67**	**1.65**	**1.64**	**1.63**	**1.62**	**1.60**	**1.60**
16	6.11	3.59	2.87	*2.53*	**2.33**	**2.11**	**1.99**	**1.91**	**1.85**	**1.81**	**1.78**	**1.76**	**1.74**	**1.72**	**1.70**	**1.69**	**1.68**	**1.67**	**1.66**	**1.65**
20	6.39	3.73	2.97	*2.61*	**2.40**	**2.17**	**2.05**	**1.96**	**1.90**	**1.86**	**1.83**	**1.80**	**1.79**	**1.76**	**1.74**	**1.73**	**1.72**	**1.71**	**1.69**	**1.68**
30	6.86	3.97	3.14	2.75	*2.53*	**2.28**	**2.15**	**2.05**	**1.98**	**1.94**	**1.91**	**1.88**	**1.86**	**1.84**	**1.82**	**1.80**	**1.79**	**1.78**	**1.76**	**1.75**
40	7.19	4.14	3.27	2.86	*2.62*	**2.36**	**2.22**	**2.11**	**2.04**	**2.00**	**1.96**	**1.94**	**1.92**	**1.89**	**1.87**	**1.85**	**1.84**	**1.83**	**1.81**	**1.80**
50	7.46	4.27	3.36	2.94	*2.69*	**2.42**	**2.27**	**2.16**	**2.09**	**2.04**	**2.01**	**1.98**	**1.96**	**1.93**	**1.91**	**1.89**	**1.88**	**1.87**	**1.85**	**1.84**
60	7.66	4.38	3.44	3.00	2.75	*2.47*	**2.31**	**2.20**	**2.13**	**2.08**	**2.04**	**2.01**	**1.99**	**1.96**	**1.94**	**1.92**	**1.91**	**1.90**	**1.88**	**1.87**
75	7.91	4.51	3.54	3.08	2.82	*2.53*	**2.37**	**2.25**	**2.18**	**2.12**	**2.08**	**2.06**	**2.03**	**2.00**	**1.98**	**1.96**	**1.94**	**1.93**	**1.92**	**1.90**
100	8.24	4.67	3.66	3.18	2.91	*2.60*	**2.44**	**2.31**	**2.23**	**2.18**	**2.14**	**2.11**	**2.08**	**2.05**	**2.02**	**2.01**	**1.99**	**1.98**	**1.96**	**1.95**
125	8.48	4.79	3.75	3.26	2.98	*2.66*	*2.49*	**2.36**	**2.28**	**2.22**	**2.18**	**2.15**	**2.12**	**2.09**	**2.06**	**2.04**	**2.03**	**2.02**	**2.00**	**1.98**
150	8.67	4.90	3.83	3.33	3.03	*2.71*	*2.53*	**2.40**	**2.32**	**2.26**	**2.21**	**2.18**	**2.16**	**2.12**	**2.09**	**2.07**	**2.06**	**2.05**	**2.03**	**2.01**
175	8.83	4.98	3.89	3.38	3.08	*2.75*	*2.57*	**2.43**	**2.35**	**2.29**	**2.24**	**2.21**	**2.19**	**2.15**	**2.12**	**2.10**	**2.08**	**2.07**	**2.05**	**2.03**
200	8.98	5.06	3.95	3.42	3.12	2.78	*2.60*	*2.46*	**2.37**	**2.31**	**2.27**	**2.23**	**2.21**	**2.17**	**2.14**	**2.12**	**2.10**	**2.09**	**2.07**	**2.06**

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Table 19-2. κ-Multipliers for 1-of-3 Interwell Prediction Limits on Observations (20 COCs, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.71	**2.38**	**1.98**	**1.78**	**1.67**	**1.54**	**1.47**	**1.42**	**1.38**	**1.36**	**1.34**	**1.33**	**1.32**	**1.30**	**1.29**	**1.28**	**1.28**	**1.27**	**1.26**	**1.26**
2	4.48	**2.77**	**2.27**	**2.03**	**1.89**	**1.73**	**1.65**	**1.59**	**1.55**	**1.52**	**1.50**	**1.48**	**1.47**	**1.45**	**1.44**	**1.43**	**1.42**	**1.41**	**1.40**	**1.39**
3	4.96	3.01	**2.44**	**2.18**	**2.02**	**1.85**	**1.75**	**1.68**	**1.64**	**1.60**	**1.58**	**1.56**	**1.55**	**1.53**	**1.52**	**1.50**	**1.50**	**1.49**	**1.48**	**1.47**
4	5.29	3.18	**2.57**	**2.28**	**2.11**	**1.92**	**1.82**	**1.75**	**1.70**	**1.67**	**1.64**	**1.62**	**1.61**	**1.59**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**
5	5.57	3.32	**2.67**	**2.36**	**2.18**	**1.98**	**1.88**	**1.80**	**1.75**	**1.71**	**1.69**	**1.67**	**1.65**	**1.63**	**1.61**	**1.60**	**1.59**	**1.58**	**1.57**	**1.56**
8	6.11	3.59	*2.87*	**2.53**	**2.33**	**2.11**	**1.99**	**1.91**	**1.85**	**1.81**	**1.78**	**1.76**	**1.74**	**1.72**	**1.70**	**1.69**	**1.68**	**1.67**	**1.66**	**1.65**
12	6.60	3.84	3.05	**2.68**	**2.46**	**2.22**	**2.09**	**2.00**	**1.94**	**1.89**	**1.86**	**1.84**	**1.82**	**1.79**	**1.77**	**1.76**	**1.75**	**1.74**	**1.73**	**1.72**
16	6.93	4.00	3.17	*2.78*	**2.55**	**2.30**	**2.16**	**2.06**	**2.00**	**1.95**	**1.92**	**1.89**	**1.88**	**1.85**	**1.83**	**1.81**	**1.80**	**1.79**	**1.77**	**1.76**
20	7.19	4.14	3.27	*2.86*	**2.62**	**2.36**	**2.22**	**2.11**	**2.04**	**2.00**	**1.96**	**1.94**	**1.92**	**1.89**	**1.87**	**1.85**	**1.84**	**1.83**	**1.81**	**1.80**
30	7.66	4.38	3.44	*3.00*	**2.75**	**2.47**	**2.31**	**2.20**	**2.13**	**2.08**	**2.04**	**2.01**	**1.99**	**1.96**	**1.94**	**1.92**	**1.91**	**1.90**	**1.88**	**1.87**
40	7.97	4.54	3.56	3.11	*2.84*	**2.54**	**2.38**	**2.26**	**2.19**	**2.14**	**2.10**	**2.07**	**2.04**	**2.01**	**1.99**	**1.97**	**1.96**	**1.94**	**1.93**	**1.91**
50	8.24	4.67	3.66	3.18	*2.91*	**2.60**	**2.44**	**2.31**	**2.23**	**2.18**	**2.14**	**2.11**	**2.08**	**2.05**	**2.02**	**2.01**	**1.99**	**1.98**	**1.96**	**1.95**
60	8.44	4.78	3.73	3.25	*2.96*	**2.65**	**2.48**	**2.35**	**2.27**	**2.21**	**2.17**	**2.14**	**2.12**	**2.08**	**2.06**	**2.04**	**2.02**	**2.01**	**1.99**	**1.98**
75	8.67	4.90	3.83	3.33	*3.03*	**2.71**	**2.53**	**2.40**	**2.32**	**2.26**	**2.21**	**2.18**	**2.16**	**2.12**	**2.09**	**2.07**	**2.06**	**2.05**	**2.03**	**2.01**
100	8.98	5.06	3.95	3.42	3.12	*2.78*	**2.60**	**2.46**	**2.37**	**2.31**	**2.27**	**2.23**	**2.21**	**2.17**	**2.14**	**2.12**	**2.10**	**2.09**	**2.07**	**2.06**
125	9.22	5.18	4.03	3.50	3.19	*2.84*	**2.65**	**2.51**	**2.42**	**2.36**	**2.31**	**2.28**	**2.25**	**2.21**	**2.18**	**2.16**	**2.14**	**2.13**	**2.10**	**2.09**
150	9.41	5.28	4.11	3.56	3.24	*2.89*	**2.70**	**2.55**	**2.45**	**2.39**	**2.34**	**2.31**	**2.28**	**2.24**	**2.21**	**2.19**	**2.17**	**2.16**	**2.13**	**2.12**
175	9.57	5.37	4.17	3.61	3.29	*2.93*	**2.73**	**2.58**	**2.49**	**2.42**	**2.37**	**2.33**	**2.30**	**2.26**	**2.23**	**2.21**	**2.19**	**2.18**	**2.16**	**2.14**
200	9.69	5.44	4.23	3.66	3.33	*2.96*	**2.76**	**2.61**	**2.51**	**2.44**	**2.40**	**2.36**	**2.33**	**2.29**	**2.25**	**2.23**	**2.21**	**2.20**	**2.18**	**2.16**

Table 19-2. κ-Multipliers for 1-of-3 Interwell Prediction Limits on Observations (40 COCs, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.05	**2.03**	**1.70**	**1.55**	**1.45**	**1.35**	**1.29**	**1.25**	**1.22**	**1.20**	**1.18**	**1.17**	**1.16**	**1.15**	**1.14**	**1.14**	**1.13**	**1.13**	**1.12**	**1.12**
2	3.84	2.41	**1.99**	**1.79**	**1.68**	**1.55**	**1.47**	**1.42**	**1.39**	**1.36**	**1.34**	**1.33**	**1.32**	**1.30**	**1.29**	**1.29**	**1.28**	**1.27**	**1.27**	**1.26**
3	4.36	2.65	*2.16*	**1.94**	**1.81**	**1.66**	**1.58**	**1.52**	**1.48**	**1.45**	**1.43**	**1.42**	**1.41**	**1.39**	**1.38**	**1.37**	**1.36**	**1.36**	**1.35**	**1.34**
4	4.72	2.83	*2.29*	**2.04**	**1.90**	**1.74**	**1.65**	**1.59**	**1.55**	**1.52**	**1.50**	**1.48**	**1.47**	**1.45**	**1.44**	**1.42**	**1.42**	**1.41**	**1.40**	**1.40**
5	5.05	2.97	2.39	**2.12**	**1.97**	**1.80**	**1.71**	**1.64**	**1.59**	**1.57**	**1.54**	**1.53**	**1.51**	**1.49**	**1.48**	**1.47**	**1.46**	**1.45**	**1.44**	**1.44**
8	5.70	3.27	2.61	*2.30*	**2.12**	**1.93**	**1.83**	**1.75**	**1.70**	**1.67**	**1.64**	**1.62**	**1.61**	**1.59**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**
12	6.30	3.54	2.79	2.45	*2.26*	**2.04**	**1.93**	**1.84**	**1.79**	**1.75**	**1.72**	**1.70**	**1.69**	**1.66**	**1.65**	**1.64**	**1.63**	**1.62**	**1.60**	**1.59**
16	6.74	3.73	2.93	2.56	*2.35*	**2.12**	**2.00**	**1.91**	**1.85**	**1.81**	**1.79**	**1.76**	**1.75**	**1.72**	**1.70**	**1.69**	**1.68**	**1.67**	**1.66**	**1.65**
20	7.07	3.90	3.04	2.64	2.42	*2.18*	**2.05**	**1.96**	**1.90**	**1.86**	**1.83**	**1.81**	**1.79**	**1.76**	**1.74**	**1.73**	**1.72**	**1.71**	**1.69**	**1.68**
30	7.67	4.17	3.23	2.80	2.56	*2.29*	*2.16*	**2.05**	**1.98**	**1.94**	**1.91**	**1.89**	**1.86**	**1.83**	**1.82**	**1.80**	**1.79**	**1.78**	**1.77**	**1.75**
40	8.11	4.36	3.37	2.91	2.65	*2.37*	*2.22*	**2.11**	**2.05**	**2.00**	**1.96**	**1.94**	**1.92**	**1.89**	**1.87**	**1.85**	**1.84**	**1.83**	**1.81**	**1.80**
50	8.44	4.51	3.46	3.00	2.72	2.44	*2.28*	*2.17*	**2.09**	**2.05**	**2.01**	**1.98**	**1.96**	**1.93**	**1.91**	**1.89**	**1.88**	**1.87**	**1.85**	**1.84**
60	8.71	4.64	3.56	3.06	2.79	2.48	*2.33*	*2.21*	*2.13*	**2.08**	**2.05**	**2.02**	**1.99**	**1.96**	**1.94**	**1.92**	**1.91**	**1.90**	**1.88**	**1.87**
75	8.98	4.79	3.65	3.15	2.86	2.54	*2.38*	*2.26*	*2.18*	*2.12*	**2.09**	**2.06**	**2.03**	**2.00**	**1.98**	**1.96**	**1.95**	**1.93**	**1.92**	**1.90**
100	9.42	4.98	3.79	3.26	2.96	2.63	2.45	*2.32*	*2.24*	*2.18*	*2.14*	*2.11*	**2.09**	**2.05**	**2.03**	**2.01**	**1.99**	**1.98**	**1.96**	**1.95**
125	9.75	5.13	3.90	3.34	3.03	2.69	2.50	*2.37*	*2.29*	*2.23*	*2.18*	*2.15*	*2.13*	**2.09**	**2.06**	**2.05**	**2.03**	**2.02**	**2.00**	**1.98**
150	10.02	5.24	3.98	3.41	3.09	2.74	2.55	*2.41*	*2.32*	*2.26*	*2.22*	*2.19*	*2.16*	*2.12*	**2.09**	**2.07**	**2.06**	**2.05**	**2.03**	**2.01**
175	10.24	5.35	4.06	3.47	3.14	2.78	2.59	2.44	*2.35*	*2.29*	*2.25*	*2.21*	*2.19*	*2.15*	*2.12*	**2.10**	**2.08**	**2.07**	**2.05**	**2.04**
200	10.41	5.43	4.12	3.52	3.19	2.81	2.62	2.47	*2.38*	*2.32*	*2.27*	*2.24*	*2.21*	*2.17*	*2.14*	*2.12*	**2.10**	**2.09**	**2.07**	**2.06**

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Table 19-2. κ-Multipliers for 1-of-3 Interwell Prediction Limits on Observations (40 COCs, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.84	2.41	1.99	1.79	1.68	1.55	1.47	1.42	1.39	1.36	1.34	1.33	1.32	1.30	1.29	1.29	1.28	1.27	1.27	1.26
2	4.72	2.83	2.29	2.04	1.90	1.74	1.65	1.59	1.55	1.52	1.50	1.48	1.47	1.45	1.44	1.42	1.42	1.41	1.40	1.40
3	5.29	3.09	2.48	2.19	2.03	1.85	1.75	1.68	1.64	1.60	1.58	1.56	1.55	1.53	1.52	1.51	1.50	1.49	1.48	1.47
4	5.70	3.27	2.61	2.30	2.12	1.93	1.83	1.75	1.70	1.67	1.64	1.62	1.61	1.59	1.57	1.56	1.55	1.54	1.53	1.52
5	6.03	3.42	2.71	2.38	2.20	1.99	1.88	1.80	1.75	1.71	1.69	1.67	1.65	1.63	1.62	1.60	1.59	1.58	1.57	1.56
8	6.74	3.73	2.93	2.56	2.35	2.12	2.00	1.91	1.85	1.81	1.79	1.76	1.75	1.72	1.70	1.69	1.68	1.67	1.66	1.65
12	7.34	4.01	3.12	2.71	2.48	2.23	2.10	2.00	1.94	1.90	1.86	1.84	1.82	1.79	1.78	1.76	1.75	1.74	1.72	1.72
16	7.78	4.20	3.26	2.83	2.58	2.31	2.17	2.07	2.00	1.96	1.92	1.90	1.88	1.85	1.83	1.81	1.80	1.79	1.78	1.77
20	8.11	4.36	3.37	2.91	2.65	2.37	2.22	2.11	2.05	2.00	1.96	1.94	1.92	1.89	1.87	1.85	1.84	1.83	1.81	1.80
30	8.71	4.64	3.56	3.06	2.79	2.48	2.33	2.21	2.13	2.08	2.05	2.02	1.99	1.96	1.94	1.92	1.91	1.90	1.88	1.87
40	9.09	4.83	3.69	3.17	2.89	2.57	2.39	2.27	2.19	2.14	2.10	2.07	2.05	2.01	1.99	1.97	1.96	1.94	1.93	1.91
50	9.42	4.98	3.79	3.26	2.96	2.63	2.45	2.32	2.24	2.18	2.14	2.11	2.09	2.05	2.03	2.01	1.99	1.98	1.96	1.95
60	9.70	5.10	3.88	3.32	3.02	2.67	2.50	2.36	2.28	2.22	2.18	2.15	2.12	2.08	2.06	2.04	2.02	2.01	1.99	1.98
75	10.02	5.24	3.98	3.41	3.09	2.74	2.55	2.41	2.32	2.26	2.22	2.19	2.16	2.12	2.09	2.07	2.06	2.05	2.03	2.01
100	10.41	5.43	4.12	3.52	3.19	2.81	2.62	2.47	2.38	2.32	2.27	2.24	2.21	2.17	2.14	2.12	2.10	2.09	2.07	2.06
125	10.73	5.59	4.23	3.61	3.26	2.87	2.67	2.52	2.43	2.36	2.31	2.28	2.25	2.21	2.18	2.16	2.14	2.13	2.10	2.09
150	10.95	5.70	4.31	3.68	3.32	2.93	2.72	2.56	2.46	2.39	2.35	2.31	2.28	2.24	2.21	2.19	2.17	2.16	2.13	2.12
175	11.17	5.81	4.38	3.73	3.37	2.97	2.75	2.59	2.49	2.43	2.37	2.34	2.31	2.26	2.23	2.21	2.19	2.18	2.16	2.14
200	11.39	5.89	4.43	3.78	3.41	3.00	2.78	2.62	2.52	2.45	2.40	2.36	2.33	2.29	2.25	2.23	2.21	2.20	2.18	2.16

Table 19-2. κ-Multipliers for 1-of-3 Interwell Prediction Limits on Observations (40 COCs, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	4.72	2.83	2.29	2.04	1.90	1.74	1.65	1.59	1.55	1.52	1.50	1.48	1.47	1.45	1.44	1.42	1.42	1.41	1.40	1.40
2	5.70	3.27	2.61	2.30	2.12	1.93	1.83	1.75	1.70	1.67	1.64	1.62	1.61	1.59	1.57	1.56	1.55	1.54	1.53	1.52
3	6.30	3.54	2.79	2.45	2.26	2.04	1.93	1.84	1.79	1.75	1.72	1.70	1.69	1.66	1.65	1.64	1.63	1.62	1.60	1.59
4	6.74	3.73	2.93	2.56	2.35	2.12	2.00	1.91	1.85	1.81	1.79	1.76	1.75	1.72	1.70	1.69	1.68	1.67	1.66	1.65
5	7.07	3.90	3.04	2.64	2.42	2.18	2.05	1.96	1.90	1.86	1.83	1.81	1.79	1.76	1.74	1.73	1.72	1.71	1.69	1.68
8	7.78	4.20	3.26	2.83	2.58	2.31	2.17	2.07	2.00	1.96	1.92	1.90	1.88	1.85	1.83	1.81	1.80	1.79	1.78	1.77
12	8.38	4.49	3.45	2.98	2.72	2.42	2.27	2.16	2.09	2.04	2.00	1.97	1.95	1.92	1.90	1.88	1.87	1.86	1.84	1.83
16	8.77	4.68	3.58	3.09	2.80	2.50	2.34	2.22	2.15	2.09	2.06	2.03	2.00	1.97	1.95	1.93	1.92	1.91	1.89	1.88
20	9.09	4.83	3.69	3.17	2.89	2.57	2.39	2.27	2.19	2.14	2.10	2.07	2.05	2.01	1.99	1.97	1.96	1.94	1.93	1.91
30	9.70	5.10	3.88	3.32	3.02	2.67	2.50	2.36	2.28	2.22	2.18	2.15	2.12	2.08	2.06	2.04	2.02	2.01	1.99	1.98
40	10.08	5.29	4.01	3.43	3.11	2.76	2.57	2.42	2.33	2.27	2.23	2.20	2.17	2.13	2.10	2.08	2.07	2.06	2.04	2.02
50	10.41	5.43	4.12	3.52	3.19	2.81	2.62	2.47	2.38	2.32	2.27	2.24	2.21	2.17	2.14	2.12	2.10	2.09	2.07	2.06
60	10.68	5.57	4.20	3.59	3.24	2.87	2.66	2.51	2.42	2.35	2.31	2.27	2.24	2.20	2.17	2.15	2.13	2.12	2.10	2.08
75	10.95	5.70	4.31	3.68	3.32	2.93	2.72	2.56	2.46	2.39	2.35	2.31	2.28	2.24	2.21	2.19	2.17	2.16	2.13	2.12
100	11.39	5.89	4.43	3.78	3.41	3.00	2.78	2.62	2.52	2.45	2.40	2.36	2.33	2.29	2.25	2.23	2.21	2.20	2.18	2.16
125	11.66	6.03	4.54	3.86	3.48	3.06	2.84	2.67	2.57	2.49	2.44	2.40	2.37	2.32	2.29	2.27	2.25	2.23	2.21	2.19
150	11.94	6.14	4.61	3.93	3.54	3.11	2.88	2.71	2.60	2.53	2.47	2.43	2.40	2.35	2.32	2.30	2.28	2.26	2.24	2.22
175	12.10	6.25	4.69	3.98	3.58	3.15	2.91	2.74	2.63	2.56	2.50	2.46	2.43	2.38	2.35	2.32	2.30	2.29	2.26	2.24
200	12.27	6.30	4.75	4.04	3.63	3.19	2.95	2.77	2.66	2.58	2.52	2.48	2.45	2.40	2.37	2.34	2.32	2.31	2.28	2.26

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Table 19-3. κ-Multipliers for 1-of-4 Interwell Prediction Limits on Observations (1 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	0.06	-0.01	-0.04	-0.07	-0.08	-0.10	-0.11	-0.12	-0.13	-0.13	-0.13	-0.14	-0.14	-0.14	-0.14	-0.15	-0.15	-0.15	-0.15	-0.15
2	0.36	0.25	0.21	0.18	0.16	0.13	0.12	0.11	0.10	0.09	0.09	0.09	0.08	0.08	0.08	0.08	0.07	0.07	0.07	0.07
3	0.52	0.40	0.34	0.31	0.29	0.26	0.24	0.23	0.22	0.21	0.21	0.20	0.20	0.20	0.19	0.19	0.19	0.19	0.18	0.18
4	0.64	0.50	0.44	0.40	0.37	0.34	0.32	0.31	0.30	0.29	0.29	0.28	0.28	0.27	0.27	0.27	0.27	0.26	0.26	0.26
5	0.73	0.58	0.51	0.47	0.44	0.41	0.39	0.37	0.36	0.35	0.35	0.34	0.34	0.33	0.33	0.33	0.32	0.32	0.32	0.32
8	0.92	0.73	0.65	0.60	0.57	0.53	0.51	0.49	0.48	0.47	0.46	0.46	0.45	0.45	0.44	0.44	0.44	0.44	0.43	0.43
12	1.08	0.86	0.77	0.72	0.68	0.64	0.61	0.59	0.58	0.57	0.56	0.55	0.55	0.54	0.54	0.53	0.53	0.53	0.52	0.52
16	1.19	0.95	0.85	0.79	0.76	0.71	0.68	0.66	0.64	0.63	0.63	0.62	0.61	0.61	0.60	0.60	0.59	0.59	0.59	0.58
20	1.28	1.02	0.91	0.85	0.81	0.76	0.73	0.71	0.69	0.68	0.67	0.67	0.66	0.66	0.65	0.65	0.64	0.64	0.63	0.63
30	1.44	1.15	1.03	0.96	0.91	0.86	0.83	0.80	0.78	0.77	0.76	0.75	0.75	0.74	0.73	0.73	0.73	0.72	0.72	0.71
40	1.55	1.23	1.10	1.03	0.98	0.93	0.89	0.86	0.84	0.83	0.82	0.81	0.81	0.80	0.79	0.79	0.78	0.78	0.77	0.77
50	1.63	1.30	1.16	1.09	1.04	0.98	0.94	0.91	0.89	0.88	0.87	0.86	0.85	0.84	0.83	0.83	0.83	0.82	0.82	0.81
60	1.70	1.35	1.21	1.13	1.08	1.02	0.98	0.95	0.93	0.91	0.90	0.89	0.89	0.88	0.87	0.86	0.86	0.86	0.85	0.85
75	1.78	1.42	1.27	1.19	1.13	1.07	1.03	0.99	0.97	0.96	0.95	0.94	0.93	0.92	0.91	0.91	0.90	0.90	0.89	0.89
100	1.89	1.50	1.34	1.26	1.20	1.13	1.09	1.05	1.03	1.01	1.00	0.99	0.98	0.97	0.96	0.96	0.95	0.95	0.94	0.94
125	1.97	1.56	1.40	1.31	1.25	1.18	1.13	1.10	1.07	1.06	1.04	1.03	1.03	1.01	1.01	1.00	0.99	0.99	0.98	0.98
150	2.03	1.61	1.44	1.35	1.29	1.21	1.17	1.13	1.11	1.09	1.08	1.07	1.06	1.05	1.04	1.03	1.03	1.02	1.01	1.01
175	*2.09*	1.66	1.48	1.39	1.32	1.25	1.20	1.16	1.14	1.12	1.11	1.10	1.09	1.07	1.06	1.06	1.05	1.05	1.04	1.03
200	2.14	1.69	1.51	1.42	1.35	1.27	1.23	1.19	1.16	1.14	1.13	1.12	1.11	1.10	1.09	1.08	1.08	1.07	1.06	1.06

Table 19-3. κ-Multipliers for 1-of-4 Interwell Prediction Limits on Observations (1 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	0.36	0.25	0.21	0.18	0.16	0.13	0.12	0.11	0.10	0.09	0.09	0.09	0.08	0.08	0.08	0.08	0.07	0.07	0.07	0.07
2	0.64	0.50	0.44	0.40	0.37	0.34	0.32	0.31	0.30	0.29	0.29	0.28	0.28	0.27	0.27	0.27	0.27	0.26	0.26	0.26
3	0.80	0.64	0.56	0.52	0.49	0.46	0.43	0.42	0.41	0.40	0.39	0.39	0.38	0.38	0.37	0.37	0.37	0.37	0.36	0.36
4	0.92	0.73	0.65	0.60	0.57	0.53	0.51	0.49	0.48	0.47	0.46	0.46	0.45	0.45	0.44	0.44	0.44	0.44	0.43	0.43
5	1.01	0.80	0.72	0.66	0.63	0.59	0.57	0.55	0.53	0.52	0.52	0.51	0.51	0.50	0.50	0.49	0.49	0.49	0.48	0.48
8	1.19	0.95	0.85	0.79	0.76	0.71	0.68	0.66	0.64	0.63	0.63	0.62	0.61	0.61	0.60	0.60	0.59	0.59	0.59	0.58
12	1.35	1.08	0.97	0.90	0.86	0.81	0.78	0.75	0.74	0.72	0.71	0.71	0.70	0.69	0.69	0.68	0.68	0.68	0.67	0.67
16	1.46	1.17	1.04	0.98	0.93	0.87	0.84	0.82	0.80	0.78	0.78	0.77	0.76	0.75	0.75	0.74	0.74	0.74	0.73	0.73
20	1.55	1.23	1.10	1.03	0.98	0.93	0.89	0.86	0.84	0.83	0.82	0.81	0.81	0.80	0.79	0.79	0.78	0.78	0.77	0.77
30	1.70	1.35	1.21	1.13	1.08	1.02	0.98	0.95	0.93	0.91	0.90	0.89	0.89	0.88	0.87	0.86	0.86	0.86	0.85	0.85
40	1.81	1.44	1.29	1.20	1.15	1.08	1.04	1.01	0.99	0.97	0.96	0.95	0.94	0.93	0.92	0.92	0.91	0.91	0.90	0.90
50	1.89	1.50	1.34	1.26	1.20	1.13	1.09	1.05	1.03	1.01	1.00	0.99	0.98	0.97	0.96	0.96	0.95	0.95	0.94	0.94
60	1.95	1.55	1.39	1.30	1.24	1.17	1.12	1.09	1.07	1.05	1.04	1.03	1.02	1.01	1.00	0.99	0.99	0.98	0.98	0.97
75	2.03	1.61	1.44	1.35	1.29	1.21	1.17	1.13	1.11	1.09	1.08	1.07	1.06	1.05	1.04	1.03	1.03	1.02	1.01	1.01
100	2.14	1.69	1.51	1.42	1.35	1.27	1.23	1.19	1.16	1.14	1.13	1.12	1.11	1.10	1.09	1.08	1.08	1.07	1.06	1.06
125	2.21	1.75	1.57	1.47	1.40	1.32	1.27	1.23	1.20	1.18	1.17	1.16	1.15	1.14	1.13	1.12	1.11	1.11	1.10	1.09
150	2.28	1.80	1.61	1.51	1.44	1.35	1.30	1.26	1.24	1.22	1.20	1.19	1.18	1.17	1.16	1.15	1.14	1.14	1.13	1.12
175	*2.33*	1.84	1.65	1.54	1.47	1.38	1.33	1.29	1.26	1.24	1.23	1.22	1.21	1.19	1.18	1.17	1.17	1.16	1.15	1.15
200	2.37	1.88	1.68	1.57	1.50	1.41	1.36	1.32	1.29	1.27	1.25	1.24	1.23	1.22	1.20	1.20	1.19	1.19	1.18	1.17

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Table 19-3. κ-Multipliers for 1-of-4 Interwell Prediction Limits on Observations (1 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	0.64	0.50	0.44	0.40	0.37	0.34	0.32	0.31	0.30	0.29	0.29	0.28	0.28	0.27	0.27	0.27	0.27	0.26	0.26	0.26
2	0.92	0.73	0.65	0.60	0.57	0.53	0.51	0.49	0.48	0.47	0.46	0.46	0.45	0.45	0.44	0.44	0.44	0.44	0.43	0.43
3	1.08	0.86	0.77	0.72	0.68	0.64	0.61	0.59	0.58	0.57	0.56	0.55	0.55	0.54	0.54	0.53	0.53	0.53	0.52	0.52
4	1.19	0.95	0.85	0.79	0.76	0.71	0.68	0.66	0.64	0.63	0.63	0.62	0.61	0.61	0.60	0.60	0.59	0.59	0.59	0.58
5	1.28	1.02	0.91	0.85	0.81	0.76	0.73	0.71	0.69	0.68	0.67	0.67	0.66	0.66	0.65	0.65	0.64	0.64	0.63	0.63
8	1.46	1.17	1.04	0.98	0.93	0.87	0.84	0.82	0.80	0.78	0.78	0.77	0.76	0.75	0.75	0.74	0.74	0.74	0.73	0.73
12	1.62	1.29	1.15	1.08	1.03	0.97	0.93	0.90	0.88	0.87	0.86	0.85	0.84	0.83	0.83	0.82	0.82	0.81	0.81	0.80
16	1.72	1.37	1.23	1.15	1.10	1.03	0.99	0.96	0.94	0.93	0.92	0.91	0.90	0.89	0.88	0.88	0.87	0.87	0.86	0.86
20	1.81	1.44	1.29	1.20	1.15	1.08	1.04	1.01	0.99	0.97	0.96	0.95	0.94	0.93	0.92	0.92	0.91	0.91	0.90	0.90
30	1.95	1.55	1.39	1.30	1.24	1.17	1.12	1.09	1.07	1.05	1.04	1.03	1.02	1.01	1.00	0.99	0.99	0.98	0.98	0.97
40	2.06	1.63	1.46	1.36	1.30	1.23	1.18	1.14	1.12	1.10	1.09	1.08	1.07	1.06	1.05	1.04	1.04	1.03	1.02	1.02
50	2.14	1.69	1.51	1.42	1.35	1.27	1.23	1.19	1.16	1.14	1.13	1.12	1.11	1.10	1.09	1.08	1.08	1.07	1.06	1.06
60	2.20	1.74	1.56	1.46	1.39	1.31	1.26	1.22	1.20	1.18	1.16	1.15	1.14	1.13	1.12	1.11	1.11	1.10	1.09	1.09
75	2.28	1.80	1.61	1.51	1.44	1.35	1.30	1.26	1.24	1.22	1.20	1.19	1.18	1.17	1.16	1.15	1.14	1.14	1.13	1.12
100	2.37	1.88	1.68	1.57	1.50	1.41	1.36	1.32	1.29	1.27	1.25	1.24	1.23	1.22	1.20	1.20	1.19	1.19	1.18	1.17
125	2.45	1.94	1.73	1.62	1.54	1.45	1.40	1.36	1.33	1.31	1.29	1.28	1.27	1.25	1.24	1.23	1.23	1.22	1.21	1.20
150	2.51	1.98	1.77	1.66	1.58	1.49	1.43	1.39	1.36	1.34	1.32	1.31	1.30	1.28	1.27	1.26	1.26	1.25	1.24	1.23
175	2.56	2.02	1.81	1.69	1.61	1.52	1.46	1.42	1.39	1.36	1.35	1.33	1.32	1.31	1.30	1.29	1.28	1.27	1.26	1.26
200	2.60	2.06	1.84	1.72	1.64	1.54	1.49	1.44	1.41	1.39	1.37	1.36	1.34	1.33	1.32	1.31	1.30	1.29	1.28	1.28

Table 19-3. κ-Multipliers for 1-of-4 Interwell Prediction Limits on Observations (2 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	0.39	0.28	0.22	0.19	0.17	0.14	0.12	0.11	0.10	0.10	0.09	0.09	0.09	0.08	0.08	0.08	0.07	0.07	0.07	0.07
2	0.70	0.53	0.46	0.41	0.39	0.35	0.33	0.31	0.30	0.30	0.29	0.29	0.28	0.28	0.27	0.27	0.27	0.27	0.26	0.26
3	0.88	0.67	0.59	0.54	0.50	0.47	0.44	0.42	0.41	0.40	0.40	0.39	0.39	0.38	0.38	0.37	0.37	0.37	0.36	0.36
4	1.01	0.78	0.68	0.62	0.59	0.54	0.52	0.50	0.48	0.47	0.47	0.46	0.46	0.45	0.45	0.44	0.44	0.44	0.43	0.43
5	1.12	0.85	0.75	0.69	0.65	0.60	0.58	0.55	0.54	0.53	0.52	0.52	0.51	0.50	0.50	0.49	0.49	0.49	0.48	0.48
8	1.33	1.02	0.89	0.82	0.78	0.72	0.69	0.67	0.65	0.64	0.63	0.62	0.62	0.61	0.60	0.60	0.60	0.59	0.59	0.59
12	1.52	1.16	1.01	0.93	0.88	0.82	0.79	0.76	0.74	0.73	0.72	0.71	0.71	0.70	0.69	0.69	0.68	0.68	0.67	0.67
16	1.66	1.26	1.10	1.01	0.96	0.89	0.86	0.83	0.81	0.79	0.78	0.77	0.77	0.76	0.75	0.74	0.74	0.74	0.73	0.73
20	1.76	1.33	1.16	1.07	1.02	0.95	0.91	0.87	0.85	0.84	0.83	0.82	0.81	0.80	0.79	0.79	0.78	0.78	0.77	0.77
30	1.95	1.47	1.28	1.18	1.12	1.04	1.00	0.96	0.94	0.92	0.91	0.90	0.89	0.88	0.87	0.87	0.86	0.86	0.85	0.85
40	*2.09*	1.56	1.36	1.26	1.19	1.11	1.06	1.02	1.00	0.98	0.97	0.96	0.95	0.94	0.93	0.92	0.92	0.91	0.90	0.90
50	2.19	1.64	1.43	1.31	1.24	1.16	1.11	1.07	1.04	1.02	1.01	1.00	0.99	0.98	0.97	0.96	0.96	0.95	0.95	0.94
60	2.27	1.70	1.48	1.36	1.29	1.20	1.15	1.11	1.08	1.06	1.04	1.03	1.02	1.01	1.00	1.00	0.99	0.99	0.98	0.97
75	2.37	1.77	1.54	1.42	1.34	1.25	1.19	1.15	1.12	1.10	1.09	1.08	1.07	1.05	1.04	1.03	1.03	1.02	1.02	1.01
100	2.50	1.86	1.62	1.49	1.41	1.31	1.25	1.21	1.18	1.16	1.14	1.13	1.12	1.10	1.09	1.08	1.08	1.07	1.07	1.06
125	2.60	1.93	1.68	1.54	1.46	1.36	1.30	1.25	1.22	1.20	1.18	1.17	1.16	1.14	1.13	1.12	1.12	1.11	1.10	1.10
150	2.68	1.99	1.73	1.59	1.50	1.40	1.33	1.29	1.25	1.23	1.21	1.20	1.19	1.17	1.16	1.15	1.15	1.14	1.13	1.13
175	2.75	*2.04*	1.77	1.63	1.54	1.43	1.37	1.32	1.28	1.26	1.24	1.23	1.22	1.20	1.19	1.18	1.17	1.17	1.16	1.15
200	2.81	*2.08*	1.81	1.66	1.57	1.46	1.39	1.34	1.31	1.28	1.26	1.25	1.24	1.22	1.21	1.20	1.19	1.19	1.18	1.17

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Table 19-3. κ-Multipliers for 1-of-4 Interwell Prediction Limits on Observations (2 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	0.70	0.53	0.46	0.41	0.39	0.35	0.33	0.31	0.30	0.30	0.29	0.29	0.28	0.28	0.27	0.27	0.27	0.27	0.26	0.26
2	1.01	0.78	0.68	0.62	0.59	0.54	0.52	0.50	0.48	0.47	0.47	0.46	0.46	0.45	0.45	0.44	0.44	0.44	0.43	0.43
3	1.20	0.92	0.80	0.74	0.70	0.65	0.62	0.60	0.58	0.57	0.56	0.56	0.55	0.55	0.54	0.54	0.53	0.53	0.53	0.52
4	1.33	1.02	0.89	0.82	0.78	0.72	0.69	0.67	0.65	0.64	0.63	0.62	0.62	0.61	0.60	0.60	0.60	0.59	0.59	0.59
5	1.44	1.10	0.96	0.88	0.84	0.78	0.75	0.72	0.70	0.69	0.68	0.67	0.67	0.66	0.65	0.65	0.64	0.64	0.64	0.63
8	1.66	1.26	1.10	1.01	0.96	0.89	0.86	0.83	0.81	0.79	0.78	0.77	0.77	0.76	0.75	0.74	0.74	0.74	0.73	0.73
12	1.85	1.39	1.22	1.12	1.06	0.99	0.95	0.91	0.89	0.88	0.86	0.86	0.85	0.84	0.83	0.82	0.82	0.82	0.81	0.81
16	1.98	1.49	1.30	1.20	1.13	1.06	1.01	0.98	0.95	0.94	0.92	0.91	0.91	0.89	0.89	0.88	0.87	0.87	0.86	0.86
20	2.09	1.56	1.36	1.26	1.19	1.11	1.06	1.02	1.00	0.98	0.97	0.96	0.95	0.94	0.93	0.92	0.92	0.91	0.90	0.90
30	2.27	1.70	1.48	1.36	1.29	1.20	1.15	1.11	1.08	1.06	1.04	1.03	1.02	1.01	1.00	1.00	0.99	0.99	0.98	0.97
40	2.40	1.79	1.56	1.43	1.36	1.26	1.21	1.16	1.13	1.11	1.10	1.09	1.08	1.06	1.05	1.05	1.04	1.04	1.03	1.02
50	2.50	1.86	1.62	1.49	1.41	1.31	1.25	1.21	1.18	1.16	1.14	1.13	1.12	1.10	1.09	1.08	1.08	1.07	1.07	1.06
60	2.59	1.92	1.67	1.53	1.45	1.35	1.29	1.24	1.21	1.19	1.17	1.16	1.15	1.14	1.12	1.12	1.11	1.10	1.10	1.09
75	2.68	1.99	1.73	1.59	1.50	1.40	1.33	1.29	1.25	1.23	1.21	1.20	1.19	1.17	1.16	1.15	1.15	1.14	1.13	1.13
100	2.81	2.08	1.81	1.66	1.57	1.46	1.39	1.34	1.31	1.28	1.26	1.25	1.24	1.22	1.21	1.20	1.19	1.19	1.18	1.17
125	2.91	2.15	1.86	1.71	1.62	1.50	1.44	1.38	1.35	1.32	1.30	1.29	1.28	1.26	1.25	1.24	1.23	1.22	1.21	1.21
150	2.99	2.20	1.91	1.76	1.66	1.54	1.47	1.42	1.38	1.35	1.34	1.32	1.31	1.29	1.28	1.27	1.26	1.25	1.24	1.24
175	3.05	2.25	1.95	1.79	1.69	1.57	1.50	1.44	1.41	1.38	1.36	1.35	1.33	1.32	1.30	1.29	1.28	1.28	1.27	1.26
200	3.11	*2.29*	1.98	1.82	1.72	1.60	1.53	1.47	1.43	1.40	1.38	1.37	1.36	1.34	1.32	1.31	1.31	1.30	1.29	1.28

Table 19-3. κ-Multipliers for 1-of-4 Interwell Prediction Limits on Observations (2 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	1.01	0.78	0.68	0.62	0.59	0.54	0.52	0.50	0.48	0.47	0.47	0.46	0.46	0.45	0.45	0.44	0.44	0.44	0.43	0.43
2	1.33	1.02	0.89	0.82	0.78	0.72	0.69	0.67	0.65	0.64	0.63	0.62	0.62	0.61	0.60	0.60	0.60	0.59	0.59	0.59
3	1.52	1.16	1.01	0.93	0.88	0.82	0.79	0.76	0.74	0.73	0.72	0.71	0.71	0.70	0.69	0.69	0.68	0.68	0.67	0.67
4	1.66	1.26	1.10	1.01	0.96	0.89	0.86	0.83	0.81	0.79	0.78	0.77	0.77	0.76	0.75	0.74	0.74	0.74	0.73	0.73
5	1.76	1.33	1.16	1.07	1.02	0.95	0.91	0.87	0.85	0.84	0.83	0.82	0.81	0.80	0.79	0.79	0.78	0.78	0.77	0.77
8	1.98	1.49	1.30	1.20	1.13	1.06	1.01	0.98	0.95	0.94	0.92	0.91	0.91	0.89	0.89	0.88	0.87	0.87	0.86	0.86
12	2.17	1.62	1.42	1.30	1.23	1.15	1.10	1.06	1.03	1.02	1.00	0.99	0.98	0.97	0.96	0.95	0.95	0.95	0.94	0.93
16	2.30	1.72	1.50	1.38	1.30	1.21	1.16	1.12	1.09	1.07	1.06	1.05	1.04	1.02	1.01	1.01	1.00	1.00	0.99	0.98
20	2.40	1.79	1.56	1.43	1.36	1.26	1.21	1.16	1.13	1.11	1.10	1.09	1.08	1.06	1.05	1.05	1.04	1.04	1.03	1.02
30	2.59	1.92	1.67	1.53	1.45	1.35	1.29	1.24	1.21	1.19	1.17	1.16	1.15	1.14	1.12	1.12	1.11	1.10	1.10	1.09
40	2.71	2.01	1.75	1.61	1.52	1.41	1.35	1.30	1.27	1.24	1.23	1.21	1.20	1.18	1.17	1.16	1.16	1.15	1.14	1.14
50	2.81	2.08	1.81	1.66	1.57	1.46	1.39	1.34	1.31	1.28	1.26	1.25	1.24	1.22	1.21	1.20	1.19	1.19	1.18	1.17
60	2.89	2.13	1.85	1.70	1.61	1.49	1.43	1.37	1.34	1.32	1.30	1.28	1.27	1.25	1.24	1.23	1.22	1.22	1.21	1.20
75	2.99	2.20	1.91	1.76	1.66	1.54	1.47	1.42	1.38	1.35	1.34	1.32	1.31	1.29	1.28	1.27	1.26	1.25	1.24	1.24
100	3.11	2.29	1.98	1.82	1.72	1.60	1.53	1.47	1.43	1.40	1.38	1.37	1.36	1.34	1.32	1.31	1.31	1.30	1.29	1.28
125	3.20	2.35	2.04	1.87	1.77	1.64	1.57	1.51	1.47	1.44	1.42	1.41	1.39	1.37	1.36	1.35	1.34	1.33	1.32	1.31
150	3.28	2.41	2.09	1.92	1.81	1.68	1.60	1.54	1.50	1.47	1.45	1.44	1.42	1.40	1.39	1.38	1.37	1.36	1.35	1.34
175	3.34	2.45	2.13	1.95	1.84	1.71	1.63	1.57	1.53	1.50	1.48	1.46	1.45	1.43	1.41	1.40	1.39	1.38	1.37	1.36
200	3.39	2.49	2.16	1.98	1.87	1.74	1.66	1.59	1.55	1.52	1.50	1.48	1.47	1.45	1.43	1.42	1.41	1.40	1.39	1.38

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Table 19-3. κ-Multipliers for 1-of-4 Interwell Prediction Limits on Observations (5 COC, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	0.85	0.63	0.54	0.49	0.46	0.42	0.40	0.38	0.37	0.36	0.35	0.35	0.34	0.34	0.33	0.33	0.33	0.32	0.32	0.32
2	1.21	0.89	0.77	0.70	0.66	0.61	0.58	0.56	0.54	0.53	0.52	0.52	0.51	0.50	0.50	0.50	0.49	0.49	0.49	0.48
3	1.43	1.04	0.90	0.82	0.77	0.72	0.68	0.66	0.64	0.63	0.62	0.61	0.61	0.60	0.59	0.59	0.58	0.58	0.58	0.57
4	1.59	1.15	0.99	0.91	0.85	0.79	0.75	0.72	0.71	0.69	0.68	0.68	0.67	0.66	0.65	0.65	0.64	0.64	0.64	0.63
5	1.71	1.24	1.06	0.97	0.91	0.85	0.81	0.78	0.76	0.74	0.73	0.72	0.72	0.71	0.70	0.70	0.69	0.69	0.68	0.68
8	1.99	1.42	1.21	1.11	1.04	0.96	0.92	0.88	0.86	0.84	0.83	0.82	0.81	0.80	0.80	0.79	0.79	0.78	0.78	0.77
12	2.24	1.58	1.34	1.22	1.15	1.06	1.01	0.97	0.95	0.93	0.91	0.90	0.90	0.88	0.88	0.87	0.86	0.86	0.85	0.85
16	2.41	1.69	1.43	1.30	1.22	1.13	1.07	1.03	1.00	0.99	0.97	0.96	0.95	0.94	0.93	0.92	0.92	0.91	0.91	0.90
20	2.55	1.77	1.50	1.36	1.28	1.18	1.12	1.08	1.05	1.03	1.02	1.00	0.99	0.98	0.97	0.96	0.96	0.95	0.95	0.94
30	2.80	1.93	1.63	1.48	1.38	1.27	1.21	1.16	1.13	1.11	1.09	1.08	1.07	1.06	1.04	1.04	1.03	1.03	1.02	1.01
40	2.97	*2.04*	1.72	1.56	1.46	1.34	1.27	1.22	1.19	1.16	1.15	1.13	1.12	1.11	1.10	1.09	1.08	1.08	1.07	1.06
50	3.11	*2.13*	1.79	1.62	1.51	1.39	1.32	1.27	1.23	1.21	1.19	1.17	1.16	1.15	1.13	1.13	1.12	1.11	1.10	1.10
60	3.22	2.20	1.85	1.67	1.56	1.43	1.36	1.30	1.27	1.24	1.22	1.21	1.20	1.18	1.17	1.16	1.15	1.14	1.13	1.13
75	3.36	2.28	1.91	1.73	1.61	1.48	1.40	1.35	1.31	1.28	1.26	1.25	1.23	1.22	1.20	1.19	1.19	1.18	1.17	1.16
100	3.53	2.39	*2.00*	1.80	1.68	1.54	1.46	1.40	1.36	1.33	1.31	1.30	1.28	1.26	1.25	1.24	1.23	1.23	1.22	1.21
125	3.67	2.47	*2.07*	1.86	1.74	1.59	1.51	1.44	1.40	1.37	1.35	1.33	1.32	1.30	1.29	1.28	1.27	1.26	1.25	1.24
150	3.77	2.54	*2.12*	1.91	1.78	1.63	1.55	1.48	1.44	1.41	1.38	1.37	1.35	1.33	1.32	1.31	1.30	1.29	1.28	1.27
175	3.86	2.60	*2.17*	1.95	1.82	1.66	1.58	1.51	1.46	1.43	1.41	1.39	1.38	1.36	1.34	1.33	1.32	1.32	1.30	1.30
200	3.94	2.65	2.21	*1.99*	1.85	1.69	1.60	1.53	1.49	1.46	1.43	1.41	1.40	1.38	1.36	1.35	1.34	1.34	1.32	1.32

Table 19-3. κ-Multipliers for 1-of-4 Interwell Prediction Limits on Observations (5 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	1.21	0.89	0.77	0.70	0.66	0.61	0.58	0.56	0.54	0.53	0.52	0.52	0.51	0.50	0.50	0.50	0.49	0.49	0.49	0.48
2	1.59	1.15	0.99	0.91	0.85	0.79	0.75	0.72	0.71	0.69	0.68	0.68	0.67	0.66	0.65	0.65	0.64	0.64	0.64	0.63
3	1.82	1.31	1.12	1.02	0.96	0.89	0.85	0.82	0.80	0.78	0.77	0.76	0.76	0.75	0.74	0.73	0.73	0.73	0.72	0.72
4	1.99	1.42	1.21	1.11	1.04	0.96	0.92	0.88	0.86	0.84	0.83	0.82	0.81	0.80	0.80	0.79	0.79	0.78	0.78	0.77
5	2.13	1.50	1.28	1.17	1.10	1.02	0.97	0.93	0.91	0.89	0.88	0.87	0.86	0.85	0.84	0.83	0.83	0.83	0.82	0.81
8	2.41	1.69	1.43	1.30	1.22	1.13	1.07	1.03	1.00	0.99	0.97	0.96	0.95	0.94	0.93	0.92	0.92	0.91	0.91	0.90
12	2.66	1.84	1.56	1.41	1.33	1.22	1.16	1.12	1.09	1.07	1.05	1.04	1.03	1.01	1.00	1.00	0.99	0.99	0.98	0.97
16	2.84	1.95	1.65	1.49	1.40	1.29	1.22	1.18	1.14	1.12	1.11	1.09	1.08	1.07	1.06	1.05	1.04	1.04	1.03	1.02
20	2.97	2.04	1.72	1.56	1.46	1.34	1.27	1.22	1.19	1.16	1.15	1.13	1.12	1.11	1.10	1.09	1.08	1.08	1.07	1.06
30	3.22	2.20	1.85	1.67	1.56	1.43	1.36	1.30	1.27	1.24	1.22	1.21	1.20	1.18	1.17	1.16	1.15	1.14	1.13	1.13
40	3.40	*2.30*	1.93	1.74	1.63	1.49	1.42	1.36	1.32	1.29	1.27	1.26	1.25	1.23	1.21	1.20	1.20	1.19	1.18	1.17
50	3.53	*2.39*	2.00	1.80	1.68	1.54	1.46	1.40	1.36	1.33	1.31	1.30	1.28	1.26	1.25	1.24	1.23	1.23	1.22	1.21
60	3.64	2.46	2.06	1.85	1.73	1.58	1.50	1.44	1.40	1.37	1.34	1.33	1.31	1.30	1.28	1.27	1.26	1.26	1.24	1.24
75	3.77	2.54	2.12	1.91	1.78	1.63	1.55	1.48	1.44	1.41	1.38	1.37	1.35	1.33	1.32	1.31	1.30	1.29	1.28	1.27
100	3.94	2.65	2.21	1.99	1.85	1.69	1.60	1.53	1.49	1.46	1.43	1.41	1.40	1.38	1.36	1.35	1.34	1.34	1.32	1.32
125	4.07	2.73	*2.27*	2.04	1.90	1.74	1.65	1.58	1.53	1.50	1.47	1.45	1.44	1.41	1.40	1.39	1.38	1.37	1.36	1.35
150	4.18	2.79	*2.33*	2.09	1.95	1.78	1.68	1.61	1.56	1.53	1.50	1.48	1.47	1.44	1.43	1.41	1.41	1.40	1.38	1.38
175	4.27	2.85	*2.37*	2.13	1.98	1.81	1.71	1.64	1.59	1.55	1.53	1.51	1.49	1.47	1.45	1.44	1.43	1.42	1.41	1.40
200	4.34	2.90	*2.41*	2.17	2.02	1.84	1.74	1.66	1.61	1.58	1.55	1.53	1.51	1.49	1.47	1.46	1.45	1.44	1.43	1.42

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Table 19-3. κ-Multipliers for 1-of-4 Interwell Prediction Limits on Observations (5 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.59**	**1.15**	**0.99**	**0.91**	**0.85**	**0.79**	**0.75**	**0.72**	**0.71**	**0.69**	**0.68**	**0.68**	**0.67**	**0.66**	**0.65**	**0.65**	**0.64**	**0.64**	**0.64**	**0.63**
2	**1.99**	**1.42**	**1.21**	**1.11**	**1.04**	**0.96**	**0.92**	**0.88**	**0.86**	**0.84**	**0.83**	**0.82**	**0.81**	**0.80**	**0.80**	**0.79**	**0.79**	**0.78**	**0.78**	**0.77**
3	**2.24**	**1.58**	**1.34**	**1.22**	**1.15**	**1.06**	**1.01**	**0.97**	**0.95**	**0.93**	**0.91**	**0.90**	**0.90**	**0.88**	**0.88**	**0.87**	**0.86**	**0.86**	**0.85**	**0.85**
4	**2.41**	**1.69**	**1.43**	**1.30**	**1.22**	**1.13**	**1.07**	**1.03**	**1.00**	**0.99**	**0.97**	**0.96**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.91**	**0.90**
5	**2.55**	**1.77**	**1.50**	**1.36**	**1.28**	**1.18**	**1.12**	**1.08**	**1.05**	**1.03**	**1.02**	**1.00**	**0.99**	**0.98**	**0.97**	**0.96**	**0.96**	**0.95**	**0.95**	**0.94**
8	2.84	**1.95**	**1.65**	**1.49**	**1.40**	**1.29**	**1.22**	**1.18**	**1.14**	**1.12**	**1.11**	**1.09**	**1.08**	**1.07**	**1.06**	**1.05**	**1.04**	**1.04**	**1.03**	**1.02**
12	3.09	**2.11**	**1.78**	**1.61**	**1.50**	**1.38**	**1.31**	**1.26**	**1.22**	**1.20**	**1.18**	**1.17**	**1.16**	**1.14**	**1.13**	**1.12**	**1.11**	**1.11**	**1.10**	**1.09**
16	3.26	**2.22**	**1.87**	**1.68**	**1.57**	**1.44**	**1.37**	**1.31**	**1.28**	**1.25**	**1.23**	**1.22**	**1.21**	**1.19**	**1.18**	**1.17**	**1.16**	**1.15**	**1.14**	**1.14**
20	3.40	**2.30**	**1.93**	**1.74**	**1.63**	**1.49**	**1.42**	**1.36**	**1.32**	**1.29**	**1.27**	**1.26**	**1.25**	**1.23**	**1.21**	**1.20**	**1.20**	**1.19**	**1.18**	**1.17**
30	3.64	**2.46**	**2.06**	**1.85**	**1.73**	**1.58**	**1.50**	**1.44**	**1.40**	**1.37**	**1.34**	**1.33**	**1.31**	**1.30**	**1.28**	**1.27**	**1.26**	**1.26**	**1.24**	**1.24**
40	3.81	**2.56**	**2.14**	**1.93**	**1.80**	**1.65**	**1.56**	**1.49**	**1.45**	**1.42**	**1.39**	**1.38**	**1.36**	**1.34**	**1.33**	**1.32**	**1.31**	**1.30**	**1.29**	**1.28**
50	3.94	*2.65*	**2.21**	**1.99**	**1.85**	**1.69**	**1.60**	**1.53**	**1.49**	**1.46**	**1.43**	**1.41**	**1.40**	**1.38**	**1.36**	**1.35**	**1.34**	**1.34**	**1.32**	**1.32**
60	4.05	2.71	**2.26**	**2.03**	**1.89**	**1.73**	**1.64**	**1.57**	**1.52**	**1.49**	**1.46**	**1.45**	**1.43**	**1.41**	**1.39**	**1.38**	**1.37**	**1.36**	**1.35**	**1.34**
75	4.18	2.79	**2.33**	**2.09**	**1.95**	**1.78**	**1.68**	**1.61**	**1.56**	**1.53**	**1.50**	**1.48**	**1.47**	**1.44**	**1.43**	**1.41**	**1.41**	**1.40**	**1.38**	**1.38**
100	4.34	2.90	**2.41**	**2.17**	**2.02**	**1.84**	**1.74**	**1.66**	**1.61**	**1.58**	**1.55**	**1.53**	**1.51**	**1.49**	**1.47**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**
125	4.47	2.97	**2.48**	**2.22**	**2.07**	**1.89**	**1.78**	**1.70**	**1.65**	**1.61**	**1.59**	**1.57**	**1.55**	**1.52**	**1.51**	**1.49**	**1.48**	**1.47**	**1.46**	**1.45**
150	4.57	3.04	**2.53**	**2.27**	**2.11**	**1.92**	**1.82**	**1.74**	**1.68**	**1.64**	**1.62**	**1.59**	**1.58**	**1.55**	**1.53**	**1.52**	**1.51**	**1.50**	**1.49**	**1.48**
175	4.66	3.09	*2.57*	**2.31**	**2.14**	**1.96**	**1.85**	**1.76**	**1.71**	**1.67**	**1.64**	**1.62**	**1.60**	**1.57**	**1.56**	**1.54**	**1.53**	**1.52**	**1.51**	**1.50**
200	4.73	3.14	*2.61*	**2.34**	**2.17**	**1.98**	**1.87**	**1.79**	**1.73**	**1.69**	**1.66**	**1.64**	**1.62**	**1.60**	**1.58**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**

Table 19-3. κ-Multipliers for 1-of-4 Interwell Prediction Limits on Observations (10 COC, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.24**	**0.91**	**0.78**	**0.71**	**0.67**	**0.61**	**0.58**	**0.56**	**0.54**	**0.53**	**0.52**	**0.52**	**0.51**	**0.51**	**0.50**	**0.50**	**0.49**	**0.49**	**0.49**	**0.48**
2	**1.66**	**1.18**	**1.01**	**0.91**	**0.86**	**0.79**	**0.76**	**0.73**	**0.71**	**0.69**	**0.68**	**0.68**	**0.67**	**0.66**	**0.65**	**0.65**	**0.65**	**0.64**	**0.64**	**0.63**
3	**1.92**	**1.34**	**1.14**	**1.03**	**0.97**	**0.90**	**0.85**	**0.82**	**0.80**	**0.78**	**0.77**	**0.76**	**0.76**	**0.75**	**0.74**	**0.73**	**0.73**	**0.73**	**0.72**	**0.72**
4	2.11	**1.46**	**1.23**	**1.12**	**1.05**	**0.97**	**0.92**	**0.88**	**0.86**	**0.84**	**0.83**	**0.82**	**0.82**	**0.80**	**0.80**	**0.79**	**0.79**	**0.78**	**0.78**	**0.77**
5	2.27	**1.55**	**1.31**	**1.18**	**1.11**	**1.02**	**0.97**	**0.93**	**0.91**	**0.89**	**0.88**	**0.87**	**0.86**	**0.85**	**0.84**	**0.83**	**0.83**	**0.83**	**0.82**	**0.81**
8	2.61	**1.75**	**1.46**	**1.32**	**1.23**	**1.13**	**1.08**	**1.04**	**1.01**	**0.99**	**0.97**	**0.96**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.91**	**0.90**
12	2.91	**1.92**	**1.60**	**1.44**	**1.34**	**1.23**	**1.17**	**1.12**	**1.09**	**1.07**	**1.05**	**1.04**	**1.03**	**1.02**	**1.01**	**1.00**	**0.99**	**0.99**	**0.98**	**0.97**
16	3.13	*2.05*	**1.70**	**1.52**	**1.42**	**1.30**	**1.23**	**1.18**	**1.15**	**1.12**	**1.11**	**1.09**	**1.08**	**1.07**	**1.06**	**1.05**	**1.04**	**1.04**	**1.03**	**1.02**
20	3.30	*2.14*	**1.77**	**1.59**	**1.48**	**1.35**	**1.28**	**1.23**	**1.19**	**1.17**	**1.15**	**1.14**	**1.12**	**1.11**	**1.10**	**1.09**	**1.08**	**1.08**	**1.07**	**1.06**
30	3.61	2.32	**1.91**	**1.70**	**1.58**	**1.44**	**1.37**	**1.31**	**1.27**	**1.24**	**1.22**	**1.21**	**1.20**	**1.18**	**1.17**	**1.16**	**1.15**	**1.14**	**1.13**	**1.13**
40	3.83	2.44	*2.00*	**1.79**	**1.66**	**1.51**	**1.43**	**1.37**	**1.32**	**1.30**	**1.28**	**1.26**	**1.25**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**
50	4.00	2.54	*2.08*	**1.85**	**1.72**	**1.56**	**1.47**	**1.41**	**1.37**	**1.34**	**1.32**	**1.30**	**1.29**	**1.27**	**1.25**	**1.24**	**1.23**	**1.23**	**1.22**	**1.21**
60	4.14	2.62	*2.14*	**1.90**	**1.76**	**1.60**	**1.51**	**1.44**	**1.40**	**1.37**	**1.35**	**1.33**	**1.32**	**1.30**	**1.28**	**1.27**	**1.26**	**1.26**	**1.25**	**1.24**
75	4.31	2.71	2.21	*1.97*	**1.82**	**1.65**	**1.56**	**1.49**	**1.44**	**1.41**	**1.39**	**1.37**	**1.35**	**1.33**	**1.32**	**1.31**	**1.30**	**1.29**	**1.28**	**1.27**
100	4.52	2.84	2.31	*2.05*	**1.89**	**1.72**	**1.62**	**1.54**	**1.50**	**1.46**	**1.44**	**1.42**	**1.40**	**1.38**	**1.37**	**1.35**	**1.34**	**1.34**	**1.32**	**1.32**
125	4.69	2.93	2.38	*2.11*	**1.95**	**1.77**	**1.66**	**1.59**	**1.54**	**1.50**	**1.48**	**1.46**	**1.44**	**1.42**	**1.40**	**1.39**	**1.38**	**1.37**	**1.36**	**1.35**
150	4.83	3.01	2.44	*2.16*	*2.00*	**1.81**	**1.70**	**1.62**	**1.57**	**1.53**	**1.51**	**1.49**	**1.47**	**1.45**	**1.43**	**1.42**	**1.41**	**1.40**	**1.39**	**1.38**
175	4.94	3.07	2.49	*2.21*	*2.04*	**1.84**	**1.73**	**1.65**	**1.60**	**1.56**	**1.53**	**1.51**	**1.49**	**1.47**	**1.45**	**1.44**	**1.43**	**1.42**	**1.41**	**1.40**
200	5.04	3.13	2.54	2.24	*2.07*	**1.87**	**1.76**	**1.68**	**1.62**	**1.58**	**1.55**	**1.53**	**1.52**	**1.49**	**1.47**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**

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Table 19-3. κ-Multipliers for 1-of-4 Interwell Prediction Limits on Observations (10 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.66**	**1.18**	**1.01**	**0.91**	**0.86**	**0.79**	**0.76**	**0.73**	**0.71**	**0.69**	**0.68**	**0.68**	**0.67**	**0.66**	**0.65**	**0.65**	**0.65**	**0.64**	**0.64**	**0.63**
2	**2.11**	**1.46**	**1.23**	**1.12**	**1.05**	**0.97**	**0.92**	**0.88**	**0.86**	**0.84**	**0.83**	**0.82**	**0.82**	**0.80**	**0.80**	**0.79**	**0.79**	**0.78**	**0.78**	**0.77**
3	2.40	**1.63**	**1.37**	**1.24**	**1.16**	**1.07**	**1.01**	**0.97**	**0.95**	**0.93**	**0.92**	**0.91**	**0.90**	**0.89**	**0.88**	**0.87**	**0.86**	**0.86**	**0.85**	**0.85**
4	2.61	**1.75**	**1.46**	**1.32**	**1.23**	**1.13**	**1.08**	**1.04**	**1.01**	**0.99**	**0.97**	**0.96**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.91**	**0.90**
5	2.77	**1.84**	**1.54**	**1.39**	**1.29**	**1.19**	**1.13**	**1.08**	**1.05**	**1.03**	**1.02**	**1.01**	**1.00**	**0.98**	**0.97**	**0.96**	**0.96**	**0.95**	**0.95**	**0.94**
8	3.13	**2.05**	**1.70**	**1.52**	**1.42**	**1.30**	**1.23**	**1.18**	**1.15**	**1.12**	**1.11**	**1.09**	**1.08**	**1.07**	**1.06**	**1.05**	**1.04**	**1.04**	**1.03**	**1.02**
12	3.44	**2.22**	**1.83**	**1.64**	**1.52**	**1.39**	**1.32**	**1.26**	**1.23**	**1.20**	**1.18**	**1.17**	**1.16**	**1.14**	**1.13**	**1.12**	**1.11**	**1.11**	**1.10**	**1.09**
16	3.66	*2.35*	**1.93**	**1.72**	**1.60**	**1.46**	**1.38**	**1.32**	**1.28**	**1.26**	**1.24**	**1.22**	**1.21**	**1.19**	**1.18**	**1.17**	**1.16**	**1.16**	**1.15**	**1.14**
20	3.83	2.44	**2.00**	**1.79**	**1.66**	**1.51**	**1.43**	**1.37**	**1.32**	**1.30**	**1.28**	**1.26**	**1.25**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**
30	4.14	2.62	**2.14**	**1.90**	**1.76**	**1.60**	**1.51**	**1.44**	**1.40**	**1.37**	**1.35**	**1.33**	**1.32**	**1.30**	**1.28**	**1.27**	**1.26**	**1.26**	**1.25**	**1.24**
40	4.36	2.74	**2.24**	**1.99**	**1.84**	**1.67**	**1.57**	**1.50**	**1.45**	**1.42**	**1.40**	**1.38**	**1.37**	**1.34**	**1.33**	**1.32**	**1.31**	**1.30**	**1.29**	**1.28**
50	4.52	2.84	*2.31*	**2.05**	**1.89**	**1.72**	**1.62**	**1.54**	**1.50**	**1.46**	**1.44**	**1.42**	**1.40**	**1.38**	**1.37**	**1.35**	**1.34**	**1.34**	**1.32**	**1.32**
60	4.66	2.92	*2.37*	**2.10**	**1.94**	**1.76**	**1.66**	**1.58**	**1.53**	**1.49**	**1.47**	**1.45**	**1.43**	**1.41**	**1.39**	**1.38**	**1.37**	**1.37**	**1.35**	**1.34**
75	4.83	3.01	*2.44*	**2.16**	**2.00**	**1.81**	**1.70**	**1.62**	**1.57**	**1.53**	**1.51**	**1.49**	**1.47**	**1.45**	**1.43**	**1.42**	**1.41**	**1.40**	**1.39**	**1.38**
100	5.04	3.13	2.54	**2.24**	**2.07**	**1.87**	**1.76**	**1.68**	**1.62**	**1.58**	**1.55**	**1.53**	**1.52**	**1.49**	**1.47**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**
125	5.20	3.22	2.61	*2.31*	**2.13**	**1.92**	**1.80**	**1.72**	**1.66**	**1.62**	**1.59**	**1.57**	**1.55**	**1.53**	**1.51**	**1.49**	**1.48**	**1.47**	**1.46**	**1.45**
150	5.34	3.30	2.67	*2.36*	**2.17**	**1.96**	**1.84**	**1.75**	**1.69**	**1.65**	**1.62**	**1.60**	**1.58**	**1.55**	**1.54**	**1.52**	**1.51**	**1.50**	**1.49**	**1.48**
175	5.45	3.36	2.71	*2.40*	**2.21**	**1.99**	**1.87**	**1.78**	**1.72**	**1.68**	**1.65**	**1.62**	**1.61**	**1.58**	**1.56**	**1.54**	**1.53**	**1.52**	**1.51**	**1.50**
200	5.54	3.42	2.76	*2.43*	**2.24**	**2.02**	**1.90**	**1.80**	**1.74**	**1.70**	**1.67**	**1.65**	**1.63**	**1.60**	**1.58**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**

Table 19-3. κ-Multipliers for 1-of-4 Interwell Prediction Limits on Observations (10 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.11**	**1.46**	**1.23**	**1.12**	**1.05**	**0.97**	**0.92**	**0.88**	**0.86**	**0.84**	**0.83**	**0.82**	**0.82**	**0.80**	**0.80**	**0.79**	**0.79**	**0.78**	**0.78**	**0.77**
2	2.61	**1.75**	**1.46**	**1.32**	**1.23**	**1.13**	**1.08**	**1.04**	**1.01**	**0.99**	**0.97**	**0.96**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.91**	**0.90**
3	2.91	**1.92**	**1.60**	**1.44**	**1.34**	**1.23**	**1.17**	**1.12**	**1.09**	**1.07**	**1.05**	**1.04**	**1.03**	**1.02**	**1.01**	**1.00**	**0.99**	**0.99**	**0.98**	**0.97**
4	3.13	**2.05**	**1.70**	**1.52**	**1.42**	**1.30**	**1.23**	**1.18**	**1.15**	**1.12**	**1.11**	**1.09**	**1.08**	**1.07**	**1.06**	**1.05**	**1.04**	**1.04**	**1.03**	**1.02**
5	3.30	**2.14**	**1.77**	**1.59**	**1.48**	**1.35**	**1.28**	**1.23**	**1.19**	**1.17**	**1.15**	**1.14**	**1.12**	**1.11**	**1.10**	**1.09**	**1.08**	**1.08**	**1.07**	**1.06**
8	3.66	**2.35**	**1.93**	**1.72**	**1.60**	**1.46**	**1.38**	**1.32**	**1.28**	**1.26**	**1.24**	**1.22**	**1.21**	**1.19**	**1.18**	**1.17**	**1.16**	**1.16**	**1.15**	**1.14**
12	3.97	**2.52**	**2.06**	**1.84**	**1.71**	**1.55**	**1.47**	**1.40**	**1.36**	**1.33**	**1.31**	**1.29**	**1.28**	**1.26**	**1.25**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**
16	4.19	*2.65*	**2.16**	**1.92**	**1.78**	**1.62**	**1.53**	**1.46**	**1.41**	**1.38**	**1.36**	**1.34**	**1.33**	**1.31**	**1.29**	**1.28**	**1.27**	**1.27**	**1.26**	**1.25**
20	4.36	2.74	**2.24**	**1.99**	**1.84**	**1.67**	**1.57**	**1.50**	**1.45**	**1.42**	**1.40**	**1.38**	**1.37**	**1.34**	**1.33**	**1.32**	**1.31**	**1.30**	**1.29**	**1.28**
30	4.66	2.92	**2.37**	**2.10**	**1.94**	**1.76**	**1.66**	**1.58**	**1.53**	**1.49**	**1.47**	**1.45**	**1.43**	**1.41**	**1.39**	**1.38**	**1.37**	**1.37**	**1.35**	**1.34**
40	4.88	3.04	**2.46**	**2.18**	**2.01**	**1.82**	**1.71**	**1.63**	**1.58**	**1.54**	**1.52**	**1.50**	**1.48**	**1.46**	**1.44**	**1.43**	**1.42**	**1.41**	**1.39**	**1.39**
50	5.04	3.13	**2.54**	**2.24**	**2.07**	**1.87**	**1.76**	**1.68**	**1.62**	**1.58**	**1.55**	**1.53**	**1.52**	**1.49**	**1.47**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**
60	5.17	3.21	*2.59*	**2.29**	**2.11**	**1.91**	**1.80**	**1.71**	**1.65**	**1.61**	**1.59**	**1.56**	**1.55**	**1.52**	**1.50**	**1.49**	**1.48**	**1.47**	**1.45**	**1.44**
75	5.34	3.30	*2.67*	**2.36**	**2.17**	**1.96**	**1.84**	**1.75**	**1.69**	**1.65**	**1.62**	**1.60**	**1.58**	**1.55**	**1.54**	**1.52**	**1.51**	**1.50**	**1.49**	**1.48**
100	5.54	3.42	*2.76*	**2.43**	**2.24**	**2.02**	**1.90**	**1.80**	**1.74**	**1.70**	**1.67**	**1.65**	**1.63**	**1.60**	**1.58**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**
125	5.70	3.51	2.83	**2.50**	**2.30**	**2.07**	**1.94**	**1.85**	**1.78**	**1.74**	**1.71**	**1.68**	**1.66**	**1.63**	**1.61**	**1.60**	**1.58**	**1.58**	**1.56**	**1.55**
150	5.83	3.58	2.88	**2.54**	**2.34**	**2.11**	**1.98**	**1.88**	**1.81**	**1.77**	**1.74**	**1.71**	**1.69**	**1.66**	**1.64**	**1.62**	**1.61**	**1.60**	**1.58**	**1.57**
175	5.94	3.64	2.93	*2.59*	**2.38**	**2.14**	**2.01**	**1.91**	**1.84**	**1.79**	**1.76**	**1.73**	**1.71**	**1.68**	**1.66**	**1.64**	**1.63**	**1.62**	**1.60**	**1.59**
200	6.03	3.70	2.97	*2.62*	**2.41**	**2.17**	**2.03**	**1.93**	**1.86**	**1.82**	**1.78**	**1.75**	**1.73**	**1.70**	**1.68**	**1.66**	**1.65**	**1.64**	**1.62**	**1.61**

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Table 19-3. κ-Multipliers for 1-of-4 Interwell Prediction Limits on Observations (20 COC, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.70**	**1.19**	**1.01**	**0.92**	**0.86**	**0.80**	**0.76**	**0.73**	**0.71**	**0.69**	**0.68**	**0.68**	**0.67**	**0.66**	**0.65**	**0.65**	**0.65**	**0.64**	**0.64**	**0.63**
2	2.20	**1.48**	**1.25**	**1.13**	**1.05**	**0.97**	**0.92**	**0.89**	**0.86**	**0.85**	**0.83**	**0.82**	**0.82**	**0.81**	**0.80**	**0.79**	**0.79**	**0.78**	**0.78**	**0.77**
3	2.51	**1.66**	**1.38**	**1.25**	**1.16**	**1.07**	**1.02**	**0.98**	**0.95**	**0.93**	**0.92**	**0.91**	**0.90**	**0.89**	**0.88**	**0.87**	**0.86**	**0.86**	**0.85**	**0.85**
4	2.75	**1.79**	**1.48**	**1.33**	**1.24**	**1.14**	**1.08**	**1.04**	**1.01**	**0.99**	**0.97**	**0.96**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.91**	**0.90**
5	2.94	**1.89**	**1.56**	**1.40**	**1.30**	**1.19**	**1.13**	**1.08**	**1.05**	**1.03**	**1.02**	**1.01**	**1.00**	**0.98**	**0.97**	**0.97**	**0.96**	**0.96**	**0.95**	**0.94**
8	3.36	*2.11*	**1.72**	**1.54**	**1.43**	**1.30**	**1.24**	**1.18**	**1.15**	**1.13**	**1.11**	**1.09**	**1.08**	**1.07**	**1.06**	**1.05**	**1.04**	**1.04**	**1.03**	**1.02**
12	3.74	2.30	**1.87**	**1.66**	**1.54**	**1.40**	**1.32**	**1.27**	**1.23**	**1.20**	**1.18**	**1.17**	**1.16**	**1.14**	**1.13**	**1.12**	**1.11**	**1.11**	**1.10**	**1.09**
16	4.01	2.44	*1.97*	**1.75**	**1.62**	**1.47**	**1.39**	**1.32**	**1.28**	**1.26**	**1.24**	**1.22**	**1.21**	**1.19**	**1.18**	**1.17**	**1.16**	**1.16**	**1.15**	**1.14**
20	4.22	2.55	*2.05*	**1.82**	**1.68**	**1.52**	**1.43**	**1.37**	**1.33**	**1.30**	**1.28**	**1.26**	**1.25**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**
30	4.61	2.75	*2.20*	**1.94**	**1.78**	**1.61**	**1.52**	**1.45**	**1.40**	**1.37**	**1.35**	**1.33**	**1.32**	**1.30**	**1.28**	**1.27**	**1.26**	**1.26**	**1.25**	**1.24**
40	4.88	2.89	2.30	*2.03*	**1.86**	**1.68**	**1.58**	**1.51**	**1.46**	**1.42**	**1.40**	**1.38**	**1.37**	**1.35**	**1.33**	**1.32**	**1.31**	**1.30**	**1.29**	**1.28**
50	5.10	3.00	2.39	*2.09*	**1.92**	**1.73**	**1.63**	**1.55**	**1.50**	**1.46**	**1.44**	**1.42**	**1.40**	**1.38**	**1.37**	**1.35**	**1.34**	**1.34**	**1.32**	**1.32**
60	5.27	3.09	2.45	*2.15*	*1.97*	**1.77**	**1.67**	**1.58**	**1.53**	**1.50**	**1.47**	**1.45**	**1.43**	**1.41**	**1.39**	**1.38**	**1.37**	**1.37**	**1.35**	**1.34**
75	5.49	3.20	2.53	*2.22*	*2.03*	**1.82**	**1.71**	**1.63**	**1.57**	**1.54**	**1.51**	**1.49**	**1.47**	**1.45**	**1.43**	**1.42**	**1.41**	**1.40**	**1.39**	**1.38**
100	5.76	3.34	2.64	2.30	*2.11*	**1.89**	**1.77**	**1.68**	**1.63**	**1.59**	**1.56**	**1.54**	**1.52**	**1.49**	**1.47**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**
125	5.97	3.45	2.72	2.37	*2.17*	**1.94**	**1.82**	**1.73**	**1.67**	**1.63**	**1.60**	**1.57**	**1.55**	**1.53**	**1.51**	**1.49**	**1.48**	**1.48**	**1.46**	**1.45**
150	6.14	3.54	2.78	2.42	*2.22*	*1.98*	**1.86**	**1.76**	**1.70**	**1.66**	**1.63**	**1.60**	**1.58**	**1.56**	**1.54**	**1.52**	**1.51**	**1.50**	**1.49**	**1.48**
175	6.28	3.61	2.84	2.47	2.26	*2.02*	**1.89**	**1.79**	**1.73**	**1.68**	**1.65**	**1.63**	**1.61**	**1.58**	**1.56**	**1.54**	**1.53**	**1.52**	**1.51**	**1.50**
200	6.41	3.68	2.88	2.51	2.29	*2.05*	**1.91**	**1.81**	**1.75**	**1.71**	**1.67**	**1.65**	**1.63**	**1.60**	**1.58**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**

Table 19-3. κ-Multipliers for 1-of-4 Interwell Prediction Limits on Observations (20 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.20**	**1.48**	**1.25**	**1.13**	**1.05**	**0.97**	**0.92**	**0.89**	**0.86**	**0.85**	**0.83**	**0.82**	**0.82**	**0.81**	**0.80**	**0.79**	**0.79**	**0.78**	**0.78**	**0.77**
2	2.75	**1.79**	**1.48**	**1.33**	**1.24**	**1.14**	**1.08**	**1.04**	**1.01**	**0.99**	**0.97**	**0.96**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.91**	**0.90**
3	3.11	**1.98**	**1.62**	**1.45**	**1.35**	**1.24**	**1.17**	**1.12**	**1.09**	**1.07**	**1.05**	**1.04**	**1.03**	**1.02**	**1.01**	**1.00**	**0.99**	**0.99**	**0.98**	**0.97**
4	3.36	**2.11**	**1.72**	**1.54**	**1.43**	**1.30**	**1.24**	**1.18**	**1.15**	**1.13**	**1.11**	**1.09**	**1.08**	**1.07**	**1.06**	**1.05**	**1.04**	**1.04**	**1.03**	**1.02**
5	3.57	**2.21**	**1.80**	**1.61**	**1.49**	**1.36**	**1.28**	**1.23**	**1.19**	**1.17**	**1.15**	**1.14**	**1.13**	**1.11**	**1.10**	**1.09**	**1.08**	**1.08**	**1.07**	**1.06**
8	4.01	2.44	**1.97**	**1.75**	**1.62**	**1.47**	**1.39**	**1.32**	**1.28**	**1.26**	**1.24**	**1.22**	**1.21**	**1.19**	**1.18**	**1.17**	**1.16**	**1.16**	**1.15**	**1.14**
12	4.39	2.64	**2.12**	**1.87**	**1.72**	**1.56**	**1.47**	**1.41**	**1.36**	**1.33**	**1.31**	**1.29**	**1.28**	**1.26**	**1.25**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**
16	4.67	2.78	**2.22**	**1.96**	**1.80**	**1.63**	**1.53**	**1.46**	**1.42**	**1.38**	**1.36**	**1.34**	**1.33**	**1.31**	**1.29**	**1.28**	**1.27**	**1.27**	**1.26**	**1.25**
20	4.88	2.89	*2.30*	**2.03**	**1.86**	**1.68**	**1.58**	**1.51**	**1.46**	**1.42**	**1.40**	**1.38**	**1.37**	**1.35**	**1.33**	**1.32**	**1.31**	**1.30**	**1.29**	**1.28**
30	5.27	3.09	*2.45*	**2.15**	**1.97**	**1.77**	**1.67**	**1.58**	**1.53**	**1.50**	**1.47**	**1.45**	**1.43**	**1.41**	**1.39**	**1.38**	**1.37**	**1.37**	**1.35**	**1.34**
40	5.55	3.23	2.56	**2.24**	**2.05**	**1.84**	**1.73**	**1.64**	**1.59**	**1.55**	**1.52**	**1.50**	**1.48**	**1.46**	**1.44**	**1.43**	**1.42**	**1.41**	**1.40**	**1.39**
50	5.76	3.34	2.64	*2.30*	**2.11**	**1.89**	**1.77**	**1.68**	**1.63**	**1.59**	**1.56**	**1.54**	**1.52**	**1.49**	**1.47**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**
60	5.93	3.43	2.70	*2.36*	**2.16**	**1.93**	**1.81**	**1.72**	**1.66**	**1.62**	**1.59**	**1.57**	**1.55**	**1.52**	**1.50**	**1.49**	**1.48**	**1.47**	**1.45**	**1.44**
75	6.14	3.54	2.78	*2.42*	**2.22**	**1.98**	**1.86**	**1.76**	**1.70**	**1.66**	**1.63**	**1.60**	**1.58**	**1.56**	**1.54**	**1.52**	**1.51**	**1.50**	**1.49**	**1.48**
100	6.41	3.68	2.88	*2.51*	*2.29*	**2.05**	**1.91**	**1.81**	**1.75**	**1.71**	**1.67**	**1.65**	**1.63**	**1.60**	**1.58**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**
125	6.61	3.78	2.96	2.58	*2.35*	**2.10**	**1.96**	**1.86**	**1.79**	**1.74**	**1.71**	**1.68**	**1.66**	**1.63**	**1.61**	**1.60**	**1.59**	**1.58**	**1.56**	**1.55**
150	6.78	3.87	3.03	2.63	*2.40*	**2.14**	**2.00**	**1.89**	**1.82**	**1.77**	**1.74**	**1.71**	**1.69**	**1.66**	**1.64**	**1.62**	**1.61**	**1.60**	**1.58**	**1.57**
175	6.92	3.94	3.08	2.68	*2.44*	**2.17**	**2.03**	**1.92**	**1.85**	**1.80**	**1.76**	**1.74**	**1.72**	**1.68**	**1.66**	**1.65**	**1.63**	**1.62**	**1.61**	**1.59**
200	7.04	4.00	3.13	2.71	*2.47*	**2.20**	**2.06**	**1.94**	**1.87**	**1.82**	**1.79**	**1.76**	**1.74**	**1.70**	**1.68**	**1.67**	**1.65**	**1.64**	**1.62**	**1.61**

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Table 19-3. κ-Multipliers for 1-of-4 Interwell Prediction Limits on Observations (20 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	2.75	**1.79**	**1.48**	**1.33**	**1.24**	**1.14**	**1.08**	**1.04**	**1.01**	**0.99**	**0.97**	**0.96**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.91**	**0.90**
2	3.36	**2.11**	**1.72**	**1.54**	**1.43**	**1.30**	**1.24**	**1.18**	**1.15**	**1.13**	**1.11**	**1.09**	**1.08**	**1.07**	**1.06**	**1.05**	**1.04**	**1.04**	**1.03**	**1.02**
3	3.74	**2.30**	**1.87**	**1.66**	**1.54**	**1.40**	**1.32**	**1.27**	**1.23**	**1.20**	**1.18**	**1.17**	**1.16**	**1.14**	**1.13**	**1.12**	**1.11**	**1.11**	**1.10**	**1.09**
4	4.01	**2.44**	**1.97**	**1.75**	**1.62**	**1.47**	**1.39**	**1.32**	**1.28**	**1.26**	**1.24**	**1.22**	**1.21**	**1.19**	**1.18**	**1.17**	**1.16**	**1.16**	**1.15**	**1.14**
5	4.22	**2.55**	**2.05**	**1.82**	**1.68**	**1.52**	**1.43**	**1.37**	**1.33**	**1.30**	**1.28**	**1.26**	**1.25**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**
8	4.67	2.78	**2.22**	**1.96**	**1.80**	**1.63**	**1.53**	**1.46**	**1.42**	**1.38**	**1.36**	**1.34**	**1.33**	**1.31**	**1.29**	**1.28**	**1.27**	**1.27**	**1.26**	**1.25**
12	5.06	2.98	**2.37**	**2.08**	**1.91**	**1.72**	**1.62**	**1.54**	**1.49**	**1.46**	**1.43**	**1.41**	**1.40**	**1.38**	**1.36**	**1.35**	**1.34**	**1.33**	**1.32**	**1.31**
16	5.34	3.12	**2.47**	**2.17**	**1.99**	**1.79**	**1.68**	**1.60**	**1.54**	**1.51**	**1.48**	**1.46**	**1.45**	**1.42**	**1.41**	**1.39**	**1.38**	**1.38**	**1.36**	**1.35**
20	5.55	3.23	*2.56*	**2.24**	**2.05**	**1.84**	**1.73**	**1.64**	**1.59**	**1.55**	**1.52**	**1.50**	**1.48**	**1.46**	**1.44**	**1.43**	**1.42**	**1.41**	**1.40**	**1.39**
30	5.93	3.43	*2.70*	**2.36**	**2.16**	**1.93**	**1.81**	**1.72**	**1.66**	**1.62**	**1.59**	**1.57**	**1.55**	**1.52**	**1.50**	**1.49**	**1.48**	**1.47**	**1.45**	**1.44**
40	6.20	3.57	2.81	**2.44**	**2.23**	**2.00**	**1.87**	**1.77**	**1.71**	**1.67**	**1.64**	**1.61**	**1.59**	**1.57**	**1.55**	**1.53**	**1.52**	**1.51**	**1.50**	**1.49**
50	6.41	3.68	2.88	**2.51**	**2.29**	**2.05**	**1.91**	**1.81**	**1.75**	**1.71**	**1.67**	**1.65**	**1.63**	**1.60**	**1.58**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**
60	6.57	3.76	2.95	*2.56*	**2.34**	**2.09**	**1.95**	**1.85**	**1.78**	**1.74**	**1.70**	**1.68**	**1.66**	**1.63**	**1.61**	**1.59**	**1.58**	**1.57**	**1.55**	**1.54**
75	6.78	3.87	3.03	*2.63*	**2.40**	**2.14**	**2.00**	**1.89**	**1.82**	**1.77**	**1.74**	**1.71**	**1.69**	**1.66**	**1.64**	**1.62**	**1.61**	**1.60**	**1.58**	**1.57**
100	7.04	4.00	3.13	*2.71*	**2.47**	**2.20**	**2.06**	**1.94**	**1.87**	**1.82**	**1.79**	**1.76**	**1.74**	**1.70**	**1.68**	**1.67**	**1.65**	**1.64**	**1.62**	**1.61**
125	7.24	4.11	3.21	*2.78*	**2.53**	**2.25**	**2.10**	**1.98**	**1.91**	**1.86**	**1.82**	**1.79**	**1.77**	**1.74**	**1.71**	**1.70**	**1.68**	**1.67**	**1.65**	**1.64**
150	7.40	4.19	3.27	2.83	*2.58*	**2.29**	**2.14**	**2.02**	**1.94**	**1.89**	**1.85**	**1.82**	**1.80**	**1.76**	**1.74**	**1.72**	**1.71**	**1.70**	**1.68**	**1.67**
175	7.54	4.26	3.32	2.88	*2.62*	**2.33**	**2.17**	**2.05**	**1.97**	**1.92**	**1.88**	**1.85**	**1.82**	**1.79**	**1.76**	**1.74**	**1.73**	**1.72**	**1.70**	**1.69**
200	7.66	4.32	3.37	2.92	*2.65*	**2.36**	**2.19**	**2.07**	**1.99**	**1.94**	**1.90**	**1.87**	**1.84**	**1.81**	**1.78**	**1.76**	**1.75**	**1.74**	**1.72**	**1.70**

Table 19-3. κ-Multipliers for 1-of-4 Interwell Prediction Limits on Observations (40 COC, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	2.25	**1.49**	**1.25**	**1.13**	**1.05**	**0.97**	**0.92**	**0.89**	**0.86**	**0.85**	**0.83**	**0.82**	**0.82**	**0.81**	**0.80**	**0.79**	**0.79**	**0.78**	**0.78**	**0.77**
2	2.85	**1.81**	**1.49**	**1.34**	**1.25**	**1.14**	**1.08**	**1.04**	**1.01**	**0.99**	**0.97**	**0.96**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.91**	**0.90**
3	3.25	*2.01*	**1.64**	**1.46**	**1.35**	**1.24**	**1.17**	**1.12**	**1.09**	**1.07**	**1.05**	**1.04**	**1.03**	**1.02**	**1.01**	**1.00**	**0.99**	**0.99**	**0.98**	**0.97**
4	3.54	*2.15*	**1.74**	**1.55**	**1.44**	**1.31**	**1.24**	**1.18**	**1.15**	**1.13**	**1.11**	**1.10**	**1.09**	**1.07**	**1.06**	**1.05**	**1.04**	**1.04**	**1.03**	**1.02**
5	3.78	2.27	**1.82**	**1.62**	**1.50**	**1.36**	**1.29**	**1.23**	**1.19**	**1.17**	**1.15**	**1.14**	**1.13**	**1.11**	**1.10**	**1.09**	**1.08**	**1.08**	**1.07**	**1.06**
8	4.30	2.51	*2.00*	**1.76**	**1.62**	**1.47**	**1.39**	**1.33**	**1.29**	**1.26**	**1.24**	**1.22**	**1.21**	**1.19**	**1.18**	**1.17**	**1.16**	**1.16**	**1.15**	**1.14**
12	4.77	2.73	*2.16*	**1.89**	**1.74**	**1.57**	**1.48**	**1.41**	**1.36**	**1.33**	**1.31**	**1.29**	**1.28**	**1.26**	**1.25**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**
16	5.11	2.89	2.27	*1.98*	**1.82**	**1.64**	**1.54**	**1.46**	**1.42**	**1.39**	**1.36**	**1.34**	**1.33**	**1.31**	**1.29**	**1.28**	**1.27**	**1.27**	**1.26**	**1.25**
20	5.37	3.01	2.35	*2.05*	**1.88**	**1.69**	**1.58**	**1.51**	**1.46**	**1.43**	**1.40**	**1.38**	**1.37**	**1.35**	**1.33**	**1.32**	**1.31**	**1.30**	**1.29**	**1.28**
30	5.86	3.23	2.51	*2.18*	*1.99*	**1.78**	**1.67**	**1.59**	**1.54**	**1.50**	**1.47**	**1.45**	**1.44**	**1.41**	**1.40**	**1.38**	**1.37**	**1.37**	**1.35**	**1.34**
40	6.21	3.39	2.63	2.27	*2.07*	**1.85**	**1.73**	**1.64**	**1.59**	**1.55**	**1.52**	**1.50**	**1.48**	**1.46**	**1.44**	**1.43**	**1.42**	**1.41**	**1.40**	**1.39**
50	6.47	3.52	2.71	2.34	*2.13*	**1.90**	**1.78**	**1.69**	**1.63**	**1.59**	**1.56**	**1.54**	**1.52**	**1.49**	**1.47**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**
60	6.70	3.62	2.79	2.40	*2.19*	*1.95*	**1.82**	**1.72**	**1.66**	**1.62**	**1.59**	**1.57**	**1.55**	**1.52**	**1.50**	**1.49**	**1.48**	**1.47**	**1.46**	**1.44**
75	6.95	3.75	2.87	2.48	2.25	*2.00*	**1.87**	**1.77**	**1.70**	**1.66**	**1.63**	**1.60**	**1.58**	**1.56**	**1.54**	**1.52**	**1.51**	**1.50**	**1.49**	**1.48**
100	7.30	3.91	2.99	2.57	2.33	*2.07*	**1.92**	**1.82**	**1.75**	**1.71**	**1.67**	**1.65**	**1.63**	**1.60**	**1.58**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**
125	7.58	4.03	3.08	2.64	2.39	*2.12*	*1.97*	**1.86**	**1.79**	**1.75**	**1.71**	**1.69**	**1.67**	**1.63**	**1.61**	**1.60**	**1.59**	**1.58**	**1.56**	**1.55**
150	7.79	4.13	3.15	2.70	2.44	*2.16*	*2.01*	**1.90**	**1.83**	**1.78**	**1.74**	**1.72**	**1.69**	**1.66**	**1.64**	**1.62**	**1.61**	**1.60**	**1.58**	**1.57**
175	7.97	4.22	3.21	2.75	2.48	*2.19*	*2.04*	**1.93**	**1.85**	**1.80**	**1.77**	**1.74**	**1.72**	**1.69**	**1.66**	**1.65**	**1.63**	**1.62**	**1.61**	**1.59**
200	8.12	4.29	3.26	2.79	2.52	*2.23*	*2.07*	*1.95*	**1.88**	**1.83**	**1.79**	**1.76**	**1.74**	**1.71**	**1.68**	**1.67**	**1.65**	**1.64**	**1.62**	**1.61**

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Table 19-3. κ-Multipliers for 1-of-4 Interwell Prediction Limits on Observations (40 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	2.85	**1.81**	**1.49**	**1.34**	**1.25**	**1.14**	**1.08**	**1.04**	**1.01**	**0.99**	**0.97**	**0.96**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.91**	**0.90**
2	3.54	**2.15**	**1.74**	**1.55**	**1.44**	**1.31**	**1.24**	**1.18**	**1.15**	**1.13**	**1.11**	**1.10**	**1.09**	**1.07**	**1.06**	**1.05**	**1.04**	**1.04**	**1.03**	**1.02**
3	3.98	*2.36*	**1.89**	**1.67**	**1.55**	**1.40**	**1.33**	**1.27**	**1.23**	**1.20**	**1.19**	**1.17**	**1.16**	**1.14**	**1.13**	**1.12**	**1.11**	**1.11**	**1.10**	**1.09**
4	4.30	2.51	**2.00**	**1.76**	**1.62**	**1.47**	**1.39**	**1.33**	**1.29**	**1.26**	**1.24**	**1.22**	**1.21**	**1.19**	**1.18**	**1.17**	**1.16**	**1.16**	**1.15**	**1.14**
5	4.56	2.63	**2.08**	**1.83**	**1.69**	**1.52**	**1.44**	**1.37**	**1.33**	**1.30**	**1.28**	**1.26**	**1.25**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**
8	5.11	2.89	*2.27*	**1.98**	**1.82**	**1.64**	**1.54**	**1.46**	**1.42**	**1.39**	**1.36**	**1.34**	**1.33**	**1.31**	**1.29**	**1.28**	**1.27**	**1.27**	**1.26**	**1.25**
12	5.59	3.11	*2.42*	**2.11**	**1.93**	**1.73**	**1.62**	**1.54**	**1.49**	**1.46**	**1.43**	**1.41**	**1.40**	**1.38**	**1.36**	**1.35**	**1.34**	**1.33**	**1.32**	**1.31**
16	5.94	3.27	2.54	**2.20**	**2.01**	**1.80**	**1.68**	**1.60**	**1.55**	**1.51**	**1.48**	**1.46**	**1.45**	**1.42**	**1.41**	**1.39**	**1.38**	**1.38**	**1.36**	**1.35**
20	6.21	3.39	2.63	*2.27*	**2.07**	**1.85**	**1.73**	**1.64**	**1.59**	**1.55**	**1.52**	**1.50**	**1.48**	**1.46**	**1.44**	**1.43**	**1.42**	**1.41**	**1.40**	**1.39**
30	6.70	3.62	2.79	*2.40*	**2.19**	**1.95**	**1.82**	**1.72**	**1.66**	**1.62**	**1.59**	**1.57**	**1.55**	**1.52**	**1.50**	**1.49**	**1.48**	**1.47**	**1.46**	**1.44**
40	7.03	3.78	2.90	*2.50*	*2.27*	**2.01**	**1.88**	**1.78**	**1.71**	**1.67**	**1.64**	**1.61**	**1.59**	**1.57**	**1.55**	**1.53**	**1.52**	**1.51**	**1.50**	**1.49**
50	7.30	3.91	2.99	2.57	*2.33*	**2.07**	**1.92**	**1.82**	**1.75**	**1.71**	**1.67**	**1.65**	**1.63**	**1.60**	**1.58**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**
60	7.52	4.01	3.06	2.63	*2.38*	**2.11**	**1.96**	**1.85**	**1.79**	**1.74**	**1.71**	**1.68**	**1.66**	**1.63**	**1.61**	**1.59**	**1.58**	**1.57**	**1.55**	**1.54**
75	7.79	4.13	3.15	2.70	*2.44*	**2.16**	**2.01**	**1.90**	**1.83**	**1.78**	**1.74**	**1.72**	**1.69**	**1.66**	**1.64**	**1.62**	**1.61**	**1.60**	**1.58**	**1.57**
100	8.12	4.29	3.26	2.79	*2.52*	**2.23**	**2.07**	**1.95**	**1.88**	**1.83**	**1.79**	**1.76**	**1.74**	**1.71**	**1.68**	**1.67**	**1.65**	**1.64**	**1.62**	**1.61**
125	8.38	4.41	3.34	2.86	2.58	*2.28*	**2.11**	**1.99**	**1.92**	**1.86**	**1.82**	**1.80**	**1.77**	**1.74**	**1.72**	**1.70**	**1.68**	**1.67**	**1.65**	**1.64**
150	8.59	4.51	3.42	2.92	2.63	*2.32*	**2.15**	**2.03**	**1.95**	**1.89**	**1.85**	**1.82**	**1.80**	**1.77**	**1.74**	**1.72**	**1.71**	**1.70**	**1.68**	**1.67**
175	8.77	4.59	3.48	2.97	2.68	*2.36*	**2.18**	**2.06**	**1.98**	**1.92**	**1.88**	**1.85**	**1.82**	**1.79**	**1.76**	**1.74**	**1.73**	**1.72**	**1.70**	**1.69**
200	8.91	4.67	3.53	3.01	2.71	*2.39*	**2.21**	**2.08**	**2.00**	**1.94**	**1.90**	**1.87**	**1.84**	**1.81**	**1.78**	**1.76**	**1.75**	**1.74**	**1.72**	**1.70**

Table 19-3. κ-Multipliers for 1-of-4 Interwell Prediction Limits on Observations (40 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.54	**2.15**	**1.74**	**1.55**	**1.44**	**1.31**	**1.24**	**1.18**	**1.15**	**1.13**	**1.11**	**1.10**	**1.09**	**1.07**	**1.06**	**1.05**	**1.04**	**1.04**	**1.03**	**1.02**
2	4.30	**2.51**	**2.00**	**1.76**	**1.62**	**1.47**	**1.39**	**1.33**	**1.29**	**1.26**	**1.24**	**1.22**	**1.21**	**1.19**	**1.18**	**1.17**	**1.16**	**1.16**	**1.15**	**1.14**
3	4.77	2.73	**2.16**	**1.89**	**1.74**	**1.57**	**1.48**	**1.41**	**1.36**	**1.33**	**1.31**	**1.29**	**1.28**	**1.26**	**1.25**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**
4	5.11	2.89	**2.27**	**1.98**	**1.82**	**1.64**	**1.54**	**1.46**	**1.42**	**1.39**	**1.36**	**1.34**	**1.33**	**1.31**	**1.29**	**1.28**	**1.27**	**1.27**	**1.26**	**1.25**
5	5.37	3.01	**2.35**	**2.05**	**1.88**	**1.69**	**1.58**	**1.51**	**1.46**	**1.43**	**1.40**	**1.38**	**1.37**	**1.35**	**1.33**	**1.32**	**1.31**	**1.30**	**1.29**	**1.28**
8	5.94	3.27	**2.54**	**2.20**	**2.01**	**1.80**	**1.68**	**1.60**	**1.55**	**1.51**	**1.48**	**1.46**	**1.45**	**1.42**	**1.41**	**1.39**	**1.38**	**1.38**	**1.36**	**1.35**
12	6.43	3.50	*2.70*	**2.33**	**2.12**	**1.89**	**1.77**	**1.68**	**1.62**	**1.58**	**1.55**	**1.53**	**1.51**	**1.49**	**1.47**	**1.46**	**1.45**	**1.44**	**1.42**	**1.41**
16	6.78	3.66	2.81	**2.42**	**2.20**	**1.96**	**1.83**	**1.73**	**1.67**	**1.63**	**1.60**	**1.58**	**1.56**	**1.53**	**1.51**	**1.50**	**1.49**	**1.48**	**1.46**	**1.45**
20	7.03	3.78	2.90	**2.50**	**2.27**	**2.01**	**1.88**	**1.78**	**1.71**	**1.67**	**1.64**	**1.61**	**1.59**	**1.57**	**1.55**	**1.53**	**1.52**	**1.51**	**1.50**	**1.49**
30	7.52	4.01	3.06	*2.63*	**2.38**	**2.11**	**1.96**	**1.85**	**1.79**	**1.74**	**1.71**	**1.68**	**1.66**	**1.63**	**1.61**	**1.59**	**1.58**	**1.57**	**1.55**	**1.54**
40	7.85	4.17	3.17	*2.72*	**2.46**	**2.18**	**2.02**	**1.91**	**1.84**	**1.79**	**1.75**	**1.72**	**1.70**	**1.67**	**1.65**	**1.63**	**1.62**	**1.61**	**1.59**	**1.58**	**1.58**
50	8.12	4.29	3.26	*2.79*	**2.52**	**2.23**	**2.07**	**1.95**	**1.88**	**1.83**	**1.79**	**1.76**	**1.74**	**1.71**	**1.68**	**1.67**	**1.65**	**1.64**	**1.62**	**1.61**
60	8.34	4.39	3.33	2.85	*2.57*	**2.27**	**2.11**	**1.98**	**1.91**	**1.86**	**1.82**	**1.79**	**1.77**	**1.73**	**1.71**	**1.69**	**1.68**	**1.67**	**1.65**	**1.64**
75	8.59	4.51	3.42	2.92	*2.63*	**2.32**	**2.15**	**2.03**	**1.95**	**1.89**	**1.85**	**1.82**	**1.80**	**1.77**	**1.74**	**1.72**	**1.71**	**1.70**	**1.68**	**1.67**
100	8.91	4.67	3.53	3.01	*2.71*	**2.39**	**2.21**	**2.08**	**2.00**	**1.94**	**1.90**	**1.87**	**1.84**	**1.81**	**1.78**	**1.76**	**1.75**	**1.74**	**1.72**	**1.70**
125	9.16	4.79	3.61	3.08	*2.77*	**2.44**	**2.26**	**2.12**	**2.04**	**1.98**	**1.94**	**1.90**	**1.88**	**1.84**	**1.81**	**1.79**	**1.78**	**1.77**	**1.75**	**1.73**
150	9.38	4.88	3.68	3.13	*2.82*	**2.48**	**2.29**	**2.16**	**2.07**	**2.01**	**1.97**	**1.93**	**1.91**	**1.87**	**1.84**	**1.82**	**1.80**	**1.79**	**1.77**	**1.76**
175	9.53	4.96	3.74	3.18	*2.87*	**2.51**	**2.33**	**2.19**	**2.10**	**2.03**	**1.99**	**1.96**	**1.93**	**1.89**	**1.86**	**1.84**	**1.82**	**1.81**	**1.79**	**1.78**
200	9.69	5.03	3.79	3.23	2.90	*2.54*	**2.35**	**2.21**	**2.12**	**2.06**	**2.01**	**1.98**	**1.95**	**1.91**	**1.88**	**1.86**	**1.84**	**1.83**	**1.81**	**1.79**

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Table 19-4. κ-Multipliers for Modified Calif. Interwell Prediction Limits on Observations (1 COC, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	0.71	0.59	0.53	0.50	0.48	0.45	0.44	0.43	0.42	0.41	0.41	0.41	0.40	0.40	0.40	0.40	0.39	0.39	0.39	0.39
2	1.07	0.88	0.81	0.76	0.73	0.70	0.68	0.66	0.65	0.64	0.64	0.63	0.63	0.62	0.62	0.62	0.61	0.61	0.61	0.61
3	1.28	1.05	0.96	0.90	0.87	0.83	0.80	0.78	0.77	0.76	0.76	0.75	0.75	0.74	0.74	0.73	0.73	0.73	0.72	0.72
4	1.43	1.17	1.06	1.00	0.96	0.92	0.89	0.87	0.85	0.84	0.84	0.83	0.83	0.82	0.81	0.81	0.81	0.81	0.80	0.80
5	1.54	1.26	1.14	1.07	1.03	0.98	0.95	0.93	0.92	0.91	0.90	0.89	0.89	0.88	0.87	0.87	0.87	0.86	0.86	0.86
8	1.78	1.44	1.30	1.23	1.18	1.12	1.09	1.06	1.04	1.03	1.02	1.01	1.01	1.00	0.99	0.99	0.98	0.98	0.97	0.97
12	1.98	1.59	1.44	1.35	1.30	1.23	1.20	1.16	1.14	1.13	1.12	1.11	1.11	1.10	1.09	1.08	1.08	1.08	1.07	1.07
16	2.11	1.70	1.53	1.44	1.38	1.31	1.27	1.24	1.22	1.20	1.19	1.18	1.17	1.16	1.15	1.15	1.14	1.14	1.13	1.13
20	2.22	1.78	1.60	1.51	1.44	1.37	1.33	1.29	1.27	1.25	1.24	1.23	1.22	1.21	1.20	1.20	1.19	1.19	1.18	1.18
30	2.41	1.92	1.73	1.62	1.56	1.48	1.43	1.39	1.36	1.35	1.33	1.32	1.31	1.30	1.29	1.28	1.28	1.28	1.27	1.26
40	2.54	2.02	1.82	1.71	1.63	1.55	1.50	1.46	1.43	1.41	1.40	1.38	1.38	1.36	1.35	1.34	1.34	1.33	1.33	1.32
50	2.64	2.10	1.88	1.77	1.69	1.60	1.55	1.51	1.48	1.46	1.44	1.43	1.42	1.41	1.40	1.39	1.38	1.38	1.37	1.37
60	2.72	2.16	1.94	1.82	1.74	1.65	1.59	1.55	1.52	1.50	1.48	1.47	1.46	1.45	1.43	1.43	1.42	1.42	1.41	1.40
75	2.81	2.23	2.00	1.88	1.80	1.70	1.64	1.60	1.57	1.55	1.53	1.52	1.51	1.49	1.48	1.47	1.46	1.46	1.45	1.44
100	2.93	2.32	2.08	1.95	1.87	1.77	1.71	1.66	1.63	1.61	1.59	1.57	1.56	1.55	1.54	1.53	1.52	1.51	1.50	1.50
125	3.03	2.39	2.15	2.01	1.93	1.82	1.76	1.71	1.67	1.65	1.63	1.62	1.61	1.59	1.58	1.57	1.56	1.56	1.54	1.54
150	3.10	2.45	2.20	2.06	1.97	1.86	1.80	1.75	1.71	1.69	1.67	1.65	1.64	1.62	1.61	1.60	1.59	1.59	1.58	1.57
175	3.16	2.50	2.24	2.10	2.01	1.90	1.83	1.78	1.74	1.72	1.70	1.68	1.67	1.65	1.64	1.63	1.62	1.62	1.61	1.60
200	3.21	2.54	2.27	2.13	2.04	1.93	1.86	1.81	1.77	1.74	1.72	1.71	1.70	1.68	1.67	1.66	1.65	1.64	1.63	1.62

Table 19-4. κ-Multipliers for Modified Calif. Interwell Prediction Limits on Observations (1 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	1.07	0.88	0.81	0.76	0.73	0.70	0.68	0.66	0.65	0.64	0.64	0.63	0.63	0.62	0.62	0.62	0.61	0.61	0.61	0.61
2	1.43	1.17	1.06	1.00	0.96	0.92	0.89	0.87	0.85	0.84	0.84	0.83	0.83	0.82	0.81	0.81	0.81	0.81	0.80	0.80
3	1.63	1.33	1.20	1.13	1.09	1.04	1.01	0.98	0.97	0.95	0.95	0.94	0.93	0.93	0.92	0.92	0.91	0.91	0.90	0.90
4	1.78	1.44	1.30	1.23	1.18	1.12	1.09	1.06	1.04	1.03	1.02	1.01	1.01	1.00	0.99	0.99	0.98	0.98	0.97	0.97
5	1.89	1.52	1.38	1.30	1.25	1.18	1.15	1.12	1.10	1.09	1.08	1.07	1.06	1.05	1.05	1.04	1.04	1.03	1.03	1.02
8	2.11	1.70	1.53	1.44	1.38	1.31	1.27	1.24	1.22	1.20	1.19	1.18	1.17	1.16	1.15	1.15	1.14	1.14	1.13	1.13
12	2.31	1.84	1.66	1.56	1.50	1.42	1.37	1.34	1.31	1.30	1.28	1.27	1.26	1.25	1.24	1.24	1.23	1.23	1.22	1.22
16	2.44	1.94	1.75	1.64	1.57	1.49	1.44	1.40	1.38	1.36	1.35	1.34	1.33	1.31	1.31	1.30	1.29	1.29	1.28	1.28
20	2.54	2.02	1.82	1.71	1.63	1.55	1.50	1.46	1.43	1.41	1.40	1.38	1.38	1.36	1.35	1.34	1.34	1.33	1.33	1.32
30	2.72	2.16	1.94	1.82	1.74	1.65	1.59	1.55	1.52	1.50	1.48	1.47	1.46	1.45	1.43	1.43	1.42	1.42	1.41	1.40
40	2.84	2.25	2.02	1.89	1.81	1.72	1.66	1.61	1.58	1.56	1.54	1.53	1.52	1.50	1.49	1.48	1.48	1.47	1.46	1.46
50	2.93	2.32	2.08	1.95	1.87	1.77	1.71	1.66	1.63	1.61	1.59	1.57	1.56	1.55	1.54	1.53	1.52	1.51	1.50	1.50
60	3.01	2.38	2.13	2.00	1.92	1.81	1.75	1.70	1.67	1.64	1.62	1.61	1.60	1.58	1.57	1.56	1.55	1.55	1.54	1.53
75	3.10	2.45	2.20	2.06	1.97	1.86	1.80	1.75	1.71	1.69	1.67	1.65	1.64	1.62	1.61	1.60	1.59	1.59	1.58	1.57
100	3.21	2.54	2.27	2.13	2.04	1.93	1.86	1.81	1.77	1.74	1.72	1.71	1.70	1.68	1.67	1.66	1.65	1.64	1.63	1.62
125	3.30	2.61	2.33	2.19	2.09	1.98	1.91	1.85	1.81	1.79	1.77	1.75	1.74	1.72	1.71	1.70	1.69	1.68	1.67	1.66
150	3.37	2.66	2.38	2.23	2.13	2.02	1.95	1.89	1.85	1.82	1.80	1.79	1.77	1.75	1.74	1.73	1.72	1.71	1.70	1.69
175	3.43	2.70	2.42	2.27	2.17	2.05	1.98	1.92	1.88	1.85	1.83	1.81	1.80	1.78	1.77	1.76	1.75	1.74	1.73	1.72
200	3.48	2.74	2.46	2.30	2.20	2.08	2.00	1.95	1.91	1.88	1.86	1.84	1.83	1.80	1.79	1.78	1.77	1.76	1.75	1.74

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Table 19-4. κ-Multipliers for Modified Calif. Interwell Prediction Limits on Observations (1 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.43**	**1.17**	**1.06**	**1.00**	**0.96**	**0.92**	**0.89**	**0.87**	**0.85**	**0.84**	**0.84**	**0.83**	**0.83**	**0.82**	**0.81**	**0.81**	**0.81**	**0.81**	**0.80**	**0.80**
2	**1.78**	**1.44**	**1.30**	**1.23**	**1.18**	**1.12**	**1.09**	**1.06**	**1.04**	**1.03**	**1.02**	**1.01**	**1.01**	**1.00**	**0.99**	**0.99**	**0.98**	**0.98**	**0.97**	**0.97**
3	**1.98**	**1.59**	**1.44**	**1.35**	**1.30**	**1.23**	**1.20**	**1.16**	**1.14**	**1.13**	**1.12**	**1.11**	**1.11**	**1.10**	**1.09**	**1.08**	**1.08**	**1.08**	**1.07**	**1.07**
4	**2.11**	**1.70**	**1.53**	**1.44**	**1.38**	**1.31**	**1.27**	**1.24**	**1.22**	**1.20**	**1.19**	**1.18**	**1.17**	**1.16**	**1.15**	**1.15**	**1.14**	**1.14**	**1.13**	**1.13**
5	**2.22**	**1.78**	**1.60**	**1.51**	**1.44**	**1.37**	**1.33**	**1.29**	**1.27**	**1.25**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**	**1.20**	**1.19**	**1.19**	**1.18**	**1.18**
8	**2.44**	**1.94**	**1.75**	**1.64**	**1.57**	**1.49**	**1.44**	**1.40**	**1.38**	**1.36**	**1.35**	**1.34**	**1.33**	**1.31**	**1.31**	**1.30**	**1.29**	**1.29**	**1.28**	**1.28**
12	**2.62**	**2.08**	**1.87**	**1.76**	**1.68**	**1.59**	**1.54**	**1.50**	**1.47**	**1.45**	**1.43**	**1.42**	**1.41**	**1.40**	**1.39**	**1.38**	**1.38**	**1.37**	**1.36**	**1.36**
16	**2.74**	**2.18**	**1.96**	**1.83**	**1.76**	**1.66**	**1.61**	**1.56**	**1.53**	**1.51**	**1.50**	**1.48**	**1.47**	**1.46**	**1.45**	**1.44**	**1.43**	**1.43**	**1.42**	**1.41**
20	**2.84**	**2.25**	**2.02**	**1.89**	**1.81**	**1.72**	**1.66**	**1.61**	**1.58**	**1.56**	**1.54**	**1.53**	**1.52**	**1.50**	**1.49**	**1.48**	**1.48**	**1.47**	**1.46**	**1.46**
30	3.01	**2.38**	**2.13**	**2.00**	**1.92**	**1.81**	**1.75**	**1.70**	**1.67**	**1.64**	**1.62**	**1.61**	**1.60**	**1.58**	**1.57**	**1.56**	**1.55**	**1.55**	**1.54**	**1.53**
40	3.13	**2.47**	**2.21**	**2.07**	**1.99**	**1.88**	**1.81**	**1.76**	**1.73**	**1.70**	**1.68**	**1.67**	**1.65**	**1.64**	**1.62**	**1.61**	**1.61**	**1.60**	**1.59**	**1.58**
50	3.21	**2.54**	**2.27**	**2.13**	**2.04**	**1.93**	**1.86**	**1.81**	**1.77**	**1.74**	**1.72**	**1.71**	**1.70**	**1.68**	**1.67**	**1.66**	**1.65**	**1.64**	**1.63**	**1.62**
60	3.29	**2.59**	**2.32**	**2.18**	**2.08**	**1.97**	**1.90**	**1.84**	**1.81**	**1.78**	**1.76**	**1.74**	**1.73**	**1.71**	**1.70**	**1.69**	**1.68**	**1.67**	**1.66**	**1.65**
75	3.37	**2.66**	**2.38**	**2.23**	**2.13**	**2.02**	**1.95**	**1.89**	**1.85**	**1.82**	**1.80**	**1.79**	**1.77**	**1.75**	**1.74**	**1.73**	**1.72**	**1.71**	**1.70**	**1.69**
100	3.48	**2.74**	**2.46**	**2.30**	**2.20**	**2.08**	**2.00**	**1.95**	**1.91**	**1.88**	**1.86**	**1.84**	**1.83**	**1.80**	**1.79**	**1.78**	**1.77**	**1.76**	**1.75**	**1.74**
125	3.57	**2.81**	**2.51**	**2.35**	**2.25**	**2.12**	**2.05**	**1.99**	**1.95**	**1.92**	**1.90**	**1.88**	**1.87**	**1.84**	**1.83**	**1.82**	**1.81**	**1.80**	**1.79**	**1.78**
150	3.63	**2.86**	**2.56**	**2.40**	**2.29**	**2.16**	**2.09**	**2.02**	**1.98**	**1.95**	**1.93**	**1.91**	**1.90**	**1.88**	**1.86**	**1.85**	**1.84**	**1.83**	**1.82**	**1.81**
175	3.69	**2.90**	**2.60**	**2.43**	**2.32**	**2.19**	**2.12**	**2.05**	**2.01**	**1.98**	**1.96**	**1.94**	**1.93**	**1.90**	**1.89**	**1.87**	**1.86**	**1.86**	**1.84**	**1.83**
200	3.74	**2.94**	**2.63**	**2.46**	**2.35**	**2.22**	**2.14**	**2.08**	**2.04**	**2.01**	**1.98**	**1.96**	**1.95**	**1.93**	**1.91**	**1.90**	**1.89**	**1.88**	**1.86**	**1.85**

Table 19-4. κ-Multipliers for Modified Calif. Interwell Prediction Limits on Observations (2 COC, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.14**	**0.92**	**0.83**	**0.78**	**0.74**	**0.71**	**0.68**	**0.66**	**0.65**	**0.64**	**0.64**	**0.63**	**0.63**	**0.62**	**0.62**	**0.62**	**0.61**	**0.61**	**0.61**	**0.61**
2	**1.55**	**1.22**	**1.09**	**1.02**	**0.98**	**0.93**	**0.90**	**0.88**	**0.86**	**0.85**	**0.84**	**0.83**	**0.83**	**0.82**	**0.82**	**0.81**	**0.81**	**0.81**	**0.80**	**0.80**
3	**1.79**	**1.40**	**1.25**	**1.16**	**1.11**	**1.05**	**1.02**	**0.99**	**0.97**	**0.96**	**0.95**	**0.94**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.91**	**0.91**	**0.90**
4	**1.97**	**1.52**	**1.35**	**1.26**	**1.20**	**1.14**	**1.10**	**1.07**	**1.05**	**1.04**	**1.02**	**1.02**	**1.01**	**1.00**	**0.99**	**0.99**	**0.99**	**0.98**	**0.98**	**0.97**
5	**2.10**	**1.62**	**1.43**	**1.34**	**1.27**	**1.20**	**1.16**	**1.13**	**1.11**	**1.09**	**1.08**	**1.07**	**1.07**	**1.06**	**1.05**	**1.04**	**1.04**	**1.04**	**1.03**	**1.02**
8	**2.39**	**1.81**	**1.60**	**1.49**	**1.42**	**1.34**	**1.29**	**1.25**	**1.23**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**	**1.16**	**1.15**	**1.15**	**1.14**	**1.14**	**1.13**
12	2.63	**1.98**	**1.74**	**1.62**	**1.54**	**1.45**	**1.39**	**1.35**	**1.32**	**1.30**	**1.29**	**1.28**	**1.27**	**1.26**	**1.25**	**1.24**	**1.24**	**1.23**	**1.22**	**1.22**
16	2.80	**2.10**	**1.84**	**1.71**	**1.62**	**1.52**	**1.47**	**1.42**	**1.39**	**1.37**	**1.36**	**1.34**	**1.33**	**1.32**	**1.31**	**1.30**	**1.30**	**1.29**	**1.28**	**1.28**
20	2.93	**2.19**	**1.92**	**1.78**	**1.69**	**1.58**	**1.52**	**1.47**	**1.44**	**1.42**	**1.41**	**1.39**	**1.38**	**1.37**	**1.36**	**1.35**	**1.34**	**1.34**	**1.33**	**1.32**
30	3.16	**2.35**	**2.06**	**1.90**	**1.80**	**1.69**	**1.62**	**1.57**	**1.54**	**1.51**	**1.49**	**1.48**	**1.47**	**1.45**	**1.44**	**1.43**	**1.42**	**1.42**	**1.41**	**1.40**
40	3.32	**2.46**	**2.15**	**1.99**	**1.88**	**1.76**	**1.69**	**1.64**	**1.60**	**1.57**	**1.55**	**1.54**	**1.53**	**1.51**	**1.50**	**1.49**	**1.48**	**1.47**	**1.46**	**1.46**
50	3.44	**2.55**	**2.22**	**2.05**	**1.94**	**1.82**	**1.74**	**1.69**	**1.65**	**1.62**	**1.60**	**1.59**	**1.57**	**1.55**	**1.54**	**1.53**	**1.52**	**1.52**	**1.51**	**1.50**
60	3.54	*2.62*	**2.28**	**2.10**	**1.99**	**1.86**	**1.79**	**1.73**	**1.69**	**1.66**	**1.64**	**1.62**	**1.61**	**1.59**	**1.58**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**
75	3.66	2.70	**2.35**	**2.17**	**2.05**	**1.92**	**1.84**	**1.78**	**1.73**	**1.71**	**1.68**	**1.67**	**1.65**	**1.63**	**1.62**	**1.61**	**1.60**	**1.59**	**1.58**	**1.57**
100	3.81	2.81	**2.44**	**2.25**	**2.13**	**1.99**	**1.90**	**1.84**	**1.79**	**1.76**	**1.74**	**1.72**	**1.71**	**1.69**	**1.67**	**1.66**	**1.65**	**1.65**	**1.63**	**1.62**
125	3.93	2.89	**2.51**	**2.31**	**2.19**	**2.04**	**1.95**	**1.89**	**1.84**	**1.81**	**1.79**	**1.77**	**1.75**	**1.73**	**1.71**	**1.70**	**1.69**	**1.69**	**1.67**	**1.66**
150	4.02	2.95	*2.57*	**2.36**	**2.23**	**2.08**	**1.99**	**1.92**	**1.88**	**1.85**	**1.82**	**1.80**	**1.79**	**1.76**	**1.75**	**1.74**	**1.73**	**1.72**	**1.70**	**1.70**
175	4.10	3.01	*2.61*	**2.40**	**2.27**	**2.12**	**2.03**	**1.96**	**1.91**	**1.88**	**1.85**	**1.83**	**1.82**	**1.79**	**1.78**	**1.76**	**1.75**	**1.74**	**1.73**	**1.72**
200	4.17	3.06	*2.65*	**2.44**	**2.31**	**2.15**	**2.06**	**1.98**	**1.94**	**1.90**	**1.88**	**1.86**	**1.84**	**1.82**	**1.80**	**1.79**	**1.78**	**1.77**	**1.75**	**1.74**

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Table 19-4. κ-Multipliers for Modified Calif. Interwell Prediction Limits on Observations (2 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.55**	**1.22**	**1.09**	**1.02**	**0.98**	**0.93**	**0.90**	**0.88**	**0.86**	**0.85**	**0.84**	**0.83**	**0.83**	**0.82**	**0.82**	**0.81**	**0.81**	**0.81**	**0.80**	**0.80**
2	**1.97**	**1.52**	**1.35**	**1.26**	**1.20**	**1.14**	**1.10**	**1.07**	**1.05**	**1.04**	**1.02**	**1.02**	**1.01**	**1.00**	**0.99**	**0.99**	**0.99**	**0.98**	**0.98**	**0.97**
3	**2.21**	**1.69**	**1.50**	**1.40**	**1.33**	**1.25**	**1.21**	**1.18**	**1.15**	**1.14**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.09**	**1.08**	**1.08**	**1.07**	**1.07**
4	**2.39**	**1.81**	**1.60**	**1.49**	**1.42**	**1.34**	**1.29**	**1.25**	**1.23**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**	**1.16**	**1.15**	**1.15**	**1.14**	**1.14**	**1.13**
5	**2.52**	**1.91**	**1.68**	**1.56**	**1.49**	**1.40**	**1.35**	**1.31**	**1.28**	**1.26**	**1.25**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**	**1.20**	**1.19**	**1.18**	**1.18**
8	2.80	**2.10**	**1.84**	**1.71**	**1.62**	**1.52**	**1.47**	**1.42**	**1.39**	**1.37**	**1.36**	**1.34**	**1.33**	**1.32**	**1.31**	**1.30**	**1.30**	**1.29**	**1.28**	**1.28**
12	3.03	**2.26**	**1.98**	**1.83**	**1.74**	**1.63**	**1.57**	**1.52**	**1.49**	**1.46**	**1.45**	**1.43**	**1.42**	**1.41**	**1.39**	**1.39**	**1.38**	**1.37**	**1.37**	**1.36**
16	3.20	**2.38**	**2.08**	**1.92**	**1.82**	**1.70**	**1.64**	**1.58**	**1.55**	**1.53**	**1.51**	**1.49**	**1.48**	**1.46**	**1.45**	**1.44**	**1.44**	**1.43**	**1.42**	**1.42**
20	3.32	**2.46**	**2.15**	**1.99**	**1.88**	**1.76**	**1.69**	**1.64**	**1.60**	**1.57**	**1.55**	**1.54**	**1.53**	**1.51**	**1.50**	**1.49**	**1.48**	**1.47**	**1.46**	**1.46**
30	3.54	**2.62**	**2.28**	**2.10**	**1.99**	**1.86**	**1.79**	**1.73**	**1.69**	**1.66**	**1.64**	**1.62**	**1.61**	**1.59**	**1.58**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**
40	3.70	**2.73**	**2.37**	**2.19**	**2.07**	**1.93**	**1.85**	**1.79**	**1.75**	**1.72**	**1.70**	**1.68**	**1.67**	**1.65**	**1.63**	**1.62**	**1.61**	**1.61**	**1.59**	**1.59**
50	3.81	**2.81**	**2.44**	**2.25**	**2.13**	**1.99**	**1.90**	**1.84**	**1.79**	**1.76**	**1.74**	**1.72**	**1.71**	**1.69**	**1.67**	**1.66**	**1.65**	**1.65**	**1.63**	**1.62**
60	3.91	*2.87*	**2.50**	**2.30**	**2.18**	**2.03**	**1.94**	**1.88**	**1.83**	**1.80**	**1.78**	**1.76**	**1.74**	**1.72**	**1.71**	**1.69**	**1.69**	**1.68**	**1.67**	**1.66**
75	4.02	2.95	**2.57**	**2.36**	**2.23**	**2.08**	**1.99**	**1.92**	**1.88**	**1.85**	**1.82**	**1.80**	**1.79**	**1.76**	**1.75**	**1.74**	**1.73**	**1.72**	**1.70**	**1.70**
100	4.17	3.06	**2.65**	**2.44**	**2.31**	**2.15**	**2.06**	**1.98**	**1.94**	**1.90**	**1.88**	**1.86**	**1.84**	**1.82**	**1.80**	**1.79**	**1.78**	**1.77**	**1.75**	**1.74**
125	4.28	3.13	**2.72**	**2.50**	**2.36**	**2.20**	**2.11**	**2.03**	**1.98**	**1.94**	**1.92**	**1.90**	**1.88**	**1.86**	**1.84**	**1.83**	**1.81**	**1.81**	**1.79**	**1.78**
150	4.37	3.19	**2.77**	**2.55**	**2.41**	**2.24**	**2.14**	**2.07**	**2.02**	**1.98**	**1.95**	**1.93**	**1.91**	**1.89**	**1.87**	**1.86**	**1.85**	**1.84**	**1.82**	**1.81**
175	4.44	3.25	*2.82*	**2.59**	**2.45**	**2.28**	**2.18**	**2.10**	**2.05**	**2.01**	**1.98**	**1.96**	**1.94**	**1.92**	**1.90**	**1.88**	**1.87**	**1.86**	**1.85**	**1.84**
200	4.51	3.29	*2.85*	**2.62**	**2.48**	**2.31**	**2.20**	**2.13**	**2.07**	**2.03**	**2.01**	**1.98**	**1.97**	**1.94**	**1.92**	**1.91**	**1.89**	**1.89**	**1.87**	**1.86**

Table 19-4. κ-Multipliers for Modified Calif. Interwell Prediction Limits on Observations (2 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.97**	**1.52**	**1.35**	**1.26**	**1.20**	**1.14**	**1.10**	**1.07**	**1.05**	**1.04**	**1.02**	**1.02**	**1.01**	**1.00**	**0.99**	**0.99**	**0.99**	**0.98**	**0.98**	**0.97**
2	**2.39**	**1.81**	**1.60**	**1.49**	**1.42**	**1.34**	**1.29**	**1.25**	**1.23**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**	**1.16**	**1.15**	**1.15**	**1.14**	**1.14**	**1.13**
3	**2.63**	**1.98**	**1.74**	**1.62**	**1.54**	**1.45**	**1.39**	**1.35**	**1.32**	**1.30**	**1.29**	**1.28**	**1.27**	**1.26**	**1.25**	**1.24**	**1.24**	**1.23**	**1.22**	**1.22**
4	**2.80**	**2.10**	**1.84**	**1.71**	**1.62**	**1.52**	**1.47**	**1.42**	**1.39**	**1.37**	**1.36**	**1.34**	**1.33**	**1.32**	**1.31**	**1.30**	**1.30**	**1.29**	**1.28**	**1.28**
5	**2.93**	**2.19**	**1.92**	**1.78**	**1.69**	**1.58**	**1.52**	**1.47**	**1.44**	**1.42**	**1.41**	**1.39**	**1.38**	**1.37**	**1.36**	**1.35**	**1.34**	**1.34**	**1.33**	**1.32**
8	3.20	**2.38**	**2.08**	**1.92**	**1.82**	**1.70**	**1.64**	**1.58**	**1.55**	**1.53**	**1.51**	**1.49**	**1.48**	**1.46**	**1.45**	**1.44**	**1.44**	**1.43**	**1.42**	**1.42**
12	3.42	**2.53**	**2.21**	**2.04**	**1.93**	**1.81**	**1.73**	**1.68**	**1.64**	**1.61**	**1.59**	**1.58**	**1.56**	**1.55**	**1.53**	**1.52**	**1.52**	**1.51**	**1.50**	**1.49**
16	3.58	**2.64**	**2.30**	**2.12**	**2.01**	**1.88**	**1.80**	**1.74**	**1.70**	**1.67**	**1.65**	**1.64**	**1.62**	**1.60**	**1.59**	**1.58**	**1.57**	**1.56**	**1.55**	**1.54**
20	3.70	**2.73**	**2.37**	**2.19**	**2.07**	**1.93**	**1.85**	**1.79**	**1.75**	**1.72**	**1.70**	**1.68**	**1.67**	**1.65**	**1.63**	**1.62**	**1.61**	**1.61**	**1.59**	**1.59**
30	3.91	**2.87**	**2.50**	**2.30**	**2.18**	**2.03**	**1.94**	**1.88**	**1.83**	**1.80**	**1.78**	**1.76**	**1.74**	**1.72**	**1.71**	**1.69**	**1.69**	**1.68**	**1.67**	**1.66**
40	4.06	**2.98**	**2.59**	**2.38**	**2.25**	**2.10**	**2.01**	**1.94**	**1.89**	**1.86**	**1.83**	**1.81**	**1.80**	**1.78**	**1.76**	**1.75**	**1.74**	**1.73**	**1.72**	**1.71**
50	4.17	**3.06**	**2.65**	**2.44**	**2.31**	**2.15**	**2.06**	**1.98**	**1.94**	**1.90**	**1.88**	**1.86**	**1.84**	**1.82**	**1.80**	**1.79**	**1.78**	**1.77**	**1.75**	**1.74**
60	4.26	*3.12*	**2.71**	**2.49**	**2.35**	**2.19**	**2.10**	**2.02**	**1.97**	**1.94**	**1.91**	**1.89**	**1.87**	**1.85**	**1.83**	**1.82**	**1.81**	**1.80**	**1.78**	**1.77**
75	4.37	3.19	**2.77**	**2.55**	**2.41**	**2.24**	**2.14**	**2.07**	**2.02**	**1.98**	**1.95**	**1.93**	**1.91**	**1.89**	**1.87**	**1.86**	**1.85**	**1.84**	**1.82**	**1.81**
100	4.51	3.29	**2.85**	**2.62**	**2.48**	**2.31**	**2.20**	**2.13**	**2.07**	**2.03**	**2.01**	**1.98**	**1.97**	**1.94**	**1.92**	**1.91**	**1.89**	**1.89**	**1.87**	**1.86**
125	4.61	3.37	**2.92**	**2.68**	**2.53**	**2.35**	**2.25**	**2.17**	**2.12**	**2.08**	**2.05**	**2.02**	**2.01**	**1.98**	**1.96**	**1.94**	**1.93**	**1.92**	**1.91**	**1.89**
150	4.69	3.43	**2.97**	**2.73**	**2.58**	**2.39**	**2.29**	**2.21**	**2.15**	**2.11**	**2.08**	**2.06**	**2.04**	**2.01**	**1.99**	**1.97**	**1.96**	**1.95**	**1.93**	**1.92**
175	4.77	3.48	**3.01**	**2.76**	**2.61**	**2.43**	**2.32**	**2.24**	**2.18**	**2.14**	**2.11**	**2.08**	**2.06**	**2.04**	**2.01**	**2.00**	**1.99**	**1.98**	**1.96**	**1.95**
200	4.83	3.52	**3.05**	**2.80**	**2.64**	**2.46**	**2.35**	**2.26**	**2.20**	**2.16**	**2.13**	**2.11**	**2.09**	**2.06**	**2.04**	**2.02**	**2.01**	**2.00**	**1.98**	**1.97**

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Table 19-4. κ-Multipliers for Modified Calif. Interwell Prediction Limits on Observations (5 COC, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.80**	**1.36**	**1.20**	**1.12**	**1.07**	**1.01**	**0.97**	**0.94**	**0.93**	**0.91**	**0.90**	**0.90**	**0.89**	**0.88**	**0.88**	**0.87**	**0.87**	**0.87**	**0.86**	**0.86**
2	**2.30**	**1.69**	**1.47**	**1.36**	**1.29**	**1.21**	**1.17**	**1.13**	**1.11**	**1.10**	**1.08**	**1.08**	**1.07**	**1.06**	**1.05**	**1.04**	**1.04**	**1.04**	**1.03**	**1.03**
3	2.62	**1.88**	**1.63**	**1.50**	**1.42**	**1.33**	**1.28**	**1.24**	**1.22**	**1.20**	**1.18**	**1.17**	**1.17**	**1.15**	**1.14**	**1.14**	**1.13**	**1.13**	**1.12**	**1.12**
4	2.84	**2.02**	**1.74**	**1.60**	**1.52**	**1.41**	**1.36**	**1.32**	**1.29**	**1.27**	**1.25**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**	**1.20**	**1.19**	**1.19**	**1.18**
5	3.02	**2.13**	**1.83**	**1.68**	**1.59**	**1.48**	**1.42**	**1.37**	**1.34**	**1.32**	**1.30**	**1.29**	**1.28**	**1.27**	**1.26**	**1.25**	**1.25**	**1.24**	**1.23**	**1.23**
8	3.39	**2.36**	**2.01**	**1.84**	**1.73**	**1.61**	**1.54**	**1.49**	**1.45**	**1.43**	**1.41**	**1.40**	**1.39**	**1.37**	**1.36**	**1.35**	**1.34**	**1.34**	**1.33**	**1.32**
12	3.71	**2.56**	**2.17**	**1.97**	**1.85**	**1.72**	**1.64**	**1.58**	**1.55**	**1.52**	**1.50**	**1.49**	**1.47**	**1.46**	**1.44**	**1.43**	**1.43**	**1.42**	**1.41**	**1.40**
16	3.94	2.69	**2.28**	**2.07**	**1.94**	**1.80**	**1.71**	**1.65**	**1.61**	**1.58**	**1.56**	**1.55**	**1.53**	**1.51**	**1.50**	**1.49**	**1.48**	**1.48**	**1.47**	**1.46**
20	4.11	2.80	**2.36**	**2.14**	**2.01**	**1.86**	**1.77**	**1.70**	**1.66**	**1.63**	**1.61**	**1.59**	**1.58**	**1.56**	**1.55**	**1.53**	**1.53**	**1.52**	**1.51**	**1.50**
30	4.43	2.99	**2.51**	**2.27**	**2.13**	**1.96**	**1.87**	**1.80**	**1.75**	**1.72**	**1.69**	**1.68**	**1.66**	**1.64**	**1.62**	**1.61**	**1.60**	**1.60**	**1.58**	**1.58**
40	4.64	3.12	*2.62*	**2.37**	**2.21**	**2.04**	**1.94**	**1.86**	**1.81**	**1.78**	**1.75**	**1.73**	**1.72**	**1.69**	**1.68**	**1.67**	**1.66**	**1.65**	**1.64**	**1.63**
50	4.81	3.22	2.70	**2.44**	**2.28**	**2.09**	**1.99**	**1.91**	**1.86**	**1.82**	**1.80**	**1.78**	**1.76**	**1.74**	**1.72**	**1.71**	**1.70**	**1.69**	**1.67**	**1.67**
60	4.94	3.31	2.76	**2.49**	**2.33**	**2.14**	**2.03**	**1.95**	**1.90**	**1.86**	**1.83**	**1.81**	**1.80**	**1.77**	**1.75**	**1.74**	**1.73**	**1.72**	**1.71**	**1.70**
75	5.10	3.40	2.84	*2.56*	**2.39**	**2.20**	**2.09**	**2.00**	**1.94**	**1.91**	**1.88**	**1.86**	**1.84**	**1.81**	**1.79**	**1.78**	**1.77**	**1.76**	**1.75**	**1.74**
100	5.31	3.53	2.95	*2.65*	**2.47**	**2.27**	**2.15**	**2.06**	**2.00**	**1.96**	**1.93**	**1.91**	**1.89**	**1.86**	**1.84**	**1.83**	**1.82**	**1.81**	**1.79**	**1.78**
125	5.46	3.63	3.02	*2.72*	*2.54*	**2.32**	**2.20**	**2.11**	**2.05**	**2.01**	**1.98**	**1.95**	**1.93**	**1.90**	**1.88**	**1.87**	**1.86**	**1.85**	**1.83**	**1.82**
150	5.59	3.71	3.09	2.78	*2.59*	**2.37**	**2.24**	**2.15**	**2.09**	**2.04**	**2.01**	**1.99**	**1.97**	**1.94**	**1.92**	**1.90**	**1.89**	**1.88**	**1.86**	**1.85**
175	5.69	3.77	3.14	2.82	*2.63*	**2.41**	**2.28**	**2.18**	**2.12**	**2.07**	**2.04**	**2.01**	**1.99**	**1.96**	**1.94**	**1.93**	**1.91**	**1.90**	**1.89**	**1.88**
200	5.79	3.83	3.18	2.86	*2.67*	**2.44**	**2.31**	**2.21**	**2.15**	**2.10**	**2.07**	**2.04**	**2.02**	**1.99**	**1.97**	**1.95**	**1.94**	**1.93**	**1.91**	**1.90**

Table 19-4. κ-Multipliers for Modified Calif. Interwell Prediction Limits on Observations (5 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.30**	**1.69**	**1.47**	**1.36**	**1.29**	**1.21**	**1.17**	**1.13**	**1.11**	**1.10**	**1.08**	**1.08**	**1.07**	**1.06**	**1.05**	**1.04**	**1.04**	**1.04**	**1.03**	**1.03**
2	2.84	**2.02**	**1.74**	**1.60**	**1.52**	**1.41**	**1.36**	**1.32**	**1.29**	**1.27**	**1.25**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**	**1.20**	**1.19**	**1.19**	**1.18**
3	3.16	**2.22**	**1.90**	**1.74**	**1.64**	**1.53**	**1.47**	**1.42**	**1.38**	**1.36**	**1.35**	**1.33**	**1.32**	**1.31**	**1.30**	**1.29**	**1.28**	**1.28**	**1.27**	**1.27**
4	3.39	**2.36**	**2.01**	**1.84**	**1.73**	**1.61**	**1.54**	**1.49**	**1.45**	**1.43**	**1.41**	**1.40**	**1.39**	**1.37**	**1.36**	**1.35**	**1.34**	**1.34**	**1.33**	**1.32**
5	3.57	**2.47**	**2.10**	**1.91**	**1.80**	**1.67**	**1.60**	**1.54**	**1.50**	**1.48**	**1.46**	**1.45**	**1.43**	**1.42**	**1.41**	**1.40**	**1.39**	**1.38**	**1.37**	**1.37**
8	3.94	**2.69**	**2.28**	**2.07**	**1.94**	**1.80**	**1.71**	**1.65**	**1.61**	**1.58**	**1.56**	**1.55**	**1.53**	**1.51**	**1.50**	**1.49**	**1.48**	**1.48**	**1.47**	**1.46**
12	4.26	*2.88*	**2.43**	**2.20**	**2.06**	**1.90**	**1.81**	**1.75**	**1.70**	**1.67**	**1.65**	**1.63**	**1.62**	**1.60**	**1.58**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**
16	4.47	3.02	**2.54**	**2.29**	**2.15**	**1.98**	**1.88**	**1.81**	**1.76**	**1.73**	**1.71**	**1.69**	**1.67**	**1.65**	**1.64**	**1.62**	**1.62**	**1.61**	**1.60**	**1.59**
20	4.64	3.12	**2.62**	**2.37**	**2.21**	**2.04**	**1.94**	**1.86**	**1.81**	**1.78**	**1.75**	**1.73**	**1.72**	**1.69**	**1.68**	**1.67**	**1.66**	**1.65**	**1.64**	**1.63**
30	4.94	3.31	**2.76**	**2.49**	**2.33**	**2.14**	**2.03**	**1.95**	**1.90**	**1.86**	**1.83**	**1.81**	**1.80**	**1.77**	**1.75**	**1.74**	**1.73**	**1.72**	**1.71**	**1.70**
40	5.15	3.43	*2.87*	**2.58**	**2.41**	**2.21**	**2.10**	**2.01**	**1.96**	**1.92**	**1.89**	**1.87**	**1.85**	**1.82**	**1.80**	**1.79**	**1.78**	**1.77**	**1.76**	**1.75**
50	5.31	3.53	*2.95*	**2.65**	**2.47**	**2.27**	**2.15**	**2.06**	**2.00**	**1.96**	**1.93**	**1.91**	**1.89**	**1.86**	**1.84**	**1.83**	**1.82**	**1.81**	**1.79**	**1.78**
60	5.43	3.61	3.01	**2.71**	**2.53**	**2.31**	**2.19**	**2.10**	**2.04**	**2.00**	**1.97**	**1.94**	**1.93**	**1.90**	**1.88**	**1.86**	**1.85**	**1.84**	**1.82**	**1.81**
75	5.59	3.71	3.09	**2.78**	**2.59**	**2.37**	**2.24**	**2.15**	**2.09**	**2.04**	**2.01**	**1.99**	**1.97**	**1.94**	**1.92**	**1.90**	**1.89**	**1.88**	**1.86**	**1.85**
100	5.79	3.83	3.18	*2.86*	**2.67**	**2.44**	**2.31**	**2.21**	**2.15**	**2.10**	**2.07**	**2.04**	**2.02**	**1.99**	**1.97**	**1.95**	**1.94**	**1.93**	**1.91**	**1.90**
125	5.94	3.92	3.26	*2.93*	**2.73**	**2.49**	**2.36**	**2.26**	**2.19**	**2.14**	**2.11**	**2.08**	**2.06**	**2.03**	**2.00**	**1.99**	**1.97**	**1.96**	**1.95**	**1.93**
150	6.05	4.00	3.32	*2.98*	**2.77**	**2.54**	**2.40**	**2.29**	**2.23**	**2.18**	**2.14**	**2.11**	**2.09**	**2.06**	**2.04**	**2.02**	**2.00**	**1.99**	**1.97**	**1.96**
175	6.16	4.06	3.37	3.02	*2.82*	**2.57**	**2.43**	**2.33**	**2.26**	**2.21**	**2.17**	**2.14**	**2.12**	**2.08**	**2.06**	**2.04**	**2.03**	**2.02**	**2.00**	**1.99**
200	6.24	4.11	3.41	3.06	*2.85*	**2.60**	**2.46**	**2.35**	**2.28**	**2.23**	**2.19**	**2.17**	**2.14**	**2.11**	**2.08**	**2.07**	**2.05**	**2.04**	**2.02**	**2.01**

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Table 19-4. κ-Multipliers for Modified Calif. Interwell Prediction Limits on Observations (5 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.84**	**2.02**	**1.74**	**1.60**	**1.52**	**1.41**	**1.36**	**1.32**	**1.29**	**1.27**	**1.25**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**	**1.20**	**1.19**	**1.19**	**1.18**
2	3.39	**2.36**	**2.01**	**1.84**	**1.73**	**1.61**	**1.54**	**1.49**	**1.45**	**1.43**	**1.41**	**1.40**	**1.39**	**1.37**	**1.36**	**1.35**	**1.34**	**1.34**	**1.33**	**1.32**
3	3.71	**2.56**	**2.17**	**1.97**	**1.85**	**1.72**	**1.64**	**1.58**	**1.55**	**1.52**	**1.50**	**1.49**	**1.47**	**1.46**	**1.44**	**1.43**	**1.43**	**1.42**	**1.41**	**1.40**
4	3.94	**2.69**	**2.28**	**2.07**	**1.94**	**1.80**	**1.71**	**1.65**	**1.61**	**1.58**	**1.56**	**1.55**	**1.53**	**1.51**	**1.50**	**1.49**	**1.48**	**1.48**	**1.47**	**1.46**
5	4.11	**2.80**	**2.36**	**2.14**	**2.01**	**1.86**	**1.77**	**1.70**	**1.66**	**1.63**	**1.61**	**1.59**	**1.58**	**1.56**	**1.55**	**1.53**	**1.53**	**1.52**	**1.51**	**1.50**
8	4.47	**3.02**	**2.54**	**2.29**	**2.15**	**1.98**	**1.88**	**1.81**	**1.76**	**1.73**	**1.71**	**1.69**	**1.67**	**1.65**	**1.64**	**1.62**	**1.62**	**1.61**	**1.60**	**1.59**
12	4.78	3.20	**2.68**	**2.42**	**2.27**	**2.08**	**1.98**	**1.90**	**1.85**	**1.82**	**1.79**	**1.77**	**1.75**	**1.73**	**1.71**	**1.70**	**1.69**	**1.68**	**1.67**	**1.66**
16	4.99	3.33	**2.79**	**2.51**	**2.35**	**2.16**	**2.05**	**1.97**	**1.91**	**1.87**	**1.85**	**1.82**	**1.81**	**1.78**	**1.76**	**1.75**	**1.74**	**1.73**	**1.72**	**1.71**
20	5.15	3.43	**2.87**	**2.58**	**2.41**	**2.21**	**2.10**	**2.01**	**1.96**	**1.92**	**1.89**	**1.87**	**1.85**	**1.82**	**1.80**	**1.79**	**1.78**	**1.77**	**1.76**	**1.75**
30	5.43	3.61	**3.01**	**2.71**	**2.53**	**2.31**	**2.19**	**2.10**	**2.04**	**2.00**	**1.97**	**1.94**	**1.93**	**1.90**	**1.88**	**1.86**	**1.85**	**1.84**	**1.82**	**1.81**
40	5.63	3.73	*3.11*	**2.79**	**2.60**	**2.38**	**2.26**	**2.16**	**2.10**	**2.06**	**2.02**	**2.00**	**1.98**	**1.95**	**1.93**	**1.91**	**1.90**	**1.89**	**1.87**	**1.86**
50	5.79	3.83	*3.18*	**2.86**	**2.67**	**2.44**	**2.31**	**2.21**	**2.15**	**2.10**	**2.07**	**2.04**	**2.02**	**1.99**	**1.97**	**1.95**	**1.94**	**1.93**	**1.91**	**1.90**
60	5.91	3.90	3.25	**2.92**	**2.71**	**2.48**	**2.35**	**2.25**	**2.18**	**2.13**	**2.10**	**2.07**	**2.05**	**2.02**	**2.00**	**1.98**	**1.97**	**1.96**	**1.94**	**1.93**
75	6.05	4.00	3.32	**2.98**	**2.77**	**2.54**	**2.40**	**2.29**	**2.23**	**2.18**	**2.14**	**2.11**	**2.09**	**2.06**	**2.04**	**2.02**	**2.00**	**1.99**	**1.97**	**1.96**
100	6.24	4.11	3.41	**3.06**	**2.85**	**2.60**	**2.46**	**2.35**	**2.28**	**2.23**	**2.19**	**2.17**	**2.14**	**2.11**	**2.08**	**2.07**	**2.05**	**2.04**	**2.02**	**2.01**
125	6.39	4.20	3.49	*3.13*	**2.91**	**2.66**	**2.51**	**2.40**	**2.33**	**2.27**	**2.23**	**2.20**	**2.18**	**2.15**	**2.12**	**2.10**	**2.09**	**2.08**	**2.05**	**2.04**
150	6.50	4.27	3.54	*3.18*	**2.96**	**2.70**	**2.55**	**2.44**	**2.36**	**2.31**	**2.27**	**2.24**	**2.21**	**2.18**	**2.15**	**2.13**	**2.12**	**2.10**	**2.08**	**2.07**
175	6.60	4.33	3.59	*3.22*	**3.00**	**2.73**	**2.58**	**2.47**	**2.39**	**2.34**	**2.30**	**2.26**	**2.24**	**2.20**	**2.18**	**2.16**	**2.14**	**2.13**	**2.11**	**2.09**
200	6.68	4.39	3.64	*3.26*	**3.03**	**2.76**	**2.61**	**2.49**	**2.42**	**2.36**	**2.32**	**2.29**	**2.26**	**2.22**	**2.20**	**2.18**	**2.16**	**2.15**	**2.13**	**2.11**

Table 19-4. κ-Multipliers for Modified Calif. Interwell Prediction Limits on Observations (10 COC, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.40**	**1.72**	**1.49**	**1.37**	**1.30**	**1.22**	**1.17**	**1.14**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**	**1.06**	**1.05**	**1.04**	**1.04**	**1.04**	**1.03**	**1.03**
2	3.01	**2.08**	**1.77**	**1.62**	**1.53**	**1.42**	**1.36**	**1.32**	**1.29**	**1.27**	**1.25**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**	**1.20**	**1.19**	**1.19**	**1.18**
3	3.40	**2.29**	**1.94**	**1.76**	**1.66**	**1.54**	**1.47**	**1.42**	**1.39**	**1.37**	**1.35**	**1.34**	**1.33**	**1.31**	**1.30**	**1.29**	**1.29**	**1.28**	**1.27**	**1.27**
4	3.68	**2.44**	**2.05**	**1.86**	**1.75**	**1.62**	**1.55**	**1.49**	**1.46**	**1.43**	**1.41**	**1.40**	**1.39**	**1.37**	**1.36**	**1.35**	**1.35**	**1.34**	**1.33**	**1.32**
5	3.89	**2.57**	**2.15**	**1.94**	**1.82**	**1.68**	**1.60**	**1.55**	**1.51**	**1.48**	**1.46**	**1.45**	**1.44**	**1.42**	**1.41**	**1.40**	**1.39**	**1.39**	**1.38**	**1.37**
8	4.36	2.82	**2.34**	**2.11**	**1.97**	**1.81**	**1.72**	**1.66**	**1.62**	**1.59**	**1.56**	**1.55**	**1.54**	**1.52**	**1.50**	**1.49**	**1.48**	**1.48**	**1.47**	**1.46**
12	4.76	3.04	**2.51**	**2.25**	**2.09**	**1.92**	**1.83**	**1.75**	**1.71**	**1.67**	**1.65**	**1.63**	**1.62**	**1.60**	**1.58**	**1.57**	**1.56**	**1.56**	**1.54**	**1.54**
16	5.04	3.20	*2.62*	**2.35**	**2.18**	**2.00**	**1.90**	**1.82**	**1.77**	**1.74**	**1.71**	**1.69**	**1.68**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**	**1.59**
20	5.26	3.32	2.72	**2.43**	**2.25**	**2.06**	**1.95**	**1.87**	**1.82**	**1.78**	**1.76**	**1.74**	**1.72**	**1.70**	**1.68**	**1.67**	**1.66**	**1.65**	**1.64**	**1.63**
30	5.65	3.53	2.88	*2.56*	**2.38**	**2.17**	**2.05**	**1.96**	**1.91**	**1.87**	**1.84**	**1.82**	**1.80**	**1.77**	**1.75**	**1.74**	**1.73**	**1.72**	**1.71**	**1.70**
40	5.92	3.69	3.00	*2.66*	**2.47**	**2.24**	**2.12**	**2.03**	**1.97**	**1.93**	**1.90**	**1.87**	**1.85**	**1.83**	**1.81**	**1.79**	**1.78**	**1.77**	**1.76**	**1.75**
50	6.13	3.80	3.08	2.74	*2.53*	**2.30**	**2.17**	**2.08**	**2.01**	**1.97**	**1.94**	**1.91**	**1.90**	**1.87**	**1.85**	**1.83**	**1.82**	**1.81**	**1.80**	**1.78**
60	6.30	3.90	3.16	2.80	*2.59*	**2.35**	**2.22**	**2.12**	**2.05**	**2.01**	**1.97**	**1.95**	**1.93**	**1.90**	**1.88**	**1.86**	**1.85**	**1.84**	**1.83**	**1.81**
75	6.50	4.01	3.24	2.87	*2.66*	**2.41**	**2.27**	**2.17**	**2.10**	**2.05**	**2.02**	**1.99**	**1.97**	**1.94**	**1.92**	**1.90**	**1.89**	**1.88**	**1.86**	**1.85**
100	6.76	4.15	3.36	2.97	*2.74*	**2.48**	**2.34**	**2.23**	**2.16**	**2.11**	**2.07**	**2.05**	**2.02**	**1.99**	**1.97**	**1.95**	**1.94**	**1.93**	**1.91**	**1.90**
125	6.96	4.27	3.44	3.04	2.81	*2.54*	**2.39**	**2.28**	**2.20**	**2.15**	**2.12**	**2.09**	**2.06**	**2.03**	**2.01**	**1.99**	**1.98**	**1.97**	**1.95**	**1.93**
150	7.12	4.35	3.51	3.10	2.86	*2.58*	**2.43**	**2.32**	**2.24**	**2.19**	**2.15**	**2.12**	**2.10**	**2.06**	**2.04**	**2.02**	**2.01**	**2.00**	**1.98**	**1.96**
175	7.25	4.43	3.57	3.15	2.90	*2.62*	**2.47**	**2.35**	**2.27**	**2.22**	**2.18**	**2.15**	**2.12**	**2.09**	**2.06**	**2.05**	**2.03**	**2.02**	**2.00**	**1.99**
200	7.36	4.49	3.62	3.19	2.94	*2.66*	**2.50**	**2.38**	**2.30**	**2.24**	**2.20**	**2.17**	**2.15**	**2.11**	**2.09**	**2.07**	**2.05**	**2.04**	**2.02**	**2.01**

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Table 19-4. κ-Multipliers for Modified Calif. Interwell Prediction Limits on Observations (10 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.01	**2.08**	**1.77**	**1.62**	**1.53**	**1.42**	**1.36**	**1.32**	**1.29**	**1.27**	**1.25**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**	**1.20**	**1.19**	**1.19**	**1.18**
2	3.68	**2.44**	**2.05**	**1.86**	**1.75**	**1.62**	**1.55**	**1.49**	**1.46**	**1.43**	**1.41**	**1.40**	**1.39**	**1.37**	**1.36**	**1.35**	**1.35**	**1.34**	**1.33**	**1.32**
3	4.08	**2.66**	**2.22**	**2.00**	**1.88**	**1.73**	**1.65**	**1.59**	**1.55**	**1.52**	**1.50**	**1.49**	**1.48**	**1.46**	**1.44**	**1.43**	**1.43**	**1.42**	**1.41**	**1.40**
4	4.36	**2.82**	**2.34**	**2.11**	**1.97**	**1.81**	**1.72**	**1.66**	**1.62**	**1.59**	**1.56**	**1.55**	**1.54**	**1.52**	**1.50**	**1.49**	**1.48**	**1.48**	**1.47**	**1.46**
5	4.58	2.94	**2.43**	**2.18**	**2.04**	**1.87**	**1.78**	**1.71**	**1.67**	**1.64**	**1.61**	**1.59**	**1.58**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**	**1.51**	**1.50**
8	5.04	3.20	**2.62**	**2.35**	**2.18**	**2.00**	**1.90**	**1.82**	**1.77**	**1.74**	**1.71**	**1.69**	**1.68**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**	**1.59**
12	5.44	3.41	**2.79**	**2.49**	**2.31**	**2.11**	**2.00**	**1.91**	**1.86**	**1.82**	**1.79**	**1.77**	**1.76**	**1.73**	**1.71**	**1.70**	**1.69**	**1.68**	**1.67**	**1.66**
16	5.71	3.57	*2.91*	**2.59**	**2.40**	**2.18**	**2.07**	**1.98**	**1.92**	**1.88**	**1.85**	**1.83**	**1.81**	**1.78**	**1.77**	**1.75**	**1.74**	**1.73**	**1.72**	**1.71**
20	5.92	3.69	3.00	**2.66**	**2.47**	**2.24**	**2.12**	**2.03**	**1.97**	**1.93**	**1.90**	**1.87**	**1.85**	**1.83**	**1.81**	**1.79**	**1.78**	**1.77**	**1.76**	**1.75**
30	6.30	3.90	3.16	*2.80*	**2.59**	**2.35**	**2.22**	**2.12**	**2.05**	**2.01**	**1.97**	**1.95**	**1.93**	**1.90**	**1.88**	**1.86**	**1.85**	**1.84**	**1.83**	**1.81**
40	6.56	4.04	3.27	*2.90*	**2.67**	**2.42**	**2.29**	**2.18**	**2.11**	**2.07**	**2.03**	**2.00**	**1.98**	**1.95**	**1.93**	**1.91**	**1.90**	**1.89**	**1.87**	**1.86**
50	6.76	4.15	3.36	*2.97*	**2.74**	**2.48**	**2.34**	**2.23**	**2.16**	**2.11**	**2.07**	**2.05**	**2.02**	**1.99**	**1.97**	**1.95**	**1.94**	**1.93**	**1.91**	**1.90**
60	6.92	4.25	3.43	3.03	**2.79**	**2.53**	**2.38**	**2.27**	**2.20**	**2.14**	**2.11**	**2.08**	**2.06**	**2.02**	**2.00**	**1.98**	**1.97**	**1.96**	**1.94**	**1.93**
75	7.12	4.35	3.51	3.10	*2.86*	**2.58**	**2.43**	**2.32**	**2.24**	**2.19**	**2.15**	**2.12**	**2.10**	**2.06**	**2.04**	**2.02**	**2.01**	**2.00**	**1.98**	**1.96**
100	7.36	4.49	3.62	3.19	*2.94*	**2.66**	**2.50**	**2.38**	**2.30**	**2.24**	**2.20**	**2.17**	**2.15**	**2.11**	**2.09**	**2.07**	**2.05**	**2.04**	**2.02**	**2.01**
125	7.55	4.60	3.70	3.27	*3.01*	**2.71**	**2.55**	**2.42**	**2.34**	**2.29**	**2.24**	**2.21**	**2.19**	**2.15**	**2.12**	**2.10**	**2.09**	**2.08**	**2.06**	**2.04**
150	7.71	4.69	3.77	3.32	*3.06*	**2.76**	**2.59**	**2.46**	**2.38**	**2.32**	**2.28**	**2.25**	**2.22**	**2.18**	**2.15**	**2.13**	**2.12**	**2.11**	**2.08**	**2.07**
175	7.83	4.76	3.82	3.37	3.10	*2.80*	**2.62**	**2.49**	**2.41**	**2.35**	**2.31**	**2.27**	**2.25**	**2.21**	**2.18**	**2.16**	**2.14**	**2.13**	**2.11**	**2.09**
200	7.94	4.82	3.87	3.41	3.14	*2.83*	**2.65**	**2.52**	**2.44**	**2.38**	**2.33**	**2.30**	**2.27**	**2.23**	**2.20**	**2.18**	**2.16**	**2.15**	**2.13**	**2.11**

Table 19-4. κ-Multipliers for Modified Calif. Interwell Prediction Limits on Observations (10 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.68	**2.44**	**2.05**	**1.86**	**1.75**	**1.62**	**1.55**	**1.49**	**1.46**	**1.43**	**1.41**	**1.40**	**1.39**	**1.37**	**1.36**	**1.35**	**1.35**	**1.34**	**1.33**	**1.32**
2	4.36	**2.82**	**2.34**	**2.11**	**1.97**	**1.81**	**1.72**	**1.66**	**1.62**	**1.59**	**1.56**	**1.55**	**1.54**	**1.52**	**1.50**	**1.49**	**1.48**	**1.48**	**1.47**	**1.46**
3	4.76	**3.04**	**2.51**	**2.25**	**2.09**	**1.92**	**1.83**	**1.75**	**1.71**	**1.67**	**1.65**	**1.63**	**1.62**	**1.60**	**1.58**	**1.57**	**1.56**	**1.56**	**1.54**	**1.54**
4	5.04	3.20	**2.62**	**2.35**	**2.18**	**2.00**	**1.90**	**1.82**	**1.77**	**1.74**	**1.71**	**1.69**	**1.68**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**	**1.59**
5	5.26	3.32	**2.72**	**2.43**	**2.25**	**2.06**	**1.95**	**1.87**	**1.82**	**1.78**	**1.76**	**1.74**	**1.72**	**1.70**	**1.68**	**1.67**	**1.66**	**1.65**	**1.64**	**1.63**
8	5.71	3.57	**2.91**	**2.59**	**2.40**	**2.18**	**2.07**	**1.98**	**1.92**	**1.88**	**1.85**	**1.83**	**1.81**	**1.78**	**1.77**	**1.75**	**1.74**	**1.73**	**1.72**	**1.71**
12	6.09	3.78	**3.07**	**2.72**	**2.52**	**2.29**	**2.16**	**2.07**	**2.01**	**1.96**	**1.93**	**1.91**	**1.89**	**1.86**	**1.84**	**1.83**	**1.81**	**1.80**	**1.79**	**1.78**
16	6.36	3.93	*3.18*	**2.82**	**2.61**	**2.37**	**2.23**	**2.13**	**2.07**	**2.02**	**1.99**	**1.96**	**1.94**	**1.91**	**1.89**	**1.88**	**1.86**	**1.85**	**1.84**	**1.83**
20	6.56	4.04	3.27	**2.90**	**2.67**	**2.42**	**2.29**	**2.18**	**2.11**	**2.07**	**2.03**	**2.00**	**1.98**	**1.95**	**1.93**	**1.91**	**1.90**	**1.89**	**1.87**	**1.86**
30	6.92	4.25	3.43	**3.03**	**2.79**	**2.53**	**2.38**	**2.27**	**2.20**	**2.14**	**2.11**	**2.08**	**2.06**	**2.02**	**2.00**	**1.98**	**1.97**	**1.96**	**1.94**	**1.93**
40	7.17	4.39	3.53	*3.12*	**2.88**	**2.60**	**2.45**	**2.33**	**2.25**	**2.20**	**2.16**	**2.13**	**2.11**	**2.07**	**2.05**	**2.03**	**2.02**	**2.01**	**1.99**	**1.97**
50	7.36	4.49	3.62	*3.19*	**2.94**	**2.66**	**2.50**	**2.38**	**2.30**	**2.24**	**2.20**	**2.17**	**2.15**	**2.11**	**2.09**	**2.07**	**2.05**	**2.04**	**2.02**	**2.01**
60	7.52	4.58	3.69	*3.25*	**2.99**	**2.70**	**2.54**	**2.41**	**2.33**	**2.28**	**2.24**	**2.21**	**2.18**	**2.14**	**2.12**	**2.10**	**2.08**	**2.07**	**2.05**	**2.04**
75	7.71	4.69	3.77	3.32	**3.06**	**2.76**	**2.59**	**2.46**	**2.38**	**2.32**	**2.28**	**2.25**	**2.22**	**2.18**	**2.15**	**2.13**	**2.12**	**2.11**	**2.08**	**2.07**
100	7.94	4.82	3.87	3.41	*3.14*	**2.83**	**2.65**	**2.52**	**2.44**	**2.38**	**2.33**	**2.30**	**2.27**	**2.23**	**2.20**	**2.18**	**2.16**	**2.15**	**2.13**	**2.11**
125	8.12	4.93	3.95	3.48	*3.20*	**2.88**	**2.70**	**2.57**	**2.48**	**2.42**	**2.37**	**2.34**	**2.31**	**2.27**	**2.24**	**2.22**	**2.20**	**2.19**	**2.16**	**2.15**
150	8.27	5.01	4.02	3.54	*3.25*	**2.93**	**2.74**	**2.60**	**2.51**	**2.45**	**2.40**	**2.37**	**2.34**	**2.30**	**2.27**	**2.24**	**2.23**	**2.21**	**2.19**	**2.17**
175	8.38	5.08	4.07	3.58	*3.29*	**2.96**	**2.78**	**2.64**	**2.54**	**2.48**	**2.43**	**2.39**	**2.37**	**2.32**	**2.29**	**2.27**	**2.25**	**2.24**	**2.21**	**2.20**
200	8.49	5.14	4.12	3.62	*3.33*	**2.99**	**2.81**	**2.66**	**2.57**	**2.50**	**2.46**	**2.42**	**2.39**	**2.34**	**2.31**	**2.29**	**2.27**	**2.26**	**2.23**	**2.22**

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Table 19-4. κ-Multipliers for Modified Calif. Interwell Prediction Limits on Observations (20 COC, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.13	**2.11**	**1.79**	**1.63**	**1.53**	**1.42**	**1.37**	**1.32**	**1.29**	**1.27**	**1.26**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**	**1.20**	**1.19**	**1.19**	**1.18**
2	3.89	**2.50**	**2.08**	**1.88**	**1.76**	**1.62**	**1.55**	**1.49**	**1.46**	**1.43**	**1.41**	**1.40**	**1.39**	**1.37**	**1.36**	**1.35**	**1.35**	**1.34**	**1.33**	**1.32**
3	4.36	2.74	**2.25**	**2.02**	**1.89**	**1.74**	**1.65**	**1.59**	**1.55**	**1.52**	**1.50**	**1.49**	**1.48**	**1.46**	**1.44**	**1.44**	**1.43**	**1.42**	**1.41**	**1.40**
4	4.71	2.91	**2.38**	**2.13**	**1.98**	**1.82**	**1.73**	**1.66**	**1.62**	**1.59**	**1.57**	**1.55**	**1.54**	**1.52**	**1.50**	**1.49**	**1.48**	**1.48**	**1.47**	**1.46**
5	4.98	3.05	**2.48**	**2.21**	**2.05**	**1.88**	**1.79**	**1.71**	**1.67**	**1.64**	**1.61**	**1.60**	**1.58**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**	**1.51**	**1.50**
8	5.56	3.34	*2.69*	**2.38**	**2.21**	**2.01**	**1.90**	**1.82**	**1.77**	**1.74**	**1.71**	**1.69**	**1.68**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**	**1.59**
12	6.06	3.59	2.87	*2.53*	**2.34**	**2.12**	**2.01**	**1.92**	**1.86**	**1.82**	**1.80**	**1.77**	**1.76**	**1.73**	**1.71**	**1.70**	**1.69**	**1.68**	**1.67**	**1.66**
16	6.42	3.76	3.00	*2.64*	**2.43**	**2.20**	**2.08**	**1.98**	**1.92**	**1.88**	**1.85**	**1.83**	**1.81**	**1.79**	**1.77**	**1.75**	**1.74**	**1.73**	**1.72**	**1.71**
20	6.69	3.90	3.10	*2.72*	**2.50**	**2.26**	**2.13**	**2.03**	**1.97**	**1.93**	**1.90**	**1.87**	**1.86**	**1.83**	**1.81**	**1.79**	**1.78**	**1.77**	**1.76**	**1.75**
30	7.19	4.15	3.28	2.87	*2.63*	**2.37**	**2.23**	**2.12**	**2.06**	**2.01**	**1.98**	**1.95**	**1.93**	**1.90**	**1.88**	**1.86**	**1.85**	**1.84**	**1.83**	**1.82**
40	7.53	4.32	3.40	2.97	*2.73*	**2.45**	**2.30**	**2.19**	**2.12**	**2.07**	**2.03**	**2.01**	**1.99**	**1.95**	**1.93**	**1.91**	**1.90**	**1.89**	**1.87**	**1.86**
50	7.79	4.45	3.50	3.05	2.80	*2.51*	**2.35**	**2.24**	**2.17**	**2.11**	**2.08**	**2.05**	**2.03**	**1.99**	**1.97**	**1.95**	**1.94**	**1.93**	**1.91**	**1.90**
60	8.00	4.56	3.58	3.12	2.85	*2.56*	**2.40**	**2.28**	**2.20**	**2.15**	**2.11**	**2.08**	**2.06**	**2.03**	**2.00**	**1.98**	**1.97**	**1.96**	**1.94**	**1.93**
75	8.25	4.69	3.67	3.20	2.92	*2.62*	**2.45**	**2.33**	**2.25**	**2.19**	**2.15**	**2.12**	**2.10**	**2.06**	**2.04**	**2.02**	**2.01**	**2.00**	**1.98**	**1.96**
100	8.58	4.86	3.80	3.30	3.01	*2.70*	*2.52*	**2.39**	**2.31**	**2.25**	**2.21**	**2.18**	**2.15**	**2.11**	**2.09**	**2.07**	**2.05**	**2.04**	**2.02**	**2.01**
125	8.83	4.98	3.89	3.38	3.08	*2.75*	*2.57*	**2.44**	**2.35**	**2.29**	**2.25**	**2.22**	**2.19**	**2.15**	**2.13**	**2.11**	**2.09**	**2.08**	**2.06**	**2.04**
150	9.02	5.09	3.97	3.44	3.14	2.80	*2.62*	**2.48**	**2.39**	**2.33**	**2.28**	**2.25**	**2.22**	**2.18**	**2.16**	**2.14**	**2.12**	**2.11**	**2.09**	**2.07**
175	9.19	5.17	4.03	3.50	3.19	2.84	*2.65*	*2.51*	**2.42**	**2.36**	**2.31**	**2.28**	**2.25**	**2.21**	**2.18**	**2.16**	**2.14**	**2.13**	**2.11**	**2.09**
200	9.33	5.25	4.09	3.54	3.23	2.88	*2.68*	*2.54*	**2.45**	**2.38**	**2.34**	**2.30**	**2.27**	**2.23**	**2.20**	**2.18**	**2.17**	**2.15**	**2.13**	**2.11**

Table 19-4. κ-Multipliers for Modified Calif. Interwell Prediction Limits on Observations (20 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.89	**2.50**	**2.08**	**1.88**	**1.76**	**1.62**	**1.55**	**1.49**	**1.46**	**1.43**	**1.41**	**1.40**	**1.39**	**1.37**	**1.36**	**1.35**	**1.35**	**1.34**	**1.33**	**1.32**
2	4.71	2.91	**2.38**	**2.13**	**1.98**	**1.82**	**1.73**	**1.66**	**1.62**	**1.59**	**1.57**	**1.55**	**1.54**	**1.52**	**1.50**	**1.49**	**1.48**	**1.48**	**1.47**	**1.46**
3	5.21	3.16	**2.56**	**2.28**	**2.11**	**1.93**	**1.83**	**1.76**	**1.71**	**1.68**	**1.65**	**1.63**	**1.62**	**1.60**	**1.58**	**1.57**	**1.56**	**1.56**	**1.54**	**1.54**
4	5.56	3.34	**2.69**	**2.38**	**2.21**	**2.01**	**1.90**	**1.82**	**1.77**	**1.74**	**1.71**	**1.69**	**1.68**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**	**1.59**
5	5.84	3.47	**2.79**	**2.46**	**2.28**	**2.07**	**1.96**	**1.88**	**1.82**	**1.79**	**1.76**	**1.74**	**1.72**	**1.70**	**1.68**	**1.67**	**1.66**	**1.65**	**1.64**	**1.63**
8	6.42	3.76	3.00	**2.64**	**2.43**	**2.20**	**2.08**	**1.98**	**1.92**	**1.88**	**1.85**	**1.83**	**1.81**	**1.79**	**1.77**	**1.75**	**1.74**	**1.73**	**1.72**	**1.71**
12	6.91	4.01	3.18	**2.79**	**2.56**	**2.31**	**2.18**	**2.08**	**2.01**	**1.97**	**1.93**	**1.91**	**1.89**	**1.86**	**1.84**	**1.83**	**1.81**	**1.81**	**1.79**	**1.78**
16	7.26	4.19	3.30	*2.89*	**2.65**	**2.39**	**2.25**	**2.14**	**2.07**	**2.03**	**1.99**	**1.96**	**1.94**	**1.91**	**1.89**	**1.88**	**1.86**	**1.85**	**1.84**	**1.83**
20	7.53	4.32	3.40	*2.97*	**2.73**	**2.45**	**2.30**	**2.19**	**2.12**	**2.07**	**2.03**	**2.01**	**1.99**	**1.95**	**1.93**	**1.91**	**1.90**	**1.89**	**1.87**	**1.86**
30	8.00	4.56	3.58	3.12	*2.85*	**2.56**	**2.40**	**2.28**	**2.20**	**2.15**	**2.11**	**2.08**	**2.06**	**2.03**	**2.00**	**1.98**	**1.97**	**1.96**	**1.94**	**1.93**
40	8.33	4.73	3.70	3.22	*2.94*	**2.64**	**2.47**	**2.34**	**2.26**	**2.21**	**2.17**	**2.14**	**2.11**	**2.08**	**2.05**	**2.03**	**2.02**	**2.01**	**1.99**	**1.97**
50	8.58	4.86	3.80	3.30	*3.01*	**2.70**	**2.52**	**2.39**	**2.31**	**2.25**	**2.21**	**2.18**	**2.15**	**2.11**	**2.09**	**2.07**	**2.05**	**2.04**	**2.02**	**2.01**
60	8.78	4.96	3.87	3.37	3.07	**2.74**	**2.56**	**2.43**	**2.35**	**2.29**	**2.24**	**2.21**	**2.18**	**2.15**	**2.12**	**2.10**	**2.08**	**2.07**	**2.05**	**2.04**
75	9.02	5.09	3.97	3.44	3.14	*2.80*	**2.62**	**2.48**	**2.39**	**2.33**	**2.28**	**2.25**	**2.22**	**2.18**	**2.16**	**2.14**	**2.12**	**2.11**	**2.09**	**2.07**
100	9.33	5.25	4.09	3.54	3.23	*2.88*	**2.68**	**2.54**	**2.45**	**2.38**	**2.34**	**2.30**	**2.27**	**2.23**	**2.20**	**2.18**	**2.17**	**2.15**	**2.13**	**2.11**
125	9.57	5.37	4.18	3.62	3.30	*2.93*	**2.74**	**2.59**	**2.49**	**2.43**	**2.38**	**2.34**	**2.31**	**2.27**	**2.24**	**2.22**	**2.20**	**2.19**	**2.16**	**2.15**
150	9.77	5.47	4.25	3.68	3.35	*2.98*	**2.78**	**2.63**	**2.53**	**2.46**	**2.41**	**2.37**	**2.34**	**2.30**	**2.27**	**2.25**	**2.23**	**2.22**	**2.19**	**2.17**
175	9.93	5.55	4.31	3.73	3.40	*3.02*	*2.81*	**2.66**	**2.56**	**2.49**	**2.44**	**2.40**	**2.37**	**2.33**	**2.29**	**2.27**	**2.25**	**2.24**	**2.21**	**2.20**
200	10.06	5.62	4.37	3.78	3.44	*3.05*	*2.85*	**2.69**	**2.59**	**2.52**	**2.46**	**2.43**	**2.39**	**2.35**	**2.32**	**2.29**	**2.27**	**2.26**	**2.23**	**2.22**

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Table 19-4. κ-Multipliers for Modified Calif. Interwell Prediction Limits on Observations (20 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	4.72	**2.92**	**2.38**	**2.13**	**1.98**	**1.82**	**1.73**	**1.66**	**1.62**	**1.59**	**1.57**	**1.55**	**1.54**	**1.52**	**1.50**	**1.49**	**1.48**	**1.48**	**1.47**	**1.46**
2	5.57	3.33	**2.69**	**2.38**	**2.21**	**2.01**	**1.90**	**1.82**	**1.77**	**1.74**	**1.71**	**1.69**	**1.68**	**1.66**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**	**1.59**
3	6.06	3.59	**2.87**	**2.53**	**2.34**	**2.12**	**2.01**	**1.92**	**1.86**	**1.82**	**1.79**	**1.77**	**1.76**	**1.73**	**1.71**	**1.70**	**1.69**	**1.68**	**1.67**	**1.66**
4	6.42	3.76	**3.00**	**2.64**	**2.43**	**2.20**	**2.08**	**1.98**	**1.92**	**1.88**	**1.85**	**1.83**	**1.81**	**1.79**	**1.77**	**1.75**	**1.74**	**1.73**	**1.72**	**1.71**
5	6.69	3.90	*3.10*	**2.72**	**2.50**	**2.26**	**2.13**	**2.03**	**1.97**	**1.93**	**1.90**	**1.88**	**1.85**	**1.83**	**1.81**	**1.79**	**1.78**	**1.77**	**1.76**	**1.75**
8	7.27	4.19	3.30	**2.89**	**2.66**	**2.39**	**2.25**	**2.14**	**2.07**	**2.03**	**1.99**	**1.96**	**1.94**	**1.91**	**1.89**	**1.88**	**1.86**	**1.85**	**1.84**	**1.83**
12	7.73	4.42	3.48	**3.04**	**2.78**	**2.50**	**2.34**	**2.23**	**2.16**	**2.11**	**2.07**	**2.04**	**2.02**	**1.99**	**1.96**	**1.95**	**1.93**	**1.92**	**1.90**	**1.89**
16	8.09	4.60	3.60	3.14	**2.87**	**2.58**	**2.41**	**2.29**	**2.22**	**2.16**	**2.12**	**2.09**	**2.07**	**2.04**	**2.01**	**2.00**	**1.98**	**1.97**	**1.95**	**1.94**
20	8.32	4.73	3.70	3.22	**2.94**	**2.64**	**2.47**	**2.34**	**2.26**	**2.21**	**2.17**	**2.14**	**2.11**	**2.08**	**2.05**	**2.03**	**2.02**	**2.01**	**1.99**	**1.97**
30	8.79	4.97	3.87	3.37	**3.07**	**2.74**	**2.56**	**2.43**	**2.35**	**2.29**	**2.24**	**2.21**	**2.18**	**2.15**	**2.12**	**2.10**	**2.08**	**2.07**	**2.05**	**2.04**
40	9.08	5.13	3.99	3.46	*3.16*	**2.82**	**2.63**	**2.49**	**2.40**	**2.34**	**2.30**	**2.26**	**2.24**	**2.20**	**2.17**	**2.15**	**2.13**	**2.12**	**2.09**	**2.08**
50	9.35	5.24	4.09	3.54	*3.23*	**2.87**	**2.68**	**2.54**	**2.45**	**2.38**	**2.34**	**2.30**	**2.27**	**2.23**	**2.20**	**2.18**	**2.17**	**2.15**	**2.13**	**2.11**
60	9.52	5.35	4.16	3.60	*3.28*	**2.92**	**2.73**	**2.58**	**2.48**	**2.42**	**2.37**	**2.33**	**2.31**	**2.26**	**2.23**	**2.21**	**2.19**	**2.18**	**2.16**	**2.14**
75	9.76	5.46	4.25	3.68	3.35	**2.98**	**2.78**	**2.63**	**2.53**	**2.46**	**2.41**	**2.37**	**2.34**	**2.30**	**2.27**	**2.25**	**2.23**	**2.22**	**2.19**	**2.17**
100	10.08	5.62	4.37	3.78	3.44	**3.05**	**2.85**	**2.69**	**2.59**	**2.52**	**2.46**	**2.42**	**2.39**	**2.35**	**2.32**	**2.29**	**2.27**	**2.26**	**2.23**	**2.22**
125	10.28	5.74	4.45	3.85	3.50	*3.11*	**2.90**	**2.73**	**2.63**	**2.56**	**2.50**	**2.46**	**2.43**	**2.38**	**2.35**	**2.33**	**2.31**	**2.29**	**2.27**	**2.25**
150	10.49	5.84	4.53	3.91	3.56	*3.16*	**2.94**	**2.77**	**2.67**	**2.59**	**2.54**	**2.50**	**2.46**	**2.42**	**2.38**	**2.35**	**2.34**	**2.32**	**2.29**	**2.27**
175	10.63	5.92	4.58	3.96	3.60	*3.20*	**2.97**	**2.80**	**2.70**	**2.62**	**2.57**	**2.52**	**2.49**	**2.44**	**2.40**	**2.38**	**2.36**	**2.34**	**2.32**	**2.30**
200	10.75	5.99	4.64	4.01	3.64	*3.23*	**3.00**	**2.83**	**2.72**	**2.64**	**2.59**	**2.55**	**2.51**	**2.46**	**2.43**	**2.40**	**2.38**	**2.36**	**2.33**	**2.32**

Table 19-4. κ-Multipliers for Modified Calif. Interwell Prediction Limits on Observations (40 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	4.02	**2.53**	**2.09**	**1.88**	**1.76**	**1.63**	**1.55**	**1.49**	**1.46**	**1.43**	**1.41**	**1.40**	**1.39**	**1.37**	**1.36**	**1.35**	**1.35**	**1.34**	**1.33**	**1.32**
2	4.97	2.97	**2.40**	**2.14**	**1.99**	**1.82**	**1.73**	**1.66**	**1.62**	**1.59**	**1.57**	**1.55**	**1.54**	**1.52**	**1.50**	**1.49**	**1.48**	**1.48**	**1.47**	**1.46**
3	5.56	3.24	*2.59*	**2.29**	**2.12**	**1.94**	**1.83**	**1.76**	**1.71**	**1.68**	**1.65**	**1.63**	**1.62**	**1.60**	**1.58**	**1.57**	**1.56**	**1.56**	**1.54**	**1.54**
4	5.99	3.43	2.73	**2.40**	**2.22**	**2.02**	**1.91**	**1.83**	**1.77**	**1.74**	**1.71**	**1.69**	**1.68**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**	**1.59**
5	6.34	3.58	2.83	**2.49**	**2.29**	**2.08**	**1.96**	**1.88**	**1.82**	**1.79**	**1.76**	**1.74**	**1.72**	**1.70**	**1.68**	**1.67**	**1.66**	**1.65**	**1.64**	**1.63**
8	7.06	3.91	3.06	*2.67*	**2.45**	**2.21**	**2.08**	**1.99**	**1.93**	**1.89**	**1.85**	**1.83**	**1.81**	**1.79**	**1.77**	**1.75**	**1.74**	**1.73**	**1.72**	**1.71**
12	7.70	4.19	3.26	2.83	*2.59*	**2.32**	**2.18**	**2.08**	**2.01**	**1.97**	**1.94**	**1.91**	**1.89**	**1.86**	**1.84**	**1.83**	**1.81**	**1.81**	**1.79**	**1.78**
16	8.14	4.40	3.40	2.94	*2.68*	**2.40**	**2.26**	**2.14**	**2.08**	**2.03**	**1.99**	**1.97**	**1.95**	**1.91**	**1.89**	**1.88**	**1.86**	**1.85**	**1.84**	**1.83**
20	8.49	4.56	3.50	3.03	2.76	**2.47**	**2.31**	**2.19**	**2.12**	**2.07**	**2.04**	**2.01**	**1.99**	**1.95**	**1.93**	**1.92**	**1.90**	**1.89**	**1.87**	**1.86**
30	9.10	4.83	3.70	3.19	2.90	*2.58*	**2.41**	**2.29**	**2.21**	**2.15**	**2.11**	**2.08**	**2.06**	**2.03**	**2.00**	**1.98**	**1.97**	**1.96**	**1.94**	**1.93**
40	9.53	5.03	3.84	3.30	2.99	*2.66*	**2.48**	**2.35**	**2.27**	**2.21**	**2.17**	**2.14**	**2.11**	**2.08**	**2.05**	**2.03**	**2.02**	**2.01**	**1.99**	**1.97**
50	9.86	5.19	3.95	3.39	3.07	*2.72*	*2.54*	**2.40**	**2.31**	**2.25**	**2.21**	**2.18**	**2.15**	**2.12**	**2.09**	**2.07**	**2.06**	**2.04**	**2.02**	**2.01**
60	10.13	5.31	4.03	3.45	3.13	*2.77*	*2.58*	**2.44**	**2.35**	**2.29**	**2.25**	**2.21**	**2.19**	**2.15**	**2.12**	**2.10**	**2.08**	**2.07**	**2.05**	**2.04**
75	10.45	5.46	4.14	3.54	3.20	2.83	*2.64*	**2.49**	**2.40**	**2.33**	**2.29**	**2.25**	**2.23**	**2.19**	**2.16**	**2.14**	**2.12**	**2.11**	**2.09**	**2.07**
100	10.86	5.65	4.27	3.65	3.30	2.91	*2.71*	*2.55*	**2.46**	**2.39**	**2.34**	**2.31**	**2.28**	**2.23**	**2.20**	**2.18**	**2.17**	**2.15**	**2.13**	**2.11**
125	11.17	5.80	4.38	3.74	3.37	2.97	*2.76*	*2.60*	*2.50*	**2.43**	**2.38**	**2.34**	**2.32**	**2.27**	**2.24**	**2.22**	**2.20**	**2.19**	**2.16**	**2.15**
150	11.43	5.92	4.46	3.80	3.43	3.02	*2.80*	*2.64*	*2.54*	**2.47**	**2.42**	**2.38**	**2.35**	**2.30**	**2.27**	**2.25**	**2.23**	**2.22**	**2.19**	**2.17**
175	11.63	6.02	4.53	3.86	3.48	3.06	2.84	*2.67*	*2.57*	*2.50*	**2.45**	**2.41**	**2.37**	**2.33**	**2.30**	**2.27**	**2.25**	**2.24**	**2.21**	**2.20**
200	11.82	6.10	4.59	3.91	3.52	3.10	2.87	*2.70*	*2.60*	*2.52*	**2.47**	**2.43**	**2.40**	**2.35**	**2.32**	**2.29**	**2.27**	**2.26**	**2.23**	**2.22**

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Table 19-4. κ-Multipliers for Modified Calif. Interwell Prediction Limits on Observations (40 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	4.97	2.97	**2.40**	**2.14**	**1.99**	**1.82**	**1.73**	**1.66**	**1.62**	**1.59**	**1.57**	**1.55**	**1.54**	**1.52**	**1.50**	**1.49**	**1.48**	**1.48**	**1.47**	**1.46**
2	5.99	3.43	**2.73**	**2.40**	**2.22**	**2.02**	**1.91**	**1.83**	**1.77**	**1.74**	**1.71**	**1.69**	**1.68**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**	**1.59**
3	6.62	3.71	*2.92*	**2.56**	**2.35**	**2.13**	**2.01**	**1.92**	**1.86**	**1.82**	**1.80**	**1.77**	**1.76**	**1.73**	**1.72**	**1.70**	**1.69**	**1.68**	**1.67**	**1.66**
4	7.06	3.91	3.06	**2.67**	**2.45**	**2.21**	**2.08**	**1.99**	**1.93**	**1.89**	**1.85**	**1.83**	**1.81**	**1.79**	**1.77**	**1.75**	**1.74**	**1.73**	**1.72**	**1.71**
5	7.41	4.07	3.17	**2.76**	**2.53**	**2.27**	**2.14**	**2.04**	**1.98**	**1.93**	**1.90**	**1.88**	**1.86**	**1.83**	**1.81**	**1.79**	**1.78**	**1.77**	**1.76**	**1.75**
8	8.14	4.40	3.40	*2.94*	**2.68**	**2.40**	**2.26**	**2.14**	**2.08**	**2.03**	**1.99**	**1.97**	**1.95**	**1.91**	**1.89**	**1.88**	**1.86**	**1.85**	**1.84**	**1.83**
12	8.76	4.68	3.59	3.10	*2.82*	**2.52**	**2.36**	**2.24**	**2.16**	**2.11**	**2.07**	**2.04**	**2.02**	**1.99**	**1.96**	**1.95**	**1.93**	**1.92**	**1.90**	**1.89**
16	9.20	4.88	3.73	3.21	*2.92*	**2.60**	**2.43**	**2.30**	**2.22**	**2.17**	**2.13**	**2.10**	**2.07**	**2.04**	**2.01**	**2.00**	**1.98**	**1.97**	**1.95**	**1.94**
20	9.53	5.03	3.84	3.30	*2.99*	**2.66**	**2.48**	**2.35**	**2.27**	**2.21**	**2.17**	**2.14**	**2.11**	**2.08**	**2.05**	**2.03**	**2.02**	**2.01**	**1.99**	**1.97**
30	10.13	5.31	4.03	3.45	3.13	**2.77**	**2.58**	**2.44**	**2.35**	**2.29**	**2.25**	**2.21**	**2.19**	**2.15**	**2.12**	**2.10**	**2.08**	**2.07**	**2.05**	**2.04**
40	10.54	5.50	4.17	3.56	3.22	*2.85*	**2.65**	**2.50**	**2.41**	**2.35**	**2.30**	**2.27**	**2.24**	**2.20**	**2.17**	**2.15**	**2.13**	**2.12**	**2.10**	**2.08**
50	10.86	5.65	4.27	3.65	3.30	*2.91*	**2.71**	**2.55**	**2.46**	**2.39**	**2.34**	**2.31**	**2.28**	**2.23**	**2.20**	**2.18**	**2.17**	**2.15**	**2.13**	**2.11**
60	11.11	5.77	4.36	3.72	3.36	*2.96*	**2.75**	**2.59**	**2.49**	**2.42**	**2.38**	**2.34**	**2.31**	**2.27**	**2.23**	**2.21**	**2.19**	**2.18**	**2.16**	**2.14**
75	11.43	5.92	4.46	3.80	3.43	*3.02*	*2.80*	**2.64**	**2.54**	**2.47**	**2.42**	**2.38**	**2.35**	**2.30**	**2.27**	**2.25**	**2.23**	**2.22**	**2.19**	**2.17**
100	11.82	6.10	4.59	3.91	3.52	*3.10*	*2.87*	**2.70**	**2.60**	**2.52**	**2.47**	**2.43**	**2.40**	**2.35**	**2.32**	**2.29**	**2.27**	**2.26**	**2.23**	**2.22**
125	12.11	6.24	4.69	3.99	3.59	3.16	*2.92*	**2.75**	**2.64**	**2.57**	**2.51**	**2.47**	**2.44**	**2.39**	**2.35**	**2.33**	**2.31**	**2.29**	**2.27**	**2.25**
150	12.35	6.36	4.78	4.06	3.65	3.21	*2.97*	*2.79*	**2.68**	**2.60**	**2.54**	**2.50**	**2.47**	**2.42**	**2.38**	**2.36**	**2.34**	**2.32**	**2.29**	**2.28**
175	12.56	6.46	4.84	4.12	3.70	3.25	*3.00*	*2.82*	**2.71**	**2.63**	**2.57**	**2.53**	**2.49**	**2.44**	**2.41**	**2.38**	**2.36**	**2.34**	**2.32**	**2.30**
200	12.73	6.53	4.90	4.17	3.75	3.28	*3.04*	*2.85*	**2.73**	**2.65**	**2.60**	**2.55**	**2.52**	**2.46**	**2.43**	**2.40**	**2.38**	**2.36**	**2.34**	**2.32**

Table 19-4. κ-Multipliers for Modified Calif. Interwell Prediction Limits on Observations (40 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	5.99	3.43	**2.73**	**2.40**	**2.22**	**2.02**	**1.91**	**1.83**	**1.77**	**1.74**	**1.71**	**1.69**	**1.68**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**	**1.59**
2	7.06	3.91	**3.06**	**2.67**	**2.45**	**2.21**	**2.08**	**1.99**	**1.93**	**1.89**	**1.85**	**1.83**	**1.81**	**1.79**	**1.77**	**1.75**	**1.74**	**1.73**	**1.72**	**1.71**
3	7.70	4.19	3.26	**2.83**	**2.59**	**2.32**	**2.18**	**2.08**	**2.01**	**1.97**	**1.94**	**1.91**	**1.89**	**1.86**	**1.84**	**1.83**	**1.81**	**1.81**	**1.79**	**1.78**
4	8.14	4.40	3.40	**2.94**	**2.68**	**2.40**	**2.26**	**2.14**	**2.08**	**2.03**	**1.99**	**1.97**	**1.95**	**1.91**	**1.89**	**1.88**	**1.86**	**1.85**	**1.84**	**1.83**
5	8.49	4.56	3.50	**3.03**	**2.76**	**2.47**	**2.31**	**2.19**	**2.12**	**2.07**	**2.04**	**2.01**	**1.99**	**1.95**	**1.93**	**1.92**	**1.90**	**1.89**	**1.87**	**1.86**
8	9.20	4.88	3.73	*3.21*	**2.92**	**2.60**	**2.43**	**2.30**	**2.22**	**2.17**	**2.13**	**2.10**	**2.07**	**2.04**	**2.01**	**2.00**	**1.98**	**1.97**	**1.95**	**1.94**
12	9.80	5.16	3.93	3.37	**3.05**	**2.71**	**2.53**	**2.39**	**2.31**	**2.25**	**2.20**	**2.17**	**2.15**	**2.11**	**2.08**	**2.06**	**2.05**	**2.04**	**2.02**	**2.00**
16	10.21	5.35	4.06	3.48	*3.15*	**2.79**	**2.60**	**2.45**	**2.36**	**2.30**	**2.26**	**2.22**	**2.20**	**2.16**	**2.13**	**2.11**	**2.10**	**2.08**	**2.06**	**2.05**
20	10.54	5.50	4.17	3.56	*3.22*	**2.85**	**2.65**	**2.50**	**2.41**	**2.35**	**2.30**	**2.27**	**2.24**	**2.20**	**2.17**	**2.15**	**2.13**	**2.12**	**2.10**	**2.08**
30	11.11	5.77	4.36	3.72	3.36	**2.96**	**2.75**	**2.59**	**2.49**	**2.42**	**2.38**	**2.34**	**2.31**	**2.27**	**2.23**	**2.21**	**2.19**	**2.18**	**2.16**	**2.14**
40	11.50	5.96	4.49	3.83	3.45	**3.04**	**2.82**	**2.65**	**2.55**	**2.48**	**2.43**	**2.39**	**2.36**	**2.31**	**2.28**	**2.26**	**2.24**	**2.23**	**2.20**	**2.18**
50	11.82	6.10	4.59	3.91	3.52	*3.10*	**2.87**	**2.70**	**2.60**	**2.52**	**2.47**	**2.43**	**2.40**	**2.35**	**2.32**	**2.29**	**2.27**	**2.26**	**2.23**	**2.22**
60	12.05	6.22	4.68	3.98	3.58	*3.15*	**2.92**	**2.74**	**2.63**	**2.56**	**2.50**	**2.46**	**2.43**	**2.38**	**2.35**	**2.32**	**2.30**	**2.29**	**2.26**	**2.24**
75	12.35	6.36	4.78	4.06	3.65	*3.21*	**2.97**	**2.79**	**2.68**	**2.60**	**2.54**	**2.50**	**2.47**	**2.42**	**2.38**	**2.36**	**2.34**	**2.32**	**2.29**	**2.28**
100	12.73	6.53	4.90	4.17	3.75	*3.28*	**3.04**	**2.85**	**2.73**	**2.65**	**2.60**	**2.55**	**2.52**	**2.46**	**2.43**	**2.40**	**2.38**	**2.36**	**2.34**	**2.32**
125	13.01	6.67	5.00	4.25	3.82	*3.34*	*3.09*	**2.90**	**2.78**	**2.70**	**2.64**	**2.59**	**2.55**	**2.50**	**2.46**	**2.43**	**2.41**	**2.40**	**2.37**	**2.35**
150	13.24	6.78	5.08	4.31	3.87	*3.39*	*3.13*	**2.94**	**2.81**	**2.73**	**2.67**	**2.62**	**2.58**	**2.53**	**2.49**	**2.46**	**2.44**	**2.42**	**2.39**	**2.37**
175	13.44	6.88	5.15	4.37	3.92	3.43	*3.17*	**2.97**	**2.84**	**2.76**	**2.70**	**2.65**	**2.61**	**2.55**	**2.51**	**2.49**	**2.46**	**2.45**	**2.42**	**2.40**
200	13.61	6.95	5.21	4.41	3.96	3.47	*3.20*	**3.00**	**2.87**	**2.78**	**2.72**	**2.67**	**2.63**	**2.58**	**2.54**	**2.51**	**2.48**	**2.47**	**2.43**	**2.41**

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D STATISTICAL TABLES

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Table 19-5. κ-Multipliers for 1-of-1 Interwell Prediction Limits on Means of Order 2 (1 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.42**	**1.21**	**1.12**	**1.07**	**1.04**	**1.01**	**0.98**	**0.97**	**0.96**	**0.95**	**0.94**	**0.94**	**0.94**	**0.93**	**0.93**	**0.93**	**0.92**	**0.92**	**0.92**	**0.92**
2	**1.89**	**1.58**	**1.45**	**1.38**	**1.34**	**1.29**	**1.26**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**	**1.20**	**1.19**	**1.18**	**1.18**	**1.18**	**1.18**	**1.17**	**1.17**
3	**2.17**	**1.79**	**1.64**	**1.56**	**1.51**	**1.45**	**1.41**	**1.39**	**1.37**	**1.36**	**1.35**	**1.34**	**1.34**	**1.33**	**1.32**	**1.32**	**1.31**	**1.31**	**1.31**	**1.30**
4	**2.37**	**1.94**	**1.77**	**1.68**	**1.62**	**1.56**	**1.52**	**1.49**	**1.47**	**1.45**	**1.44**	**1.44**	**1.43**	**1.42**	**1.41**	**1.41**	**1.40**	**1.40**	**1.40**	**1.39**
5	**2.52**	**2.05**	**1.87**	**1.77**	**1.71**	**1.64**	**1.60**	**1.56**	**1.54**	**1.53**	**1.52**	**1.51**	**1.50**	**1.49**	**1.48**	**1.48**	**1.47**	**1.47**	**1.46**	**1.46**
8	**2.83**	**2.28**	**2.07**	**1.96**	**1.89**	**1.80**	**1.76**	**1.72**	**1.69**	**1.68**	**1.66**	**1.65**	**1.64**	**1.63**	**1.62**	**1.62**	**1.61**	**1.61**	**1.60**	**1.60**
12	3.09	**2.48**	**2.24**	**2.12**	**2.04**	**1.94**	**1.89**	**1.85**	**1.82**	**1.80**	**1.78**	**1.77**	**1.76**	**1.75**	**1.74**	**1.73**	**1.73**	**1.72**	**1.71**	**1.71**
16	3.27	**2.61**	**2.36**	**2.22**	**2.14**	**2.04**	**1.98**	**1.93**	**1.90**	**1.88**	**1.86**	**1.85**	**1.84**	**1.83**	**1.82**	**1.81**	**1.80**	**1.80**	**1.79**	**1.78**
20	3.40	**2.71**	**2.45**	**2.31**	**2.22**	**2.11**	**2.05**	**2.00**	**1.97**	**1.94**	**1.93**	**1.91**	**1.90**	**1.89**	**1.88**	**1.87**	**1.86**	**1.86**	**1.85**	**1.84**
30	3.64	**2.89**	**2.61**	**2.45**	**2.36**	**2.24**	**2.17**	**2.12**	**2.08**	**2.06**	**2.04**	**2.02**	**2.01**	**1.99**	**1.98**	**1.97**	**1.96**	**1.96**	**1.95**	**1.94**
40	3.81	**3.02**	**2.72**	**2.55**	**2.45**	**2.33**	**2.26**	**2.20**	**2.16**	**2.13**	**2.11**	**2.10**	**2.09**	**2.07**	**2.05**	**2.04**	**2.04**	**2.03**	**2.02**	**2.01**
50	3.93	3.11	**2.80**	**2.63**	**2.52**	**2.40**	**2.32**	**2.26**	**2.22**	**2.19**	**2.17**	**2.16**	**2.14**	**2.12**	**2.11**	**2.10**	**2.09**	**2.08**	**2.07**	**2.06**
60	4.03	3.19	**2.87**	**2.69**	**2.58**	**2.45**	**2.37**	**2.31**	**2.27**	**2.24**	**2.22**	**2.20**	**2.19**	**2.17**	**2.15**	**2.14**	**2.13**	**2.13**	**2.11**	**2.11**
75	4.15	3.28	**2.95**	**2.77**	**2.65**	**2.52**	**2.43**	**2.37**	**2.33**	**2.30**	**2.28**	**2.26**	**2.24**	**2.22**	**2.21**	**2.19**	**2.19**	**2.18**	**2.17**	**2.16**
100	4.31	3.40	*3.05*	**2.86**	**2.74**	**2.60**	**2.51**	**2.45**	**2.40**	**2.37**	**2.35**	**2.33**	**2.31**	**2.29**	**2.27**	**2.26**	**2.25**	**2.24**	**2.23**	**2.22**
125	4.42	3.48	3.13	**2.93**	**2.81**	**2.66**	**2.57**	**2.51**	**2.46**	**2.43**	**2.40**	**2.38**	**2.37**	**2.34**	**2.32**	**2.31**	**2.30**	**2.29**	**2.28**	**2.27**
150	4.51	3.55	3.19	**2.99**	**2.86**	**2.71**	**2.62**	**2.55**	**2.50**	**2.47**	**2.44**	**2.42**	**2.41**	**2.38**	**2.37**	**2.35**	**2.34**	**2.33**	**2.32**	**2.31**
175	4.59	3.61	3.24	*3.04*	**2.91**	**2.76**	**2.66**	**2.59**	**2.54**	**2.51**	**2.48**	**2.46**	**2.44**	**2.42**	**2.40**	**2.39**	**2.38**	**2.37**	**2.35**	**2.34**
200	4.66	3.66	3.28	*3.08*	**2.95**	**2.79**	**2.70**	**2.62**	**2.58**	**2.54**	**2.51**	**2.49**	**2.47**	**2.45**	**2.43**	**2.42**	**2.41**	**2.40**	**2.38**	**2.37**

Table 19-5. κ-Multipliers for 1-of-1 Interwell Prediction Limits on Means of Order 2 (1 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.89**	**1.58**	**1.45**	**1.38**	**1.34**	**1.29**	**1.26**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**	**1.20**	**1.19**	**1.18**	**1.18**	**1.18**	**1.18**	**1.17**	**1.17**
2	**2.37**	**1.94**	**1.77**	**1.68**	**1.62**	**1.56**	**1.52**	**1.49**	**1.47**	**1.45**	**1.44**	**1.44**	**1.43**	**1.42**	**1.41**	**1.41**	**1.40**	**1.40**	**1.40**	**1.39**
3	**2.64**	**2.14**	**1.95**	**1.84**	**1.78**	**1.70**	**1.66**	**1.62**	**1.60**	**1.59**	**1.57**	**1.56**	**1.56**	**1.55**	**1.54**	**1.53**	**1.53**	**1.52**	**1.52**	**1.51**
4	**2.83**	**2.28**	**2.07**	**1.96**	**1.89**	**1.80**	**1.76**	**1.72**	**1.69**	**1.68**	**1.66**	**1.65**	**1.64**	**1.63**	**1.62**	**1.62**	**1.61**	**1.61**	**1.60**	**1.60**
5	**2.97**	**2.39**	**2.17**	**2.05**	**1.97**	**1.88**	**1.83**	**1.79**	**1.76**	**1.74**	**1.73**	**1.72**	**1.71**	**1.70**	**1.69**	**1.68**	**1.67**	**1.67**	**1.66**	**1.66**
8	3.27	**2.61**	**2.36**	**2.22**	**2.14**	**2.04**	**1.98**	**1.93**	**1.90**	**1.88**	**1.86**	**1.85**	**1.84**	**1.83**	**1.82**	**1.81**	**1.80**	**1.80**	**1.79**	**1.78**
12	3.51	**2.79**	**2.52**	**2.37**	**2.28**	**2.17**	**2.10**	**2.05**	**2.02**	**2.00**	**1.98**	**1.96**	**1.95**	**1.94**	**1.92**	**1.92**	**1.91**	**1.90**	**1.89**	**1.89**
16	3.68	**2.92**	**2.63**	**2.48**	**2.38**	**2.26**	**2.19**	**2.14**	**2.10**	**2.07**	**2.06**	**2.04**	**2.03**	**2.01**	**2.00**	**1.99**	**1.98**	**1.98**	**1.96**	**1.96**
20	3.81	**3.02**	**2.72**	**2.55**	**2.45**	**2.33**	**2.26**	**2.20**	**2.16**	**2.13**	**2.11**	**2.10**	**2.09**	**2.07**	**2.05**	**2.04**	**2.04**	**2.03**	**2.02**	**2.01**
30	4.03	**3.19**	**2.87**	**2.69**	**2.58**	**2.45**	**2.37**	**2.31**	**2.27**	**2.24**	**2.22**	**2.20**	**2.19**	**2.17**	**2.15**	**2.14**	**2.13**	**2.13**	**2.11**	**2.11**
40	4.19	3.31	**2.97**	**2.79**	**2.67**	**2.53**	**2.45**	**2.39**	**2.35**	**2.31**	**2.29**	**2.27**	**2.26**	**2.24**	**2.22**	**2.21**	**2.20**	**2.19**	**2.18**	**2.17**
50	4.31	3.40	**3.05**	**2.86**	**2.74**	**2.60**	**2.51**	**2.45**	**2.40**	**2.37**	**2.35**	**2.33**	**2.31**	**2.29**	**2.27**	**2.26**	**2.25**	**2.24**	**2.23**	**2.22**
60	4.40	3.47	**3.11**	**2.92**	**2.80**	**2.65**	**2.56**	**2.49**	**2.45**	**2.42**	**2.39**	**2.37**	**2.36**	**2.33**	**2.32**	**2.30**	**2.29**	**2.28**	**2.27**	**2.26**
75	4.51	3.55	**3.19**	**2.99**	**2.86**	**2.71**	**2.62**	**2.55**	**2.50**	**2.47**	**2.44**	**2.42**	**2.41**	**2.38**	**2.37**	**2.35**	**2.34**	**2.33**	**2.32**	**2.31**
100	4.66	3.66	**3.28**	**3.08**	**2.95**	**2.79**	**2.70**	**2.62**	**2.58**	**2.54**	**2.51**	**2.49**	**2.47**	**2.45**	**2.43**	**2.42**	**2.41**	**2.40**	**2.38**	**2.37**
125	4.77	3.75	*3.36*	**3.15**	**3.01**	**2.85**	**2.76**	**2.68**	**2.63**	**2.59**	**2.56**	**2.54**	**2.53**	**2.50**	**2.48**	**2.46**	**2.45**	**2.44**	**2.43**	**2.42**
150	4.85	3.81	3.42	**3.20**	**3.07**	**2.90**	**2.80**	**2.73**	**2.67**	**2.63**	**2.61**	**2.58**	**2.57**	**2.54**	**2.52**	**2.50**	**2.49**	**2.48**	**2.47**	**2.45**
175	4.93	3.87	3.47	**3.25**	**3.11**	**2.94**	**2.84**	**2.76**	**2.71**	**2.67**	**2.64**	**2.62**	**2.60**	**2.57**	**2.55**	**2.54**	**2.52**	**2.51**	**2.50**	**2.49**
200	4.99	3.92	3.51	*3.29*	**3.15**	**2.98**	**2.88**	**2.79**	**2.74**	**2.70**	**2.67**	**2.65**	**2.63**	**2.60**	**2.58**	**2.56**	**2.55**	**2.54**	**2.52**	**2.51**

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Table 19-5. κ-Multipliers for 1-of-1 Interwell Prediction Limits on Means of Order 2 (1 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.37**	**1.94**	**1.77**	**1.68**	**1.62**	**1.56**	**1.52**	**1.49**	**1.47**	**1.45**	**1.44**	**1.44**	**1.43**	**1.42**	**1.41**	**1.41**	**1.40**	**1.40**	**1.40**	**1.39**
2	**2.83**	**2.28**	**2.07**	**1.96**	**1.89**	**1.80**	**1.76**	**1.72**	**1.69**	**1.68**	**1.66**	**1.65**	**1.64**	**1.63**	**1.62**	**1.62**	**1.61**	**1.61**	**1.60**	**1.60**
3	**3.09**	**2.48**	**2.24**	**2.12**	**2.04**	**1.94**	**1.89**	**1.85**	**1.82**	**1.80**	**1.78**	**1.77**	**1.76**	**1.75**	**1.74**	**1.73**	**1.73**	**1.72**	**1.71**	**1.71**
4	**3.27**	**2.61**	**2.36**	**2.22**	**2.14**	**2.04**	**1.98**	**1.93**	**1.90**	**1.88**	**1.86**	**1.85**	**1.84**	**1.83**	**1.82**	**1.81**	**1.80**	**1.80**	**1.79**	**1.78**
5	3.40	**2.71**	**2.45**	**2.31**	**2.22**	**2.11**	**2.05**	**2.00**	**1.97**	**1.94**	**1.93**	**1.91**	**1.90**	**1.89**	**1.88**	**1.87**	**1.86**	**1.86**	**1.85**	**1.84**
8	3.68	**2.92**	**2.63**	**2.48**	**2.38**	**2.26**	**2.19**	**2.14**	**2.10**	**2.07**	**2.06**	**2.04**	**2.03**	**2.01**	**2.00**	**1.99**	**1.98**	**1.98**	**1.96**	**1.96**
12	3.91	**3.10**	**2.78**	**2.62**	**2.51**	**2.38**	**2.31**	**2.25**	**2.21**	**2.18**	**2.16**	**2.15**	**2.13**	**2.11**	**2.10**	**2.09**	**2.08**	**2.07**	**2.06**	**2.05**
16	4.07	**3.22**	**2.89**	**2.71**	**2.60**	**2.47**	**2.39**	**2.33**	**2.29**	**2.26**	**2.24**	**2.22**	**2.20**	**2.18**	**2.17**	**2.16**	**2.15**	**2.14**	**2.13**	**2.12**
20	4.19	**3.31**	**2.97**	**2.79**	**2.67**	**2.53**	**2.45**	**2.39**	**2.35**	**2.31**	**2.29**	**2.27**	**2.26**	**2.24**	**2.22**	**2.21**	**2.20**	**2.19**	**2.18**	**2.17**
30	4.40	**3.47**	**3.11**	**2.92**	**2.80**	**2.65**	**2.56**	**2.49**	**2.45**	**2.42**	**2.39**	**2.37**	**2.36**	**2.33**	**2.32**	**2.30**	**2.29**	**2.28**	**2.27**	**2.26**
40	4.55	3.58	**3.21**	**3.01**	**2.88**	**2.73**	**2.64**	**2.57**	**2.52**	**2.49**	**2.46**	**2.44**	**2.42**	**2.40**	**2.38**	**2.37**	**2.36**	**2.35**	**2.33**	**2.32**
50	4.66	3.66	**3.28**	**3.08**	**2.95**	**2.79**	**2.70**	**2.62**	**2.58**	**2.54**	**2.51**	**2.49**	**2.47**	**2.45**	**2.43**	**2.42**	**2.41**	**2.40**	**2.38**	**2.37**
60	4.75	3.73	**3.34**	**3.13**	**3.00**	**2.84**	**2.75**	**2.67**	**2.62**	**2.58**	**2.56**	**2.53**	**2.52**	**2.49**	**2.47**	**2.46**	**2.44**	**2.44**	**2.42**	**2.41**
75	4.85	3.81	**3.42**	**3.20**	**3.07**	**2.90**	**2.80**	**2.73**	**2.67**	**2.63**	**2.61**	**2.58**	**2.57**	**2.54**	**2.52**	**2.50**	**2.49**	**2.48**	**2.47**	**2.45**
100	4.99	3.92	**3.51**	**3.29**	**3.15**	**2.98**	**2.88**	**2.79**	**2.74**	**2.70**	**2.67**	**2.65**	**2.63**	**2.60**	**2.58**	**2.56**	**2.55**	**2.54**	**2.52**	**2.51**
125	5.09	4.00	**3.58**	**3.35**	**3.21**	**3.03**	**2.93**	**2.85**	**2.79**	**2.75**	**2.72**	**2.70**	**2.68**	**2.65**	**2.63**	**2.61**	**2.60**	**2.59**	**2.57**	**2.56**
150	5.18	4.06	3.63	**3.40**	**3.26**	**3.08**	**2.98**	**2.89**	**2.83**	**2.79**	**2.76**	**2.74**	**2.72**	**2.69**	**2.67**	**2.65**	**2.64**	**2.63**	**2.61**	**2.59**
175	5.24	4.11	3.68	**3.45**	**3.30**	**3.12**	**3.01**	**2.93**	**2.87**	**2.83**	**2.80**	**2.77**	**2.75**	**2.72**	**2.70**	**2.68**	**2.67**	**2.66**	**2.64**	**2.62**
200	5.30	4.16	3.72	**3.49**	**3.34**	**3.15**	**3.04**	**2.96**	**2.90**	**2.86**	**2.82**	**2.80**	**2.78**	**2.75**	**2.72**	**2.71**	**2.69**	**2.68**	**2.66**	**2.65**

Table 19-5. κ-Multipliers for 1-of-1 Interwell Prediction Limits on Means of Order 2 (2 COC, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.01**	**1.63**	**1.48**	**1.41**	**1.36**	**1.30**	**1.27**	**1.25**	**1.23**	**1.22**	**1.21**	**1.20**	**1.20**	**1.19**	**1.19**	**1.18**	**1.18**	**1.18**	**1.17**	**1.17**
2	**2.57**	**2.02**	**1.82**	**1.71**	**1.65**	**1.57**	**1.53**	**1.50**	**1.48**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**	**1.42**	**1.41**	**1.41**	**1.40**	**1.40**	**1.39**
3	**2.90**	**2.25**	**2.01**	**1.89**	**1.81**	**1.72**	**1.67**	**1.64**	**1.61**	**1.59**	**1.58**	**1.57**	**1.56**	**1.55**	**1.54**	**1.54**	**1.53**	**1.53**	**1.52**	**1.52**
4	3.14	**2.41**	**2.15**	**2.01**	**1.93**	**1.83**	**1.77**	**1.73**	**1.70**	**1.68**	**1.67**	**1.66**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.61**	**1.60**	**1.60**
5	3.33	**2.54**	**2.25**	**2.10**	**2.01**	**1.91**	**1.85**	**1.80**	**1.77**	**1.75**	**1.74**	**1.72**	**1.72**	**1.70**	**1.69**	**1.68**	**1.68**	**1.67**	**1.67**	**1.66**
8	3.71	**2.79**	**2.47**	**2.30**	**2.19**	**2.07**	**2.00**	**1.95**	**1.92**	**1.89**	**1.87**	**1.86**	**1.85**	**1.83**	**1.82**	**1.81**	**1.81**	**1.80**	**1.79**	**1.79**
12	4.03	**3.01**	**2.65**	**2.46**	**2.35**	**2.21**	**2.13**	**2.07**	**2.04**	**2.01**	**1.99**	**1.97**	**1.96**	**1.94**	**1.93**	**1.92**	**1.91**	**1.91**	**1.90**	**1.89**
16	4.25	3.16	**2.78**	**2.57**	**2.45**	**2.31**	**2.22**	**2.16**	**2.12**	**2.09**	**2.07**	**2.05**	**2.04**	**2.02**	**2.00**	**1.99**	**1.99**	**1.98**	**1.97**	**1.96**
20	4.42	3.28	**2.87**	**2.66**	**2.53**	**2.38**	**2.29**	**2.23**	**2.18**	**2.15**	**2.13**	**2.11**	**2.10**	**2.08**	**2.06**	**2.05**	**2.04**	**2.03**	**2.02**	**2.01**
30	4.72	3.48	*3.04*	**2.82**	**2.68**	**2.51**	**2.42**	**2.34**	**2.29**	**2.26**	**2.23**	**2.22**	**2.20**	**2.18**	**2.16**	**2.15**	**2.14**	**2.13**	**2.12**	**2.11**
40	4.93	3.63	3.16	**2.92**	**2.77**	**2.60**	**2.50**	**2.42**	**2.37**	**2.34**	**2.31**	**2.29**	**2.27**	**2.25**	**2.23**	**2.22**	**2.21**	**2.20**	**2.18**	**2.17**
50	5.08	3.74	3.26	*3.01*	**2.85**	**2.67**	**2.57**	**2.48**	**2.43**	**2.39**	**2.37**	**2.34**	**2.33**	**2.30**	**2.28**	**2.27**	**2.26**	**2.25**	**2.23**	**2.22**
60	5.21	3.82	3.33	*3.07*	**2.91**	**2.73**	**2.62**	**2.53**	**2.48**	**2.44**	**2.41**	**2.39**	**2.37**	**2.34**	**2.32**	**2.31**	**2.30**	**2.29**	**2.27**	**2.26**
75	5.36	3.93	3.42	*3.15*	*2.99*	**2.79**	**2.68**	**2.59**	**2.54**	**2.50**	**2.47**	**2.44**	**2.42**	**2.40**	**2.38**	**2.36**	**2.35**	**2.34**	**2.32**	**2.31**
100	5.55	4.06	3.53	3.25	*3.08*	**2.88**	**2.76**	**2.67**	**2.61**	**2.57**	**2.54**	**2.51**	**2.49**	**2.46**	**2.44**	**2.43**	**2.41**	**2.40**	**2.39**	**2.37**
125	5.70	4.16	3.61	3.33	*3.15*	**2.94**	**2.82**	**2.73**	**2.67**	**2.62**	**2.59**	**2.56**	**2.54**	**2.51**	**2.49**	**2.47**	**2.46**	**2.45**	**2.43**	**2.42**
150	5.82	4.24	3.68	3.39	3.21	*3.00*	**2.87**	**2.78**	**2.71**	**2.67**	**2.63**	**2.61**	**2.59**	**2.55**	**2.53**	**2.51**	**2.50**	**2.49**	**2.47**	**2.46**
175	5.91	4.31	3.74	3.44	3.26	*3.04*	**2.92**	**2.82**	**2.75**	**2.70**	**2.67**	**2.64**	**2.62**	**2.59**	**2.56**	**2.55**	**2.53**	**2.52**	**2.50**	**2.49**
200	6.00	4.37	3.79	3.49	3.30	*3.08*	**2.95**	**2.85**	**2.78**	**2.74**	**2.70**	**2.67**	**2.65**	**2.62**	**2.59**	**2.58**	**2.56**	**2.55**	**2.53**	**2.52**

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Table 19-5. κ-Multipliers for 1-of-1 Interwell Prediction Limits on Means of Order 2 (2 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.57**	**2.02**	**1.82**	**1.71**	**1.65**	**1.57**	**1.53**	**1.50**	**1.48**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**	**1.42**	**1.41**	**1.41**	**1.40**	**1.40**	**1.39**
2	3.14	**2.41**	**2.15**	**2.01**	**1.93**	**1.83**	**1.77**	**1.73**	**1.70**	**1.68**	**1.67**	**1.66**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.61**	**1.60**	**1.60**
3	3.47	**2.64**	**2.34**	**2.18**	**2.08**	**1.97**	**1.91**	**1.86**	**1.83**	**1.81**	**1.79**	**1.78**	**1.77**	**1.75**	**1.74**	**1.73**	**1.73**	**1.72**	**1.71**	**1.71**
4	3.71	**2.79**	**2.47**	**2.30**	**2.19**	**2.07**	**2.00**	**1.95**	**1.92**	**1.89**	**1.87**	**1.86**	**1.85**	**1.83**	**1.82**	**1.81**	**1.81**	**1.80**	**1.79**	**1.79**
5	3.88	**2.91**	**2.57**	**2.39**	**2.28**	**2.15**	**2.08**	**2.02**	**1.98**	**1.96**	**1.94**	**1.92**	**1.91**	**1.89**	**1.88**	**1.87**	**1.87**	**1.86**	**1.85**	**1.84**
8	4.25	**3.16**	**2.78**	**2.57**	**2.45**	**2.31**	**2.22**	**2.16**	**2.12**	**2.09**	**2.07**	**2.05**	**2.04**	**2.02**	**2.00**	**1.99**	**1.99**	**1.98**	**1.97**	**1.96**
12	4.56	3.37	**2.95**	**2.73**	**2.60**	**2.44**	**2.35**	**2.28**	**2.23**	**2.20**	**2.18**	**2.16**	**2.14**	**2.12**	**2.11**	**2.09**	**2.09**	**2.08**	**2.07**	**2.06**
16	4.77	3.52	**3.07**	**2.84**	**2.70**	**2.53**	**2.43**	**2.36**	**2.31**	**2.28**	**2.25**	**2.23**	**2.22**	**2.19**	**2.18**	**2.16**	**2.15**	**2.15**	**2.13**	**2.12**
20	4.93	3.63	**3.16**	**2.92**	**2.77**	**2.60**	**2.50**	**2.42**	**2.37**	**2.34**	**2.31**	**2.29**	**2.27**	**2.25**	**2.23**	**2.22**	**2.21**	**2.20**	**2.18**	**2.17**
30	5.21	3.82	*3.33*	**3.07**	**2.91**	**2.73**	**2.62**	**2.53**	**2.48**	**2.44**	**2.41**	**2.39**	**2.37**	**2.34**	**2.32**	**2.31**	**2.30**	**2.29**	**2.27**	**2.26**
40	5.40	3.96	3.44	**3.17**	**3.01**	**2.81**	**2.70**	**2.61**	**2.55**	**2.51**	**2.48**	**2.46**	**2.44**	**2.41**	**2.39**	**2.38**	**2.36**	**2.35**	**2.34**	**2.33**
50	5.55	4.06	3.53	**3.25**	**3.08**	**2.88**	**2.76**	**2.67**	**2.61**	**2.57**	**2.54**	**2.51**	**2.49**	**2.46**	**2.44**	**2.43**	**2.41**	**2.40**	**2.39**	**2.37**
60	5.67	4.14	3.60	*3.32*	**3.14**	**2.93**	**2.81**	**2.72**	**2.66**	**2.61**	**2.58**	**2.55**	**2.53**	**2.50**	**2.48**	**2.47**	**2.45**	**2.44**	**2.42**	**2.41**
75	5.82	4.24	3.68	*3.39*	**3.21**	**3.00**	**2.87**	**2.78**	**2.71**	**2.67**	**2.63**	**2.61**	**2.59**	**2.55**	**2.53**	**2.51**	**2.50**	**2.49**	**2.47**	**2.46**
100	6.00	4.37	3.79	3.49	*3.30*	**3.08**	**2.95**	**2.85**	**2.78**	**2.74**	**2.70**	**2.67**	**2.65**	**2.62**	**2.59**	**2.58**	**2.56**	**2.55**	**2.53**	**2.52**
125	6.13	4.47	3.87	3.56	*3.37*	**3.14**	**3.01**	**2.91**	**2.84**	**2.79**	**2.75**	**2.72**	**2.70**	**2.67**	**2.64**	**2.62**	**2.61**	**2.60**	**2.58**	**2.56**
150	6.24	4.54	3.94	3.62	*3.43*	**3.19**	**3.06**	**2.95**	**2.88**	**2.83**	**2.79**	**2.76**	**2.74**	**2.71**	**2.68**	**2.66**	**2.65**	**2.63**	**2.61**	**2.60**
175	6.34	4.61	3.99	3.67	3.47	**3.24**	**3.10**	**2.99**	**2.92**	**2.87**	**2.83**	**2.80**	**2.77**	**2.74**	**2.71**	**2.69**	**2.68**	**2.67**	**2.64**	**2.63**
200	6.42	4.66	4.04	3.72	3.51	*3.27*	**3.13**	**3.02**	**2.95**	**2.90**	**2.86**	**2.83**	**2.80**	**2.77**	**2.74**	**2.72**	**2.70**	**2.69**	**2.67**	**2.65**

Table 19-5. κ-Multipliers for 1-of-1 Interwell Prediction Limits on Means of Order 2 (2 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**3.14**	**2.41**	**2.15**	**2.01**	**1.93**	**1.83**	**1.77**	**1.73**	**1.70**	**1.68**	**1.67**	**1.66**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.61**	**1.60**	**1.60**
2	3.71	**2.79**	**2.47**	**2.30**	**2.19**	**2.07**	**2.00**	**1.95**	**1.92**	**1.89**	**1.87**	**1.86**	**1.85**	**1.83**	**1.82**	**1.81**	**1.81**	**1.80**	**1.79**	**1.79**
3	4.03	**3.01**	**2.65**	**2.46**	**2.35**	**2.21**	**2.13**	**2.07**	**2.04**	**2.01**	**1.99**	**1.97**	**1.96**	**1.94**	**1.93**	**1.92**	**1.91**	**1.91**	**1.90**	**1.89**
4	4.25	**3.16**	**2.78**	**2.57**	**2.45**	**2.31**	**2.22**	**2.16**	**2.12**	**2.09**	**2.07**	**2.05**	**2.04**	**2.02**	**2.00**	**1.99**	**1.99**	**1.98**	**1.97**	**1.96**
5	4.42	**3.28**	**2.87**	**2.66**	**2.53**	**2.38**	**2.29**	**2.23**	**2.18**	**2.15**	**2.13**	**2.11**	**2.10**	**2.08**	**2.06**	**2.05**	**2.04**	**2.03**	**2.02**	**2.01**
8	4.77	**3.52**	**3.07**	**2.84**	**2.70**	**2.53**	**2.43**	**2.36**	**2.31**	**2.28**	**2.25**	**2.23**	**2.22**	**2.19**	**2.18**	**2.16**	**2.15**	**2.15**	**2.13**	**2.12**
12	5.06	3.72	**3.24**	**2.99**	**2.84**	**2.66**	**2.55**	**2.47**	**2.42**	**2.38**	**2.36**	**2.33**	**2.32**	**2.29**	**2.27**	**2.26**	**2.25**	**2.24**	**2.23**	**2.22**
16	5.25	3.85	**3.35**	**3.09**	**2.93**	**2.75**	**2.64**	**2.55**	**2.50**	**2.46**	**2.43**	**2.40**	**2.39**	**2.36**	**2.34**	**2.33**	**2.31**	**2.31**	**2.29**	**2.28**
20	5.40	3.96	**3.44**	**3.17**	**3.01**	**2.81**	**2.70**	**2.61**	**2.55**	**2.51**	**2.48**	**2.46**	**2.44**	**2.41**	**2.39**	**2.38**	**2.36**	**2.35**	**2.34**	**2.33**
30	5.67	4.14	*3.60*	**3.32**	**3.14**	**2.93**	**2.81**	**2.72**	**2.66**	**2.61**	**2.58**	**2.55**	**2.53**	**2.50**	**2.48**	**2.47**	**2.45**	**2.44**	**2.42**	**2.41**
40	5.86	4.27	3.71	**3.41**	**3.23**	**3.02**	**2.89**	**2.79**	**2.73**	**2.68**	**2.65**	**2.62**	**2.60**	**2.57**	**2.55**	**2.53**	**2.51**	**2.50**	**2.48**	**2.47**
50	6.00	4.37	3.79	**3.49**	**3.30**	**3.08**	**2.95**	**2.85**	**2.78**	**2.74**	**2.70**	**2.67**	**2.65**	**2.62**	**2.59**	**2.58**	**2.56**	**2.55**	**2.53**	**2.52**
60	6.10	4.45	3.86	**3.55**	**3.36**	**3.13**	**3.00**	**2.90**	**2.83**	**2.78**	**2.74**	**2.71**	**2.69**	**2.66**	**2.63**	**2.61**	**2.60**	**2.59**	**2.57**	**2.55**
75	6.24	4.54	3.94	*3.62*	**3.43**	**3.19**	**3.06**	**2.95**	**2.88**	**2.83**	**2.79**	**2.76**	**2.74**	**2.71**	**2.68**	**2.66**	**2.65**	**2.63**	**2.61**	**2.60**
100	6.42	4.66	4.04	3.72	**3.51**	**3.27**	**3.13**	**3.02**	**2.95**	**2.90**	**2.86**	**2.83**	**2.80**	**2.77**	**2.74**	**2.72**	**2.70**	**2.69**	**2.67**	**2.65**
125	6.55	4.76	4.12	3.79	**3.58**	**3.33**	**3.19**	**3.08**	**3.00**	**2.95**	**2.91**	**2.88**	**2.85**	**2.81**	**2.79**	**2.77**	**2.75**	**2.74**	**2.71**	**2.70**
150	6.65	4.83	4.18	3.84	*3.63*	**3.38**	**3.24**	**3.12**	**3.04**	**2.99**	**2.95**	**2.92**	**2.89**	**2.85**	**2.82**	**2.80**	**2.79**	**2.77**	**2.75**	**2.73**
175	6.74	4.89	4.23	3.89	*3.68*	**3.42**	**3.28**	**3.16**	**3.08**	**3.02**	**2.98**	**2.95**	**2.92**	**2.88**	**2.85**	**2.83**	**2.82**	**2.80**	**2.78**	**2.76**
200	6.82	4.94	4.28	3.93	*3.72*	**3.46**	**3.31**	**3.19**	**3.11**	**3.05**	**3.01**	**2.98**	**2.95**	**2.91**	**2.88**	**2.86**	**2.84**	**2.83**	**2.80**	**2.79**

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Table 19-5. κ-Multipliers for 1-of-1 Interwell Prediction Limits on Means of Order 2 (5 COC, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.97**	**2.22**	**1.97**	**1.84**	**1.76**	**1.67**	**1.62**	**1.58**	**1.56**	**1.54**	**1.53**	**1.52**	**1.51**	**1.50**	**1.49**	**1.48**	**1.48**	**1.47**	**1.47**	**1.46**
2	3.68	**2.66**	**2.32**	**2.15**	**2.04**	**1.93**	**1.86**	**1.81**	**1.78**	**1.76**	**1.74**	**1.73**	**1.72**	**1.70**	**1.69**	**1.69**	**1.68**	**1.67**	**1.67**	**1.66**
3	4.12	**2.92**	**2.52**	**2.33**	**2.21**	**2.07**	**2.00**	**1.94**	**1.91**	**1.88**	**1.86**	**1.85**	**1.84**	**1.82**	**1.81**	**1.80**	**1.79**	**1.79**	**1.78**	**1.77**
4	4.43	3.10	**2.67**	**2.45**	**2.32**	**2.18**	**2.09**	**2.03**	**1.99**	**1.96**	**1.94**	**1.93**	**1.92**	**1.90**	**1.88**	**1.88**	**1.87**	**1.86**	**1.85**	**1.84**
5	4.68	3.25	**2.78**	**2.55**	**2.41**	**2.25**	**2.17**	**2.10**	**2.06**	**2.03**	**2.01**	**1.99**	**1.98**	**1.96**	**1.94**	**1.93**	**1.93**	**1.92**	**1.91**	**1.90**
8	5.19	3.55	*3.02*	**2.75**	**2.60**	**2.42**	**2.32**	**2.24**	**2.20**	**2.16**	**2.14**	**2.12**	**2.10**	**2.08**	**2.06**	**2.05**	**2.04**	**2.04**	**2.02**	**2.02**
12	5.62	3.81	3.22	**2.93**	**2.75**	**2.56**	**2.45**	**2.36**	**2.31**	**2.27**	**2.25**	**2.22**	**2.21**	**2.18**	**2.17**	**2.15**	**2.14**	**2.13**	**2.12**	**2.11**
16	5.92	3.99	3.36	*3.05*	**2.86**	**2.65**	**2.54**	**2.45**	**2.39**	**2.35**	**2.32**	**2.30**	**2.28**	**2.25**	**2.23**	**2.22**	**2.21**	**2.20**	**2.19**	**2.18**
20	6.15	4.12	3.47	*3.14*	**2.95**	**2.73**	**2.61**	**2.51**	**2.45**	**2.41**	**2.38**	**2.35**	**2.34**	**2.31**	**2.29**	**2.27**	**2.26**	**2.25**	**2.24**	**2.23**
30	6.55	4.37	3.66	3.31	*3.10*	**2.86**	**2.73**	**2.63**	**2.56**	**2.51**	**2.48**	**2.45**	**2.43**	**2.40**	**2.38**	**2.37**	**2.35**	**2.34**	**2.33**	**2.32**
40	6.83	4.54	3.80	3.43	3.21	**2.96**	**2.81**	**2.71**	**2.64**	**2.59**	**2.55**	**2.53**	**2.50**	**2.47**	**2.45**	**2.43**	**2.42**	**2.41**	**2.39**	**2.38**
50	7.04	4.67	3.90	3.52	3.29	*3.03*	**2.88**	**2.77**	**2.70**	**2.65**	**2.61**	**2.58**	**2.56**	**2.52**	**2.50**	**2.48**	**2.47**	**2.46**	**2.44**	**2.42**
60	7.21	4.77	3.98	3.59	3.36	*3.09*	**2.93**	**2.82**	**2.74**	**2.69**	**2.65**	**2.62**	**2.60**	**2.56**	**2.54**	**2.52**	**2.51**	**2.50**	**2.48**	**2.46**
75	7.42	4.90	4.08	3.68	3.44	*3.16*	*3.00*	**2.88**	**2.80**	**2.75**	**2.71**	**2.67**	**2.65**	**2.61**	**2.59**	**2.57**	**2.55**	**2.54**	**2.52**	**2.51**
100	7.68	5.06	4.21	3.79	3.54	3.25	*3.08*	*2.96*	**2.87**	**2.82**	**2.77**	**2.74**	**2.72**	**2.68**	**2.65**	**2.63**	**2.61**	**2.60**	**2.58**	**2.57**
125	7.88	5.18	4.31	3.88	3.62	3.31	*3.15*	*3.02*	**2.93**	**2.87**	**2.83**	**2.79**	**2.77**	**2.73**	**2.70**	**2.68**	**2.66**	**2.65**	**2.63**	**2.61**
150	8.04	5.28	4.39	3.95	3.68	3.37	*3.20*	*3.06*	*2.98*	**2.92**	**2.87**	**2.84**	**2.81**	**2.77**	**2.74**	**2.72**	**2.70**	**2.69**	**2.66**	**2.65**
175	8.17	5.36	4.45	4.00	3.73	3.42	*3.24*	*3.10*	*3.01*	*2.95*	**2.91**	**2.87**	**2.84**	**2.80**	**2.77**	**2.75**	**2.73**	**2.72**	**2.69**	**2.68**
200	8.28	5.43	4.51	4.05	3.78	3.46	3.28	*3.14*	*3.05*	*2.98*	**2.94**	**2.90**	**2.87**	**2.83**	**2.80**	**2.78**	**2.76**	**2.74**	**2.72**	**2.70**

Table 19-5. κ-Multipliers for 1-of-1 Interwell Prediction Limits on Means of Order 2 (5 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.68	**2.66**	**2.32**	**2.15**	**2.04**	**1.93**	**1.86**	**1.81**	**1.78**	**1.76**	**1.74**	**1.73**	**1.72**	**1.70**	**1.69**	**1.69**	**1.68**	**1.67**	**1.67**	**1.66**
2	4.43	**3.10**	**2.67**	**2.45**	**2.32**	**2.18**	**2.09**	**2.03**	**1.99**	**1.96**	**1.94**	**1.93**	**1.92**	**1.90**	**1.88**	**1.88**	**1.87**	**1.86**	**1.85**	**1.84**
3	4.88	3.37	**2.87**	**2.63**	**2.48**	**2.32**	**2.23**	**2.16**	**2.11**	**2.08**	**2.06**	**2.04**	**2.03**	**2.01**	**1.99**	**1.98**	**1.97**	**1.97**	**1.95**	**1.95**
4	5.19	3.55	**3.02**	**2.75**	**2.60**	**2.42**	**2.32**	**2.24**	**2.20**	**2.16**	**2.14**	**2.12**	**2.10**	**2.08**	**2.06**	**2.05**	**2.04**	**2.04**	**2.02**	**2.02**
5	5.42	3.69	**3.13**	**2.85**	**2.68**	**2.49**	**2.39**	**2.31**	**2.26**	**2.22**	**2.20**	**2.18**	**2.16**	**2.14**	**2.12**	**2.11**	**2.10**	**2.09**	**2.08**	**2.07**
8	5.92	3.99	3.36	**3.05**	**2.86**	**2.65**	**2.54**	**2.45**	**2.39**	**2.35**	**2.32**	**2.30**	**2.28**	**2.25**	**2.23**	**2.22**	**2.21**	**2.20**	**2.19**	**2.18**
12	6.33	4.23	3.56	**3.22**	**3.02**	**2.79**	**2.66**	**2.56**	**2.50**	**2.46**	**2.42**	**2.40**	**2.38**	**2.35**	**2.33**	**2.32**	**2.30**	**2.29**	**2.28**	**2.27**
16	6.61	4.41	3.69	*3.34*	**3.13**	**2.88**	**2.75**	**2.64**	**2.58**	**2.53**	**2.50**	**2.47**	**2.45**	**2.42**	**2.40**	**2.38**	**2.37**	**2.36**	**2.34**	**2.33**
20	6.83	4.54	3.80	3.43	**3.21**	**2.96**	**2.81**	**2.71**	**2.64**	**2.59**	**2.55**	**2.53**	**2.50**	**2.47**	**2.45**	**2.43**	**2.42**	**2.41**	**2.39**	**2.38**
30	7.21	4.77	3.98	3.59	*3.36*	**3.09**	**2.93**	**2.82**	**2.74**	**2.69**	**2.65**	**2.62**	**2.60**	**2.56**	**2.54**	**2.52**	**2.51**	**2.50**	**2.48**	**2.46**
40	7.48	4.94	4.11	3.70	*3.46*	**3.18**	**3.02**	**2.90**	**2.82**	**2.76**	**2.72**	**2.69**	**2.67**	**2.63**	**2.60**	**2.58**	**2.57**	**2.56**	**2.53**	**2.52**
50	7.68	5.06	4.21	3.79	3.54	**3.25**	**3.08**	**2.96**	**2.87**	**2.82**	**2.77**	**2.74**	**2.72**	**2.68**	**2.65**	**2.63**	**2.61**	**2.60**	**2.58**	**2.57**
60	7.84	5.16	4.29	3.86	3.60	*3.30*	**3.13**	**3.00**	**2.92**	**2.86**	**2.82**	**2.78**	**2.76**	**2.72**	**2.69**	**2.67**	**2.65**	**2.64**	**2.62**	**2.60**
75	8.04	5.28	4.39	3.95	3.68	*3.37*	**3.20**	**3.06**	**2.98**	**2.92**	**2.87**	**2.84**	**2.81**	**2.77**	**2.74**	**2.72**	**2.70**	**2.69**	**2.66**	**2.65**
100	8.28	5.43	4.51	4.05	3.78	*3.46*	*3.28*	**3.14**	**3.05**	**2.98**	**2.94**	**2.90**	**2.87**	**2.83**	**2.80**	**2.78**	**2.76**	**2.74**	**2.72**	**2.70**
125	8.47	5.55	4.61	4.14	3.85	*3.52*	*3.34*	**3.20**	**3.10**	**3.04**	**2.99**	**2.95**	**2.92**	**2.88**	**2.84**	**2.82**	**2.80**	**2.79**	**2.76**	**2.74**
150	8.62	5.64	4.68	4.20	3.91	3.58	*3.39*	**3.24**	**3.15**	**3.08**	**3.03**	**2.99**	**2.96**	**2.91**	**2.88**	**2.86**	**2.84**	**2.82**	**2.80**	**2.78**
175	8.75	5.72	4.74	4.26	3.96	3.62	*3.43*	*3.28*	**3.18**	**3.12**	**3.06**	**3.02**	**2.99**	**2.95**	**2.91**	**2.89**	**2.87**	**2.85**	**2.83**	**2.81**
200	8.85	5.79	4.80	4.31	4.01	3.66	*3.47*	*3.31*	**3.22**	**3.15**	**3.09**	**3.05**	**3.02**	**2.97**	**2.94**	**2.91**	**2.90**	**2.88**	**2.85**	**2.83**

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Table 19-5. κ-Multipliers for 1-of-1 Interwell Prediction Limits on Means of Order 2 (5 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	4.43	**3.10**	**2.67**	**2.45**	**2.32**	**2.18**	**2.09**	**2.03**	**1.99**	**1.96**	**1.94**	**1.93**	**1.92**	**1.90**	**1.88**	**1.88**	**1.87**	**1.86**	**1.85**	**1.84**
2	5.19	3.55	**3.02**	**2.75**	**2.60**	**2.42**	**2.32**	**2.24**	**2.20**	**2.16**	**2.14**	**2.12**	**2.10**	**2.08**	**2.06**	**2.05**	**2.04**	**2.04**	**2.02**	**2.02**
3	5.62	3.81	**3.22**	**2.93**	**2.75**	**2.56**	**2.45**	**2.36**	**2.31**	**2.27**	**2.25**	**2.22**	**2.21**	**2.18**	**2.17**	**2.15**	**2.14**	**2.13**	**2.12**	**2.11**
4	5.92	3.99	**3.36**	**3.05**	**2.86**	**2.65**	**2.54**	**2.45**	**2.39**	**2.35**	**2.32**	**2.30**	**2.28**	**2.25**	**2.23**	**2.22**	**2.21**	**2.20**	**2.19**	**2.18**
5	6.15	4.12	**3.47**	**3.14**	**2.95**	**2.73**	**2.61**	**2.51**	**2.45**	**2.41**	**2.38**	**2.35**	**2.34**	**2.31**	**2.29**	**2.27**	**2.26**	**2.25**	**2.24**	**2.23**
8	6.61	4.41	3.69	**3.34**	**3.13**	**2.88**	**2.75**	**2.64**	**2.58**	**2.53**	**2.50**	**2.47**	**2.45**	**2.42**	**2.40**	**2.38**	**2.37**	**2.36**	**2.34**	**2.33**
12	7.00	4.65	3.88	**3.50**	**3.28**	**3.01**	**2.87**	**2.76**	**2.69**	**2.63**	**2.60**	**2.57**	**2.55**	**2.51**	**2.49**	**2.47**	**2.46**	**2.45**	**2.43**	**2.42**
16	7.27	4.81	4.01	*3.62*	**3.38**	**3.11**	**2.95**	**2.84**	**2.76**	**2.71**	**2.67**	**2.64**	**2.61**	**2.58**	**2.55**	**2.53**	**2.52**	**2.51**	**2.49**	**2.48**
20	7.48	4.94	4.11	3.70	**3.46**	**3.18**	**3.02**	**2.90**	**2.82**	**2.76**	**2.72**	**2.69**	**2.67**	**2.63**	**2.60**	**2.58**	**2.57**	**2.56**	**2.53**	**2.52**
30	7.84	5.16	4.29	3.86	*3.60*	**3.30**	**3.13**	**3.00**	**2.92**	**2.86**	**2.82**	**2.78**	**2.76**	**2.72**	**2.69**	**2.67**	**2.65**	**2.64**	**2.62**	**2.60**
40	8.09	5.32	4.42	3.97	*3.70*	**3.39**	**3.21**	**3.08**	**2.99**	**2.93**	**2.89**	**2.85**	**2.82**	**2.78**	**2.75**	**2.73**	**2.71**	**2.70**	**2.67**	**2.66**
50	8.28	5.43	4.51	4.05	3.78	**3.46**	**3.28**	**3.14**	**3.05**	**2.98**	**2.94**	**2.90**	**2.87**	**2.83**	**2.80**	**2.78**	**2.76**	**2.74**	**2.72**	**2.70**
60	8.43	5.53	4.59	4.12	3.84	**3.51**	**3.33**	**3.19**	**3.09**	**3.03**	**2.98**	**2.94**	**2.91**	**2.87**	**2.84**	**2.81**	**2.79**	**2.78**	**2.75**	**2.74**
75	8.62	5.64	4.68	4.20	3.91	*3.58*	**3.39**	**3.24**	**3.15**	**3.08**	**3.03**	**2.99**	**2.96**	**2.91**	**2.88**	**2.86**	**2.84**	**2.82**	**2.80**	**2.78**
100	8.85	5.79	4.80	4.31	4.01	*3.66*	**3.47**	**3.31**	**3.22**	**3.15**	**3.09**	**3.05**	**3.02**	**2.97**	**2.94**	**2.91**	**2.90**	**2.88**	**2.85**	**2.83**
125	9.03	5.90	4.89	4.38	4.08	*3.73*	**3.53**	**3.37**	**3.27**	**3.20**	**3.14**	**3.10**	**3.07**	**3.02**	**2.99**	**2.96**	**2.94**	**2.92**	**2.89**	**2.87**
150	9.18	5.99	4.96	4.45	4.14	*3.78*	**3.57**	**3.42**	**3.31**	**3.24**	**3.18**	**3.14**	**3.11**	**3.06**	**3.02**	**2.99**	**2.97**	**2.96**	**2.93**	**2.91**
175	9.29	6.07	5.02	4.50	4.19	*3.82*	*3.62*	**3.45**	**3.35**	**3.27**	**3.22**	**3.17**	**3.14**	**3.09**	**3.05**	**3.02**	**3.00**	**2.99**	**2.96**	**2.94**
200	9.40	6.13	5.07	4.55	4.23	3.86	*3.65*	**3.49**	**3.38**	**3.30**	**3.25**	**3.20**	**3.17**	**3.12**	**3.08**	**3.05**	**3.03**	**3.01**	**2.98**	**2.96**

Table 19-5. κ-Multipliers for 1-of-1 Interwell Prediction Limits on Means of Order 2 (10 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.86	**2.71**	**2.34**	**2.16**	**2.06**	**1.93**	**1.87**	**1.82**	**1.78**	**1.76**	**1.74**	**1.73**	**1.72**	**1.71**	**1.69**	**1.69**	**1.68**	**1.68**	**1.67**	**1.66**
2	4.75	3.20	**2.71**	**2.48**	**2.34**	**2.19**	**2.10**	**2.04**	**2.00**	**1.97**	**1.95**	**1.93**	**1.92**	**1.90**	**1.89**	**1.88**	**1.87**	**1.86**	**1.85**	**1.84**
3	5.29	3.49	**2.93**	**2.66**	**2.51**	**2.33**	**2.24**	**2.16**	**2.12**	**2.08**	**2.06**	**2.04**	**2.03**	**2.01**	**1.99**	**1.98**	**1.97**	**1.97**	**1.95**	**1.95**
4	5.68	3.69	*3.09*	**2.80**	**2.62**	**2.43**	**2.33**	**2.25**	**2.20**	**2.17**	**2.14**	**2.12**	**2.10**	**2.08**	**2.07**	**2.05**	**2.04**	**2.04**	**2.02**	**2.02**
5	5.99	3.86	3.21	**2.90**	**2.72**	**2.51**	**2.40**	**2.32**	**2.26**	**2.23**	**2.20**	**2.18**	**2.16**	**2.14**	**2.12**	**2.11**	**2.10**	**2.09**	**2.08**	**2.07**
8	6.62	4.20	3.46	*3.11*	**2.91**	**2.68**	**2.55**	**2.46**	**2.40**	**2.35**	**2.32**	**2.30**	**2.28**	**2.26**	**2.24**	**2.22**	**2.21**	**2.20**	**2.19**	**2.18**
12	7.16	4.49	3.68	3.29	*3.07*	**2.82**	**2.68**	**2.57**	**2.51**	**2.46**	**2.43**	**2.40**	**2.38**	**2.35**	**2.33**	**2.32**	**2.31**	**2.30**	**2.28**	**2.27**
16	7.54	4.69	3.83	3.42	3.18	**2.91**	**2.77**	**2.66**	**2.59**	**2.54**	**2.50**	**2.48**	**2.45**	**2.42**	**2.40**	**2.38**	**2.37**	**2.36**	**2.34**	**2.33**
20	7.83	4.85	3.95	3.52	3.27	*2.99*	**2.84**	**2.72**	**2.65**	**2.60**	**2.56**	**2.53**	**2.51**	**2.47**	**2.45**	**2.43**	**2.42**	**2.41**	**2.39**	**2.38**
30	8.33	5.13	4.17	3.70	3.43	*3.13*	*2.96*	**2.84**	**2.76**	**2.70**	**2.66**	**2.63**	**2.60**	**2.57**	**2.54**	**2.52**	**2.51**	**2.50**	**2.48**	**2.46**
40	8.69	5.33	4.31	3.83	3.54	3.22	*3.05*	**2.92**	**2.83**	**2.77**	**2.73**	**2.70**	**2.67**	**2.63**	**2.61**	**2.59**	**2.57**	**2.56**	**2.54**	**2.52**
50	8.95	5.48	4.43	3.92	3.63	3.30	*3.12*	*2.98*	**2.89**	**2.83**	**2.78**	**2.75**	**2.72**	**2.68**	**2.65**	**2.63**	**2.62**	**2.60**	**2.58**	**2.57**
60	9.17	5.60	4.52	4.00	3.70	3.36	*3.16*	*3.03*	**2.94**	**2.81**	**2.83**	**2.79**	**2.76**	**2.72**	**2.69**	**2.67**	**2.66**	**2.64**	**2.62**	**2.60**
75	9.43	5.74	4.63	4.10	3.78	3.43	*3.24*	*3.09*	*2.99*	**2.93**	**2.88**	**2.84**	**2.81**	**2.77**	**2.74**	**2.72**	**2.70**	**2.69**	**2.66**	**2.65**
100	9.76	5.93	4.77	4.22	3.89	3.52	3.32	*3.17*	*3.07*	*3.00*	*2.95*	**2.91**	**2.88**	**2.83**	**2.80**	**2.78**	**2.76**	**2.75**	**2.72**	**2.70**
125	10.01	6.07	4.88	4.31	3.97	3.59	3.39	*3.23*	*3.12*	*3.05*	*3.00*	*2.96*	**2.93**	**2.88**	**2.85**	**2.82**	**2.81**	**2.79**	**2.76**	**2.75**
150	10.21	6.18	4.97	4.38	4.04	3.65	3.44	3.27	*3.17*	*3.10*	*3.04*	*3.00*	*2.97*	**2.92**	**2.89**	**2.86**	**2.84**	**2.83**	**2.80**	**2.78**
175	10.37	6.28	5.04	4.45	4.10	3.70	3.48	3.32	*3.21*	*3.13*	*3.08*	*3.04*	*3.00*	*2.95*	**2.92**	**2.89**	**2.87**	**2.86**	**2.83**	**2.81**
200	10.52	6.36	5.10	4.50	4.15	3.74	3.52	3.35	*3.24*	*3.16*	*3.11*	*3.07*	*3.03*	*2.98*	*2.95*	**2.92**	**2.90**	**2.88**	**2.85**	**2.83**

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Table 19-5. κ-Multipliers for 1-of-1 Interwell Prediction Limits on Means of Order 2 (10 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	4.75	**3.20**	**2.71**	**2.48**	**2.34**	**2.19**	**2.10**	**2.04**	**2.00**	**1.97**	**1.95**	**1.93**	**1.92**	**1.90**	**1.89**	**1.88**	**1.87**	**1.86**	**1.85**	**1.84**
2	5.68	3.69	**3.09**	**2.80**	**2.62**	**2.43**	**2.33**	**2.25**	**2.20**	**2.17**	**2.14**	**2.12**	**2.10**	**2.08**	**2.07**	**2.05**	**2.04**	**2.04**	**2.02**	**2.02**
3	6.23	3.99	*3.31*	**2.98**	**2.79**	**2.58**	**2.46**	**2.37**	**2.32**	**2.28**	**2.25**	**2.23**	**2.21**	**2.18**	**2.17**	**2.15**	**2.14**	**2.14**	**2.12**	**2.11**
4	6.62	4.20	3.46	**3.11**	**2.91**	**2.68**	**2.55**	**2.46**	**2.40**	**2.35**	**2.32**	**2.30**	**2.28**	**2.26**	**2.24**	**2.22**	**2.21**	**2.20**	**2.19**	**2.18**
5	6.92	4.36	3.58	**3.21**	**3.00**	**2.75**	**2.62**	**2.52**	**2.46**	**2.41**	**2.38**	**2.36**	**2.34**	**2.31**	**2.29**	**2.27**	**2.26**	**2.25**	**2.24**	**2.23**
8	7.54	4.69	3.83	3.42	**3.18**	**2.91**	**2.77**	**2.66**	**2.59**	**2.54**	**2.50**	**2.48**	**2.45**	**2.42**	**2.40**	**2.38**	**2.37**	**2.36**	**2.34**	**2.33**
12	8.06	4.98	4.05	3.60	*3.34*	**3.05**	**2.89**	**2.77**	**2.70**	**2.64**	**2.60**	**2.57**	**2.55**	**2.52**	**2.49**	**2.47**	**2.46**	**2.45**	**2.43**	**2.42**
16	8.42	5.18	4.20	3.73	*3.46*	**3.15**	**2.98**	**2.85**	**2.77**	**2.72**	**2.68**	**2.64**	**2.62**	**2.58**	**2.56**	**2.54**	**2.52**	**2.51**	**2.49**	**2.48**
20	8.69	5.33	4.31	3.83	3.54	**3.22**	**3.05**	**2.92**	**2.83**	**2.77**	**2.73**	**2.70**	**2.67**	**2.63**	**2.61**	**2.59**	**2.57**	**2.56**	**2.54**	**2.52**
30	9.17	5.60	4.52	4.00	3.70	*3.36*	**3.16**	**3.03**	**2.94**	**2.81**	**2.83**	**2.79**	**2.76**	**2.72**	**2.69**	**2.67**	**2.66**	**2.64**	**2.62**	**2.60**
40	9.50	5.78	4.66	4.12	3.81	*3.45*	**3.25**	**3.11**	**3.01**	**2.94**	**2.90**	**2.86**	**2.83**	**2.79**	**2.76**	**2.73**	**2.71**	**2.70**	**2.68**	**2.66**
50	9.76	5.93	4.77	4.22	3.89	*3.52*	*3.32*	**3.17**	**3.07**	**3.00**	**2.95**	**2.91**	**2.88**	**2.83**	**2.80**	**2.78**	**2.76**	**2.75**	**2.72**	**2.70**
60	9.96	6.04	4.86	4.29	3.96	3.58	*3.37*	**3.22**	**3.11**	**3.04**	**2.99**	**2.95**	**2.92**	**2.87**	**2.84**	**2.82**	**2.80**	**2.78**	**2.76**	**2.74**
75	10.21	6.18	4.97	4.38	4.04	3.65	*3.44*	*3.27*	**3.17**	**3.10**	**3.04**	**3.00**	**2.97**	**2.92**	**2.89**	**2.86**	**2.84**	**2.83**	**2.80**	**2.78**
100	10.52	6.36	5.10	4.50	4.15	3.74	*3.52*	*3.35*	**3.24**	**3.16**	**3.11**	**3.07**	**3.03**	**2.98**	**2.95**	**2.92**	**2.90**	**2.88**	**2.85**	**2.83**
125	10.76	6.49	5.21	4.59	4.23	3.81	3.58	*3.41*	*3.30*	**3.22**	**3.16**	**3.12**	**3.08**	**3.03**	**2.99**	**2.96**	**2.94**	**2.93**	**2.90**	**2.88**
150	10.95	6.60	5.29	4.66	4.29	3.87	3.64	*3.46*	*3.34*	*3.26*	**3.20**	**3.16**	**3.12**	**3.07**	**3.03**	**3.00**	**2.98**	**2.96**	**2.93**	**2.91**
175	11.10	6.69	5.36	4.72	4.35	3.92	3.68	*3.50*	*3.38*	*3.30*	**3.24**	**3.19**	**3.15**	**3.10**	**3.06**	**3.03**	**3.01**	**2.99**	**2.96**	**2.94**
200	11.24	6.77	5.42	4.77	4.39	3.96	3.72	*3.53*	*3.41*	*3.33*	*3.27*	**3.22**	**3.18**	**3.12**	**3.09**	**3.06**	**3.03**	**3.02**	**2.98**	**2.96**

Table 19-5. κ-Multipliers for 1-of-1 Interwell Prediction Limits on Means of Order 2 (10 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	5.68	3.69	**3.09**	**2.80**	**2.62**	**2.43**	**2.33**	**2.25**	**2.20**	**2.17**	**2.14**	**2.12**	**2.10**	**2.08**	**2.07**	**2.05**	**2.04**	**2.04**	**2.02**	**2.02**
2	6.62	4.20	**3.46**	**3.11**	**2.91**	**2.68**	**2.55**	**2.46**	**2.40**	**2.35**	**2.32**	**2.30**	**2.28**	**2.26**	**2.24**	**2.22**	**2.21**	**2.20**	**2.19**	**2.18**
3	7.16	4.49	3.68	**3.29**	**3.07**	**2.82**	**2.68**	**2.57**	**2.51**	**2.46**	**2.43**	**2.40**	**2.38**	**2.35**	**2.33**	**2.32**	**2.31**	**2.30**	**2.28**	**2.27**
4	7.54	4.69	3.83	**3.42**	**3.18**	**2.91**	**2.77**	**2.66**	**2.59**	**2.54**	**2.50**	**2.48**	**2.45**	**2.42**	**2.40**	**2.38**	**2.37**	**2.36**	**2.34**	**2.33**
5	7.83	4.85	3.95	**3.52**	**3.27**	**2.99**	**2.84**	**2.72**	**2.65**	**2.60**	**2.56**	**2.53**	**2.51**	**2.47**	**2.45**	**2.43**	**2.42**	**2.41**	**2.39**	**2.38**
8	8.42	5.18	4.20	3.73	**3.46**	**3.15**	**2.98**	**2.85**	**2.77**	**2.72**	**2.68**	**2.64**	**2.62**	**2.58**	**2.56**	**2.54**	**2.52**	**2.51**	**2.49**	**2.48**
12	8.91	5.45	4.41	3.91	*3.61*	**3.28**	**3.10**	**2.97**	**2.88**	**2.82**	**2.77**	**2.74**	**2.71**	**2.67**	**2.65**	**2.62**	**2.61**	**2.60**	**2.57**	**2.56**
16	9.25	5.64	4.55	4.03	*3.72*	**3.38**	**3.19**	**3.05**	**2.95**	**2.89**	**2.84**	**2.81**	**2.78**	**2.74**	**2.71**	**2.69**	**2.67**	**2.66**	**2.63**	**2.62**
20	9.50	5.78	4.66	4.12	3.81	**3.45**	**3.25**	**3.11**	**3.01**	**2.94**	**2.90**	**2.86**	**2.83**	**2.79**	**2.76**	**2.73**	**2.71**	**2.70**	**2.68**	**2.66**
30	9.96	6.04	4.86	4.29	3.96	*3.58*	**3.37**	**3.22**	**3.11**	**3.04**	**2.99**	**2.95**	**2.92**	**2.87**	**2.84**	**2.82**	**2.80**	**2.78**	**2.76**	**2.74**
40	10.28	6.22	5.00	4.41	4.06	*3.67*	**3.46**	**3.29**	**3.19**	**3.11**	**3.06**	**3.02**	**2.98**	**2.93**	**2.90**	**2.87**	**2.85**	**2.84**	**2.81**	**2.79**
50	10.52	6.36	5.10	4.50	4.15	*3.74*	**3.52**	**3.35**	**3.24**	**3.16**	**3.11**	**3.07**	**3.03**	**2.98**	**2.95**	**2.92**	**2.90**	**2.88**	**2.85**	**2.83**
60	10.71	6.47	5.19	4.57	4.21	*3.80*	**3.57**	**3.40**	**3.29**	**3.21**	**3.15**	**3.11**	**3.07**	**3.02**	**2.98**	**2.96**	**2.93**	**2.92**	**2.89**	**2.87**
75	10.95	6.60	5.29	4.66	4.29	3.87	*3.64*	**3.46**	**3.34**	**3.26**	**3.20**	**3.16**	**3.12**	**3.07**	**3.03**	**3.00**	**2.98**	**2.96**	**2.93**	**2.91**
100	11.24	6.77	5.42	4.77	4.39	3.96	*3.72*	**3.53**	**3.41**	**3.33**	**3.27**	**3.22**	**3.18**	**3.12**	**3.09**	**3.06**	**3.03**	**3.02**	**2.98**	**2.96**
125	11.47	6.90	5.52	4.86	4.47	4.02	*3.78*	*3.59*	**3.46**	**3.38**	**3.32**	**3.27**	**3.23**	**3.17**	**3.13**	**3.10**	**3.08**	**3.06**	**3.02**	**3.00**
150	11.65	7.00	5.60	4.93	4.53	4.08	*3.83*	*3.63*	**3.51**	**3.42**	**3.36**	**3.31**	**3.27**	**3.21**	**3.17**	**3.13**	**3.11**	**3.09**	**3.06**	**3.03**
175	11.80	7.09	5.67	4.99	4.58	4.12	*3.87*	*3.67*	**3.54**	**3.46**	**3.39**	**3.34**	**3.30**	**3.24**	**3.20**	**3.16**	**3.14**	**3.12**	**3.09**	**3.06**
200	11.93	7.16	5.73	5.04	4.63	4.16	3.90	*3.71*	*3.58*	**3.49**	**3.42**	**3.37**	**3.33**	**3.26**	**3.22**	**3.19**	**3.16**	**3.14**	**3.11**	**3.09**

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Table 19-5. κ-Multipliers for 1-of-1 Interwell Prediction Limits on Means of Order 2 (20 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	4.97	3.25	2.74	2.49	2.35	2.19	2.10	2.04	2.00	1.97	1.95	1.93	1.92	1.90	1.89	1.88	1.87	1.86	1.85	1.84
2	6.07	3.79	3.13	2.82	2.64	2.44	2.33	2.25	2.20	2.17	2.14	2.12	2.11	2.08	2.07	2.05	2.05	2.04	2.02	2.02
3	6.75	4.12	3.36	3.01	2.81	2.59	2.47	2.38	2.32	2.28	2.25	2.23	2.21	2.19	2.17	2.15	2.14	2.14	2.12	2.11
4	7.24	4.35	3.53	3.15	2.93	2.69	2.56	2.46	2.40	2.36	2.33	2.30	2.28	2.26	2.24	2.22	2.21	2.20	2.19	2.18
5	7.62	4.54	3.66	3.26	3.02	2.77	2.63	2.53	2.46	2.42	2.38	2.36	2.34	2.31	2.29	2.28	2.26	2.25	2.24	2.23
8	8.41	4.92	3.94	3.48	3.22	2.93	2.78	2.66	2.59	2.54	2.51	2.48	2.46	2.42	2.40	2.38	2.37	2.36	2.34	2.33
12	9.09	5.26	4.18	3.68	3.39	3.08	2.91	2.78	2.70	2.65	2.61	2.58	2.55	2.52	2.49	2.47	2.46	2.45	2.43	2.42
16	9.57	5.49	4.34	3.81	3.51	3.18	3.00	2.86	2.78	2.72	2.68	2.65	2.62	2.58	2.56	2.54	2.52	2.51	2.49	2.48
20	9.93	5.67	4.47	3.92	3.60	3.25	3.07	2.93	2.84	2.78	2.73	2.70	2.67	2.63	2.61	2.59	2.57	2.56	2.54	2.52
30	10.57	5.99	4.71	4.11	3.77	3.39	3.19	3.04	2.95	2.88	2.83	2.80	2.77	2.72	2.70	2.67	2.66	2.64	2.62	2.60
40	11.01	6.22	4.87	4.25	3.89	3.49	3.28	3.12	3.02	2.95	2.90	2.86	2.83	2.79	2.76	2.73	2.72	2.70	2.68	2.66
50	11.35	6.39	5.00	4.35	3.98	3.57	3.35	3.18	3.08	3.01	2.95	2.89	2.88	2.84	2.80	2.78	2.76	2.75	2.72	2.70
60	11.62	6.53	5.10	4.43	4.05	3.63	3.40	3.23	3.13	3.05	3.00	2.96	2.92	2.88	2.84	2.82	2.80	2.78	2.76	2.74
75	11.95	6.69	5.22	4.54	4.14	3.71	3.47	3.30	3.18	3.11	3.05	3.01	2.97	2.92	2.89	2.86	2.84	2.83	2.80	2.78
100	12.36	6.91	5.38	4.67	4.26	3.80	3.56	3.37	3.26	3.18	3.12	3.07	3.04	2.98	2.95	2.92	2.90	2.88	2.85	2.84
125	12.68	7.07	5.50	4.77	4.34	3.88	3.62	3.43	3.31	3.23	3.17	3.12	3.09	3.03	2.99	2.97	2.94	2.93	2.90	2.88
150	12.93	7.20	5.59	4.85	4.42	3.94	3.68	3.48	3.36	3.27	3.21	3.16	3.13	3.07	3.03	3.00	2.98	2.96	2.93	2.91
175	13.14	7.31	5.67	4.91	4.48	3.99	3.72	3.52	3.40	3.31	3.25	3.20	3.16	3.10	3.06	3.03	3.01	2.99	2.96	2.94
200	13.32	7.40	5.74	4.97	4.53	4.03	3.76	3.56	3.43	3.34	3.28	3.23	3.19	3.13	3.09	3.06	3.04	3.02	2.98	2.96

Table 19-5. κ-Multipliers for 1-of-1 Interwell Prediction Limits on Means of Order 2 (20 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	6.07	3.79	3.13	2.82	2.64	2.44	2.33	2.25	2.20	2.17	2.14	2.12	2.11	2.08	2.07	2.05	2.05	2.04	2.02	2.02
2	7.24	4.35	3.53	3.15	2.93	2.69	2.56	2.46	2.40	2.36	2.33	2.30	2.28	2.26	2.24	2.22	2.21	2.20	2.19	2.18
3	7.93	4.69	3.77	3.34	3.10	2.83	2.69	2.58	2.51	2.47	2.43	2.41	2.39	2.36	2.33	2.32	2.31	2.30	2.28	2.27
4	8.41	4.92	3.94	3.48	3.22	2.93	2.78	2.66	2.59	2.54	2.51	2.48	2.46	2.42	2.40	2.38	2.37	2.36	2.34	2.33
5	8.79	5.11	4.07	3.59	3.31	3.01	2.85	2.73	2.65	2.60	2.56	2.53	2.51	2.48	2.45	2.43	2.42	2.41	2.39	2.38
8	9.57	5.49	4.34	3.81	3.51	3.18	3.00	2.86	2.78	2.72	2.68	2.65	2.62	2.58	2.56	2.54	2.52	2.51	2.49	2.48
12	10.22	5.82	4.58	4.01	3.68	3.32	3.12	2.98	2.89	2.82	2.78	2.74	2.72	2.68	2.65	2.63	2.61	2.60	2.57	2.56
16	10.67	6.04	4.74	4.14	3.80	3.42	3.21	3.06	2.96	2.90	2.85	2.81	2.78	2.74	2.71	2.69	2.67	2.66	2.63	2.62
20	11.01	6.22	4.87	4.25	3.89	3.49	3.28	3.12	3.02	2.95	2.90	2.86	2.83	2.79	2.76	2.73	2.72	2.70	2.68	2.66
30	11.62	6.53	5.10	4.43	4.05	3.63	3.40	3.23	3.13	3.05	3.00	2.96	2.92	2.88	2.84	2.82	2.80	2.78	2.76	2.74
40	12.04	6.74	5.25	4.57	4.17	3.73	3.49	3.31	3.20	3.12	3.07	3.02	2.99	2.94	2.90	2.88	2.86	2.84	2.81	2.79
50	12.36	6.91	5.38	4.67	4.26	3.80	3.56	3.37	3.26	3.18	3.12	3.07	3.04	2.98	2.95	2.92	2.90	2.88	2.85	2.84
60	12.62	7.04	5.47	4.75	4.33	3.86	3.61	3.42	3.30	3.22	3.16	3.11	3.08	3.02	2.99	2.96	2.94	2.92	2.89	2.87
75	12.93	7.20	5.59	4.85	4.42	3.94	3.68	3.48	3.36	3.27	3.21	3.16	3.13	3.07	3.03	3.00	2.98	2.96	2.93	2.91
100	13.32	7.40	5.74	4.97	4.53	4.03	3.76	3.56	3.43	3.34	3.28	3.23	3.19	3.13	3.09	3.06	3.04	3.02	2.98	2.96
125	13.62	7.56	5.86	5.07	4.61	4.10	3.83	3.62	3.49	3.39	3.33	3.28	3.24	3.18	3.13	3.10	3.08	3.06	3.03	3.00
150	13.86	7.68	5.95	5.15	4.68	4.16	3.88	3.67	3.53	3.44	3.37	3.32	3.27	3.21	3.17	3.14	3.11	3.09	3.06	3.04
175	14.06	7.79	6.03	5.21	4.74	4.21	3.93	3.71	3.57	3.47	3.40	3.35	3.31	3.24	3.20	3.17	3.14	3.12	3.09	3.06
200	14.23	7.88	6.10	5.27	4.79	4.26	3.96	3.74	3.60	3.50	3.43	3.38	3.33	3.27	3.23	3.19	3.17	3.15	3.11	3.09

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Table 19-5. κ-Multipliers for 1-of-1 Interwell Prediction Limits on Means of Order 2 (20 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	7.24	4.35	**3.53**	**3.15**	**2.93**	**2.69**	**2.56**	**2.46**	**2.40**	**2.36**	**2.33**	**2.30**	**2.28**	**2.26**	**2.24**	**2.22**	**2.21**	**2.20**	**2.19**	**2.18**
2	8.41	4.92	3.94	**3.48**	**3.22**	**2.93**	**2.78**	**2.66**	**2.59**	**2.54**	**2.51**	**2.48**	**2.46**	**2.42**	**2.40**	**2.38**	**2.37**	**2.36**	**2.34**	**2.33**
3	9.09	5.26	4.18	*3.68*	**3.39**	**3.08**	**2.91**	**2.78**	**2.70**	**2.65**	**2.61**	**2.58**	**2.55**	**2.52**	**2.49**	**2.47**	**2.46**	**2.45**	**2.43**	**2.42**
4	9.57	5.49	4.34	3.81	**3.51**	**3.18**	**3.00**	**2.86**	**2.78**	**2.72**	**2.68**	**2.65**	**2.62**	**2.58**	**2.56**	**2.54**	**2.52**	**2.51**	**2.49**	**2.48**
5	9.93	5.67	4.47	3.92	*3.60*	**3.25**	**3.07**	**2.93**	**2.84**	**2.78**	**2.73**	**2.70**	**2.67**	**2.63**	**2.61**	**2.59**	**2.57**	**2.56**	**2.54**	**2.52**
8	10.67	6.04	4.74	4.14	3.80	**3.42**	**3.21**	**3.06**	**2.96**	**2.90**	**2.85**	**2.81**	**2.78**	**2.74**	**2.71**	**2.69**	**2.67**	**2.66**	**2.63**	**2.62**
12	11.29	6.36	4.97	4.33	3.96	**3.56**	**3.34**	**3.17**	**3.07**	**3.00**	**2.94**	**2.91**	**2.87**	**2.83**	**2.80**	**2.77**	**2.75**	**2.74**	**2.71**	**2.70**
16	11.72	6.57	5.13	4.46	4.08	*3.65*	**3.42**	**3.25**	**3.14**	**3.07**	**3.01**	**2.97**	**2.94**	**2.89**	**2.86**	**2.83**	**2.81**	**2.80**	**2.77**	**2.75**
20	12.04	6.74	5.25	4.57	4.17	*3.73*	**3.49**	**3.31**	**3.20**	**3.12**	**3.07**	**3.02**	**2.99**	**2.94**	**2.90**	**2.88**	**2.86**	**2.84**	**2.81**	**2.79**
30	12.62	7.04	5.47	4.75	4.33	3.86	*3.61*	**3.42**	**3.30**	**3.22**	**3.16**	**3.11**	**3.08**	**3.02**	**2.99**	**2.96**	**2.94**	**2.92**	**2.89**	**2.87**
40	13.02	7.24	5.63	4.87	4.44	3.96	*3.70*	**3.50**	**3.38**	**3.29**	**3.23**	**3.18**	**3.14**	**3.08**	**3.04**	**3.01**	**2.99**	**2.97**	**2.94**	**2.92**
50	13.32	7.40	5.74	4.97	4.53	4.03	*3.76*	**3.56**	**3.43**	**3.34**	**3.28**	**3.23**	**3.19**	**3.13**	**3.09**	**3.06**	**3.04**	**3.02**	**2.98**	**2.96**
60	13.56	7.53	5.84	5.05	4.60	4.09	*3.82*	*3.61*	**3.48**	**3.39**	**3.32**	**3.27**	**3.23**	**3.17**	**3.13**	**3.09**	**3.07**	**3.05**	**3.02**	**3.00**
75	13.86	7.68	5.95	5.15	4.68	4.16	*3.88*	*3.67*	**3.53**	**3.44**	**3.37**	**3.32**	**3.27**	**3.21**	**3.17**	**3.14**	**3.11**	**3.09**	**3.06**	**3.04**
100	14.23	7.88	6.10	5.27	4.79	4.26	3.96	*3.74*	*3.60*	**3.50**	**3.43**	**3.38**	**3.33**	**3.27**	**3.23**	**3.19**	**3.17**	**3.15**	**3.11**	**3.09**
125	14.52	8.03	6.21	5.36	4.87	4.33	4.03	*3.80*	*3.66*	**3.56**	**3.48**	**3.43**	**3.38**	**3.32**	**3.27**	**3.23**	**3.21**	**3.19**	**3.15**	**3.13**
150	14.74	8.15	6.30	5.44	4.94	4.38	4.08	*3.85*	*3.70*	*3.60*	**3.52**	**3.46**	**3.42**	**3.35**	**3.30**	**3.27**	**3.24**	**3.22**	**3.18**	**3.16**
175	14.94	8.25	6.37	5.50	5.00	4.43	4.12	*3.89*	*3.74*	*3.63*	**3.56**	**3.50**	**3.45**	**3.38**	**3.33**	**3.30**	**3.27**	**3.25**	**3.21**	**3.18**
200	15.10	8.33	6.44	5.55	5.04	4.47	4.16	*3.92*	*3.77*	*3.66*	*3.59*	**3.53**	**3.48**	**3.41**	**3.36**	**3.32**	**3.30**	**3.27**	**3.23**	**3.21**

Table 19-5. κ-Multipliers for 1-of-1 Interwell Prediction Limits on Means of Order 2 (40 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	6.34	3.85	3.15	**2.83**	**2.65**	**2.45**	**2.34**	**2.26**	**2.20**	**2.17**	**2.14**	**2.12**	**2.11**	**2.08**	**2.07**	**2.05**	**2.05**	**2.04**	**2.02**	**2.02**
2	7.72	4.46	3.57	3.17	**2.94**	**2.70**	**2.56**	**2.46**	**2.40**	**2.36**	**2.33**	**2.30**	**2.29**	**2.26**	**2.24**	**2.22**	**2.21**	**2.20**	**2.19**	**2.18**
3	8.57	4.83	3.83	3.37	*3.12*	**2.84**	**2.69**	**2.58**	**2.52**	**2.47**	**2.43**	**2.41**	**2.39**	**2.36**	**2.33**	**2.32**	**2.31**	**2.30**	**2.28**	**2.27**
4	9.18	5.10	4.01	3.52	3.24	**2.94**	**2.79**	**2.67**	**2.59**	**2.54**	**2.51**	**2.48**	**2.46**	**2.42**	**2.40**	**2.38**	**2.37**	**2.36**	**2.34**	**2.33**
5	9.66	5.30	4.15	3.63	3.34	*3.02*	**2.86**	**2.73**	**2.66**	**2.60**	**2.56**	**2.53**	**2.51**	**2.48**	**2.45**	**2.43**	**2.42**	**2.41**	**2.39**	**2.38**
8	10.66	5.75	4.45	3.87	3.55	*3.19*	*3.01*	**2.87**	**2.78**	**2.72**	**2.68**	**2.65**	**2.62**	**2.58**	**2.56**	**2.54**	**2.52**	**2.51**	**2.49**	**2.48**
12	11.51	6.13	4.71	4.08	3.72	3.34	*3.14*	*2.99*	**2.89**	**2.83**	**2.78**	**2.75**	**2.72**	**2.68**	**2.65**	**2.63**	**2.61**	**2.60**	**2.57**	**2.56**
16	12.11	6.39	4.90	4.22	3.85	3.44	*3.23*	*3.07*	*2.97*	**2.90**	**2.85**	**2.81**	**2.78**	**2.74**	**2.71**	**2.69**	**2.67**	**2.66**	**2.63**	**2.62**
20	12.56	6.60	5.04	4.34	3.95	3.52	3.30	*3.13*	*3.03*	*2.96*	**2.90**	**2.87**	**2.83**	**2.79**	**2.76**	**2.73**	**2.72**	**2.70**	**2.68**	**2.66**
30	13.37	6.97	5.29	4.54	4.12	3.66	3.42	*3.24*	*3.13*	*3.06*	*3.00*	*2.96*	**2.93**	**2.88**	**2.84**	**2.82**	**2.80**	**2.78**	**2.76**	**2.74**
40	13.93	7.22	5.47	4.69	4.25	3.77	3.51	3.33	*3.21*	*3.13*	*3.07*	*3.03*	*2.99*	*2.94*	**2.90**	**2.88**	**2.86**	**2.84**	**2.81**	**2.79**
50	14.35	7.42	5.61	4.80	4.34	3.85	3.58	3.32	*3.27*	*3.18*	*3.12*	*3.08*	*3.04*	*2.99*	*2.95*	**2.92**	**2.90**	**2.88**	**2.86**	**2.84**
60	14.70	7.58	5.72	4.89	4.42	3.91	3.64	3.44	3.31	*3.23*	*3.16*	*3.12*	*3.08*	*3.03*	*2.99*	*2.96*	*2.94*	**2.92**	**2.89**	**2.87**
75	15.11	7.77	5.86	5.00	4.51	3.99	3.71	3.50	3.37	*3.28*	*3.22*	*3.17*	*3.13*	*3.07*	*3.03*	*3.00*	*2.98*	*2.96*	**2.93**	**2.91**
100	15.63	8.02	6.03	5.14	4.64	4.09	3.80	3.58	3.44	3.35	*3.28*	*3.23*	*3.19*	*3.13*	*3.09*	*3.06*	*3.04*	*3.02*	*2.99*	*2.96*
125	16.02	8.20	6.16	5.25	4.73	4.16	3.86	3.64	3.50	3.40	3.33	*3.28*	*3.24*	*3.18*	*3.14*	*3.10*	*3.08*	*3.06*	*3.03*	*3.00*
150	16.34	8.35	6.27	5.33	4.80	4.23	3.92	3.69	3.55	3.45	3.38	3.32	*3.28*	*3.22*	*3.17*	*3.14*	*3.11*	*3.09*	*3.06*	*3.04*
175	16.61	8.48	6.36	5.41	4.87	4.28	3.97	3.73	3.59	3.48	3.41	3.36	*3.31*	*3.25*	*3.20*	*3.17*	*3.14*	*3.12*	*3.09*	*3.06*
200	16.84	8.59	6.44	5.47	4.92	4.33	4.01	3.77	3.62	3.52	3.44	3.38	3.34	*3.27*	*3.23*	*3.19*	*3.17*	*3.15*	*3.11*	*3.09*

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Table 19-5. κ-Multipliers for 1-of-1 Interwell Prediction Limits on Means of Order 2 (40 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	7.72	4.46	3.57	**3.17**	**2.94**	**2.70**	**2.56**	**2.46**	**2.40**	**2.36**	**2.33**	**2.30**	**2.29**	**2.26**	**2.24**	**2.22**	**2.21**	**2.20**	**2.19**	**2.18**
2	9.18	5.10	4.01	3.52	**3.24**	**2.94**	**2.79**	**2.67**	**2.59**	**2.54**	**2.51**	**2.48**	**2.46**	**2.42**	**2.40**	**2.38**	**2.37**	**2.36**	**2.34**	**2.33**
3	10.05	5.48	4.27	3.72	*3.42*	**3.09**	**2.92**	**2.79**	**2.71**	**2.65**	**2.61**	**2.58**	**2.55**	**2.52**	**2.49**	**2.48**	**2.46**	**2.45**	**2.43**	**2.42**
4	10.66	5.75	4.45	3.87	3.55	**3.19**	**3.01**	**2.87**	**2.78**	**2.72**	**2.68**	**2.65**	**2.62**	**2.58**	**2.56**	**2.54**	**2.52**	**2.51**	**2.49**	**2.48**
5	11.13	5.95	4.59	3.99	3.64	*3.27*	**3.08**	**2.93**	**2.84**	**2.78**	**2.74**	**2.70**	**2.68**	**2.64**	**2.61**	**2.59**	**2.57**	**2.56**	**2.54**	**2.52**
8	12.11	6.39	4.90	4.22	3.85	*3.44*	**3.23**	**3.07**	**2.97**	**2.90**	**2.85**	**2.81**	**2.78**	**2.74**	**2.71**	**2.69**	**2.67**	**2.66**	**2.63**	**2.62**
12	12.93	6.76	5.15	4.43	4.02	3.59	*3.35*	**3.18**	**3.08**	**3.00**	**2.95**	**2.91**	**2.88**	**2.83**	**2.80**	**2.77**	**2.75**	**2.74**	**2.71**	**2.70**
16	13.50	7.03	5.33	4.58	4.15	3.69	*3.44*	*3.26*	**3.15**	**3.07**	**3.02**	**2.97**	**2.94**	**2.89**	**2.86**	**2.83**	**2.81**	**2.80**	**2.77**	**2.75**
20	13.93	7.22	5.47	4.69	4.25	3.77	*3.51*	*3.33*	**3.21**	**3.13**	**3.07**	**3.03**	**2.99**	**2.94**	**2.90**	**2.88**	**2.86**	**2.84**	**2.81**	**2.79**
30	14.70	7.58	5.72	4.89	4.42	3.91	3.64	*3.44*	*3.31*	**3.23**	**3.16**	**3.12**	**3.08**	**3.03**	**2.99**	**2.96**	**2.94**	**2.92**	**2.89**	**2.87**
40	15.23	7.83	5.90	5.03	4.54	4.01	3.73	*3.52*	*3.39*	*3.30*	**3.23**	**3.18**	**3.14**	**3.09**	**3.05**	**3.02**	**2.99**	**2.98**	**2.94**	**2.92**
50	15.63	8.02	6.03	5.14	4.64	4.09	3.80	*3.58*	*3.44*	*3.35*	*3.28*	**3.23**	**3.19**	**3.13**	**3.09**	**3.06**	**3.04**	**3.02**	**2.99**	**2.96**
60	15.95	8.17	6.14	5.23	4.71	4.15	3.85	3.63	*3.49*	*3.39*	*3.32*	*3.27*	**3.23**	**3.17**	**3.13**	**3.10**	**3.07**	**3.05**	**3.02**	**3.00**
75	16.34	8.35	6.27	5.33	4.80	4.23	3.92	3.69	*3.55*	*3.45*	*3.38*	*3.32*	*3.28*	**3.22**	**3.17**	**3.14**	**3.11**	**3.09**	**3.06**	**3.04**
100	16.84	8.59	6.44	5.47	4.92	4.33	4.01	3.77	*3.62*	*3.52*	*3.44*	*3.38*	*3.34*	*3.27*	**3.23**	**3.19**	**3.17**	**3.15**	**3.11**	**3.09**
125	17.21	8.77	6.56	5.57	5.01	4.40	4.07	3.83	3.67	*3.57*	*3.49*	*3.43*	*3.39*	*3.32*	*3.27*	**3.24**	**3.21**	**3.19**	**3.15**	**3.13**
150	17.52	8.91	6.67	5.66	5.09	4.46	4.13	3.88	3.72	*3.61*	*3.53*	*3.47*	*3.43*	*3.36*	*3.31*	*3.27*	**3.24**	**3.22**	**3.18**	**3.16**
175	17.77	9.03	6.75	5.73	5.15	4.51	4.17	3.92	3.76	*3.65*	*3.57*	*3.51*	*3.46*	*3.39*	*3.34*	*3.30*	*3.27*	**3.25**	**3.21**	**3.18**
200	17.99	9.14	6.83	5.79	5.20	4.56	4.21	3.95	3.79	3.68	*3.60*	*3.53*	*3.49*	*3.41*	*3.36*	*3.33*	*3.30*	*3.27*	**3.23**	**3.21**

Table 19-5. κ-Multipliers for 1-of-1 Interwell Prediction Limits on Means of Order 2 (40 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	9.18	5.10	4.01	**3.52**	**3.24**	**2.94**	**2.79**	**2.67**	**2.59**	**2.54**	**2.51**	**2.48**	**2.46**	**2.42**	**2.40**	**2.38**	**2.37**	**2.36**	**2.34**	**2.33**
2	10.66	5.75	4.45	3.87	**3.55**	**3.19**	**3.01**	**2.87**	**2.78**	**2.72**	**2.68**	**2.65**	**2.62**	**2.58**	**2.56**	**2.54**	**2.52**	**2.51**	**2.49**	**2.48**
3	11.51	6.13	4.71	4.08	*3.72*	**3.34**	**3.14**	**2.99**	**2.89**	**2.83**	**2.78**	**2.75**	**2.72**	**2.68**	**2.65**	**2.63**	**2.61**	**2.60**	**2.57**	**2.56**
4	12.11	6.39	4.90	4.22	3.85	**3.44**	**3.23**	**3.07**	**2.97**	**2.90**	**2.85**	**2.81**	**2.78**	**2.74**	**2.71**	**2.69**	**2.67**	**2.66**	**2.63**	**2.62**
5	12.56	6.60	5.04	4.34	3.95	**3.52**	**3.30**	**3.13**	**3.03**	**2.96**	**2.90**	**2.87**	**2.83**	**2.79**	**2.76**	**2.73**	**2.72**	**2.70**	**2.68**	**2.66**
8	13.50	7.03	5.33	4.58	4.15	*3.69*	**3.44**	**3.26**	**3.15**	**3.07**	**3.02**	**2.97**	**2.94**	**2.89**	**2.86**	**2.83**	**2.81**	**2.80**	**2.77**	**2.75**
12	14.28	7.39	5.59	4.78	4.32	*3.83*	**3.57**	**3.38**	**3.26**	**3.17**	**3.11**	**3.07**	**3.03**	**2.98**	**2.94**	**2.91**	**2.89**	**2.88**	**2.85**	**2.83**
16	14.82	7.64	5.76	4.92	4.45	3.93	*3.66*	**3.46**	**3.33**	**3.24**	**3.18**	**3.13**	**3.09**	**3.04**	**3.00**	**2.97**	**2.95**	**2.93**	**2.90**	**2.87**
20	15.23	7.83	5.90	5.03	4.54	4.01	*3.73*	**3.52**	**3.39**	**3.30**	**3.23**	**3.18**	**3.14**	**3.09**	**3.05**	**3.02**	**2.99**	**2.98**	**2.94**	**2.92**
30	15.95	8.17	6.14	5.23	4.71	4.15	*3.85*	*3.63*	**3.49**	**3.39**	**3.32**	**3.27**	**3.23**	**3.17**	**3.13**	**3.10**	**3.07**	**3.05**	**3.02**	**3.00**
40	16.46	8.41	6.31	5.36	4.83	4.25	3.94	*3.71*	**3.56**	**3.46**	**3.39**	**3.34**	**3.29**	**3.23**	**3.18**	**3.15**	**3.13**	**3.11**	**3.07**	**3.05**
50	16.84	8.59	6.44	5.47	4.92	4.33	4.01	*3.77*	*3.62*	**3.52**	**3.44**	**3.38**	**3.34**	**3.27**	**3.23**	**3.19**	**3.17**	**3.15**	**3.11**	**3.09**
60	17.15	8.73	6.54	5.55	5.00	4.39	4.06	*3.82*	*3.66*	**3.56**	**3.48**	**3.42**	**3.38**	**3.31**	**3.26**	**3.23**	**3.20**	**3.18**	**3.14**	**3.12**
75	17.52	8.91	6.67	5.66	5.09	4.46	4.13	*3.88*	*3.72*	*3.61*	**3.53**	**3.47**	**3.43**	**3.36**	**3.31**	**3.27**	**3.24**	**3.22**	**3.18**	**3.16**
100	17.99	9.14	6.83	5.79	5.20	4.56	4.21	3.95	*3.79*	*3.68*	*3.60*	**3.53**	**3.49**	**3.41**	**3.36**	**3.33**	**3.30**	**3.27**	**3.23**	**3.21**
125	18.34	9.31	6.95	5.89	5.29	4.63	4.28	4.01	*3.85*	*3.73*	*3.65*	*3.58*	**3.53**	**3.46**	**3.41**	**3.37**	**3.34**	**3.31**	**3.27**	**3.25**
150	18.63	9.44	7.05	5.97	5.36	4.69	4.33	4.06	*3.89*	*3.77*	*3.69*	*3.62*	**3.57**	**3.49**	**3.44**	**3.40**	**3.37**	**3.35**	**3.30**	**3.28**
175	18.88	9.56	7.13	6.04	5.42	4.74	4.38	4.10	*3.93*	*3.81*	*3.72*	*3.65*	*3.60*	**3.52**	**3.47**	**3.43**	**3.40**	**3.37**	**3.33**	**3.30**
200	19.08	9.66	7.21	6.10	5.47	4.79	4.42	4.14	*3.96*	*3.84*	*3.75*	*3.68*	*3.63*	**3.55**	**3.49**	**3.45**	**3.42**	**3.40**	**3.35**	**3.33**

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Table 19-6. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Means of Order 2 (1 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	0.69	0.56	0.50	0.47	0.45	0.42	0.40	0.39	0.38	0.37	0.37	0.37	0.36	0.36	0.36	0.35	0.35	0.35	0.35	0.35
2	1.02	0.83	0.75	0.70	0.67	0.64	0.62	0.60	0.59	0.58	0.57	0.57	0.56	0.56	0.55	0.55	0.55	0.55	0.54	0.54
3	1.21	0.98	0.89	0.83	0.80	0.76	0.73	0.71	0.70	0.69	0.68	0.68	0.67	0.66	0.66	0.66	0.65	0.65	0.65	0.64
4	1.34	1.09	0.98	0.92	0.88	0.84	0.81	0.79	0.77	0.76	0.75	0.75	0.74	0.74	0.73	0.73	0.72	0.72	0.72	0.71
5	1.44	1.17	1.05	0.99	0.95	0.90	0.87	0.84	0.83	0.82	0.81	0.80	0.80	0.79	0.78	0.78	0.78	0.77	0.77	0.77
8	1.65	1.33	1.20	1.12	1.08	1.02	0.99	0.96	0.94	0.93	0.92	0.91	0.90	0.90	0.89	0.88	0.88	0.88	0.87	0.87
12	1.83	1.47	1.32	1.24	1.19	1.12	1.08	1.05	1.03	1.02	1.01	1.00	0.99	0.98	0.98	0.97	0.97	0.96	0.96	0.95
16	1.95	1.56	1.40	1.32	1.26	1.19	1.15	1.12	1.10	1.08	1.07	1.06	1.05	1.04	1.04	1.03	1.03	1.02	1.01	1.01
20	2.05	1.63	1.47	1.38	1.32	1.24	1.20	1.17	1.15	1.13	1.12	1.11	1.10	1.09	1.08	1.07	1.07	1.07	1.06	1.05
30	2.21	1.76	1.58	1.48	1.42	1.34	1.29	1.25	1.23	1.21	1.20	1.19	1.18	1.17	1.16	1.15	1.15	1.14	1.13	1.13
40	2.33	1.85	1.66	1.55	1.49	1.40	1.35	1.31	1.29	1.27	1.26	1.24	1.24	1.22	1.21	1.21	1.20	1.20	1.19	1.18
50	2.41	1.92	1.72	1.61	1.54	1.45	1.40	1.36	1.33	1.31	1.30	1.29	1.28	1.26	1.25	1.25	1.24	1.24	1.23	1.22
60	2.48	1.97	1.77	1.65	1.58	1.49	1.44	1.40	1.37	1.35	1.33	1.32	1.31	1.30	1.29	1.28	1.27	1.27	1.26	1.25
75	2.57	2.03	1.82	1.71	1.63	1.54	1.48	1.44	1.41	1.39	1.37	1.36	1.35	1.34	1.33	1.32	1.31	1.31	1.30	1.29
100	2.68	2.12	1.90	1.77	1.70	1.60	1.54	1.50	1.47	1.44	1.43	1.41	1.40	1.39	1.38	1.37	1.36	1.36	1.35	1.34
125	2.76	2.18	1.95	1.83	1.74	1.65	1.59	1.54	1.51	1.48	1.47	1.45	1.44	1.43	1.41	1.41	1.40	1.39	1.38	1.38
150	2.82	2.23	2.00	1.87	1.78	1.68	1.62	1.57	1.54	1.52	1.50	1.49	1.47	1.46	1.44	1.44	1.43	1.42	1.41	1.40
175	2.88	2.27	2.03	1.90	1.82	1.71	1.65	1.60	1.57	1.54	1.53	1.51	1.50	1.48	1.47	1.46	1.45	1.45	1.44	1.43
200	2.92	2.31	2.06	1.93	1.85	1.74	1.68	1.63	1.59	1.57	1.55	1.53	1.52	1.51	1.49	1.48	1.47	1.47	1.46	1.45

Table 19-6. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Means of Order 2 (1 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	1.02	0.83	0.75	0.70	0.67	0.64	0.62	0.60	0.59	0.58	0.57	0.57	0.56	0.56	0.55	0.55	0.55	0.55	0.54	0.54
2	1.34	1.09	0.98	0.92	0.88	0.84	0.81	0.79	0.77	0.76	0.75	0.75	0.74	0.74	0.73	0.73	0.72	0.72	0.72	0.71
3	1.52	1.23	1.11	1.04	1.00	0.94	0.91	0.89	0.87	0.86	0.85	0.84	0.84	0.83	0.83	0.82	0.82	0.81	0.81	0.81
4	1.65	1.33	1.20	1.12	1.08	1.02	0.99	0.96	0.94	0.93	0.92	0.91	0.90	0.90	0.89	0.88	0.88	0.88	0.87	0.87
5	1.75	1.41	1.26	1.19	1.14	1.08	1.04	1.01	0.99	0.98	0.97	0.96	0.95	0.94	0.94	0.93	0.93	0.93	0.92	0.92
8	1.95	1.56	1.40	1.32	1.26	1.19	1.15	1.12	1.10	1.08	1.07	1.06	1.05	1.04	1.04	1.03	1.03	1.02	1.01	1.01
12	2.12	1.69	1.52	1.42	1.36	1.29	1.24	1.21	1.18	1.17	1.15	1.14	1.14	1.12	1.12	1.11	1.10	1.10	1.09	1.09
16	2.24	1.78	1.60	1.50	1.43	1.35	1.31	1.27	1.24	1.23	1.21	1.20	1.19	1.18	1.17	1.16	1.16	1.15	1.15	1.14
20	2.33	1.85	1.66	1.55	1.49	1.40	1.35	1.31	1.29	1.27	1.26	1.24	1.24	1.22	1.21	1.21	1.20	1.20	1.19	1.18
30	2.48	1.97	1.77	1.65	1.58	1.49	1.44	1.40	1.37	1.35	1.33	1.32	1.31	1.30	1.29	1.28	1.27	1.27	1.26	1.25
40	2.59	2.05	1.84	1.72	1.65	1.55	1.50	1.45	1.42	1.40	1.39	1.37	1.36	1.35	1.34	1.33	1.32	1.32	1.31	1.30
50	2.68	2.12	1.90	1.77	1.70	1.60	1.54	1.50	1.47	1.44	1.43	1.41	1.40	1.39	1.38	1.37	1.36	1.36	1.35	1.34
60	2.74	2.17	1.94	1.82	1.74	1.64	1.58	1.53	1.50	1.48	1.46	1.45	1.44	1.42	1.41	1.40	1.39	1.39	1.38	1.37
75	2.82	2.23	2.00	1.87	1.78	1.68	1.62	1.57	1.54	1.52	1.50	1.49	1.47	1.46	1.44	1.44	1.43	1.42	1.41	1.40
100	2.92	2.31	2.06	1.93	1.85	1.74	1.68	1.63	1.59	1.57	1.55	1.53	1.52	1.51	1.49	1.48	1.47	1.47	1.46	1.45
125	3.00	2.37	2.12	1.98	1.89	1.78	1.72	1.67	1.63	1.61	1.59	1.57	1.56	1.54	1.53	1.52	1.51	1.50	1.49	1.48
150	3.06	2.41	2.16	2.02	1.93	1.82	1.75	1.70	1.66	1.64	1.62	1.60	1.59	1.57	1.56	1.55	1.54	1.53	1.52	1.51
175	3.11	2.45	2.19	2.05	1.96	1.85	1.78	1.73	1.69	1.66	1.64	1.63	1.62	1.60	1.58	1.57	1.56	1.56	1.54	1.54
200	3.16	2.49	2.23	2.08	1.99	1.87	1.81	1.75	1.71	1.69	1.67	1.65	1.64	1.62	1.60	1.59	1.58	1.58	1.56	1.56

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Table 19-6. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Means of Order 2 (1 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	1.34	1.09	0.98	0.92	0.88	0.84	0.81	0.79	0.77	0.76	0.75	0.75	0.74	0.74	0.73	0.73	0.72	0.72	0.72	0.71
2	1.65	1.33	1.20	1.12	1.08	1.02	0.99	0.96	0.94	0.93	0.92	0.91	0.90	0.90	0.89	0.88	0.88	0.88	0.87	0.87
3	1.83	1.47	1.32	1.24	1.19	1.12	1.08	1.05	1.03	1.02	1.01	1.00	0.99	0.98	0.98	0.97	0.97	0.96	0.96	0.95
4	1.95	1.56	1.40	1.32	1.26	1.19	1.15	1.12	1.10	1.08	1.07	1.06	1.05	1.04	1.04	1.03	1.03	1.02	1.01	1.01
5	2.05	1.63	1.47	1.38	1.32	1.24	1.20	1.17	1.15	1.13	1.12	1.11	1.10	1.09	1.08	1.07	1.07	1.07	1.06	1.05
8	2.24	1.78	1.60	1.50	1.43	1.35	1.31	1.27	1.24	1.23	1.21	1.20	1.19	1.18	1.17	1.16	1.16	1.15	1.15	1.14
12	2.40	1.90	1.71	1.60	1.53	1.44	1.39	1.35	1.32	1.31	1.29	1.28	1.27	1.26	1.25	1.24	1.23	1.23	1.22	1.21
16	2.51	1.99	1.78	1.67	1.60	1.51	1.45	1.41	1.38	1.36	1.35	1.33	1.32	1.31	1.30	1.29	1.28	1.28	1.27	1.26
20	2.59	2.05	1.84	1.72	1.65	1.55	1.50	1.45	1.42	1.40	1.39	1.37	1.36	1.35	1.34	1.33	1.32	1.32	1.31	1.30
30	2.74	2.17	1.94	1.82	1.74	1.64	1.58	1.53	1.50	1.48	1.46	1.45	1.44	1.42	1.41	1.40	1.39	1.39	1.38	1.37
40	2.85	2.25	2.01	1.88	1.80	1.70	1.64	1.59	1.55	1.53	1.51	1.50	1.49	1.47	1.46	1.45	1.44	1.43	1.42	1.41
50	2.92	2.31	2.06	1.93	1.85	1.74	1.68	1.63	1.59	1.57	1.55	1.53	1.52	1.51	1.49	1.48	1.47	1.47	1.46	1.45
60	2.99	2.36	2.11	1.97	1.88	1.78	1.71	1.66	1.63	1.60	1.58	1.57	1.55	1.54	1.52	1.51	1.50	1.50	1.49	1.48
75	3.06	2.41	2.16	2.02	1.93	1.82	1.75	1.70	1.66	1.64	1.62	1.60	1.59	1.57	1.56	1.55	1.54	1.53	1.52	1.51
100	3.16	2.49	2.23	2.08	1.99	1.87	1.81	1.75	1.71	1.69	1.67	1.65	1.64	1.62	1.60	1.59	1.58	1.58	1.56	1.56
125	3.23	2.54	2.28	2.13	2.03	1.92	1.85	1.79	1.75	1.72	1.70	1.69	1.67	1.65	1.64	1.63	1.62	1.61	1.60	1.59
150	3.29	2.59	2.32	2.17	2.07	1.95	1.88	1.82	1.78	1.75	1.73	1.72	1.70	1.68	1.67	1.65	1.64	1.64	1.62	1.62
175	3.34	2.63	2.35	2.20	2.10	1.98	1.91	1.85	1.81	1.78	1.76	1.74	1.73	1.70	1.69	1.68	1.67	1.66	1.65	1.64
200	3.38	2.66	2.38	2.22	2.12	2.00	1.93	1.87	1.83	1.80	1.78	1.76	1.75	1.72	1.71	1.70	1.69	1.68	1.67	1.66

Table 19-6. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Means of Order 2 (2 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	1.10	0.87	0.77	0.72	0.69	0.65	0.62	0.60	0.59	0.58	0.58	0.57	0.57	0.56	0.56	0.55	0.55	0.55	0.55	0.54
2	1.47	1.14	1.02	0.95	0.90	0.85	0.82	0.79	0.78	0.77	0.76	0.75	0.75	0.74	0.73	0.73	0.73	0.72	0.72	0.72
3	1.69	1.30	1.15	1.07	1.02	0.96	0.93	0.90	0.88	0.87	0.86	0.85	0.84	0.83	0.83	0.82	0.82	0.82	0.81	0.81
4	1.85	1.42	1.25	1.16	1.10	1.04	1.00	0.97	0.95	0.93	0.92	0.92	0.91	0.90	0.89	0.89	0.88	0.88	0.87	0.87
5	1.97	1.50	1.32	1.23	1.17	1.10	1.05	1.02	1.00	0.99	0.97	0.97	0.96	0.95	0.94	0.94	0.93	0.93	0.92	0.92
8	2.22	1.68	1.48	1.37	1.30	1.22	1.17	1.13	1.11	1.09	1.08	1.07	1.06	1.05	1.04	1.03	1.03	1.02	1.02	1.01
12	2.44	1.83	1.60	1.48	1.41	1.32	1.26	1.22	1.20	1.18	1.16	1.15	1.14	1.13	1.12	1.11	1.11	1.10	1.10	1.09
16	2.59	1.94	1.69	1.56	1.48	1.39	1.33	1.29	1.26	1.24	1.22	1.21	1.20	1.19	1.18	1.17	1.16	1.16	1.15	1.14
20	2.71	2.02	1.76	1.63	1.54	1.44	1.38	1.33	1.30	1.28	1.27	1.25	1.24	1.23	1.22	1.21	1.20	1.20	1.19	1.18
30	2.91	2.16	1.88	1.74	1.64	1.53	1.47	1.42	1.39	1.36	1.34	1.33	1.32	1.30	1.29	1.28	1.28	1.27	1.26	1.25
40	3.05	2.26	1.97	1.81	1.72	1.60	1.53	1.48	1.44	1.42	1.40	1.38	1.37	1.36	1.34	1.33	1.33	1.32	1.31	1.30
50	3.16	2.34	2.03	1.87	1.77	1.65	1.58	1.52	1.49	1.46	1.44	1.43	1.41	1.40	1.38	1.37	1.37	1.36	1.35	1.34
60	3.25	2.40	2.08	1.92	1.81	1.69	1.62	1.56	1.52	1.49	1.47	1.46	1.45	1.43	1.41	1.40	1.40	1.39	1.38	1.37
75	3.35	2.47	2.15	1.98	1.87	1.74	1.66	1.60	1.56	1.54	1.51	1.50	1.49	1.47	1.45	1.44	1.43	1.43	1.41	1.41
100	3.49	2.57	2.23	2.05	1.93	1.80	1.72	1.66	1.62	1.59	1.57	1.55	1.54	1.51	1.50	1.49	1.48	1.47	1.46	1.45
125	3.59	2.64	2.29	2.10	1.99	1.85	1.77	1.70	1.66	1.63	1.61	1.59	1.57	1.55	1.54	1.53	1.52	1.51	1.50	1.49
150	3.67	*2.69*	2.34	2.15	2.03	1.89	1.80	1.74	1.69	1.66	1.64	1.62	1.60	1.58	1.57	1.55	1.55	1.54	1.52	1.52
175	3.74	*2.74*	2.38	2.18	2.06	1.92	1.83	1.76	1.72	1.69	1.66	1.64	1.63	1.61	1.59	1.58	1.57	1.56	1.55	1.54
200	3.80	2.78	2.41	2.22	2.09	1.94	1.86	1.79	1.74	1.71	1.69	1.67	1.65	1.63	1.61	1.60	1.59	1.58	1.57	1.56

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Table 19-6. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Means of Order 2 (2 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	1.47	1.14	1.02	0.95	0.90	0.85	0.82	0.79	0.78	0.77	0.76	0.75	0.75	0.74	0.73	0.73	0.73	0.72	0.72	0.72
2	1.85	1.42	1.25	1.16	1.10	1.04	1.00	0.97	0.95	0.93	0.92	0.92	0.91	0.90	0.89	0.89	0.88	0.88	0.87	0.87
3	2.07	1.57	1.38	1.28	1.22	1.14	1.10	1.07	1.04	1.03	1.01	1.01	1.00	0.99	0.98	0.97	0.97	0.97	0.96	0.95
4	2.22	1.68	1.48	1.37	1.30	1.22	1.17	1.13	1.11	1.09	1.08	1.07	1.06	1.05	1.04	1.03	1.03	1.02	1.02	1.01
5	2.34	1.76	1.55	1.43	1.36	1.27	1.22	1.18	1.16	1.14	1.12	1.11	1.11	1.09	1.08	1.08	1.07	1.07	1.06	1.06
8	2.59	1.94	1.69	1.56	1.48	1.39	1.33	1.29	1.26	1.24	1.22	1.21	1.20	1.19	1.18	1.17	1.16	1.16	1.15	1.14
12	2.80	2.08	1.82	1.68	1.59	1.48	1.42	1.37	1.34	1.32	1.30	1.29	1.28	1.26	1.25	1.24	1.24	1.23	1.22	1.22
16	2.94	2.18	1.90	1.75	1.66	1.55	1.48	1.43	1.40	1.37	1.36	1.34	1.33	1.32	1.30	1.29	1.29	1.28	1.27	1.27
20	3.05	2.26	1.97	1.81	1.72	1.60	1.53	1.48	1.44	1.42	1.40	1.38	1.37	1.36	1.34	1.33	1.33	1.32	1.31	1.30
30	3.25	2.40	2.08	1.92	1.81	1.69	1.62	1.56	1.52	1.49	1.47	1.46	1.45	1.43	1.41	1.40	1.40	1.39	1.38	1.37
40	3.38	2.49	2.17	1.99	1.88	1.75	1.68	1.62	1.58	1.55	1.53	1.51	1.50	1.48	1.46	1.45	1.44	1.44	1.43	1.42
50	3.49	2.57	2.23	2.05	1.93	1.80	1.72	1.66	1.62	1.59	1.57	1.55	1.54	1.51	1.50	1.49	1.48	1.47	1.46	1.45
60	3.57	2.62	2.28	2.09	1.98	1.84	1.76	1.69	1.65	1.62	1.60	1.58	1.57	1.55	1.53	1.52	1.51	1.50	1.49	1.48
75	3.67	2.69	2.34	2.15	2.03	1.89	1.80	1.74	1.69	1.66	1.64	1.62	1.60	1.58	1.57	1.55	1.55	1.54	1.52	1.52
100	3.80	2.78	2.41	2.22	2.09	1.94	1.86	1.79	1.74	1.71	1.69	1.67	1.65	1.63	1.61	1.60	1.59	1.58	1.57	1.56
125	3.90	2.85	2.47	2.27	2.14	1.99	1.90	1.83	1.78	1.75	1.72	1.70	1.69	1.66	1.65	1.63	1.62	1.62	1.60	1.59
150	3.97	*2.91*	2.52	2.31	2.18	2.03	1.94	1.86	1.82	1.78	1.75	1.73	1.72	1.69	1.68	1.66	1.65	1.64	1.63	1.62
175	4.04	2.95	2.56	2.35	2.22	2.06	1.96	1.89	1.84	1.81	1.78	1.76	1.74	1.72	1.70	1.69	1.68	1.67	1.65	1.64
200	4.09	2.99	2.59	2.38	2.24	2.08	1.99	1.92	1.87	1.83	1.80	1.78	1.76	1.74	1.72	1.71	1.70	1.69	1.67	1.66

Table 19-6. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Means of Order 2 (2 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	1.85	1.42	1.25	1.16	1.10	1.04	1.00	0.97	0.95	0.93	0.92	0.92	0.91	0.90	0.89	0.89	0.88	0.88	0.87	0.87
2	2.22	1.68	1.48	1.37	1.30	1.22	1.17	1.13	1.11	1.09	1.08	1.07	1.06	1.05	1.04	1.03	1.03	1.02	1.02	1.01
3	2.44	1.83	1.60	1.48	1.41	1.32	1.26	1.22	1.20	1.18	1.16	1.15	1.14	1.13	1.12	1.11	1.11	1.10	1.10	1.09
4	2.59	1.94	1.69	1.56	1.48	1.39	1.33	1.29	1.26	1.24	1.22	1.21	1.20	1.19	1.18	1.17	1.16	1.16	1.15	1.14
5	2.71	2.02	1.76	1.63	1.54	1.44	1.38	1.33	1.30	1.28	1.27	1.25	1.24	1.23	1.22	1.21	1.20	1.20	1.19	1.18
8	2.94	2.18	1.90	1.75	1.66	1.55	1.48	1.43	1.40	1.37	1.36	1.34	1.33	1.32	1.30	1.29	1.29	1.28	1.27	1.27
12	3.14	2.32	2.02	1.86	1.76	1.64	1.57	1.51	1.48	1.45	1.43	1.42	1.41	1.39	1.38	1.37	1.36	1.35	1.34	1.33
16	3.28	2.42	2.10	1.93	1.83	1.70	1.63	1.57	1.53	1.51	1.49	1.47	1.46	1.44	1.42	1.41	1.41	1.40	1.39	1.38
20	3.38	2.49	2.17	1.99	1.88	1.75	1.68	1.62	1.58	1.55	1.53	1.51	1.50	1.48	1.46	1.45	1.44	1.44	1.43	1.42
30	3.57	2.62	2.28	2.09	1.98	1.84	1.76	1.69	1.65	1.62	1.60	1.58	1.57	1.55	1.53	1.52	1.51	1.50	1.49	1.48
40	3.70	2.71	2.35	2.16	2.04	1.90	1.81	1.75	1.70	1.67	1.65	1.63	1.61	1.59	1.58	1.56	1.56	1.55	1.53	1.53
50	3.80	2.78	2.41	2.22	2.09	1.94	1.86	1.79	1.74	1.71	1.69	1.67	1.65	1.63	1.61	1.60	1.59	1.58	1.57	1.56
60	3.88	2.84	2.46	2.26	2.13	1.98	1.89	1.82	1.78	1.74	1.72	1.70	1.68	1.66	1.64	1.63	1.62	1.61	1.60	1.59
75	3.97	2.91	2.52	2.31	2.18	2.03	1.94	1.86	1.82	1.78	1.75	1.73	1.72	1.69	1.68	1.66	1.65	1.64	1.63	1.62
100	4.09	2.99	2.59	2.38	2.24	2.08	1.99	1.92	1.87	1.83	1.80	1.78	1.76	1.74	1.72	1.71	1.70	1.69	1.67	1.66
125	4.19	3.06	2.65	2.43	2.29	2.13	2.03	1.95	1.90	1.87	1.84	1.82	1.80	1.77	1.75	1.74	1.73	1.72	1.70	1.69
150	4.26	*3.11*	2.69	2.47	2.33	2.16	2.06	1.99	1.93	1.90	1.87	1.85	1.83	1.80	1.78	1.77	1.76	1.75	1.73	1.72
175	4.32	3.15	2.73	2.50	2.36	2.19	2.09	2.01	1.96	1.92	1.89	1.87	1.85	1.82	1.80	1.79	1.78	1.77	1.75	1.74
200	4.38	3.19	2.76	2.53	2.39	2.22	2.12	2.04	1.98	1.94	1.91	1.89	1.87	1.84	1.82	1.81	1.80	1.79	1.77	1.76

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Table 19-6. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Means of Order 2 (5 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.72**	**1.28**	**1.12**	**1.04**	**0.98**	**0.92**	**0.88**	**0.86**	**0.84**	**0.83**	**0.82**	**0.81**	**0.80**	**0.79**	**0.79**	**0.78**	**0.78**	**0.78**	**0.77**	**0.77**
2	**2.19**	**1.58**	**1.37**	**1.26**	**1.19**	**1.11**	**1.06**	**1.03**	**1.01**	**0.99**	**0.98**	**0.97**	**0.96**	**0.95**	**0.94**	**0.94**	**0.93**	**0.93**	**0.92**	**0.92**
3	**2.47**	**1.76**	**1.51**	**1.39**	**1.31**	**1.22**	**1.17**	**1.13**	**1.10**	**1.08**	**1.07**	**1.06**	**1.05**	**1.04**	**1.03**	**1.02**	**1.02**	**1.01**	**1.01**	**1.00**
4	**2.67**	**1.89**	**1.61**	**1.48**	**1.39**	**1.29**	**1.24**	**1.19**	**1.16**	**1.14**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**	**1.07**	**1.06**	**1.06**
5	2.83	**1.98**	**1.69**	**1.54**	**1.45**	**1.35**	**1.29**	**1.24**	**1.21**	**1.19**	**1.18**	**1.16**	**1.15**	**1.14**	**1.13**	**1.12**	**1.12**	**1.11**	**1.10**	**1.10**
8	3.17	**2.19**	**1.86**	**1.69**	**1.59**	**1.47**	**1.40**	**1.35**	**1.31**	**1.29**	**1.27**	**1.26**	**1.25**	**1.23**	**1.22**	**1.21**	**1.21**	**1.20**	**1.19**	**1.18**
12	3.45	**2.37**	**2.00**	**1.81**	**1.70**	**1.57**	**1.49**	**1.43**	**1.40**	**1.37**	**1.35**	**1.34**	**1.33**	**1.31**	**1.30**	**1.29**	**1.28**	**1.27**	**1.26**	**1.26**
16	3.65	**2.49**	**2.10**	**1.90**	**1.78**	**1.64**	**1.56**	**1.50**	**1.46**	**1.43**	**1.41**	**1.39**	**1.38**	**1.36**	**1.35**	**1.34**	**1.33**	**1.32**	**1.31**	**1.31**
20	3.81	**2.58**	**2.17**	**1.96**	**1.84**	**1.69**	**1.61**	**1.54**	**1.50**	**1.47**	**1.45**	**1.43**	**1.42**	**1.40**	**1.39**	**1.38**	**1.37**	**1.36**	**1.35**	**1.34**
30	4.08	*2.75*	**2.31**	**2.08**	**1.94**	**1.78**	**1.69**	**1.63**	**1.58**	**1.55**	**1.53**	**1.51**	**1.49**	**1.47**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**	**1.41**
40	4.27	2.87	**2.40**	**2.16**	**2.02**	**1.85**	**1.76**	**1.68**	**1.64**	**1.60**	**1.58**	**1.56**	**1.54**	**1.52**	**1.50**	**1.49**	**1.48**	**1.48**	**1.46**	**1.45**
50	4.42	2.96	**2.47**	**2.23**	**2.08**	**1.90**	**1.80**	**1.73**	**1.68**	**1.64**	**1.62**	**1.60**	**1.58**	**1.56**	**1.54**	**1.53**	**1.52**	**1.51**	**1.50**	**1.49**
60	4.54	3.03	**2.53**	**2.28**	**2.12**	**1.94**	**1.84**	**1.76**	**1.71**	**1.68**	**1.65**	**1.63**	**1.61**	**1.59**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**
75	4.68	3.12	**2.60**	**2.34**	**2.18**	**1.99**	**1.89**	**1.81**	**1.75**	**1.72**	**1.69**	**1.67**	**1.65**	**1.63**	**1.61**	**1.59**	**1.58**	**1.58**	**1.56**	**1.55**
100	4.86	3.23	*2.69*	**2.42**	**2.25**	**2.06**	**1.95**	**1.86**	**1.81**	**1.77**	**1.74**	**1.72**	**1.70**	**1.67**	**1.65**	**1.64**	**1.63**	**1.62**	**1.60**	**1.59**
125	5.00	3.32	*2.76*	**2.48**	**2.31**	**2.11**	**1.99**	**1.91**	**1.85**	**1.81**	**1.78**	**1.75**	**1.74**	**1.71**	**1.69**	**1.67**	**1.66**	**1.65**	**1.64**	**1.63**
150	5.11	3.39	*2.82*	**2.53**	**2.35**	**2.15**	**2.03**	**1.94**	**1.88**	**1.84**	**1.81**	**1.79**	**1.77**	**1.74**	**1.72**	**1.70**	**1.69**	**1.68**	**1.66**	**1.65**
175	5.20	3.44	2.86	**2.57**	**2.39**	**2.18**	**2.06**	**1.97**	**1.91**	**1.87**	**1.84**	**1.81**	**1.79**	**1.76**	**1.74**	**1.73**	**1.71**	**1.70**	**1.69**	**1.67**
200	5.28	3.49	2.90	*2.60*	**2.42**	**2.21**	**2.09**	**2.00**	**1.93**	**1.89**	**1.86**	**1.83**	**1.81**	**1.78**	**1.76**	**1.75**	**1.73**	**1.72**	**1.71**	**1.70**

Table 19-6. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Means of Order 2 (5 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.19**	**1.58**	**1.37**	**1.26**	**1.19**	**1.11**	**1.06**	**1.03**	**1.01**	**0.99**	**0.98**	**0.97**	**0.96**	**0.95**	**0.94**	**0.94**	**0.93**	**0.93**	**0.92**	**0.92**
2	**2.67**	**1.89**	**1.61**	**1.48**	**1.39**	**1.29**	**1.24**	**1.19**	**1.16**	**1.14**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**	**1.07**	**1.06**	**1.06**
3	2.96	**2.06**	**1.76**	**1.60**	**1.50**	**1.39**	**1.33**	**1.28**	**1.25**	**1.23**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**	**1.16**	**1.15**	**1.15**	**1.14**	**1.13**
4	3.17	**2.19**	**1.86**	**1.69**	**1.59**	**1.47**	**1.40**	**1.35**	**1.31**	**1.29**	**1.27**	**1.26**	**1.25**	**1.23**	**1.22**	**1.21**	**1.21**	**1.20**	**1.19**	**1.18**
5	3.32	**2.29**	**1.93**	**1.76**	**1.65**	**1.52**	**1.45**	**1.40**	**1.36**	**1.33**	**1.32**	**1.30**	**1.29**	**1.27**	**1.26**	**1.25**	**1.25**	**1.24**	**1.23**	**1.22**
8	3.65	**2.49**	**2.10**	**1.90**	**1.78**	**1.64**	**1.56**	**1.50**	**1.46**	**1.43**	**1.41**	**1.39**	**1.38**	**1.36**	**1.35**	**1.34**	**1.33**	**1.32**	**1.31**	**1.31**
12	3.93	**2.66**	**2.23**	**2.02**	**1.88**	**1.73**	**1.65**	**1.58**	**1.54**	**1.51**	**1.48**	**1.47**	**1.45**	**1.43**	**1.42**	**1.41**	**1.40**	**1.39**	**1.38**	**1.37**
16	4.13	**2.78**	**2.33**	**2.10**	**1.96**	**1.80**	**1.71**	**1.64**	**1.59**	**1.56**	**1.54**	**1.52**	**1.50**	**1.48**	**1.47**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**
20	4.27	*2.87*	**2.40**	**2.16**	**2.02**	**1.85**	**1.76**	**1.68**	**1.64**	**1.60**	**1.58**	**1.56**	**1.54**	**1.52**	**1.50**	**1.49**	**1.48**	**1.48**	**1.46**	**1.45**
30	4.54	3.03	**2.53**	**2.28**	**2.12**	**1.94**	**1.84**	**1.76**	**1.71**	**1.68**	**1.65**	**1.63**	**1.61**	**1.59**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**
40	4.72	3.15	**2.62**	**2.36**	**2.20**	**2.01**	**1.90**	**1.82**	**1.77**	**1.73**	**1.70**	**1.68**	**1.66**	**1.64**	**1.62**	**1.60**	**1.59**	**1.59**	**1.57**	**1.56**
50	4.86	3.23	**2.69**	**2.42**	**2.25**	**2.06**	**1.95**	**1.86**	**1.81**	**1.77**	**1.74**	**1.72**	**1.70**	**1.67**	**1.65**	**1.64**	**1.63**	**1.62**	**1.60**	**1.59**
60	4.97	3.30	**2.75**	**2.47**	**2.30**	**2.10**	**1.99**	**1.90**	**1.84**	**1.80**	**1.77**	**1.75**	**1.73**	**1.70**	**1.68**	**1.67**	**1.66**	**1.65**	**1.63**	**1.62**
75	5.11	3.39	**2.82**	**2.53**	**2.35**	**2.15**	**2.03**	**1.94**	**1.88**	**1.84**	**1.81**	**1.79**	**1.77**	**1.74**	**1.72**	**1.70**	**1.69**	**1.68**	**1.66**	**1.65**
100	5.28	3.49	*2.90*	**2.60**	**2.42**	**2.21**	**2.09**	**2.00**	**1.93**	**1.89**	**1.86**	**1.83**	**1.81**	**1.78**	**1.76**	**1.75**	**1.73**	**1.72**	**1.71**	**1.70**
125	5.41	3.58	*2.97*	**2.66**	**2.48**	**2.26**	**2.13**	**2.04**	**1.97**	**1.93**	**1.89**	**1.87**	**1.85**	**1.82**	**1.80**	**1.78**	**1.77**	**1.76**	**1.74**	**1.73**
150	5.52	3.64	3.02	**2.71**	**2.52**	**2.30**	**2.17**	**2.07**	**2.01**	**1.96**	**1.92**	**1.90**	**1.88**	**1.85**	**1.82**	**1.81**	**1.79**	**1.78**	**1.76**	**1.75**
175	5.61	3.70	3.07	**2.75**	**2.56**	**2.33**	**2.20**	**2.10**	**2.03**	**1.99**	**1.95**	**1.92**	**1.90**	**1.87**	**1.85**	**1.83**	**1.82**	**1.81**	**1.79**	**1.77**
200	5.68	3.75	3.11	**2.78**	**2.59**	**2.36**	**2.23**	**2.12**	**2.06**	**2.01**	**1.97**	**1.94**	**1.92**	**1.89**	**1.87**	**1.85**	**1.84**	**1.82**	**1.80**	**1.79**

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Table 19-6. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Means of Order 2 (5 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.67**	**1.89**	**1.61**	**1.48**	**1.39**	**1.29**	**1.24**	**1.19**	**1.16**	**1.14**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**	**1.07**	**1.06**	**1.06**
2	3.17	**2.19**	**1.86**	**1.69**	**1.59**	**1.47**	**1.40**	**1.35**	**1.31**	**1.29**	**1.27**	**1.26**	**1.25**	**1.23**	**1.22**	**1.21**	**1.21**	**1.20**	**1.19**	**1.18**
3	3.45	**2.37**	**2.00**	**1.81**	**1.70**	**1.57**	**1.49**	**1.43**	**1.40**	**1.37**	**1.35**	**1.34**	**1.33**	**1.31**	**1.30**	**1.29**	**1.28**	**1.27**	**1.26**	**1.26**
4	3.65	**2.49**	**2.10**	**1.90**	**1.78**	**1.64**	**1.56**	**1.50**	**1.46**	**1.43**	**1.41**	**1.39**	**1.38**	**1.36**	**1.35**	**1.34**	**1.33**	**1.32**	**1.31**	**1.31**
5	3.81	**2.58**	**2.17**	**1.96**	**1.84**	**1.69**	**1.61**	**1.54**	**1.50**	**1.47**	**1.45**	**1.43**	**1.42**	**1.40**	**1.39**	**1.38**	**1.37**	**1.36**	**1.35**	**1.34**
8	4.13	**2.78**	**2.33**	**2.10**	**1.96**	**1.80**	**1.71**	**1.64**	**1.59**	**1.56**	**1.54**	**1.52**	**1.50**	**1.48**	**1.47**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**
12	4.39	**2.94**	**2.46**	**2.21**	**2.07**	**1.89**	**1.80**	**1.72**	**1.67**	**1.64**	**1.61**	**1.59**	**1.58**	**1.55**	**1.54**	**1.52**	**1.51**	**1.51**	**1.49**	**1.48**
16	4.58	**3.06**	**2.55**	**2.30**	**2.14**	**1.96**	**1.86**	**1.78**	**1.73**	**1.69**	**1.66**	**1.64**	**1.62**	**1.60**	**1.58**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**
20	4.72	3.15	**2.62**	**2.36**	**2.20**	**2.01**	**1.90**	**1.82**	**1.77**	**1.73**	**1.70**	**1.68**	**1.66**	**1.64**	**1.62**	**1.60**	**1.59**	**1.59**	**1.57**	**1.56**
30	4.97	3.30	**2.75**	**2.47**	**2.30**	**2.10**	**1.99**	**1.90**	**1.84**	**1.80**	**1.77**	**1.75**	**1.73**	**1.70**	**1.68**	**1.67**	**1.66**	**1.65**	**1.63**	**1.62**
40	5.15	3.41	**2.84**	**2.55**	**2.37**	**2.16**	**2.04**	**1.95**	**1.89**	**1.85**	**1.82**	**1.80**	**1.78**	**1.75**	**1.73**	**1.71**	**1.70**	**1.69**	**1.67**	**1.66**
50	5.28	3.49	**2.90**	**2.60**	**2.42**	**2.21**	**2.09**	**2.00**	**1.93**	**1.89**	**1.86**	**1.83**	**1.81**	**1.78**	**1.76**	**1.75**	**1.73**	**1.72**	**1.71**	**1.70**
60	5.39	3.56	**2.96**	**2.65**	**2.47**	**2.25**	**2.13**	**2.03**	**1.97**	**1.92**	**1.89**	**1.86**	**1.84**	**1.81**	**1.79**	**1.77**	**1.76**	**1.75**	**1.73**	**1.72**
75	5.52	3.64	**3.02**	**2.71**	**2.52**	**2.30**	**2.17**	**2.07**	**2.01**	**1.96**	**1.92**	**1.90**	**1.88**	**1.85**	**1.82**	**1.81**	**1.79**	**1.78**	**1.76**	**1.75**
100	5.68	3.75	*3.11*	**2.78**	**2.59**	**2.36**	**2.23**	**2.12**	**2.06**	**2.01**	**1.97**	**1.94**	**1.92**	**1.89**	**1.87**	**1.85**	**1.84**	**1.82**	**1.80**	**1.79**
125	5.81	3.82	*3.17*	**2.84**	**2.64**	**2.40**	**2.27**	**2.16**	**2.09**	**2.04**	**2.01**	**1.98**	**1.96**	**1.92**	**1.90**	**1.88**	**1.87**	**1.86**	**1.84**	**1.82**
150	5.91	3.89	*3.22*	**2.88**	**2.68**	**2.44**	**2.30**	**2.20**	**2.12**	**2.07**	**2.04**	**2.01**	**1.99**	**1.95**	**1.93**	**1.91**	**1.89**	**1.88**	**1.86**	**1.85**
175	5.99	3.94	3.26	**2.92**	**2.71**	**2.47**	**2.33**	**2.22**	**2.15**	**2.10**	**2.06**	**2.03**	**2.01**	**1.97**	**1.95**	**1.93**	**1.91**	**1.90**	**1.88**	**1.87**
200	6.07	3.99	3.30	**2.96**	**2.74**	**2.50**	**2.36**	**2.25**	**2.17**	**2.12**	**2.08**	**2.05**	**2.03**	**1.99**	**1.97**	**1.95**	**1.93**	**1.92**	**1.90**	**1.89**

Table 19-6. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Means of Order 2 (10 COC, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.29**	**1.62**	**1.39**	**1.27**	**1.20**	**1.11**	**1.07**	**1.03**	**1.01**	**0.99**	**0.98**	**0.97**	**0.96**	**0.95**	**0.94**	**0.94**	**0.93**	**0.93**	**0.92**	**0.92**
2	2.86	**1.94**	**1.64**	**1.49**	**1.40**	**1.30**	**1.24**	**1.20**	**1.17**	**1.15**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**	**1.07**	**1.06**	**1.06**
3	3.21	**2.14**	**1.79**	**1.62**	**1.52**	**1.40**	**1.34**	**1.29**	**1.26**	**1.23**	**1.22**	**1.20**	**1.19**	**1.18**	**1.17**	**1.16**	**1.15**	**1.15**	**1.14**	**1.13**
4	3.46	**2.28**	**1.90**	**1.72**	**1.60**	**1.48**	**1.41**	**1.35**	**1.32**	**1.29**	**1.27**	**1.26**	**1.25**	**1.23**	**1.22**	**1.21**	**1.21**	**1.20**	**1.19**	**1.19**
5	3.66	**2.39**	**1.99**	**1.79**	**1.67**	**1.53**	**1.46**	**1.40**	**1.36**	**1.34**	**1.32**	**1.30**	**1.29**	**1.28**	**1.26**	**1.25**	**1.25**	**1.24**	**1.23**	**1.22**
8	4.07	**2.62**	**2.16**	**1.94**	**1.80**	**1.65**	**1.57**	**1.50**	**1.46**	**1.43**	**1.41**	**1.39**	**1.38**	**1.36**	**1.35**	**1.34**	**1.33**	**1.32**	**1.31**	**1.31**
12	4.43	2.82	**2.31**	**2.06**	**1.92**	**1.75**	**1.66**	**1.59**	**1.54**	**1.51**	**1.49**	**1.47**	**1.46**	**1.43**	**1.42**	**1.41**	**1.40**	**1.39**	**1.38**	**1.37**
16	4.68	2.96	**2.42**	**2.15**	**2.00**	**1.82**	**1.72**	**1.65**	**1.60**	**1.57**	**1.54**	**1.52**	**1.51**	**1.48**	**1.47**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**
20	4.87	3.06	**2.50**	**2.22**	**2.06**	**1.87**	**1.77**	**1.69**	**1.64**	**1.61**	**1.58**	**1.56**	**1.55**	**1.52**	**1.51**	**1.49**	**1.49**	**1.48**	**1.46**	**1.46**
30	5.22	3.26	*2.65*	**2.35**	**2.17**	**1.97**	**1.86**	**1.78**	**1.72**	**1.68**	**1.66**	**1.63**	**1.62**	**1.59**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**
40	5.46	3.39	*2.75*	**2.44**	**2.25**	**2.04**	**1.92**	**1.83**	**1.78**	**1.74**	**1.71**	**1.68**	**1.67**	**1.64**	**1.62**	**1.61**	**1.60**	**1.59**	**1.57**	**1.56**
50	5.64	3.49	2.83	**2.50**	**2.31**	**2.09**	**1.97**	**1.88**	**1.82**	**1.78**	**1.75**	**1.72**	**1.70**	**1.68**	**1.66**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**
60	5.79	3.58	2.89	**2.56**	**2.36**	**2.14**	**2.01**	**1.91**	**1.85**	**1.81**	**1.78**	**1.75**	**1.73**	**1.71**	**1.69**	**1.67**	**1.66**	**1.65**	**1.63**	**1.62**
75	5.97	3.68	2.97	*2.63*	**2.42**	**2.19**	**2.06**	**1.96**	**1.89**	**1.85**	**1.82**	**1.79**	**1.77**	**1.74**	**1.72**	**1.70**	**1.69**	**1.68**	**1.67**	**1.65**
100	6.19	3.81	3.07	*2.71*	**2.50**	**2.25**	**2.12**	**2.01**	**1.95**	**1.90**	**1.87**	**1.84**	**1.82**	**1.79**	**1.76**	**1.75**	**1.74**	**1.73**	**1.71**	**1.70**
125	6.37	3.90	3.15	*2.78*	**2.56**	**2.30**	**2.16**	**2.06**	**1.99**	**1.94**	**1.90**	**1.88**	**1.85**	**1.82**	**1.80**	**1.78**	**1.77**	**1.76**	**1.74**	**1.73**
150	6.51	3.98	3.21	*2.83*	*2.60*	**2.35**	**2.20**	**2.09**	**2.02**	**1.97**	**1.93**	**1.91**	**1.88**	**1.85**	**1.83**	**1.81**	**1.80**	**1.78**	**1.77**	**1.75**
175	6.62	4.05	3.26	2.87	*2.64*	**2.38**	**2.23**	**2.12**	**2.05**	**2.00**	**1.96**	**1.93**	**1.91**	**1.87**	**1.85**	**1.83**	**1.82**	**1.81**	**1.79**	**1.77**
200	6.72	4.11	3.30	2.91	*2.68*	**2.41**	**2.26**	**2.15**	**2.07**	**2.02**	**1.98**	**1.95**	**1.93**	**1.89**	**1.87**	**1.85**	**1.84**	**1.83**	**1.81**	**1.79**

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Table 19-6. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Means of Order 2 (10 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	2.86	**1.94**	**1.64**	**1.49**	**1.40**	**1.30**	**1.24**	**1.20**	**1.17**	**1.15**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**	**1.07**	**1.06**	**1.06**
2	3.46	**2.28**	**1.90**	**1.72**	**1.60**	**1.48**	**1.41**	**1.35**	**1.32**	**1.29**	**1.27**	**1.26**	**1.25**	**1.23**	**1.22**	**1.21**	**1.21**	**1.20**	**1.19**	**1.19**
3	3.82	**2.48**	**2.05**	**1.84**	**1.72**	**1.58**	**1.50**	**1.44**	**1.40**	**1.37**	**1.35**	**1.34**	**1.33**	**1.31**	**1.30**	**1.29**	**1.28**	**1.27**	**1.26**	**1.26**
4	4.07	**2.62**	**2.16**	**1.94**	**1.80**	**1.65**	**1.57**	**1.50**	**1.46**	**1.43**	**1.41**	**1.39**	**1.38**	**1.36**	**1.35**	**1.34**	**1.33**	**1.32**	**1.31**	**1.31**
5	4.27	**2.73**	**2.24**	**2.01**	**1.87**	**1.71**	**1.62**	**1.55**	**1.51**	**1.48**	**1.45**	**1.44**	**1.42**	**1.40**	**1.39**	**1.38**	**1.37**	**1.36**	**1.35**	**1.34**
8	4.68	2.96	**2.42**	**2.15**	**2.00**	**1.82**	**1.72**	**1.65**	**1.60**	**1.57**	**1.54**	**1.52**	**1.51**	**1.48**	**1.47**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**
12	5.03	3.15	**2.57**	**2.28**	**2.11**	**1.92**	**1.81**	**1.73**	**1.68**	**1.64**	**1.62**	**1.59**	**1.58**	**1.55**	**1.54**	**1.52**	**1.51**	**1.51**	**1.49**	**1.48**
16	5.27	3.29	**2.67**	**2.37**	**2.19**	**1.99**	**1.87**	**1.79**	**1.73**	**1.70**	**1.67**	**1.65**	**1.63**	**1.60**	**1.58**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**
20	5.46	3.39	**2.75**	**2.44**	**2.25**	**2.04**	**1.92**	**1.83**	**1.78**	**1.74**	**1.71**	**1.68**	**1.67**	**1.64**	**1.62**	**1.61**	**1.60**	**1.59**	**1.57**	**1.56**
30	5.79	3.58	*2.89*	**2.56**	**2.36**	**2.14**	**2.01**	**1.91**	**1.85**	**1.81**	**1.78**	**1.75**	**1.73**	**1.71**	**1.69**	**1.67**	**1.66**	**1.65**	**1.63**	**1.62**
40	6.02	3.71	*2.99*	**2.65**	**2.44**	**2.20**	**2.07**	**1.97**	**1.91**	**1.86**	**1.83**	**1.80**	**1.78**	**1.75**	**1.73**	**1.71**	**1.70**	**1.69**	**1.68**	**1.66**
50	6.19	3.81	3.07	**2.71**	**2.50**	**2.25**	**2.12**	**2.01**	**1.95**	**1.90**	**1.87**	**1.84**	**1.82**	**1.79**	**1.76**	**1.75**	**1.74**	**1.73**	**1.71**	**1.70**
60	6.34	3.89	3.13	**2.76**	**2.54**	**2.30**	**2.16**	**2.05**	**1.98**	**1.93**	**1.90**	**1.87**	**1.85**	**1.82**	**1.79**	**1.78**	**1.76**	**1.75**	**1.73**	**1.72**
75	6.51	3.98	3.21	*2.83*	**2.60**	**2.35**	**2.20**	**2.09**	**2.02**	**1.97**	**1.93**	**1.91**	**1.88**	**1.85**	**1.83**	**1.81**	**1.80**	**1.78**	**1.77**	**1.75**
100	6.72	4.11	3.30	*2.91*	**2.68**	**2.41**	**2.26**	**2.15**	**2.07**	**2.02**	**1.98**	**1.95**	**1.93**	**1.89**	**1.87**	**1.85**	**1.84**	**1.83**	**1.81**	**1.79**
125	6.89	4.20	3.38	*2.97*	**2.73**	**2.46**	**2.31**	**2.19**	**2.11**	**2.06**	**2.02**	**1.99**	**1.96**	**1.93**	**1.90**	**1.88**	**1.87**	**1.86**	**1.84**	**1.82**
150	7.02	4.28	3.43	*3.02*	**2.78**	**2.50**	**2.34**	**2.22**	**2.14**	**2.09**	**2.05**	**2.02**	**1.99**	**1.96**	**1.93**	**1.91**	**1.90**	**1.88**	**1.86**	**1.85**
175	7.13	4.34	3.48	*3.07*	**2.82**	**2.53**	**2.37**	**2.25**	**2.17**	**2.12**	**2.07**	**2.04**	**2.02**	**1.98**	**1.95**	**1.93**	**1.92**	**1.90**	**1.88**	**1.87**
200	7.23	4.40	3.53	3.10	*2.85*	**2.56**	**2.40**	**2.28**	**2.19**	**2.14**	**2.10**	**2.06**	**2.04**	**2.00**	**1.97**	**1.95**	**1.94**	**1.92**	**1.90**	**1.89**

Table 19-6. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Means of Order 2 (10 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.46	**2.28**	**1.90**	**1.72**	**1.60**	**1.48**	**1.41**	**1.35**	**1.32**	**1.29**	**1.27**	**1.26**	**1.25**	**1.23**	**1.22**	**1.21**	**1.21**	**1.20**	**1.19**	**1.19**
2	4.07	**2.62**	**2.16**	**1.94**	**1.80**	**1.65**	**1.57**	**1.50**	**1.46**	**1.43**	**1.41**	**1.39**	**1.38**	**1.36**	**1.35**	**1.34**	**1.33**	**1.32**	**1.31**	**1.31**
3	4.43	**2.82**	**2.31**	**2.06**	**1.92**	**1.75**	**1.66**	**1.59**	**1.54**	**1.51**	**1.49**	**1.47**	**1.46**	**1.43**	**1.42**	**1.41**	**1.40**	**1.39**	**1.38**	**1.37**
4	4.68	**2.96**	**2.42**	**2.15**	**2.00**	**1.82**	**1.72**	**1.65**	**1.60**	**1.57**	**1.54**	**1.52**	**1.51**	**1.48**	**1.47**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**
5	4.87	**3.06**	**2.50**	**2.22**	**2.06**	**1.87**	**1.77**	**1.69**	**1.64**	**1.61**	**1.58**	**1.56**	**1.55**	**1.52**	**1.51**	**1.49**	**1.49**	**1.48**	**1.46**	**1.46**
8	5.27	3.29	**2.67**	**2.37**	**2.19**	**1.99**	**1.87**	**1.79**	**1.73**	**1.70**	**1.67**	**1.65**	**1.63**	**1.60**	**1.58**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**
12	5.61	3.48	**2.81**	**2.49**	**2.30**	**2.08**	**1.96**	**1.87**	**1.81**	**1.77**	**1.74**	**1.72**	**1.70**	**1.67**	**1.65**	**1.64**	**1.62**	**1.62**	**1.60**	**1.59**
16	5.84	3.61	**2.92**	**2.58**	**2.38**	**2.15**	**2.02**	**1.93**	**1.86**	**1.82**	**1.79**	**1.76**	**1.74**	**1.72**	**1.70**	**1.68**	**1.67**	**1.66**	**1.64**	**1.63**
20	6.02	3.71	**2.99**	**2.65**	**2.44**	**2.20**	**2.07**	**1.97**	**1.91**	**1.86**	**1.83**	**1.80**	**1.78**	**1.75**	**1.73**	**1.71**	**1.70**	**1.69**	**1.68**	**1.66**
30	6.34	3.89	*3.13*	**2.76**	**2.54**	**2.30**	**2.16**	**2.05**	**1.98**	**1.93**	**1.90**	**1.87**	**1.85**	**1.82**	**1.79**	**1.78**	**1.76**	**1.75**	**1.73**	**1.72**
40	6.56	4.01	3.23	**2.85**	**2.62**	**2.36**	**2.22**	**2.10**	**2.03**	**1.98**	**1.94**	**1.92**	**1.89**	**1.86**	**1.84**	**1.82**	**1.81**	**1.79**	**1.77**	**1.76**
50	6.72	4.11	3.30	**2.91**	**2.68**	**2.41**	**2.26**	**2.15**	**2.07**	**2.02**	**1.98**	**1.95**	**1.93**	**1.89**	**1.87**	**1.85**	**1.84**	**1.83**	**1.81**	**1.79**
60	6.86	4.18	3.36	**2.96**	**2.72**	**2.45**	**2.30**	**2.18**	**2.10**	**2.05**	**2.01**	**1.98**	**1.96**	**1.92**	**1.90**	**1.88**	**1.86**	**1.85**	**1.83**	**1.82**
75	7.02	4.28	3.43	**3.02**	**2.78**	**2.50**	**2.34**	**2.22**	**2.14**	**2.09**	**2.05**	**2.02**	**1.99**	**1.96**	**1.93**	**1.91**	**1.90**	**1.88**	**1.86**	**1.85**
100	7.23	4.40	3.53	*3.10*	**2.85**	**2.56**	**2.40**	**2.28**	**2.19**	**2.14**	**2.10**	**2.06**	**2.04**	**2.00**	**1.97**	**1.95**	**1.94**	**1.92**	**1.90**	**1.89**
125	7.39	4.49	3.60	*3.16*	**2.91**	**2.61**	**2.44**	**2.32**	**2.23**	**2.17**	**2.13**	**2.10**	**2.07**	**2.03**	**2.00**	**1.98**	**1.97**	**1.95**	**1.93**	**1.92**
150	7.52	4.56	3.65	*3.21*	**2.95**	**2.65**	**2.48**	**2.35**	**2.26**	**2.20**	**2.16**	**2.13**	**2.10**	**2.06**	**2.03**	**2.01**	**1.99**	**1.98**	**1.96**	**1.93**
175	7.62	4.62	3.70	*3.25*	**2.99**	**2.68**	**2.51**	**2.38**	**2.29**	**2.23**	**2.18**	**2.15**	**2.12**	**2.08**	**2.05**	**2.03**	**2.01**	**2.00**	**1.98**	**1.96**
200	7.71	4.67	3.74	*3.29*	**3.02**	**2.71**	**2.54**	**2.40**	**2.31**	**2.25**	**2.21**	**2.17**	**2.14**	**2.10**	**2.07**	**2.05**	**2.03**	**2.02**	**1.99**	**1.98**

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Table 19-6. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Means of Order 2 (20 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	2.99	1.98	1.66	1.50	1.41	1.30	1.24	1.20	1.17	1.15	1.13	1.12	1.11	1.10	1.09	1.08	1.07	1.07	1.06	1.06
2	3.68	2.34	1.93	1.73	1.61	1.48	1.41	1.35	1.32	1.29	1.28	1.26	1.25	1.23	1.22	1.21	1.21	1.20	1.19	1.19
3	4.12	2.56	2.09	1.87	1.73	1.59	1.50	1.44	1.40	1.38	1.36	1.34	1.33	1.31	1.30	1.29	1.28	1.27	1.26	1.26
4	4.43	*2.71*	2.20	1.96	1.82	1.66	1.57	1.51	1.46	1.43	1.41	1.40	1.38	1.36	1.35	1.34	1.33	1.32	1.31	1.31
5	4.68	2.84	2.29	2.04	1.88	1.72	1.62	1.55	1.51	1.48	1.45	1.44	1.42	1.40	1.39	1.38	1.37	1.36	1.35	1.34
8	5.20	3.10	2.48	2.19	2.02	1.83	1.73	1.65	1.60	1.57	1.54	1.52	1.51	1.49	1.47	1.46	1.45	1.44	1.43	1.42
12	5.65	3.32	*2.65*	2.33	2.14	1.93	1.82	1.74	1.68	1.65	1.62	1.60	1.58	1.56	1.54	1.53	1.52	1.51	1.49	1.48
16	5.96	3.48	*2.76*	2.42	2.23	2.01	1.89	1.80	1.74	1.70	1.67	1.65	1.63	1.60	1.59	1.57	1.56	1.55	1.54	1.53
20	6.20	3.60	2.85	2.50	2.29	2.06	1.94	1.84	1.78	1.74	1.71	1.69	1.67	1.64	1.62	1.61	1.60	1.59	1.57	1.56
30	6.63	3.82	3.01	*2.63*	2.41	2.16	2.02	1.92	1.86	1.81	1.78	1.76	1.74	1.71	1.69	1.67	1.66	1.65	1.63	1.62
40	6.94	3.98	3.12	*2.72*	2.49	2.23	2.09	1.98	1.91	1.87	1.83	1.80	1.78	1.75	1.73	1.72	1.70	1.69	1.68	1.66
50	7.17	4.09	3.21	*2.80*	2.55	2.28	2.14	2.03	1.95	1.91	1.87	1.84	1.82	1.79	1.77	1.75	1.74	1.73	1.71	1.70
60	7.35	4.19	3.28	*2.85*	*2.61*	2.33	2.18	2.06	1.99	1.94	1.90	1.87	1.85	1.82	1.79	1.78	1.76	1.75	1.73	1.72
75	7.58	4.31	3.37	2.92	*2.67*	2.38	2.22	2.11	2.03	1.98	1.94	1.91	1.89	1.85	1.83	1.81	1.80	1.79	1.77	1.75
100	7.86	4.45	3.48	3.02	*2.75*	2.45	2.28	2.16	2.08	2.03	1.99	1.96	1.93	1.90	1.87	1.85	1.84	1.83	1.81	1.79
125	8.08	4.56	3.56	3.09	*2.81*	2.50	2.33	2.20	2.12	2.07	2.02	1.99	1.97	1.93	1.90	1.89	1.87	1.86	1.84	1.82
150	8.26	4.66	3.63	3.14	*2.86*	2.54	2.37	2.24	2.16	2.10	2.06	2.02	2.00	1.96	1.93	1.91	1.90	1.88	1.86	1.85
175	8.40	4.73	3.68	3.19	2.90	*2.58*	2.40	2.27	2.18	2.12	2.08	2.05	2.02	1.98	1.95	1.93	1.92	1.91	1.88	1.87
200	8.53	4.80	3.73	3.23	2.94	*2.61*	2.43	2.29	2.21	2.15	2.10	2.07	2.04	2.00	1.97	1.95	1.94	1.92	1.90	1.89

Table 19-6. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Means of Order 2 (20 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.68	2.34	1.93	1.73	1.61	1.48	1.41	1.35	1.32	1.29	1.28	1.26	1.25	1.23	1.22	1.21	1.21	1.20	1.19	1.19
2	4.43	2.71	2.20	1.96	1.82	1.66	1.57	1.51	1.46	1.43	1.41	1.40	1.38	1.36	1.35	1.34	1.33	1.32	1.31	1.31
3	4.88	2.94	2.37	2.10	1.94	1.76	1.66	1.59	1.55	1.51	1.49	1.47	1.46	1.44	1.42	1.41	1.40	1.39	1.38	1.37
4	5.20	3.10	2.48	2.19	2.02	1.83	1.73	1.65	1.60	1.57	1.54	1.52	1.51	1.49	1.47	1.46	1.45	1.44	1.43	1.42
5	5.44	3.22	2.57	2.27	2.09	1.89	1.78	1.70	1.65	1.61	1.58	1.56	1.55	1.52	1.51	1.50	1.49	1.48	1.46	1.46
8	5.96	3.48	2.76	2.42	2.23	2.01	1.89	1.80	1.74	1.70	1.67	1.65	1.63	1.60	1.59	1.57	1.56	1.55	1.54	1.53
12	6.40	3.70	*2.92*	2.56	2.34	2.11	1.98	1.88	1.82	1.77	1.74	1.72	1.70	1.67	1.65	1.64	1.63	1.62	1.60	1.59
16	6.70	3.86	3.04	2.65	2.43	2.18	2.04	1.94	1.87	1.83	1.79	1.77	1.75	1.72	1.70	1.68	1.67	1.66	1.64	1.63
20	6.94	3.98	3.12	2.72	2.49	2.23	2.09	1.98	1.91	1.87	1.83	1.80	1.78	1.75	1.73	1.72	1.70	1.69	1.68	1.66
30	7.35	4.19	3.28	*2.85*	2.61	2.33	2.18	2.06	1.99	1.94	1.90	1.87	1.85	1.82	1.79	1.78	1.76	1.75	1.73	1.72
40	7.64	4.34	3.39	*2.95*	2.69	2.40	2.24	2.12	2.04	1.99	1.95	1.92	1.90	1.86	1.84	1.82	1.81	1.80	1.78	1.76
50	7.86	4.45	3.48	*3.02*	2.75	2.45	2.28	2.16	2.08	2.03	1.99	1.96	1.93	1.90	1.87	1.85	1.84	1.83	1.81	1.79
60	8.04	4.54	3.54	3.07	2.80	2.49	2.32	2.20	2.12	2.06	2.02	1.99	1.96	1.92	1.90	1.88	1.86	1.85	1.83	1.82
75	8.26	4.66	3.63	3.14	*2.86*	2.54	2.37	2.24	2.16	2.10	2.06	2.02	2.00	1.96	1.93	1.91	1.90	1.88	1.86	1.85
100	8.53	4.80	3.73	3.23	*2.94*	2.61	2.43	2.29	2.21	2.15	2.10	2.07	2.04	2.00	1.97	1.95	1.94	1.92	1.90	1.89
125	8.74	4.91	3.81	3.30	*3.00*	2.66	2.48	2.34	2.25	2.18	2.14	2.10	2.08	2.04	2.01	1.98	1.97	1.96	1.93	1.92
150	8.91	4.99	3.88	3.35	*3.05*	2.70	2.51	2.37	2.28	2.22	2.17	2.13	2.10	2.06	2.03	2.01	1.99	1.98	1.96	1.94
175	9.05	5.07	3.93	3.40	*3.09*	2.74	2.55	2.40	2.31	2.24	2.19	2.16	2.13	2.08	2.05	2.03	2.02	2.00	1.98	1.96
200	9.17	5.13	3.98	3.44	3.12	2.77	2.57	2.43	2.33	2.26	2.22	2.18	2.15	2.10	2.07	2.05	2.03	2.02	1.99	1.98

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Table 19-6. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Means of Order 2 (20 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	4.43	**2.71**	**2.20**	**1.96**	**1.82**	**1.66**	**1.57**	**1.51**	**1.46**	**1.43**	**1.41**	**1.40**	**1.38**	**1.36**	**1.35**	**1.34**	**1.33**	**1.32**	**1.31**	**1.31**
2	5.20	**3.10**	**2.48**	**2.19**	**2.02**	**1.83**	**1.73**	**1.65**	**1.60**	**1.57**	**1.54**	**1.52**	**1.51**	**1.49**	**1.47**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**
3	5.65	3.32	**2.65**	**2.33**	**2.14**	**1.93**	**1.82**	**1.74**	**1.68**	**1.65**	**1.62**	**1.60**	**1.58**	**1.56**	**1.54**	**1.53**	**1.52**	**1.51**	**1.49**	**1.48**
4	5.96	3.48	**2.76**	**2.42**	**2.23**	**2.01**	**1.89**	**1.80**	**1.74**	**1.70**	**1.67**	**1.65**	**1.63**	**1.60**	**1.59**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**
5	6.20	3.60	**2.85**	**2.50**	**2.29**	**2.06**	**1.94**	**1.84**	**1.78**	**1.74**	**1.71**	**1.69**	**1.67**	**1.64**	**1.62**	**1.61**	**1.60**	**1.59**	**1.57**	**1.56**
8	6.70	3.86	**3.04**	**2.65**	**2.43**	**2.18**	**2.04**	**1.94**	**1.87**	**1.83**	**1.79**	**1.77**	**1.75**	**1.72**	**1.70**	**1.68**	**1.67**	**1.66**	**1.64**	**1.63**
12	7.12	4.07	*3.19*	**2.78**	**2.54**	**2.27**	**2.13**	**2.02**	**1.95**	**1.90**	**1.86**	**1.84**	**1.81**	**1.78**	**1.76**	**1.74**	**1.73**	**1.72**	**1.70**	**1.69**
16	7.42	4.22	3.31	**2.87**	**2.62**	**2.34**	**2.19**	**2.07**	**2.00**	**1.95**	**1.91**	**1.88**	**1.86**	**1.83**	**1.80**	**1.79**	**1.77**	**1.76**	**1.74**	**1.73**
20	7.64	4.34	3.39	**2.95**	**2.69**	**2.40**	**2.24**	**2.12**	**2.04**	**1.99**	**1.95**	**1.92**	**1.90**	**1.86**	**1.84**	**1.82**	**1.81**	**1.80**	**1.78**	**1.76**
30	8.04	4.54	3.54	**3.07**	**2.80**	**2.49**	**2.32**	**2.20**	**2.12**	**2.06**	**2.02**	**1.99**	**1.96**	**1.92**	**1.90**	**1.88**	**1.86**	**1.85**	**1.83**	**1.82**
40	8.32	4.69	3.65	*3.16*	**2.88**	**2.56**	**2.38**	**2.25**	**2.17**	**2.11**	**2.07**	**2.03**	**2.01**	**1.97**	**1.94**	**1.92**	**1.91**	**1.89**	**1.87**	**1.86**
50	8.53	4.80	3.73	*3.23*	**2.94**	**2.61**	**2.43**	**2.29**	**2.21**	**2.15**	**2.10**	**2.07**	**2.04**	**2.00**	**1.97**	**1.95**	**1.94**	**1.92**	**1.90**	**1.89**
60	8.70	4.89	3.80	*3.29*	**2.99**	**2.65**	**2.47**	**2.33**	**2.24**	**2.18**	**2.13**	**2.10**	**2.07**	**2.03**	**2.00**	**1.98**	**1.96**	**1.95**	**1.93**	**1.91**
75	8.91	4.99	3.88	3.35	**3.05**	**2.70**	**2.51**	**2.37**	**2.28**	**2.22**	**2.17**	**2.13**	**2.10**	**2.06**	**2.03**	**2.01**	**1.99**	**1.98**	**1.96**	**1.94**
100	9.17	5.13	3.98	3.44	*3.12*	**2.77**	**2.57**	**2.43**	**2.33**	**2.26**	**2.22**	**2.18**	**2.15**	**2.10**	**2.07**	**2.05**	**2.03**	**2.02**	**1.99**	**1.98**
125	9.37	5.23	4.06	3.50	*3.18*	**2.82**	**2.62**	**2.47**	**2.37**	**2.30**	**2.25**	**2.21**	**2.18**	**2.14**	**2.11**	**2.08**	**2.06**	**2.05**	**2.02**	**2.01**
150	9.53	5.32	4.12	3.56	*3.23*	**2.86**	**2.66**	**2.50**	**2.40**	**2.33**	**2.28**	**2.24**	**2.21**	**2.16**	**2.13**	**2.11**	**2.09**	**2.07**	**2.05**	**2.03**
175	9.66	5.39	4.17	3.60	*3.27*	**2.89**	**2.69**	**2.53**	**2.43**	**2.36**	**2.30**	**2.26**	**2.23**	**2.19**	**2.15**	**2.13**	**2.11**	**2.09**	**2.07**	**2.05**
200	9.78	5.45	4.22	3.64	*3.30*	**2.92**	**2.71**	**2.55**	**2.45**	**2.38**	**2.33**	**2.28**	**2.25**	**2.20**	**2.17**	**2.15**	**2.13**	**2.11**	**2.08**	**2.07**

Table 19-6. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Means of Order 2 (40 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.84	**2.38**	**1.94**	**1.74**	**1.62**	**1.49**	**1.41**	**1.36**	**1.32**	**1.29**	**1.28**	**1.26**	**1.25**	**1.23**	**1.22**	**1.21**	**1.21**	**1.20**	**1.19**	**1.19**
2	4.71	2.78	**2.23**	**1.98**	**1.83**	**1.66**	**1.57**	**1.51**	**1.46**	**1.43**	**1.41**	**1.40**	**1.38**	**1.36**	**1.35**	**1.34**	**1.33**	**1.32**	**1.31**	**1.31**
3	5.25	3.02	**2.40**	**2.12**	**1.95**	**1.77**	**1.67**	**1.59**	**1.55**	**1.51**	**1.49**	**1.47**	**1.46**	**1.44**	**1.42**	**1.41**	**1.40**	**1.39**	**1.38**	**1.37**
4	5.64	3.20	**2.53**	**2.22**	**2.04**	**1.84**	**1.73**	**1.65**	**1.60**	**1.57**	**1.54**	**1.52**	**1.51**	**1.49**	**1.47**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**
5	5.95	3.34	*2.62*	**2.29**	**2.10**	**1.90**	**1.79**	**1.70**	**1.65**	**1.61**	**1.59**	**1.56**	**1.55**	**1.52**	**1.51**	**1.50**	**1.49**	**1.48**	**1.46**	**1.46**
8	6.60	3.64	2.83	**2.46**	**2.25**	**2.02**	**1.89**	**1.80**	**1.74**	**1.70**	**1.67**	**1.65**	**1.63**	**1.60**	**1.59**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**
12	7.16	3.89	3.00	*2.60*	**2.37**	**2.12**	**1.98**	**1.88**	**1.82**	**1.78**	**1.74**	**1.72**	**1.70**	**1.67**	**1.65**	**1.64**	**1.63**	**1.62**	**1.60**	**1.59**
16	7.56	4.07	3.13	*2.70*	**2.46**	**2.19**	**2.05**	**1.94**	**1.87**	**1.83**	**1.79**	**1.77**	**1.75**	**1.72**	**1.70**	**1.68**	**1.67**	**1.66**	**1.64**	**1.63**
20	7.86	4.21	3.23	*2.78*	**2.53**	**2.25**	**2.10**	**1.99**	**1.92**	**1.87**	**1.83**	**1.81**	**1.79**	**1.75**	**1.73**	**1.72**	**1.70**	**1.69**	**1.68**	**1.66**
30	8.41	4.46	3.40	2.92	*2.65*	**2.35**	**2.19**	**2.07**	**1.99**	**1.94**	**1.90**	**1.87**	**1.85**	**1.82**	**1.80**	**1.78**	**1.76**	**1.75**	**1.74**	**1.72**
40	8.79	4.64	3.53	3.02	*2.73*	**2.42**	**2.25**	**2.13**	**2.05**	**1.99**	**1.95**	**1.92**	**1.90**	**1.86**	**1.84**	**1.82**	**1.81**	**1.80**	**1.78**	**1.76**
50	9.08	4.77	3.62	3.10	*2.80*	**2.48**	**2.30**	**2.17**	**2.09**	**2.03**	**1.99**	**1.96**	**1.93**	**1.90**	**1.87**	**1.85**	**1.84**	**1.83**	**1.81**	**1.79**
60	9.31	4.88	3.70	3.16	*2.86*	**2.52**	**2.34**	**2.21**	**2.12**	**2.06**	**2.02**	**1.99**	**1.96**	**1.93**	**1.90**	**1.88**	**1.87**	**1.85**	**1.83**	**1.82**
75	9.59	5.01	3.79	3.24	2.92	**2.58**	**2.39**	**2.25**	**2.16**	**2.10**	**2.06**	**2.03**	**2.00**	**1.96**	**1.93**	**1.91**	**1.90**	**1.89**	**1.86**	**1.85**
100	9.95	5.18	3.91	3.34	3.01	*2.65*	**2.45**	**2.31**	**2.22**	**2.15**	**2.11**	**2.07**	**2.04**	**2.00**	**1.98**	**1.95**	**1.94**	**1.93**	**1.90**	**1.89**
125	10.23	5.31	4.00	3.41	3.07	*2.70*	**2.50**	**2.35**	**2.26**	**2.19**	**2.14**	**2.11**	**2.08**	**2.04**	**2.01**	**1.99**	**1.97**	**1.96**	**1.93**	**1.92**
150	10.45	5.42	4.08	3.47	3.13	*2.74*	**2.54**	**2.39**	**2.29**	**2.22**	**2.17**	**2.14**	**2.11**	**2.06**	**2.03**	**2.01**	**1.99**	**1.98**	**1.96**	**1.94**
175	10.63	5.50	4.14	3.52	3.17	*2.78*	*2.57*	**2.42**	**2.32**	**2.25**	**2.20**	**2.16**	**2.13**	**2.09**	**2.06**	**2.03**	**2.02**	**2.00**	**1.98**	**1.96**
200	10.79	5.58	4.20	3.57	3.21	*2.81*	*2.60*	**2.44**	**2.34**	**2.27**	**2.22**	**2.18**	**2.15**	**2.11**	**2.08**	**2.05**	**2.03**	**2.02**	**1.99**	**1.98**

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Table 19-6. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Means of Order 2 (40 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	4.71	2.78	2.23	1.98	1.83	1.66	1.57	1.51	1.46	1.43	1.41	1.40	1.38	1.36	1.35	1.34	1.33	1.32	1.31	1.31
2	5.64	3.20	2.53	2.22	2.04	1.84	1.73	1.65	1.60	1.57	1.54	1.52	1.51	1.49	1.47	1.46	1.45	1.44	1.43	1.42
3	6.20	3.45	2.70	2.36	2.16	1.94	1.83	1.74	1.68	1.65	1.62	1.60	1.58	1.56	1.54	1.53	1.52	1.51	1.49	1.48
4	6.60	3.64	2.83	2.46	2.25	2.02	1.89	1.80	1.74	1.70	1.67	1.65	1.63	1.60	1.59	1.57	1.56	1.55	1.54	1.53
5	6.91	3.78	*2.92*	2.54	2.32	2.07	1.94	1.85	1.78	1.74	1.71	1.69	1.67	1.64	1.62	1.61	1.60	1.59	1.57	1.56
8	7.56	4.07	3.13	2.70	2.46	2.19	2.05	1.94	1.87	1.83	1.79	1.77	1.75	1.72	1.70	1.68	1.67	1.66	1.64	1.63
12	8.11	4.32	3.31	*2.84*	2.58	2.29	2.14	2.02	1.95	1.90	1.87	1.84	1.82	1.78	1.76	1.74	1.73	1.72	1.70	1.69
16	8.49	4.50	3.43	*2.94*	2.67	2.36	2.20	2.08	2.01	1.95	1.91	1.89	1.86	1.83	1.81	1.79	1.77	1.76	1.74	1.73
20	8.79	4.64	3.53	*3.02*	2.73	2.42	2.25	2.13	2.05	1.99	1.95	1.92	1.90	1.86	1.84	1.82	1.81	1.80	1.78	1.76
30	9.31	4.88	3.70	3.16	*2.86*	2.52	2.34	2.21	2.12	2.06	2.02	1.99	1.96	1.93	1.90	1.88	1.87	1.85	1.83	1.82
40	9.68	5.05	3.82	3.26	*2.94*	2.59	2.40	2.26	2.17	2.11	2.07	2.04	2.01	1.97	1.94	1.92	1.91	1.89	1.87	1.86
50	9.95	5.18	3.91	3.34	*3.01*	2.65	2.45	2.31	2.22	2.15	2.11	2.07	2.04	2.00	1.98	1.95	1.94	1.93	1.90	1.89
60	10.18	5.29	3.99	3.40	*3.06*	2.69	2.49	2.34	2.25	2.18	2.14	2.10	2.07	2.03	2.00	1.98	1.96	1.95	1.93	1.91
75	10.45	5.42	4.08	3.47	3.13	2.74	2.54	2.39	2.29	2.22	2.17	2.14	2.11	2.06	2.03	2.01	1.99	1.98	1.96	1.94
100	10.79	5.58	4.20	3.57	3.21	2.81	2.60	2.44	2.34	2.27	2.22	2.18	2.15	2.11	2.08	2.05	2.03	2.02	1.99	1.98
125	11.05	5.70	4.28	3.64	3.27	*2.87*	2.65	2.48	2.38	2.31	2.26	2.22	2.19	2.14	2.11	2.08	2.06	2.05	2.02	2.01
150	11.27	5.81	4.36	3.70	3.32	*2.91*	2.69	2.52	2.41	2.34	2.29	2.25	2.21	2.17	2.13	2.11	2.09	2.07	2.05	2.03
175	11.44	5.89	4.42	3.75	3.37	*2.95*	2.72	2.55	2.44	2.37	2.31	2.27	2.24	2.19	2.15	2.13	2.11	2.09	2.07	2.05
200	11.60	5.96	4.47	3.79	3.41	*2.98*	2.75	2.57	2.46	2.39	2.33	2.29	2.26	2.21	2.17	2.15	2.13	2.11	2.08	2.07

Table 19-6. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Means of Order 2 (40 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	5.64	3.20	2.53	2.22	2.04	1.84	1.73	1.65	1.60	1.57	1.54	1.52	1.51	1.49	1.47	1.46	1.45	1.44	1.43	1.42
2	6.60	3.64	2.83	2.46	2.25	2.02	1.89	1.80	1.74	1.70	1.67	1.65	1.63	1.60	1.59	1.57	1.56	1.55	1.54	1.53
3	7.16	3.89	3.00	2.60	2.37	2.12	1.98	1.88	1.82	1.78	1.74	1.72	1.70	1.67	1.65	1.64	1.63	1.62	1.60	1.59
4	7.56	4.07	*3.13*	2.70	2.46	2.19	2.05	1.94	1.87	1.83	1.79	1.77	1.75	1.72	1.70	1.68	1.67	1.66	1.64	1.63
5	7.86	4.21	3.23	2.78	2.53	2.25	2.10	1.99	1.92	1.87	1.83	1.81	1.79	1.75	1.73	1.72	1.70	1.69	1.68	1.66
8	8.49	4.50	3.43	2.94	2.67	2.36	2.20	2.08	2.01	1.95	1.91	1.89	1.86	1.83	1.81	1.79	1.77	1.76	1.74	1.73
12	9.02	4.75	3.60	*3.09*	2.79	2.47	2.29	2.16	2.08	2.02	1.98	1.95	1.93	1.89	1.87	1.85	1.83	1.82	1.79	1.79
16	9.39	4.92	3.73	*3.18*	2.88	2.54	2.35	2.22	2.13	2.08	2.03	2.00	1.97	1.94	1.91	1.89	1.87	1.86	1.84	1.83
20	9.68	5.05	3.82	*3.26*	2.94	2.59	2.40	2.26	2.17	2.11	2.07	2.04	2.01	1.97	1.94	1.92	1.91	1.89	1.87	1.86
30	10.18	5.29	3.99	3.40	3.06	2.69	2.49	2.34	2.25	2.18	2.14	2.10	2.07	2.03	2.00	1.98	1.96	1.95	1.93	1.91
40	10.53	5.45	4.11	3.49	*3.14*	2.76	2.55	2.40	2.30	2.23	2.18	2.15	2.12	2.07	2.04	2.02	2.00	1.99	1.97	1.95
50	10.79	5.58	4.20	3.57	*3.21*	2.81	2.60	2.44	2.34	2.27	2.22	2.18	2.15	2.11	2.08	2.05	2.03	2.02	1.99	1.98
60	11.01	5.68	4.27	3.63	*3.26*	2.86	2.64	2.48	2.37	2.30	2.25	2.21	2.18	2.13	2.10	2.08	2.06	2.04	2.02	2.00
75	11.27	5.81	4.36	3.70	*3.32*	2.91	2.69	2.52	2.41	2.34	2.29	2.25	2.21	2.17	2.13	2.11	2.09	2.07	2.05	2.03
100	11.60	5.96	4.47	3.79	3.41	2.98	2.75	2.57	2.46	2.39	2.33	2.29	2.26	2.21	2.17	2.15	2.13	2.11	2.08	2.07
125	11.85	6.08	4.56	3.86	3.47	3.03	2.79	2.62	2.50	2.43	2.37	2.32	2.29	2.24	2.20	2.18	2.16	2.14	2.11	2.09
150	12.05	6.18	4.63	3.92	3.52	*3.07*	2.83	2.65	2.54	2.46	2.40	2.35	2.32	2.27	2.23	2.20	2.18	2.17	2.14	2.12
175	12.22	6.26	4.68	3.97	3.56	*3.11*	2.86	2.68	2.56	2.48	2.42	2.38	2.34	2.29	2.25	2.22	2.20	2.19	2.16	2.14
200	12.37	6.33	4.74	4.01	3.60	*3.14*	2.89	2.70	2.59	2.50	2.44	2.40	2.36	2.31	2.27	2.24	2.22	2.20	2.17	2.15

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Table 19-7. κ-Multipliers for 1-of-3 Interwell Prediction Limits on Means of Order 2 (1 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	0.37	0.27	0.22	0.19	0.17	0.14	0.13	0.11	0.11	0.10	0.10	0.09	0.09	0.08	0.08	0.08	0.08	0.08	0.07	0.07
2	0.64	0.50	0.43	0.39	0.36	0.33	0.31	0.30	0.29	0.28	0.27	0.27	0.26	0.26	0.25	0.25	0.25	0.25	0.24	0.24
3	0.79	0.62	0.54	0.50	0.47	0.43	0.41	0.39	0.38	0.37	0.37	0.36	0.36	0.35	0.35	0.34	0.34	0.34	0.33	0.33
4	0.90	0.71	0.62	0.57	0.54	0.50	0.48	0.46	0.45	0.44	0.43	0.42	0.42	0.41	0.41	0.40	0.40	0.40	0.39	0.39
5	0.98	0.77	0.68	0.63	0.60	0.55	0.53	0.51	0.49	0.48	0.48	0.47	0.47	0.46	0.45	0.45	0.45	0.44	0.44	0.44
8	1.15	0.91	0.80	0.75	0.71	0.66	0.63	0.61	0.59	0.58	0.57	0.56	0.56	0.55	0.54	0.54	0.54	0.53	0.53	0.53
12	1.29	1.02	0.90	0.84	0.80	0.74	0.71	0.69	0.67	0.66	0.65	0.64	0.63	0.63	0.62	0.61	0.61	0.61	0.60	0.60
16	1.38	1.10	0.97	0.90	0.86	0.80	0.77	0.74	0.72	0.71	0.70	0.69	0.69	0.68	0.67	0.66	0.66	0.66	0.65	0.65
20	1.46	1.15	1.03	0.95	0.91	0.85	0.81	0.78	0.76	0.75	0.74	0.73	0.73	0.72	0.71	0.70	0.70	0.69	0.69	0.68
30	1.59	1.26	1.12	1.04	0.99	0.93	0.89	0.86	0.84	0.82	0.81	0.80	0.79	0.78	0.78	0.77	0.76	0.76	0.75	0.75
40	1.68	1.33	1.18	1.10	1.05	0.98	0.94	0.91	0.89	0.87	0.86	0.85	0.84	0.83	0.82	0.81	0.81	0.81	0.80	0.79
50	1.75	1.38	1.23	1.15	1.09	1.02	0.98	0.95	0.92	0.91	0.89	0.88	0.88	0.86	0.86	0.85	0.84	0.84	0.83	0.83
60	1.81	1.43	1.27	1.18	1.13	1.06	1.01	0.98	0.95	0.94	0.92	0.91	0.91	0.89	0.88	0.88	0.87	0.87	0.86	0.85
75	1.87	1.48	1.32	1.23	1.17	1.10	1.05	1.01	0.99	0.97	0.96	0.95	0.94	0.93	0.92	0.91	0.91	0.90	0.89	0.89
100	1.96	1.55	1.38	1.28	1.22	1.15	1.10	1.06	1.04	1.02	1.00	0.99	0.98	0.97	0.96	0.95	0.95	0.94	0.93	0.93
125	2.02	1.60	1.42	1.33	1.26	1.18	1.14	1.10	1.07	1.05	1.04	1.03	1.02	1.00	0.99	0.98	0.98	0.97	0.97	0.96
150	2.08	1.64	1.46	1.36	1.30	1.21	1.17	1.13	1.10	1.08	1.06	1.05	1.04	1.03	1.02	1.01	1.00	1.00	0.99	0.98
175	2.12	1.67	1.49	1.39	1.32	1.24	1.19	1.15	1.12	1.10	1.09	1.08	1.07	1.05	1.04	1.03	1.03	1.02	1.01	1.00
200	2.16	1.70	1.52	1.41	1.35	1.26	1.21	1.17	1.14	1.12	1.11	1.09	1.08	1.07	1.06	1.05	1.04	1.04	1.03	1.02

Table 19-7. κ-Multipliers for 1-of-3 Interwell Prediction Limits on Means of Order 2 (1 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	0.64	0.50	0.43	0.39	0.36	0.33	0.31	0.30	0.29	0.28	0.27	0.27	0.26	0.26	0.25	0.25	0.25	0.25	0.24	0.24
2	0.90	0.71	0.62	0.57	0.54	0.50	0.48	0.46	0.45	0.44	0.43	0.42	0.42	0.41	0.41	0.40	0.40	0.40	0.39	0.39
3	1.04	0.83	0.73	0.68	0.64	0.59	0.57	0.55	0.53	0.52	0.51	0.51	0.50	0.49	0.49	0.49	0.48	0.48	0.48	0.47
4	1.15	0.91	0.80	0.75	0.71	0.66	0.63	0.61	0.59	0.58	0.57	0.56	0.56	0.55	0.54	0.54	0.54	0.53	0.53	0.53
5	1.22	0.97	0.86	0.80	0.76	0.71	0.68	0.65	0.63	0.62	0.61	0.61	0.60	0.59	0.59	0.58	0.58	0.57	0.57	0.57
8	1.38	1.10	0.97	0.90	0.86	0.80	0.77	0.74	0.72	0.71	0.70	0.69	0.69	0.68	0.67	0.66	0.66	0.66	0.65	0.65
12	1.52	1.20	1.07	0.99	0.94	0.88	0.85	0.82	0.80	0.78	0.77	0.76	0.76	0.75	0.74	0.73	0.73	0.73	0.72	0.71
16	1.61	1.27	1.13	1.05	1.00	0.94	0.90	0.87	0.85	0.83	0.82	0.81	0.80	0.79	0.79	0.78	0.77	0.77	0.76	0.76
20	1.68	1.33	1.18	1.10	1.05	0.98	0.94	0.91	0.89	0.87	0.86	0.85	0.84	0.83	0.82	0.81	0.81	0.81	0.80	0.79
30	1.81	1.43	1.27	1.18	1.13	1.06	1.01	0.98	0.95	0.94	0.92	0.91	0.91	0.89	0.88	0.88	0.87	0.87	0.86	0.85
40	1.89	1.50	1.33	1.24	1.18	1.11	1.06	1.03	1.00	0.98	0.97	0.96	0.95	0.94	0.93	0.92	0.91	0.91	0.90	0.90
50	1.96	1.55	1.38	1.28	1.22	1.15	1.10	1.06	1.04	1.02	1.00	0.99	0.98	0.97	0.96	0.95	0.95	0.94	0.93	0.93
60	2.01	1.59	1.42	1.32	1.26	1.18	1.13	1.09	1.06	1.05	1.03	1.02	1.01	1.00	0.99	0.98	0.97	0.97	0.96	0.95
75	2.08	1.64	1.46	1.36	1.30	1.21	1.17	1.13	1.10	1.08	1.06	1.05	1.04	1.03	1.02	1.01	1.00	1.00	0.99	0.98
100	2.16	1.70	1.52	1.41	1.35	1.26	1.21	1.17	1.14	1.12	1.11	1.09	1.08	1.07	1.06	1.05	1.04	1.04	1.03	1.02
125	2.22	1.75	1.56	1.45	1.38	1.30	1.25	1.20	1.18	1.15	1.14	1.13	1.12	1.10	1.09	1.08	1.07	1.07	1.06	1.05
150	2.27	1.79	1.60	1.49	1.42	1.33	1.28	1.23	1.20	1.18	1.16	1.15	1.14	1.13	1.11	1.11	1.10	1.09	1.08	1.08
175	2.31	1.82	1.62	1.51	1.44	1.35	1.30	1.25	1.22	1.20	1.19	1.17	1.16	1.15	1.13	1.13	1.12	1.11	1.10	1.10
200	2.35	1.85	1.65	1.54	1.46	1.37	1.32	1.27	1.24	1.22	1.20	1.19	1.18	1.16	1.15	1.14	1.14	1.13	1.12	1.11

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Table 19-7. κ-Multipliers for 1-of-3 Interwell Prediction Limits on Means of Order 2 (1 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	0.90	0.71	0.62	0.57	0.54	0.50	0.48	0.46	0.45	0.44	0.43	0.42	0.42	0.41	0.41	0.40	0.40	0.40	0.39	0.39
2	1.15	0.91	0.80	0.75	0.71	0.66	0.63	0.61	0.59	0.58	0.57	0.56	0.56	0.55	0.54	0.54	0.54	0.53	0.53	0.53
3	1.29	1.02	0.90	0.84	0.80	0.74	0.71	0.69	0.67	0.66	0.65	0.64	0.63	0.63	0.62	0.61	0.61	0.61	0.60	0.60
4	1.38	1.10	0.97	0.90	0.86	0.80	0.77	0.74	0.72	0.71	0.70	0.69	0.69	0.68	0.67	0.66	0.66	0.66	0.65	0.65
5	1.46	1.15	1.03	0.95	0.91	0.85	0.81	0.78	0.76	0.75	0.74	0.73	0.73	0.72	0.71	0.70	0.70	0.69	0.69	0.68
8	1.61	1.27	1.13	1.05	1.00	0.94	0.90	0.87	0.85	0.83	0.82	0.81	0.80	0.79	0.79	0.78	0.77	0.77	0.76	0.76
12	1.74	1.37	1.22	1.14	1.08	1.01	0.97	0.94	0.92	0.90	0.89	0.88	0.87	0.86	0.85	0.84	0.84	0.83	0.83	0.82
16	1.83	1.44	1.29	1.20	1.14	1.07	1.02	0.99	0.96	0.95	0.93	0.92	0.92	0.90	0.89	0.89	0.88	0.88	0.87	0.86
20	1.89	1.50	1.33	1.24	1.18	1.11	1.06	1.03	1.00	0.98	0.97	0.96	0.95	0.94	0.93	0.92	0.91	0.91	0.90	0.90
30	2.01	1.59	1.42	1.32	1.26	1.18	1.13	1.09	1.06	1.05	1.03	1.02	1.01	1.00	0.99	0.98	0.97	0.97	0.96	0.95
40	2.09	1.65	1.47	1.37	1.31	1.23	1.18	1.14	1.11	1.09	1.07	1.06	1.05	1.04	1.03	1.02	1.01	1.01	1.00	0.99
50	2.16	1.70	1.52	1.41	1.35	1.26	1.21	1.17	1.14	1.12	1.11	1.09	1.08	1.07	1.06	1.05	1.04	1.04	1.03	1.02
60	2.21	1.74	1.55	1.45	1.38	1.29	1.24	1.20	1.17	1.15	1.13	1.12	1.11	1.09	1.08	1.08	1.07	1.06	1.05	1.05
75	2.27	1.79	1.60	1.49	1.42	1.33	1.28	1.23	1.20	1.18	1.16	1.15	1.14	1.13	1.11	1.11	1.10	1.09	1.08	1.08
100	2.35	1.85	1.65	1.54	1.46	1.37	1.32	1.27	1.24	1.22	1.20	1.19	1.18	1.16	1.15	1.14	1.14	1.13	1.12	1.11
125	2.41	1.90	1.69	1.58	1.50	1.41	1.35	1.31	1.28	1.25	1.24	1.22	1.21	1.19	1.18	1.17	1.16	1.16	1.15	1.14
150	2.46	1.93	1.72	1.61	1.53	1.44	1.38	1.33	1.30	1.28	1.26	1.25	1.24	1.22	1.21	1.20	1.19	1.18	1.17	1.16
175	2.50	1.96	1.75	1.63	1.56	1.46	1.40	1.36	1.32	1.30	1.28	1.27	1.26	1.24	1.22	1.21	1.21	1.20	1.19	1.18
200	2.53	1.99	1.78	1.66	1.58	1.48	1.42	1.37	1.34	1.32	1.30	1.28	1.27	1.25	1.24	1.23	1.22	1.22	1.21	1.20

Table 19-7. κ-Multipliers for 1-of-3 Interwell Prediction Limits on Means of Order 2 (2 COC, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	0.71	0.53	0.45	0.41	0.38	0.34	0.32	0.30	0.29	0.28	0.28	0.27	0.27	0.26	0.26	0.25	0.25	0.25	0.25	0.24
2	1.00	0.76	0.66	0.60	0.56	0.51	0.49	0.47	0.45	0.44	0.43	0.43	0.42	0.41	0.41	0.41	0.40	0.40	0.40	0.39
3	1.17	0.89	0.77	0.70	0.66	0.61	0.58	0.55	0.54	0.53	0.52	0.51	0.51	0.50	0.49	0.49	0.48	0.48	0.48	0.47
4	1.30	0.98	0.85	0.78	0.73	0.68	0.64	0.62	0.60	0.59	0.58	0.57	0.56	0.55	0.55	0.54	0.54	0.54	0.53	0.53
5	1.39	1.05	0.91	0.83	0.78	0.72	0.69	0.66	0.64	0.63	0.62	0.61	0.60	0.60	0.59	0.58	0.58	0.58	0.57	0.57
8	1.59	1.19	1.04	0.95	0.89	0.83	0.79	0.75	0.73	0.72	0.71	0.70	0.69	0.68	0.67	0.67	0.66	0.66	0.65	0.65
12	1.76	1.31	1.14	1.04	0.98	0.91	0.87	0.83	0.81	0.79	0.78	0.77	0.76	0.75	0.74	0.74	0.73	0.73	0.72	0.72
16	1.88	1.40	1.21	1.11	1.05	0.97	0.92	0.88	0.86	0.84	0.83	0.82	0.81	0.80	0.79	0.78	0.78	0.77	0.77	0.76
20	1.97	1.46	1.27	1.16	1.09	1.01	0.96	0.92	0.90	0.88	0.87	0.86	0.85	0.83	0.83	0.82	0.81	0.81	0.80	0.80
30	2.13	1.58	1.37	1.25	1.18	1.09	1.04	1.00	0.97	0.95	0.93	0.92	0.91	0.90	0.89	0.88	0.88	0.87	0.86	0.86
40	2.24	1.66	1.44	1.32	1.24	1.15	1.09	1.05	1.02	1.00	0.98	0.97	0.96	0.94	0.93	0.92	0.92	0.91	0.90	0.90
50	2.33	1.72	1.49	1.36	1.28	1.19	1.13	1.08	1.05	1.03	1.02	1.00	0.99	0.98	0.97	0.96	0.95	0.95	0.94	0.93
60	2.40	1.77	1.53	1.40	1.32	1.22	1.16	1.11	1.08	1.06	1.04	1.03	1.02	1.00	0.99	0.98	0.98	0.97	0.96	0.96
75	2.48	1.83	1.58	1.45	1.36	1.26	1.20	1.15	1.12	1.10	1.08	1.06	1.05	1.04	1.02	1.02	1.01	1.00	0.99	0.99
100	2.59	1.90	1.65	1.51	1.42	1.31	1.25	1.20	1.16	1.14	1.12	1.11	1.10	1.08	1.07	1.06	1.05	1.04	1.03	1.03
125	2.67	1.96	1.70	1.55	1.46	1.35	1.29	1.23	1.20	1.17	1.15	1.14	1.13	1.11	1.10	1.09	1.08	1.07	1.06	1.05
150	2.73	2.01	1.74	1.59	1.50	1.38	1.32	1.26	1.23	1.20	1.18	1.17	1.15	1.13	1.12	1.11	1.10	1.10	1.09	1.08
175	2.79	2.05	1.77	1.62	1.52	1.41	1.34	1.29	1.25	1.22	1.20	1.19	1.17	1.16	1.14	1.13	1.12	1.12	1.11	1.10
200	2.83	2.08	1.80	1.65	1.55	1.43	1.36	1.31	1.27	1.24	1.22	1.21	1.19	1.17	1.16	1.15	1.14	1.14	1.12	1.12

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Table 19-7. κ-Multipliers for 1-of-3 Interwell Prediction Limits on Means of Order 2 (2 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	1.00	0.76	0.66	0.60	0.56	0.51	0.49	0.47	0.45	0.44	0.43	0.43	0.42	0.41	0.41	0.41	0.40	0.40	0.40	0.39
2	1.30	0.98	0.85	0.78	0.73	0.68	0.64	0.62	0.60	0.59	0.58	0.57	0.56	0.55	0.55	0.54	0.54	0.54	0.53	0.53
3	1.47	1.10	0.96	0.88	0.83	0.76	0.73	0.70	0.68	0.66	0.65	0.65	0.64	0.63	0.62	0.62	0.61	0.61	0.60	0.60
4	1.59	1.19	1.04	0.95	0.89	0.83	0.79	0.75	0.73	0.72	0.71	0.70	0.69	0.68	0.67	0.67	0.66	0.66	0.65	0.65
5	1.68	1.26	1.09	1.00	0.94	0.87	0.83	0.80	0.77	0.76	0.75	0.74	0.73	0.72	0.71	0.71	0.70	0.70	0.69	0.69
8	1.88	1.40	1.21	1.11	1.05	0.97	0.92	0.88	0.86	0.84	0.83	0.82	0.81	0.80	0.79	0.78	0.78	0.77	0.77	0.76
12	2.04	1.52	1.31	1.20	1.13	1.05	1.00	0.96	0.93	0.91	0.90	0.89	0.88	0.86	0.85	0.85	0.84	0.84	0.83	0.82
16	2.15	1.60	1.38	1.27	1.19	1.10	1.05	1.01	0.98	0.96	0.94	0.93	0.92	0.91	0.90	0.89	0.89	0.88	0.87	0.87
20	2.24	1.66	1.44	1.32	1.24	1.15	1.09	1.05	1.02	1.00	0.98	0.97	0.96	0.94	0.93	0.92	0.92	0.91	0.90	0.90
30	2.40	1.77	1.53	1.40	1.32	1.22	1.16	1.11	1.08	1.06	1.04	1.03	1.02	1.00	0.99	0.98	0.98	0.97	0.96	0.96
40	2.50	1.85	1.60	1.46	1.38	1.27	1.21	1.16	1.13	1.11	1.09	1.07	1.06	1.05	1.03	1.02	1.02	1.01	1.00	1.00
50	2.59	1.90	1.65	1.51	1.42	1.31	1.25	1.20	1.16	1.14	1.12	1.11	1.10	1.08	1.07	1.06	1.05	1.04	1.03	1.03
60	2.65	1.95	1.69	1.54	1.45	1.34	1.28	1.23	1.19	1.17	1.15	1.13	1.12	1.10	1.09	1.08	1.07	1.07	1.06	1.05
75	2.73	2.01	1.74	1.59	1.50	1.38	1.32	1.26	1.23	1.20	1.18	1.17	1.15	1.13	1.12	1.11	1.10	1.10	1.09	1.08
100	2.83	2.08	1.80	1.65	1.55	1.43	1.36	1.31	1.27	1.24	1.22	1.21	1.19	1.17	1.16	1.15	1.14	1.14	1.12	1.12
125	2.91	2.14	1.85	1.69	1.59	1.47	1.40	1.34	1.30	1.27	1.25	1.24	1.22	1.20	1.19	1.18	1.17	1.16	1.15	1.14
150	2.97	2.18	1.88	1.72	1.62	1.50	1.43	1.37	1.33	1.30	1.28	1.26	1.25	1.23	1.21	1.20	1.19	1.19	1.17	1.17
175	3.03	2.22	1.92	1.75	1.65	1.53	1.45	1.39	1.35	1.32	1.30	1.28	1.27	1.25	1.23	1.22	1.21	1.21	1.19	1.19
200	3.07	2.25	1.94	1.78	1.67	1.55	1.47	1.41	1.37	1.34	1.32	1.30	1.29	1.27	1.25	1.24	1.23	1.22	1.21	1.20

Table 19-7. κ-Multipliers for 1-of-3 Interwell Prediction Limits on Means of Order 2 (2 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	1.30	0.98	0.85	0.78	0.73	0.68	0.64	0.62	0.60	0.59	0.58	0.57	0.56	0.55	0.55	0.54	0.54	0.54	0.53	0.53
2	1.59	1.19	1.04	0.95	0.89	0.83	0.79	0.75	0.73	0.72	0.71	0.70	0.69	0.68	0.67	0.67	0.66	0.66	0.65	0.65
3	1.76	1.31	1.14	1.04	0.98	0.91	0.87	0.83	0.81	0.79	0.78	0.77	0.76	0.75	0.74	0.74	0.73	0.73	0.72	0.72
4	1.88	1.40	1.21	1.11	1.05	0.97	0.92	0.88	0.86	0.84	0.83	0.82	0.81	0.80	0.79	0.78	0.78	0.77	0.77	0.76
5	1.97	1.46	1.27	1.16	1.09	1.01	0.96	0.92	0.90	0.88	0.87	0.86	0.85	0.83	0.83	0.82	0.81	0.81	0.80	0.80
8	2.15	1.60	1.38	1.27	1.19	1.10	1.05	1.01	0.98	0.96	0.94	0.93	0.92	0.91	0.90	0.89	0.89	0.88	0.87	0.87
12	2.31	1.71	1.48	1.35	1.28	1.18	1.12	1.08	1.05	1.03	1.01	1.00	0.99	0.97	0.96	0.95	0.95	0.94	0.93	0.92
16	2.42	1.79	1.55	1.42	1.33	1.23	1.17	1.12	1.09	1.07	1.05	1.04	1.03	1.01	1.00	0.99	0.99	0.98	0.97	0.96
20	2.50	1.85	1.60	1.46	1.38	1.27	1.21	1.16	1.13	1.11	1.09	1.07	1.06	1.05	1.03	1.02	1.02	1.01	1.00	1.00
30	2.65	1.95	1.69	1.54	1.45	1.34	1.28	1.23	1.19	1.17	1.15	1.13	1.12	1.10	1.09	1.08	1.07	1.07	1.06	1.05
40	2.75	2.02	1.75	1.60	1.51	1.39	1.33	1.27	1.24	1.21	1.19	1.17	1.16	1.14	1.13	1.12	1.11	1.11	1.09	1.09
50	2.83	2.08	1.80	1.65	1.55	1.43	1.36	1.31	1.27	1.24	1.22	1.21	1.19	1.17	1.16	1.15	1.14	1.14	1.12	1.12
60	2.90	2.13	1.84	1.68	1.58	1.46	1.39	1.33	1.30	1.27	1.25	1.23	1.22	1.20	1.18	1.17	1.17	1.16	1.15	1.14
75	2.97	2.18	1.88	1.72	1.62	1.50	1.43	1.37	1.33	1.30	1.28	1.26	1.25	1.23	1.21	1.20	1.19	1.19	1.17	1.17
100	3.07	2.25	1.94	1.78	1.67	1.55	1.47	1.41	1.37	1.34	1.32	1.30	1.29	1.27	1.25	1.24	1.23	1.22	1.21	1.20
125	3.14	2.30	1.99	1.82	1.71	1.58	1.51	1.44	1.40	1.37	1.35	1.33	1.32	1.30	1.28	1.27	1.26	1.25	1.24	1.23
150	3.20	2.35	2.03	1.85	1.74	1.61	1.53	1.47	1.43	1.40	1.37	1.36	1.34	1.32	1.30	1.29	1.28	1.27	1.26	1.25
175	3.25	2.38	2.06	1.88	1.77	1.64	1.56	1.49	1.45	1.42	1.39	1.38	1.36	1.34	1.32	1.31	1.30	1.29	1.28	1.27
200	3.30	2.41	2.08	1.91	1.79	1.66	1.58	1.51	1.47	1.44	1.41	1.39	1.38	1.36	1.34	1.33	1.32	1.31	1.29	1.28

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Table 19-7. κ-Multipliers for 1-of-3 Interwell Prediction Limits on Means of Order 2 (5 COC, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	1.20	0.87	0.74	0.67	0.63	0.58	0.54	0.52	0.50	0.49	0.48	0.48	0.47	0.46	0.46	0.45	0.45	0.45	0.44	0.44
2	1.56	1.11	0.95	0.86	0.80	0.74	0.70	0.67	0.65	0.63	0.62	0.61	0.61	0.60	0.59	0.59	0.58	0.58	0.57	0.57
3	1.78	1.26	1.07	0.97	0.90	0.83	0.78	0.75	0.73	0.71	0.70	0.69	0.68	0.67	0.66	0.66	0.65	0.65	0.64	0.64
4	1.93	1.36	1.15	1.04	0.97	0.89	0.84	0.81	0.78	0.76	0.75	0.74	0.73	0.72	0.71	0.71	0.70	0.70	0.69	0.69
5	2.05	1.44	1.21	1.10	1.02	0.94	0.89	0.85	0.82	0.80	0.79	0.78	0.77	0.76	0.75	0.74	0.74	0.74	0.73	0.72
8	2.31	1.60	1.35	1.21	1.13	1.04	0.98	0.94	0.91	0.89	0.87	0.86	0.85	0.84	0.83	0.82	0.82	0.81	0.80	0.80
12	2.53	1.74	1.46	1.31	1.22	1.12	1.06	1.01	0.98	0.96	0.94	0.93	0.92	0.90	0.89	0.88	0.88	0.87	0.86	0.86
16	2.69	1.84	1.54	1.38	1.29	1.18	1.11	1.06	1.03	1.00	0.99	0.97	0.96	0.95	0.94	0.93	0.92	0.92	0.91	0.90
20	2.81	1.91	1.60	1.44	1.34	1.22	1.15	1.10	1.07	1.04	1.02	1.01	1.00	0.98	0.97	0.96	0.95	0.95	0.94	0.93
30	3.02	2.05	1.71	1.53	1.43	1.30	1.23	1.17	1.13	1.11	1.09	1.07	1.06	1.04	1.03	1.02	1.01	1.01	1.00	0.99
40	3.17	2.14	1.78	1.60	1.49	1.35	1.28	1.22	1.18	1.15	1.13	1.11	1.10	1.08	1.07	1.06	1.05	1.05	1.03	1.03
50	3.29	2.21	1.84	1.65	1.53	1.40	1.32	1.26	1.21	1.19	1.16	1.15	1.13	1.12	1.10	1.09	1.08	1.08	1.06	1.06
60	3.38	2.27	1.89	1.69	1.57	1.43	1.35	1.29	1.24	1.21	1.19	1.17	1.16	1.14	1.13	1.12	1.11	1.10	1.09	1.08
75	3.49	2.34	1.95	1.74	1.62	1.47	1.39	1.32	1.28	1.25	1.22	1.21	1.19	1.17	1.16	1.15	1.14	1.13	1.12	1.11
100	3.63	2.43	2.02	1.81	1.68	1.53	1.44	1.37	1.32	1.29	1.27	1.25	1.23	1.21	1.20	1.18	1.17	1.17	1.15	1.15
125	3.74	2.50	2.07	1.86	1.72	1.57	1.47	1.40	1.36	1.32	1.30	1.28	1.26	1.24	1.23	1.21	1.20	1.20	1.18	1.17
150	3.83	2.55	2.12	1.90	1.76	1.60	1.51	1.43	1.38	1.35	1.32	1.31	1.29	1.27	1.25	1.24	1.23	1.22	1.20	1.20
175	3.90	2.60	2.16	1.93	1.79	1.63	1.53	1.46	1.41	1.37	1.35	1.33	1.31	1.29	1.27	1.26	1.25	1.24	1.22	1.21
200	3.97	2.64	2.19	1.96	1.82	1.65	1.55	1.48	1.43	1.39	1.37	1.34	1.33	1.30	1.29	1.27	1.26	1.25	1.24	1.23

Table 19-7. κ-Multipliers for 1-of-3 Interwell Prediction Limits on Means of Order 2 (5 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	1.56	1.11	0.95	0.86	0.80	0.74	0.70	0.67	0.65	0.63	0.62	0.61	0.61	0.60	0.59	0.59	0.58	0.58	0.57	0.57
2	1.93	1.36	1.15	1.04	0.97	0.89	0.84	0.81	0.78	0.76	0.75	0.74	0.73	0.72	0.71	0.71	0.70	0.70	0.69	0.69
3	2.15	1.50	1.26	1.14	1.07	0.98	0.92	0.88	0.86	0.84	0.82	0.81	0.80	0.79	0.78	0.77	0.77	0.77	0.76	0.75
4	2.31	1.60	1.35	1.21	1.13	1.04	0.98	0.94	0.91	0.89	0.87	0.86	0.85	0.84	0.83	0.82	0.82	0.81	0.80	0.80
5	2.43	1.68	1.41	1.27	1.18	1.08	1.02	0.98	0.95	0.93	0.91	0.90	0.89	0.87	0.86	0.86	0.85	0.85	0.84	0.83
8	2.69	1.84	1.54	1.38	1.29	1.18	1.11	1.06	1.03	1.00	0.99	0.97	0.96	0.95	0.94	0.93	0.92	0.92	0.91	0.90
12	2.91	1.97	1.65	1.48	1.38	1.26	1.19	1.13	1.10	1.07	1.05	1.04	1.03	1.01	1.00	0.99	0.98	0.97	0.96	0.96
16	3.06	2.07	1.72	1.55	1.44	1.31	1.24	1.18	1.14	1.12	1.10	1.08	1.07	1.05	1.04	1.03	1.02	1.01	1.00	1.00
20	3.17	2.14	1.78	1.60	1.49	1.35	1.28	1.22	1.18	1.15	1.13	1.11	1.10	1.08	1.07	1.06	1.05	1.05	1.03	1.03
30	3.38	2.27	1.89	1.69	1.57	1.43	1.35	1.29	1.24	1.21	1.19	1.17	1.16	1.14	1.13	1.12	1.11	1.10	1.09	1.08
40	3.52	2.36	1.96	1.76	1.63	1.48	1.40	1.33	1.29	1.26	1.23	1.22	1.20	1.18	1.17	1.15	1.15	1.14	1.13	1.12
50	3.63	2.43	2.02	1.81	1.68	1.53	1.44	1.37	1.32	1.29	1.27	1.25	1.23	1.21	1.20	1.18	1.17	1.17	1.15	1.15
60	3.72	2.49	2.06	1.85	1.72	1.56	1.47	1.40	1.35	1.32	1.29	1.27	1.26	1.24	1.22	1.21	1.20	1.19	1.18	1.17
75	3.83	2.55	2.12	1.90	1.76	1.60	1.51	1.43	1.38	1.35	1.32	1.31	1.29	1.27	1.25	1.24	1.23	1.22	1.20	1.20
100	3.97	*2.64*	2.19	1.96	1.82	1.65	1.55	1.48	1.43	1.39	1.37	1.34	1.33	1.30	1.29	1.27	1.26	1.25	1.24	1.23
125	4.07	*2.71*	2.24	2.01	1.86	1.69	1.59	1.51	1.46	1.42	1.40	1.38	1.36	1.33	1.31	1.30	1.29	1.28	1.27	1.26
150	4.16	*2.76*	2.29	2.04	1.90	1.72	1.62	1.54	1.49	1.45	1.42	1.40	1.38	1.36	1.34	1.32	1.31	1.30	1.29	1.28
175	4.23	2.80	2.32	2.08	1.93	1.75	1.64	1.56	1.51	1.47	1.44	1.42	1.40	1.38	1.36	1.34	1.33	1.32	1.31	1.30
200	4.29	2.84	2.35	2.10	1.95	1.77	1.67	1.58	1.53	1.49	1.46	1.44	1.42	1.39	1.37	1.36	1.35	1.34	1.32	1.31

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Table 19-7. κ-Multipliers for 1-of-3 Interwell Prediction Limits on Means of Order 2 (5 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.93**	**1.36**	**1.15**	**1.04**	**0.97**	**0.89**	**0.84**	**0.81**	**0.78**	**0.76**	**0.75**	**0.74**	**0.73**	**0.72**	**0.71**	**0.71**	**0.70**	**0.70**	**0.69**	**0.69**
2	**2.31**	**1.60**	**1.35**	**1.21**	**1.13**	**1.04**	**0.98**	**0.94**	**0.91**	**0.89**	**0.87**	**0.86**	**0.85**	**0.84**	**0.83**	**0.82**	**0.82**	**0.81**	**0.80**	**0.80**
3	**2.53**	**1.74**	**1.46**	**1.31**	**1.22**	**1.12**	**1.06**	**1.01**	**0.98**	**0.96**	**0.94**	**0.93**	**0.92**	**0.90**	**0.89**	**0.88**	**0.88**	**0.87**	**0.86**	**0.86**
4	**2.69**	**1.84**	**1.54**	**1.38**	**1.29**	**1.18**	**1.11**	**1.06**	**1.03**	**1.00**	**0.99**	**0.97**	**0.96**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.90**
5	2.81	**1.91**	**1.60**	**1.44**	**1.34**	**1.22**	**1.15**	**1.10**	**1.07**	**1.04**	**1.02**	**1.01**	**1.00**	**0.98**	**0.97**	**0.96**	**0.95**	**0.95**	**0.94**	**0.93**
8	3.06	**2.07**	**1.72**	**1.55**	**1.44**	**1.31**	**1.24**	**1.18**	**1.14**	**1.12**	**1.10**	**1.08**	**1.07**	**1.05**	**1.04**	**1.03**	**1.02**	**1.01**	**1.00**	**1.00**
12	3.27	**2.20**	**1.83**	**1.64**	**1.53**	**1.39**	**1.31**	**1.25**	**1.21**	**1.18**	**1.16**	**1.14**	**1.13**	**1.11**	**1.10**	**1.08**	**1.08**	**1.07**	**1.06**	**1.05**
16	3.41	**2.29**	**1.91**	**1.71**	**1.59**	**1.44**	**1.36**	**1.30**	**1.25**	**1.22**	**1.20**	**1.18**	**1.17**	**1.15**	**1.14**	**1.12**	**1.12**	**1.11**	**1.10**	**1.09**
20	3.52	**2.36**	**1.96**	**1.76**	**1.63**	**1.48**	**1.40**	**1.33**	**1.29**	**1.26**	**1.23**	**1.22**	**1.20**	**1.18**	**1.17**	**1.15**	**1.15**	**1.14**	**1.13**	**1.12**
30	3.72	**2.49**	**2.06**	**1.85**	**1.72**	**1.56**	**1.47**	**1.40**	**1.35**	**1.32**	**1.29**	**1.27**	**1.26**	**1.24**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**
40	3.86	**2.57**	**2.14**	**1.91**	**1.77**	**1.61**	**1.52**	**1.44**	**1.39**	**1.36**	**1.33**	**1.31**	**1.30**	**1.27**	**1.26**	**1.24**	**1.23**	**1.23**	**1.21**	**1.20**
50	3.97	**2.64**	**2.19**	**1.96**	**1.82**	**1.65**	**1.55**	**1.48**	**1.43**	**1.39**	**1.37**	**1.34**	**1.33**	**1.30**	**1.29**	**1.27**	**1.26**	**1.25**	**1.24**	**1.23**
60	4.05	**2.69**	**2.23**	**2.00**	**1.85**	**1.68**	**1.58**	**1.51**	**1.45**	**1.42**	**1.39**	**1.37**	**1.35**	**1.33**	**1.31**	**1.30**	**1.29**	**1.28**	**1.26**	**1.25**
75	4.16	**2.76**	**2.29**	**2.04**	**1.90**	**1.72**	**1.62**	**1.54**	**1.49**	**1.45**	**1.42**	**1.40**	**1.38**	**1.36**	**1.34**	**1.32**	**1.31**	**1.30**	**1.29**	**1.28**
100	4.29	**2.84**	**2.35**	**2.10**	**1.95**	**1.77**	**1.67**	**1.58**	**1.53**	**1.49**	**1.46**	**1.44**	**1.42**	**1.39**	**1.37**	**1.36**	**1.35**	**1.34**	**1.32**	**1.31**
125	4.39	*2.91*	**2.41**	**2.15**	**1.99**	**1.81**	**1.70**	**1.62**	**1.56**	**1.52**	**1.49**	**1.47**	**1.45**	**1.42**	**1.40**	**1.39**	**1.37**	**1.37**	**1.35**	**1.34**
150	4.47	2.96	**2.45**	**2.19**	**2.03**	**1.84**	**1.73**	**1.64**	**1.59**	**1.55**	**1.52**	**1.49**	**1.47**	**1.44**	**1.42**	**1.41**	**1.40**	**1.39**	**1.37**	**1.36**
175	4.54	3.00	**2.48**	**2.22**	**2.06**	**1.86**	**1.75**	**1.67**	**1.61**	**1.57**	**1.54**	**1.51**	**1.49**	**1.46**	**1.44**	**1.43**	**1.41**	**1.41**	**1.39**	**1.38**
200	4.60	3.04	**2.51**	**2.24**	**2.08**	**1.89**	**1.77**	**1.69**	**1.63**	**1.58**	**1.55**	**1.53**	**1.51**	**1.48**	**1.46**	**1.44**	**1.43**	**1.42**	**1.40**	**1.39**

Table 19-7. κ-Multipliers for 1-of-3 Interwell Prediction Limits on Means of Order 2 (10 COC, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.64**	**1.14**	**0.96**	**0.87**	**0.81**	**0.74**	**0.70**	**0.67**	**0.65**	**0.63**	**0.62**	**0.62**	**0.61**	**0.60**	**0.59**	**0.59**	**0.58**	**0.58**	**0.57**	**0.57**
2	**2.07**	**1.40**	**1.17**	**1.05**	**0.98**	**0.90**	**0.85**	**0.81**	**0.78**	**0.77**	**0.75**	**0.74**	**0.74**	**0.72**	**0.71**	**0.71**	**0.70**	**0.70**	**0.69**	**0.69**
3	**2.34**	**1.56**	**1.29**	**1.16**	**1.08**	**0.98**	**0.93**	**0.89**	**0.86**	**0.84**	**0.83**	**0.81**	**0.81**	**0.79**	**0.78**	**0.78**	**0.77**	**0.77**	**0.76**	**0.75**
4	**2.53**	**1.67**	**1.38**	**1.24**	**1.15**	**1.04**	**0.99**	**0.94**	**0.91**	**0.89**	**0.87**	**0.86**	**0.85**	**0.84**	**0.83**	**0.82**	**0.82**	**0.81**	**0.80**	**0.80**
5	2.68	**1.76**	**1.45**	**1.29**	**1.20**	**1.09**	**1.03**	**0.98**	**0.95**	**0.93**	**0.91**	**0.90**	**0.89**	**0.88**	**0.86**	**0.86**	**0.85**	**0.85**	**0.84**	**0.83**
8	3.00	**1.94**	**1.59**	**1.42**	**1.31**	**1.19**	**1.12**	**1.07**	**1.03**	**1.01**	**0.99**	**0.98**	**0.97**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.90**
12	3.27	**2.09**	**1.71**	**1.52**	**1.40**	**1.27**	**1.20**	**1.14**	**1.10**	**1.07**	**1.05**	**1.04**	**1.03**	**1.01**	**1.00**	**0.99**	**0.98**	**0.98**	**0.96**	**0.96**
16	3.47	**2.20**	**1.80**	**1.59**	**1.47**	**1.33**	**1.25**	**1.19**	**1.15**	**1.12**	**1.10**	**1.08**	**1.07**	**1.05**	**1.04**	**1.03**	**1.02**	**1.02**	**1.00**	**1.00**
20	3.62	**2.29**	**1.86**	**1.65**	**1.52**	**1.37**	**1.29**	**1.23**	**1.19**	**1.16**	**1.13**	**1.12**	**1.10**	**1.09**	**1.07**	**1.06**	**1.05**	**1.05**	**1.04**	**1.03**
30	3.88	**2.44**	**1.98**	**1.75**	**1.61**	**1.45**	**1.36**	**1.30**	**1.25**	**1.22**	**1.20**	**1.18**	**1.16**	**1.14**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.08**
40	4.07	*2.55*	**2.06**	**1.82**	**1.68**	**1.51**	**1.42**	**1.34**	**1.30**	**1.26**	**1.24**	**1.22**	**1.21**	**1.18**	**1.17**	**1.16**	**1.15**	**1.14**	**1.13**	**1.12**
50	4.21	2.63	**2.13**	**1.88**	**1.73**	**1.55**	**1.46**	**1.38**	**1.33**	**1.30**	**1.27**	**1.25**	**1.24**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**	**1.16**	**1.15**
60	4.33	2.70	**2.18**	**1.92**	**1.77**	**1.59**	**1.49**	**1.41**	**1.36**	**1.32**	**1.30**	**1.28**	**1.26**	**1.24**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**
75	4.47	2.78	**2.24**	**1.97**	**1.81**	**1.63**	**1.53**	**1.45**	**1.39**	**1.36**	**1.33**	**1.31**	**1.29**	**1.27**	**1.25**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**
100	4.65	2.88	**2.32**	**2.04**	**1.88**	**1.68**	**1.58**	**1.49**	**1.44**	**1.40**	**1.37**	**1.35**	**1.33**	**1.31**	**1.29**	**1.28**	**1.26**	**1.26**	**1.24**	**1.23**
125	4.78	2.96	**2.38**	**2.10**	**1.92**	**1.73**	**1.61**	**1.53**	**1.47**	**1.43**	**1.40**	**1.38**	**1.36**	**1.34**	**1.32**	**1.30**	**1.29**	**1.28**	**1.27**	**1.26**
150	4.90	3.02	*2.43*	**2.14**	**1.96**	**1.76**	**1.65**	**1.56**	**1.50**	**1.46**	**1.43**	**1.41**	**1.39**	**1.36**	**1.34**	**1.33**	**1.32**	**1.31**	**1.29**	**1.28**
175	4.99	3.07	*2.47*	**2.17**	**1.99**	**1.79**	**1.67**	**1.58**	**1.52**	**1.48**	**1.45**	**1.43**	**1.41**	**1.38**	**1.36**	**1.35**	**1.33**	**1.32**	**1.31**	**1.30**
200	5.07	3.12	*2.51*	**2.20**	**2.02**	**1.81**	**1.69**	**1.60**	**1.54**	**1.50**	**1.47**	**1.44**	**1.43**	**1.40**	**1.38**	**1.36**	**1.35**	**1.34**	**1.32**	**1.31**

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Table 19-7. κ-Multipliers for 1-of-3 Interwell Prediction Limits on Means of Order 2 (10 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.07**	**1.40**	**1.17**	**1.05**	**0.98**	**0.90**	**0.85**	**0.81**	**0.78**	**0.77**	**0.75**	**0.74**	**0.74**	**0.72**	**0.71**	**0.71**	**0.70**	**0.70**	**0.69**	**0.69**
2	**2.53**	**1.67**	**1.38**	**1.24**	**1.15**	**1.04**	**0.99**	**0.94**	**0.91**	**0.89**	**0.87**	**0.86**	**0.85**	**0.84**	**0.83**	**0.82**	**0.82**	**0.81**	**0.80**	**0.80**
3	2.80	**1.83**	**1.50**	**1.34**	**1.24**	**1.13**	**1.06**	**1.01**	**0.98**	**0.96**	**0.94**	**0.93**	**0.92**	**0.90**	**0.89**	**0.88**	**0.88**	**0.87**	**0.86**	**0.86**
4	3.00	**1.94**	**1.59**	**1.42**	**1.31**	**1.19**	**1.12**	**1.07**	**1.03**	**1.01**	**0.99**	**0.98**	**0.97**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.90**
5	3.15	**2.02**	**1.66**	**1.47**	**1.36**	**1.23**	**1.16**	**1.11**	**1.07**	**1.04**	**1.03**	**1.01**	**1.00**	**0.98**	**0.97**	**0.96**	**0.95**	**0.95**	**0.94**	**0.93**
8	3.47	**2.20**	**1.80**	**1.59**	**1.47**	**1.33**	**1.25**	**1.19**	**1.15**	**1.12**	**1.10**	**1.08**	**1.07**	**1.05**	**1.04**	**1.03**	**1.02**	**1.02**	**1.00**	**1.00**
12	3.74	**2.36**	**1.91**	**1.70**	**1.56**	**1.41**	**1.32**	**1.26**	**1.21**	**1.18**	**1.16**	**1.15**	**1.13**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**	**1.06**	**1.05**
16	3.93	**2.46**	**2.00**	**1.77**	**1.63**	**1.47**	**1.38**	**1.31**	**1.26**	**1.23**	**1.21**	**1.19**	**1.17**	**1.15**	**1.14**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**
20	4.07	**2.55**	**2.06**	**1.82**	**1.68**	**1.51**	**1.42**	**1.34**	**1.30**	**1.26**	**1.24**	**1.22**	**1.21**	**1.18**	**1.17**	**1.16**	**1.15**	**1.14**	**1.13**	**1.12**
30	4.33	*2.70*	**2.18**	**1.92**	**1.77**	**1.59**	**1.49**	**1.41**	**1.36**	**1.32**	**1.30**	**1.28**	**1.26**	**1.24**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**
40	4.51	2.80	**2.26**	**1.99**	**1.83**	**1.64**	**1.54**	**1.46**	**1.40**	**1.37**	**1.34**	**1.32**	**1.30**	**1.28**	**1.26**	**1.25**	**1.24**	**1.23**	**1.21**	**1.20**
50	4.65	2.88	**2.32**	**2.04**	**1.88**	**1.68**	**1.58**	**1.49**	**1.44**	**1.40**	**1.37**	**1.35**	**1.33**	**1.31**	**1.29**	**1.28**	**1.26**	**1.26**	**1.24**	**1.23**
60	4.76	2.94	**2.37**	**2.09**	**1.92**	**1.72**	**1.61**	**1.52**	**1.47**	**1.43**	**1.40**	**1.38**	**1.36**	**1.33**	**1.31**	**1.30**	**1.29**	**1.28**	**1.26**	**1.25**
75	4.90	3.02	**2.43**	**2.14**	**1.96**	**1.76**	**1.65**	**1.56**	**1.50**	**1.46**	**1.43**	**1.41**	**1.39**	**1.36**	**1.34**	**1.33**	**1.32**	**1.31**	**1.29**	**1.28**
100	5.07	3.12	**2.51**	**2.20**	**2.02**	**1.81**	**1.69**	**1.60**	**1.54**	**1.50**	**1.47**	**1.44**	**1.43**	**1.40**	**1.38**	**1.36**	**1.35**	**1.34**	**1.32**	**1.31**
125	5.20	3.19	**2.57**	**2.26**	**2.07**	**1.85**	**1.73**	**1.64**	**1.58**	**1.53**	**1.50**	**1.47**	**1.45**	**1.43**	**1.40**	**1.39**	**1.38**	**1.37**	**1.35**	**1.34**
150	5.30	3.26	*2.61*	**2.30**	**2.11**	**1.89**	**1.76**	**1.66**	**1.60**	**1.56**	**1.52**	**1.50**	**1.48**	**1.45**	**1.43**	**1.41**	**1.40**	**1.39**	**1.37**	**1.36**
175	5.39	3.31	*2.65*	**2.33**	**2.14**	**1.91**	**1.79**	**1.69**	**1.62**	**1.58**	**1.55**	**1.52**	**1.50**	**1.47**	**1.45**	**1.43**	**1.42**	**1.41**	**1.39**	**1.38**
200	5.47	3.35	*2.69*	**2.36**	**2.16**	**1.94**	**1.81**	**1.71**	**1.64**	**1.60**	**1.56**	**1.54**	**1.52**	**1.48**	**1.46**	**1.45**	**1.43**	**1.42**	**1.40**	**1.39**

Table 19-7. κ-Multipliers for 1-of-3 Interwell Prediction Limits on Means of Order 2 (10 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.53**	**1.67**	**1.38**	**1.24**	**1.15**	**1.04**	**0.99**	**0.94**	**0.91**	**0.89**	**0.87**	**0.86**	**0.85**	**0.84**	**0.83**	**0.82**	**0.82**	**0.81**	**0.80**	**0.80**
2	3.00	**1.94**	**1.59**	**1.42**	**1.31**	**1.19**	**1.12**	**1.07**	**1.03**	**1.01**	**0.99**	**0.98**	**0.97**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.90**
3	3.27	**2.09**	**1.71**	**1.52**	**1.40**	**1.27**	**1.20**	**1.14**	**1.10**	**1.07**	**1.05**	**1.04**	**1.03**	**1.01**	**1.00**	**0.99**	**0.98**	**0.98**	**0.96**	**0.96**
4	3.47	**2.20**	**1.80**	**1.59**	**1.47**	**1.33**	**1.25**	**1.19**	**1.15**	**1.12**	**1.10**	**1.08**	**1.07**	**1.05**	**1.04**	**1.03**	**1.02**	**1.02**	**1.00**	**1.00**
5	3.62	**2.29**	**1.86**	**1.65**	**1.52**	**1.37**	**1.29**	**1.23**	**1.19**	**1.16**	**1.13**	**1.12**	**1.10**	**1.09**	**1.07**	**1.06**	**1.05**	**1.05**	**1.04**	**1.03**
8	3.93	**2.46**	**2.00**	**1.77**	**1.63**	**1.47**	**1.38**	**1.31**	**1.26**	**1.23**	**1.21**	**1.19**	**1.17**	**1.15**	**1.14**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**
12	4.19	**2.61**	**2.11**	**1.87**	**1.72**	**1.54**	**1.45**	**1.37**	**1.32**	**1.29**	**1.27**	**1.25**	**1.23**	**1.21**	**1.19**	**1.18**	**1.17**	**1.16**	**1.15**	**1.14**
16	4.37	**2.72**	**2.20**	**1.94**	**1.78**	**1.60**	**1.50**	**1.42**	**1.37**	**1.33**	**1.31**	**1.29**	**1.27**	**1.25**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**
20	4.51	**2.80**	**2.26**	**1.99**	**1.83**	**1.64**	**1.54**	**1.46**	**1.40**	**1.37**	**1.34**	**1.32**	**1.30**	**1.28**	**1.26**	**1.25**	**1.24**	**1.23**	**1.21**	**1.20**
30	4.76	2.94	**2.37**	**2.09**	**1.92**	**1.72**	**1.61**	**1.52**	**1.47**	**1.43**	**1.40**	**1.38**	**1.36**	**1.33**	**1.31**	**1.30**	**1.29**	**1.28**	**1.26**	**1.25**
40	4.93	3.04	**2.45**	**2.15**	**1.98**	**1.77**	**1.66**	**1.57**	**1.51**	**1.47**	**1.44**	**1.41**	**1.40**	**1.37**	**1.35**	**1.33**	**1.32**	**1.31**	**1.30**	**1.29**
50	5.07	3.12	**2.51**	**2.20**	**2.02**	**1.81**	**1.69**	**1.60**	**1.54**	**1.50**	**1.47**	**1.44**	**1.43**	**1.40**	**1.38**	**1.36**	**1.35**	**1.34**	**1.32**	**1.31**
60	5.17	3.18	**2.55**	**2.25**	**2.06**	**1.85**	**1.72**	**1.63**	**1.57**	**1.53**	**1.49**	**1.47**	**1.45**	**1.42**	**1.40**	**1.38**	**1.37**	**1.36**	**1.35**	**1.33**
75	5.30	3.26	**2.61**	**2.30**	**2.11**	**1.89**	**1.76**	**1.66**	**1.60**	**1.56**	**1.52**	**1.50**	**1.48**	**1.45**	**1.43**	**1.41**	**1.40**	**1.39**	**1.37**	**1.36**
100	5.47	3.35	**2.69**	**2.36**	**2.16**	**1.94**	**1.81**	**1.71**	**1.64**	**1.60**	**1.56**	**1.54**	**1.52**	**1.48**	**1.46**	**1.45**	**1.43**	**1.42**	**1.40**	**1.39**
125	5.60	3.42	**2.74**	**2.41**	**2.21**	**1.98**	**1.84**	**1.74**	**1.68**	**1.63**	**1.59**	**1.57**	**1.54**	**1.51**	**1.49**	**1.47**	**1.46**	**1.45**	**1.43**	**1.42**
150	5.70	3.48	**2.79**	**2.45**	**2.25**	**2.01**	**1.87**	**1.77**	**1.70**	**1.65**	**1.62**	**1.59**	**1.57**	**1.53**	**1.51**	**1.49**	**1.48**	**1.47**	**1.45**	**1.44**
175	5.78	3.53	**2.83**	**2.48**	**2.28**	**2.04**	**1.90**	**1.79**	**1.72**	**1.67**	**1.64**	**1.61**	**1.59**	**1.55**	**1.53**	**1.51**	**1.50**	**1.49**	**1.47**	**1.45**
200	5.86	3.57	*2.86*	**2.51**	**2.30**	**2.06**	**1.92**	**1.81**	**1.74**	**1.69**	**1.66**	**1.63**	**1.60**	**1.57**	**1.55**	**1.53**	**1.51**	**1.50**	**1.48**	**1.47**

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Table 19-7. κ-Multipliers for 1-of-3 Interwell Prediction Limits on Means of Order 2 (20 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	2.16	1.43	1.19	1.06	0.99	0.90	0.85	0.81	0.78	0.77	0.75	0.74	0.74	0.72	0.71	0.71	0.70	0.70	0.69	0.69
2	2.69	1.72	1.40	1.25	1.16	1.05	0.99	0.94	0.91	0.89	0.88	0.86	0.85	0.84	0.83	0.82	0.82	0.81	0.80	0.80
3	3.02	1.89	1.53	1.36	1.25	1.14	1.07	1.02	0.98	0.96	0.94	0.93	0.92	0.90	0.89	0.89	0.88	0.87	0.86	0.86
4	3.26	2.01	1.62	1.44	1.32	1.20	1.12	1.07	1.03	1.01	0.99	0.98	0.97	0.95	0.94	0.93	0.92	0.92	0.91	0.90
5	3.45	2.11	1.70	1.50	1.38	1.24	1.17	1.11	1.07	1.05	1.03	1.01	1.00	0.98	0.97	0.96	0.95	0.95	0.94	0.93
8	3.84	2.31	1.85	1.62	1.49	1.34	1.26	1.19	1.15	1.12	1.10	1.09	1.07	1.05	1.04	1.03	1.02	1.02	1.00	1.00
12	4.19	*2.49*	1.98	1.73	1.59	1.42	1.33	1.26	1.22	1.19	1.16	1.15	1.13	1.11	1.10	1.09	1.08	1.07	1.06	1.05
16	4.43	*2.61*	2.07	1.81	1.65	1.48	1.38	1.31	1.26	1.23	1.21	1.19	1.17	1.15	1.14	1.13	1.12	1.11	1.10	1.09
20	4.62	2.71	2.14	1.87	1.71	1.53	1.43	1.35	1.30	1.27	1.24	1.22	1.21	1.18	1.17	1.16	1.15	1.14	1.13	1.12
30	4.95	2.88	2.27	1.97	1.80	1.61	1.50	1.42	1.36	1.33	1.30	1.28	1.26	1.24	1.22	1.21	1.20	1.19	1.18	1.17
40	5.19	3.00	2.36	2.05	1.87	1.66	1.55	1.47	1.41	1.37	1.34	1.32	1.30	1.28	1.26	1.25	1.24	1.23	1.21	1.20
50	5.37	3.10	*2.43*	2.11	1.92	1.71	1.59	1.50	1.44	1.40	1.38	1.35	1.34	1.31	1.29	1.28	1.27	1.26	1.24	1.23
60	5.51	3.17	*2.48*	2.16	1.96	1.74	1.62	1.53	1.47	1.43	1.40	1.38	1.36	1.33	1.31	1.30	1.29	1.28	1.26	1.25
75	5.69	3.26	*2.55*	2.21	2.01	1.79	1.66	1.57	1.51	1.46	1.43	1.41	1.39	1.36	1.34	1.33	1.32	1.31	1.29	1.28
100	5.91	3.38	*2.64*	2.29	2.08	1.84	1.71	1.61	1.55	1.51	1.47	1.45	1.43	1.40	1.38	1.36	1.35	1.34	1.32	1.31
125	6.08	3.47	2.71	2.34	2.13	1.89	1.75	1.65	1.58	1.54	1.50	1.48	1.46	1.43	1.41	1.39	1.38	1.37	1.35	1.34
150	6.22	3.54	2.76	2.39	2.17	1.92	1.78	1.68	1.61	1.56	1.53	1.50	1.48	1.45	1.43	1.41	1.40	1.39	1.37	1.36
175	6.34	3.60	2.81	*2.43*	2.20	1.95	1.81	1.70	1.63	1.59	1.55	1.52	1.50	1.47	1.45	1.43	1.42	1.41	1.39	1.38
200	6.44	3.66	2.85	*2.46*	2.23	1.98	1.83	1.72	1.65	1.61	1.57	1.54	1.52	1.49	1.46	1.45	1.43	1.42	1.41	1.39

Table 19-7. κ-Multipliers for 1-of-3 Interwell Prediction Limits on Means of Order 2 (20 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	2.69	1.72	1.40	1.25	1.16	1.05	0.99	0.94	0.91	0.89	0.88	0.86	0.85	0.84	0.83	0.82	0.82	0.81	0.80	0.80
2	3.26	2.01	1.62	1.44	1.32	1.20	1.12	1.07	1.03	1.01	0.99	0.98	0.97	0.95	0.94	0.93	0.92	0.92	0.91	0.90
3	3.60	2.19	1.75	1.55	1.42	1.28	1.20	1.14	1.10	1.08	1.06	1.04	1.03	1.01	1.00	0.99	0.98	0.98	0.96	0.96
4	3.84	2.31	1.85	1.62	1.49	1.34	1.26	1.19	1.15	1.12	1.10	1.09	1.07	1.05	1.04	1.03	1.02	1.02	1.00	1.00
5	4.03	2.41	1.92	1.68	1.54	1.39	1.30	1.23	1.19	1.16	1.14	1.12	1.11	1.09	1.07	1.06	1.05	1.05	1.04	1.03
8	4.43	2.61	2.07	1.81	1.65	1.48	1.38	1.31	1.26	1.23	1.21	1.19	1.17	1.15	1.14	1.13	1.12	1.11	1.10	1.09
12	4.77	2.79	2.20	1.92	1.75	1.56	1.46	1.38	1.33	1.29	1.27	1.25	1.23	1.21	1.19	1.18	1.17	1.16	1.15	1.14
16	5.00	2.91	2.29	1.99	1.82	1.62	1.51	1.43	1.38	1.34	1.31	1.29	1.27	1.25	1.23	1.22	1.21	1.20	1.19	1.18
20	5.19	3.00	2.36	2.05	1.87	1.66	1.55	1.47	1.41	1.37	1.34	1.32	1.30	1.28	1.26	1.25	1.24	1.23	1.21	1.20
30	5.51	3.17	2.48	2.16	1.96	1.74	1.62	1.53	1.47	1.43	1.40	1.38	1.36	1.33	1.31	1.30	1.29	1.28	1.26	1.25
40	5.74	3.29	2.57	2.23	2.03	1.80	1.67	1.58	1.52	1.47	1.44	1.42	1.40	1.37	1.35	1.34	1.32	1.31	1.30	1.29
50	5.91	3.38	*2.64*	2.29	2.08	1.84	1.71	1.61	1.55	1.51	1.47	1.45	1.43	1.40	1.38	1.36	1.35	1.34	1.32	1.31
60	6.05	3.45	*2.69*	2.33	2.12	1.88	1.74	1.64	1.58	1.53	1.50	1.47	1.45	1.42	1.40	1.39	1.37	1.36	1.35	1.33
75	6.22	3.54	*2.76*	2.39	2.17	1.92	1.78	1.68	1.61	1.56	1.53	1.50	1.48	1.45	1.43	1.41	1.40	1.39	1.37	1.36
100	6.44	3.66	2.85	2.46	2.23	1.98	1.83	1.72	1.65	1.61	1.57	1.54	1.52	1.49	1.46	1.45	1.43	1.42	1.41	1.39
125	6.61	3.74	2.91	2.51	2.28	2.02	1.87	1.76	1.69	1.64	1.60	1.57	1.55	1.51	1.49	1.47	1.46	1.45	1.43	1.42
150	6.74	3.81	2.96	2.56	2.32	2.05	1.90	1.79	1.71	1.66	1.62	1.59	1.57	1.54	1.51	1.50	1.48	1.47	1.45	1.44
175	6.85	3.87	3.01	2.60	2.35	2.08	1.93	1.81	1.74	1.68	1.64	1.62	1.59	1.56	1.53	1.51	1.50	1.49	1.47	1.45
200	6.95	3.92	3.04	*2.63*	2.38	2.10	1.95	1.83	1.76	1.70	1.66	1.63	1.61	1.57	1.55	1.53	1.51	1.50	1.48	1.47

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Table 19-7. κ-Multipliers for 1-of-3 Interwell Prediction Limits on Means of Order 2 (20 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.26	**2.01**	**1.62**	**1.44**	**1.32**	**1.20**	**1.12**	**1.07**	**1.03**	**1.01**	**0.99**	**0.98**	**0.97**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.90**
2	3.84	**2.31**	**1.85**	**1.62**	**1.49**	**1.34**	**1.26**	**1.19**	**1.15**	**1.12**	**1.10**	**1.09**	**1.07**	**1.05**	**1.04**	**1.03**	**1.02**	**1.02**	**1.00**	**1.00**
3	4.19	**2.49**	**1.98**	**1.73**	**1.59**	**1.42**	**1.33**	**1.26**	**1.22**	**1.19**	**1.16**	**1.15**	**1.13**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**	**1.06**	**1.05**
4	4.43	**2.61**	**2.07**	**1.81**	**1.65**	**1.48**	**1.38**	**1.31**	**1.26**	**1.23**	**1.21**	**1.19**	**1.17**	**1.15**	**1.14**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**
5	4.62	**2.71**	**2.14**	**1.87**	**1.71**	**1.53**	**1.43**	**1.35**	**1.30**	**1.27**	**1.24**	**1.22**	**1.21**	**1.18**	**1.17**	**1.16**	**1.15**	**1.14**	**1.13**	**1.12**
8	5.00	*2.91*	**2.29**	**1.99**	**1.82**	**1.62**	**1.51**	**1.43**	**1.38**	**1.34**	**1.31**	**1.29**	**1.27**	**1.25**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**
12	5.33	3.08	**2.42**	**2.10**	**1.91**	**1.70**	**1.58**	**1.50**	**1.44**	**1.40**	**1.37**	**1.35**	**1.33**	**1.30**	**1.28**	**1.27**	**1.26**	**1.25**	**1.24**	**1.23**
16	5.56	3.20	**2.50**	**2.17**	**1.98**	**1.76**	**1.63**	**1.54**	**1.48**	**1.44**	**1.41**	**1.39**	**1.37**	**1.34**	**1.32**	**1.31**	**1.30**	**1.29**	**1.27**	**1.26**
20	5.74	3.29	**2.57**	**2.23**	**2.03**	**1.80**	**1.67**	**1.58**	**1.52**	**1.47**	**1.44**	**1.42**	**1.40**	**1.37**	**1.35**	**1.34**	**1.32**	**1.31**	**1.30**	**1.29**
30	6.05	3.45	**2.69**	**2.33**	**2.12**	**1.88**	**1.74**	**1.64**	**1.58**	**1.53**	**1.50**	**1.47**	**1.45**	**1.42**	**1.40**	**1.39**	**1.37**	**1.36**	**1.35**	**1.33**
40	6.27	3.57	**2.78**	**2.40**	**2.18**	**1.93**	**1.79**	**1.69**	**1.62**	**1.57**	**1.54**	**1.51**	**1.49**	**1.46**	**1.44**	**1.42**	**1.41**	**1.40**	**1.38**	**1.37**
50	6.44	3.66	*2.85*	**2.46**	**2.23**	**1.98**	**1.83**	**1.72**	**1.65**	**1.61**	**1.57**	**1.54**	**1.52**	**1.49**	**1.46**	**1.45**	**1.43**	**1.42**	**1.41**	**1.39**
60	6.57	3.73	*2.90*	**2.50**	**2.27**	**2.01**	**1.86**	**1.75**	**1.68**	**1.63**	**1.59**	**1.57**	**1.54**	**1.51**	**1.49**	**1.47**	**1.46**	**1.44**	**1.43**	**1.41**
75	6.74	3.81	*2.96*	**2.56**	**2.32**	**2.05**	**1.90**	**1.79**	**1.71**	**1.66**	**1.62**	**1.59**	**1.57**	**1.54**	**1.51**	**1.50**	**1.48**	**1.47**	**1.45**	**1.44**
100	6.95	3.92	3.04	**2.63**	**2.38**	**2.10**	**1.95**	**1.83**	**1.76**	**1.70**	**1.66**	**1.63**	**1.61**	**1.57**	**1.55**	**1.53**	**1.51**	**1.50**	**1.48**	**1.47**
125	7.11	4.01	3.11	**2.68**	**2.43**	**2.15**	**1.99**	**1.87**	**1.79**	**1.73**	**1.69**	**1.66**	**1.64**	**1.60**	**1.57**	**1.55**	**1.54**	**1.53**	**1.51**	**1.49**
150	7.24	4.07	3.16	**2.72**	**2.47**	**2.18**	**2.02**	**1.89**	**1.81**	**1.76**	**1.72**	**1.68**	**1.66**	**1.62**	**1.60**	**1.58**	**1.56**	**1.55**	**1.53**	**1.51**
175	7.34	4.13	3.20	**2.76**	**2.50**	**2.21**	**2.04**	**1.92**	**1.84**	**1.78**	**1.74**	**1.70**	**1.68**	**1.64**	**1.61**	**1.59**	**1.58**	**1.57**	**1.54**	**1.53**
200	7.44	4.18	3.24	**2.79**	**2.53**	**2.23**	**2.06**	**1.94**	**1.85**	**1.80**	**1.75**	**1.72**	**1.70**	**1.66**	**1.63**	**1.61**	**1.59**	**1.58**	**1.56**	**1.54**

Table 19-7. κ-Multipliers for 1-of-3 Interwell Prediction Limits on Means of Order 2 (40 COC, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	2.81	**1.74**	**1.42**	**1.26**	**1.16**	**1.05**	**0.99**	**0.94**	**0.91**	**0.89**	**0.88**	**0.86**	**0.85**	**0.84**	**0.83**	**0.82**	**0.82**	**0.81**	**0.80**	**0.80**
2	3.46	**2.06**	**1.65**	**1.45**	**1.33**	**1.20**	**1.13**	**1.07**	**1.04**	**1.01**	**0.99**	**0.98**	**0.97**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.90**
3	3.87	**2.25**	**1.78**	**1.56**	**1.43**	**1.28**	**1.20**	**1.14**	**1.10**	**1.08**	**1.06**	**1.04**	**1.03**	**1.01**	**1.00**	**0.99**	**0.98**	**0.98**	**0.97**	**0.96**
4	4.17	**2.39**	**1.88**	**1.64**	**1.50**	**1.35**	**1.26**	**1.19**	**1.15**	**1.12**	**1.10**	**1.09**	**1.07**	**1.05**	**1.04**	**1.03**	**1.02**	**1.02**	**1.01**	**1.00**
5	4.40	*2.50*	**1.96**	**1.70**	**1.56**	**1.39**	**1.30**	**1.23**	**1.19**	**1.16**	**1.14**	**1.12**	**1.11**	**1.09**	**1.07**	**1.06**	**1.05**	**1.05**	**1.04**	**1.03**
8	4.90	2.73	**2.12**	**1.84**	**1.67**	**1.49**	**1.39**	**1.31**	**1.27**	**1.23**	**1.21**	**1.19**	**1.18**	**1.15**	**1.14**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**
12	5.33	2.93	**2.26**	**1.95**	**1.77**	**1.57**	**1.47**	**1.38**	**1.33**	**1.30**	**1.27**	**1.25**	**1.23**	**1.21**	**1.19**	**1.18**	**1.17**	**1.16**	**1.15**	**1.14**
16	5.63	3.07	**2.36**	**2.03**	**1.84**	**1.63**	**1.52**	**1.43**	**1.38**	**1.34**	**1.31**	**1.29**	**1.27**	**1.25**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**
20	5.86	3.18	*2.44*	**2.09**	**1.90**	**1.68**	**1.56**	**1.47**	**1.41**	**1.37**	**1.35**	**1.32**	**1.31**	**1.28**	**1.26**	**1.25**	**1.24**	**1.23**	**1.21**	**1.20**
30	6.29	3.38	*2.58*	**2.21**	**2.00**	**1.76**	**1.63**	**1.54**	**1.48**	**1.43**	**1.40**	**1.38**	**1.36**	**1.33**	**1.31**	**1.30**	**1.29**	**1.28**	**1.26**	**1.25**
40	6.58	3.51	2.68	**2.29**	**2.07**	**1.82**	**1.69**	**1.59**	**1.52**	**1.48**	**1.44**	**1.42**	**1.40**	**1.37**	**1.35**	**1.34**	**1.32**	**1.32**	**1.30**	**1.29**
50	6.81	3.62	2.75	**2.35**	**2.12**	**1.86**	**1.73**	**1.62**	**1.56**	**1.51**	**1.48**	**1.45**	**1.43**	**1.40**	**1.38**	**1.36**	**1.35**	**1.34**	**1.33**	**1.31**
60	6.99	3.71	2.81	**2.40**	**2.16**	**1.90**	**1.76**	**1.65**	**1.58**	**1.54**	**1.50**	**1.48**	**1.45**	**1.42**	**1.40**	**1.39**	**1.37**	**1.36**	**1.35**	**1.34**
75	7.21	3.81	2.89	*2.46*	**2.22**	**1.95**	**1.80**	**1.69**	**1.62**	**1.57**	**1.53**	**1.51**	**1.48**	**1.45**	**1.43**	**1.41**	**1.40**	**1.39**	**1.37**	**1.36**
100	7.49	3.95	2.98	*2.54*	**2.29**	**2.00**	**1.85**	**1.73**	**1.66**	**1.61**	**1.57**	**1.54**	**1.52**	**1.49**	**1.47**	**1.45**	**1.43**	**1.42**	**1.41**	**1.39**
125	7.71	4.05	3.06	*2.60*	**2.34**	**2.05**	**1.89**	**1.77**	**1.69**	**1.64**	**1.60**	**1.57**	**1.55**	**1.52**	**1.49**	**1.47**	**1.46**	**1.45**	**1.43**	**1.42**
150	7.89	4.13	3.12	*2.65*	**2.38**	**2.08**	**1.92**	**1.80**	**1.72**	**1.67**	**1.63**	**1.60**	**1.57**	**1.54**	**1.51**	**1.50**	**1.48**	**1.47**	**1.45**	**1.44**
175	8.03	4.20	3.17	*2.69*	*2.42*	**2.11**	**1.95**	**1.82**	**1.74**	**1.69**	**1.65**	**1.62**	**1.59**	**1.56**	**1.53**	**1.51**	**1.50**	**1.49**	**1.47**	**1.45**
200	8.16	4.26	3.21	2.73	*2.45*	**2.14**	**1.97**	**1.84**	**1.76**	**1.71**	**1.67**	**1.64**	**1.61**	**1.57**	**1.55**	**1.53**	**1.52**	**1.50**	**1.48**	**1.47**

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Table 19-7. κ-Multipliers for 1-of-3 Interwell Prediction Limits on Means of Order 2 (40 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.46	2.06	1.65	1.45	1.33	1.20	1.13	1.07	1.04	1.01	0.99	0.98	0.97	0.95	0.94	0.93	0.92	0.92	0.91	0.90
2	4.17	2.39	1.88	1.64	1.50	1.35	1.26	1.19	1.15	1.12	1.10	1.09	1.07	1.05	1.04	1.03	1.02	1.02	1.01	1.00
3	4.59	2.59	2.02	1.76	1.60	1.43	1.34	1.27	1.22	1.19	1.17	1.15	1.13	1.11	1.10	1.09	1.08	1.07	1.06	1.05
4	4.90	*2.73*	2.12	1.84	1.67	1.49	1.39	1.31	1.27	1.23	1.21	1.19	1.18	1.15	1.14	1.13	1.12	1.11	1.10	1.09
5	5.13	2.84	2.20	1.90	1.73	1.54	1.43	1.35	1.30	1.27	1.24	1.22	1.21	1.18	1.17	1.16	1.15	1.14	1.13	1.12
8	5.63	3.07	2.36	2.03	1.84	1.63	1.52	1.43	1.38	1.34	1.31	1.29	1.27	1.25	1.23	1.22	1.21	1.20	1.19	1.18
12	6.06	3.27	2.50	2.15	1.94	1.72	1.59	1.50	1.44	1.40	1.37	1.35	1.33	1.30	1.29	1.27	1.26	1.25	1.24	1.23
16	6.35	3.41	2.60	2.23	2.01	1.77	1.65	1.55	1.49	1.44	1.41	1.39	1.37	1.34	1.32	1.31	1.30	1.29	1.27	1.26
20	6.58	3.51	*2.68*	2.29	2.07	1.82	1.69	1.59	1.52	1.48	1.44	1.42	1.40	1.37	1.35	1.34	1.32	1.32	1.30	1.29
30	6.99	3.71	*2.81*	2.40	2.16	1.90	1.76	1.65	1.58	1.54	1.50	1.48	1.45	1.42	1.40	1.39	1.37	1.36	1.35	1.34
40	7.28	3.84	2.91	2.48	2.23	1.96	1.81	1.70	1.63	1.58	1.54	1.51	1.49	1.46	1.44	1.42	1.41	1.40	1.38	1.37
50	7.49	3.95	2.98	2.54	2.29	2.00	1.85	1.73	1.66	1.61	1.57	1.54	1.52	1.49	1.47	1.45	1.43	1.42	1.41	1.39
60	7.67	4.03	3.04	2.59	2.33	2.04	1.88	1.76	1.69	1.64	1.60	1.57	1.55	1.51	1.49	1.47	1.46	1.45	1.43	1.41
75	7.89	4.13	3.12	*2.65*	2.38	2.08	1.92	1.80	1.72	1.67	1.63	1.60	1.57	1.54	1.51	1.50	1.48	1.47	1.45	1.44
100	8.16	4.26	3.21	*2.73*	2.45	2.14	1.97	1.84	1.76	1.71	1.67	1.64	1.61	1.57	1.55	1.53	1.52	1.50	1.48	1.47
125	8.37	4.36	3.28	*2.79*	2.50	2.18	2.01	1.88	1.80	1.74	1.70	1.66	1.64	1.60	1.58	1.56	1.54	1.53	1.51	1.49
150	8.53	4.44	3.34	*2.83*	2.54	2.22	2.04	1.91	1.82	1.76	1.72	1.69	1.66	1.62	1.60	1.58	1.56	1.55	1.53	1.51
175	8.68	4.51	3.39	*2.87*	2.58	2.25	2.07	1.93	1.85	1.79	1.74	1.71	1.68	1.64	1.61	1.59	1.58	1.57	1.54	1.53
200	8.80	4.57	3.43	2.91	*2.61*	2.27	2.09	1.95	1.87	1.80	1.76	1.73	1.70	1.66	1.63	1.61	1.59	1.58	1.56	1.54

Table 19-7. κ-Multipliers for 1-of-3 Interwell Prediction Limits on Means of Order 2 (40 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	4.17	2.39	1.88	1.64	1.50	1.35	1.26	1.19	1.15	1.12	1.10	1.09	1.07	1.05	1.04	1.03	1.02	1.02	1.01	1.00
2	4.90	2.73	2.12	1.84	1.67	1.49	1.39	1.31	1.27	1.23	1.21	1.19	1.18	1.15	1.14	1.13	1.12	1.11	1.10	1.09
3	5.33	*2.93*	2.26	1.95	1.77	1.57	1.47	1.38	1.33	1.30	1.27	1.25	1.23	1.21	1.19	1.18	1.17	1.16	1.15	1.14
4	5.63	3.07	2.36	2.03	1.84	1.63	1.52	1.43	1.38	1.34	1.31	1.29	1.27	1.25	1.23	1.22	1.21	1.20	1.19	1.18
5	5.86	3.18	2.44	2.09	1.90	1.68	1.56	1.47	1.41	1.37	1.35	1.32	1.31	1.28	1.26	1.25	1.24	1.23	1.21	1.20
8	6.35	3.41	2.60	2.23	2.01	1.77	1.65	1.55	1.49	1.44	1.41	1.39	1.37	1.34	1.32	1.31	1.30	1.29	1.27	1.26
12	6.77	3.60	2.74	2.34	2.11	1.86	1.72	1.61	1.55	1.50	1.47	1.44	1.42	1.40	1.37	1.36	1.35	1.34	1.32	1.31
16	7.06	3.74	*2.83*	2.42	2.18	1.91	1.77	1.66	1.59	1.55	1.51	1.48	1.46	1.43	1.41	1.39	1.38	1.37	1.35	1.34
20	7.28	3.84	*2.91*	2.48	2.23	1.96	1.81	1.70	1.63	1.58	1.54	1.51	1.49	1.46	1.44	1.42	1.41	1.40	1.38	1.37
30	7.67	4.03	3.04	2.59	2.33	2.04	1.88	1.76	1.69	1.64	1.60	1.57	1.55	1.51	1.49	1.47	1.46	1.45	1.43	1.41
40	7.95	4.16	3.14	2.67	2.40	2.10	1.93	1.81	1.73	1.68	1.64	1.61	1.58	1.55	1.52	1.50	1.49	1.48	1.46	1.45
50	8.16	4.26	3.21	2.73	2.45	2.14	1.97	1.84	1.76	1.71	1.67	1.64	1.61	1.57	1.55	1.53	1.52	1.50	1.48	1.47
60	8.33	4.34	3.27	2.77	2.49	2.18	2.00	1.87	1.79	1.73	1.69	1.66	1.63	1.60	1.57	1.55	1.54	1.52	1.50	1.49
75	8.53	4.44	3.34	*2.83*	2.54	2.22	2.04	1.91	1.82	1.76	1.72	1.69	1.66	1.62	1.60	1.58	1.56	1.55	1.53	1.51
100	8.80	4.57	3.43	*2.91*	2.61	2.27	2.09	1.95	1.87	1.80	1.76	1.73	1.70	1.66	1.63	1.61	1.59	1.58	1.56	1.54
125	9.00	4.67	3.50	*2.97*	2.66	2.32	2.13	1.99	1.90	1.84	1.79	1.75	1.73	1.69	1.66	1.64	1.62	1.61	1.58	1.57
150	9.16	4.74	3.56	*3.01*	2.70	2.35	2.16	2.02	1.92	1.86	1.81	1.78	1.75	1.71	1.68	1.66	1.64	1.63	1.60	1.59
175	9.29	4.81	3.60	*3.05*	2.73	2.38	2.19	2.04	1.95	1.88	1.83	1.80	1.77	1.73	1.69	1.67	1.66	1.64	1.62	1.60
200	9.41	4.86	3.64	*3.08*	2.76	2.40	2.21	2.06	1.97	1.90	1.85	1.81	1.78	1.74	1.71	1.69	1.67	1.66	1.63	1.62

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Table 19-8. κ-Multipliers for 1-of-1 Interwell Prediction Limits on Means of Order 3 (1 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	1.25	1.04	0.96	0.91	0.88	0.84	0.82	0.81	0.79	0.79	0.78	0.78	0.77	0.77	0.76	0.76	0.76	0.76	0.75	0.75
2	1.65	1.35	1.24	1.17	1.13	1.08	1.05	1.03	1.01	1.00	1.00	0.99	0.99	0.98	0.97	0.97	0.97	0.96	0.96	0.96
3	1.87	1.53	1.39	1.32	1.27	1.21	1.18	1.15	1.13	1.12	1.11	1.11	1.10	1.09	1.09	1.08	1.08	1.07	1.07	1.07
4	2.03	1.65	1.50	1.42	1.36	1.30	1.26	1.23	1.22	1.20	1.19	1.18	1.18	1.17	1.16	1.16	1.15	1.15	1.14	1.14
5	2.16	1.74	1.58	1.49	1.43	1.37	1.33	1.30	1.28	1.26	1.25	1.24	1.24	1.23	1.22	1.21	1.21	1.21	1.20	1.20
8	2.41	1.93	1.75	1.65	1.58	1.50	1.46	1.42	1.40	1.38	1.37	1.36	1.35	1.34	1.33	1.33	1.32	1.32	1.31	1.31
12	2.62	2.09	1.89	1.77	1.70	1.62	1.57	1.53	1.50	1.48	1.47	1.46	1.45	1.44	1.43	1.42	1.42	1.41	1.40	1.40
16	2.76	2.20	1.98	1.86	1.79	1.70	1.64	1.60	1.57	1.55	1.54	1.53	1.52	1.50	1.49	1.48	1.48	1.47	1.47	1.46
20	2.87	2.28	2.05	1.93	1.85	1.76	1.70	1.65	1.63	1.60	1.59	1.58	1.57	1.55	1.54	1.53	1.53	1.52	1.51	1.51
30	3.06	2.43	2.18	2.05	1.96	1.86	1.80	1.75	1.72	1.70	1.68	1.67	1.65	1.64	1.63	1.62	1.61	1.61	1.60	1.59
40	3.19	2.53	2.27	2.13	2.04	1.93	1.87	1.82	1.78	1.76	1.74	1.73	1.72	1.70	1.69	1.68	1.67	1.66	1.65	1.65
50	3.29	2.61	2.34	2.19	2.10	1.99	1.92	1.87	1.83	1.81	1.79	1.77	1.76	1.74	1.73	1.72	1.71	1.71	1.70	1.69
60	3.38	2.67	2.39	2.24	2.15	2.03	1.96	1.91	1.87	1.85	1.83	1.81	1.80	1.78	1.77	1.76	1.75	1.74	1.73	1.72
75	3.47	2.74	2.46	2.30	2.21	2.09	2.02	1.96	1.92	1.89	1.87	1.86	1.84	1.83	1.81	1.80	1.79	1.79	1.77	1.77
100	3.59	2.83	2.54	2.38	2.28	2.15	2.08	2.02	1.98	1.95	1.93	1.92	1.90	1.88	1.87	1.86	1.85	1.84	1.83	1.82
125	3.69	2.90	2.60	2.44	2.33	2.21	2.13	2.07	2.03	2.00	1.98	1.96	1.94	1.92	1.91	1.90	1.89	1.88	1.87	1.86
150	3.76	2.96	2.65	2.48	2.38	2.25	2.17	2.11	2.07	2.04	2.01	1.99	1.98	1.96	1.94	1.93	1.92	1.91	1.90	1.89
175	3.82	3.01	2.69	2.52	2.41	2.28	2.20	2.14	2.10	2.07	2.04	2.02	2.01	1.99	1.97	1.96	1.95	1.94	1.93	1.92
200	3.88	3.05	2.73	2.56	2.45	2.31	2.23	2.17	2.12	2.09	2.07	2.05	2.03	2.01	1.99	1.98	1.97	1.96	1.95	1.94

Table 19-8. κ-Multipliers for 1-of-1 Interwell Prediction Limits on Means of Order 3 (1 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	1.65	1.35	1.24	1.17	1.13	1.08	1.05	1.03	1.01	1.00	1.00	0.99	0.99	0.98	0.97	0.97	0.97	0.96	0.96	0.96
2	2.03	1.65	1.50	1.42	1.36	1.30	1.26	1.23	1.22	1.20	1.19	1.18	1.18	1.17	1.16	1.16	1.15	1.15	1.14	1.14
3	2.25	1.82	1.65	1.55	1.49	1.42	1.38	1.35	1.32	1.31	1.30	1.29	1.28	1.27	1.26	1.26	1.25	1.25	1.24	1.24
4	2.41	1.93	1.75	1.65	1.58	1.50	1.46	1.42	1.40	1.38	1.37	1.36	1.35	1.34	1.33	1.33	1.32	1.32	1.31	1.31
5	2.52	2.02	1.82	1.72	1.65	1.57	1.52	1.48	1.46	1.44	1.43	1.42	1.41	1.39	1.39	1.38	1.37	1.37	1.36	1.36
8	2.76	2.20	1.98	1.86	1.79	1.70	1.64	1.60	1.57	1.55	1.54	1.53	1.52	1.50	1.49	1.48	1.48	1.47	1.47	1.46
12	2.96	2.35	2.11	1.98	1.90	1.80	1.74	1.70	1.67	1.65	1.63	1.62	1.61	1.59	1.58	1.57	1.57	1.56	1.55	1.54
16	3.09	2.45	2.20	2.07	1.98	1.88	1.82	1.77	1.73	1.71	1.69	1.68	1.67	1.65	1.64	1.63	1.62	1.62	1.61	1.60
20	3.19	2.53	2.27	2.13	2.04	1.93	1.87	1.82	1.78	1.76	1.74	1.73	1.72	1.70	1.69	1.68	1.67	1.66	1.65	1.65
30	3.38	2.67	2.39	2.24	2.15	2.03	1.96	1.91	1.87	1.85	1.83	1.81	1.80	1.78	1.77	1.76	1.75	1.74	1.73	1.72
40	3.50	2.76	2.48	2.32	2.22	2.10	2.03	1.97	1.94	1.91	1.89	1.87	1.86	1.84	1.82	1.81	1.80	1.80	1.79	1.78
50	3.59	2.83	2.54	2.38	2.28	2.15	2.08	2.02	1.98	1.95	1.93	1.92	1.90	1.88	1.87	1.86	1.85	1.84	1.83	1.82
60	3.67	2.89	2.59	2.43	2.32	2.20	2.12	2.06	2.02	1.99	1.97	1.95	1.94	1.92	1.90	1.89	1.88	1.87	1.86	1.85
75	3.76	2.96	2.65	2.48	2.38	2.25	2.17	2.11	2.07	2.04	2.01	1.99	1.98	1.96	1.94	1.93	1.92	1.91	1.90	1.89
100	3.88	3.05	2.73	2.56	2.45	2.31	2.23	2.17	2.12	2.09	2.07	2.05	2.03	2.01	1.99	1.98	1.97	1.96	1.95	1.94
125	3.96	3.12	2.79	2.61	2.50	2.36	2.28	2.21	2.17	2.13	2.11	2.09	2.08	2.05	2.03	2.02	2.01	2.00	1.99	1.98
150	4.03	3.17	2.84	2.66	2.54	2.40	2.32	2.25	2.20	2.17	2.14	2.12	2.11	2.08	2.07	2.05	2.04	2.03	2.02	2.01
175	4.09	3.22	2.88	2.69	2.58	2.43	2.35	2.28	2.23	2.20	2.17	2.15	2.14	2.11	2.09	2.08	2.07	2.06	2.05	2.03
200	4.14	3.25	2.91	2.73	2.61	2.46	2.37	2.31	2.26	2.22	2.20	2.18	2.16	2.14	2.12	2.10	2.09	2.08	2.07	2.06

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Table 19-8. κ-Multipliers for 1-of-1 Interwell Prediction Limits on Means of Order 3 (1 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.03**	**1.65**	**1.50**	**1.42**	**1.36**	**1.30**	**1.26**	**1.23**	**1.22**	**1.20**	**1.19**	**1.18**	**1.18**	**1.17**	**1.16**	**1.16**	**1.15**	**1.15**	**1.14**	**1.14**
2	**2.41**	**1.93**	**1.75**	**1.65**	**1.58**	**1.50**	**1.46**	**1.42**	**1.40**	**1.38**	**1.37**	**1.36**	**1.35**	**1.34**	**1.33**	**1.33**	**1.32**	**1.32**	**1.31**	**1.31**
3	**2.62**	**2.09**	**1.89**	**1.77**	**1.70**	**1.62**	**1.57**	**1.53**	**1.50**	**1.48**	**1.47**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**	**1.42**	**1.41**	**1.40**	**1.40**
4	**2.76**	**2.20**	**1.98**	**1.86**	**1.79**	**1.70**	**1.64**	**1.60**	**1.57**	**1.55**	**1.54**	**1.53**	**1.52**	**1.50**	**1.49**	**1.48**	**1.48**	**1.47**	**1.47**	**1.46**
5	**2.87**	**2.28**	**2.05**	**1.93**	**1.85**	**1.76**	**1.70**	**1.65**	**1.63**	**1.60**	**1.59**	**1.58**	**1.57**	**1.55**	**1.54**	**1.53**	**1.53**	**1.52**	**1.51**	**1.51**
8	**3.09**	**2.45**	**2.20**	**2.07**	**1.98**	**1.88**	**1.82**	**1.77**	**1.73**	**1.71**	**1.69**	**1.68**	**1.67**	**1.65**	**1.64**	**1.63**	**1.62**	**1.62**	**1.61**	**1.60**
12	**3.28**	**2.59**	**2.33**	**2.18**	**2.09**	**1.98**	**1.91**	**1.86**	**1.82**	**1.80**	**1.78**	**1.77**	**1.75**	**1.74**	**1.72**	**1.71**	**1.71**	**1.70**	**1.69**	**1.68**
16	3.40	**2.69**	**2.41**	**2.26**	**2.16**	**2.05**	**1.98**	**1.92**	**1.89**	**1.86**	**1.84**	**1.83**	**1.81**	**1.79**	**1.78**	**1.77**	**1.76**	**1.76**	**1.74**	**1.74**
20	3.50	**2.76**	**2.48**	**2.32**	**2.22**	**2.10**	**2.03**	**1.97**	**1.94**	**1.91**	**1.89**	**1.87**	**1.86**	**1.84**	**1.82**	**1.81**	**1.80**	**1.80**	**1.79**	**1.78**
30	3.67	**2.89**	**2.59**	**2.43**	**2.32**	**2.20**	**2.12**	**2.06**	**2.02**	**1.99**	**1.97**	**1.95**	**1.94**	**1.92**	**1.90**	**1.89**	**1.88**	**1.87**	**1.86**	**1.85**
40	3.79	**2.98**	**2.67**	**2.50**	**2.39**	**2.26**	**2.18**	**2.12**	**2.08**	**2.05**	**2.02**	**2.01**	**1.99**	**1.97**	**1.95**	**1.94**	**1.93**	**1.92**	**1.91**	**1.90**
50	3.88	**3.05**	**2.73**	**2.56**	**2.45**	**2.31**	**2.23**	**2.17**	**2.12**	**2.09**	**2.07**	**2.05**	**2.03**	**2.01**	**1.99**	**1.98**	**1.97**	**1.96**	**1.95**	**1.94**
60	3.95	**3.10**	**2.78**	**2.60**	**2.49**	**2.35**	**2.27**	**2.20**	**2.16**	**2.13**	**2.10**	**2.08**	**2.07**	**2.04**	**2.03**	**2.01**	**2.00**	**2.00**	**1.98**	**1.97**
75	4.03	**3.17**	**2.84**	**2.66**	**2.54**	**2.40**	**2.32**	**2.25**	**2.20**	**2.17**	**2.14**	**2.12**	**2.11**	**2.08**	**2.07**	**2.05**	**2.04**	**2.03**	**2.02**	**2.01**
100	4.14	**3.25**	**2.91**	**2.73**	**2.61**	**2.46**	**2.37**	**2.31**	**2.26**	**2.22**	**2.20**	**2.18**	**2.16**	**2.14**	**2.12**	**2.10**	**2.09**	**2.08**	**2.07**	**2.06**
125	4.23	**3.32**	**2.97**	**2.78**	**2.66**	**2.51**	**2.42**	**2.35**	**2.30**	**2.27**	**2.24**	**2.22**	**2.20**	**2.17**	**2.16**	**2.14**	**2.13**	**2.12**	**2.10**	**2.09**
150	4.29	**3.37**	**3.01**	**2.82**	**2.70**	**2.55**	**2.46**	**2.38**	**2.33**	**2.30**	**2.27**	**2.25**	**2.23**	**2.21**	**2.19**	**2.17**	**2.16**	**2.15**	**2.13**	**2.12**
175	4.35	**3.41**	**3.05**	**2.86**	**2.73**	**2.58**	**2.49**	**2.41**	**2.36**	**2.33**	**2.30**	**2.28**	**2.26**	**2.23**	**2.21**	**2.20**	**2.19**	**2.18**	**2.16**	**2.15**
200	4.40	3.45	**3.08**	**2.89**	**2.76**	**2.60**	**2.51**	**2.44**	**2.39**	**2.35**	**2.32**	**2.30**	**2.28**	**2.25**	**2.24**	**2.22**	**2.21**	**2.20**	**2.18**	**2.17**

Table 19-8. κ-Multipliers for 1-of-1 Interwell Prediction Limits on Means of Order 3 (2 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.78**	**1.41**	**1.27**	**1.20**	**1.15**	**1.09**	**1.06**	**1.04**	**1.02**	**1.01**	**1.00**	**0.99**	**0.99**	**0.98**	**0.98**	**0.97**	**0.97**	**0.97**	**0.96**	**0.96**
2	**2.24**	**1.74**	**1.55**	**1.45**	**1.39**	**1.32**	**1.28**	**1.24**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**	**1.16**	**1.16**	**1.15**	**1.15**	**1.15**	**1.14**
3	**2.52**	**1.93**	**1.71**	**1.60**	**1.53**	**1.44**	**1.40**	**1.36**	**1.33**	**1.32**	**1.30**	**1.29**	**1.29**	**1.28**	**1.27**	**1.26**	**1.26**	**1.25**	**1.25**	**1.24**
4	**2.71**	**2.06**	**1.82**	**1.70**	**1.62**	**1.53**	**1.48**	**1.44**	**1.41**	**1.39**	**1.38**	**1.37**	**1.36**	**1.35**	**1.34**	**1.33**	**1.33**	**1.32**	**1.31**	**1.31**
5	**2.86**	**2.16**	**1.91**	**1.78**	**1.69**	**1.60**	**1.54**	**1.50**	**1.47**	**1.45**	**1.43**	**1.42**	**1.41**	**1.40**	**1.39**	**1.38**	**1.38**	**1.37**	**1.36**	**1.36**
8	3.17	**2.38**	**2.09**	**1.94**	**1.84**	**1.73**	**1.67**	**1.62**	**1.59**	**1.56**	**1.55**	**1.53**	**1.52**	**1.51**	**1.50**	**1.49**	**1.48**	**1.48**	**1.47**	**1.46**
12	3.43	**2.55**	**2.24**	**2.07**	**1.97**	**1.84**	**1.77**	**1.72**	**1.68**	**1.66**	**1.64**	**1.63**	**1.61**	**1.60**	**1.59**	**1.58**	**1.57**	**1.56**	**1.55**	**1.55**
16	3.60	**2.68**	**2.34**	**2.16**	**2.05**	**1.92**	**1.85**	**1.79**	**1.75**	**1.73**	**1.71**	**1.69**	**1.68**	**1.66**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**
20	3.74	**2.77**	**2.42**	**2.23**	**2.12**	**1.98**	**1.91**	**1.84**	**1.80**	**1.78**	**1.76**	**1.74**	**1.73**	**1.71**	**1.69**	**1.68**	**1.67**	**1.67**	**1.66**	**1.65**
30	3.98	**2.94**	**2.56**	**2.36**	**2.24**	**2.09**	**2.01**	**1.94**	**1.90**	**1.87**	**1.84**	**1.83**	**1.81**	**1.79**	**1.77**	**1.76**	**1.75**	**1.75**	**1.74**	**1.73**
40	4.15	**3.05**	**2.65**	**2.45**	**2.32**	**2.16**	**2.08**	**2.01**	**1.96**	**1.93**	**1.90**	**1.89**	**1.87**	**1.85**	**1.83**	**1.82**	**1.81**	**1.80**	**1.79**	**1.78**
50	4.27	3.14	**2.73**	**2.51**	**2.38**	**2.22**	**2.13**	**2.06**	**2.01**	**1.98**	**1.95**	**1.93**	**1.92**	**1.89**	**1.87**	**1.86**	**1.85**	**1.84**	**1.83**	**1.82**
60	4.37	3.21	**2.79**	**2.57**	**2.43**	**2.27**	**2.17**	**2.10**	**2.05**	**2.01**	**1.99**	**1.97**	**1.95**	**1.93**	**1.91**	**1.90**	**1.89**	**1.88**	**1.86**	**1.85**
75	4.49	3.29	**2.86**	**2.63**	**2.49**	**2.32**	**2.22**	**2.15**	**2.10**	**2.06**	**2.03**	**2.01**	**2.00**	**1.97**	**1.95**	**1.94**	**1.93**	**1.92**	**1.90**	**1.89**
100	4.65	3.40	**2.95**	**2.71**	**2.57**	**2.39**	**2.29**	**2.21**	**2.16**	**2.12**	**2.09**	**2.07**	**2.05**	**2.02**	**2.01**	**1.99**	**1.98**	**1.97**	**1.96**	**1.94**
125	4.76	3.48	**3.02**	**2.78**	**2.63**	**2.45**	**2.34**	**2.26**	**2.20**	**2.16**	**2.13**	**2.11**	**2.09**	**2.07**	**2.05**	**2.03**	**2.02**	**2.01**	**1.99**	**1.98**
150	4.86	3.55	*3.07*	**2.83**	**2.67**	**2.49**	**2.38**	**2.30**	**2.24**	**2.20**	**2.17**	**2.15**	**2.13**	**2.10**	**2.08**	**2.06**	**2.05**	**2.04**	**2.03**	**2.01**
175	4.94	3.60	*3.12*	**2.87**	**2.71**	**2.52**	**2.42**	**2.33**	**2.27**	**2.23**	**2.20**	**2.18**	**2.16**	**2.13**	**2.11**	**2.09**	**2.08**	**2.07**	**2.05**	**2.04**
200	5.00	3.65	*3.16*	**2.91**	**2.75**	**2.56**	**2.44**	**2.36**	**2.30**	**2.26**	**2.23**	**2.20**	**2.18**	**2.15**	**2.13**	**2.11**	**2.10**	**2.09**	**2.07**	**2.06**

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Table 19-8. κ-Multipliers for 1-of-1 Interwell Prediction Limits on Means of Order 3 (2 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.24**	**1.74**	**1.55**	**1.45**	**1.39**	**1.32**	**1.28**	**1.24**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**	**1.16**	**1.16**	**1.15**	**1.15**	**1.15**	**1.14**
2	**2.71**	**2.06**	**1.82**	**1.70**	**1.62**	**1.53**	**1.48**	**1.44**	**1.41**	**1.39**	**1.38**	**1.37**	**1.36**	**1.35**	**1.34**	**1.33**	**1.33**	**1.32**	**1.31**	**1.31**
3	**2.98**	**2.25**	**1.98**	**1.84**	**1.75**	**1.65**	**1.59**	**1.54**	**1.51**	**1.49**	**1.48**	**1.47**	**1.46**	**1.44**	**1.43**	**1.42**	**1.42**	**1.41**	**1.41**	**1.40**
4	3.17	**2.38**	**2.09**	**1.94**	**1.84**	**1.73**	**1.67**	**1.62**	**1.59**	**1.56**	**1.55**	**1.53**	**1.52**	**1.51**	**1.50**	**1.49**	**1.48**	**1.48**	**1.47**	**1.46**
5	3.31	**2.47**	**2.17**	**2.01**	**1.91**	**1.79**	**1.73**	**1.67**	**1.64**	**1.62**	**1.60**	**1.59**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**	**1.53**	**1.52**	**1.51**
8	3.60	**2.68**	**2.34**	**2.16**	**2.05**	**1.92**	**1.85**	**1.79**	**1.75**	**1.73**	**1.71**	**1.69**	**1.68**	**1.66**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**
12	3.85	**2.84**	**2.48**	**2.29**	**2.17**	**2.03**	**1.95**	**1.89**	**1.85**	**1.82**	**1.80**	**1.78**	**1.76**	**1.74**	**1.73**	**1.72**	**1.71**	**1.70**	**1.69**	**1.68**
16	4.02	**2.96**	**2.58**	**2.38**	**2.25**	**2.11**	**2.02**	**1.96**	**1.91**	**1.88**	**1.86**	**1.84**	**1.82**	**1.80**	**1.79**	**1.78**	**1.77**	**1.76**	**1.75**	**1.74**
20	4.15	**3.05**	**2.65**	**2.45**	**2.32**	**2.16**	**2.08**	**2.01**	**1.96**	**1.93**	**1.90**	**1.89**	**1.87**	**1.85**	**1.83**	**1.82**	**1.81**	**1.80**	**1.79**	**1.78**
30	4.37	**3.21**	**2.79**	**2.57**	**2.43**	**2.27**	**2.17**	**2.10**	**2.05**	**2.01**	**1.99**	**1.97**	**1.95**	**1.93**	**1.91**	**1.90**	**1.89**	**1.88**	**1.86**	**1.85**
40	4.53	3.32	**2.88**	**2.65**	**2.51**	**2.34**	**2.24**	**2.16**	**2.11**	**2.07**	**2.05**	**2.02**	**2.01**	**1.98**	**1.96**	**1.95**	**1.94**	**1.93**	**1.92**	**1.91**
50	4.65	3.40	**2.95**	**2.71**	**2.57**	**2.39**	**2.29**	**2.21**	**2.16**	**2.12**	**2.09**	**2.07**	**2.05**	**2.02**	**2.01**	**1.99**	**1.98**	**1.97**	**1.96**	**1.94**
60	4.74	3.47	**3.01**	**2.77**	**2.62**	**2.44**	**2.33**	**2.25**	**2.19**	**2.16**	**2.13**	**2.10**	**2.09**	**2.06**	**2.04**	**2.02**	**2.01**	**2.00**	**1.99**	**1.98**
75	4.86	3.55	**3.07**	**2.83**	**2.67**	**2.49**	**2.38**	**2.30**	**2.24**	**2.20**	**2.17**	**2.15**	**2.13**	**2.10**	**2.08**	**2.06**	**2.05**	**2.04**	**2.03**	**2.01**
100	5.00	3.65	**3.16**	**2.91**	**2.75**	**2.56**	**2.44**	**2.36**	**2.30**	**2.26**	**2.23**	**2.20**	**2.18**	**2.15**	**2.13**	**2.11**	**2.10**	**2.09**	**2.07**	**2.06**
125	5.11	3.73	**3.23**	**2.97**	**2.80**	**2.61**	**2.49**	**2.40**	**2.34**	**2.30**	**2.27**	**2.24**	**2.22**	**2.19**	**2.17**	**2.15**	**2.14**	**2.13**	**2.11**	**2.10**
150	5.20	3.79	*3.28*	**3.01**	**2.85**	**2.65**	**2.53**	**2.44**	**2.38**	**2.33**	**2.30**	**2.28**	**2.25**	**2.22**	**2.20**	**2.18**	**2.17**	**2.16**	**2.14**	**2.13**
175	5.28	3.84	*3.32*	**3.05**	**2.88**	**2.68**	**2.56**	**2.47**	**2.41**	**2.36**	**2.33**	**2.30**	**2.28**	**2.25**	**2.23**	**2.21**	**2.20**	**2.19**	**2.17**	**2.15**
200	5.34	3.89	3.36	**3.09**	**2.92**	**2.71**	**2.59**	**2.50**	**2.43**	**2.39**	**2.35**	**2.33**	**2.31**	**2.27**	**2.25**	**2.23**	**2.22**	**2.21**	**2.19**	**2.17**

Table 19-8. κ-Multipliers for 1-of-1 Interwell Prediction Limits on Means of Order 3 (2 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.71**	**2.06**	**1.82**	**1.70**	**1.62**	**1.53**	**1.48**	**1.44**	**1.41**	**1.39**	**1.38**	**1.37**	**1.36**	**1.35**	**1.34**	**1.33**	**1.33**	**1.32**	**1.31**	**1.31**
2	**3.17**	**2.38**	**2.09**	**1.94**	**1.84**	**1.73**	**1.67**	**1.62**	**1.59**	**1.56**	**1.55**	**1.53**	**1.52**	**1.51**	**1.50**	**1.49**	**1.48**	**1.48**	**1.47**	**1.46**
3	3.43	**2.55**	**2.24**	**2.07**	**1.97**	**1.84**	**1.77**	**1.72**	**1.68**	**1.66**	**1.64**	**1.63**	**1.61**	**1.60**	**1.59**	**1.58**	**1.57**	**1.56**	**1.55**	**1.55**
4	3.60	**2.68**	**2.34**	**2.16**	**2.05**	**1.92**	**1.85**	**1.79**	**1.75**	**1.73**	**1.71**	**1.69**	**1.68**	**1.66**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**
5	3.74	**2.77**	**2.42**	**2.23**	**2.12**	**1.98**	**1.91**	**1.84**	**1.80**	**1.78**	**1.76**	**1.74**	**1.73**	**1.71**	**1.69**	**1.68**	**1.67**	**1.67**	**1.66**	**1.65**
8	4.02	**2.96**	**2.58**	**2.38**	**2.25**	**2.11**	**2.02**	**1.96**	**1.91**	**1.88**	**1.86**	**1.84**	**1.82**	**1.80**	**1.79**	**1.78**	**1.77**	**1.76**	**1.75**	**1.74**
12	4.25	**3.12**	**2.71**	**2.50**	**2.37**	**2.21**	**2.12**	**2.05**	**2.00**	**1.97**	**1.94**	**1.92**	**1.91**	**1.88**	**1.87**	**1.85**	**1.84**	**1.84**	**1.82**	**1.81**
16	4.41	**3.23**	**2.81**	**2.59**	**2.45**	**2.28**	**2.19**	**2.11**	**2.06**	**2.03**	**2.00**	**1.98**	**1.96**	**1.94**	**1.92**	**1.91**	**1.90**	**1.89**	**1.88**	**1.87**
20	4.53	**3.32**	**2.88**	**2.65**	**2.51**	**2.34**	**2.24**	**2.16**	**2.11**	**2.07**	**2.05**	**2.02**	**2.01**	**1.98**	**1.96**	**1.95**	**1.94**	**1.93**	**1.92**	**1.91**
30	4.74	3.47	**3.01**	**2.77**	**2.62**	**2.44**	**2.33**	**2.25**	**2.19**	**2.16**	**2.13**	**2.10**	**2.09**	**2.06**	**2.04**	**2.02**	**2.01**	**2.00**	**1.99**	**1.98**
40	4.89	3.57	**3.09**	**2.84**	**2.69**	**2.50**	**2.40**	**2.31**	**2.25**	**2.21**	**2.18**	**2.16**	**2.14**	**2.11**	**2.09**	**2.07**	**2.06**	**2.05**	**2.04**	**2.02**
50	5.00	3.65	**3.16**	**2.91**	**2.75**	**2.56**	**2.44**	**2.36**	**2.30**	**2.26**	**2.23**	**2.20**	**2.18**	**2.15**	**2.13**	**2.11**	**2.10**	**2.09**	**2.07**	**2.06**
60	5.09	3.71	**3.22**	**2.95**	**2.79**	**2.60**	**2.48**	**2.39**	**2.33**	**2.29**	**2.26**	**2.23**	**2.21**	**2.18**	**2.16**	**2.15**	**2.13**	**2.12**	**2.10**	**2.09**
75	5.20	3.79	**3.28**	**3.01**	**2.85**	**2.65**	**2.53**	**2.44**	**2.38**	**2.33**	**2.30**	**2.28**	**2.25**	**2.22**	**2.20**	**2.18**	**2.17**	**2.16**	**2.14**	**2.13**
100	5.34	3.89	**3.36**	**3.09**	**2.92**	**2.71**	**2.59**	**2.50**	**2.43**	**2.39**	**2.35**	**2.33**	**2.31**	**2.27**	**2.25**	**2.23**	**2.22**	**2.21**	**2.19**	**2.17**
125	5.44	3.96	**3.43**	**3.15**	**2.97**	**2.76**	**2.64**	**2.54**	**2.48**	**2.43**	**2.40**	**2.37**	**2.35**	**2.31**	**2.29**	**2.27**	**2.26**	**2.24**	**2.22**	**2.21**
150	5.53	4.02	*3.48*	**3.19**	**3.01**	**2.80**	**2.68**	**2.58**	**2.51**	**2.46**	**2.43**	**2.40**	**2.38**	**2.34**	**2.32**	**2.30**	**2.29**	**2.27**	**2.25**	**2.24**
175	5.60	4.07	*3.52*	**3.23**	**3.05**	**2.83**	**2.71**	**2.61**	**2.54**	**2.49**	**2.46**	**2.43**	**2.40**	**2.37**	**2.34**	**2.32**	**2.31**	**2.30**	**2.28**	**2.26**
200	5.66	4.11	3.56	**3.26**	**3.08**	**2.86**	**2.74**	**2.63**	**2.57**	**2.52**	**2.48**	**2.45**	**2.43**	**2.39**	**2.37**	**2.35**	**2.33**	**2.32**	**2.30**	**2.28**

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Table 19-8. κ-Multipliers for 1-of-1 Interwell Prediction Limits on Means of Order 3 (5 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.62**	**1.92**	**1.68**	**1.56**	**1.49**	**1.40**	**1.35**	**1.31**	**1.29**	**1.27**	**1.26**	**1.25**	**1.24**	**1.23**	**1.22**	**1.22**	**1.21**	**1.21**	**1.20**	**1.20**
2	3.22	**2.29**	**1.98**	**1.82**	**1.73**	**1.62**	**1.55**	**1.51**	**1.48**	**1.45**	**1.44**	**1.43**	**1.42**	**1.40**	**1.39**	**1.38**	**1.38**	**1.37**	**1.37**	**1.36**
3	3.58	**2.51**	**2.15**	**1.97**	**1.86**	**1.74**	**1.67**	**1.61**	**1.58**	**1.56**	**1.54**	**1.52**	**1.51**	**1.50**	**1.49**	**1.48**	**1.47**	**1.46**	**1.46**	**1.45**
4	3.83	**2.66**	**2.27**	**2.08**	**1.96**	**1.82**	**1.75**	**1.69**	**1.65**	**1.63**	**1.61**	**1.59**	**1.58**	**1.56**	**1.55**	**1.54**	**1.53**	**1.53**	**1.52**	**1.51**
5	4.03	**2.78**	**2.36**	**2.16**	**2.03**	**1.89**	**1.81**	**1.75**	**1.71**	**1.68**	**1.66**	**1.64**	**1.63**	**1.61**	**1.60**	**1.59**	**1.58**	**1.57**	**1.56**	**1.56**
8	4.44	**3.03**	**2.56**	**2.32**	**2.18**	**2.02**	**1.93**	**1.86**	**1.82**	**1.79**	**1.76**	**1.75**	**1.73**	**1.71**	**1.70**	**1.69**	**1.68**	**1.67**	**1.66**	**1.65**
12	4.79	3.23	**2.72**	**2.47**	**2.31**	**2.14**	**2.04**	**1.96**	**1.91**	**1.88**	**1.85**	**1.83**	**1.82**	**1.80**	**1.78**	**1.77**	**1.76**	**1.75**	**1.74**	**1.73**
16	5.03	3.38	**2.84**	**2.57**	**2.40**	**2.22**	**2.11**	**2.03**	**1.98**	**1.94**	**1.92**	**1.89**	**1.88**	**1.85**	**1.84**	**1.82**	**1.81**	**1.81**	**1.79**	**1.78**
20	5.21	3.49	**2.93**	**2.64**	**2.47**	**2.28**	**2.17**	**2.08**	**2.03**	**1.99**	**1.96**	**1.94**	**1.92**	**1.90**	**1.88**	**1.87**	**1.86**	**1.85**	**1.83**	**1.82**
30	5.53	3.69	*3.08*	**2.78**	**2.60**	**2.39**	**2.27**	**2.18**	**2.12**	**2.08**	**2.05**	**2.02**	**2.01**	**1.98**	**1.96**	**1.94**	**1.93**	**1.92**	**1.91**	**1.90**
40	5.76	3.83	3.19	**2.88**	**2.69**	**2.46**	**2.34**	**2.24**	**2.18**	**2.14**	**2.11**	**2.08**	**2.06**	**2.03**	**2.01**	**2.00**	**1.98**	**1.98**	**1.96**	**1.95**
50	5.93	3.93	3.28	**2.95**	**2.75**	**2.52**	**2.39**	**2.30**	**2.23**	**2.19**	**2.15**	**2.13**	**2.11**	**2.07**	**2.05**	**2.04**	**2.02**	**2.01**	**2.00**	**1.99**
60	6.07	4.02	3.35	*3.01*	**2.81**	**2.57**	**2.44**	**2.34**	**2.27**	**2.22**	**2.19**	**2.16**	**2.14**	**2.11**	**2.09**	**2.07**	**2.06**	**2.05**	**2.03**	**2.02**
75	6.23	4.12	3.43	*3.08*	**2.87**	**2.63**	**2.49**	**2.39**	**2.32**	**2.27**	**2.23**	**2.20**	**2.18**	**2.15**	**2.13**	**2.11**	**2.10**	**2.09**	**2.07**	**2.05**
100	6.44	4.25	3.53	*3.17*	**2.95**	**2.70**	**2.56**	**2.45**	**2.38**	**2.33**	**2.29**	**2.26**	**2.24**	**2.20**	**2.18**	**2.16**	**2.15**	**2.13**	**2.11**	**2.10**
125	6.60	4.35	3.61	3.24	*3.02*	**2.76**	**2.61**	**2.50**	**2.42**	**2.37**	**2.33**	**2.30**	**2.28**	**2.24**	**2.22**	**2.20**	**2.18**	**2.17**	**2.15**	**2.14**
150	6.72	4.42	3.67	3.30	*3.07*	**2.80**	**2.65**	**2.54**	**2.46**	**2.41**	**2.37**	**2.34**	**2.31**	**2.28**	**2.25**	**2.23**	**2.21**	**2.20**	**2.18**	**2.17**
175	6.83	4.49	3.73	3.34	*3.11*	**2.84**	**2.69**	**2.57**	**2.49**	**2.44**	**2.40**	**2.37**	**2.34**	**2.30**	**2.28**	**2.26**	**2.24**	**2.23**	**2.21**	**2.19**
200	6.92	4.55	3.77	3.38	*3.15*	**2.87**	**2.72**	**2.60**	**2.52**	**2.46**	**2.42**	**2.39**	**2.36**	**2.33**	**2.30**	**2.28**	**2.26**	**2.25**	**2.23**	**2.21**

Table 19-8. κ-Multipliers for 1-of-1 Interwell Prediction Limits on Means of Order 3 (5 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.22	**2.29**	**1.98**	**1.82**	**1.73**	**1.62**	**1.55**	**1.51**	**1.48**	**1.45**	**1.44**	**1.43**	**1.42**	**1.40**	**1.39**	**1.38**	**1.38**	**1.37**	**1.37**	**1.36**
2	3.83	**2.66**	**2.27**	**2.08**	**1.96**	**1.82**	**1.75**	**1.69**	**1.65**	**1.63**	**1.61**	**1.59**	**1.58**	**1.56**	**1.55**	**1.54**	**1.53**	**1.53**	**1.52**	**1.51**
3	4.19	**2.88**	**2.44**	**2.22**	**2.09**	**1.94**	**1.86**	**1.79**	**1.75**	**1.72**	**1.70**	**1.68**	**1.67**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**	**1.59**
4	4.44	**3.03**	**2.56**	**2.32**	**2.18**	**2.02**	**1.93**	**1.86**	**1.82**	**1.79**	**1.76**	**1.75**	**1.73**	**1.71**	**1.70**	**1.69**	**1.68**	**1.67**	**1.66**	**1.65**
5	4.63	**3.14**	**2.65**	**2.40**	**2.26**	**2.09**	**1.99**	**1.92**	**1.87**	**1.84**	**1.81**	**1.79**	**1.78**	**1.76**	**1.74**	**1.73**	**1.72**	**1.72**	**1.70**	**1.69**
8	5.03	3.38	**2.84**	**2.57**	**2.40**	**2.22**	**2.11**	**2.03**	**1.98**	**1.94**	**1.92**	**1.89**	**1.88**	**1.85**	**1.84**	**1.82**	**1.81**	**1.81**	**1.79**	**1.78**
12	5.36	3.58	**3.00**	**2.71**	**2.53**	**2.33**	**2.21**	**2.13**	**2.07**	**2.03**	**2.00**	**1.98**	**1.96**	**1.93**	**1.92**	**1.90**	**1.89**	**1.88**	**1.87**	**1.86**
16	5.59	3.72	**3.11**	**2.80**	**2.62**	**2.41**	**2.29**	**2.19**	**2.13**	**2.09**	**2.06**	**2.04**	**2.02**	**1.99**	**1.97**	**1.96**	**1.94**	**1.93**	**1.92**	**1.91**
20	5.76	3.83	**3.19**	**2.88**	**2.69**	**2.46**	**2.34**	**2.24**	**2.18**	**2.14**	**2.11**	**2.08**	**2.06**	**2.03**	**2.01**	**2.00**	**1.98**	**1.98**	**1.96**	**1.95**
30	6.07	4.02	3.35	**3.01**	**2.81**	**2.57**	**2.44**	**2.34**	**2.27**	**2.22**	**2.19**	**2.16**	**2.14**	**2.11**	**2.09**	**2.07**	**2.06**	**2.05**	**2.03**	**2.02**
40	6.28	4.15	3.45	**3.10**	**2.89**	**2.65**	**2.51**	**2.40**	**2.33**	**2.28**	**2.25**	**2.22**	**2.20**	**2.16**	**2.14**	**2.12**	**2.11**	**2.10**	**2.08**	**2.06**
50	6.44	4.25	3.53	**3.17**	**2.95**	**2.70**	**2.56**	**2.45**	**2.38**	**2.33**	**2.29**	**2.26**	**2.24**	**2.20**	**2.18**	**2.16**	**2.15**	**2.13**	**2.11**	**2.10**
60	6.57	4.33	3.59	*3.23*	**3.01**	**2.75**	**2.60**	**2.49**	**2.42**	**2.36**	**2.32**	**2.29**	**2.27**	**2.24**	**2.21**	**2.19**	**2.17**	**2.17**	**2.14**	**2.13**
75	6.72	4.42	3.67	*3.30*	**3.07**	**2.80**	**2.65**	**2.54**	**2.46**	**2.41**	**2.37**	**2.34**	**2.31**	**2.28**	**2.25**	**2.23**	**2.21**	**2.20**	**2.18**	**2.17**
100	6.92	4.55	3.77	*3.38*	**3.15**	**2.87**	**2.72**	**2.60**	**2.52**	**2.46**	**2.42**	**2.39**	**2.36**	**2.33**	**2.30**	**2.28**	**2.26**	**2.25**	**2.23**	**2.21**
125	7.07	4.64	3.85	3.45	**3.21**	**2.93**	**2.77**	**2.65**	**2.56**	**2.51**	**2.46**	**2.43**	**2.40**	**2.36**	**2.33**	**2.32**	**2.30**	**2.29**	**2.26**	**2.25**
150	7.19	4.72	3.91	3.50	*3.26*	**2.97**	**2.81**	**2.68**	**2.60**	**2.54**	**2.50**	**2.46**	**2.44**	**2.40**	**2.37**	**2.35**	**2.33**	**2.32**	**2.29**	**2.28**
175	7.29	4.78	3.96	3.55	*3.30*	**3.01**	**2.84**	**2.72**	**2.63**	**2.57**	**2.53**	**2.49**	**2.46**	**2.42**	**2.39**	**2.37**	**2.35**	**2.34**	**2.32**	**2.30**
200	7.34	4.83	4.00	3.59	*3.34*	**3.04**	**2.87**	**2.74**	**2.66**	**2.60**	**2.55**	**2.52**	**2.49**	**2.45**	**2.42**	**2.39**	**2.38**	**2.36**	**2.34**	**2.32**

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Table 19-8. κ-Multipliers for 1-of-1 Interwell Prediction Limits on Means of Order 3 (5 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.83	2.66	2.27	2.08	1.96	1.82	1.75	1.69	1.65	1.63	1.61	1.59	1.58	1.56	1.55	1.54	1.53	1.53	1.52	1.51
2	4.44	3.03	2.56	2.32	2.18	2.02	1.93	1.86	1.82	1.79	1.76	1.75	1.73	1.71	1.70	1.69	1.68	1.67	1.66	1.65
3	4.79	3.23	2.72	2.47	2.31	2.14	2.04	1.96	1.91	1.88	1.85	1.83	1.82	1.80	1.78	1.77	1.76	1.75	1.74	1.73
4	5.03	3.38	2.84	2.57	2.40	2.22	2.11	2.03	1.98	1.94	1.92	1.89	1.88	1.85	1.84	1.82	1.81	1.81	1.79	1.78
5	5.21	3.49	2.93	2.64	2.47	2.28	2.17	2.08	2.03	1.99	1.96	1.94	1.92	1.90	1.88	1.87	1.86	1.85	1.83	1.82
8	5.59	3.72	3.11	2.80	2.62	2.41	2.29	2.19	2.13	2.09	2.06	2.04	2.02	1.99	1.97	1.96	1.94	1.93	1.92	1.91
12	5.90	3.91	3.26	2.94	2.74	2.51	2.38	2.29	2.22	2.18	2.14	2.12	2.10	2.07	2.05	2.03	2.02	2.01	1.99	1.98
16	6.11	4.05	3.37	3.03	2.83	2.59	2.45	2.35	2.28	2.24	2.20	2.17	2.15	2.12	2.10	2.08	2.07	2.06	2.04	2.03
20	6.28	4.15	3.45	3.10	2.89	2.65	2.51	2.40	2.33	2.28	2.25	2.22	2.20	2.16	2.14	2.12	2.11	2.10	2.08	2.06
30	6.57	4.33	3.59	3.23	3.01	2.75	2.60	2.49	2.42	2.36	2.32	2.29	2.27	2.24	2.21	2.19	2.17	2.17	2.14	2.13
40	6.77	4.45	3.70	3.32	3.09	2.82	2.67	2.55	2.47	2.42	2.38	2.35	2.32	2.29	2.26	2.24	2.23	2.21	2.19	2.18
50	6.92	4.55	3.77	3.38	3.15	2.87	2.72	2.60	2.52	2.46	2.42	2.39	2.36	2.33	2.30	2.28	2.26	2.25	2.23	2.21
60	7.04	4.62	3.83	3.44	3.20	2.92	2.76	2.64	2.56	2.50	2.46	2.42	2.40	2.36	2.33	2.31	2.29	2.28	2.26	2.24
75	7.19	4.72	3.91	*3.50*	3.26	2.97	2.81	2.68	2.60	2.54	2.50	2.46	2.44	2.40	2.37	2.35	2.33	2.32	2.29	2.28
100	7.34	4.83	4.00	*3.59*	3.34	3.04	2.87	2.74	2.66	2.60	2.55	2.52	2.49	2.45	2.42	2.39	2.38	2.36	2.34	2.32
125	7.52	4.92	4.08	3.65	3.39	3.09	2.92	2.79	2.70	2.64	2.59	2.56	2.53	2.48	2.45	2.43	2.41	2.40	2.37	2.35
150	7.64	5.00	4.13	3.70	3.44	3.14	2.96	2.83	2.74	2.67	2.62	2.59	2.56	2.51	2.48	2.46	2.44	2.43	2.40	2.38
175	7.73	5.06	4.18	3.75	*3.48*	3.17	2.99	2.86	2.77	2.70	2.65	2.61	2.58	2.54	2.51	2.48	2.46	2.45	2.42	2.40
200	7.82	5.11	4.23	3.78	*3.52*	3.20	3.02	2.88	2.79	2.73	2.68	2.64	2.61	2.56	2.53	2.50	2.49	2.47	2.44	2.42

Table 19-8. κ-Multipliers for 1-of-1 Interwell Prediction Limits on Means of Order 3 (10 COC, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.41	2.35	2.01	1.84	1.74	1.62	1.56	1.51	1.48	1.46	1.44	1.43	1.42	1.40	1.39	1.39	1.38	1.37	1.37	1.36
2	4.15	2.76	2.32	2.10	1.98	1.83	1.75	1.69	1.65	1.63	1.61	1.59	1.58	1.56	1.55	1.54	1.53	1.53	1.52	1.51
3	4.60	3.00	2.50	2.26	2.12	1.95	1.86	1.80	1.75	1.72	1.70	1.69	1.67	1.65	1.64	1.63	1.62	1.61	1.60	1.59
4	4.92	3.17	2.63	2.37	2.21	2.04	1.94	1.87	1.82	1.79	1.77	1.75	1.73	1.71	1.70	1.69	1.68	1.67	1.66	1.65
5	5.16	3.30	2.73	2.45	2.29	2.10	2.00	1.93	1.88	1.84	1.82	1.80	1.78	1.76	1.74	1.73	1.72	1.72	1.70	1.69
8	5.68	3.58	2.94	2.63	2.45	2.24	2.13	2.04	1.99	1.95	1.92	1.90	1.88	1.86	1.84	1.83	1.82	1.81	1.79	1.78
12	6.11	3.82	*3.12*	2.78	2.58	2.36	2.23	2.14	2.08	2.04	2.01	1.98	1.96	1.94	1.92	1.90	1.89	1.88	1.87	1.86
16	6.41	3.99	3.24	2.89	2.68	2.44	2.31	2.21	2.14	2.10	2.07	2.04	2.02	1.99	1.97	1.96	1.95	1.94	1.92	1.91
20	6.64	4.11	3.34	2.97	2.75	2.50	2.36	2.26	2.19	2.15	2.11	2.09	2.07	2.04	2.01	2.00	1.99	1.98	1.96	1.95
30	7.05	4.34	3.51	*3.11*	2.88	2.61	2.47	2.35	2.28	2.23	2.20	2.17	2.15	2.11	2.09	2.07	2.06	2.05	2.03	2.02
40	7.33	4.50	3.63	*3.22*	2.97	2.69	2.54	2.42	2.34	2.29	2.25	2.22	2.20	2.17	2.14	2.12	2.11	2.10	2.08	2.07
50	7.55	4.62	3.73	3.30	*3.04*	2.75	2.59	2.47	2.39	2.34	2.30	2.27	2.24	2.21	2.18	2.16	2.15	2.14	2.12	2.10
60	7.72	4.71	3.80	3.36	*3.10*	2.80	2.63	2.50	2.43	2.38	2.33	2.30	2.28	2.24	2.21	2.19	2.18	2.17	2.15	2.13
75	7.93	4.83	3.89	3.44	*3.17*	2.86	2.69	2.56	2.48	2.42	2.38	2.34	2.32	2.28	2.25	2.23	2.22	2.20	2.18	2.17
100	8.19	4.98	4.00	3.53	3.25	2.94	2.76	2.63	2.54	2.48	2.43	2.40	2.37	2.33	2.30	2.28	2.27	2.25	2.23	2.21
125	8.39	5.09	4.09	3.61	3.32	*2.99*	2.81	2.67	2.58	2.52	2.48	2.44	2.41	2.37	2.34	2.32	2.30	2.29	2.27	2.25
150	8.55	5.18	4.16	3.67	3.38	*3.04*	2.86	2.71	2.62	2.56	2.51	2.47	2.45	2.40	2.37	2.35	2.33	2.32	2.29	2.28
175	8.68	5.26	4.22	3.72	3.42	*3.08*	2.89	2.75	2.65	2.59	2.54	2.50	2.47	2.43	2.40	2.38	2.36	2.34	2.32	2.30
200	8.80	5.32	4.27	3.76	3.46	*3.12*	2.92	2.78	2.68	2.61	2.57	2.53	2.50	2.45	2.42	2.40	2.38	2.36	2.34	2.26

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Table 19-8. κ-Multipliers for 1-of-1 Interwell Prediction Limits on Means of Order 3 (10 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	4.15	**2.76**	**2.32**	**2.10**	**1.98**	**1.83**	**1.75**	**1.69**	**1.65**	**1.63**	**1.61**	**1.59**	**1.58**	**1.56**	**1.55**	**1.54**	**1.53**	**1.53**	**1.52**	**1.51**
2	4.92	**3.17**	**2.63**	**2.37**	**2.21**	**2.04**	**1.94**	**1.87**	**1.82**	**1.79**	**1.77**	**1.75**	**1.73**	**1.71**	**1.70**	**1.69**	**1.68**	**1.67**	**1.66**	**1.65**
3	5.36	3.41	**2.81**	**2.52**	**2.35**	**2.16**	**2.05**	**1.97**	**1.92**	**1.88**	**1.86**	**1.84**	**1.82**	**1.80**	**1.78**	**1.77**	**1.76**	**1.75**	**1.74**	**1.73**
4	5.68	3.58	**2.94**	**2.63**	**2.45**	**2.24**	**2.13**	**2.04**	**1.99**	**1.95**	**1.92**	**1.90**	**1.88**	**1.86**	**1.84**	**1.83**	**1.82**	**1.81**	**1.79**	**1.78**
5	5.92	3.71	**3.04**	**2.71**	**2.52**	**2.30**	**2.18**	**2.09**	**2.04**	**2.00**	**1.97**	**1.95**	**1.93**	**1.90**	**1.88**	**1.87**	**1.86**	**1.85**	**1.83**	**1.82**
8	6.41	3.99	*3.24*	**2.89**	**2.68**	**2.44**	**2.31**	**2.21**	**2.14**	**2.10**	**2.07**	**2.04**	**2.02**	**1.99**	**1.97**	**1.96**	**1.95**	**1.94**	**1.92**	**1.91**
12	6.83	4.22	3.42	**3.03**	**2.81**	**2.55**	**2.41**	**2.30**	**2.23**	**2.19**	**2.15**	**2.12**	**2.10**	**2.07**	**2.05**	**2.03**	**2.02**	**2.01**	**1.99**	**1.98**
16	7.11	4.38	3.54	**3.14**	**2.90**	**2.63**	**2.48**	**2.37**	**2.30**	**2.25**	**2.21**	**2.18**	**2.16**	**2.12**	**2.10**	**2.08**	**2.07**	**2.06**	**2.04**	**2.03**
20	7.33	4.50	3.63	*3.22*	**2.97**	**2.69**	**2.54**	**2.42**	**2.34**	**2.29**	**2.25**	**2.22**	**2.20**	**2.17**	**2.14**	**2.12**	**2.11**	**2.10**	**2.08**	**2.07**
30	7.72	4.71	3.80	*3.36*	**3.10**	**2.80**	**2.63**	**2.50**	**2.43**	**2.38**	**2.33**	**2.30**	**2.28**	**2.24**	**2.21**	**2.19**	**2.18**	**2.17**	**2.15**	**2.13**
40	7.99	4.87	3.92	3.46	**3.19**	**2.88**	**2.71**	**2.58**	**2.49**	**2.43**	**2.39**	**2.36**	**2.33**	**2.29**	**2.26**	**2.24**	**2.23**	**2.22**	**2.19**	**2.18**
50	8.19	4.98	4.00	3.53	*3.25*	**2.94**	**2.76**	**2.63**	**2.54**	**2.48**	**2.43**	**2.40**	**2.37**	**2.33**	**2.30**	**2.28**	**2.27**	**2.25**	**2.23**	**2.21**
60	8.35	5.07	4.08	3.59	*3.31*	**2.98**	**2.80**	**2.67**	**2.58**	**2.51**	**2.47**	**2.43**	**2.41**	**2.36**	**2.33**	**2.31**	**2.30**	**2.28**	**2.26**	**2.24**
75	8.55	5.18	4.16	3.67	*3.38*	**3.04**	**2.86**	**2.71**	**2.62**	**2.56**	**2.51**	**2.47**	**2.45**	**2.40**	**2.37**	**2.35**	**2.33**	**2.32**	**2.29**	**2.28**
100	8.80	5.32	4.27	3.76	3.46	**3.12**	**2.92**	**2.78**	**2.68**	**2.61**	**2.57**	**2.53**	**2.50**	**2.45**	**2.42**	**2.40**	**2.38**	**2.36**	**2.34**	**2.26**
125	8.99	5.43	4.36	3.83	3.53	**3.17**	**2.98**	**2.82**	**2.73**	**2.66**	**2.61**	**2.57**	**2.54**	**2.49**	**2.46**	**2.43**	**2.42**	**2.40**	**2.37**	**2.36**
150	9.14	5.52	4.42	3.89	3.58	*3.22*	**3.02**	**2.86**	**2.76**	**2.69**	**2.64**	**2.60**	**2.57**	**2.52**	**2.49**	**2.46**	**2.44**	**2.43**	**2.40**	**2.38**
175	9.27	5.60	4.48	3.94	3.62	*3.26*	**3.05**	**2.90**	**2.79**	**2.72**	**2.67**	**2.63**	**2.60**	**2.55**	**2.51**	**2.49**	**2.47**	**2.45**	**2.42**	**2.41**
200	9.38	5.66	4.53	3.98	3.66	*3.29*	**3.08**	**2.92**	**2.82**	**2.75**	**2.69**	**2.65**	**2.62**	**2.57**	**2.54**	**2.51**	**2.49**	**2.47**	**2.45**	**2.43**

Table 19-8. κ-Multipliers for 1-of-1 Interwell Prediction Limits on Means of Order 3 (10 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	4.92	**3.17**	**2.63**	**2.37**	**2.21**	**2.04**	**1.94**	**1.87**	**1.82**	**1.79**	**1.77**	**1.75**	**1.73**	**1.71**	**1.70**	**1.69**	**1.68**	**1.67**	**1.66**	**1.65**
2	5.68	3.58	**2.94**	**2.63**	**2.45**	**2.24**	**2.13**	**2.04**	**1.99**	**1.95**	**1.92**	**1.90**	**1.88**	**1.86**	**1.84**	**1.83**	**1.82**	**1.81**	**1.79**	**1.78**
3	6.11	3.82	**3.12**	**2.78**	**2.58**	**2.36**	**2.23**	**2.14**	**2.08**	**2.04**	**2.01**	**1.98**	**1.96**	**1.94**	**1.92**	**1.90**	**1.89**	**1.88**	**1.87**	**1.86**
4	6.41	3.99	**3.24**	**2.89**	**2.68**	**2.44**	**2.31**	**2.21**	**2.14**	**2.10**	**2.07**	**2.04**	**2.02**	**1.99**	**1.97**	**1.96**	**1.95**	**1.94**	**1.92**	**1.91**
5	6.64	4.11	**3.34**	**2.97**	**2.75**	**2.50**	**2.36**	**2.26**	**2.19**	**2.15**	**2.11**	**2.09**	**2.07**	**2.04**	**2.01**	**2.00**	**1.99**	**1.98**	**1.96**	**1.95**
8	7.11	4.38	*3.54*	**3.14**	**2.90**	**2.63**	**2.48**	**2.37**	**2.30**	**2.25**	**2.21**	**2.18**	**2.16**	**2.12**	**2.10**	**2.08**	**2.07**	**2.06**	**2.04**	**2.03**
12	7.51	4.60	3.71	**3.28**	**3.03**	**2.74**	**2.58**	**2.46**	**2.38**	**2.33**	**2.29**	**2.26**	**2.24**	**2.20**	**2.17**	**2.16**	**2.14**	**2.13**	**2.11**	**2.10**
16	7.78	4.75	3.83	**3.38**	**3.12**	**2.82**	**2.65**	**2.53**	**2.44**	**2.39**	**2.35**	**2.31**	**2.29**	**2.25**	**2.23**	**2.21**	**2.19**	**2.18**	**2.16**	**2.14**
20	7.99	4.87	3.92	**3.46**	**3.19**	**2.88**	**2.71**	**2.58**	**2.49**	**2.43**	**2.39**	**2.36**	**2.33**	**2.29**	**2.26**	**2.24**	**2.23**	**2.22**	**2.19**	**2.18**
30	8.35	5.07	4.08	*3.59*	**3.31**	**2.98**	**2.80**	**2.67**	**2.58**	**2.51**	**2.47**	**2.43**	**2.41**	**2.36**	**2.33**	**2.31**	**2.30**	**2.28**	**2.26**	**2.24**
40	8.60	5.22	4.19	3.69	**3.39**	**3.06**	**2.87**	**2.73**	**2.64**	**2.57**	**2.52**	**2.49**	**2.46**	**2.41**	**2.38**	**2.36**	**2.34**	**2.33**	**2.30**	**2.29**
50	8.80	5.32	4.27	3.76	**3.46**	**3.12**	**2.92**	**2.78**	**2.68**	**2.61**	**2.57**	**2.53**	**2.50**	**2.45**	**2.42**	**2.40**	**2.38**	**2.36**	**2.34**	**2.26**
60	8.95	5.42	4.34	3.82	*3.51*	**3.16**	**2.97**	**2.82**	**2.72**	**2.65**	**2.60**	**2.56**	**2.53**	**2.48**	**2.45**	**2.43**	**2.41**	**2.39**	**2.37**	**2.35**
75	9.14	5.52	4.42	3.89	*3.58*	**3.22**	**3.02**	**2.86**	**2.76**	**2.69**	**2.64**	**2.60**	**2.57**	**2.52**	**2.49**	**2.46**	**2.44**	**2.43**	**2.40**	**2.38**
100	9.38	5.66	4.53	3.98	*3.66*	**3.29**	**3.08**	**2.92**	**2.82**	**2.75**	**2.69**	**2.65**	**2.62**	**2.57**	**2.54**	**2.51**	**2.49**	**2.47**	**2.45**	**2.43**
125	9.56	5.76	4.61	4.05	3.72	**3.34**	**3.13**	**2.97**	**2.86**	**2.79**	**2.73**	**2.69**	**2.66**	**2.61**	**2.57**	**2.54**	**2.52**	**2.51**	**2.48**	**2.46**
150	9.70	5.85	4.68	4.11	3.77	**3.39**	**3.17**	**3.01**	**2.90**	**2.82**	**2.77**	**2.72**	**2.69**	**2.64**	**2.60**	**2.57**	**2.55**	**2.54**	**2.51**	**2.49**
175	9.82	5.91	4.73	4.16	3.82	**3.43**	**3.21**	**3.04**	**2.93**	**2.85**	**2.80**	**2.75**	**2.72**	**2.66**	**2.63**	**2.60**	**2.58**	**2.56**	**2.53**	**2.51**
200	9.93	5.97	4.77	4.20	3.85	**3.46**	**3.24**	**3.07**	**2.96**	**2.88**	**2.82**	**2.77**	**2.74**	**2.68**	**2.65**	**2.62**	**2.60**	**2.58**	**2.55**	**2.53**

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Table 19-8. κ-Multipliers for 1-of-1 Interwell Prediction Limits on Means of Order 3 (20 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	4.38	**2.82**	**2.34**	**2.12**	**1.99**	**1.84**	**1.76**	**1.70**	**1.66**	**1.63**	**1.61**	**1.59**	**1.58**	**1.56**	**1.55**	**1.54**	**1.53**	**1.53**	**1.52**	**1.51**
2	5.31	3.27	**2.67**	**2.39**	**2.23**	**2.05**	**1.95**	**1.87**	**1.83**	**1.79**	**1.77**	**1.75**	**1.74**	**1.71**	**1.70**	**1.69**	**1.68**	**1.67**	**1.66**	**1.65**
3	5.86	3.54	**2.87**	**2.55**	**2.37**	**2.17**	**2.06**	**1.97**	**1.92**	**1.89**	**1.86**	**1.84**	**1.82**	**1.80**	**1.78**	**1.77**	**1.76**	**1.75**	**1.74**	**1.73**
4	6.26	3.74	**3.01**	**2.67**	**2.47**	**2.25**	**2.13**	**2.05**	**1.99**	**1.95**	**1.92**	**1.90**	**1.88**	**1.86**	**1.84**	**1.83**	**1.82**	**1.81**	**1.79**	**1.78**
5	6.57	3.89	*3.12*	**2.76**	**2.55**	**2.32**	**2.19**	**2.10**	**2.04**	**2.00**	**1.97**	**1.95**	**1.93**	**1.90**	**1.88**	**1.87**	**1.86**	**1.85**	**1.83**	**1.82**
8	7.22	4.21	3.35	**2.95**	**2.71**	**2.46**	**2.32**	**2.21**	**2.15**	**2.10**	**2.07**	**2.04**	**2.02**	**1.99**	**1.97**	**1.96**	**1.95**	**1.94**	**1.92**	**1.91**
12	7.76	4.48	3.54	*3.11*	**2.85**	**2.57**	**2.42**	**2.31**	**2.24**	**2.19**	**2.15**	**2.13**	**2.10**	**2.07**	**2.05**	**2.03**	**2.02**	**2.01**	**1.99**	**1.98**
16	8.14	4.67	3.68	3.22	**2.95**	**2.66**	**2.50**	**2.38**	**2.30**	**2.25**	**2.21**	**2.18**	**2.16**	**2.13**	**2.10**	**2.08**	**2.07**	**2.06**	**2.04**	**2.03**
20	8.43	4.81	3.78	3.31	*3.03*	**2.72**	**2.56**	**2.43**	**2.35**	**2.30**	**2.26**	**2.23**	**2.20**	**2.17**	**2.14**	**2.12**	**2.11**	**2.10**	**2.08**	**2.07**
30	8.94	5.07	3.97	3.46	*3.17*	**2.84**	**2.66**	**2.53**	**2.44**	**2.38**	**2.34**	**2.31**	**2.28**	**2.24**	**2.22**	**2.20**	**2.18**	**2.17**	**2.15**	**2.13**
40	9.30	5.25	4.11	3.57	3.26	**2.92**	**2.73**	**2.59**	**2.50**	**2.44**	**2.40**	**2.36**	**2.33**	**2.29**	**2.27**	**2.25**	**2.23**	**2.22**	**2.17**	**2.18**
50	9.57	5.39	4.21	3.66	3.34	*2.98*	**2.79**	**2.64**	**2.55**	**2.49**	**2.44**	**2.40**	**2.38**	**2.33**	**2.31**	**2.28**	**2.27**	**2.25**	**2.23**	**2.21**
60	9.79	5.50	4.29	3.72	3.40	*3.03*	**2.83**	**2.68**	**2.59**	**2.52**	**2.48**	**2.44**	**2.41**	**2.37**	**2.34**	**2.31**	**2.30**	**2.28**	**2.26**	**2.24**
75	10.05	5.64	4.39	3.81	3.47	*3.09*	**2.89**	**2.73**	**2.64**	**2.57**	**2.52**	**2.48**	**2.45**	**2.41**	**2.37**	**2.35**	**2.33**	**2.32**	**2.29**	**2.26**
100	10.38	5.81	4.52	3.91	3.56	*3.17*	**2.96**	**2.80**	**2.70**	**2.63**	**2.57**	**2.53**	**2.50**	**2.46**	**2.42**	**2.40**	**2.38**	**2.37**	**2.34**	**2.32**
125	10.63	5.94	4.61	3.99	3.63	*3.23*	*3.01*	**2.85**	**2.74**	**2.67**	**2.62**	**2.57**	**2.54**	**2.49**	**2.46**	**2.44**	**2.42**	**2.40**	**2.37**	**2.36**
150	10.83	6.04	4.69	4.06	3.69	*3.28*	*3.06*	**2.89**	**2.78**	**2.71**	**2.65**	**2.61**	**2.58**	**2.53**	**2.49**	**2.47**	**2.45**	**2.43**	**2.40**	**2.38**
175	11.00	6.13	4.76	4.11	3.74	3.32	*3.10*	**2.92**	**2.81**	**2.74**	**2.68**	**2.64**	**2.60**	**2.55**	**2.52**	**2.49**	**2.47**	**2.45**	**2.43**	**2.41**
200	11.15	6.20	4.81	4.16	3.78	3.36	*3.13*	**2.95**	**2.84**	**2.76**	**2.70**	**2.66**	**2.63**	**2.57**	**2.54**	**2.51**	**2.49**	**2.48**	**2.45**	**2.43**

Table 19-8. κ-Multipliers for 1-of-1 Interwell Prediction Limits on Means of Order 3 (20 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	5.31	3.27	**2.67**	**2.39**	**2.23**	**2.05**	**1.95**	**1.87**	**1.83**	**1.79**	**1.77**	**1.75**	**1.74**	**1.71**	**1.70**	**1.69**	**1.68**	**1.67**	**1.66**	**1.65**
2	6.26	3.74	**3.01**	**2.67**	**2.47**	**2.25**	**2.13**	**2.05**	**1.99**	**1.95**	**1.92**	**1.90**	**1.88**	**1.86**	**1.84**	**1.83**	**1.82**	**1.81**	**1.79**	**1.78**
3	6.82	4.01	**3.21**	**2.83**	**2.61**	**2.37**	**2.24**	**2.14**	**2.08**	**2.04**	**2.01**	**1.98**	**1.97**	**1.94**	**1.92**	**1.90**	**1.89**	**1.88**	**1.87**	**1.86**
4	7.22	4.21	3.35	**2.95**	**2.71**	**2.46**	**2.32**	**2.21**	**2.15**	**2.10**	**2.07**	**2.04**	**2.02**	**1.99**	**1.97**	**1.96**	**1.95**	**1.94**	**1.92**	**1.91**
5	7.52	4.36	3.45	**3.03**	**2.79**	**2.52**	**2.38**	**2.27**	**2.20**	**2.15**	**2.12**	**2.09**	**2.07**	**2.04**	**2.02**	**2.00**	**1.99**	**1.98**	**1.96**	**1.95**
8	8.14	4.67	3.68	*3.22*	**2.95**	**2.66**	**2.50**	**2.38**	**2.30**	**2.25**	**2.21**	**2.18**	**2.16**	**2.13**	**2.10**	**2.08**	**2.07**	**2.06**	**2.04**	**2.03**
12	8.66	4.93	3.87	*3.38*	**3.09**	**2.77**	**2.60**	**2.47**	**2.39**	**2.34**	**2.29**	**2.26**	**2.24**	**2.20**	**2.18**	**2.16**	**2.14**	**2.13**	**2.11**	**2.10**
16	9.02	5.11	4.00	3.49	**3.19**	**2.86**	**2.68**	**2.54**	**2.45**	**2.40**	**2.35**	**2.32**	**2.29**	**2.25**	**2.23**	**2.21**	**2.19**	**2.18**	**2.16**	**2.14**
20	9.30	5.25	4.11	3.57	*3.26*	**2.92**	**2.73**	**2.59**	**2.50**	**2.44**	**2.40**	**2.36**	**2.33**	**2.29**	**2.27**	**2.25**	**2.23**	**2.22**	**2.17**	**2.18**
30	9.79	5.50	4.29	3.72	*3.40*	**3.03**	**2.83**	**2.68**	**2.59**	**2.52**	**2.48**	**2.44**	**2.41**	**2.37**	**2.34**	**2.31**	**2.30**	**2.28**	**2.26**	**2.24**
40	10.12	5.68	4.42	3.83	3.49	**3.11**	**2.90**	**2.75**	**2.65**	**2.58**	**2.53**	**2.49**	**2.46**	**2.42**	**2.39**	**2.36**	**2.34**	**2.33**	**2.31**	**2.29**
50	10.38	5.81	4.52	3.91	3.56	**3.17**	**2.96**	**2.80**	**2.70**	**2.63**	**2.57**	**2.53**	**2.50**	**2.46**	**2.42**	**2.40**	**2.38**	**2.37**	**2.34**	**2.32**
60	10.58	5.91	4.59	3.98	3.62	*3.22*	**3.00**	**2.84**	**2.73**	**2.66**	**2.61**	**2.57**	**2.54**	**2.49**	**2.45**	**2.43**	**2.41**	**2.40**	**2.37**	**2.35**
75	10.83	6.04	4.69	4.06	3.69	*3.28*	**3.06**	**2.89**	**2.78**	**2.71**	**2.65**	**2.61**	**2.58**	**2.53**	**2.49**	**2.47**	**2.45**	**2.43**	**2.40**	**2.38**
100	11.15	6.20	4.81	4.16	3.78	*3.36*	**3.13**	**2.95**	**2.84**	**2.76**	**2.70**	**2.66**	**2.63**	**2.57**	**2.54**	**2.51**	**2.49**	**2.48**	**2.45**	**2.43**
125	11.38	6.33	4.90	4.24	3.85	*3.42*	**3.18**	**3.00**	**2.89**	**2.81**	**2.75**	**2.70**	**2.67**	**2.61**	**2.58**	**2.55**	**2.53**	**2.51**	**2.48**	**2.46**
150	11.58	6.43	4.98	4.30	3.91	*3.47*	*3.22*	**3.04**	**2.92**	**2.84**	**2.78**	**2.73**	**2.70**	**2.64**	**2.60**	**2.58**	**2.56**	**2.54**	**2.51**	**2.49**
175	11.74	6.52	5.04	4.35	3.95	*3.51*	*3.26*	**3.07**	**2.95**	**2.87**	**2.81**	**2.76**	**2.72**	**2.67**	**2.63**	**2.60**	**2.58**	**2.56**	**2.53**	**2.51**
200	11.88	6.59	5.10	4.40	3.99	3.54	*3.29*	**3.10**	**2.98**	**2.90**	**2.83**	**2.78**	**2.75**	**2.69**	**2.65**	**2.62**	**2.60**	**2.58**	**2.55**	**2.53**

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Table 19-8. κ-Multipliers for 1-of-1 Interwell Prediction Limits on Means of Order 3 (20 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	6.26	3.74	**3.01**	**2.67**	**2.47**	**2.25**	**2.13**	**2.05**	**1.99**	**1.95**	**1.92**	**1.90**	**1.88**	**1.86**	**1.84**	**1.83**	**1.82**	**1.81**	**1.79**	**1.78**
2	7.22	4.21	**3.35**	**2.95**	**2.71**	**2.46**	**2.32**	**2.21**	**2.15**	**2.10**	**2.07**	**2.04**	**2.02**	**1.99**	**1.97**	**1.96**	**1.95**	**1.94**	**1.92**	**1.91**
3	7.76	4.48	*3.54*	**3.11**	**2.85**	**2.57**	**2.42**	**2.31**	**2.24**	**2.19**	**2.15**	**2.13**	**2.10**	**2.07**	**2.05**	**2.03**	**2.02**	**2.01**	**1.99**	**1.98**
4	8.14	4.67	3.68	**3.22**	**2.95**	**2.66**	**2.50**	**2.38**	**2.30**	**2.25**	**2.21**	**2.18**	**2.16**	**2.13**	**2.10**	**2.08**	**2.07**	**2.06**	**2.04**	**2.03**
5	8.43	4.81	3.78	**3.31**	**3.03**	**2.72**	**2.56**	**2.43**	**2.35**	**2.30**	**2.26**	**2.23**	**2.20**	**2.17**	**2.14**	**2.12**	**2.11**	**2.10**	**2.08**	**2.07**
8	9.02	5.11	4.00	*3.49*	**3.19**	**2.86**	**2.68**	**2.54**	**2.45**	**2.40**	**2.35**	**2.32**	**2.29**	**2.25**	**2.23**	**2.21**	**2.19**	**2.18**	**2.16**	**2.14**
12	9.52	5.37	4.19	3.64	**3.32**	**2.97**	**2.78**	**2.63**	**2.54**	**2.48**	**2.43**	**2.40**	**2.37**	**2.31**	**2.30**	**2.28**	**2.26**	**2.25**	**2.22**	**2.21**
16	9.86	5.54	4.32	3.75	**3.42**	**3.05**	**2.85**	**2.70**	**2.60**	**2.54**	**2.49**	**2.45**	**2.42**	**2.38**	**2.35**	**2.33**	**2.31**	**2.29**	**2.27**	**2.25**
20	10.12	5.68	4.42	3.83	*3.49*	**3.11**	**2.90**	**2.75**	**2.65**	**2.58**	**2.53**	**2.49**	**2.46**	**2.42**	**2.39**	**2.36**	**2.34**	**2.33**	**2.31**	**2.29**
30	10.58	5.91	4.59	3.98	*3.62*	**3.22**	**3.00**	**2.84**	**2.73**	**2.66**	**2.61**	**2.57**	**2.54**	**2.49**	**2.45**	**2.43**	**2.41**	**2.40**	**2.37**	**2.35**
40	10.90	6.08	4.72	4.08	3.71	**3.30**	**3.07**	**2.90**	**2.79**	**2.72**	**2.66**	**2.62**	**2.59**	**2.54**	**2.50**	**2.48**	**2.46**	**2.44**	**2.41**	**2.39**
50	11.15	6.20	4.81	4.16	3.78	**3.36**	**3.13**	**2.95**	**2.84**	**2.76**	**2.70**	**2.66**	**2.63**	**2.57**	**2.54**	**2.51**	**2.49**	**2.48**	**2.45**	**2.43**
60	11.34	6.31	4.89	4.22	3.84	**3.41**	**3.17**	**2.99**	**2.88**	**2.80**	**2.74**	**2.69**	**2.66**	**2.61**	**2.57**	**2.54**	**2.52**	**2.50**	**2.47**	**2.45**
75	11.58	6.43	4.98	4.30	3.91	*3.47*	**3.22**	**3.04**	**2.92**	**2.84**	**2.78**	**2.73**	**2.70**	**2.64**	**2.60**	**2.58**	**2.56**	**2.54**	**2.51**	**2.49**
100	11.88	6.59	5.10	4.40	3.99	*3.54*	**3.29**	**3.10**	**2.98**	**2.90**	**2.83**	**2.78**	**2.75**	**2.69**	**2.65**	**2.62**	**2.60**	**2.58**	**2.55**	**2.53**
125	12.10	6.71	5.19	4.48	4.06	*3.60*	**3.34**	**3.15**	**3.02**	**2.94**	**2.87**	**2.82**	**2.79**	**2.73**	**2.69**	**2.66**	**2.63**	**2.62**	**2.58**	**2.56**
150	12.29	6.80	5.26	4.54	4.12	*3.64*	**3.39**	**3.19**	**3.06**	**2.97**	**2.91**	**2.86**	**2.82**	**2.76**	**2.72**	**2.69**	**2.66**	**2.64**	**2.61**	**2.59**
175	12.44	6.89	5.32	4.59	4.16	*3.68*	**3.42**	**3.22**	**3.09**	**3.00**	**2.93**	**2.88**	**2.84**	**2.78**	**2.74**	**2.71**	**2.68**	**2.67**	**2.63**	**2.61**
200	12.57	6.95	5.37	4.63	4.20	*3.69*	**3.45**	**3.25**	**3.12**	**3.03**	**2.96**	**2.91**	**2.87**	**2.80**	**2.76**	**2.73**	**2.70**	**2.69**	**2.65**	**2.63**

Table 19-8. κ-Multipliers for 1-of-1 Interwell Prediction Limits on Means of Order 3 (40 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	5.59	3.33	**2.70**	**2.41**	**2.24**	**2.05**	**1.95**	**1.88**	**1.83**	**1.79**	**1.77**	**1.75**	**1.74**	**1.71**	**1.70**	**1.69**	**1.68**	**1.67**	**1.66**	**1.65**
2	6.75	3.85	*3.05*	**2.69**	**2.49**	**2.26**	**2.14**	**2.05**	**1.99**	**1.95**	**1.92**	**1.90**	**1.88**	**1.86**	**1.84**	**1.83**	**1.82**	**1.81**	**1.79**	**1.78**
3	7.45	4.16	3.27	**2.86**	**2.63**	**2.38**	**2.25**	**2.15**	**2.09**	**2.04**	**2.01**	**1.99**	**1.97**	**1.94**	**1.92**	**1.90**	**1.89**	**1.88**	**1.87**	**1.86**
4	7.95	4.38	3.42	**2.98**	**2.74**	**2.47**	**2.32**	**2.22**	**2.15**	**2.10**	**2.07**	**2.05**	**2.02**	**2.00**	**1.97**	**1.96**	**1.95**	**1.94**	**1.92**	**1.91**
5	8.33	4.55	3.54	*3.08*	**2.82**	**2.53**	**2.38**	**2.27**	**2.20**	**2.15**	**2.12**	**2.09**	**2.07**	**2.04**	**2.02**	**2.00**	**1.99**	**1.98**	**1.96**	**1.95**
8	9.15	4.91	3.78	3.28	**2.99**	**2.67**	**2.51**	**2.38**	**2.31**	**2.25**	**2.21**	**2.19**	**2.16**	**2.13**	**2.10**	**2.09**	**2.07**	**2.06**	**2.04**	**2.03**
12	9.83	5.22	4.00	3.45	**3.13**	**2.79**	**2.61**	**2.48**	**2.40**	**2.34**	**2.30**	**2.27**	**2.24**	**2.20**	**2.18**	**2.16**	**2.14**	**2.13**	**2.11**	**2.10**
16	10.31	5.44	4.15	3.57	*3.24*	**2.88**	**2.69**	**2.55**	**2.46**	**2.40**	**2.35**	**2.32**	**2.29**	**2.26**	**2.23**	**2.21**	**2.19**	**2.18**	**2.16**	**2.14**
20	10.67	5.60	4.26	3.66	3.32	**2.95**	**2.75**	**2.60**	**2.51**	**2.45**	**2.40**	**2.36**	**2.34**	**2.30**	**2.27**	**2.25**	**2.23**	**2.22**	**2.19**	**2.18**
30	11.32	5.90	4.47	3.83	3.46	*3.06*	**2.85**	**2.70**	**2.60**	**2.53**	**2.48**	**2.44**	**2.41**	**2.37**	**2.34**	**2.32**	**2.30**	**2.28**	**2.26**	**2.20**
40	11.77	6.11	4.62	3.95	3.56	*3.15*	**2.93**	**2.76**	**2.66**	**2.59**	**2.54**	**2.50**	**2.46**	**2.42**	**2.39**	**2.33**	**2.35**	**2.33**	**2.31**	**2.29**
50	12.10	6.27	4.73	4.04	3.64	*3.20*	*2.98*	**2.81**	**2.71**	**2.63**	**2.58**	**2.54**	**2.51**	**2.46**	**2.42**	**2.40**	**2.38**	**2.37**	**2.34**	**2.32**
60	12.38	6.40	4.82	4.11	3.71	*3.27*	*3.03*	**2.85**	**2.74**	**2.67**	**2.61**	**2.57**	**2.54**	**2.49**	**2.46**	**2.43**	**2.41**	**2.40**	**2.37**	**2.34**
75	12.71	6.55	4.93	4.20	3.78	3.33	*3.09*	**2.91**	**2.79**	**2.71**	**2.66**	**2.61**	**2.58**	**2.53**	**2.49**	**2.47**	**2.44**	**2.43**	**2.40**	**2.38**
100	13.12	6.75	5.07	4.31	3.88	3.41	*3.16*	*2.97*	**2.85**	**2.77**	**2.71**	**2.67**	**2.63**	**2.58**	**2.54**	**2.51**	**2.49**	**2.48**	**2.45**	**2.43**
125	13.44	6.90	5.18	4.40	3.96	3.47	*3.22*	*3.02*	**2.90**	**2.81**	**2.75**	**2.71**	**2.67**	**2.62**	**2.58**	**2.55**	**2.53**	**2.51**	**2.48**	**2.46**
150	13.70	7.02	5.26	4.47	4.02	3.53	*3.26*	*3.06*	**2.94**	**2.85**	**2.79**	**2.74**	**2.70**	**2.65**	**2.61**	**2.58**	**2.56**	**2.52**	**2.51**	**2.49**
175	13.91	7.12	5.31	4.53	4.07	3.57	*3.30*	*3.10*	*2.97*	**2.88**	**2.82**	**2.77**	**2.73**	**2.67**	**2.63**	**2.60**	**2.58**	**2.56**	**2.53**	**2.51**
200	14.09	7.21	5.40	4.58	4.12	3.61	3.33	*3.13*	*3.00*	**2.91**	**2.84**	**2.79**	**2.75**	**2.69**	**2.65**	**2.62**	**2.60**	**2.58**	**2.54**	**2.53**

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Table 19-8. κ-Multipliers for 1-of-1 Interwell Prediction Limits on Means of Order 3 (40 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	6.75	3.85	**3.05**	**2.69**	**2.49**	**2.26**	**2.14**	**2.05**	**1.99**	**1.95**	**1.92**	**1.90**	**1.88**	**1.86**	**1.84**	**1.83**	**1.82**	**1.81**	**1.79**	**1.78**
2	7.95	4.38	3.42	**2.98**	**2.74**	**2.47**	**2.32**	**2.22**	**2.15**	**2.10**	**2.07**	**2.05**	**2.02**	**2.00**	**1.97**	**1.96**	**1.95**	**1.94**	**1.92**	**1.91**
3	8.65	4.69	3.63	**3.15**	**2.88**	**2.59**	**2.43**	**2.32**	**2.24**	**2.19**	**2.16**	**2.13**	**2.11**	**2.07**	**2.05**	**2.03**	**2.02**	**2.01**	**1.99**	**1.98**
4	9.15	4.91	3.78	*3.28*	**2.99**	**2.67**	**2.51**	**2.38**	**2.31**	**2.25**	**2.21**	**2.19**	**2.16**	**2.13**	**2.10**	**2.09**	**2.07**	**2.06**	**2.04**	**2.03**
5	9.52	5.08	3.90	*3.37*	**3.07**	**2.74**	**2.57**	**2.44**	**2.36**	**2.30**	**2.26**	**2.23**	**2.20**	**2.17**	**2.14**	**2.13**	**2.11**	**2.10**	**2.08**	**2.07**
8	10.31	5.44	4.15	3.57	*3.24*	**2.88**	**2.69**	**2.55**	**2.46**	**2.40**	**2.35**	**2.32**	**2.29**	**2.26**	**2.23**	**2.21**	**2.19**	**2.18**	**2.16**	**2.14**
12	10.96	5.74	4.36	3.74	*3.38*	**3.00**	**2.79**	**2.64**	**2.55**	**2.48**	**2.44**	**2.40**	**2.37**	**2.33**	**2.30**	**2.28**	**2.26**	**2.25**	**2.22**	**2.21**
16	11.42	5.95	4.51	3.85	3.49	**3.08**	**2.87**	**2.71**	**2.61**	**2.54**	**2.49**	**2.45**	**2.42**	**2.38**	**2.35**	**2.33**	**2.31**	**2.30**	**2.26**	**2.25**
20	11.77	6.11	4.62	3.95	3.56	**3.15**	**2.93**	**2.76**	**2.66**	**2.59**	**2.54**	**2.50**	**2.46**	**2.42**	**2.39**	**2.33**	**2.35**	**2.33**	**2.31**	**2.29**
30	12.38	6.40	4.82	4.11	3.71	*3.27*	**3.03**	**2.85**	**2.74**	**2.67**	**2.61**	**2.57**	**2.54**	**2.49**	**2.46**	**2.43**	**2.41**	**2.40**	**2.37**	**2.34**
40	12.80	6.60	4.96	4.22	3.81	*3.35*	**3.10**	**2.92**	**2.81**	**2.73**	**2.67**	**2.62**	**2.59**	**2.54**	**2.50**	**2.48**	**2.46**	**2.44**	**2.41**	**2.39**
50	13.12	6.75	5.07	4.31	3.88	*3.41*	**3.16**	**2.97**	**2.85**	**2.77**	**2.71**	**2.67**	**2.63**	**2.58**	**2.54**	**2.51**	**2.49**	**2.48**	**2.45**	**2.43**
60	13.38	6.87	5.16	4.38	3.94	*3.46*	*3.20*	**3.01**	**2.89**	**2.81**	**2.75**	**2.70**	**2.66**	**2.61**	**2.57**	**2.54**	**2.52**	**2.50**	**2.47**	**2.45**
75	13.70	7.02	5.26	4.47	4.02	3.53	*3.26*	**3.06**	**2.94**	**2.85**	**2.79**	**2.74**	**2.70**	**2.65**	**2.61**	**2.58**	**2.56**	**2.52**	**2.51**	**2.46**
100	14.09	7.21	5.40	4.58	4.12	3.61	*3.33*	**3.13**	**3.00**	**2.91**	**2.84**	**2.79**	**2.75**	**2.69**	**2.65**	**2.62**	**2.60**	**2.58**	**2.54**	**2.47**
125	14.39	7.35	5.50	4.66	4.19	3.67	*3.39*	**3.18**	**3.04**	**2.95**	**2.88**	**2.83**	**2.79**	**2.73**	**2.69**	**2.66**	**2.64**	**2.62**	**2.58**	**2.56**
150	14.64	7.47	5.58	4.73	4.25	3.72	*3.43*	*3.22*	**3.08**	**2.99**	**2.92**	**2.86**	**2.82**	**2.76**	**2.72**	**2.69**	**2.66**	**2.64**	**2.57**	**2.59**
175	14.84	7.56	5.65	4.79	4.30	3.76	*3.47*	*3.25*	**3.11**	**3.01**	**2.94**	**2.89**	**2.85**	**2.77**	**2.74**	**2.71**	**2.69**	**2.67**	**2.63**	**2.61**
200	15.01	7.65	5.71	4.84	4.34	3.80	*3.50*	*3.28*	**3.14**	**3.04**	**2.97**	**2.91**	**2.87**	**2.81**	**2.76**	**2.73**	**2.71**	**2.69**	**2.65**	**2.60**

Table 19-8. κ-Multipliers for 1-of-1 Interwell Prediction Limits on Means of Order 3 (40 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	7.95	4.38	**3.42**	**2.98**	**2.74**	**2.47**	**2.32**	**2.22**	**2.15**	**2.10**	**2.07**	**2.05**	**2.02**	**2.00**	**1.97**	**1.96**	**1.95**	**1.94**	**1.92**	**1.91**
2	9.15	4.91	3.78	**3.28**	**2.99**	**2.67**	**2.51**	**2.38**	**2.31**	**2.25**	**2.21**	**2.19**	**2.16**	**2.13**	**2.10**	**2.09**	**2.07**	**2.06**	**2.04**	**2.03**
3	9.83	5.22	4.00	**3.45**	**3.13**	**2.79**	**2.61**	**2.48**	**2.40**	**2.34**	**2.30**	**2.27**	**2.24**	**2.20**	**2.18**	**2.16**	**2.14**	**2.13**	**2.11**	**2.10**
4	10.31	5.44	4.15	*3.57*	**3.24**	**2.88**	**2.69**	**2.55**	**2.46**	**2.40**	**2.35**	**2.32**	**2.29**	**2.26**	**2.23**	**2.21**	**2.19**	**2.18**	**2.16**	**2.14**
5	10.67	5.60	4.26	3.66	**3.32**	**2.95**	**2.75**	**2.60**	**2.51**	**2.45**	**2.40**	**2.36**	**2.34**	**2.30**	**2.27**	**2.25**	**2.23**	**2.22**	**2.19**	**2.18**
8	11.42	5.95	4.51	3.85	*3.49*	**3.08**	**2.87**	**2.71**	**2.61**	**2.54**	**2.49**	**2.45**	**2.42**	**2.38**	**2.35**	**2.33**	**2.31**	**2.30**	**2.26**	**2.20**
12	12.04	6.24	4.69	4.02	*3.63*	**3.20**	**2.97**	**2.80**	**2.69**	**2.62**	**2.57**	**2.53**	**2.50**	**2.45**	**2.42**	**2.39**	**2.38**	**2.36**	**2.33**	**2.32**
16	12.48	6.44	4.85	4.14	3.73	**3.28**	**3.05**	**2.87**	**2.76**	**2.68**	**2.63**	**2.58**	**2.55**	**2.50**	**2.47**	**2.44**	**2.42**	**2.41**	**2.38**	**2.32**
20	12.80	6.60	4.96	4.22	3.81	**3.35**	**3.10**	**2.92**	**2.81**	**2.73**	**2.67**	**2.62**	**2.59**	**2.54**	**2.50**	**2.48**	**2.46**	**2.44**	**2.41**	**2.39**
30	13.38	6.87	5.16	4.38	3.94	*3.46*	**3.20**	**3.01**	**2.89**	**2.81**	**2.75**	**2.70**	**2.66**	**2.61**	**2.57**	**2.54**	**2.52**	**2.50**	**2.47**	**2.46**
40	13.79	7.06	5.29	4.50	4.04	*3.54*	**3.28**	**3.08**	**2.95**	**2.86**	**2.80**	**2.75**	**2.71**	**2.66**	**2.62**	**2.58**	**2.57**	**2.55**	**2.52**	**2.50**
50	14.09	7.21	5.40	4.58	4.12	*3.61*	**3.33**	**3.13**	**3.00**	**2.91**	**2.84**	**2.79**	**2.75**	**2.69**	**2.65**	**2.62**	**2.60**	**2.58**	**2.54**	**2.53**
60	14.34	7.32	5.48	4.65	4.18	*3.66*	**3.38**	**3.17**	**3.03**	**2.94**	**2.87**	**2.82**	**2.78**	**2.72**	**2.68**	**2.65**	**2.63**	**2.61**	**2.58**	**2.56**
75	14.64	7.47	5.58	4.73	4.25	*3.72*	**3.43**	**3.22**	**3.08**	**2.99**	**2.92**	**2.86**	**2.82**	**2.76**	**2.72**	**2.69**	**2.66**	**2.64**	**2.61**	**2.59**
100	15.01	7.65	5.71	4.84	4.34	3.80	*3.50*	**3.28**	**3.14**	**3.04**	**2.97**	**2.91**	**2.87**	**2.81**	**2.76**	**2.73**	**2.71**	**2.69**	**2.65**	**2.63**
125	15.30	7.78	5.81	4.92	4.41	3.86	*3.55*	**3.33**	**3.18**	**3.08**	**3.01**	**2.95**	**2.91**	**2.84**	**2.80**	**2.77**	**2.74**	**2.72**	**2.68**	**2.66**
150	15.48	7.90	5.89	4.99	4.47	3.90	*3.60*	**3.37**	**3.22**	**3.12**	**3.04**	**2.99**	**2.94**	**2.87**	**2.83**	**2.79**	**2.77**	**2.75**	**2.71**	**2.68**
175	15.73	7.99	5.96	5.04	4.52	3.95	*3.63*	**3.40**	**3.25**	**3.15**	**3.07**	**3.01**	**2.97**	**2.90**	**2.85**	**2.82**	**2.79**	**2.77**	**2.73**	**2.71**
200	15.89	8.07	6.02	5.09	4.56	3.98	*3.67*	**3.43**	**3.28**	**3.17**	**3.09**	**3.04**	**2.99**	**2.92**	**2.87**	**2.84**	**2.81**	**2.79**	**2.75**	**2.73**

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Table 19-9. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Means of Order 3 (1 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	0.67	0.53	0.46	0.42	0.40	0.37	0.35	0.34	0.33	0.32	0.31	0.31	0.31	0.30	0.30	0.29	0.29	0.29	0.29	0.29
2	0.95	0.75	0.67	0.62	0.59	0.55	0.53	0.51	0.50	0.49	0.48	0.48	0.47	0.47	0.46	0.46	0.45	0.45	0.45	0.45
3	1.11	0.88	0.79	0.73	0.69	0.65	0.62	0.60	0.59	0.58	0.57	0.56	0.56	0.55	0.55	0.54	0.54	0.54	0.53	0.53
4	1.22	0.97	0.86	0.80	0.77	0.72	0.69	0.67	0.65	0.64	0.63	0.62	0.62	0.61	0.61	0.60	0.60	0.60	0.59	0.59
5	1.30	1.04	0.92	0.86	0.82	0.77	0.74	0.71	0.70	0.68	0.68	0.67	0.66	0.65	0.65	0.64	0.64	0.64	0.63	0.63
8	1.47	1.17	1.05	0.97	0.93	0.87	0.84	0.81	0.79	0.78	0.77	0.76	0.75	0.74	0.74	0.73	0.73	0.72	0.72	0.71
12	1.62	1.28	1.15	1.07	1.02	0.95	0.92	0.89	0.87	0.85	0.84	0.83	0.83	0.82	0.81	0.80	0.80	0.79	0.79	0.78
16	1.72	1.36	1.21	1.13	1.08	1.01	0.97	0.94	0.92	0.90	0.89	0.88	0.88	0.86	0.86	0.85	0.85	0.84	0.84	0.83
20	1.79	1.42	1.27	1.18	1.13	1.06	1.02	0.98	0.96	0.94	0.93	0.92	0.91	0.90	0.89	0.89	0.88	0.88	0.87	0.87
30	1.92	1.52	1.36	1.27	1.21	1.13	1.09	1.05	1.03	1.01	1.00	0.99	0.98	0.97	0.96	0.95	0.95	0.94	0.93	0.93
40	2.02	1.59	1.42	1.33	1.26	1.19	1.14	1.10	1.08	1.06	1.05	1.03	1.03	1.01	1.00	1.00	0.99	0.98	0.98	0.97
50	2.09	1.65	1.47	1.37	1.31	1.23	1.18	1.14	1.11	1.09	1.08	1.07	1.06	1.05	1.04	1.03	1.02	1.02	1.01	1.00
60	2.14	1.69	1.51	1.41	1.34	1.26	1.21	1.17	1.14	1.12	1.11	1.10	1.09	1.07	1.06	1.06	1.05	1.04	1.04	1.03
75	2.21	1.74	1.56	1.45	1.38	1.30	1.25	1.21	1.18	1.16	1.14	1.13	1.12	1.11	1.10	1.09	1.08	1.08	1.07	1.06
100	2.29	1.81	1.62	1.51	1.44	1.35	1.30	1.25	1.22	1.20	1.19	1.17	1.16	1.15	1.14	1.13	1.12	1.12	1.11	1.10
125	2.36	1.86	1.66	1.55	1.48	1.39	1.33	1.29	1.26	1.24	1.22	1.21	1.20	1.18	1.17	1.16	1.15	1.15	1.14	1.13
150	2.41	1.90	1.70	1.58	1.51	1.42	1.36	1.32	1.29	1.26	1.25	1.23	1.22	1.21	1.19	1.18	1.18	1.17	1.16	1.15
175	2.45	1.93	1.73	1.61	1.53	1.44	1.38	1.34	1.31	1.29	1.27	1.25	1.24	1.23	1.21	1.20	1.20	1.19	1.18	1.17
200	2.49	1.96	1.75	1.63	1.56	1.46	1.41	1.36	1.33	1.30	1.29	1.27	1.26	1.24	1.23	1.22	1.22	1.21	1.20	1.19

Table 19-9. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Means of Order 3 (1 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	0.95	0.75	0.67	0.62	0.59	0.55	0.53	0.51	0.50	0.49	0.48	0.48	0.47	0.47	0.46	0.46	0.45	0.45	0.45	0.45
2	1.22	0.97	0.86	0.80	0.77	0.72	0.69	0.67	0.65	0.64	0.63	0.62	0.62	0.61	0.61	0.60	0.60	0.60	0.59	0.59
3	1.37	1.09	0.97	0.91	0.86	0.81	0.78	0.75	0.73	0.72	0.71	0.70	0.70	0.69	0.68	0.68	0.67	0.67	0.67	0.66
4	1.47	1.17	1.05	0.97	0.93	0.87	0.84	0.81	0.79	0.78	0.77	0.76	0.75	0.74	0.74	0.73	0.73	0.72	0.72	0.71
5	1.55	1.23	1.10	1.03	0.98	0.92	0.88	0.85	0.83	0.82	0.81	0.80	0.79	0.78	0.78	0.77	0.77	0.76	0.76	0.75
8	1.72	1.36	1.21	1.13	1.08	1.01	0.97	0.94	0.92	0.90	0.89	0.88	0.88	0.86	0.86	0.85	0.85	0.84	0.84	0.83
12	1.85	1.47	1.31	1.22	1.16	1.09	1.05	1.01	0.99	0.97	0.96	0.95	0.94	0.93	0.92	0.92	0.91	0.91	0.90	0.89
16	1.94	1.54	1.37	1.28	1.22	1.15	1.10	1.06	1.04	1.02	1.01	1.00	0.99	0.98	0.97	0.96	0.96	0.95	0.94	0.94
20	2.02	1.59	1.42	1.33	1.26	1.19	1.14	1.10	1.08	1.06	1.05	1.03	1.03	1.01	1.00	1.00	0.99	0.98	0.98	0.97
30	2.14	1.69	1.51	1.41	1.34	1.26	1.21	1.17	1.14	1.12	1.11	1.10	1.09	1.07	1.06	1.06	1.05	1.04	1.04	1.03
40	2.23	1.76	1.57	1.46	1.40	1.31	1.26	1.22	1.19	1.17	1.15	1.14	1.13	1.12	1.10	1.10	1.09	1.08	1.08	1.07
50	2.29	1.81	1.62	1.51	1.44	1.35	1.30	1.25	1.22	1.20	1.19	1.17	1.16	1.15	1.14	1.13	1.12	1.12	1.11	1.10
60	2.35	1.85	1.65	1.54	1.47	1.38	1.33	1.28	1.25	1.23	1.21	1.20	1.19	1.17	1.16	1.15	1.15	1.14	1.13	1.12
75	2.41	1.90	1.70	1.58	1.51	1.42	1.36	1.32	1.29	1.26	1.25	1.23	1.22	1.21	1.19	1.18	1.18	1.17	1.16	1.15
100	2.49	1.96	1.75	1.63	1.56	1.46	1.41	1.36	1.33	1.30	1.29	1.27	1.26	1.24	1.23	1.22	1.22	1.21	1.20	1.19
125	2.55	2.01	1.79	1.67	1.60	1.50	1.44	1.39	1.36	1.34	1.32	1.30	1.29	1.27	1.26	1.25	1.24	1.24	1.23	1.22
150	2.60	2.05	1.83	1.71	1.63	1.53	1.47	1.42	1.39	1.36	1.34	1.33	1.32	1.30	1.29	1.28	1.27	1.26	1.25	1.24
175	2.64	2.08	1.86	1.73	1.65	1.55	1.49	1.44	1.41	1.38	1.36	1.35	1.34	1.32	1.31	1.30	1.29	1.28	1.27	1.26
200	2.68	2.11	1.88	1.75	1.67	1.57	1.51	1.46	1.43	1.40	1.38	1.37	1.36	1.34	1.32	1.31	1.30	1.30	1.29	1.28

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Table 19-9. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Means of Order 3 (1 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	1.22	0.97	0.86	0.80	0.77	0.72	0.69	0.67	0.65	0.64	0.63	0.62	0.62	0.61	0.61	0.60	0.60	0.60	0.59	0.59
2	1.47	1.17	1.05	0.97	0.93	0.87	0.84	0.81	0.79	0.78	0.77	0.76	0.75	0.74	0.74	0.73	0.73	0.72	0.72	0.71
3	1.62	1.28	1.15	1.07	1.02	0.95	0.92	0.89	0.87	0.85	0.84	0.83	0.83	0.82	0.81	0.80	0.80	0.79	0.79	0.78
4	1.72	1.36	1.21	1.13	1.08	1.01	0.97	0.94	0.92	0.90	0.89	0.88	0.88	0.86	0.86	0.85	0.85	0.84	0.84	0.83
5	1.79	1.42	1.27	1.18	1.13	1.06	1.02	0.98	0.96	0.94	0.93	0.92	0.91	0.90	0.89	0.89	0.88	0.88	0.87	0.87
8	1.94	1.54	1.37	1.28	1.22	1.15	1.10	1.06	1.04	1.02	1.01	1.00	0.99	0.98	0.97	0.96	0.96	0.95	0.94	0.94
12	2.07	1.64	1.46	1.36	1.30	1.22	1.17	1.13	1.11	1.09	1.07	1.06	1.05	1.04	1.03	1.02	1.02	1.01	1.00	1.00
16	2.16	1.71	1.52	1.42	1.35	1.27	1.22	1.18	1.15	1.13	1.12	1.11	1.10	1.08	1.07	1.06	1.06	1.05	1.04	1.04
20	2.23	1.76	1.57	1.46	1.40	1.31	1.26	1.22	1.19	1.17	1.15	1.14	1.13	1.12	1.10	1.10	1.09	1.08	1.08	1.07
30	2.35	1.85	1.65	1.54	1.47	1.38	1.33	1.28	1.25	1.23	1.21	1.20	1.19	1.17	1.16	1.15	1.15	1.14	1.13	1.12
40	2.43	1.91	1.71	1.59	1.52	1.43	1.37	1.33	1.29	1.27	1.26	1.24	1.23	1.21	1.20	1.19	1.19	1.18	1.17	1.16
50	2.49	1.96	1.75	1.63	1.56	1.46	1.41	1.36	1.33	1.30	1.29	1.27	1.26	1.24	1.23	1.22	1.22	1.21	1.20	1.19
60	2.54	2.00	1.79	1.67	1.59	1.49	1.43	1.39	1.35	1.33	1.31	1.30	1.29	1.27	1.26	1.25	1.24	1.23	1.22	1.21
75	2.60	2.05	1.83	1.71	1.63	1.53	1.47	1.42	1.39	1.36	1.34	1.33	1.32	1.30	1.29	1.28	1.27	1.26	1.25	1.24
100	2.68	2.11	1.88	1.75	1.67	1.57	1.51	1.46	1.43	1.40	1.38	1.37	1.36	1.34	1.32	1.31	1.30	1.30	1.29	1.28
125	2.74	2.15	1.92	1.79	1.71	1.61	1.54	1.49	1.46	1.43	1.41	1.40	1.38	1.37	1.35	1.34	1.33	1.33	1.31	1.30
150	2.79	2.19	1.95	1.82	1.74	1.63	1.57	1.52	1.48	1.46	1.44	1.42	1.41	1.39	1.37	1.36	1.35	1.35	1.33	1.33
175	2.82	2.22	1.98	1.85	1.76	1.66	1.59	1.54	1.50	1.48	1.46	1.44	1.43	1.41	1.39	1.38	1.37	1.37	1.35	1.34
200	2.86	2.25	2.00	1.87	1.78	1.68	1.61	1.56	1.52	1.49	1.47	1.46	1.44	1.42	1.41	1.40	1.39	1.38	1.37	1.36

Table 19-9. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Means of Order 3 (2 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	1.04	0.80	0.70	0.64	0.61	0.56	0.54	0.52	0.50	0.49	0.49	0.48	0.47	0.47	0.46	0.46	0.46	0.45	0.45	0.45
2	1.36	1.04	0.91	0.84	0.79	0.73	0.70	0.67	0.66	0.64	0.64	0.63	0.62	0.61	0.61	0.60	0.60	0.60	0.59	0.59
3	1.55	1.17	1.02	0.94	0.89	0.83	0.79	0.76	0.74	0.73	0.72	0.71	0.70	0.69	0.69	0.68	0.68	0.67	0.67	0.66
4	1.68	1.27	1.11	1.02	0.96	0.89	0.85	0.82	0.80	0.78	0.77	0.76	0.76	0.75	0.74	0.73	0.73	0.73	0.72	0.72
5	1.78	1.34	1.17	1.07	1.01	0.94	0.90	0.87	0.84	0.83	0.82	0.81	0.80	0.79	0.78	0.77	0.77	0.77	0.76	0.75
8	1.99	1.49	1.29	1.19	1.12	1.04	0.99	0.96	0.93	0.91	0.90	0.89	0.88	0.87	0.86	0.85	0.85	0.84	0.84	0.83
12	2.17	1.61	1.40	1.29	1.21	1.12	1.07	1.03	1.00	0.99	0.97	0.96	0.95	0.94	0.93	0.92	0.91	0.91	0.90	0.90
16	2.29	1.70	1.47	1.35	1.28	1.18	1.13	1.08	1.06	1.03	1.02	1.01	1.00	0.98	0.97	0.97	0.96	0.95	0.95	0.94
20	2.38	1.76	1.53	1.40	1.32	1.23	1.17	1.12	1.09	1.07	1.06	1.04	1.03	1.02	1.01	1.00	0.99	0.99	0.98	0.97
30	2.54	1.88	1.63	1.49	1.41	1.30	1.24	1.19	1.16	1.14	1.12	1.11	1.10	1.08	1.07	1.06	1.05	1.05	1.04	1.03
40	2.66	1.96	1.70	1.56	1.47	1.36	1.29	1.24	1.21	1.18	1.17	1.15	1.14	1.12	1.11	1.10	1.09	1.09	1.08	1.07
50	2.74	2.02	1.75	1.60	1.51	1.40	1.33	1.28	1.25	1.22	1.20	1.19	1.17	1.16	1.14	1.13	1.13	1.12	1.11	1.10
60	2.81	2.07	1.79	1.64	1.55	1.43	1.36	1.31	1.27	1.25	1.23	1.21	1.20	1.18	1.17	1.16	1.15	1.15	1.13	1.13
75	2.90	2.13	1.84	1.69	1.59	1.47	1.40	1.35	1.31	1.28	1.26	1.25	1.23	1.21	1.20	1.19	1.18	1.18	1.16	1.16
100	3.00	2.21	1.91	1.75	1.65	1.52	1.45	1.39	1.35	1.33	1.30	1.29	1.27	1.25	1.24	1.23	1.22	1.21	1.20	1.19
125	3.08	2.26	1.96	1.79	1.69	1.56	1.49	1.43	1.39	1.36	1.34	1.32	1.31	1.29	1.27	1.26	1.25	1.24	1.23	1.22
150	3.15	2.31	2.00	1.83	1.72	1.59	1.52	1.46	1.41	1.39	1.36	1.35	1.33	1.31	1.29	1.28	1.27	1.27	1.25	1.25
175	3.20	2.35	2.03	1.86	1.75	1.62	1.54	1.48	1.44	1.41	1.38	1.37	1.35	1.33	1.32	1.30	1.29	1.29	1.27	1.26
200	3.25	2.38	2.06	1.88	1.77	1.64	1.56	1.50	1.46	1.43	1.40	1.39	1.37	1.35	1.33	1.32	1.31	1.30	1.29	1.28

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Table 19-9. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Means of Order 3 (2 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	1.36	1.04	0.91	0.84	0.79	0.73	0.70	0.67	0.66	0.64	0.64	0.63	0.62	0.61	0.61	0.60	0.60	0.60	0.59	0.59
2	1.68	1.27	1.11	1.02	0.96	0.89	0.85	0.82	0.80	0.78	0.77	0.76	0.76	0.75	0.74	0.73	0.73	0.73	0.72	0.72
3	1.86	1.40	1.22	1.12	1.06	0.98	0.94	0.90	0.88	0.86	0.85	0.84	0.83	0.82	0.81	0.81	0.80	0.80	0.79	0.78
4	1.99	1.49	1.29	1.19	1.12	1.04	0.99	0.96	0.93	0.91	0.90	0.89	0.88	0.87	0.86	0.85	0.85	0.84	0.84	0.83
5	2.09	1.56	1.35	1.24	1.17	1.09	1.04	1.00	0.97	0.95	0.94	0.93	0.92	0.91	0.90	0.89	0.89	0.88	0.87	0.87
8	2.29	1.70	1.47	1.35	1.28	1.18	1.13	1.08	1.06	1.03	1.02	1.01	1.00	0.98	0.97	0.97	0.96	0.95	0.95	0.94
12	2.45	1.82	1.57	1.44	1.36	1.26	1.20	1.16	1.12	1.10	1.09	1.07	1.06	1.05	1.04	1.03	1.02	1.02	1.01	1.00
16	2.57	1.90	1.64	1.51	1.42	1.32	1.25	1.21	1.17	1.15	1.13	1.12	1.11	1.09	1.08	1.07	1.06	1.06	1.05	1.04
20	2.66	1.96	1.70	1.56	1.47	1.36	1.29	1.24	1.21	1.18	1.17	1.15	1.14	1.12	1.11	1.10	1.09	1.09	1.08	1.07
30	2.81	2.07	1.79	1.64	1.55	1.43	1.36	1.31	1.27	1.25	1.23	1.21	1.20	1.18	1.17	1.16	1.15	1.15	1.13	1.13
40	2.92	2.15	1.86	1.70	1.60	1.48	1.41	1.36	1.32	1.29	1.27	1.26	1.24	1.22	1.21	1.20	1.19	1.18	1.17	1.16
50	3.00	2.21	1.91	1.75	1.65	1.52	1.45	1.39	1.35	1.33	1.30	1.29	1.27	1.25	1.24	1.23	1.22	1.21	1.20	1.19
60	3.07	2.25	1.95	1.78	1.68	1.55	1.48	1.42	1.38	1.35	1.33	1.31	1.30	1.28	1.27	1.25	1.25	1.24	1.23	1.22
75	3.15	2.31	2.00	1.83	1.72	1.59	1.52	1.46	1.41	1.39	1.36	1.35	1.33	1.31	1.29	1.28	1.27	1.27	1.25	1.25
100	3.25	2.38	2.06	1.88	1.77	1.64	1.56	1.50	1.46	1.43	1.40	1.39	1.37	1.35	1.33	1.32	1.31	1.30	1.29	1.28
125	3.33	2.44	2.10	1.93	1.81	1.68	1.60	1.53	1.49	1.46	1.43	1.42	1.40	1.38	1.36	1.35	1.34	1.33	1.32	1.31
150	3.39	2.48	2.14	1.96	1.85	1.71	1.63	1.56	1.52	1.48	1.46	1.44	1.43	1.40	1.39	1.37	1.36	1.35	1.34	1.33
175	3.44	2.52	2.17	1.99	1.87	1.73	1.65	1.58	1.54	1.51	1.48	1.46	1.45	1.42	1.40	1.39	1.38	1.37	1.36	1.35
200	3.49	2.55	2.20	2.01	1.90	1.75	1.67	1.60	1.56	1.52	1.50	1.48	1.46	1.44	1.42	1.41	1.40	1.39	1.37	1.36

Table 19-9. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Means of Order 3 (2 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	1.68	1.27	1.11	1.02	0.96	0.89	0.85	0.82	0.80	0.78	0.77	0.76	0.76	0.75	0.74	0.73	0.73	0.73	0.72	0.72
2	1.99	1.49	1.29	1.19	1.12	1.04	0.99	0.96	0.93	0.91	0.90	0.89	0.88	0.87	0.86	0.85	0.85	0.84	0.84	0.83
3	2.17	1.61	1.40	1.29	1.21	1.12	1.07	1.03	1.00	0.99	0.97	0.96	0.95	0.94	0.93	0.92	0.91	0.91	0.90	0.90
4	2.29	1.70	1.47	1.35	1.28	1.18	1.13	1.08	1.06	1.03	1.02	1.01	1.00	0.98	0.97	0.97	0.96	0.95	0.95	0.94
5	2.38	1.76	1.53	1.40	1.32	1.23	1.17	1.12	1.09	1.07	1.06	1.04	1.03	1.02	1.01	1.00	0.99	0.99	0.98	0.97
8	2.57	1.90	1.64	1.51	1.42	1.32	1.25	1.21	1.17	1.15	1.13	1.12	1.11	1.09	1.08	1.07	1.06	1.06	1.05	1.04
12	2.73	2.01	1.74	1.60	1.50	1.39	1.33	1.27	1.24	1.21	1.19	1.18	1.17	1.15	1.14	1.13	1.12	1.11	1.10	1.10
16	2.84	2.09	1.81	1.66	1.56	1.44	1.38	1.32	1.28	1.26	1.24	1.22	1.21	1.19	1.18	1.17	1.16	1.15	1.14	1.14
20	2.92	2.15	1.86	1.70	1.60	1.48	1.41	1.36	1.32	1.29	1.27	1.26	1.24	1.22	1.21	1.20	1.19	1.18	1.17	1.16
30	3.07	2.25	1.95	1.78	1.68	1.55	1.48	1.42	1.38	1.35	1.33	1.31	1.30	1.28	1.27	1.25	1.25	1.24	1.23	1.22
40	3.17	2.33	2.01	1.84	1.73	1.60	1.53	1.47	1.42	1.39	1.37	1.35	1.34	1.32	1.30	1.29	1.28	1.28	1.26	1.25
50	3.25	2.38	2.06	1.88	1.77	1.64	1.56	1.50	1.46	1.43	1.40	1.39	1.37	1.35	1.33	1.32	1.31	1.30	1.29	1.28
60	3.31	2.43	2.10	1.92	1.81	1.67	1.59	1.53	1.48	1.45	1.43	1.41	1.40	1.37	1.36	1.34	1.33	1.33	1.31	1.30
75	3.39	2.48	2.14	1.96	1.85	1.71	1.63	1.56	1.52	1.48	1.46	1.44	1.43	1.40	1.39	1.37	1.36	1.35	1.34	1.33
100	3.49	2.55	2.20	2.01	1.90	1.75	1.67	1.60	1.56	1.52	1.50	1.48	1.46	1.44	1.42	1.41	1.40	1.39	1.37	1.36
125	3.56	2.60	2.24	2.06	1.94	1.79	1.70	1.63	1.59	1.55	1.53	1.51	1.49	1.47	1.45	1.44	1.42	1.42	1.40	1.39
150	3.62	2.64	2.28	2.09	1.97	1.82	1.73	1.66	1.61	1.58	1.55	1.53	1.52	1.49	1.47	1.46	1.45	1.44	1.42	1.41
175	3.67	2.68	2.31	2.12	1.99	1.84	1.75	1.68	1.63	1.60	1.57	1.55	1.53	1.51	1.49	1.48	1.47	1.46	1.44	1.43
200	3.71	2.71	2.34	2.14	2.01	1.86	1.77	1.70	1.65	1.62	1.59	1.57	1.55	1.53	1.51	1.49	1.48	1.47	1.46	1.44

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Table 19-9. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Means of Order 3 (5 COC, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.62**	**1.17**	**1.01**	**0.92**	**0.86**	**0.80**	**0.76**	**0.73**	**0.71**	**0.70**	**0.68**	**0.68**	**0.67**	**0.66**	**0.65**	**0.65**	**0.64**	**0.64**	**0.64**	**0.63**
2	**2.02**	**1.43**	**1.22**	**1.11**	**1.04**	**0.96**	**0.91**	**0.87**	**0.85**	**0.83**	**0.82**	**0.81**	**0.80**	**0.79**	**0.78**	**0.78**	**0.77**	**0.77**	**0.76**	**0.76**
3	**2.26**	**1.58**	**1.34**	**1.22**	**1.14**	**1.05**	**1.00**	**0.95**	**0.93**	**0.91**	**0.89**	**0.88**	**0.87**	**0.86**	**0.85**	**0.85**	**0.84**	**0.84**	**0.83**	**0.82**
4	**2.43**	**1.69**	**1.43**	**1.29**	**1.21**	**1.11**	**1.05**	**1.01**	**0.98**	**0.96**	**0.95**	**0.93**	**0.92**	**0.91**	**0.90**	**0.89**	**0.89**	**0.88**	**0.87**	**0.87**
5	**2.57**	**1.77**	**1.50**	**1.35**	**1.26**	**1.16**	**1.10**	**1.05**	**1.02**	**1.00**	**0.98**	**0.97**	**0.96**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.90**
8	2.84	**1.94**	**1.63**	**1.47**	**1.37**	**1.26**	**1.19**	**1.14**	**1.11**	**1.08**	**1.06**	**1.05**	**1.04**	**1.02**	**1.01**	**1.00**	**1.00**	**0.99**	**0.98**	**0.97**
12	3.07	**2.09**	**1.75**	**1.57**	**1.47**	**1.34**	**1.27**	**1.21**	**1.18**	**1.15**	**1.13**	**1.12**	**1.10**	**1.09**	**1.07**	**1.06**	**1.06**	**1.05**	**1.04**	**1.03**
16	3.24	**2.19**	**1.83**	**1.65**	**1.53**	**1.40**	**1.32**	**1.26**	**1.22**	**1.20**	**1.18**	**1.16**	**1.15**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**
20	3.36	**2.27**	**1.89**	**1.70**	**1.58**	**1.44**	**1.36**	**1.30**	**1.26**	**1.23**	**1.21**	**1.19**	**1.18**	**1.16**	**1.15**	**1.14**	**1.13**	**1.12**	**1.11**	**1.10**
30	3.58	**2.40**	**2.00**	**1.80**	**1.67**	**1.52**	**1.44**	**1.37**	**1.33**	**1.30**	**1.27**	**1.26**	**1.24**	**1.22**	**1.21**	**1.19**	**1.19**	**1.18**	**1.17**	**1.16**
40	3.73	**2.50**	**2.08**	**1.86**	**1.73**	**1.58**	**1.49**	**1.42**	**1.37**	**1.34**	**1.32**	**1.30**	**1.28**	**1.26**	**1.25**	**1.23**	**1.22**	**1.22**	**1.20**	**1.20**
50	3.85	**2.57**	**2.14**	**1.92**	**1.78**	**1.62**	**1.53**	**1.46**	**1.41**	**1.38**	**1.35**	**1.33**	**1.32**	**1.29**	**1.28**	**1.26**	**1.25**	**1.25**	**1.23**	**1.22**
60	3.94	**2.63**	**2.19**	**1.96**	**1.82**	**1.65**	**1.56**	**1.49**	**1.44**	**1.40**	**1.38**	**1.36**	**1.34**	**1.32**	**1.30**	**1.29**	**1.28**	**1.27**	**1.26**	**1.25**
75	4.06	**2.70**	**2.24**	**2.01**	**1.86**	**1.70**	**1.60**	**1.52**	**1.47**	**1.44**	**1.41**	**1.39**	**1.37**	**1.35**	**1.33**	**1.32**	**1.31**	**1.30**	**1.29**	**1.28**
100	4.20	*2.79*	**2.32**	**2.07**	**1.92**	**1.75**	**1.65**	**1.57**	**1.52**	**1.48**	**1.45**	**1.43**	**1.41**	**1.39**	**1.37**	**1.36**	**1.34**	**1.34**	**1.32**	**1.31**
125	4.31	*2.86*	**2.37**	**2.12**	**1.97**	**1.79**	**1.68**	**1.60**	**1.55**	**1.51**	**1.48**	**1.46**	**1.44**	**1.42**	**1.40**	**1.38**	**1.37**	**1.36**	**1.35**	**1.34**
150	4.40	2.91	**2.42**	**2.16**	**2.01**	**1.82**	**1.72**	**1.63**	**1.58**	**1.54**	**1.51**	**1.49**	**1.47**	**1.44**	**1.42**	**1.41**	**1.40**	**1.39**	**1.37**	**1.36**
175	4.47	2.96	**2.45**	**2.19**	**2.04**	**1.85**	**1.74**	**1.66**	**1.60**	**1.56**	**1.53**	**1.51**	**1.49**	**1.46**	**1.44**	**1.43**	**1.41**	**1.41**	**1.39**	**1.38**
200	4.53	3.00	**2.49**	**2.22**	**2.06**	**1.87**	**1.76**	**1.68**	**1.62**	**1.58**	**1.55**	**1.52**	**1.51**	**1.48**	**1.46**	**1.44**	**1.43**	**1.42**	**1.40**	**1.39**

Table 19-9. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Means of Order 3 (5 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.02**	**1.43**	**1.22**	**1.11**	**1.04**	**0.96**	**0.91**	**0.87**	**0.85**	**0.83**	**0.82**	**0.81**	**0.80**	**0.79**	**0.78**	**0.78**	**0.77**	**0.77**	**0.76**	**0.76**
2	**2.43**	**1.69**	**1.43**	**1.29**	**1.21**	**1.11**	**1.05**	**1.01**	**0.98**	**0.96**	**0.95**	**0.93**	**0.92**	**0.91**	**0.90**	**0.89**	**0.89**	**0.88**	**0.87**	**0.87**
3	**2.67**	**1.84**	**1.55**	**1.40**	**1.31**	**1.20**	**1.13**	**1.09**	**1.05**	**1.03**	**1.02**	**1.00**	**0.99**	**0.98**	**0.97**	**0.96**	**0.95**	**0.95**	**0.94**	**0.93**
4	2.84	**1.94**	**1.63**	**1.47**	**1.37**	**1.26**	**1.19**	**1.14**	**1.11**	**1.08**	**1.06**	**1.05**	**1.04**	**1.02**	**1.01**	**1.00**	**1.00**	**0.99**	**0.98**	**0.97**
5	2.97	**2.02**	**1.70**	**1.53**	**1.42**	**1.30**	**1.23**	**1.18**	**1.14**	**1.12**	**1.10**	**1.09**	**1.07**	**1.06**	**1.05**	**1.04**	**1.03**	**1.02**	**1.01**	**1.01**
8	3.24	**2.19**	**1.83**	**1.65**	**1.53**	**1.40**	**1.32**	**1.26**	**1.22**	**1.20**	**1.18**	**1.16**	**1.15**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**
12	3.46	**2.33**	**1.94**	**1.74**	**1.62**	**1.48**	**1.40**	**1.33**	**1.29**	**1.26**	**1.24**	**1.22**	**1.21**	**1.19**	**1.17**	**1.16**	**1.16**	**1.15**	**1.14**	**1.13**
16	3.61	**2.43**	**2.02**	**1.81**	**1.68**	**1.53**	**1.45**	**1.38**	**1.34**	**1.31**	**1.28**	**1.27**	**1.25**	**1.23**	**1.21**	**1.20**	**1.19**	**1.19**	**1.18**	**1.17**
20	3.73	**2.50**	**2.08**	**1.86**	**1.73**	**1.58**	**1.49**	**1.42**	**1.37**	**1.34**	**1.32**	**1.30**	**1.28**	**1.26**	**1.25**	**1.23**	**1.22**	**1.22**	**1.20**	**1.20**
30	3.94	**2.63**	**2.19**	**1.96**	**1.82**	**1.65**	**1.56**	**1.49**	**1.44**	**1.40**	**1.38**	**1.36**	**1.34**	**1.32**	**1.30**	**1.29**	**1.28**	**1.27**	**1.26**	**1.25**
40	4.09	**2.72**	**2.26**	**2.02**	**1.88**	**1.71**	**1.61**	**1.53**	**1.48**	**1.45**	**1.42**	**1.40**	**1.38**	**1.36**	**1.34**	**1.33**	**1.32**	**1.31**	**1.29**	**1.28**
50	4.20	**2.79**	**2.32**	**2.07**	**1.92**	**1.75**	**1.65**	**1.57**	**1.52**	**1.48**	**1.45**	**1.43**	**1.41**	**1.39**	**1.37**	**1.36**	**1.34**	**1.34**	**1.32**	**1.31**
60	4.29	**2.85**	**2.36**	**2.11**	**1.96**	**1.78**	**1.68**	**1.60**	**1.54**	**1.51**	**1.48**	**1.46**	**1.44**	**1.41**	**1.39**	**1.38**	**1.37**	**1.36**	**1.34**	**1.33**
75	4.40	*2.91*	**2.42**	**2.16**	**2.01**	**1.82**	**1.72**	**1.63**	**1.58**	**1.54**	**1.51**	**1.49**	**1.47**	**1.44**	**1.42**	**1.41**	**1.40**	**1.39**	**1.37**	**1.36**
100	4.53	3.00	**2.49**	**2.22**	**2.06**	**1.87**	**1.76**	**1.68**	**1.62**	**1.58**	**1.55**	**1.52**	**1.51**	**1.48**	**1.46**	**1.44**	**1.43**	**1.42**	**1.40**	**1.39**
125	4.64	3.07	**2.54**	**2.27**	**2.11**	**1.91**	**1.80**	**1.71**	**1.65**	**1.61**	**1.58**	**1.55**	**1.54**	**1.51**	**1.49**	**1.47**	**1.46**	**1.45**	**1.43**	**1.42**
150	4.72	3.12	**2.58**	**2.31**	**2.14**	**1.94**	**1.83**	**1.74**	**1.68**	**1.64**	**1.60**	**1.58**	**1.56**	**1.53**	**1.51**	**1.49**	**1.48**	**1.47**	**1.45**	**1.44**
175	4.79	3.16	**2.62**	**2.34**	**2.17**	**1.97**	**1.85**	**1.76**	**1.70**	**1.66**	**1.62**	**1.60**	**1.58**	**1.55**	**1.53**	**1.51**	**1.50**	**1.49**	**1.47**	**1.46**
200	4.85	3.20	**2.65**	**2.37**	**2.19**	**1.99**	**1.87**	**1.78**	**1.72**	**1.68**	**1.64**	**1.62**	**1.60**	**1.57**	**1.54**	**1.53**	**1.51**	**1.50**	**1.49**	**1.47**

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Table 19-9. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Means of Order 3 (5 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.43**	**1.69**	**1.43**	**1.29**	**1.21**	**1.11**	**1.05**	**1.01**	**0.98**	**0.96**	**0.95**	**0.93**	**0.92**	**0.91**	**0.90**	**0.89**	**0.89**	**0.88**	**0.87**	**0.87**
2	**2.84**	**1.94**	**1.63**	**1.47**	**1.37**	**1.26**	**1.19**	**1.14**	**1.11**	**1.08**	**1.06**	**1.05**	**1.04**	**1.02**	**1.01**	**1.00**	**1.00**	**0.99**	**0.98**	**0.97**
3	3.07	**2.09**	**1.75**	**1.57**	**1.47**	**1.34**	**1.27**	**1.21**	**1.18**	**1.15**	**1.13**	**1.12**	**1.10**	**1.09**	**1.07**	**1.06**	**1.06**	**1.05**	**1.04**	**1.03**
4	3.24	**2.19**	**1.83**	**1.65**	**1.53**	**1.40**	**1.32**	**1.26**	**1.22**	**1.20**	**1.18**	**1.16**	**1.15**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**
5	3.36	**2.27**	**1.89**	**1.70**	**1.58**	**1.44**	**1.36**	**1.30**	**1.26**	**1.23**	**1.21**	**1.19**	**1.18**	**1.16**	**1.15**	**1.14**	**1.13**	**1.12**	**1.11**	**1.10**
8	3.61	**2.43**	**2.02**	**1.81**	**1.68**	**1.53**	**1.45**	**1.38**	**1.34**	**1.31**	**1.28**	**1.27**	**1.25**	**1.23**	**1.21**	**1.20**	**1.19**	**1.19**	**1.18**	**1.17**
12	3.83	**2.56**	**2.13**	**1.91**	**1.77**	**1.61**	**1.52**	**1.45**	**1.40**	**1.37**	**1.34**	**1.33**	**1.31**	**1.29**	**1.27**	**1.26**	**1.25**	**1.24**	**1.23**	**1.22**
16	3.98	**2.65**	**2.20**	**1.97**	**1.83**	**1.67**	**1.57**	**1.50**	**1.45**	**1.41**	**1.39**	**1.37**	**1.35**	**1.33**	**1.31**	**1.30**	**1.29**	**1.28**	**1.27**	**1.26**
20	4.09	**2.72**	**2.26**	**2.02**	**1.88**	**1.71**	**1.61**	**1.53**	**1.48**	**1.45**	**1.42**	**1.40**	**1.38**	**1.36**	**1.34**	**1.33**	**1.32**	**1.31**	**1.29**	**1.28**
30	4.29	**2.85**	**2.36**	**2.11**	**1.96**	**1.78**	**1.68**	**1.60**	**1.54**	**1.51**	**1.48**	**1.46**	**1.44**	**1.41**	**1.39**	**1.38**	**1.37**	**1.36**	**1.34**	**1.33**
40	4.43	**2.93**	**2.43**	**2.18**	**2.02**	**1.83**	**1.73**	**1.64**	**1.59**	**1.55**	**1.52**	**1.49**	**1.48**	**1.45**	**1.43**	**1.41**	**1.40**	**1.39**	**1.38**	**1.37**
50	4.53	**3.00**	**2.49**	**2.22**	**2.06**	**1.87**	**1.76**	**1.68**	**1.62**	**1.58**	**1.55**	**1.52**	**1.51**	**1.48**	**1.46**	**1.44**	**1.43**	**1.42**	**1.40**	**1.39**
60	4.62	**3.05**	**2.53**	**2.26**	**2.10**	**1.90**	**1.79**	**1.70**	**1.65**	**1.60**	**1.57**	**1.55**	**1.53**	**1.50**	**1.48**	**1.47**	**1.45**	**1.44**	**1.43**	**1.41**
75	4.72	*3.12*	**2.58**	**2.31**	**2.14**	**1.94**	**1.83**	**1.74**	**1.68**	**1.64**	**1.60**	**1.58**	**1.56**	**1.53**	**1.51**	**1.49**	**1.48**	**1.47**	**1.45**	**1.44**
100	4.85	3.20	**2.65**	**2.37**	**2.19**	**1.99**	**1.87**	**1.78**	**1.72**	**1.68**	**1.64**	**1.62**	**1.60**	**1.57**	**1.54**	**1.53**	**1.51**	**1.50**	**1.49**	**1.47**
125	4.95	3.26	**2.70**	**2.41**	**2.24**	**2.03**	**1.91**	**1.81**	**1.75**	**1.71**	**1.67**	**1.65**	**1.62**	**1.59**	**1.57**	**1.55**	**1.54**	**1.53**	**1.51**	**1.50**
150	5.03	3.31	**2.74**	**2.45**	**2.27**	**2.06**	**1.94**	**1.84**	**1.78**	**1.73**	**1.70**	**1.67**	**1.65**	**1.62**	**1.59**	**1.58**	**1.56**	**1.55**	**1.53**	**1.52**
175	5.10	3.36	**2.78**	**2.48**	**2.30**	**2.08**	**1.96**	**1.86**	**1.80**	**1.75**	**1.72**	**1.69**	**1.67**	**1.63**	**1.61**	**1.59**	**1.58**	**1.57**	**1.55**	**1.53**
200	5.16	3.39	**2.81**	**2.51**	**2.32**	**2.11**	**1.98**	**1.88**	**1.82**	**1.77**	**1.73**	**1.71**	**1.68**	**1.65**	**1.63**	**1.61**	**1.59**	**1.58**	**1.56**	**1.55**

Table 19-9. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Means of Order 3 (10 COC, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.15**	**1.48**	**1.24**	**1.12**	**1.05**	**0.96**	**0.91**	**0.88**	**0.85**	**0.83**	**0.82**	**0.81**	**0.80**	**0.79**	**0.78**	**0.78**	**0.77**	**0.77**	**0.76**	**0.76**
2	**2.64**	**1.76**	**1.46**	**1.31**	**1.22**	**1.12**	**1.06**	**1.01**	**0.98**	**0.96**	**0.95**	**0.94**	**0.93**	**0.91**	**0.90**	**0.89**	**0.89**	**0.88**	**0.87**	**0.87**
3	2.94	**1.93**	**1.59**	**1.43**	**1.32**	**1.21**	**1.14**	**1.09**	**1.06**	**1.03**	**1.02**	**1.00**	**0.99**	**0.98**	**0.97**	**0.96**	**0.95**	**0.95**	**0.94**	**0.93**
4	3.15	**2.04**	**1.68**	**1.50**	**1.40**	**1.27**	**1.20**	**1.14**	**1.11**	**1.08**	**1.07**	**1.05**	**1.04**	**1.02**	**1.01**	**1.00**	**1.00**	**0.99**	**0.98**	**0.97**
5	3.32	**2.14**	**1.75**	**1.56**	**1.45**	**1.32**	**1.24**	**1.19**	**1.15**	**1.12**	**1.10**	**1.09**	**1.08**	**1.06**	**1.05**	**1.04**	**1.03**	**1.02**	**1.01**	**1.01**
8	3.66	**2.33**	**1.90**	**1.69**	**1.56**	**1.42**	**1.33**	**1.27**	**1.23**	**1.20**	**1.18**	**1.16**	**1.15**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**
12	3.95	**2.49**	**2.03**	**1.80**	**1.66**	**1.50**	**1.41**	**1.34**	**1.30**	**1.27**	**1.24**	**1.23**	**1.21**	**1.19**	**1.18**	**1.16**	**1.16**	**1.15**	**1.14**	**1.13**
16	4.15	**2.61**	**2.12**	**1.87**	**1.73**	**1.56**	**1.46**	**1.39**	**1.35**	**1.31**	**1.29**	**1.27**	**1.25**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**
20	4.31	**2.69**	**2.18**	**1.93**	**1.78**	**1.60**	**1.51**	**1.43**	**1.38**	**1.35**	**1.32**	**1.30**	**1.29**	**1.26**	**1.25**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**
30	4.58	*2.85*	**2.30**	**2.03**	**1.87**	**1.68**	**1.58**	**1.50**	**1.45**	**1.41**	**1.38**	**1.36**	**1.35**	**1.32**	**1.30**	**1.29**	**1.28**	**1.27**	**1.26**	**1.25**
40	4.77	2.96	**2.39**	**2.11**	**1.94**	**1.74**	**1.63**	**1.55**	**1.49**	**1.45**	**1.43**	**1.40**	**1.39**	**1.36**	**1.34**	**1.33**	**1.32**	**1.31**	**1.29**	**1.28**
50	4.92	3.04	**2.45**	**2.16**	**1.99**	**1.78**	**1.67**	**1.58**	**1.53**	**1.49**	**1.46**	**1.44**	**1.42**	**1.39**	**1.37**	**1.36**	**1.35**	**1.34**	**1.32**	**1.31**
60	5.04	3.11	**2.50**	**2.21**	**2.03**	**1.82**	**1.70**	**1.61**	**1.56**	**1.51**	**1.48**	**1.46**	**1.44**	**1.41**	**1.40**	**1.38**	**1.37**	**1.36**	**1.34**	**1.33**
75	5.18	3.19	**2.57**	**2.26**	**2.08**	**1.86**	**1.74**	**1.65**	**1.59**	**1.55**	**1.52**	**1.49**	**1.47**	**1.44**	**1.42**	**1.41**	**1.40**	**1.39**	**1.37**	**1.36**
100	5.36	3.29	**2.65**	**2.33**	**2.14**	**1.92**	**1.79**	**1.70**	**1.63**	**1.59**	**1.56**	**1.53**	**1.51**	**1.48**	**1.46**	**1.45**	**1.43**	**1.42**	**1.41**	**1.39**
125	5.50	3.37	*2.71*	**2.38**	**2.18**	**1.96**	**1.83**	**1.73**	**1.67**	**1.62**	**1.59**	**1.56**	**1.54**	**1.51**	**1.49**	**1.47**	**1.46**	**1.45**	**1.43**	**1.42**
150	5.61	3.43	*2.76*	**2.42**	**2.22**	**1.99**	**1.86**	**1.76**	**1.69**	**1.65**	**1.61**	**1.59**	**1.57**	**1.53**	**1.51**	**1.50**	**1.48**	**1.47**	**1.45**	**1.44**
175	5.70	3.49	*2.80*	**2.46**	**2.26**	**2.02**	**1.89**	**1.78**	**1.72**	**1.67**	**1.64**	**1.61**	**1.59**	**1.55**	**1.53**	**1.51**	**1.50**	**1.49**	**1.47**	**1.46**
200	5.78	3.53	*2.83*	**2.49**	**2.28**	**2.05**	**1.91**	**1.81**	**1.74**	**1.69**	**1.65**	**1.63**	**1.60**	**1.57**	**1.55**	**1.53**	**1.52**	**1.51**	**1.49**	**1.47**

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Table 19-9. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Means of Order 3 (10 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	2.64	1.76	1.46	1.31	1.22	1.12	1.06	1.01	0.98	0.96	0.95	0.94	0.93	0.91	0.90	0.89	0.89	0.88	0.87	0.87
2	3.15	2.04	1.68	1.50	1.40	1.27	1.20	1.14	1.11	1.08	1.07	1.05	1.04	1.02	1.01	1.00	1.00	0.99	0.98	0.97
3	3.45	2.21	1.81	1.61	1.49	1.36	1.28	1.22	1.18	1.15	1.13	1.12	1.11	1.09	1.07	1.06	1.06	1.05	1.04	1.03
4	3.66	2.33	1.90	1.69	1.56	1.42	1.33	1.27	1.23	1.20	1.18	1.16	1.15	1.13	1.12	1.11	1.10	1.09	1.08	1.07
5	3.82	2.42	1.97	1.75	1.62	1.46	1.38	1.31	1.27	1.24	1.21	1.20	1.18	1.16	1.15	1.14	1.13	1.12	1.11	1.10
8	4.15	2.61	2.12	1.87	1.73	1.56	1.46	1.39	1.35	1.31	1.29	1.27	1.25	1.23	1.22	1.21	1.20	1.19	1.18	1.17
12	4.43	2.76	2.24	1.98	1.82	1.64	1.54	1.46	1.41	1.38	1.35	1.33	1.31	1.29	1.27	1.26	1.25	1.24	1.23	1.22
16	4.63	2.87	2.32	2.05	1.89	1.70	1.59	1.51	1.46	1.42	1.39	1.37	1.35	1.33	1.31	1.30	1.29	1.28	1.27	1.26
20	4.77	*2.96*	2.39	2.11	1.94	1.74	1.63	1.55	1.49	1.45	1.43	1.40	1.39	1.36	1.34	1.33	1.32	1.31	1.29	1.28
30	5.04	3.11	2.50	2.21	2.03	1.82	1.70	1.61	1.56	1.51	1.48	1.46	1.44	1.41	1.40	1.38	1.37	1.36	1.34	1.33
40	5.22	3.21	2.58	2.28	2.09	1.87	1.75	1.66	1.60	1.56	1.53	1.50	1.48	1.45	1.43	1.42	1.41	1.40	1.38	1.37
50	5.36	3.29	2.65	2.33	2.14	1.92	1.79	1.70	1.63	1.59	1.56	1.53	1.51	1.48	1.46	1.45	1.43	1.42	1.41	1.39
60	5.47	3.36	2.70	2.37	2.18	1.95	1.82	1.73	1.66	1.62	1.58	1.56	1.54	1.51	1.48	1.47	1.46	1.45	1.43	1.42
75	5.61	3.43	2.76	2.42	2.22	1.99	1.86	1.76	1.69	1.65	1.61	1.59	1.57	1.53	1.51	1.50	1.48	1.47	1.45	1.44
100	5.78	3.53	2.83	2.49	2.28	2.05	1.91	1.81	1.74	1.69	1.65	1.63	1.60	1.57	1.55	1.53	1.52	1.51	1.49	1.47
125	5.91	3.61	*2.89*	2.54	2.33	2.09	1.95	1.84	1.77	1.72	1.68	1.66	1.63	1.60	1.57	1.56	1.54	1.53	1.51	1.50
150	6.02	3.67	*2.94*	2.58	2.37	2.12	1.98	1.87	1.80	1.75	1.71	1.68	1.66	1.62	1.60	1.58	1.56	1.55	1.53	1.52
175	6.10	3.72	*2.98*	2.62	2.40	2.15	2.00	1.89	1.82	1.77	1.73	1.70	1.68	1.64	1.62	1.60	1.58	1.57	1.55	1.54
200	6.18	3.76	*3.01*	2.65	2.42	2.17	2.02	1.91	1.84	1.79	1.75	1.72	1.69	1.66	1.63	1.61	1.60	1.59	1.56	1.55

Table 19-9. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Means of Order 3 (10 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.15	2.04	1.68	1.50	1.40	1.27	1.20	1.14	1.11	1.08	1.07	1.05	1.04	1.02	1.01	1.00	1.00	0.99	0.98	0.97
2	3.66	2.33	1.90	1.69	1.56	1.42	1.33	1.27	1.23	1.20	1.18	1.16	1.15	1.13	1.12	1.11	1.10	1.09	1.08	1.07
3	3.95	2.49	2.03	1.80	1.66	1.50	1.41	1.34	1.30	1.27	1.24	1.23	1.21	1.19	1.18	1.16	1.16	1.15	1.14	1.13
4	4.15	2.61	2.12	1.87	1.73	1.56	1.46	1.39	1.35	1.31	1.29	1.27	1.25	1.23	1.22	1.21	1.20	1.19	1.18	1.17
5	4.31	2.69	2.18	1.93	1.78	1.60	1.51	1.43	1.38	1.35	1.32	1.30	1.29	1.26	1.25	1.24	1.23	1.22	1.21	1.20
8	4.63	2.87	2.32	2.05	1.89	1.70	1.59	1.51	1.46	1.42	1.39	1.37	1.35	1.33	1.31	1.30	1.29	1.28	1.27	1.26
12	4.89	3.03	2.44	2.15	1.98	1.78	1.66	1.58	1.52	1.48	1.45	1.43	1.41	1.38	1.37	1.35	1.34	1.33	1.32	1.31
16	5.08	3.13	2.52	2.22	2.04	1.83	1.72	1.62	1.57	1.52	1.49	1.47	1.45	1.42	1.40	1.39	1.38	1.37	1.35	1.34
20	5.22	3.21	2.58	2.28	2.09	1.87	1.75	1.66	1.60	1.56	1.53	1.50	1.48	1.45	1.43	1.42	1.41	1.40	1.38	1.37
30	5.47	3.36	2.70	2.37	2.18	1.95	1.82	1.73	1.66	1.62	1.58	1.56	1.54	1.51	1.48	1.47	1.46	1.45	1.43	1.42
40	5.65	3.46	2.77	2.44	2.24	2.00	1.87	1.77	1.70	1.66	1.62	1.60	1.57	1.54	1.52	1.50	1.49	1.48	1.46	1.45
50	5.78	3.53	2.83	2.49	2.28	2.05	1.91	1.81	1.74	1.69	1.65	1.63	1.60	1.57	1.55	1.53	1.52	1.51	1.49	1.47
60	5.89	3.60	2.88	2.53	2.32	2.08	1.94	1.83	1.76	1.71	1.68	1.65	1.63	1.59	1.57	1.55	1.54	1.53	1.51	1.49
75	6.02	3.67	2.94	2.58	2.37	2.12	1.98	1.87	1.80	1.75	1.71	1.68	1.66	1.62	1.60	1.58	1.56	1.55	1.53	1.52
100	6.18	3.76	3.01	2.65	2.42	2.17	2.02	1.91	1.84	1.79	1.75	1.72	1.69	1.66	1.63	1.61	1.60	1.59	1.56	1.55
125	6.31	3.84	*3.07*	2.69	2.47	2.21	2.06	1.95	1.87	1.82	1.78	1.75	1.72	1.68	1.66	1.64	1.62	1.61	1.59	1.57
150	6.41	3.90	*3.12*	2.73	2.51	2.24	2.09	1.97	1.90	1.84	1.80	1.77	1.74	1.71	1.68	1.66	1.64	1.63	1.61	1.59
175	6.49	3.94	*3.16*	2.77	2.54	2.27	2.11	2.00	1.92	1.86	1.82	1.79	1.76	1.72	1.70	1.68	1.66	1.65	1.63	1.61
200	6.56	3.99	*3.19*	2.80	2.56	2.29	2.13	2.01	1.94	1.88	1.84	1.81	1.78	1.74	1.71	1.69	1.68	1.66	1.64	1.63

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Table 19-9. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Means of Order 3 (20 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	2.80	1.80	1.48	1.33	1.23	1.12	1.06	1.02	0.99	0.96	0.95	0.94	0.93	0.91	0.90	0.89	0.89	0.88	0.88	0.87
2	3.41	2.12	1.72	1.52	1.41	1.28	1.20	1.15	1.11	1.09	1.07	1.05	1.04	1.02	1.01	1.00	1.00	0.99	0.98	0.97
3	3.78	2.30	1.85	1.64	1.51	1.36	1.28	1.22	1.18	1.16	1.13	1.12	1.11	1.09	1.07	1.07	1.06	1.05	1.04	1.03
4	4.04	2.44	1.95	1.72	1.58	1.43	1.34	1.27	1.23	1.20	1.18	1.16	1.15	1.13	1.12	1.11	1.10	1.09	1.08	1.07
5	4.24	2.54	2.03	1.78	1.64	1.47	1.38	1.31	1.27	1.24	1.22	1.20	1.19	1.17	1.15	1.14	1.13	1.12	1.11	1.10
8	4.67	*2.76*	2.19	1.91	1.75	1.57	1.47	1.40	1.35	1.32	1.29	1.27	1.26	1.23	1.22	1.21	1.20	1.19	1.18	1.17
12	5.04	2.94	2.32	2.03	1.85	1.66	1.55	1.47	1.42	1.38	1.35	1.33	1.32	1.29	1.27	1.26	1.25	1.24	1.23	1.22
16	5.29	3.07	2.42	2.11	1.92	1.72	1.60	1.52	1.46	1.42	1.40	1.37	1.36	1.33	1.31	1.30	1.29	1.28	1.27	1.26
20	5.48	3.17	2.49	2.17	1.98	1.76	1.65	1.56	1.50	1.46	1.43	1.41	1.39	1.36	1.34	1.33	1.32	1.31	1.29	1.28
30	5.83	3.35	2.62	2.28	2.08	1.85	1.72	1.62	1.56	1.52	1.49	1.46	1.45	1.42	1.40	1.38	1.37	1.36	1.34	1.33
40	6.07	3.47	*2.72*	2.36	2.14	1.90	1.77	1.67	1.61	1.56	1.53	1.50	1.48	1.46	1.43	1.42	1.41	1.40	1.38	1.37
50	6.25	3.57	*2.79*	2.41	2.20	1.95	1.81	1.71	1.64	1.60	1.56	1.54	1.52	1.48	1.46	1.45	1.43	1.42	1.41	1.39
60	6.40	3.65	*2.84*	2.46	2.24	1.99	1.85	1.74	1.67	1.62	1.59	1.56	1.54	1.51	1.49	1.47	1.46	1.45	1.43	1.42
75	6.58	3.74	*2.91*	2.52	2.29	2.03	1.89	1.78	1.71	1.66	1.62	1.59	1.57	1.54	1.51	1.50	1.48	1.47	1.45	1.44
100	6.81	3.86	3.00	2.59	2.36	2.09	1.94	1.82	1.75	1.70	1.66	1.63	1.61	1.57	1.55	1.53	1.52	1.51	1.49	1.47
125	6.98	3.95	3.07	2.65	2.41	2.13	1.98	1.86	1.78	1.73	1.69	1.66	1.64	1.60	1.58	1.56	1.54	1.53	1.51	1.50
150	7.12	4.02	3.12	*2.70*	2.45	2.16	2.01	1.89	1.81	1.76	1.72	1.69	1.66	1.62	1.60	1.58	1.57	1.55	1.53	1.52
175	7.24	4.08	3.17	*2.74*	2.48	2.19	2.03	1.91	1.83	1.78	1.74	1.71	1.68	1.64	1.62	1.60	1.58	1.57	1.55	1.54
200	7.34	4.13	3.21	*2.77*	2.51	2.22	2.06	1.93	1.85	1.80	1.75	1.72	1.70	1.66	1.63	1.61	1.60	1.59	1.57	1.55

Table 19-9. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Means of Order 3 (20 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.41	2.12	1.72	1.52	1.41	1.28	1.20	1.15	1.11	1.09	1.07	1.05	1.04	1.02	1.01	1.00	1.00	0.99	0.98	0.97
2	4.04	2.44	1.95	1.72	1.58	1.43	1.34	1.27	1.23	1.20	1.18	1.16	1.15	1.13	1.12	1.11	1.10	1.09	1.08	1.07
3	4.41	2.62	2.09	1.83	1.68	1.51	1.42	1.35	1.30	1.27	1.25	1.23	1.21	1.19	1.18	1.17	1.16	1.15	1.14	1.13
4	4.67	2.76	2.19	1.91	1.75	1.57	1.47	1.40	1.35	1.32	1.29	1.27	1.26	1.23	1.22	1.21	1.20	1.19	1.18	1.17
5	4.87	2.86	2.26	1.98	1.81	1.62	1.52	1.44	1.39	1.35	1.32	1.30	1.29	1.27	1.25	1.24	1.23	1.22	1.21	1.20
8	5.29	3.07	2.42	2.11	1.92	1.72	1.60	1.52	1.46	1.42	1.40	1.37	1.36	1.33	1.31	1.30	1.29	1.28	1.27	1.26
12	5.64	3.25	2.55	2.22	2.02	1.80	1.68	1.59	1.53	1.49	1.46	1.43	1.41	1.39	1.37	1.35	1.34	1.33	1.32	1.31
16	5.89	3.38	2.64	2.30	2.09	1.86	1.73	1.64	1.57	1.53	1.50	1.47	1.45	1.43	1.41	1.39	1.38	1.37	1.35	1.34
20	6.07	3.47	2.72	2.36	2.14	1.90	1.77	1.67	1.61	1.56	1.53	1.50	1.48	1.46	1.43	1.42	1.41	1.40	1.38	1.37
30	6.40	3.65	2.84	2.46	2.24	1.99	1.85	1.74	1.67	1.62	1.59	1.56	1.54	1.51	1.49	1.47	1.46	1.45	1.43	1.42
40	6.63	3.77	*2.93*	2.54	2.30	2.04	1.90	1.79	1.72	1.67	1.63	1.60	1.58	1.55	1.52	1.50	1.49	1.48	1.46	1.45
50	6.81	3.86	*3.00*	2.59	2.36	2.09	1.94	1.82	1.75	1.70	1.66	1.63	1.61	1.57	1.55	1.53	1.52	1.51	1.49	1.47
60	6.95	3.93	3.06	2.64	2.40	2.12	1.97	1.85	1.78	1.72	1.69	1.66	1.63	1.60	1.57	1.55	1.54	1.53	1.51	1.49
75	7.12	4.02	3.12	2.70	2.45	2.16	2.01	1.89	1.81	1.76	1.72	1.69	1.66	1.62	1.60	1.58	1.57	1.55	1.53	1.52
100	7.34	4.13	3.21	2.77	2.51	2.22	2.06	1.93	1.85	1.80	1.75	1.72	1.70	1.66	1.63	1.61	1.60	1.59	1.57	1.55
125	7.50	4.22	3.27	2.82	2.56	2.26	2.09	1.97	1.89	1.83	1.79	1.75	1.73	1.69	1.66	1.64	1.62	1.61	1.59	1.58
150	7.64	4.29	3.33	*2.87*	2.60	2.29	2.13	2.00	1.91	1.85	1.81	1.78	1.75	1.71	1.68	1.66	1.65	1.63	1.61	1.60
175	7.75	4.35	3.37	*2.90*	2.63	2.32	2.15	2.02	1.93	1.87	1.83	1.80	1.77	1.73	1.70	1.68	1.66	1.65	1.63	1.61
200	7.84	4.40	3.41	*2.94*	2.66	2.35	2.17	2.04	1.95	1.89	1.85	1.81	1.79	1.75	1.72	1.69	1.68	1.67	1.64	1.63

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Table 19-9. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Means of Order 3 (20 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	4.04	**2.44**	**1.95**	**1.72**	**1.58**	**1.43**	**1.34**	**1.27**	**1.23**	**1.20**	**1.18**	**1.16**	**1.15**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**
2	4.67	**2.76**	**2.19**	**1.91**	**1.75**	**1.57**	**1.47**	**1.40**	**1.35**	**1.32**	**1.29**	**1.27**	**1.26**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**
3	5.04	**2.94**	**2.32**	**2.03**	**1.85**	**1.66**	**1.55**	**1.47**	**1.42**	**1.38**	**1.35**	**1.33**	**1.32**	**1.29**	**1.27**	**1.26**	**1.25**	**1.24**	**1.23**	**1.22**
4	5.29	**3.07**	**2.42**	**2.11**	**1.92**	**1.72**	**1.60**	**1.52**	**1.46**	**1.42**	**1.40**	**1.37**	**1.36**	**1.33**	**1.31**	**1.30**	**1.29**	**1.28**	**1.27**	**1.26**
5	5.48	3.17	**2.49**	**2.17**	**1.98**	**1.76**	**1.65**	**1.56**	**1.50**	**1.46**	**1.43**	**1.41**	**1.39**	**1.36**	**1.34**	**1.33**	**1.32**	**1.31**	**1.29**	**1.28**
8	5.89	3.38	**2.64**	**2.30**	**2.09**	**1.86**	**1.73**	**1.64**	**1.57**	**1.53**	**1.50**	**1.47**	**1.45**	**1.43**	**1.41**	**1.39**	**1.38**	**1.37**	**1.35**	**1.34**
12	6.22	3.55	**2.77**	**2.40**	**2.19**	**1.94**	**1.81**	**1.70**	**1.64**	**1.59**	**1.56**	**1.53**	**1.51**	**1.48**	**1.46**	**1.44**	**1.43**	**1.42**	**1.40**	**1.39**
16	6.46	3.67	**2.86**	**2.48**	**2.25**	**2.00**	**1.86**	**1.75**	**1.68**	**1.63**	**1.60**	**1.57**	**1.55**	**1.52**	**1.49**	**1.48**	**1.46**	**1.45**	**1.44**	**1.42**
20	6.63	3.77	**2.93**	**2.54**	**2.30**	**2.04**	**1.90**	**1.79**	**1.72**	**1.67**	**1.63**	**1.60**	**1.58**	**1.55**	**1.52**	**1.50**	**1.49**	**1.48**	**1.46**	**1.45**
30	6.95	3.93	*3.06*	**2.64**	**2.40**	**2.12**	**1.97**	**1.85**	**1.78**	**1.72**	**1.69**	**1.66**	**1.63**	**1.60**	**1.57**	**1.55**	**1.54**	**1.53**	**1.51**	**1.49**
40	7.17	4.05	*3.14*	**2.71**	**2.46**	**2.18**	**2.02**	**1.90**	**1.82**	**1.76**	**1.72**	**1.69**	**1.67**	**1.63**	**1.61**	**1.59**	**1.57**	**1.56**	**1.54**	**1.53**
50	7.34	4.13	*3.21*	**2.77**	**2.51**	**2.22**	**2.06**	**1.93**	**1.85**	**1.80**	**1.75**	**1.72**	**1.70**	**1.66**	**1.63**	**1.61**	**1.60**	**1.59**	**1.57**	**1.55**
60	7.47	4.20	3.26	**2.81**	**2.55**	**2.25**	**2.09**	**1.96**	**1.88**	**1.82**	**1.78**	**1.75**	**1.72**	**1.68**	**1.66**	**1.64**	**1.62**	**1.61**	**1.59**	**1.57**
75	7.64	4.29	3.33	**2.87**	**2.60**	**2.29**	**2.13**	**2.00**	**1.91**	**1.85**	**1.81**	**1.78**	**1.75**	**1.71**	**1.68**	**1.66**	**1.65**	**1.63**	**1.61**	**1.60**
100	7.84	4.40	3.41	**2.94**	**2.66**	**2.35**	**2.17**	**2.04**	**1.95**	**1.89**	**1.85**	**1.81**	**1.79**	**1.75**	**1.72**	**1.69**	**1.68**	**1.67**	**1.64**	**1.63**
125	8.00	4.48	3.47	**2.99**	**2.71**	**2.39**	**2.21**	**2.07**	**1.99**	**1.92**	**1.88**	**1.84**	**1.81**	**1.77**	**1.74**	**1.72**	**1.70**	**1.69**	**1.67**	**1.65**
150	8.13	4.55	3.52	**3.03**	**2.75**	**2.42**	**2.24**	**2.10**	**2.01**	**1.95**	**1.90**	**1.87**	**1.84**	**1.79**	**1.76**	**1.74**	**1.72**	**1.71**	**1.68**	**1.67**
175	8.23	4.61	3.56	*3.07*	**2.78**	**2.45**	**2.27**	**2.13**	**2.03**	**1.97**	**1.92**	**1.88**	**1.86**	**1.81**	**1.78**	**1.76**	**1.74**	**1.73**	**1.70**	**1.68**
200	8.33	4.65	3.60	*3.10*	**2.81**	**2.47**	**2.29**	**2.15**	**2.05**	**1.99**	**1.94**	**1.90**	**1.87**	**1.83**	**1.80**	**1.77**	**1.76**	**1.74**	**1.72**	**1.70**

Table 19-9. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Means of Order 3 (40 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.60	**2.16**	**1.74**	**1.53**	**1.42**	**1.28**	**1.21**	**1.15**	**1.11**	**1.09**	**1.07**	**1.05**	**1.04**	**1.03**	**1.01**	**1.00**	**1.00**	**0.99**	**0.98**	**0.98**
2	4.35	**2.51**	**1.98**	**1.74**	**1.59**	**1.43**	**1.34**	**1.28**	**1.23**	**1.20**	**1.18**	**1.17**	**1.15**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**
3	4.81	**2.72**	**2.13**	**1.86**	**1.70**	**1.52**	**1.42**	**1.35**	**1.30**	**1.27**	**1.25**	**1.23**	**1.21**	**1.19**	**1.18**	**1.17**	**1.16**	**1.15**	**1.14**	**1.13**
4	5.14	2.87	**2.24**	**1.94**	**1.77**	**1.58**	**1.48**	**1.40**	**1.35**	**1.32**	**1.29**	**1.27**	**1.26**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**
5	5.40	2.99	**2.32**	**2.01**	**1.83**	**1.63**	**1.52**	**1.44**	**1.39**	**1.35**	**1.33**	**1.31**	**1.29**	**1.27**	**1.25**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**
8	5.94	3.24	**2.49**	**2.15**	**1.95**	**1.73**	**1.61**	**1.52**	**1.47**	**1.43**	**1.40**	**1.38**	**1.36**	**1.33**	**1.31**	**1.30**	**1.29**	**1.28**	**1.27**	**1.26**
12	6.39	3.45	**2.64**	**2.27**	**2.05**	**1.82**	**1.69**	**1.59**	**1.53**	**1.49**	**1.46**	**1.43**	**1.42**	**1.39**	**1.37**	**1.35**	**1.34**	**1.33**	**1.32**	**1.31**
16	6.71	3.60	*2.74*	**2.35**	**2.13**	**1.88**	**1.74**	**1.64**	**1.58**	**1.53**	**1.50**	**1.48**	**1.46**	**1.43**	**1.41**	**1.39**	**1.38**	**1.37**	**1.35**	**1.34**
20	6.96	3.71	*2.82*	**2.42**	**2.18**	**1.92**	**1.78**	**1.68**	**1.61**	**1.57**	**1.53**	**1.51**	**1.49**	**1.46**	**1.43**	**1.42**	**1.41**	**1.40**	**1.38**	**1.37**
30	7.39	3.91	2.97	**2.53**	**2.29**	**2.01**	**1.86**	**1.75**	**1.68**	**1.63**	**1.59**	**1.56**	**1.54**	**1.51**	**1.49**	**1.47**	**1.46**	**1.45**	**1.43**	**1.42**
40	7.70	4.06	3.07	**2.62**	**2.36**	**2.07**	**1.91**	**1.80**	**1.72**	**1.67**	**1.63**	**1.60**	**1.58**	**1.55**	**1.52**	**1.51**	**1.49**	**1.48**	**1.46**	**1.45**
50	7.93	4.16	3.15	*2.68*	**2.41**	**2.12**	**1.95**	**1.83**	**1.76**	**1.70**	**1.66**	**1.63**	**1.61**	**1.58**	**1.55**	**1.53**	**1.52**	**1.51**	**1.49**	**1.47**
60	8.11	4.25	3.21	*2.73*	**2.46**	**2.15**	**1.99**	**1.86**	**1.78**	**1.73**	**1.69**	**1.66**	**1.63**	**1.60**	**1.57**	**1.55**	**1.54**	**1.53**	**1.51**	**1.50**
75	8.34	4.36	3.29	*2.79*	**2.51**	**2.20**	**2.03**	**1.90**	**1.82**	**1.76**	**1.72**	**1.69**	**1.66**	**1.63**	**1.60**	**1.58**	**1.57**	**1.55**	**1.53**	**1.52**
100	8.62	4.49	3.38	*2.87*	**2.58**	**2.26**	**2.08**	**1.95**	**1.86**	**1.80**	**1.76**	**1.73**	**1.70**	**1.66**	**1.64**	**1.62**	**1.60**	**1.59**	**1.57**	**1.55**
125	8.84	4.60	3.46	*2.93*	**2.63**	**2.30**	**2.12**	**1.98**	**1.90**	**1.83**	**1.79**	**1.76**	**1.73**	**1.69**	**1.66**	**1.64**	**1.63**	**1.61**	**1.59**	**1.58**
150	9.01	4.68	3.52	2.98	*2.68*	**2.34**	**2.15**	**2.01**	**1.92**	**1.86**	**1.82**	**1.78**	**1.75**	**1.71**	**1.68**	**1.66**	**1.65**	**1.63**	**1.61**	**1.60**
175	9.16	4.75	3.57	3.03	*2.71*	**2.37**	**2.18**	**2.04**	**1.95**	**1.88**	**1.84**	**1.80**	**1.77**	**1.73**	**1.70**	**1.68**	**1.66**	**1.65**	**1.63**	**1.61**
200	9.29	4.81	3.61	3.06	*2.75*	**2.39**	**2.20**	**2.06**	**1.97**	**1.90**	**1.86**	**1.82**	**1.79**	**1.75**	**1.72**	**1.70**	**1.68**	**1.67**	**1.64**	**1.62**

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Table 19-9. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Means of Order 3 (40 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	4.35	**2.51**	**1.98**	**1.74**	**1.59**	**1.43**	**1.34**	**1.28**	**1.23**	**1.20**	**1.18**	**1.17**	**1.15**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**
2	5.14	**2.87**	**2.24**	**1.94**	**1.77**	**1.58**	**1.48**	**1.40**	**1.35**	**1.32**	**1.29**	**1.27**	**1.26**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**
3	5.61	3.09	**2.39**	**2.06**	**1.88**	**1.67**	**1.56**	**1.47**	**1.42**	**1.38**	**1.35**	**1.33**	**1.32**	**1.29**	**1.27**	**1.26**	**1.25**	**1.24**	**1.23**	**1.22**
4	5.94	3.24	**2.49**	**2.15**	**1.95**	**1.73**	**1.61**	**1.52**	**1.47**	**1.43**	**1.40**	**1.38**	**1.36**	**1.33**	**1.31**	**1.30**	**1.29**	**1.28**	**1.27**	**1.26**
5	6.19	3.35	**2.57**	**2.21**	**2.01**	**1.78**	**1.65**	**1.56**	**1.50**	**1.46**	**1.43**	**1.41**	**1.39**	**1.36**	**1.34**	**1.33**	**1.32**	**1.31**	**1.29**	**1.28**
8	6.71	3.60	**2.74**	**2.35**	**2.13**	**1.88**	**1.74**	**1.64**	**1.58**	**1.53**	**1.50**	**1.48**	**1.46**	**1.43**	**1.41**	**1.39**	**1.38**	**1.37**	**1.35**	**1.34**
12	7.15	3.80	*2.89*	**2.47**	**2.23**	**1.96**	**1.82**	**1.71**	**1.64**	**1.59**	**1.56**	**1.53**	**1.51**	**1.48**	**1.46**	**1.44**	**1.43**	**1.42**	**1.40**	**1.39**
16	7.46	3.95	*2.99*	**2.55**	**2.30**	**2.02**	**1.87**	**1.76**	**1.69**	**1.64**	**1.60**	**1.57**	**1.55**	**1.52**	**1.49**	**1.48**	**1.46**	**1.45**	**1.44**	**1.42**
20	7.70	4.06	3.07	**2.62**	**2.36**	**2.07**	**1.91**	**1.80**	**1.72**	**1.67**	**1.63**	**1.60**	**1.58**	**1.55**	**1.52**	**1.51**	**1.49**	**1.48**	**1.46**	**1.45**
30	8.11	4.25	3.21	**2.73**	**2.46**	**2.15**	**1.99**	**1.86**	**1.78**	**1.73**	**1.69**	**1.66**	**1.63**	**1.60**	**1.57**	**1.55**	**1.54**	**1.53**	**1.51**	**1.50**
40	8.40	4.39	3.31	**2.81**	**2.53**	**2.21**	**2.04**	**1.91**	**1.83**	**1.77**	**1.73**	**1.70**	**1.67**	**1.63**	**1.61**	**1.59**	**1.57**	**1.56**	**1.54**	**1.53**
50	8.62	4.49	3.38	*2.87*	**2.58**	**2.26**	**2.08**	**1.95**	**1.86**	**1.80**	**1.76**	**1.73**	**1.70**	**1.66**	**1.64**	**1.62**	**1.60**	**1.59**	**1.57**	**1.55**
60	8.80	4.58	3.44	*2.92*	**2.62**	**2.29**	**2.11**	**1.98**	**1.89**	**1.83**	**1.78**	**1.75**	**1.72**	**1.69**	**1.66**	**1.64**	**1.62**	**1.61**	**1.59**	**1.57**
75	9.01	4.68	3.52	*2.98*	**2.68**	**2.34**	**2.15**	**2.01**	**1.92**	**1.86**	**1.82**	**1.78**	**1.75**	**1.71**	**1.68**	**1.66**	**1.65**	**1.63**	**1.61**	**1.60**
100	9.29	4.81	3.61	*3.06*	**2.75**	**2.39**	**2.20**	**2.06**	**1.97**	**1.90**	**1.86**	**1.82**	**1.79**	**1.75**	**1.72**	**1.70**	**1.68**	**1.67**	**1.64**	**1.62**
125	9.50	4.91	3.68	3.12	**2.80**	**2.44**	**2.24**	**2.09**	**2.00**	**1.93**	**1.89**	**1.85**	**1.82**	**1.77**	**1.74**	**1.72**	**1.70**	**1.69**	**1.67**	**1.65**
150	9.67	4.99	3.74	3.17	**2.84**	**2.47**	**2.27**	**2.12**	**2.03**	**1.96**	**1.91**	**1.87**	**1.84**	**1.80**	**1.77**	**1.74**	**1.72**	**1.71**	**1.69**	**1.67**
175	9.81	5.06	3.79	3.21	*2.87*	**2.50**	**2.30**	**2.15**	**2.05**	**1.98**	**1.93**	**1.89**	**1.86**	**1.82**	**1.78**	**1.76**	**1.74**	**1.73**	**1.70**	**1.69**
200	9.93	5.12	3.83	3.24	*2.90*	**2.53**	**2.32**	**2.17**	**2.07**	**2.00**	**1.95**	**1.91**	**1.88**	**1.83**	**1.80**	**1.77**	**1.76**	**1.74**	**1.72**	**1.70**

Table 19-9. κ-Multipliers for 1-of-2 Interwell Prediction Limits on Means of Order 3 (40 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	5.14	**2.87**	**2.24**	**1.94**	**1.77**	**1.58**	**1.48**	**1.40**	**1.35**	**1.32**	**1.29**	**1.27**	**1.26**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**
2	5.94	3.24	**2.49**	**2.15**	**1.95**	**1.73**	**1.61**	**1.52**	**1.47**	**1.43**	**1.40**	**1.38**	**1.36**	**1.33**	**1.31**	**1.30**	**1.29**	**1.28**	**1.27**	**1.26**
3	6.39	3.45	**2.64**	**2.27**	**2.05**	**1.82**	**1.69**	**1.59**	**1.53**	**1.49**	**1.46**	**1.43**	**1.42**	**1.39**	**1.37**	**1.35**	**1.34**	**1.33**	**1.32**	**1.31**
4	6.71	3.60	**2.74**	**2.35**	**2.13**	**1.88**	**1.74**	**1.64**	**1.58**	**1.53**	**1.50**	**1.48**	**1.46**	**1.43**	**1.41**	**1.39**	**1.38**	**1.37**	**1.35**	**1.34**
5	6.96	3.71	**2.82**	**2.42**	**2.18**	**1.92**	**1.78**	**1.68**	**1.61**	**1.57**	**1.53**	**1.51**	**1.49**	**1.46**	**1.43**	**1.42**	**1.41**	**1.40**	**1.38**	**1.37**
8	7.46	3.95	**2.99**	**2.55**	**2.30**	**2.02**	**1.87**	**1.76**	**1.69**	**1.64**	**1.60**	**1.57**	**1.55**	**1.52**	**1.49**	**1.48**	**1.46**	**1.45**	**1.44**	**1.42**
12	7.88	4.14	*3.13*	**2.67**	**2.40**	**2.11**	**1.95**	**1.83**	**1.75**	**1.70**	**1.66**	**1.63**	**1.60**	**1.57**	**1.55**	**1.53**	**1.51**	**1.50**	**1.48**	**1.47**
16	8.18	4.28	3.23	**2.75**	**2.47**	**2.17**	**2.00**	**1.87**	**1.79**	**1.74**	**1.70**	**1.67**	**1.64**	**1.61**	**1.58**	**1.56**	**1.55**	**1.54**	**1.52**	**1.50**
20	8.40	4.39	3.31	**2.81**	**2.53**	**2.21**	**2.04**	**1.91**	**1.83**	**1.77**	**1.73**	**1.70**	**1.67**	**1.63**	**1.61**	**1.59**	**1.57**	**1.56**	**1.54**	**1.53**
30	8.80	4.58	3.44	**2.92**	**2.62**	**2.29**	**2.11**	**1.98**	**1.89**	**1.83**	**1.78**	**1.75**	**1.72**	**1.69**	**1.66**	**1.64**	**1.62**	**1.61**	**1.59**	**1.57**
40	9.08	4.71	3.54	**3.00**	**2.69**	**2.35**	**2.16**	**2.02**	**1.93**	**1.87**	**1.82**	**1.79**	**1.76**	**1.72**	**1.69**	**1.67**	**1.65**	**1.64**	**1.62**	**1.60**
50	9.29	4.81	3.61	*3.06*	**2.75**	**2.39**	**2.20**	**2.06**	**1.97**	**1.90**	**1.86**	**1.82**	**1.79**	**1.75**	**1.72**	**1.70**	**1.68**	**1.67**	**1.64**	**1.62**
60	9.46	4.89	3.67	*3.11*	**2.79**	**2.43**	**2.23**	**2.09**	**1.99**	**1.93**	**1.88**	**1.84**	**1.81**	**1.77**	**1.74**	**1.72**	**1.70**	**1.69**	**1.66**	**1.65**
75	9.67	4.99	3.74	*3.17*	**2.84**	**2.47**	**2.27**	**2.12**	**2.03**	**1.96**	**1.91**	**1.87**	**1.84**	**1.80**	**1.77**	**1.74**	**1.72**	**1.71**	**1.69**	**1.67**
100	9.93	5.12	3.83	*3.24*	**2.90**	**2.53**	**2.32**	**2.17**	**2.07**	**2.00**	**1.95**	**1.91**	**1.88**	**1.83**	**1.80**	**1.77**	**1.76**	**1.74**	**1.72**	**1.70**
125	10.12	5.21	3.90	3.30	**2.95**	**2.57**	**2.36**	**2.20**	**2.10**	**2.03**	**1.98**	**1.94**	**1.90**	**1.86**	**1.82**	**1.80**	**1.78**	**1.77**	**1.74**	**1.72**
150	10.29	5.29	3.96	3.35	**3.00**	**2.61**	**2.39**	**2.23**	**2.13**	**2.05**	**2.00**	**1.96**	**1.93**	**1.88**	**1.85**	**1.82**	**1.80**	**1.79**	**1.76**	**1.74**
175	10.42	5.36	4.00	3.39	**3.03**	**2.63**	**2.42**	**2.25**	**2.15**	**2.07**	**2.02**	**1.98**	**1.95**	**1.90**	**1.86**	**1.84**	**1.82**	**1.80**	**1.77**	**1.76**
200	10.54	5.41	4.04	3.42	*3.06*	**2.66**	**2.44**	**2.27**	**2.17**	**2.09**	**2.04**	**2.00**	**1.96**	**1.91**	**1.88**	**1.85**	**1.83**	**1.82**	**1.79**	**1.77**

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D STATISTICAL TABLES

D.3 TABLES FROM CHAPTER 19: INTRAWELL PREDICTION LIMITS FOR FUTURE OBSERVATIONS

TABLE 19-10 κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Observations.....D-118

TABLE 19-11 κ-Multipliers for 1-of-3 Intrawell Prediction Limits on Observations.....D-127

TABLE 19-12 κ-Multipliers for 1-of-4 Intrawell Prediction Limits on Observations.....D-136

TABLE 19-13 κ-Multipliers for Mod. Cal. Intrawell Prediction Limits on Observations.....D-145

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Table 19-10. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Observations (1 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**0.78**	**0.67**	**0.61**	**0.58**	**0.57**	**0.54**	**0.53**	**0.52**	**0.51**	**0.51**	**0.50**	**0.50**	**0.50**	**0.50**	**0.49**	**0.49**	**0.49**	**0.49**	**0.49**	**0.49**
2	**1.27**	**1.05**	**0.97**	**0.92**	**0.89**	**0.85**	**0.83**	**0.81**	**0.80**	**0.79**	**0.79**	**0.78**	**0.78**	**0.78**	**0.77**	**0.77**	**0.77**	**0.77**	**0.76**	**0.76**
3	**1.59**	**1.28**	**1.17**	**1.10**	**1.06**	**1.02**	**0.99**	**0.97**	**0.96**	**0.95**	**0.94**	**0.94**	**0.93**	**0.93**	**0.92**	**0.92**	**0.91**	**0.91**	**0.91**	**0.91**
4	**1.82**	**1.45**	**1.31**	**1.23**	**1.19**	**1.13**	**1.10**	**1.08**	**1.06**	**1.05**	**1.04**	**1.04**	**1.03**	**1.03**	**1.02**	**1.02**	**1.01**	**1.01**	**1.01**	**1.00**
5	**2.02**	**1.58**	**1.41**	**1.33**	**1.28**	**1.22**	**1.19**	**1.16**	**1.14**	**1.13**	**1.12**	**1.11**	**1.11**	**1.10**	**1.09**	**1.09**	**1.09**	**1.08**	**1.08**	**1.08**
8	2.47	**1.86**	**1.65**	**1.54**	**1.47**	**1.40**	**1.36**	**1.32**	**1.30**	**1.29**	**1.28**	**1.27**	**1.26**	**1.25**	**1.24**	**1.24**	**1.24**	**1.23**	**1.23**	**1.22**
12	2.90	**2.11**	**1.85**	**1.72**	**1.64**	**1.55**	**1.50**	**1.46**	**1.43**	**1.42**	**1.40**	**1.39**	**1.39**	**1.38**	**1.37**	**1.36**	**1.36**	**1.35**	**1.35**	**1.34**
16	3.24	**2.30**	**1.99**	**1.84**	**1.75**	**1.65**	**1.60**	**1.55**	**1.53**	**1.51**	**1.49**	**1.48**	**1.47**	**1.46**	**1.45**	**1.44**	**1.44**	**1.43**	**1.43**	**1.42**
20	3.52	**2.45**	**2.11**	**1.94**	**1.84**	**1.73**	**1.67**	**1.62**	**1.59**	**1.57**	**1.56**	**1.55**	**1.54**	**1.52**	**1.51**	**1.51**	**1.50**	**1.50**	**1.49**	**1.48**
30	4.09	2.73	**2.32**	**2.12**	**2.01**	**1.88**	**1.80**	**1.75**	**1.72**	**1.69**	**1.68**	**1.66**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.61**	**1.60**	**1.59**
40	4.54	2.94	*2.47*	**2.25**	**2.12**	**1.98**	**1.90**	**1.84**	**1.80**	**1.78**	**1.76**	**1.74**	**1.73**	**1.71**	**1.70**	**1.69**	**1.69**	**1.68**	**1.67**	**1.66**
50	4.91	3.11	2.59	**2.35**	**2.21**	**2.06**	**1.97**	**1.91**	**1.87**	**1.84**	**1.82**	**1.80**	**1.79**	**1.77**	**1.76**	**1.75**	**1.74**	**1.74**	**1.73**	**1.72**
60	5.24	3.26	2.70	*2.43*	**2.29**	**2.12**	**2.03**	**1.96**	**1.92**	**1.89**	**1.87**	**1.85**	**1.84**	**1.82**	**1.81**	**1.80**	**1.79**	**1.78**	**1.77**	**1.76**
75	5.67	3.44	2.82	*2.54*	**2.38**	**2.20**	**2.10**	**2.03**	**1.98**	**1.95**	**1.93**	**1.91**	**1.90**	**1.88**	**1.86**	**1.85**	**1.84**	**1.84**	**1.83**	**1.82**
100	6.26	3.68	2.99	2.67	*2.49*	**2.30**	**2.19**	**2.11**	**2.07**	**2.03**	**2.01**	**1.99**	**1.97**	**1.95**	**1.93**	**1.92**	**1.91**	**1.91**	**1.89**	**1.89**
125	6.76	3.88	3.12	2.78	*2.59*	**2.37**	**2.26**	**2.18**	**2.13**	**2.09**	**2.07**	**2.05**	**2.03**	**2.01**	**1.99**	**1.98**	**1.97**	**1.96**	**1.95**	**1.94**
150	7.20	4.05	3.23	2.87	2.66	*2.44*	**2.32**	**2.23**	**2.18**	**2.14**	**2.11**	**2.09**	**2.07**	**2.05**	**2.03**	**2.02**	**2.01**	**2.00**	**1.99**	**1.98**
175	7.59	4.19	3.33	2.94	2.72	*2.49*	**2.37**	**2.28**	**2.22**	**2.18**	**2.15**	**2.13**	**2.11**	**2.09**	**2.07**	**2.06**	**2.05**	**2.04**	**2.02**	**2.01**
200	7.95	4.32	3.41	3.01	2.78	*2.54*	*2.41*	**2.32**	**2.26**	**2.22**	**2.19**	**2.16**	**2.15**	**2.12**	**2.10**	**2.09**	**2.08**	**2.07**	**2.05**	**2.04**

Table 19-10. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Observations (1 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.21**	**1.03**	**0.95**	**0.90**	**0.88**	**0.84**	**0.82**	**0.81**	**0.80**	**0.79**	**0.79**	**0.78**	**0.78**	**0.77**	**0.77**	**0.77**	**0.77**	**0.76**	**0.76**	**0.76**
2	**1.76**	**1.42**	**1.29**	**1.22**	**1.18**	**1.13**	**1.10**	**1.08**	**1.06**	**1.05**	**1.04**	**1.04**	**1.03**	**1.02**	**1.02**	**1.02**	**1.01**	**1.01**	**1.01**	**1.00**
3	**2.11**	**1.66**	**1.49**	**1.40**	**1.35**	**1.28**	**1.25**	**1.22**	**1.20**	**1.19**	**1.18**	**1.17**	**1.17**	**1.16**	**1.15**	**1.15**	**1.14**	**1.14**	**1.14**	**1.13**
4	**2.39**	**1.83**	**1.63**	**1.53**	**1.47**	**1.39**	**1.35**	**1.32**	**1.30**	**1.29**	**1.27**	**1.27**	**1.26**	**1.25**	**1.24**	**1.24**	**1.23**	**1.23**	**1.23**	**1.22**
5	**2.62**	**1.97**	**1.74**	**1.63**	**1.56**	**1.48**	**1.43**	**1.40**	**1.37**	**1.36**	**1.35**	**1.34**	**1.33**	**1.32**	**1.31**	**1.31**	**1.30**	**1.30**	**1.29**	**1.29**
8	3.15	**2.27**	**1.98**	**1.83**	**1.75**	**1.65**	**1.59**	**1.55**	**1.52**	**1.50**	**1.49**	**1.48**	**1.47**	**1.46**	**1.45**	**1.44**	**1.44**	**1.43**	**1.43**	**1.42**
12	3.67	**2.55**	**2.19**	**2.01**	**1.91**	**1.79**	**1.73**	**1.68**	**1.65**	**1.63**	**1.61**	**1.60**	**1.59**	**1.57**	**1.56**	**1.56**	**1.55**	**1.55**	**1.54**	**1.53**
16	4.08	**2.75**	**2.34**	**2.14**	**2.03**	**1.90**	**1.82**	**1.77**	**1.74**	**1.71**	**1.69**	**1.68**	**1.67**	**1.65**	**1.64**	**1.63**	**1.63**	**1.62**	**1.61**	**1.61**
20	4.42	2.91	**2.46**	**2.24**	**2.12**	**1.98**	**1.90**	**1.84**	**1.80**	**1.78**	**1.76**	**1.74**	**1.73**	**1.71**	**1.70**	**1.69**	**1.69**	**1.68**	**1.67**	**1.66**
30	5.11	3.23	**2.68**	**2.43**	**2.28**	**2.12**	**2.03**	**1.96**	**1.92**	**1.89**	**1.87**	**1.85**	**1.84**	**1.82**	**1.81**	**1.80**	**1.79**	**1.78**	**1.77**	**1.76**
40	5.65	3.46	*2.85*	**2.56**	**2.40**	**2.22**	**2.12**	**2.05**	**2.00**	**1.97**	**1.95**	**1.93**	**1.91**	**1.89**	**1.88**	**1.87**	**1.86**	**1.85**	**1.84**	**1.83**
50	6.11	3.65	2.98	**2.67**	**2.49**	**2.30**	**2.19**	**2.11**	**2.06**	**2.03**	**2.01**	**1.99**	**1.97**	**1.95**	**1.93**	**1.92**	**1.91**	**1.91**	**1.89**	**1.89**
60	6.50	3.81	3.08	**2.75**	**2.56**	**2.36**	**2.25**	**2.17**	**2.12**	**2.08**	**2.05**	**2.03**	**2.02**	**2.00**	**1.98**	**1.97**	**1.96**	**1.95**	**1.94**	**1.93**
75	7.02	4.02	3.22	*2.86*	**2.66**	**2.44**	**2.32**	**2.23**	**2.18**	**2.14**	**2.11**	**2.09**	**2.07**	**2.05**	**2.03**	**2.02**	**2.01**	**2.00**	**1.99**	**1.98**
100	7.75	4.29	3.40	3.00	*2.78*	**2.54**	**2.41**	**2.32**	**2.26**	**2.22**	**2.19**	**2.16**	**2.15**	**2.12**	**2.10**	**2.09**	**2.08**	**2.07**	**2.05**	**2.04**
125	8.36	4.51	3.54	3.11	*2.87*	**2.62**	**2.48**	**2.38**	**2.32**	**2.27**	**2.24**	**2.22**	**2.20**	**2.17**	**2.15**	**2.14**	**2.13**	**2.12**	**2.10**	**2.09**
150	8.91	4.70	3.66	3.20	*2.95*	**2.68**	**2.54**	**2.43**	**2.37**	**2.32**	**2.29**	**2.26**	**2.24**	**2.22**	**2.20**	**2.18**	**2.17**	**2.16**	**2.14**	**2.13**
175	9.38	4.86	3.76	3.28	3.02	**2.73**	**2.59**	**2.48**	**2.41**	**2.36**	**2.33**	**2.30**	**2.28**	**2.25**	**2.23**	**2.22**	**2.20**	**2.19**	**2.18**	**2.17**
200	9.81	5.01	3.85	3.35	3.07	*2.78*	**2.63**	**2.51**	**2.44**	**2.40**	**2.36**	**2.33**	**2.31**	**2.28**	**2.26**	**2.24**	**2.23**	**2.22**	**2.21**	**2.19**

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Table 19-10. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Observations (1 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.65**	**1.37**	**1.26**	**1.20**	**1.16**	**1.12**	**1.09**	**1.07**	**1.06**	**1.05**	**1.04**	**1.03**	**1.03**	**1.02**	**1.02**	**1.01**	**1.01**	**1.01**	**1.00**	**1.00**
2	**2.27**	**1.78**	**1.61**	**1.51**	**1.45**	**1.39**	**1.35**	**1.32**	**1.30**	**1.28**	**1.27**	**1.26**	**1.26**	**1.25**	**1.24**	**1.24**	**1.23**	**1.23**	**1.23**	**1.22**
3	**2.68**	**2.04**	**1.81**	**1.69**	**1.62**	**1.54**	**1.49**	**1.45**	**1.43**	**1.41**	**1.40**	**1.39**	**1.38**	**1.37**	**1.37**	**1.36**	**1.36**	**1.35**	**1.34**	**1.34**
4	3.00	**2.22**	**1.96**	**1.82**	**1.74**	**1.64**	**1.59**	**1.55**	**1.52**	**1.50**	**1.49**	**1.48**	**1.47**	**1.46**	**1.45**	**1.44**	**1.44**	**1.43**	**1.43**	**1.42**
5	3.27	**2.37**	**2.07**	**1.92**	**1.83**	**1.72**	**1.66**	**1.62**	**1.59**	**1.57**	**1.56**	**1.54**	**1.54**	**1.52**	**1.51**	**1.51**	**1.50**	**1.50**	**1.49**	**1.48**
8	3.90	**2.70**	**2.32**	**2.13**	**2.02**	**1.89**	**1.82**	**1.77**	**1.73**	**1.71**	**1.69**	**1.68**	**1.67**	**1.65**	**1.64**	**1.63**	**1.63**	**1.62**	**1.61**	**1.61**
12	4.52	**3.00**	**2.54**	**2.31**	**2.18**	**2.03**	**1.95**	**1.89**	**1.85**	**1.83**	**1.81**	**1.79**	**1.78**	**1.76**	**1.75**	**1.74**	**1.73**	**1.73**	**1.72**	**1.71**
16	5.01	3.23	**2.70**	**2.45**	**2.30**	**2.14**	**2.05**	**1.98**	**1.94**	**1.91**	**1.89**	**1.87**	**1.86**	**1.84**	**1.82**	**1.81**	**1.80**	**1.80**	**1.79**	**1.78**
20	5.42	3.41	**2.83**	**2.55**	**2.39**	**2.21**	**2.12**	**2.05**	**2.00**	**1.97**	**1.95**	**1.93**	**1.91**	**1.89**	**1.88**	**1.87**	**1.86**	**1.85**	**1.84**	**1.83**
30	6.24	3.76	**3.06**	**2.74**	**2.56**	**2.36**	**2.25**	**2.17**	**2.11**	**2.08**	**2.05**	**2.03**	**2.02**	**2.00**	**1.98**	**1.97**	**1.96**	**1.95**	**1.94**	**1.93**
40	6.89	4.02	3.24	**2.88**	**2.68**	**2.46**	**2.34**	**2.25**	**2.19**	**2.16**	**2.13**	**2.11**	**2.09**	**2.07**	**2.05**	**2.04**	**2.03**	**2.02**	**2.00**	**1.99**
50	7.45	4.23	3.38	**2.99**	**2.77**	**2.53**	**2.41**	**2.32**	**2.26**	**2.22**	**2.19**	**2.16**	**2.15**	**2.12**	**2.10**	**2.09**	**2.08**	**2.07**	**2.05**	**2.04**
60	7.92	4.41	3.49	**3.08**	**2.85**	**2.60**	**2.47**	**2.37**	**2.31**	**2.26**	**2.23**	**2.21**	**2.19**	**2.16**	**2.14**	**2.13**	**2.12**	**2.11**	**2.09**	**2.08**
75	8.55	4.64	3.64	*3.19*	**2.94**	**2.68**	**2.54**	**2.43**	**2.37**	**2.32**	**2.29**	**2.26**	**2.24**	**2.22**	**2.20**	**2.18**	**2.17**	**2.16**	**2.14**	**2.13**
100	9.43	4.95	3.83	3.34	**3.07**	**2.78**	**2.63**	**2.51**	**2.44**	**2.40**	**2.36**	**2.33**	**2.31**	**2.28**	**2.26**	**2.24**	**2.23**	**2.22**	**2.21**	**2.19**
125	10.17	5.20	3.98	3.46	*3.17*	**2.86**	**2.70**	**2.58**	**2.50**	**2.45**	**2.42**	**2.39**	**2.37**	**2.33**	**2.31**	**2.29**	**2.28**	**2.27**	**2.25**	**2.24**
150	10.82	5.41	4.11	3.55	*3.25*	**2.92**	**2.75**	**2.63**	**2.55**	**2.50**	**2.46**	**2.43**	**2.41**	**2.37**	**2.35**	**2.33**	**2.32**	**2.31**	**2.29**	**2.28**
175	11.40	5.59	4.22	3.64	*3.32*	**2.98**	**2.80**	**2.67**	**2.59**	**2.54**	**2.50**	**2.47**	**2.44**	**2.41**	**2.39**	**2.37**	**2.35**	**2.34**	**2.32**	**2.31**
200	11.92	5.76	4.32	3.71	3.37	**3.02**	**2.84**	**2.71**	**2.63**	**2.57**	**2.53**	**2.50**	**2.48**	**2.44**	**2.42**	**2.40**	**2.38**	**2.37**	**2.35**	**2.34**

Table 19-10. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Observations (2 COC, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.27**	**1.05**	**0.97**	**0.92**	**0.89**	**0.85**	**0.83**	**0.81**	**0.80**	**0.79**	**0.79**	**0.78**	**0.78**	**0.78**	**0.77**	**0.77**	**0.77**	**0.77**	**0.76**	**0.76**
2	**1.82**	**1.45**	**1.31**	**1.23**	**1.19**	**1.13**	**1.10**	**1.08**	**1.06**	**1.05**	**1.04**	**1.04**	**1.03**	**1.03**	**1.02**	**1.02**	**1.01**	**1.01**	**1.01**	**1.00**
3	**2.19**	**1.68**	**1.50**	**1.41**	**1.35**	**1.29**	**1.25**	**1.22**	**1.20**	**1.19**	**1.18**	**1.17**	**1.17**	**1.16**	**1.15**	**1.15**	**1.15**	**1.14**	**1.14**	**1.13**
4	2.47	**1.86**	**1.65**	**1.54**	**1.47**	**1.40**	**1.36**	**1.32**	**1.30**	**1.29**	**1.28**	**1.27**	**1.26**	**1.25**	**1.24**	**1.24**	**1.24**	**1.23**	**1.23**	**1.22**
5	2.70	**1.99**	**1.76**	**1.64**	**1.56**	**1.48**	**1.43**	**1.40**	**1.38**	**1.36**	**1.35**	**1.34**	**1.33**	**1.32**	**1.31**	**1.31**	**1.30**	**1.30**	**1.29**	**1.29**
8	3.24	**2.30**	**1.99**	**1.84**	**1.75**	**1.65**	**1.60**	**1.55**	**1.53**	**1.51**	**1.49**	**1.48**	**1.47**	**1.46**	**1.45**	**1.44**	**1.44**	**1.43**	**1.43**	**1.42**
12	3.77	2.57	**2.20**	**2.02**	**1.92**	**1.80**	**1.73**	**1.68**	**1.65**	**1.63**	**1.61**	**1.60**	**1.59**	**1.57**	**1.56**	**1.56**	**1.55**	**1.55**	**1.54**	**1.53**
16	4.19	2.78	**2.35**	**2.15**	**2.03**	**1.90**	**1.83**	**1.77**	**1.74**	**1.71**	**1.69**	**1.68**	**1.67**	**1.65**	**1.64**	**1.63**	**1.63**	**1.62**	**1.61**	**1.61**
20	4.54	2.94	*2.47*	**2.25**	**2.12**	**1.98**	**1.90**	**1.84**	**1.80**	**1.78**	**1.76**	**1.74**	**1.73**	**1.71**	**1.70**	**1.69**	**1.69**	**1.68**	**1.67**	**1.66**
30	5.24	3.26	2.70	*2.43*	**2.29**	**2.12**	**2.03**	**1.96**	**1.92**	**1.89**	**1.87**	**1.85**	**1.84**	**1.82**	**1.81**	**1.80**	**1.79**	**1.78**	**1.77**	**1.76**
40	5.80	3.49	2.86	*2.57*	**2.40**	**2.22**	**2.12**	**2.05**	**2.00**	**1.97**	**1.95**	**1.93**	**1.91**	**1.89**	**1.88**	**1.87**	**1.86**	**1.85**	**1.84**	**1.83**
50	6.26	3.68	2.99	2.67	*2.49*	**2.30**	**2.19**	**2.11**	**2.07**	**2.03**	**2.01**	**1.99**	**1.97**	**1.95**	**1.93**	**1.92**	**1.91**	**1.91**	**1.89**	**1.89**
60	6.67	3.84	3.10	2.76	*2.57*	**2.36**	**2.25**	**2.17**	**2.12**	**2.08**	**2.05**	**2.03**	**2.02**	**2.00**	**1.98**	**1.97**	**1.96**	**1.95**	**1.93**	**1.92**
75	7.20	4.05	3.23	2.87	2.66	*2.44*	**2.32**	**2.23**	**2.18**	**2.14**	**2.11**	**2.09**	**2.08**	**2.05**	**2.03**	**2.02**	**2.01**	**2.00**	**1.99**	**1.98**
100	7.95	4.32	3.41	3.01	2.78	*2.54*	*2.41*	**2.32**	**2.26**	**2.22**	**2.19**	**2.16**	**2.15**	**2.12**	**2.10**	**2.09**	**2.08**	**2.07**	**2.05**	**2.04**
125	8.57	4.55	3.55	3.12	2.88	*2.62*	*2.48*	**2.38**	**2.32**	**2.27**	**2.24**	**2.22**	**2.20**	**2.17**	**2.15**	**2.14**	**2.13**	**2.12**	**2.10**	**2.09**
150	9.12	4.74	3.67	3.21	2.95	2.68	*2.54*	*2.43*	**2.37**	**2.32**	**2.29**	**2.26**	**2.24**	**2.22**	**2.20**	**2.18**	**2.17**	**2.16**	**2.14**	**2.13**
175	9.61	4.90	3.77	3.29	3.02	2.73	*2.59*	*2.48*	*2.41*	**2.36**	**2.33**	**2.30**	**2.28**	**2.25**	**2.23**	**2.22**	**2.20**	**2.19**	**2.18**	**2.17**
200	10.06	5.04	3.86	3.35	3.08	2.78	*2.63*	*2.51*	*2.44*	*2.40*	**2.36**	**2.33**	**2.31**	**2.28**	**2.26**	**2.24**	**2.23**	**2.22**	**2.21**	**2.19**

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Table 19-10. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Observations (2 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	1.76	1.42	1.29	1.22	1.18	1.13	1.10	1.08	1.06	1.05	1.04	1.04	1.03	1.02	1.02	1.02	1.01	1.01	1.01	1.00
2	2.39	1.83	1.63	1.53	1.47	1.39	1.35	1.32	1.30	1.29	1.28	1.27	1.26	1.25	1.24	1.24	1.23	1.23	1.23	1.22
3	2.82	2.08	1.83	1.71	1.63	1.54	1.49	1.46	1.43	1.42	1.40	1.39	1.39	1.37	1.37	1.36	1.36	1.35	1.35	1.34
4	3.15	2.27	1.98	1.83	1.75	1.65	1.59	1.55	1.52	1.50	1.49	1.48	1.47	1.46	1.45	1.44	1.44	1.43	1.43	1.42
5	3.43	2.42	2.09	1.93	1.84	1.73	1.67	1.62	1.59	1.57	1.56	1.55	1.54	1.52	1.51	1.51	1.50	1.50	1.49	1.48
8	4.08	2.75	2.34	2.14	2.03	1.90	1.82	1.77	1.74	1.71	1.69	1.68	1.67	1.65	1.64	1.63	1.63	1.62	1.61	1.61
12	4.72	3.05	2.56	2.33	2.19	2.04	1.96	1.89	1.86	1.83	1.81	1.79	1.78	1.76	1.75	1.74	1.73	1.73	1.72	1.71
16	5.22	3.28	2.72	2.46	2.31	2.14	2.05	1.98	1.94	1.91	1.89	1.87	1.86	1.84	1.82	1.81	1.81	1.80	1.79	1.78
20	5.65	3.46	*2.85*	2.56	2.40	2.22	2.12	2.05	2.00	1.97	1.95	1.93	1.91	1.89	1.88	1.87	1.86	1.85	1.84	1.83
30	6.50	3.81	3.08	2.75	2.57	2.36	2.25	2.17	2.12	2.08	2.05	2.03	2.02	2.00	1.98	1.97	1.96	1.95	1.93	1.92
40	7.18	4.08	3.26	*2.89*	2.68	2.46	2.34	2.25	2.20	2.16	2.13	2.11	2.09	2.07	2.05	2.04	2.03	2.02	2.00	1.99
50	7.75	4.29	3.40	3.00	*2.78*	2.54	2.41	2.32	2.26	2.22	2.19	2.16	2.15	2.12	2.10	2.09	2.08	2.07	2.05	2.04
60	8.25	4.47	3.51	3.09	*2.86*	2.60	2.47	2.37	2.31	2.26	2.23	2.21	2.19	2.16	2.14	2.13	2.12	2.11	2.09	2.08
75	8.91	4.70	3.66	3.20	*2.95*	2.68	2.54	2.43	2.37	2.32	2.29	2.26	2.24	2.22	2.20	2.18	2.17	2.16	2.14	2.13
100	9.81	5.01	3.85	3.35	3.07	*2.78*	2.63	2.51	2.44	2.40	2.36	2.33	2.31	2.28	2.26	2.24	2.23	2.22	2.21	2.19
125	10.59	5.26	4.00	3.47	3.17	*2.86*	2.70	2.58	2.50	2.45	2.42	2.39	2.37	2.33	2.31	2.29	2.28	2.27	2.25	2.24
150	11.25	5.47	4.13	3.56	3.25	*2.92*	2.75	2.63	2.55	2.50	2.46	2.43	2.41	2.38	2.35	2.33	2.32	2.31	2.29	2.28
175	11.86	5.66	4.24	3.65	3.32	*2.98*	*2.80*	2.67	2.59	2.54	2.50	2.47	2.45	2.41	2.39	2.37	2.35	2.34	2.32	2.31
200	12.40	5.82	4.34	3.72	3.38	3.03	*2.84*	2.71	2.63	2.57	2.53	2.50	2.48	2.44	2.41	2.40	2.38	2.37	2.35	2.34

Table 19-10. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Observations (2 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	2.27	1.78	1.61	1.51	1.45	1.39	1.35	1.32	1.30	1.28	1.27	1.26	1.26	1.25	1.24	1.24	1.23	1.23	1.23	1.22
2	3.00	2.22	1.96	1.82	1.74	1.64	1.59	1.55	1.52	1.50	1.49	1.48	1.47	1.46	1.45	1.44	1.44	1.43	1.43	1.42
3	3.51	2.50	2.17	2.00	1.90	1.79	1.73	1.68	1.65	1.63	1.61	1.60	1.59	1.57	1.56	1.56	1.55	1.55	1.54	1.53
4	3.90	2.70	2.32	2.13	2.02	1.89	1.82	1.77	1.73	1.71	1.69	1.68	1.67	1.65	1.64	1.63	1.63	1.62	1.61	1.61
5	4.23	2.87	2.44	2.23	2.11	1.97	1.89	1.84	1.80	1.77	1.76	1.74	1.73	1.71	1.70	1.69	1.69	1.68	1.67	1.66
8	5.01	3.23	2.70	2.45	2.30	2.14	2.05	1.98	1.94	1.91	1.89	1.87	1.86	1.84	1.82	1.81	1.80	1.80	1.79	1.78
12	5.78	3.57	2.93	2.64	2.47	2.28	2.18	2.10	2.05	2.02	1.99	1.98	1.96	1.94	1.92	1.91	1.90	1.90	1.89	1.88
16	6.38	3.82	3.10	2.77	2.59	2.38	2.27	2.19	2.13	2.10	2.07	2.05	2.03	2.01	1.99	1.98	1.97	1.97	1.95	1.94
20	6.89	4.02	3.24	2.88	2.68	2.46	2.34	2.25	2.19	2.16	2.13	2.11	2.09	2.07	2.05	2.04	2.03	2.02	2.00	1.99
30	7.92	4.41	3.49	3.08	2.85	2.60	2.47	2.37	2.31	2.26	2.23	2.21	2.19	2.16	2.14	2.13	2.12	2.11	2.09	2.08
40	8.74	4.71	3.68	*3.23*	2.97	2.70	2.56	2.45	2.38	2.34	2.30	2.28	2.26	2.23	2.21	2.19	2.18	2.17	2.16	2.15
50	9.43	4.95	3.83	3.34	3.07	2.78	2.63	2.51	2.44	2.40	2.36	2.33	2.31	2.28	2.26	2.24	2.23	2.22	2.21	2.19
60	10.03	5.15	3.95	3.44	*3.15*	2.84	2.68	2.57	2.49	2.44	2.41	2.38	2.36	2.32	2.30	2.29	2.27	2.26	2.24	2.23
75	10.82	5.41	4.11	3.55	*3.25*	2.92	2.75	2.63	2.55	2.50	2.46	2.43	2.41	2.37	2.35	2.33	2.32	2.31	2.29	2.28
100	11.92	5.76	4.32	3.71	3.38	3.02	2.84	2.71	2.63	2.57	2.53	2.50	2.48	2.44	2.41	2.40	2.38	2.37	2.35	2.34
125	12.85	6.04	4.48	3.83	3.48	3.10	2.91	2.77	2.69	2.63	2.58	2.55	2.53	2.49	2.46	2.44	2.43	2.42	2.40	2.38
150	13.67	6.28	4.62	3.93	3.56	*3.17*	2.97	2.82	2.73	2.67	2.63	2.60	2.57	2.53	2.50	2.48	2.47	2.45	2.43	2.42
175	14.39	6.49	4.74	4.02	3.63	*3.23*	3.02	2.87	2.77	2.71	2.67	2.63	2.60	2.56	2.54	2.51	2.50	2.49	2.46	2.45
200	15.04	6.68	4.85	4.10	3.69	*3.27*	3.06	2.91	2.81	2.74	2.70	2.66	2.63	2.59	2.56	2.54	2.53	2.51	2.49	2.48

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Table 19-10. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Observations (5 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.02**	**1.58**	**1.41**	**1.33**	**1.28**	**1.22**	**1.19**	**1.16**	**1.14**	**1.13**	**1.12**	**1.11**	**1.11**	**1.10**	**1.09**	**1.09**	**1.09**	**1.08**	**1.08**	**1.08**
2	2.70	**1.99**	**1.76**	**1.64**	**1.56**	**1.48**	**1.43**	**1.40**	**1.38**	**1.36**	**1.35**	**1.34**	**1.33**	**1.32**	**1.31**	**1.31**	**1.30**	**1.30**	**1.29**	**1.29**
3	3.16	**2.25**	**1.96**	**1.81**	**1.73**	**1.63**	**1.57**	**1.53**	**1.50**	**1.49**	**1.47**	**1.46**	**1.45**	**1.44**	**1.43**	**1.43**	**1.42**	**1.42**	**1.41**	**1.40**
4	3.52	**2.45**	**2.11**	**1.94**	**1.84**	**1.73**	**1.67**	**1.62**	**1.59**	**1.57**	**1.56**	**1.55**	**1.54**	**1.52**	**1.51**	**1.51**	**1.50**	**1.50**	**1.49**	**1.48**
5	3.83	2.60	**2.22**	**2.04**	**1.93**	**1.81**	**1.74**	**1.69**	**1.66**	**1.64**	**1.62**	**1.61**	**1.60**	**1.59**	**1.58**	**1.57**	**1.56**	**1.56**	**1.55**	**1.54**
8	4.54	2.94	*2.47*	**2.25**	**2.12**	**1.98**	**1.90**	**1.84**	**1.80**	**1.78**	**1.76**	**1.74**	**1.73**	**1.71**	**1.70**	**1.69**	**1.69**	**1.68**	**1.67**	**1.66**
12	5.24	3.26	2.69	*2.43*	**2.29**	**2.12**	**2.03**	**1.96**	**1.92**	**1.89**	**1.87**	**1.85**	**1.84**	**1.82**	**1.81**	**1.80**	**1.79**	**1.78**	**1.77**	**1.76**
16	5.80	3.49	2.86	*2.57*	**2.40**	**2.22**	**2.12**	**2.05**	**2.00**	**1.97**	**1.95**	**1.93**	**1.91**	**1.89**	**1.88**	**1.87**	**1.86**	**1.85**	**1.84**	**1.83**
20	6.26	3.68	2.99	2.67	*2.49*	**2.30**	**2.19**	**2.11**	**2.07**	**2.03**	**2.01**	**1.99**	**1.97**	**1.95**	**1.93**	**1.92**	**1.91**	**1.91**	**1.89**	**1.89**
30	7.20	4.05	3.23	2.87	2.66	*2.44*	**2.32**	**2.23**	**2.18**	**2.14**	**2.11**	**2.09**	**2.08**	**2.05**	**2.03**	**2.02**	**2.01**	**2.00**	**1.99**	**1.98**
40	7.95	4.32	3.41	3.01	2.78	*2.54*	*2.41*	**2.32**	**2.26**	**2.22**	**2.19**	**2.16**	**2.15**	**2.12**	**2.10**	**2.09**	**2.08**	**2.07**	**2.05**	**2.04**
50	8.57	4.55	3.55	3.12	2.87	*2.62*	*2.48*	**2.38**	**2.32**	**2.28**	**2.24**	**2.22**	**2.20**	**2.17**	**2.15**	**2.14**	**2.13**	**2.12**	**2.10**	**2.09**
60	9.12	4.74	3.67	3.21	2.95	2.68	*2.54*	*2.43*	**2.37**	**2.32**	**2.29**	**2.26**	**2.24**	**2.22**	**2.20**	**2.18**	**2.17**	**2.16**	**2.14**	**2.13**
75	9.84	4.97	3.82	3.32	3.05	2.76	*2.61*	*2.50*	*2.43*	**2.38**	**2.35**	**2.32**	**2.30**	**2.27**	**2.25**	**2.23**	**2.22**	**2.21**	**2.19**	**2.18**
100	10.84	5.30	4.02	3.47	3.17	2.86	2.70	*2.58*	*2.50*	*2.45*	*2.42*	*2.39*	**2.37**	**2.33**	**2.31**	**2.29**	**2.28**	**2.27**	**2.25**	**2.24**
125	11.67	5.57	4.17	3.59	3.27	2.94	2.77	*2.64*	*2.56*	*2.51*	*2.47*	*2.44*	*2.42*	*2.38*	**2.36**	**2.34**	**2.33**	**2.32**	**2.30**	**2.29**
150	12.45	5.79	4.30	3.69	3.36	3.00	2.83	2.69	*2.61*	*2.56*	*2.51*	*2.48*	*2.46*	*2.43*	*2.40*	*2.38*	**2.37**	**2.36**	**2.34**	**2.33**
175	13.09	5.98	4.42	3.77	3.42	3.06	2.87	2.73	*2.65*	*2.59*	*2.55*	*2.52*	*2.50*	*2.46*	*2.44*	*2.42*	*2.40*	*2.39*	**2.37**	**2.36**
200	13.67	6.15	4.52	3.85	3.49	3.11	2.91	2.77	2.69	*2.63*	*2.58*	*2.55*	*2.53*	*2.49*	*2.46*	*2.44*	*2.43*	*2.42*	*2.40*	*2.38*

Table 19-10. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Observations (5 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.62**	**1.97**	**1.74**	**1.63**	**1.56**	**1.48**	**1.43**	**1.40**	**1.37**	**1.36**	**1.35**	**1.34**	**1.33**	**1.32**	**1.31**	**1.31**	**1.30**	**1.30**	**1.29**	**1.29**
2	3.43	**2.42**	**2.09**	**1.93**	**1.84**	**1.73**	**1.67**	**1.62**	**1.59**	**1.57**	**1.56**	**1.55**	**1.54**	**1.52**	**1.51**	**1.51**	**1.50**	**1.50**	**1.49**	**1.48**
3	3.98	**2.70**	**2.31**	**2.11**	**2.00**	**1.87**	**1.80**	**1.75**	**1.72**	**1.69**	**1.68**	**1.66**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.61**	**1.60**	**1.59**
4	4.42	2.91	**2.46**	**2.24**	**2.12**	**1.98**	**1.90**	**1.84**	**1.80**	**1.78**	**1.76**	**1.74**	**1.73**	**1.71**	**1.70**	**1.69**	**1.69**	**1.68**	**1.67**	**1.66**
5	4.79	3.08	**2.58**	**2.35**	**2.21**	**2.05**	**1.97**	**1.91**	**1.87**	**1.84**	**1.82**	**1.80**	**1.79**	**1.77**	**1.76**	**1.75**	**1.74**	**1.74**	**1.73**	**1.72**
8	5.65	3.46	*2.85*	**2.56**	**2.40**	**2.22**	**2.12**	**2.05**	**2.00**	**1.97**	**1.95**	**1.93**	**1.91**	**1.89**	**1.88**	**1.87**	**1.86**	**1.85**	**1.84**	**1.83**
12	6.50	3.81	3.08	**2.75**	**2.57**	**2.36**	**2.25**	**2.17**	**2.12**	**2.08**	**2.05**	**2.03**	**2.02**	**2.00**	**1.98**	**1.97**	**1.96**	**1.95**	**1.93**	**1.93**
16	7.18	4.08	3.26	*2.89*	**2.68**	**2.46**	**2.34**	**2.25**	**2.20**	**2.16**	**2.13**	**2.11**	**2.09**	**2.07**	**2.05**	**2.04**	**2.03**	**2.02**	**2.00**	**1.99**
20	7.75	4.29	3.40	3.00	*2.78*	**2.54**	**2.41**	**2.32**	**2.26**	**2.22**	**2.19**	**2.16**	**2.15**	**2.12**	**2.10**	**2.09**	**2.08**	**2.07**	**2.05**	**2.04**
30	8.90	4.70	3.66	3.20	*2.95*	**2.68**	**2.54**	**2.43**	**2.37**	**2.32**	**2.29**	**2.26**	**2.24**	**2.22**	**2.20**	**2.18**	**2.17**	**2.16**	**2.14**	**2.13**
40	9.81	5.01	3.85	3.35	3.07	*2.78*	**2.63**	**2.51**	**2.44**	**2.40**	**2.36**	**2.33**	**2.31**	**2.28**	**2.26**	**2.25**	**2.23**	**2.22**	**2.21**	**2.19**
50	10.58	5.26	4.00	3.47	3.17	*2.86*	**2.70**	**2.58**	**2.50**	**2.45**	**2.42**	**2.39**	**2.37**	**2.33**	**2.31**	**2.29**	**2.28**	**2.27**	**2.25**	**2.24**
60	11.25	5.47	4.13	3.56	3.25	*2.92*	*2.75*	**2.63**	**2.55**	**2.50**	**2.46**	**2.43**	**2.41**	**2.38**	**2.35**	**2.33**	**2.32**	**2.31**	**2.29**	**2.28**
75	12.13	5.74	4.29	3.68	3.35	*3.00*	*2.82*	**2.69**	**2.61**	**2.56**	**2.51**	**2.48**	**2.46**	**2.43**	**2.40**	**2.38**	**2.37**	**2.36**	**2.34**	**2.33**
100	13.38	6.12	4.50	3.84	3.48	3.11	*2.91*	*2.77*	**2.69**	**2.63**	**2.58**	**2.55**	**2.53**	**2.49**	**2.46**	**2.44**	**2.43**	**2.42**	**2.40**	**2.38**
125	14.40	6.41	4.68	3.97	3.58	3.19	*2.98*	*2.84*	**2.75**	**2.68**	**2.64**	**2.60**	**2.58**	**2.54**	**2.51**	**2.49**	**2.47**	**2.46**	**2.44**	**2.43**
150	15.33	6.67	4.82	4.06	3.67	3.25	*3.04*	*2.89*	*2.79*	**2.73**	**2.68**	**2.65**	**2.62**	**2.58**	**2.55**	**2.53**	**2.51**	**2.50**	**2.48**	**2.46**
175	16.11	6.88	4.94	4.16	3.74	3.31	3.09	*2.93*	*2.83*	*2.76*	**2.72**	**2.68**	**2.66**	**2.61**	**2.58**	**2.56**	**2.55**	**2.53**	**2.50**	**2.48**
200	16.89	7.08	5.05	4.24	3.80	3.36	3.13	*2.97*	*2.87*	*2.80*	*2.75*	**2.71**	**2.69**	**2.64**	**2.61**	**2.59**	**2.56**	**2.54**	**2.50**	**2.48**

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Table 19-10. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Observations (5 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.27	2.37	2.07	1.92	1.83	1.72	1.66	1.62	1.59	1.57	1.56	1.54	1.54	1.52	1.51	1.51	1.50	1.50	1.49	1.48
2	4.23	2.87	2.44	2.23	2.11	1.97	1.89	1.84	1.80	1.77	1.76	1.74	1.73	1.71	1.70	1.69	1.69	1.68	1.67	1.66
3	4.89	3.18	2.66	2.42	2.27	2.11	2.03	1.96	1.92	1.89	1.87	1.85	1.84	1.82	1.81	1.80	1.79	1.78	1.77	1.76
4	5.42	3.41	2.83	2.55	2.39	2.21	2.12	2.05	2.00	1.97	1.95	1.93	1.91	1.89	1.88	1.87	1.86	1.85	1.84	1.83
5	5.86	3.60	2.96	2.66	2.48	2.29	2.19	2.11	2.06	2.03	2.01	1.99	1.97	1.95	1.93	1.92	1.91	1.91	1.89	1.89
8	6.89	4.02	3.24	2.88	2.68	2.46	2.34	2.25	2.19	2.16	2.13	2.11	2.09	2.07	2.05	2.04	2.03	2.02	2.00	1.99
12	7.93	4.41	3.49	3.08	2.85	2.60	2.47	2.37	2.31	2.26	2.23	2.21	2.19	2.16	2.14	2.13	2.12	2.11	2.09	2.08
16	8.74	4.71	3.68	*3.23*	2.97	2.70	2.56	2.45	2.38	2.34	2.30	2.28	2.26	2.23	2.21	2.19	2.18	2.17	2.16	2.15
20	9.43	4.95	3.83	3.34	3.07	2.78	2.63	2.51	2.44	2.40	2.36	2.33	2.31	2.28	2.26	2.24	2.23	2.22	2.21	2.19
30	10.82	5.41	4.11	3.55	*3.25*	2.92	2.75	2.63	2.55	2.50	2.46	2.43	2.41	2.38	2.35	2.33	2.32	2.31	2.29	2.28
40	11.93	5.76	4.32	3.71	3.38	3.02	2.84	2.71	2.63	2.57	2.53	2.50	2.48	2.44	2.41	2.40	2.38	2.37	2.35	2.34
50	12.85	6.04	4.48	3.83	3.48	3.10	2.91	2.77	2.69	2.63	2.58	2.55	2.53	2.49	2.46	2.44	2.43	2.42	2.40	2.38
60	13.67	6.28	4.62	3.93	3.56	*3.17*	2.97	2.82	2.73	2.67	2.63	2.59	2.57	2.53	2.50	2.48	2.47	2.46	2.43	2.42
75	14.75	6.59	4.80	4.06	3.66	*3.25*	3.04	2.89	2.79	2.73	2.68	2.65	2.62	2.58	2.55	2.53	2.51	2.50	2.48	2.46
100	16.21	6.99	5.03	4.22	3.80	*3.36*	*3.13*	2.97	2.87	2.80	2.75	2.71	2.68	2.64	2.61	2.59	2.57	2.55	2.51	2.48
125	17.48	7.34	5.21	4.36	3.91	3.44	*3.20*	3.03	2.92	2.85	2.80	2.76	2.73	2.69	2.65	2.62	2.62	2.60	2.58	2.56
150	18.55	7.62	5.37	4.47	3.99	3.50	*3.26*	3.08	2.97	2.90	2.84	2.81	2.77	2.73	2.69	2.67	2.66	2.64	2.62	2.60
175	19.53	7.86	5.51	4.57	4.06	3.56	*3.31*	*3.12*	3.02	2.94	2.88	2.84	2.81	2.76	2.73	2.70	2.69	2.67	2.64	2.63
200	20.51	8.11	5.62	4.65	4.14	3.61	*3.35*	*3.16*	3.05	2.97	2.92	2.87	2.84	2.79	2.76	2.73	2.71	2.69	2.67	2.65

Table 19-10. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Observations (10 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	2.70	1.99	1.76	1.64	1.56	1.48	1.43	1.40	1.38	1.36	1.35	1.34	1.33	1.32	1.31	1.31	1.30	1.30	1.29	1.29
2	3.52	2.45	2.11	1.94	1.84	1.73	1.67	1.62	1.59	1.57	1.56	1.55	1.54	1.52	1.51	1.51	1.50	1.50	1.49	1.48
3	4.09	2.73	2.32	2.12	2.01	1.88	1.80	1.75	1.72	1.69	1.68	1.66	1.65	1.64	1.63	1.62	1.61	1.61	1.60	1.59
4	4.54	2.94	*2.47*	2.25	2.12	1.98	1.90	1.84	1.80	1.78	1.76	1.74	1.73	1.71	1.70	1.69	1.69	1.68	1.67	1.66
5	4.91	3.11	2.59	2.35	2.21	2.06	1.97	1.91	1.87	1.84	1.82	1.80	1.79	1.77	1.76	1.75	1.74	1.74	1.73	1.72
8	5.79	3.49	2.86	*2.57*	2.40	2.22	2.12	2.05	2.00	1.97	1.95	1.93	1.92	1.89	1.88	1.87	1.86	1.85	1.84	1.83
12	6.67	3.84	3.10	2.76	*2.57*	2.36	2.25	2.17	2.12	2.08	2.05	2.03	2.02	2.00	1.98	1.97	1.96	1.95	1.93	1.92
16	7.36	4.11	3.27	2.90	2.69	*2.46*	2.34	2.25	2.20	2.16	2.13	2.11	2.09	2.07	2.05	2.04	2.03	2.02	2.00	1.99
20	7.95	4.32	3.41	3.01	2.78	*2.54*	*2.41*	2.32	2.26	2.22	2.19	2.16	2.15	2.12	2.10	2.09	2.08	2.07	2.05	2.04
30	9.13	4.73	3.67	3.21	2.95	2.68	*2.54*	*2.43*	2.37	2.32	2.29	2.26	2.24	2.22	2.20	2.18	2.17	2.16	2.14	2.13
40	10.05	5.05	3.86	3.35	3.08	2.78	*2.63*	*2.51*	*2.44*	*2.40*	2.36	2.33	2.31	2.28	2.26	2.24	2.23	2.22	2.21	2.19
50	10.84	5.30	4.01	3.47	3.18	2.86	2.70	*2.58*	*2.50*	*2.45*	*2.42*	*2.39*	2.37	2.33	2.31	2.29	2.28	2.27	2.25	2.24
60	11.54	5.51	4.15	3.57	3.26	2.93	2.75	*2.63*	*2.55*	*2.50*	*2.46*	*2.43*	*2.41*	2.37	2.35	2.33	2.32	2.31	2.29	2.28
75	12.42	5.79	4.31	3.68	3.35	3.00	2.82	2.69	*2.61*	*2.56*	*2.52*	*2.48*	*2.46*	*2.42*	*2.40*	*2.38*	2.37	2.36	2.34	2.33
100	13.71	6.15	4.51	3.85	3.49	3.11	2.92	2.77	2.69	*2.63*	*2.59*	*2.55*	*2.53*	*2.49*	*2.46*	*2.44*	*2.43*	*2.42*	*2.40*	*2.38*
125	14.77	6.45	4.69	3.97	3.59	3.19	2.98	2.83	2.75	2.68	*2.64*	*2.60*	*2.58*	*2.54*	*2.51*	*2.49*	*2.48*	*2.46*	*2.44*	*2.43*
150	15.70	6.71	4.83	4.07	3.67	3.25	3.04	2.89	2.79	2.73	2.68	*2.64*	*2.62*	*2.58*	*2.55*	*2.53*	*2.51*	*2.50*	*2.48*	*2.46*
175	16.52	6.91	4.95	4.16	3.74	3.31	3.09	2.93	2.83	2.77	2.72	2.68	*2.65*	*2.61*	*2.59*	*2.56*	*2.54*	*2.52*	*2.51*	*2.49*
200	17.34	7.12	5.07	4.25	3.81	3.35	3.13	2.97	2.87	2.80	2.75	2.71	*2.68*	*2.64*	*2.61*	*2.59*	*2.57*	*2.54*	*2.53*	*2.52*

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Table 19-10. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Observations (10 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.43	2.42	2.09	1.93	1.84	1.73	1.67	1.62	1.59	1.57	1.56	1.55	1.54	1.52	1.51	1.51	1.50	1.50	1.49	1.48
2	4.42	2.91	2.46	2.24	2.12	1.98	1.90	1.84	1.80	1.78	1.76	1.74	1.73	1.71	1.70	1.69	1.69	1.68	1.67	1.66
3	5.11	3.23	2.68	2.43	2.28	2.12	2.03	1.96	1.92	1.89	1.87	1.85	1.84	1.82	1.81	1.80	1.79	1.78	1.77	1.76
4	5.65	3.46	2.85	2.56	2.40	2.22	2.12	2.05	2.00	1.97	1.95	1.93	1.91	1.89	1.88	1.87	1.86	1.85	1.84	1.83
5	6.11	3.65	2.98	2.67	2.49	2.30	2.19	2.11	2.06	2.03	2.01	1.99	1.97	1.95	1.93	1.92	1.91	1.91	1.89	1.89
8	7.18	4.08	3.26	2.89	2.68	2.46	2.34	2.25	2.20	2.16	2.13	2.11	2.09	2.07	2.05	2.04	2.03	2.02	2.00	1.99
12	8.25	4.47	3.51	3.09	2.86	2.60	2.47	2.37	2.31	2.26	2.23	2.21	2.19	2.16	2.14	2.13	2.12	2.11	2.09	2.08
16	9.10	4.77	3.70	3.24	2.98	2.70	2.56	2.45	2.38	2.34	2.31	2.28	2.26	2.23	2.21	2.19	2.18	2.17	2.16	2.15
20	9.81	5.01	3.85	3.35	3.07	2.78	2.63	2.51	2.44	2.40	2.36	2.33	2.31	2.28	2.26	2.24	2.23	2.22	2.21	2.19
30	11.25	5.47	4.13	3.56	3.25	2.92	2.75	2.63	2.55	2.50	2.46	2.43	2.41	2.37	2.35	2.33	2.32	2.31	2.29	2.28
40	12.39	5.82	4.34	3.72	3.38	3.03	2.84	2.71	2.63	2.57	2.53	2.50	2.48	2.44	2.42	2.40	2.38	2.37	2.35	2.34
50	13.36	6.11	4.50	3.84	3.48	3.11	2.91	2.77	2.69	2.63	2.59	2.55	2.53	2.49	2.46	2.44	2.43	2.42	2.40	2.38
60	14.24	6.36	4.64	3.94	3.56	3.17	2.97	2.82	2.74	2.67	2.63	2.59	2.57	2.53	2.50	2.48	2.47	2.46	2.43	2.42
75	15.35	6.67	4.82	4.06	3.67	3.25	3.04	2.89	2.79	2.73	2.68	2.65	2.62	2.58	2.55	2.53	2.51	2.50	2.48	2.46
100	16.88	7.08	5.05	4.23	3.80	3.36	3.13	2.97	2.87	2.80	2.75	2.71	2.68	2.64	2.61	2.59	2.56	2.54	2.50	2.52
125	18.16	7.41	5.24	4.37	3.91	3.44	3.20	3.03	2.93	2.85	2.80	2.76	2.73	2.68	2.65	2.62	2.60	2.60	2.58	2.56
150	19.34	7.71	5.39	4.48	4.00	3.51	3.26	3.08	2.97	2.90	2.85	2.81	2.78	2.72	2.69	2.67	2.66	2.64	2.61	2.60
175	20.39	7.97	5.54	4.57	4.07	3.57	3.31	3.13	3.02	2.94	2.89	2.84	2.81	2.76	2.72	2.70	2.68	2.67	2.64	2.63
200	21.33	8.20	5.65	4.66	4.13	3.62	3.35	3.16	3.05	2.97	2.92	2.87	2.84	2.79	2.75	2.73	2.71	2.70	2.67	2.65

Table 19-10. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Observations (10 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	4.23	2.87	2.44	2.23	2.11	1.97	1.89	1.84	1.80	1.77	1.76	1.74	1.73	1.71	1.70	1.69	1.69	1.68	1.67	1.66
2	5.42	3.41	2.83	2.55	2.39	2.21	2.12	2.05	2.00	1.97	1.95	1.93	1.91	1.89	1.88	1.87	1.86	1.85	1.84	1.83
3	6.24	3.76	3.06	2.74	2.56	2.36	2.25	2.17	2.11	2.08	2.05	2.03	2.02	2.00	1.98	1.97	1.96	1.95	1.94	1.93
4	6.89	4.02	3.24	2.88	2.68	2.46	2.34	2.25	2.19	2.16	2.13	2.11	2.09	2.07	2.05	2.04	2.03	2.02	2.00	1.99
5	7.45	4.23	3.38	2.99	2.77	2.53	2.41	2.32	2.26	2.22	2.19	2.16	2.15	2.12	2.10	2.09	2.08	2.07	2.05	2.04
8	8.74	4.71	3.68	3.23	2.97	2.70	2.56	2.45	2.38	2.34	2.31	2.28	2.26	2.23	2.21	2.19	2.18	2.17	2.16	2.15
12	10.03	5.15	3.95	3.44	3.15	2.84	2.68	2.57	2.49	2.44	2.41	2.38	2.36	2.32	2.30	2.29	2.27	2.26	2.24	2.23
16	11.06	5.49	4.16	3.59	3.28	2.95	2.77	2.65	2.57	2.52	2.48	2.45	2.42	2.39	2.37	2.35	2.33	2.32	2.30	2.29
20	11.92	5.76	4.32	3.71	3.37	3.02	2.84	2.71	2.63	2.57	2.53	2.50	2.48	2.44	2.42	2.40	2.38	2.37	2.35	2.34
30	13.67	6.28	4.62	3.93	3.56	3.17	2.97	2.82	2.73	2.67	2.63	2.59	2.57	2.53	2.50	2.48	2.47	2.46	2.43	2.42
40	15.06	6.68	4.85	4.10	3.69	3.27	3.06	2.90	2.81	2.74	2.70	2.66	2.63	2.59	2.56	2.54	2.53	2.51	2.49	2.48
50	16.23	7.00	5.03	4.23	3.80	3.35	3.13	2.97	2.87	2.80	2.75	2.71	2.68	2.64	2.61	2.59	2.57	2.55	2.51	2.48
60	17.23	7.27	5.18	4.34	3.89	3.42	3.19	3.02	2.92	2.84	2.79	2.75	2.72	2.68	2.64	2.61	2.61	2.57	2.57	2.55
75	18.57	7.62	5.37	4.47	3.99	3.50	3.26	3.08	2.97	2.90	2.85	2.81	2.77	2.72	2.70	2.67	2.65	2.64	2.61	2.60
100	20.51	8.09	5.62	4.64	4.13	3.61	3.35	3.16	3.05	2.97	2.92	2.87	2.84	2.79	2.75	2.73	2.71	2.70	2.67	2.65
125	22.03	8.47	5.83	4.79	4.25	3.70	3.42	3.23	3.11	3.03	2.97	2.93	2.89	2.83	2.80	2.78	2.75	2.74	2.71	2.69
150	23.44	8.79	5.99	4.91	4.34	3.76	3.48	3.28	3.16	3.07	3.01	2.96	2.93	2.87	2.84	2.81	2.79	2.78	2.75	2.72
175	24.61	9.08	6.15	5.01	4.41	3.82	3.53	3.33	3.19	3.11	3.05	3.00	2.96	2.91	2.87	2.84	2.82	2.81	2.77	2.75
200	25.78	9.32	6.27	5.10	4.48	3.88	3.57	3.36	3.23	3.14	3.08	3.02	2.99	2.93	2.89	2.87	2.84	2.82	2.78	2.75

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Table 19-10. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Observations (20 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.52	2.45	2.11	1.94	1.84	1.73	1.67	1.62	1.59	1.57	1.56	1.55	1.54	1.52	1.51	1.51	1.50	1.50	1.49	1.48
2	4.54	2.94	2.47	2.25	2.12	1.98	1.90	1.84	1.80	1.78	1.76	1.74	1.73	1.71	1.70	1.69	1.69	1.68	1.67	1.66
3	5.24	3.26	2.70	2.43	2.28	2.12	2.03	1.96	1.92	1.89	1.87	1.85	1.84	1.82	1.81	1.80	1.79	1.78	1.77	1.76
4	5.79	3.49	2.86	2.57	2.40	2.22	2.12	2.05	2.00	1.97	1.95	1.93	1.92	1.89	1.88	1.87	1.86	1.85	1.84	1.83
5	6.26	3.68	2.99	2.67	2.49	2.30	2.19	2.11	2.07	2.03	2.01	1.99	1.97	1.95	1.93	1.92	1.91	1.91	1.89	1.89
8	7.36	4.11	3.27	2.90	2.69	2.46	2.34	2.25	2.20	2.16	2.13	2.11	2.09	2.07	2.05	2.04	2.03	2.02	2.00	1.99
12	8.45	4.50	3.52	3.10	2.86	2.60	2.47	2.37	2.31	2.26	2.23	2.21	2.19	2.16	2.14	2.13	2.12	2.11	2.09	2.08
16	9.32	4.80	3.71	3.24	2.98	2.70	2.56	2.45	2.38	2.34	2.31	2.28	2.26	2.23	2.21	2.20	2.18	2.17	2.16	2.15
20	10.05	5.04	3.86	3.36	3.08	2.78	2.63	2.51	2.44	2.40	2.36	2.33	2.31	2.28	2.26	2.25	2.23	2.22	2.21	2.19
30	11.53	5.51	4.14	3.57	3.25	2.92	2.75	2.63	2.55	2.50	2.46	2.43	2.41	2.38	2.35	2.33	2.32	2.31	2.29	2.28
40	12.71	5.86	4.35	3.72	3.38	3.03	2.84	2.71	2.63	2.57	2.53	2.50	2.48	2.44	2.42	2.40	2.38	2.37	2.35	2.34
50	13.69	6.15	4.52	3.85	3.48	3.11	2.91	2.77	2.69	2.63	2.58	2.55	2.53	2.49	2.46	2.44	2.43	2.42	2.40	2.38
60	14.57	6.39	4.66	3.95	3.57	3.17	2.97	2.82	2.73	2.67	2.63	2.60	2.57	2.53	2.50	2.48	2.47	2.45	2.43	2.42
75	15.70	6.70	4.83	4.07	3.67	3.25	3.04	2.89	2.79	2.73	2.68	2.65	2.62	2.58	2.55	2.53	2.51	2.50	2.48	2.46
100	17.27	7.12	5.06	4.24	3.80	3.36	3.13	2.97	2.87	2.80	2.75	2.71	2.68	2.64	2.60	2.58	2.55	2.54	2.50	2.48
125	18.59	7.46	5.24	4.37	3.91	3.44	3.20	3.03	2.93	2.86	2.80	2.76	2.73	2.69	2.65	2.62	2.60	2.58	2.58	2.56
150	19.77	7.75	5.40	4.48	4.00	3.51	3.26	3.08	2.97	2.90	2.85	2.81	2.77	2.72	2.69	2.66	2.64	2.64	2.61	2.60
175	20.86	8.01	5.54	4.58	4.07	3.56	3.31	3.13	3.02	2.94	2.88	2.84	2.81	2.76	2.72	2.70	2.68	2.67	2.64	2.63
200	21.80	8.24	5.65	4.66	4.14	3.61	3.35	3.16	3.05	2.97	2.92	2.87	2.84	2.79	2.76	2.73	2.71	2.70	2.67	2.65

Table 19-10. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Observations (20 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	4.42	2.91	2.46	2.24	2.12	1.97	1.90	1.84	1.80	1.78	1.76	1.74	1.73	1.71	1.70	1.69	1.69	1.68	1.67	1.66
2	5.65	3.46	2.85	2.56	2.40	2.22	2.12	2.05	2.00	1.97	1.95	1.93	1.91	1.89	1.88	1.87	1.86	1.85	1.84	1.83
3	6.50	3.81	3.08	2.75	2.57	2.36	2.25	2.17	2.12	2.08	2.05	2.03	2.02	2.00	1.98	1.97	1.96	1.95	1.93	1.92
4	7.18	4.08	3.26	2.89	2.68	2.46	2.34	2.25	2.20	2.16	2.13	2.11	2.09	2.07	2.05	2.04	2.03	2.02	2.00	1.99
5	7.75	4.29	3.40	3.00	2.78	2.54	2.41	2.32	2.26	2.22	2.19	2.16	2.15	2.12	2.10	2.09	2.08	2.07	2.05	2.04
8	9.10	4.77	3.70	3.24	2.98	2.70	2.56	2.45	2.38	2.34	2.31	2.28	2.26	2.23	2.21	2.20	2.18	2.17	2.16	2.15
12	10.44	5.21	3.97	3.44	3.15	2.84	2.68	2.57	2.49	2.44	2.41	2.38	2.36	2.32	2.30	2.29	2.27	2.26	2.24	2.23
16	11.50	5.55	4.18	3.60	3.28	2.95	2.77	2.65	2.57	2.52	2.48	2.45	2.42	2.39	2.37	2.35	2.33	2.32	2.30	2.29
20	12.40	5.83	4.34	3.72	3.38	3.03	2.84	2.71	2.63	2.57	2.53	2.50	2.48	2.44	2.42	2.40	2.38	2.37	2.35	2.34
30	14.22	6.35	4.64	3.94	3.56	3.17	2.97	2.82	2.73	2.67	2.63	2.60	2.57	2.53	2.50	2.48	2.47	2.46	2.43	2.42
40	15.66	6.75	4.87	4.11	3.70	3.28	3.06	2.91	2.81	2.74	2.70	2.66	2.63	2.59	2.56	2.54	2.53	2.51	2.49	2.48
50	16.88	7.08	5.05	4.23	3.80	3.36	3.13	2.97	2.87	2.80	2.75	2.71	2.68	2.64	2.61	2.59	2.56	2.54	2.50	2.48
60	17.93	7.35	5.20	4.34	3.89	3.43	3.19	3.02	2.92	2.84	2.79	2.75	2.72	2.68	2.64	2.61	2.59	2.57	2.54	2.55
75	19.34	7.71	5.39	4.48	4.00	3.51	3.26	3.08	2.97	2.90	2.85	2.81	2.77	2.72	2.69	2.67	2.65	2.64	2.61	2.60
100	21.25	8.18	5.64	4.65	4.14	3.61	3.35	3.16	3.05	2.97	2.92	2.87	2.84	2.79	2.75	2.73	2.71	2.70	2.67	2.65
125	22.97	8.55	5.85	4.79	4.25	3.70	3.42	3.23	3.11	3.03	2.97	2.92	2.89	2.83	2.80	2.77	2.75	2.74	2.71	2.69
150	24.38	8.91	6.02	4.91	4.34	3.77	3.48	3.28	3.15	3.07	3.01	2.97	2.93	2.87	2.84	2.81	2.79	2.77	2.74	2.73
175	25.62	9.18	6.17	5.01	4.42	3.83	3.53	3.33	3.20	3.11	3.05	3.01	2.96	2.91	2.87	2.84	2.81	2.80	2.77	2.76
200	26.88	9.45	6.29	5.10	4.49	3.88	3.57	3.36	3.23	3.14	3.08	3.04	2.99	2.93	2.89	2.86	2.84	2.83	2.80	2.78

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Table 19-10. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Observations (20 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	5.42	3.41	**2.83**	**2.55**	**2.39**	**2.21**	**2.12**	**2.05**	**2.00**	**1.97**	**1.95**	**1.93**	**1.91**	**1.89**	**1.88**	**1.87**	**1.86**	**1.85**	**1.84**	**1.83**
2	6.89	4.02	3.24	**2.88**	**2.68**	**2.46**	**2.34**	**2.25**	**2.19**	**2.16**	**2.13**	**2.11**	**2.09**	**2.07**	**2.05**	**2.04**	**2.03**	**2.02**	**2.00**	**1.99**
3	7.92	4.41	3.49	**3.08**	**2.85**	**2.60**	**2.47**	**2.37**	**2.31**	**2.26**	**2.23**	**2.21**	**2.19**	**2.16**	**2.14**	**2.13**	**2.12**	**2.11**	**2.09**	**2.08**
4	8.74	4.71	3.68	*3.23*	**2.97**	**2.70**	**2.56**	**2.45**	**2.38**	**2.34**	**2.30**	**2.28**	**2.26**	**2.23**	**2.21**	**2.19**	**2.18**	**2.17**	**2.16**	**2.15**
5	9.43	4.95	3.83	3.34	**3.07**	**2.78**	**2.63**	**2.51**	**2.44**	**2.40**	**2.36**	**2.33**	**2.31**	**2.28**	**2.26**	**2.24**	**2.23**	**2.22**	**2.21**	**2.19**
8	11.06	5.49	4.16	3.59	*3.28*	**2.94**	**2.77**	**2.65**	**2.57**	**2.52**	**2.48**	**2.45**	**2.42**	**2.39**	**2.37**	**2.35**	**2.33**	**2.32**	**2.30**	**2.29**
12	12.68	5.99	4.45	3.81	3.46	**3.09**	**2.90**	**2.76**	**2.68**	**2.62**	**2.57**	**2.54**	**2.52**	**2.48**	**2.45**	**2.44**	**2.42**	**2.41**	**2.39**	**2.37**
16	13.96	6.37	4.67	3.97	3.59	*3.19*	**2.99**	**2.84**	**2.75**	**2.69**	**2.64**	**2.61**	**2.58**	**2.54**	**2.52**	**2.50**	**2.48**	**2.47**	**2.45**	**2.43**
20	15.06	6.68	4.85	4.10	3.69	*3.27*	**3.06**	**2.90**	**2.81**	**2.74**	**2.70**	**2.66**	**2.63**	**2.59**	**2.56**	**2.54**	**2.53**	**2.51**	**2.49**	**2.48**
30	17.25	7.27	5.18	4.33	3.89	3.42	*3.19*	**3.02**	**2.91**	**2.84**	**2.79**	**2.75**	**2.72**	**2.68**	**2.64**	**2.61**	**2.59**	**2.57**	**2.57**	**2.55**
40	18.98	7.72	5.42	4.51	4.02	3.53	*3.28*	**3.10**	**2.99**	**2.91**	**2.86**	**2.82**	**2.79**	**2.74**	**2.71**	**2.68**	**2.67**	**2.65**	**2.63**	**2.61**
50	20.47	8.10	5.62	4.64	4.13	3.61	*3.35*	*3.16*	**3.05**	**2.97**	**2.92**	**2.87**	**2.84**	**2.79**	**2.76**	**2.73**	**2.71**	**2.70**	**2.67**	**2.65**
60	21.76	8.40	5.79	4.76	4.22	3.68	*3.41*	*3.22*	**3.10**	**3.02**	**2.96**	**2.92**	**2.88**	**2.83**	**2.79**	**2.77**	**2.75**	**2.73**	**2.70**	**2.69**
75	23.44	8.81	6.00	4.90	4.34	3.76	3.48	*3.28*	*3.16*	**3.07**	**3.01**	**2.96**	**2.92**	**2.87**	**2.84**	**2.81**	**2.79**	**2.77**	**2.75**	**2.73**
100	25.78	9.34	6.27	5.09	4.48	3.88	3.57	*3.36*	*3.23*	*3.14*	**3.08**	**3.02**	**2.99**	**2.93**	**2.90**	**2.87**	**2.84**	**2.82**	**2.78**	**2.76**
125	27.81	9.77	6.48	5.24	4.60	3.96	3.65	*3.42*	*3.29*	*3.20*	*3.12*	**3.08**	**3.04**	**2.98**	**2.94**	**2.91**	**2.88**	**2.86**	**2.82**	**2.80**
150	29.53	10.16	6.68	5.37	4.70	4.03	3.71	*3.48*	*3.34*	*3.24*	*3.17*	**3.12**	**3.08**	**3.02**	**2.97**	**2.94**	**2.92**	**2.90**	**2.87**	**2.85**
175	31.09	10.47	6.84	5.47	4.79	4.09	3.75	3.52	*3.38*	*3.28*	*3.20*	*3.15*	**3.11**	**3.05**	**3.01**	**2.98**	**2.95**	**2.93**	**2.90**	**2.88**
200	32.50	10.78	6.97	5.57	4.85	4.15	3.80	3.55	*3.41*	*3.32*	*3.25*	*3.18*	*3.14*	**3.08**	**3.04**	**3.00**	**2.98**	**2.96**	**2.92**	**2.90**

Table 19-10. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Observations (40 COC, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	4.54	2.94	*2.47*	**2.25**	**2.12**	**1.98**	**1.90**	**1.84**	**1.80**	**1.78**	**1.76**	**1.74**	**1.73**	**1.71**	**1.70**	**1.69**	**1.69**	**1.68**	**1.67**	**1.66**
2	5.79	3.49	2.86	*2.57*	**2.40**	**2.22**	**2.12**	**2.05**	**2.00**	**1.97**	**1.95**	**1.93**	**1.92**	**1.89**	**1.88**	**1.87**	**1.86**	**1.85**	**1.84**	**1.83**
3	6.67	3.84	3.10	2.76	*2.57*	**2.36**	**2.25**	**2.17**	**2.12**	**2.08**	**2.05**	**2.03**	**2.02**	**2.00**	**1.98**	**1.97**	**1.96**	**1.95**	**1.93**	**1.92**
4	7.36	4.11	3.27	2.90	2.69	*2.46*	**2.34**	**2.25**	**2.20**	**2.16**	**2.13**	**2.11**	**2.09**	**2.07**	**2.05**	**2.04**	**2.03**	**2.02**	**2.00**	**1.99**
5	7.95	4.32	3.41	3.01	2.78	*2.54*	*2.41*	**2.32**	**2.26**	**2.22**	**2.19**	**2.16**	**2.15**	**2.12**	**2.10**	**2.09**	**2.08**	**2.07**	**2.05**	**2.04**
8	9.32	4.80	3.71	3.24	2.98	2.70	*2.56*	*2.45*	*2.38*	**2.34**	**2.31**	**2.28**	**2.26**	**2.23**	**2.21**	**2.20**	**2.18**	**2.17**	**2.16**	**2.15**
12	10.70	5.25	3.99	3.45	3.16	2.85	2.68	*2.57*	*2.49*	*2.44*	*2.41*	**2.38**	**2.36**	**2.32**	**2.30**	**2.29**	**2.27**	**2.26**	**2.24**	**2.23**
16	11.79	5.59	4.19	3.60	3.28	2.95	2.77	*2.65*	*2.57*	*2.52*	*2.48*	*2.45*	*2.42*	*2.39*	**2.37**	**2.35**	**2.33**	**2.32**	**2.31**	**2.29**
20	12.71	5.86	4.35	3.72	3.38	3.03	2.84	2.71	*2.63*	*2.57*	*2.53*	*2.50*	*2.48*	*2.44*	*2.41*	*2.40*	*2.38*	**2.37**	**2.35**	**2.34**
30	14.56	6.39	4.66	3.95	3.57	3.17	2.97	2.82	2.73	2.67	*2.63*	*2.59*	*2.57*	*2.53*	*2.50*	*2.48*	*2.47*	*2.46*	*2.43*	*2.42*
40	16.04	6.80	4.88	4.11	3.70	3.28	3.06	2.91	2.81	2.74	2.70	*2.66*	*2.63*	*2.59*	*2.56*	*2.54*	*2.53*	*2.51*	*2.49*	*2.46*
50	17.29	7.12	5.06	4.24	3.81	3.36	3.13	2.97	2.87	2.80	2.75	2.71	*2.68*	*2.64*	*2.60*	*2.58*	*2.56*	*2.54*	*2.50*	*2.48*
60	18.37	7.40	5.21	4.35	3.89	3.42	3.19	3.02	2.92	2.85	2.79	2.75	2.72	*2.68*	*2.64*	*2.61*	*2.59*	*2.57*	*2.54*	*2.56*
75	19.80	7.76	5.41	4.48	4.00	3.51	3.26	3.08	2.97	2.90	2.85	2.81	2.77	2.73	*2.69*	*2.66*	*2.64*	*2.64*	*2.61*	*2.60*
100	21.80	8.23	5.66	4.66	4.14	3.61	3.35	3.16	3.05	2.97	2.92	2.87	2.84	2.79	2.76	2.73	2.71	*2.70*	*2.67*	*2.65*
125	23.47	8.61	5.86	4.80	4.25	3.70	3.42	3.23	3.11	3.03	2.97	2.93	2.89	2.84	2.81	2.77	2.76	2.74	2.71	*2.69*
150	24.96	8.94	6.03	4.92	4.35	3.77	3.48	3.28	3.16	3.07	3.01	2.97	2.93	2.88	2.85	2.80	2.79	2.77	2.75	2.72
175	26.28	9.23	6.17	5.02	4.42	3.83	3.53	3.32	3.20	3.11	3.05	3.00	2.97	2.92	2.89	2.84	2.82	2.80	2.77	2.76
200	27.42	9.49	6.31	5.11	4.49	3.88	3.58	3.36	3.23	3.14	3.08	3.04	3.00	2.95	2.92	2.86	2.84	2.82	2.79	2.78

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Table 19-10. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Observations (40 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	5.65	3.46	*2.85*	**2.56**	**2.40**	**2.22**	**2.12**	**2.05**	**2.00**	**1.97**	**1.95**	**1.93**	**1.91**	**1.89**	**1.88**	**1.87**	**1.86**	**1.85**	**1.84**	**1.83**
2	7.18	4.08	3.26	*2.89*	**2.68**	**2.46**	**2.34**	**2.25**	**2.20**	**2.16**	**2.13**	**2.11**	**2.09**	**2.07**	**2.05**	**2.04**	**2.03**	**2.02**	**2.00**	**1.99**
3	8.25	4.47	3.51	3.09	*2.86*	**2.60**	**2.47**	**2.37**	**2.31**	**2.26**	**2.23**	**2.21**	**2.19**	**2.16**	**2.14**	**2.13**	**2.12**	**2.11**	**2.09**	**2.08**
4	9.10	4.77	3.70	3.24	2.98	**2.70**	**2.56**	**2.45**	**2.38**	**2.34**	**2.31**	**2.28**	**2.26**	**2.23**	**2.21**	**2.20**	**2.18**	**2.17**	**2.16**	**2.15**
5	9.81	5.01	3.85	3.35	3.07	*2.78*	**2.63**	**2.51**	**2.44**	**2.40**	**2.36**	**2.33**	**2.31**	**2.28**	**2.26**	**2.25**	**2.23**	**2.22**	**2.21**	**2.19**
8	11.51	5.55	4.18	3.60	3.28	*2.95*	*2.77*	**2.65**	**2.57**	**2.52**	**2.48**	**2.45**	**2.42**	**2.39**	**2.37**	**2.35**	**2.33**	**2.32**	**2.30**	**2.29**
12	13.19	6.06	4.47	3.82	3.46	3.09	*2.90*	*2.76*	**2.68**	**2.62**	**2.57**	**2.54**	**2.52**	**2.48**	**2.45**	**2.44**	**2.42**	**2.41**	**2.39**	**2.37**
16	14.53	6.44	4.69	3.98	3.59	3.19	*2.99*	*2.84*	*2.75*	**2.69**	**2.64**	**2.61**	**2.58**	**2.54**	**2.52**	**2.50**	**2.48**	**2.47**	**2.45**	**2.43**
20	15.66	6.75	4.87	4.10	3.70	3.28	3.06	2.91	2.81	***2.74***	***2.70***	***2.66***	***2.63***	***2.59***	***2.56***	***2.54***	***2.53***	***2.51***	***2.49***	***2.48***
30	17.94	7.35	5.20	4.34	3.89	3.42	3.19	3.02	2.91	2.84	2.79	2.75	***2.72***	***2.68***	***2.64***	***2.61***	***2.59***	***2.60***	***2.57***	***2.55***
40	19.75	7.81	5.45	4.52	4.03	3.53	3.28	3.10	*2.99*	*2.92*	*2.86*	*2.82*	*2.79*	**2.74**	**2.70**	**2.68**	**2.67**	**2.65**	**2.63**	**2.61**
50	21.27	8.18	5.64	4.65	4.14	3.61	3.35	3.16	*3.05*	*2.97*	*2.92*	*2.87*	*2.84*	*2.79*	*2.75*	**2.73**	**2.71**	**2.70**	**2.67**	**2.65**
60	22.63	8.49	5.81	4.77	4.23	3.68	3.41	3.22	*3.10*	*3.02*	*2.96*	*2.92*	*2.88*	*2.83*	*2.79*	*2.77*	**2.75**	**2.73**	**2.70**	**2.69**
75	24.39	8.90	6.02	4.91	4.34	3.77	3.48	3.28	3.16	*3.07*	*3.01*	*2.97*	*2.93*	*2.87*	*2.84*	*2.81*	*2.79*	*2.77*	**2.75**	**2.73**
100	26.81	9.44	6.30	5.10	4.49	3.88	3.57	3.36	3.23	3.14	*3.08*	*3.04*	*2.99*	*2.93*	*2.89*	*2.86*	*2.84*	*2.82*	*2.78*	*2.75*
125	28.92	9.89	6.51	5.25	4.60	3.96	3.65	3.42	3.29	3.20	3.14	*3.09*	*3.04*	*2.98*	*2.94*	*2.91*	*2.88*	*2.86*	*2.82*	*2.80*
150	30.76	10.26	6.70	5.37	4.70	4.03	3.71	3.48	3.34	3.24	3.18	*3.13*	*3.10*	*3.02*	*2.97*	*2.94*	*2.92*	*2.90*	*2.86*	*2.83*
175	32.34	10.59	6.87	5.48	4.78	4.09	3.76	3.52	3.38	3.28	3.22	3.17	*3.13*	*3.05*	*3.01*	*2.97*	*2.95*	*2.93*	*2.89*	*2.87*
200	33.75	10.88	7.01	5.58	4.86	4.15	3.80	3.56	3.41	3.32	3.25	3.20	3.16	*3.08*	*3.03*	*3.00*	*2.98*	*2.96*	*2.92*	*2.90*

Table 19-10. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Observations (40 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	6.89	4.02	3.24	**2.88**	**2.68**	**2.46**	**2.34**	**2.25**	**2.19**	**2.16**	**2.13**	**2.11**	**2.09**	**2.07**	**2.05**	**2.04**	**2.03**	**2.02**	**2.00**	**1.99**
2	8.74	4.71	3.68	*3.23*	**2.97**	**2.70**	**2.56**	**2.45**	**2.38**	**2.34**	**2.30**	**2.28**	**2.26**	**2.23**	**2.21**	**2.19**	**2.18**	**2.17**	**2.16**	**2.15**
3	10.03	5.15	3.95	3.44	*3.15*	**2.84**	**2.68**	**2.57**	**2.49**	**2.44**	**2.41**	**2.38**	**2.36**	**2.32**	**2.30**	**2.29**	**2.27**	**2.26**	**2.24**	**2.23**
4	11.06	5.49	4.16	3.59	*3.28*	**2.94**	**2.77**	**2.65**	**2.57**	**2.52**	**2.48**	**2.45**	**2.42**	**2.39**	**2.37**	**2.35**	**2.33**	**2.32**	**2.30**	**2.29**
5	11.92	5.76	4.32	3.71	3.38	**3.02**	**2.84**	**2.71**	**2.63**	**2.57**	**2.53**	**2.50**	**2.48**	**2.44**	**2.41**	**2.40**	**2.38**	**2.37**	**2.35**	**2.34**
8	13.97	6.37	4.67	3.97	3.59	*3.19*	**2.99**	**2.84**	**2.75**	**2.69**	**2.64**	**2.61**	**2.58**	**2.54**	**2.52**	**2.50**	**2.48**	**2.47**	**2.45**	**2.43**
12	16.00	6.94	5.00	4.20	3.78	*3.34*	*3.12*	**2.96**	**2.86**	**2.79**	**2.74**	**2.70**	**2.67**	**2.63**	**2.60**	**2.58**	**2.56**	**2.55**	**2.51**	**2.51**
16	17.62	7.37	5.23	4.37	3.92	3.45	*3.21*	**3.04**	**2.93**	**2.86**	**2.81**	**2.77**	**2.74**	**2.69**	**2.66**	**2.63**	**2.62**	**2.61**	**2.58**	**2.57**
20	19.00	7.72	5.42	4.51	4.02	3.53	*3.28*	**3.10**	**2.99**	**2.91**	**2.86**	**2.82**	**2.79**	**2.74**	**2.71**	**2.68**	**2.67**	**2.65**	**2.63**	**2.61**
30	21.75	8.40	5.79	4.76	4.22	3.68	*3.41*	*3.22*	**3.10**	**3.02**	**2.96**	**2.92**	**2.88**	**2.83**	**2.79**	**2.77**	**2.75**	**2.73**	**2.70**	**2.69**
40	23.95	8.92	6.05	4.94	4.37	3.79	3.50	*3.30*	*3.17*	**3.09**	**3.03**	**2.98**	**2.94**	**2.89**	**2.85**	**2.82**	**2.80**	**2.79**	**2.76**	**2.74**
50	25.80	9.34	6.27	5.09	4.49	3.88	3.57	*3.36*	*3.23*	*3.14*	**3.08**	**3.02**	**2.99**	**2.93**	**2.89**	**2.87**	**2.84**	**2.82**	**2.78**	**2.76**
60	27.42	9.70	6.45	5.21	4.58	3.95	3.63	*3.41*	*3.28*	*3.19*	*3.12*	**3.07**	**3.03**	**2.97**	**2.93**	**2.90**	**2.87**	**2.85**	**2.82**	**2.79**
75	29.53	10.15	6.67	5.37	4.70	4.03	3.71	*3.48*	*3.34*	*3.25*	*3.17*	*3.12*	**3.08**	**3.02**	**2.98**	**2.94**	**2.92**	**2.90**	**2.87**	**2.85**
100	32.52	10.77	6.98	5.56	4.85	4.14	3.80	3.56	*3.41*	*3.32*	*3.25*	*3.18*	*3.14*	**3.08**	**3.03**	**3.00**	**2.98**	**2.96**	**2.93**	**2.90**
125	35.07	11.27	7.22	5.72	4.98	4.24	3.87	3.62	*3.47*	*3.37*	*3.30*	*3.23*	*3.19*	*3.13*	**3.08**	**3.05**	**3.02**	**3.00**	**2.96**	**2.94**
150	37.27	11.69	7.43	5.86	5.08	4.31	3.93	3.67	3.52	*3.41*	*3.34*	*3.27*	*3.23*	*3.16*	*3.12*	**3.09**	**3.05**	**3.03**	**2.99**	**2.96**
175	39.20	12.08	7.60	5.98	5.16	4.37	3.98	3.72	3.56	*3.45*	*3.38*	*3.32*	*3.26*	*3.20*	*3.15*	*3.12*	**3.08**	**3.06**	**3.03**	**3.00**
200	40.96	12.39	7.76	6.08	5.24	4.42	4.03	3.76	3.59	*3.48*	*3.41*	*3.35*	*3.31*	*3.22*	*3.18*	*3.15*	**3.11**	**3.09**	**3.05**	**3.03**

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Table 19-11. κ-Multipliers for 1-of-3 Intrawell Prediction Limits on Observations (1 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	0.33	0.25	0.21	0.18	0.17	0.15	0.14	0.13	0.12	0.12	0.11	0.11	0.11	0.11	0.10	0.10	0.10	0.10	0.10	0.10
2	0.71	0.57	0.50	0.46	0.44	0.41	0.39	0.38	0.37	0.37	0.36	0.36	0.35	0.35	0.35	0.34	0.34	0.34	0.34	0.34
3	0.95	0.75	0.67	0.62	0.59	0.55	0.53	0.52	0.51	0.50	0.49	0.49	0.48	0.48	0.47	0.47	0.47	0.47	0.46	0.46
4	1.13	0.88	0.78	0.73	0.69	0.65	0.63	0.61	0.60	0.59	0.58	0.58	0.57	0.57	0.56	0.56	0.56	0.55	0.55	0.55
5	1.27	0.98	0.87	0.81	0.77	0.72	0.70	0.68	0.66	0.65	0.65	0.64	0.64	0.63	0.62	0.62	0.62	0.62	0.61	0.61
8	1.60	1.20	1.05	0.98	0.93	0.87	0.84	0.82	0.80	0.79	0.78	0.77	0.77	0.76	0.75	0.75	0.75	0.74	0.74	0.74
12	1.91	1.39	1.21	1.12	1.06	1.00	0.96	0.93	0.91	0.90	0.89	0.88	0.87	0.86	0.86	0.85	0.85	0.85	0.84	0.84
16	2.15	1.54	1.33	1.22	1.16	1.08	1.04	1.01	0.99	0.97	0.96	0.95	0.95	0.94	0.93	0.92	0.92	0.92	0.91	0.91
20	2.35	1.65	1.42	1.30	1.23	1.15	1.10	1.07	1.05	1.03	1.02	1.01	1.00	0.99	0.98	0.98	0.97	0.97	0.96	0.96
30	2.75	1.86	1.58	1.44	1.36	1.27	1.21	1.17	1.15	1.13	1.12	1.11	1.10	1.09	1.08	1.07	1.07	1.06	1.06	1.05
40	3.06	2.02	1.70	1.55	1.45	1.35	1.29	1.25	1.22	1.20	1.19	1.17	1.17	1.15	1.14	1.14	1.13	1.13	1.12	1.11
50	3.32	2.15	1.80	1.63	1.53	1.41	1.35	1.30	1.27	1.25	1.24	1.23	1.22	1.20	1.19	1.19	1.18	1.17	1.17	1.16
60	3.55	*2.26*	1.87	1.69	1.59	1.47	1.40	1.35	1.32	1.30	1.28	1.27	1.26	1.24	1.23	1.22	1.22	1.21	1.21	1.20
75	3.84	2.39	1.97	1.77	1.66	1.53	1.46	1.40	1.37	1.35	1.33	1.32	1.31	1.29	1.28	1.27	1.27	1.26	1.25	1.25
100	4.26	2.57	2.10	1.88	1.75	1.61	1.53	1.48	1.44	1.41	1.39	1.38	1.37	1.35	1.34	1.33	1.32	1.32	1.31	1.30
125	4.60	2.72	*2.20*	1.96	1.82	1.67	1.59	1.53	1.49	1.46	1.44	1.43	1.42	1.40	1.39	1.38	1.37	1.36	1.35	1.35
150	4.90	2.84	*2.28*	2.03	1.88	1.72	1.64	1.57	1.53	1.50	1.48	1.47	1.45	1.44	1.42	1.41	1.41	1.40	1.39	1.38
175	5.17	2.95	2.35	2.09	1.93	1.77	1.68	1.61	1.57	1.54	1.52	1.50	1.49	1.47	1.45	1.44	1.44	1.43	1.42	1.41
200	5.42	3.04	2.42	2.14	1.98	1.80	1.71	1.64	1.60	1.57	1.54	1.53	1.51	1.49	1.48	1.47	1.46	1.46	1.44	1.44

Table 19-11. κ-Multipliers for 1-of-3 Intrawell Prediction Limits on Observations (1 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	0.67	0.54	0.49	0.45	0.43	0.41	0.39	0.38	0.37	0.36	0.36	0.36	0.35	0.35	0.35	0.34	0.34	0.34	0.34	0.34
2	1.08	0.86	0.77	0.72	0.69	0.65	0.62	0.61	0.59	0.59	0.58	0.57	0.57	0.56	0.56	0.56	0.55	0.55	0.55	0.55
3	1.35	1.05	0.93	0.87	0.83	0.78	0.75	0.73	0.71	0.70	0.70	0.69	0.69	0.68	0.68	0.67	0.67	0.67	0.66	0.66
4	1.55	1.18	1.04	0.97	0.92	0.87	0.84	0.81	0.80	0.79	0.78	0.77	0.77	0.76	0.75	0.75	0.75	0.74	0.74	0.74
5	1.71	1.29	1.13	1.05	1.00	0.94	0.90	0.88	0.86	0.85	0.84	0.83	0.83	0.82	0.81	0.81	0.80	0.80	0.80	0.79
8	2.09	1.52	1.32	1.22	1.15	1.08	1.04	1.01	0.99	0.97	0.96	0.95	0.95	0.94	0.93	0.92	0.92	0.92	0.91	0.91
12	2.46	1.73	1.48	1.36	1.29	1.20	1.15	1.12	1.09	1.07	1.06	1.05	1.05	1.03	1.03	1.02	1.02	1.01	1.01	1.00
16	2.75	1.88	1.60	1.46	1.38	1.28	1.23	1.19	1.16	1.15	1.13	1.12	1.11	1.10	1.09	1.09	1.08	1.08	1.07	1.07
20	2.99	2.00	1.69	1.54	1.45	1.35	1.29	1.25	1.22	1.20	1.19	1.17	1.17	1.15	1.14	1.14	1.13	1.13	1.12	1.11
30	3.47	2.24	1.87	1.69	1.58	1.46	1.40	1.35	1.32	1.30	1.28	1.27	1.26	1.24	1.23	1.22	1.22	1.21	1.21	1.20
40	3.84	2.41	1.99	1.79	1.68	1.55	1.47	1.42	1.39	1.36	1.34	1.33	1.32	1.30	1.29	1.28	1.28	1.27	1.26	1.26
50	4.16	*2.55*	2.09	1.87	1.75	1.61	1.53	1.47	1.44	1.41	1.39	1.38	1.37	1.35	1.34	1.33	1.32	1.32	1.31	1.30
60	4.44	2.67	2.17	1.94	1.81	1.66	1.58	1.52	1.48	1.45	1.43	1.42	1.41	1.39	1.38	1.37	1.36	1.36	1.35	1.34
75	4.80	2.82	2.28	2.03	1.88	1.72	1.64	1.57	1.53	1.50	1.48	1.47	1.45	1.44	1.42	1.41	1.41	1.40	1.39	1.38
100	5.30	3.02	2.41	2.13	1.98	1.80	1.71	1.64	1.60	1.57	1.54	1.53	1.51	1.49	1.48	1.47	1.46	1.46	1.44	1.44
125	5.73	3.19	*2.52*	2.22	2.05	1.87	1.77	1.69	1.65	1.61	1.59	1.57	1.56	1.54	1.52	1.51	1.50	1.50	1.49	1.48
150	6.10	3.32	*2.61*	2.29	2.11	1.92	1.81	1.74	1.69	1.65	1.63	1.61	1.60	1.57	1.56	1.55	1.54	1.53	1.52	1.51
175	6.43	3.44	2.69	2.35	2.16	1.96	1.85	1.77	1.72	1.69	1.66	1.64	1.63	1.60	1.59	1.58	1.57	1.56	1.55	1.54
200	6.73	3.55	2.75	2.40	2.21	2.00	1.89	1.80	1.75	1.72	1.69	1.67	1.65	1.63	1.61	1.60	1.59	1.59	1.57	1.56

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Table 19-11. κ-Multipliers for 1-of-3 Intrawell Prediction Limits on Observations (1 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.01**	**0.82**	**0.75**	**0.70**	**0.67**	**0.64**	**0.62**	**0.60**	**0.59**	**0.58**	**0.58**	**0.57**	**0.57**	**0.56**	**0.56**	**0.56**	**0.55**	**0.55**	**0.55**	**0.55**
2	**1.47**	**1.15**	**1.02**	**0.96**	**0.91**	**0.86**	**0.83**	**0.81**	**0.79**	**0.78**	**0.78**	**0.77**	**0.76**	**0.76**	**0.75**	**0.75**	**0.74**	**0.74**	**0.74**	**0.73**
3	**1.77**	**1.34**	**1.19**	**1.10**	**1.05**	**0.99**	**0.95**	**0.93**	**0.91**	**0.89**	**0.89**	**0.88**	**0.87**	**0.86**	**0.86**	**0.85**	**0.85**	**0.85**	**0.84**	**0.84**
4	**2.00**	**1.49**	**1.30**	**1.21**	**1.15**	**1.08**	**1.04**	**1.00**	**0.98**	**0.97**	**0.96**	**0.95**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.92**	**0.91**	**0.91**
5	**2.19**	**1.60**	**1.39**	**1.29**	**1.22**	**1.14**	**1.10**	**1.06**	**1.04**	**1.03**	**1.02**	**1.01**	**1.00**	**0.99**	**0.98**	**0.98**	**0.97**	**0.97**	**0.96**	**0.96**
8	**2.64**	**1.85**	**1.59**	**1.45**	**1.37**	**1.28**	**1.23**	**1.19**	**1.16**	**1.14**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.09**	**1.08**	**1.08**	**1.07**	**1.07**
12	3.07	**2.08**	**1.76**	**1.60**	**1.50**	**1.40**	**1.34**	**1.29**	**1.26**	**1.24**	**1.23**	**1.22**	**1.21**	**1.19**	**1.18**	**1.18**	**1.17**	**1.17**	**1.16**	**1.15**
16	3.42	**2.24**	**1.88**	**1.70**	**1.60**	**1.48**	**1.41**	**1.36**	**1.33**	**1.31**	**1.29**	**1.28**	**1.27**	**1.26**	**1.25**	**1.24**	**1.23**	**1.23**	**1.22**	**1.21**
20	3.70	**2.38**	**1.98**	**1.78**	**1.67**	**1.54**	**1.47**	**1.42**	**1.39**	**1.36**	**1.34**	**1.33**	**1.32**	**1.30**	**1.29**	**1.28**	**1.28**	**1.27**	**1.26**	**1.26**
30	4.28	**2.64**	**2.16**	**1.93**	**1.80**	**1.66**	**1.58**	**1.52**	**1.48**	**1.45**	**1.43**	**1.42**	**1.41**	**1.39**	**1.38**	**1.37**	**1.36**	**1.36**	**1.35**	**1.34**
40	4.74	*2.83*	**2.29**	**2.04**	**1.90**	**1.74**	**1.65**	**1.59**	**1.55**	**1.52**	**1.50**	**1.48**	**1.47**	**1.45**	**1.44**	**1.43**	**1.42**	**1.41**	**1.40**	**1.39**
50	5.12	2.99	**2.40**	**2.13**	**1.97**	**1.80**	**1.71**	**1.64**	**1.60**	**1.57**	**1.54**	**1.53**	**1.51**	**1.49**	**1.48**	**1.47**	**1.46**	**1.46**	**1.44**	**1.44**
60	5.45	3.12	**2.49**	**2.20**	**2.03**	**1.85**	**1.76**	**1.68**	**1.64**	**1.61**	**1.58**	**1.56**	**1.55**	**1.53**	**1.52**	**1.51**	**1.50**	**1.49**	**1.48**	**1.47**
75	5.89	3.29	**2.60**	**2.28**	**2.11**	**1.92**	**1.81**	**1.74**	**1.69**	**1.65**	**1.63**	**1.61**	**1.60**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**	**1.51**
100	6.50	3.51	**2.74**	**2.40**	**2.21**	**2.00**	**1.89**	**1.80**	**1.75**	**1.72**	**1.69**	**1.67**	**1.65**	**1.63**	**1.61**	**1.60**	**1.59**	**1.59**	**1.57**	**1.56**
125	7.02	3.70	*2.86*	**2.49**	**2.28**	**2.06**	**1.94**	**1.85**	**1.80**	**1.76**	**1.73**	**1.71**	**1.70**	**1.67**	**1.66**	**1.64**	**1.63**	**1.63**	**1.61**	**1.60**
150	7.46	3.85	2.95	**2.56**	**2.34**	**2.11**	**1.99**	**1.90**	**1.84**	**1.80**	**1.77**	**1.75**	**1.73**	**1.71**	**1.69**	**1.68**	**1.67**	**1.66**	**1.64**	**1.64**
175	7.87	3.98	3.04	**2.63**	**2.40**	**2.15**	**2.03**	**1.93**	**1.87**	**1.83**	**1.80**	**1.78**	**1.76**	**1.74**	**1.72**	**1.71**	**1.69**	**1.69**	**1.67**	**1.66**
200	8.23	4.10	3.11	**2.68**	**2.44**	**2.19**	**2.06**	**1.96**	**1.90**	**1.86**	**1.83**	**1.81**	**1.79**	**1.76**	**1.74**	**1.73**	**1.72**	**1.71**	**1.69**	**1.69**

Table 19-11. κ-Multipliers for 1-of-3 Intrawell Prediction Limits on Observations (2 COC, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**0.71**	**0.57**	**0.50**	**0.46**	**0.44**	**0.41**	**0.39**	**0.38**	**0.37**	**0.37**	**0.36**	**0.36**	**0.35**	**0.35**	**0.35**	**0.34**	**0.34**	**0.34**	**0.34**	**0.34**
2	**1.13**	**0.88**	**0.78**	**0.73**	**0.69**	**0.65**	**0.63**	**0.61**	**0.60**	**0.59**	**0.58**	**0.58**	**0.57**	**0.57**	**0.56**	**0.56**	**0.56**	**0.55**	**0.55**	**0.55**
3	**1.39**	**1.07**	**0.94**	**0.87**	**0.83**	**0.78**	**0.75**	**0.73**	**0.72**	**0.71**	**0.70**	**0.69**	**0.69**	**0.68**	**0.68**	**0.67**	**0.67**	**0.67**	**0.66**	**0.66**
4	**1.60**	**1.20**	**1.05**	**0.98**	**0.93**	**0.87**	**0.84**	**0.82**	**0.80**	**0.79**	**0.78**	**0.77**	**0.77**	**0.76**	**0.75**	**0.75**	**0.75**	**0.74**	**0.74**	**0.74**
5	**1.76**	**1.31**	**1.14**	**1.06**	**1.00**	**0.94**	**0.91**	**0.88**	**0.86**	**0.85**	**0.84**	**0.83**	**0.83**	**0.82**	**0.81**	**0.81**	**0.80**	**0.80**	**0.80**	**0.79**
8	**2.15**	**1.54**	**1.33**	**1.22**	**1.16**	**1.08**	**1.04**	**1.01**	**0.99**	**0.97**	**0.96**	**0.95**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.92**	**0.91**	**0.91**
12	2.52	**1.74**	**1.49**	**1.37**	**1.29**	**1.20**	**1.15**	**1.12**	**1.09**	**1.08**	**1.06**	**1.05**	**1.05**	**1.03**	**1.03**	**1.02**	**1.02**	**1.01**	**1.01**	**1.00**
16	2.81	**1.90**	**1.61**	**1.47**	**1.38**	**1.29**	**1.23**	**1.19**	**1.16**	**1.15**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.09**	**1.08**	**1.08**	**1.07**	**1.07**
20	3.06	**2.02**	**1.70**	**1.55**	**1.45**	**1.35**	**1.29**	**1.25**	**1.22**	**1.20**	**1.19**	**1.17**	**1.17**	**1.15**	**1.14**	**1.14**	**1.13**	**1.13**	**1.12**	**1.11**
30	3.55	*2.26*	**1.87**	**1.69**	**1.59**	**1.47**	**1.40**	**1.35**	**1.32**	**1.30**	**1.28**	**1.27**	**1.26**	**1.24**	**1.23**	**1.22**	**1.22**	**1.21**	**1.21**	**1.20**
40	3.93	2.43	**2.00**	**1.80**	**1.68**	**1.55**	**1.47**	**1.42**	**1.39**	**1.36**	**1.34**	**1.33**	**1.32**	**1.30**	**1.29**	**1.28**	**1.28**	**1.27**	**1.26**	**1.26**
50	4.26	2.57	**2.10**	**1.88**	**1.75**	**1.61**	**1.53**	**1.48**	**1.44**	**1.41**	**1.39**	**1.38**	**1.37**	**1.35**	**1.34**	**1.33**	**1.32**	**1.32**	**1.31**	**1.30**
60	4.54	2.69	*2.18*	**1.95**	**1.81**	**1.66**	**1.58**	**1.52**	**1.48**	**1.45**	**1.43**	**1.42**	**1.41**	**1.39**	**1.38**	**1.37**	**1.36**	**1.36**	**1.35**	**1.34**
75	4.90	2.84	*2.28*	**2.03**	**1.88**	**1.72**	**1.64**	**1.57**	**1.53**	**1.50**	**1.48**	**1.47**	**1.45**	**1.44**	**1.42**	**1.41**	**1.41**	**1.40**	**1.39**	**1.38**
100	5.42	3.04	2.42	**2.14**	**1.98**	**1.80**	**1.71**	**1.64**	**1.60**	**1.57**	**1.54**	**1.53**	**1.51**	**1.49**	**1.48**	**1.47**	**1.46**	**1.46**	**1.44**	**1.44**
125	5.85	3.20	2.53	*2.22*	**2.05**	**1.87**	**1.77**	**1.69**	**1.65**	**1.61**	**1.59**	**1.57**	**1.56**	**1.54**	**1.52**	**1.51**	**1.50**	**1.50**	**1.49**	**1.48**
150	6.23	3.34	2.61	*2.29*	**2.11**	**1.92**	**1.81**	**1.74**	**1.69**	**1.65**	**1.63**	**1.61**	**1.60**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**	**1.51**
175	6.56	3.46	2.69	*2.35*	**2.17**	**1.96**	**1.85**	**1.77**	**1.72**	**1.69**	**1.66**	**1.64**	**1.63**	**1.60**	**1.59**	**1.58**	**1.57**	**1.56**	**1.55**	**1.54**
200	6.87	3.57	2.76	2.41	*2.21*	**2.00**	**1.89**	**1.80**	**1.75**	**1.72**	**1.69**	**1.67**	**1.65**	**1.63**	**1.61**	**1.60**	**1.59**	**1.59**	**1.57**	**1.56**

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Table 19-11. κ-Multipliers for 1-of-3 Intrawell Prediction Limits on Observations (2 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.08**	**0.86**	**0.77**	**0.72**	**0.69**	**0.65**	**0.62**	**0.61**	**0.59**	**0.59**	**0.58**	**0.57**	**0.57**	**0.56**	**0.56**	**0.56**	**0.55**	**0.55**	**0.55**	**0.55**
2	**1.55**	**1.18**	**1.04**	**0.97**	**0.92**	**0.87**	**0.84**	**0.81**	**0.80**	**0.79**	**0.78**	**0.77**	**0.77**	**0.76**	**0.75**	**0.75**	**0.75**	**0.74**	**0.74**	**0.74**
3	**1.85**	**1.38**	**1.20**	**1.11**	**1.06**	**0.99**	**0.96**	**0.93**	**0.91**	**0.90**	**0.89**	**0.88**	**0.87**	**0.86**	**0.86**	**0.85**	**0.85**	**0.85**	**0.84**	**0.84**
4	**2.09**	**1.52**	**1.32**	**1.22**	**1.15**	**1.08**	**1.04**	**1.01**	**0.99**	**0.97**	**0.96**	**0.95**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.92**	**0.91**	**0.91**
5	**2.29**	**1.63**	**1.41**	**1.30**	**1.23**	**1.15**	**1.10**	**1.07**	**1.04**	**1.03**	**1.02**	**1.01**	**1.00**	**0.99**	**0.98**	**0.98**	**0.97**	**0.97**	**0.96**	**0.96**
8	2.75	**1.88**	**1.60**	**1.46**	**1.38**	**1.28**	**1.23**	**1.19**	**1.16**	**1.15**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.09**	**1.08**	**1.08**	**1.07**	**1.07**
12	3.19	**2.11**	**1.77**	**1.61**	**1.51**	**1.40**	**1.34**	**1.29**	**1.26**	**1.24**	**1.23**	**1.22**	**1.21**	**1.19**	**1.18**	**1.18**	**1.17**	**1.17**	**1.16**	**1.15**
16	3.55	**2.28**	**1.89**	**1.71**	**1.60**	**1.48**	**1.42**	**1.37**	**1.33**	**1.31**	**1.29**	**1.28**	**1.27**	**1.26**	**1.25**	**1.24**	**1.23**	**1.23**	**1.22**	**1.21**
20	3.84	**2.41**	**1.99**	**1.79**	**1.68**	**1.55**	**1.47**	**1.42**	**1.39**	**1.36**	**1.34**	**1.33**	**1.32**	**1.30**	**1.29**	**1.28**	**1.28**	**1.27**	**1.26**	**1.26**
30	4.44	2.67	**2.17**	**1.94**	**1.81**	**1.66**	**1.58**	**1.52**	**1.48**	**1.45**	**1.43**	**1.42**	**1.41**	**1.39**	**1.38**	**1.37**	**1.36**	**1.36**	**1.35**	**1.34**
40	4.91	2.87	**2.31**	**2.05**	**1.90**	**1.74**	**1.65**	**1.59**	**1.55**	**1.52**	**1.50**	**1.48**	**1.47**	**1.45**	**1.44**	**1.43**	**1.42**	**1.41**	**1.40**	**1.39**
50	5.30	3.02	**2.41**	**2.13**	**1.98**	**1.80**	**1.71**	**1.64**	**1.60**	**1.57**	**1.54**	**1.53**	**1.51**	**1.49**	**1.48**	**1.47**	**1.46**	**1.46**	**1.44**	**1.44**
60	5.65	3.15	*2.50*	**2.20**	**2.04**	**1.85**	**1.76**	**1.68**	**1.64**	**1.61**	**1.58**	**1.57**	**1.55**	**1.53**	**1.52**	**1.51**	**1.50**	**1.49**	**1.48**	**1.47**
75	6.10	3.32	*2.61*	**2.29**	**2.11**	**1.92**	**1.81**	**1.74**	**1.69**	**1.65**	**1.63**	**1.61**	**1.60**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**	**1.51**
100	6.73	3.55	2.75	**2.40**	**2.21**	**2.00**	**1.89**	**1.80**	**1.75**	**1.72**	**1.69**	**1.67**	**1.65**	**1.63**	**1.61**	**1.60**	**1.59**	**1.59**	**1.57**	**1.56**
125	7.27	3.73	2.87	*2.49*	**2.29**	**2.06**	**1.94**	**1.85**	**1.80**	**1.76**	**1.73**	**1.71**	**1.70**	**1.67**	**1.66**	**1.64**	**1.63**	**1.63**	**1.61**	**1.60**
150	7.73	3.89	2.97	*2.57*	**2.35**	**2.11**	**1.99**	**1.90**	**1.84**	**1.80**	**1.77**	**1.75**	**1.73**	**1.71**	**1.69**	**1.68**	**1.67**	**1.66**	**1.64**	**1.64**
175	8.14	4.02	3.05	*2.63*	**2.40**	**2.16**	**2.03**	**1.93**	**1.87**	**1.83**	**1.80**	**1.78**	**1.76**	**1.74**	**1.72**	**1.70**	**1.69**	**1.69**	**1.67**	**1.66**
200	8.53	4.15	3.12	*2.69*	**2.45**	**2.19**	**2.06**	**1.96**	**1.90**	**1.86**	**1.83**	**1.81**	**1.79**	**1.76**	**1.74**	**1.73**	**1.72**	**1.71**	**1.69**	**1.68**

Table 19-11. κ-Multipliers for 1-of-3 Intrawell Prediction Limits on Observations (2 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.47**	**1.15**	**1.02**	**0.96**	**0.91**	**0.86**	**0.83**	**0.81**	**0.79**	**0.78**	**0.78**	**0.77**	**0.76**	**0.76**	**0.75**	**0.75**	**0.74**	**0.74**	**0.74**	**0.73**
2	**2.00**	**1.49**	**1.30**	**1.21**	**1.15**	**1.08**	**1.04**	**1.00**	**0.98**	**0.97**	**0.96**	**0.95**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.92**	**0.91**	**0.91**
3	**2.36**	**1.70**	**1.47**	**1.35**	**1.28**	**1.20**	**1.15**	**1.11**	**1.09**	**1.07**	**1.06**	**1.05**	**1.04**	**1.03**	**1.03**	**1.02**	**1.02**	**1.01**	**1.01**	**1.00**
4	**2.64**	**1.85**	**1.59**	**1.45**	**1.37**	**1.28**	**1.23**	**1.19**	**1.16**	**1.14**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.09**	**1.08**	**1.08**	**1.07**	**1.07**
5	2.87	**1.97**	**1.68**	**1.53**	**1.45**	**1.34**	**1.29**	**1.25**	**1.22**	**1.20**	**1.18**	**1.17**	**1.16**	**1.15**	**1.14**	**1.14**	**1.13**	**1.13**	**1.12**	**1.11**
8	3.42	**2.24**	**1.88**	**1.70**	**1.60**	**1.48**	**1.41**	**1.36**	**1.33**	**1.31**	**1.29**	**1.28**	**1.27**	**1.26**	**1.25**	**1.24**	**1.23**	**1.23**	**1.22**	**1.21**
12	3.95	**2.49**	**2.06**	**1.85**	**1.73**	**1.59**	**1.52**	**1.46**	**1.43**	**1.40**	**1.38**	**1.37**	**1.36**	**1.34**	**1.33**	**1.32**	**1.32**	**1.31**	**1.30**	**1.29**
16	4.38	**2.68**	**2.19**	**1.96**	**1.82**	**1.68**	**1.59**	**1.53**	**1.49**	**1.47**	**1.45**	**1.43**	**1.42**	**1.40**	**1.39**	**1.38**	**1.37**	**1.37**	**1.36**	**1.35**
20	4.74	*2.83*	**2.29**	**2.04**	**1.90**	**1.74**	**1.65**	**1.59**	**1.55**	**1.52**	**1.50**	**1.48**	**1.47**	**1.45**	**1.44**	**1.43**	**1.42**	**1.41**	**1.40**	**1.39**
30	5.45	3.12	**2.49**	**2.20**	**2.03**	**1.85**	**1.76**	**1.68**	**1.64**	**1.61**	**1.58**	**1.56**	**1.55**	**1.53**	**1.52**	**1.51**	**1.50**	**1.49**	**1.48**	**1.47**
40	6.02	3.34	**2.63**	**2.31**	**2.13**	**1.93**	**1.83**	**1.75**	**1.70**	**1.67**	**1.64**	**1.62**	**1.61**	**1.59**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**
50	6.50	3.51	**2.74**	**2.40**	**2.21**	**2.00**	**1.89**	**1.80**	**1.75**	**1.72**	**1.69**	**1.67**	**1.65**	**1.63**	**1.61**	**1.60**	**1.59**	**1.59**	**1.57**	**1.56**
60	6.92	3.66	*2.84*	**2.47**	**2.27**	**2.05**	**1.93**	**1.85**	**1.79**	**1.75**	**1.73**	**1.71**	**1.69**	**1.67**	**1.65**	**1.64**	**1.63**	**1.62**	**1.60**	**1.60**
75	7.46	3.85	2.95	**2.56**	**2.34**	**2.11**	**1.99**	**1.90**	**1.84**	**1.80**	**1.77**	**1.75**	**1.73**	**1.71**	**1.69**	**1.68**	**1.67**	**1.66**	**1.64**	**1.64**
100	8.23	4.10	3.11	**2.68**	**2.44**	**2.19**	**2.06**	**1.96**	**1.90**	**1.86**	**1.83**	**1.81**	**1.79**	**1.76**	**1.74**	**1.73**	**1.72**	**1.71**	**1.69**	**1.69**
125	8.88	4.31	3.23	*2.78*	**2.52**	**2.26**	**2.12**	**2.01**	**1.95**	**1.91**	**1.87**	**1.85**	**1.83**	**1.80**	**1.78**	**1.77**	**1.76**	**1.75**	**1.73**	**1.72**
150	9.43	4.48	3.34	*2.85*	**2.59**	**2.31**	**2.16**	**2.06**	**1.99**	**1.94**	**1.91**	**1.89**	**1.87**	**1.84**	**1.82**	**1.80**	**1.79**	**1.78**	**1.76**	**1.75**
175	9.95	4.64	3.43	*2.92*	**2.64**	**2.35**	**2.20**	**2.09**	**2.02**	**1.98**	**1.94**	**1.92**	**1.90**	**1.86**	**1.84**	**1.83**	**1.82**	**1.81**	**1.79**	**1.78**
200	10.40	4.78	3.51	*2.98*	**2.69**	**2.39**	**2.23**	**2.12**	**2.05**	**2.00**	**1.97**	**1.94**	**1.92**	**1.89**	**1.87**	**1.85**	**1.84**	**1.83**	**1.81**	**1.80**

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Table 19-11. κ-Multipliers for 1-of-3 Intrawell Prediction Limits on Observations (5 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.27**	**0.98**	**0.87**	**0.81**	**0.77**	**0.72**	**0.70**	**0.68**	**0.66**	**0.65**	**0.65**	**0.64**	**0.64**	**0.63**	**0.62**	**0.62**	**0.62**	**0.62**	**0.61**	**0.61**
2	**1.76**	**1.31**	**1.14**	**1.06**	**1.00**	**0.94**	**0.91**	**0.88**	**0.86**	**0.85**	**0.84**	**0.83**	**0.83**	**0.82**	**0.81**	**0.81**	**0.80**	**0.80**	**0.80**	**0.79**
3	**2.09**	**1.50**	**1.30**	**1.20**	**1.14**	**1.06**	**1.02**	**0.99**	**0.97**	**0.96**	**0.95**	**0.94**	**0.93**	**0.92**	**0.91**	**0.91**	**0.90**	**0.90**	**0.90**	**0.89**
4	2.35	**1.65**	**1.42**	**1.30**	**1.23**	**1.15**	**1.10**	**1.07**	**1.05**	**1.03**	**1.02**	**1.01**	**1.00**	**0.99**	**0.98**	**0.98**	**0.97**	**0.97**	**0.96**	**0.96**
5	2.56	**1.77**	**1.51**	**1.38**	**1.30**	**1.21**	**1.16**	**1.13**	**1.10**	**1.09**	**1.07**	**1.06**	**1.06**	**1.04**	**1.04**	**1.03**	**1.03**	**1.02**	**1.01**	**1.01**
8	3.06	**2.02**	**1.70**	**1.55**	**1.45**	**1.35**	**1.29**	**1.25**	**1.22**	**1.20**	**1.19**	**1.17**	**1.17**	**1.15**	**1.14**	**1.14**	**1.13**	**1.13**	**1.12**	**1.11**
12	3.55	*2.26*	**1.87**	**1.69**	**1.59**	**1.47**	**1.40**	**1.35**	**1.32**	**1.30**	**1.28**	**1.27**	**1.26**	**1.24**	**1.23**	**1.22**	**1.22**	**1.21**	**1.21**	**1.20**
16	3.93	2.43	**2.00**	**1.80**	**1.68**	**1.55**	**1.47**	**1.42**	**1.39**	**1.36**	**1.34**	**1.33**	**1.32**	**1.30**	**1.29**	**1.28**	**1.28**	**1.27**	**1.26**	**1.26**
20	4.26	2.57	**2.10**	**1.88**	**1.75**	**1.61**	**1.53**	**1.48**	**1.44**	**1.41**	**1.39**	**1.38**	**1.37**	**1.35**	**1.34**	**1.33**	**1.32**	**1.32**	**1.31**	**1.30**
30	4.90	2.84	*2.28*	**2.03**	**1.88**	**1.72**	**1.64**	**1.57**	**1.53**	**1.50**	**1.48**	**1.47**	**1.45**	**1.44**	**1.42**	**1.41**	**1.41**	**1.40**	**1.39**	**1.38**
40	5.42	3.04	2.42	**2.14**	**1.98**	**1.80**	**1.71**	**1.64**	**1.60**	**1.57**	**1.54**	**1.53**	**1.51**	**1.49**	**1.48**	**1.47**	**1.46**	**1.46**	**1.44**	**1.44**
50	5.85	3.20	2.53	*2.22*	**2.05**	**1.87**	**1.77**	**1.69**	**1.65**	**1.61**	**1.59**	**1.57**	**1.56**	**1.54**	**1.52**	**1.51**	**1.50**	**1.50**	**1.49**	**1.48**
60	6.23	3.34	2.61	*2.29*	**2.11**	**1.92**	**1.81**	**1.74**	**1.69**	**1.65**	**1.63**	**1.61**	**1.60**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**	**1.51**
75	6.72	3.52	2.73	2.38	*2.19*	**1.98**	**1.87**	**1.79**	**1.74**	**1.70**	**1.68**	**1.66**	**1.64**	**1.62**	**1.60**	**1.59**	**1.58**	**1.57**	**1.56**	**1.55**
100	7.41	3.76	2.88	2.50	*2.29*	**2.06**	**1.94**	**1.85**	**1.80**	**1.76**	**1.74**	**1.71**	**1.70**	**1.67**	**1.66**	**1.64**	**1.63**	**1.63**	**1.61**	**1.60**
125	8.00	3.95	3.00	2.59	*2.36*	**2.12**	**2.00**	**1.91**	**1.85**	**1.81**	**1.78**	**1.76**	**1.74**	**1.72**	**1.70**	**1.68**	**1.67**	**1.67**	**1.65**	**1.64**
150	8.50	4.11	3.09	2.66	2.43	*2.18*	**2.04**	**1.95**	**1.89**	**1.85**	**1.82**	**1.79**	**1.78**	**1.75**	**1.73**	**1.72**	**1.71**	**1.70**	**1.68**	**1.67**
175	8.96	4.25	3.18	2.72	2.48	*2.22*	**2.08**	**1.98**	**1.92**	**1.88**	**1.85**	**1.82**	**1.81**	**1.78**	**1.76**	**1.74**	**1.74**	**1.72**	**1.71**	**1.70**
200	9.38	4.38	3.25	2.78	2.53	*2.26*	**2.12**	**2.01**	**1.95**	**1.91**	**1.88**	**1.85**	**1.83**	**1.80**	**1.78**	**1.77**	**1.76**	**1.75**	**1.73**	**1.72**

Table 19-11. κ-Multipliers for 1-of-3 Intrawell Prediction Limits on Observations (5 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.71**	**1.29**	**1.13**	**1.05**	**1.00**	**0.94**	**0.90**	**0.88**	**0.86**	**0.85**	**0.84**	**0.83**	**0.83**	**0.82**	**0.81**	**0.81**	**0.80**	**0.80**	**0.80**	**0.79**
2	**2.29**	**1.63**	**1.41**	**1.30**	**1.23**	**1.15**	**1.10**	**1.07**	**1.04**	**1.03**	**1.02**	**1.01**	**1.00**	**0.99**	**0.98**	**0.98**	**0.97**	**0.97**	**0.96**	**0.96**
3	2.68	**1.85**	**1.57**	**1.44**	**1.36**	**1.27**	**1.21**	**1.17**	**1.15**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**	**1.07**	**1.06**	**1.06**	**1.05**
4	2.99	**2.00**	**1.69**	**1.54**	**1.45**	**1.35**	**1.29**	**1.25**	**1.22**	**1.20**	**1.19**	**1.17**	**1.17**	**1.15**	**1.14**	**1.14**	**1.13**	**1.13**	**1.12**	**1.11**
5	3.24	**2.13**	**1.79**	**1.62**	**1.52**	**1.41**	**1.35**	**1.30**	**1.27**	**1.25**	**1.24**	**1.23**	**1.22**	**1.20**	**1.19**	**1.18**	**1.18**	**1.17**	**1.17**	**1.16**
8	3.84	**2.41**	**1.99**	**1.79**	**1.68**	**1.55**	**1.47**	**1.42**	**1.39**	**1.36**	**1.34**	**1.33**	**1.32**	**1.30**	**1.29**	**1.28**	**1.28**	**1.27**	**1.26**	**1.26**
12	4.44	2.67	**2.17**	**1.94**	**1.81**	**1.66**	**1.58**	**1.52**	**1.48**	**1.45**	**1.43**	**1.42**	**1.41**	**1.39**	**1.38**	**1.37**	**1.36**	**1.36**	**1.35**	**1.34**
16	4.91	2.87	**2.31**	**2.05**	**1.90**	**1.74**	**1.65**	**1.59**	**1.55**	**1.52**	**1.50**	**1.48**	**1.47**	**1.45**	**1.44**	**1.43**	**1.42**	**1.41**	**1.40**	**1.39**
20	5.30	3.02	**2.41**	**2.13**	**1.98**	**1.80**	**1.71**	**1.64**	**1.60**	**1.57**	**1.54**	**1.53**	**1.51**	**1.49**	**1.48**	**1.47**	**1.46**	**1.46**	**1.44**	**1.44**
30	6.10	3.32	*2.61*	**2.29**	**2.11**	**1.92**	**1.81**	**1.74**	**1.69**	**1.65**	**1.63**	**1.61**	**1.60**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**	**1.51**
40	6.73	3.55	2.75	**2.40**	**2.21**	**2.00**	**1.89**	**1.80**	**1.75**	**1.72**	**1.69**	**1.67**	**1.65**	**1.63**	**1.61**	**1.60**	**1.59**	**1.59**	**1.57**	**1.56**
50	7.27	3.73	2.87	*2.49*	**2.29**	**2.06**	**1.94**	**1.85**	**1.80**	**1.76**	**1.73**	**1.71**	**1.70**	**1.67**	**1.66**	**1.64**	**1.63**	**1.63**	**1.61**	**1.60**
60	7.73	3.89	2.97	*2.57*	**2.35**	**2.11**	**1.99**	**1.90**	**1.84**	**1.80**	**1.77**	**1.75**	**1.73**	**1.71**	**1.69**	**1.68**	**1.67**	**1.66**	**1.64**	**1.64**
75	8.33	4.09	3.09	*2.66*	**2.42**	**2.18**	**2.05**	**1.95**	**1.89**	**1.85**	**1.82**	**1.79**	**1.78**	**1.75**	**1.73**	**1.72**	**1.71**	**1.70**	**1.68**	**1.67**
100	9.20	4.35	3.25	2.78	*2.53*	**2.26**	**2.12**	**2.01**	**1.95**	**1.91**	**1.88**	**1.85**	**1.83**	**1.80**	**1.78**	**1.77**	**1.76**	**1.75**	**1.73**	**1.72**
125	9.90	4.57	3.38	2.88	*2.61*	**2.32**	**2.17**	**2.07**	**2.00**	**1.95**	**1.92**	**1.89**	**1.87**	**1.84**	**1.82**	**1.81**	**1.80**	**1.79**	**1.77**	**1.76**
150	10.55	4.75	3.49	2.96	*2.67*	**2.37**	**2.22**	**2.11**	**2.04**	**1.99**	**1.96**	**1.93**	**1.91**	**1.88**	**1.86**	**1.84**	**1.83**	**1.82**	**1.80**	**1.79**
175	11.07	4.91	3.57	3.02	*2.72*	**2.42**	**2.26**	**2.14**	**2.07**	**2.02**	**1.98**	**1.96**	**1.94**	**1.90**	**1.88**	**1.87**	**1.85**	**1.85**	**1.83**	**1.82**
200	11.60	5.05	3.65	3.08	2.78	*2.45*	**2.29**	**2.17**	**2.10**	**2.05**	**2.01**	**1.98**	**1.96**	**1.93**	**1.91**	**1.89**	**1.88**	**1.87**	**1.85**	**1.84**

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Table 19-11. κ-Multipliers for 1-of-3 Intrawell Prediction Limits on Observations (5 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.19**	**1.60**	**1.39**	**1.29**	**1.22**	**1.14**	**1.10**	**1.06**	**1.04**	**1.03**	**1.02**	**1.01**	**1.00**	**0.99**	**0.98**	**0.98**	**0.97**	**0.97**	**0.96**	**0.96**
2	2.87	**1.97**	**1.68**	**1.53**	**1.45**	**1.34**	**1.29**	**1.25**	**1.22**	**1.20**	**1.18**	**1.17**	**1.16**	**1.15**	**1.14**	**1.14**	**1.13**	**1.13**	**1.12**	**1.11**
3	3.34	**2.21**	**1.85**	**1.68**	**1.58**	**1.46**	**1.40**	**1.35**	**1.32**	**1.29**	**1.28**	**1.27**	**1.26**	**1.24**	**1.23**	**1.22**	**1.22**	**1.21**	**1.20**	**1.20**
4	3.70	**2.38**	**1.98**	**1.78**	**1.67**	**1.54**	**1.47**	**1.42**	**1.39**	**1.36**	**1.34**	**1.33**	**1.32**	**1.30**	**1.29**	**1.28**	**1.28**	**1.27**	**1.26**	**1.26**
5	4.01	**2.52**	**2.08**	**1.87**	**1.74**	**1.61**	**1.53**	**1.47**	**1.44**	**1.41**	**1.39**	**1.38**	**1.37**	**1.35**	**1.34**	**1.33**	**1.32**	**1.32**	**1.31**	**1.30**
8	4.74	*2.83*	**2.29**	**2.04**	**1.90**	**1.74**	**1.65**	**1.59**	**1.55**	**1.52**	**1.50**	**1.48**	**1.47**	**1.45**	**1.44**	**1.43**	**1.42**	**1.41**	**1.40**	**1.39**
12	5.45	3.12	**2.49**	**2.20**	**2.03**	**1.85**	**1.76**	**1.68**	**1.64**	**1.61**	**1.58**	**1.56**	**1.55**	**1.53**	**1.52**	**1.51**	**1.50**	**1.49**	**1.48**	**1.47**
16	6.02	3.34	**2.63**	**2.31**	**2.13**	**1.93**	**1.83**	**1.75**	**1.70**	**1.67**	**1.64**	**1.62**	**1.61**	**1.59**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**
20	6.50	3.51	**2.74**	**2.40**	**2.21**	**2.00**	**1.89**	**1.80**	**1.75**	**1.72**	**1.69**	**1.67**	**1.65**	**1.63**	**1.61**	**1.60**	**1.59**	**1.59**	**1.57**	**1.56**
30	7.46	3.85	2.95	**2.56**	**2.34**	**2.11**	**1.99**	**1.90**	**1.84**	**1.80**	**1.77**	**1.75**	**1.73**	**1.71**	**1.69**	**1.68**	**1.67**	**1.66**	**1.64**	**1.64**
40	8.23	4.10	3.11	**2.68**	**2.44**	**2.19**	**2.06**	**1.96**	**1.90**	**1.86**	**1.83**	**1.81**	**1.79**	**1.76**	**1.74**	**1.73**	**1.72**	**1.71**	**1.69**	**1.69**
50	8.88	4.31	3.23	*2.78*	**2.52**	**2.26**	**2.12**	**2.01**	**1.95**	**1.91**	**1.87**	**1.85**	**1.83**	**1.80**	**1.78**	**1.77**	**1.76**	**1.75**	**1.73**	**1.72**
60	9.43	4.48	3.34	*2.85*	**2.59**	**2.31**	**2.16**	**2.06**	**1.99**	**1.94**	**1.91**	**1.89**	**1.87**	**1.84**	**1.82**	**1.80**	**1.79**	**1.78**	**1.76**	**1.75**
75	10.18	4.71	3.47	*2.95*	**2.67**	**2.37**	**2.22**	**2.11**	**2.04**	**1.99**	**1.95**	**1.93**	**1.91**	**1.88**	**1.86**	**1.84**	**1.83**	**1.82**	**1.80**	**1.79**
100	11.22	5.01	3.64	3.08	*2.77*	**2.45**	**2.29**	**2.17**	**2.10**	**2.05**	**2.01**	**1.98**	**1.96**	**1.93**	**1.91**	**1.89**	**1.88**	**1.87**	**1.85**	**1.84**
125	12.07	5.25	3.78	3.18	*2.86*	**2.52**	**2.35**	**2.22**	**2.15**	**2.09**	**2.05**	**2.03**	**2.00**	**1.97**	**1.95**	**1.93**	**1.92**	**1.90**	**1.89**	**1.87**
150	12.83	5.46	3.90	3.26	*2.92*	**2.57**	**2.40**	**2.26**	**2.18**	**2.13**	**2.09**	**2.06**	**2.04**	**2.00**	**1.98**	**1.96**	**1.95**	**1.94**	**1.92**	**1.90**
175	13.54	5.64	4.00	3.33	*2.98*	**2.62**	**2.43**	**2.30**	**2.22**	**2.16**	**2.12**	**2.09**	**2.06**	**2.03**	**2.00**	**1.98**	**1.97**	**1.96**	**1.94**	**1.93**
200	14.18	5.80	4.09	3.40	*3.03*	**2.66**	**2.47**	**2.33**	**2.24**	**2.19**	**2.15**	**2.11**	**2.09**	**2.05**	**2.03**	**2.01**	**1.99**	**1.98**	**1.96**	**1.95**

Table 19-11. κ-Multipliers for 1-of-3 Intrawell Prediction Limits on Observations (10 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.76**	**1.31**	**1.14**	**1.06**	**1.00**	**0.94**	**0.91**	**0.88**	**0.86**	**0.85**	**0.84**	**0.83**	**0.83**	**0.82**	**0.81**	**0.81**	**0.80**	**0.80**	**0.80**	**0.79**
2	2.35	**1.65**	**1.42**	**1.30**	**1.23**	**1.15**	**1.10**	**1.07**	**1.05**	**1.03**	**1.02**	**1.01**	**1.00**	**0.99**	**0.98**	**0.98**	**0.97**	**0.97**	**0.96**	**0.96**
3	2.75	**1.86**	**1.58**	**1.44**	**1.36**	**1.27**	**1.21**	**1.17**	**1.15**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**	**1.07**	**1.06**	**1.06**	**1.05**
4	3.06	**2.02**	**1.70**	**1.55**	**1.45**	**1.35**	**1.29**	**1.25**	**1.22**	**1.20**	**1.19**	**1.17**	**1.17**	**1.15**	**1.14**	**1.14**	**1.13**	**1.13**	**1.12**	**1.11**
5	3.32	**2.15**	**1.80**	**1.63**	**1.53**	**1.41**	**1.35**	**1.30**	**1.27**	**1.25**	**1.24**	**1.23**	**1.22**	**1.20**	**1.19**	**1.19**	**1.18**	**1.17**	**1.17**	**1.16**
8	3.93	2.43	**2.00**	**1.80**	**1.68**	**1.55**	**1.47**	**1.42**	**1.39**	**1.36**	**1.34**	**1.33**	**1.32**	**1.30**	**1.29**	**1.29**	**1.28**	**1.27**	**1.26**	**1.26**
12	4.53	2.69	*2.18*	**1.95**	**1.81**	**1.66**	**1.58**	**1.52**	**1.48**	**1.45**	**1.43**	**1.42**	**1.41**	**1.39**	**1.38**	**1.37**	**1.36**	**1.36**	**1.35**	**1.34**
16	5.02	2.88	*2.31*	**2.05**	**1.90**	**1.74**	**1.65**	**1.59**	**1.55**	**1.52**	**1.50**	**1.48**	**1.47**	**1.45**	**1.44**	**1.43**	**1.42**	**1.41**	**1.40**	**1.39**
20	5.42	3.04	2.42	**2.14**	**1.98**	**1.80**	**1.71**	**1.64**	**1.60**	**1.57**	**1.54**	**1.53**	**1.51**	**1.49**	**1.48**	**1.47**	**1.46**	**1.46**	**1.44**	**1.44**
30	6.23	3.34	2.62	*2.29*	**2.11**	**1.92**	**1.81**	**1.74**	**1.69**	**1.65**	**1.63**	**1.61**	**1.60**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**	**1.51**
40	6.87	3.57	2.76	2.41	*2.21*	**2.00**	**1.89**	**1.80**	**1.75**	**1.72**	**1.69**	**1.67**	**1.65**	**1.63**	**1.61**	**1.60**	**1.59**	**1.59**	**1.57**	**1.56**
50	7.42	3.75	2.87	2.50	*2.29*	**2.06**	**1.94**	**1.86**	**1.80**	**1.76**	**1.73**	**1.71**	**1.70**	**1.67**	**1.66**	**1.64**	**1.63**	**1.63**	**1.61**	**1.60**
60	7.89	3.91	2.97	2.57	*2.35*	**2.11**	**1.99**	**1.90**	**1.84**	**1.80**	**1.77**	**1.75**	**1.73**	**1.71**	**1.69**	**1.68**	**1.67**	**1.66**	**1.64**	**1.64**
75	8.50	4.11	3.09	2.66	2.43	*2.18*	**2.04**	**1.95**	**1.89**	**1.85**	**1.82**	**1.79**	**1.78**	**1.75**	**1.73**	**1.72**	**1.71**	**1.70**	**1.68**	**1.67**
100	9.38	4.37	3.25	2.78	2.53	*2.26*	**2.12**	**2.01**	**1.95**	**1.91**	**1.87**	**1.85**	**1.83**	**1.80**	**1.78**	**1.77**	**1.76**	**1.75**	**1.73**	**1.72**
125	10.11	4.59	3.38	2.88	2.61	*2.32*	*2.17*	**2.07**	**2.00**	**1.95**	**1.92**	**1.89**	**1.87**	**1.84**	**1.82**	**1.81**	**1.80**	**1.79**	**1.77**	**1.76**
150	10.74	4.79	3.49	2.95	2.67	*2.37*	*2.22*	**2.11**	**2.04**	**1.99**	**1.95**	**1.93**	**1.91**	**1.88**	**1.86**	**1.84**	**1.83**	**1.82**	**1.80**	**1.79**
175	11.33	4.93	3.59	3.03	2.73	2.42	*2.26*	*2.14*	**2.07**	**2.02**	**1.98**	**1.96**	**1.93**	**1.90**	**1.88**	**1.87**	**1.86**	**1.84**	**1.83**	**1.82**
200	11.82	5.08	3.66	3.09	2.78	2.45	*2.29*	*2.17*	**2.10**	**2.04**	**2.01**	**1.98**	**1.96**	**1.93**	**1.90**	**1.89**	**1.88**	**1.87**	**1.85**	**1.84**

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Table 19-11. κ-Multipliers for 1-of-3 Intrawell Prediction Limits on Observations (10 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.29**	**1.63**	**1.41**	**1.30**	**1.23**	**1.15**	**1.10**	**1.07**	**1.04**	**1.03**	**1.02**	**1.01**	**1.00**	**0.99**	**0.98**	**0.98**	**0.97**	**0.97**	**0.96**	**0.96**
2	2.99	**2.00**	**1.69**	**1.54**	**1.45**	**1.35**	**1.29**	**1.25**	**1.22**	**1.20**	**1.19**	**1.17**	**1.17**	**1.15**	**1.14**	**1.14**	**1.13**	**1.13**	**1.12**	**1.11**
3	3.47	**2.24**	**1.87**	**1.69**	**1.58**	**1.46**	**1.40**	**1.35**	**1.32**	**1.30**	**1.28**	**1.27**	**1.26**	**1.24**	**1.23**	**1.22**	**1.22**	**1.21**	**1.21**	**1.20**
4	3.84	**2.41**	**1.99**	**1.79**	**1.68**	**1.55**	**1.47**	**1.42**	**1.39**	**1.36**	**1.34**	**1.33**	**1.32**	**1.30**	**1.29**	**1.28**	**1.28**	**1.27**	**1.26**	**1.26**
5	4.16	*2.55*	**2.09**	**1.87**	**1.75**	**1.61**	**1.53**	**1.47**	**1.44**	**1.41**	**1.39**	**1.38**	**1.37**	**1.35**	**1.34**	**1.33**	**1.32**	**1.32**	**1.31**	**1.30**
8	4.91	2.87	**2.31**	**2.05**	**1.90**	**1.74**	**1.65**	**1.59**	**1.55**	**1.52**	**1.50**	**1.48**	**1.47**	**1.45**	**1.44**	**1.43**	**1.42**	**1.41**	**1.40**	**1.39**
12	5.65	3.16	*2.50*	**2.20**	**2.04**	**1.85**	**1.76**	**1.68**	**1.64**	**1.61**	**1.58**	**1.57**	**1.55**	**1.53**	**1.52**	**1.51**	**1.50**	**1.49**	**1.48**	**1.47**
16	6.24	3.37	*2.64*	**2.32**	**2.13**	**1.94**	**1.83**	**1.75**	**1.70**	**1.67**	**1.64**	**1.62**	**1.61**	**1.59**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**
20	6.73	3.55	2.75	**2.40**	**2.21**	**2.00**	**1.89**	**1.80**	**1.75**	**1.72**	**1.69**	**1.67**	**1.65**	**1.63**	**1.61**	**1.60**	**1.59**	**1.59**	**1.57**	**1.56**
30	7.73	3.89	2.97	*2.57*	**2.35**	**2.11**	**1.99**	**1.90**	**1.84**	**1.80**	**1.77**	**1.75**	**1.73**	**1.71**	**1.69**	**1.68**	**1.67**	**1.66**	**1.64**	**1.63**
40	8.52	4.14	3.12	*2.69*	**2.45**	**2.19**	**2.06**	**1.96**	**1.90**	**1.86**	**1.83**	**1.81**	**1.79**	**1.76**	**1.74**	**1.73**	**1.72**	**1.71**	**1.70**	**1.68**
50	9.18	4.35	3.25	2.78	*2.53*	**2.26**	**2.12**	**2.01**	**1.95**	**1.91**	**1.87**	**1.85**	**1.83**	**1.80**	**1.78**	**1.77**	**1.76**	**1.75**	**1.73**	**1.72**
60	9.77	4.53	3.35	2.86	*2.59*	**2.31**	**2.16**	**2.06**	**1.99**	**1.94**	**1.91**	**1.89**	**1.87**	**1.84**	**1.82**	**1.80**	**1.79**	**1.78**	**1.76**	**1.75**
75	10.55	4.75	3.48	2.95	*2.67*	**2.37**	**2.22**	**2.11**	**2.04**	**1.99**	**1.95**	**1.93**	**1.91**	**1.88**	**1.86**	**1.84**	**1.83**	**1.82**	**1.80**	**1.79**
100	11.62	5.05	3.66	3.08	2.78	*2.46*	**2.29**	**2.17**	**2.10**	**2.05**	**2.01**	**1.98**	**1.96**	**1.93**	**1.91**	**1.89**	**1.88**	**1.87**	**1.85**	**1.84**
125	12.50	5.30	3.80	3.19	2.86	*2.52*	**2.35**	**2.22**	**2.15**	**2.09**	**2.05**	**2.03**	**2.00**	**1.97**	**1.95**	**1.93**	**1.92**	**1.90**	**1.89**	**1.87**
150	13.28	5.52	3.91	3.27	2.93	*2.58*	**2.39**	**2.26**	**2.19**	**2.13**	**2.09**	**2.06**	**2.04**	**2.00**	**1.98**	**1.96**	**1.95**	**1.93**	**1.92**	**1.90**
175	13.96	5.69	4.00	3.34	2.98	*2.62*	**2.44**	**2.30**	**2.22**	**2.16**	**2.12**	**2.09**	**2.06**	**2.03**	**2.00**	**1.98**	**1.97**	**1.96**	**1.94**	**1.93**
200	14.65	5.86	4.10	3.41	3.04	*2.66*	*2.47*	**2.33**	**2.25**	**2.19**	**2.14**	**2.11**	**2.09**	**2.05**	**2.03**	**2.01**	**2.00**	**1.98**	**1.96**	**1.95**

Table 19-11. κ-Multipliers for 1-of-3 Intrawell Prediction Limits on Observations (10 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	2.87	**1.97**	**1.68**	**1.53**	**1.45**	**1.34**	**1.29**	**1.25**	**1.22**	**1.20**	**1.18**	**1.17**	**1.16**	**1.15**	**1.14**	**1.14**	**1.13**	**1.13**	**1.12**	**1.11**
2	3.70	**2.38**	**1.98**	**1.78**	**1.67**	**1.54**	**1.47**	**1.42**	**1.39**	**1.36**	**1.34**	**1.33**	**1.32**	**1.30**	**1.29**	**1.28**	**1.28**	**1.27**	**1.26**	**1.26**
3	4.28	**2.64**	**2.16**	**1.93**	**1.80**	**1.66**	**1.58**	**1.52**	**1.48**	**1.45**	**1.43**	**1.42**	**1.41**	**1.39**	**1.38**	**1.37**	**1.36**	**1.36**	**1.35**	**1.34**
4	4.74	*2.83*	**2.29**	**2.04**	**1.90**	**1.74**	**1.65**	**1.59**	**1.55**	**1.52**	**1.50**	**1.48**	**1.47**	**1.45**	**1.44**	**1.43**	**1.42**	**1.41**	**1.40**	**1.39**
5	5.12	2.99	**2.40**	**2.13**	**1.97**	**1.80**	**1.71**	**1.64**	**1.60**	**1.57**	**1.54**	**1.53**	**1.51**	**1.49**	**1.48**	**1.47**	**1.46**	**1.46**	**1.44**	**1.44**
8	6.02	3.34	**2.63**	**2.31**	**2.13**	**1.93**	**1.83**	**1.75**	**1.70**	**1.67**	**1.64**	**1.62**	**1.61**	**1.59**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**
12	6.92	3.66	*2.84*	**2.47**	**2.27**	**2.05**	**1.93**	**1.85**	**1.79**	**1.75**	**1.73**	**1.71**	**1.69**	**1.67**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**
16	7.63	3.90	2.99	**2.59**	**2.37**	**2.13**	**2.00**	**1.91**	**1.85**	**1.81**	**1.78**	**1.76**	**1.75**	**1.72**	**1.70**	**1.69**	**1.68**	**1.67**	**1.66**	**1.65**
20	8.23	4.10	3.11	**2.68**	**2.44**	**2.19**	**2.06**	**1.96**	**1.90**	**1.86**	**1.83**	**1.81**	**1.79**	**1.76**	**1.74**	**1.73**	**1.72**	**1.71**	**1.69**	**1.68**
30	9.44	4.49	3.34	*2.85*	**2.59**	**2.31**	**2.16**	**2.06**	**1.99**	**1.94**	**1.91**	**1.89**	**1.87**	**1.84**	**1.82**	**1.80**	**1.79**	**1.78**	**1.76**	**1.75**
40	10.40	4.77	3.51	*2.98*	**2.69**	**2.39**	**2.23**	**2.12**	**2.05**	**2.00**	**1.97**	**1.94**	**1.92**	**1.89**	**1.87**	**1.85**	**1.84**	**1.83**	**1.81**	**1.80**
50	11.21	5.00	3.64	3.08	*2.77*	**2.46**	**2.29**	**2.17**	**2.10**	**2.05**	**2.01**	**1.98**	**1.96**	**1.93**	**1.91**	**1.89**	**1.88**	**1.87**	**1.85**	**1.84**
60	11.91	5.21	3.75	3.16	*2.84*	**2.51**	**2.34**	**2.21**	**2.14**	**2.08**	**2.05**	**2.02**	**1.99**	**1.96**	**1.94**	**1.92**	**1.91**	**1.90**	**1.88**	**1.87**
75	12.84	5.46	3.89	3.26	*2.92*	**2.57**	**2.39**	**2.26**	**2.18**	**2.13**	**2.09**	**2.06**	**2.04**	**2.00**	**1.98**	**1.96**	**1.95**	**1.93**	**1.92**	**1.90**
100	14.16	5.80	4.09	3.40	*3.03*	**2.66**	**2.47**	**2.33**	**2.24**	**2.19**	**2.15**	**2.11**	**2.09**	**2.05**	**2.03**	**2.01**	**1.99**	**1.98**	**1.96**	**1.95**
125	15.23	6.08	4.24	3.50	3.12	**2.72**	**2.52**	**2.38**	**2.29**	**2.23**	**2.19**	**2.15**	**2.13**	**2.09**	**2.06**	**2.04**	**2.03**	**2.02**	**2.00**	**1.98**
150	16.21	6.32	4.37	3.59	3.19	*2.78*	**2.57**	**2.42**	**2.33**	**2.26**	**2.22**	**2.19**	**2.16**	**2.12**	**2.09**	**2.07**	**2.06**	**2.05**	**2.02**	**2.01**
175	17.09	6.52	4.47	3.67	3.25	*2.82*	**2.61**	**2.45**	**2.36**	**2.29**	**2.25**	**2.22**	**2.19**	**2.15**	**2.12**	**2.10**	**2.08**	**2.07**	**2.05**	**2.03**
200	17.77	6.69	4.57	3.74	3.31	*2.86*	**2.64**	**2.48**	**2.39**	**2.33**	**2.28**	**2.24**	**2.21**	**2.17**	**2.14**	**2.12**	**2.11**	**2.09**	**2.07**	**2.05**

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Table 19-11. κ-Multipliers for 1-of-3 Intrawell Prediction Limits on Observations (20 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	2.35	**1.65**	**1.42**	**1.30**	**1.23**	**1.15**	**1.10**	**1.07**	**1.05**	**1.03**	**1.02**	**1.01**	**1.00**	**0.99**	**0.98**	**0.98**	**0.97**	**0.97**	**0.96**	**0.96**
2	3.06	**2.02**	**1.70**	**1.55**	**1.45**	**1.35**	**1.29**	**1.25**	**1.22**	**1.20**	**1.19**	**1.17**	**1.17**	**1.15**	**1.14**	**1.14**	**1.13**	**1.13**	**1.12**	**1.11**
3	3.55	*2.26*	**1.87**	**1.69**	**1.59**	**1.47**	**1.40**	**1.35**	**1.32**	**1.30**	**1.28**	**1.27**	**1.26**	**1.24**	**1.23**	**1.22**	**1.22**	**1.21**	**1.21**	**1.20**
4	3.93	2.43	**2.00**	**1.80**	**1.68**	**1.55**	**1.47**	**1.42**	**1.39**	**1.36**	**1.34**	**1.33**	**1.32**	**1.30**	**1.29**	**1.29**	**1.28**	**1.27**	**1.26**	**1.26**
5	4.25	2.57	**2.10**	**1.88**	**1.75**	**1.61**	**1.53**	**1.48**	**1.44**	**1.41**	**1.39**	**1.38**	**1.37**	**1.35**	**1.34**	**1.33**	**1.32**	**1.32**	**1.31**	**1.30**
8	5.02	2.88	*2.31*	**2.05**	**1.90**	**1.74**	**1.65**	**1.59**	**1.55**	**1.52**	**1.50**	**1.48**	**1.47**	**1.45**	**1.44**	**1.43**	**1.42**	**1.41**	**1.40**	**1.39**
12	5.77	3.17	2.51	*2.21*	**2.04**	**1.86**	**1.76**	**1.68**	**1.64**	**1.61**	**1.58**	**1.57**	**1.55**	**1.53**	**1.52**	**1.51**	**1.50**	**1.49**	**1.48**	**1.47**
16	6.37	3.39	2.65	*2.32*	*2.14*	**1.94**	**1.83**	**1.75**	**1.70**	**1.67**	**1.64**	**1.62**	**1.61**	**1.59**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**
20	6.87	3.57	2.76	2.41	*2.21*	**2.00**	**1.89**	**1.80**	**1.75**	**1.72**	**1.69**	**1.67**	**1.65**	**1.63**	**1.61**	**1.60**	**1.59**	**1.59**	**1.57**	**1.56**
30	7.89	3.91	2.97	2.57	*2.35*	**2.11**	**1.99**	**1.90**	**1.84**	**1.80**	**1.77**	**1.75**	**1.73**	**1.71**	**1.69**	**1.68**	**1.67**	**1.66**	**1.64**	**1.64**
40	8.69	4.17	3.13	2.69	2.45	*2.19*	**2.06**	**1.96**	**1.90**	**1.86**	**1.83**	**1.81**	**1.79**	**1.76**	**1.74**	**1.73**	**1.72**	**1.71**	**1.69**	**1.68**
50	9.38	4.38	3.25	2.78	2.53	*2.26*	**2.12**	**2.01**	**1.95**	**1.91**	**1.87**	**1.85**	**1.83**	**1.80**	**1.78**	**1.77**	**1.76**	**1.75**	**1.73**	**1.72**
60	9.97	4.55	3.36	2.86	2.59	*2.31*	*2.16*	**2.06**	**1.99**	**1.94**	**1.91**	**1.89**	**1.87**	**1.84**	**1.82**	**1.80**	**1.79**	**1.78**	**1.76**	**1.75**
75	10.74	4.78	3.49	2.96	2.67	*2.37*	*2.22*	**2.11**	**2.04**	**1.99**	**1.95**	**1.93**	**1.91**	**1.88**	**1.86**	**1.84**	**1.83**	**1.82**	**1.80**	**1.79**
100	11.84	5.08	3.66	3.09	2.78	2.46	*2.29*	*2.17*	**2.10**	**2.05**	**2.01**	**1.98**	**1.96**	**1.93**	**1.91**	**1.89**	**1.88**	**1.87**	**1.85**	**1.84**
125	12.74	5.32	3.80	3.19	2.86	2.52	*2.35*	*2.22*	*2.15*	**2.09**	**2.05**	**2.02**	**2.00**	**1.97**	**1.95**	**1.93**	**1.91**	**1.90**	**1.89**	**1.87**
150	13.57	5.54	3.92	3.27	2.93	2.58	*2.39*	*2.26*	*2.18*	*2.13*	**2.09**	**2.06**	**2.04**	**2.00**	**1.98**	**1.96**	**1.95**	**1.93**	**1.92**	**1.90**
175	14.26	5.71	4.02	3.34	2.98	2.62	2.43	*2.30*	*2.22*	*2.16*	*2.12*	**2.09**	**2.06**	**2.03**	**2.00**	**1.98**	**1.97**	**1.96**	**1.94**	**1.93**
200	14.94	5.88	4.11	3.41	3.04	2.66	2.47	*2.33*	*2.24*	*2.19*	*2.15*	*2.11*	**2.09**	**2.05**	**2.03**	**2.01**	**1.99**	**1.98**	**1.96**	**1.95**

Table 19-11. κ-Multipliers for 1-of-3 Intrawell Prediction Limits on Observations (20 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	2.99	**2.00**	**1.69**	**1.54**	**1.45**	**1.35**	**1.29**	**1.25**	**1.22**	**1.20**	**1.19**	**1.17**	**1.17**	**1.15**	**1.14**	**1.14**	**1.13**	**1.13**	**1.12**	**1.11**
2	3.84	**2.41**	**1.99**	**1.79**	**1.68**	**1.55**	**1.47**	**1.42**	**1.39**	**1.36**	**1.34**	**1.33**	**1.32**	**1.30**	**1.29**	**1.28**	**1.28**	**1.27**	**1.26**	**1.26**
3	4.44	2.67	**2.17**	**1.94**	**1.81**	**1.66**	**1.58**	**1.52**	**1.48**	**1.45**	**1.43**	**1.42**	**1.41**	**1.39**	**1.38**	**1.37**	**1.36**	**1.36**	**1.35**	**1.34**
4	4.91	2.87	**2.31**	**2.05**	**1.90**	**1.74**	**1.65**	**1.59**	**1.55**	**1.52**	**1.50**	**1.48**	**1.47**	**1.45**	**1.44**	**1.43**	**1.42**	**1.41**	**1.40**	**1.39**
5	5.30	3.02	**2.41**	**2.13**	**1.98**	**1.80**	**1.71**	**1.64**	**1.60**	**1.57**	**1.54**	**1.53**	**1.51**	**1.49**	**1.48**	**1.47**	**1.46**	**1.46**	**1.44**	**1.44**
8	6.24	3.37	*2.64*	**2.32**	**2.13**	**1.94**	**1.83**	**1.75**	**1.70**	**1.67**	**1.64**	**1.62**	**1.61**	**1.59**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**
12	7.16	3.70	2.85	*2.48*	**2.27**	**2.05**	**1.93**	**1.85**	**1.79**	**1.75**	**1.73**	**1.71**	**1.69**	**1.67**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**
16	7.90	3.94	3.00	*2.59*	**2.37**	**2.13**	**2.00**	**1.91**	**1.85**	**1.81**	**1.79**	**1.76**	**1.75**	**1.72**	**1.70**	**1.69**	**1.68**	**1.67**	**1.66**	**1.65**
20	8.52	4.14	3.12	*2.69*	*2.45*	**2.19**	**2.06**	**1.96**	**1.90**	**1.86**	**1.83**	**1.81**	**1.79**	**1.76**	**1.74**	**1.73**	**1.72**	**1.71**	**1.69**	**1.68**
30	9.77	4.53	3.35	2.86	*2.59*	**2.31**	**2.16**	**2.06**	**1.99**	**1.94**	**1.91**	**1.89**	**1.87**	**1.84**	**1.82**	**1.80**	**1.79**	**1.78**	**1.76**	**1.75**
40	10.77	4.82	3.52	2.98	*2.69*	**2.39**	**2.24**	**2.12**	**2.05**	**2.00**	**1.97**	**1.94**	**1.92**	**1.89**	**1.87**	**1.85**	**1.84**	**1.83**	**1.81**	**1.80**
50	11.60	5.05	3.66	3.08	2.78	*2.46*	**2.29**	**2.17**	**2.10**	**2.05**	**2.01**	**1.98**	**1.96**	**1.93**	**1.91**	**1.89**	**1.88**	**1.87**	**1.85**	**1.84**
60	12.33	5.26	3.77	3.16	2.84	*2.51*	**2.34**	**2.21**	**2.14**	**2.08**	**2.05**	**2.02**	**2.00**	**1.96**	**1.94**	**1.92**	**1.91**	**1.90**	**1.88**	**1.87**
75	13.28	5.51	3.91	3.27	2.93	*2.57*	**2.39**	**2.26**	**2.18**	**2.13**	**2.09**	**2.06**	**2.04**	**2.00**	**1.98**	**1.96**	**1.95**	**1.93**	**1.92**	**1.90**
100	14.65	5.85	4.10	3.40	3.04	*2.66*	*2.47*	**2.33**	**2.24**	**2.19**	**2.14**	**2.11**	**2.09**	**2.05**	**2.03**	**2.01**	**1.99**	**1.98**	**1.96**	**1.95**
125	15.77	6.14	4.25	3.51	3.12	*2.73*	*2.52*	**2.38**	**2.29**	**2.23**	**2.19**	**2.15**	**2.13**	**2.09**	**2.06**	**2.04**	**2.03**	**2.02**	**1.99**	**1.98**
150	16.80	6.37	4.38	3.60	3.19	2.78	*2.57*	**2.42**	**2.33**	**2.27**	**2.22**	**2.19**	**2.16**	**2.12**	**2.09**	**2.07**	**2.06**	**2.05**	**2.03**	**2.01**
175	17.68	6.58	4.49	3.67	3.25	2.83	*2.61*	*2.46*	**2.36**	**2.30**	**2.25**	**2.22**	**2.19**	**2.15**	**2.12**	**2.10**	**2.08**	**2.07**	**2.05**	**2.03**
200	18.46	6.76	4.58	3.74	3.31	2.86	*2.64*	*2.48*	**2.39**	**2.32**	**2.28**	**2.24**	**2.21**	**2.17**	**2.14**	**2.12**	**2.10**	**2.09**	**2.07**	**2.05**

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Table 19-11. κ-Multipliers for 1-of-3 Intrawell Prediction Limits on Observations (20 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.70	**2.38**	**1.98**	**1.78**	**1.67**	**1.54**	**1.47**	**1.42**	**1.39**	**1.36**	**1.34**	**1.33**	**1.32**	**1.30**	**1.29**	**1.28**	**1.28**	**1.27**	**1.26**	**1.26**
2	4.74	*2.83*	**2.29**	**2.04**	**1.90**	**1.74**	**1.65**	**1.59**	**1.55**	**1.52**	**1.50**	**1.48**	**1.47**	**1.45**	**1.44**	**1.43**	**1.42**	**1.41**	**1.40**	**1.39**
3	5.45	3.12	**2.49**	**2.20**	**2.03**	**1.85**	**1.76**	**1.68**	**1.64**	**1.61**	**1.58**	**1.56**	**1.55**	**1.53**	**1.52**	**1.50**	**1.50**	**1.49**	**1.48**	**1.47**
4	6.02	3.34	**2.63**	**2.31**	**2.13**	**1.93**	**1.83**	**1.75**	**1.70**	**1.67**	**1.64**	**1.62**	**1.61**	**1.59**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**
5	6.50	3.51	**2.74**	**2.40**	**2.21**	**2.00**	**1.89**	**1.80**	**1.75**	**1.72**	**1.69**	**1.67**	**1.65**	**1.63**	**1.61**	**1.60**	**1.59**	**1.59**	**1.57**	**1.56**
8	7.63	3.91	2.99	**2.59**	**2.37**	**2.13**	**2.00**	**1.91**	**1.85**	**1.81**	**1.78**	**1.76**	**1.75**	**1.72**	**1.70**	**1.69**	**1.68**	**1.67**	**1.66**	**1.65**
12	8.76	4.27	3.21	**2.76**	**2.51**	**2.24**	**2.11**	**2.00**	**1.94**	**1.90**	**1.87**	**1.84**	**1.82**	**1.80**	**1.78**	**1.76**	**1.75**	**1.74**	**1.73**	**1.72**
16	9.65	4.55	3.38	*2.88*	**2.61**	**2.33**	**2.18**	**2.07**	**2.00**	**1.96**	**1.92**	**1.90**	**1.88**	**1.85**	**1.83**	**1.81**	**1.80**	**1.79**	**1.78**	**1.76**
20	10.40	4.77	3.51	*2.98*	**2.69**	**2.39**	**2.23**	**2.12**	**2.05**	**2.00**	**1.97**	**1.94**	**1.92**	**1.89**	**1.87**	**1.85**	**1.84**	**1.83**	**1.81**	**1.80**
30	11.93	5.21	3.76	3.16	*2.84*	**2.51**	**2.34**	**2.21**	**2.14**	**2.08**	**2.05**	**2.02**	**1.99**	**1.96**	**1.94**	**1.92**	**1.91**	**1.90**	**1.88**	**1.87**
40	13.13	5.54	3.94	3.29	*2.95*	**2.59**	**2.41**	**2.28**	**2.20**	**2.14**	**2.10**	**2.07**	**2.05**	**2.01**	**1.99**	**1.97**	**1.96**	**1.95**	**1.93**	**1.91**
50	14.16	5.80	4.09	3.40	*3.03*	**2.66**	**2.47**	**2.33**	**2.24**	**2.19**	**2.14**	**2.11**	**2.09**	**2.05**	**2.03**	**2.01**	**1.99**	**1.98**	**1.96**	**1.95**
60	15.04	6.03	4.21	3.49	3.10	**2.71**	**2.51**	**2.37**	**2.28**	**2.22**	**2.18**	**2.15**	**2.12**	**2.08**	**2.06**	**2.04**	**2.02**	**2.01**	**1.99**	**1.98**
75	16.21	6.32	4.36	3.59	3.19	*2.78*	**2.57**	**2.42**	**2.33**	**2.27**	**2.22**	**2.19**	**2.16**	**2.12**	**2.09**	**2.07**	**2.06**	**2.04**	**2.02**	**2.00**
100	17.87	6.70	4.57	3.74	3.30	*2.86*	**2.64**	**2.49**	**2.39**	**2.32**	**2.28**	**2.24**	**2.21**	**2.17**	**2.14**	**2.12**	**2.10**	**2.09**	**2.06**	**2.04**
125	19.24	7.03	4.74	3.85	3.39	*2.93*	**2.70**	**2.54**	**2.44**	**2.37**	**2.32**	**2.28**	**2.25**	**2.21**	**2.18**	**2.16**	**2.14**	**2.13**	**2.10**	**2.09**
150	20.41	7.30	4.87	3.94	3.47	*2.98*	**2.75**	**2.58**	**2.47**	**2.40**	**2.35**	**2.31**	**2.28**	**2.24**	**2.21**	**2.19**	**2.17**	**2.15**	**2.13**	**2.12**
175	21.48	7.53	4.99	4.03	3.53	*3.03*	*2.79*	**2.61**	**2.51**	**2.43**	**2.38**	**2.34**	**2.31**	**2.27**	**2.24**	**2.21**	**2.19**	**2.18**	**2.16**	**2.14**
200	22.46	7.74	5.09	4.10	3.58	*3.08*	*2.82*	**2.64**	**2.53**	**2.46**	**2.40**	**2.37**	**2.33**	**2.29**	**2.26**	**2.23**	**2.22**	**2.20**	**2.18**	**2.16**

Table 19-11. κ-Multipliers for 1-of-3 Intrawell Prediction Limits on Observations (40 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.06	**2.02**	**1.70**	**1.55**	**1.45**	**1.35**	**1.29**	**1.25**	**1.22**	**1.20**	**1.19**	**1.17**	**1.17**	**1.15**	**1.14**	**1.14**	**1.13**	**1.13**	**1.12**	**1.11**
2	3.93	2.43	**2.00**	**1.80**	**1.68**	**1.55**	**1.47**	**1.42**	**1.39**	**1.36**	**1.34**	**1.33**	**1.32**	**1.30**	**1.29**	**1.29**	**1.28**	**1.27**	**1.26**	**1.26**
3	4.54	2.69	*2.18*	**1.95**	**1.81**	**1.66**	**1.58**	**1.52**	**1.48**	**1.45**	**1.43**	**1.42**	**1.41**	**1.39**	**1.38**	**1.37**	**1.36**	**1.36**	**1.35**	**1.34**
4	5.02	2.88	*2.31*	**2.05**	**1.90**	**1.74**	**1.65**	**1.59**	**1.55**	**1.52**	**1.50**	**1.48**	**1.47**	**1.45**	**1.44**	**1.43**	**1.42**	**1.41**	**1.40**	**1.39**
5	5.42	3.04	2.42	**2.14**	**1.98**	**1.80**	**1.71**	**1.64**	**1.60**	**1.57**	**1.54**	**1.53**	**1.51**	**1.49**	**1.48**	**1.47**	**1.46**	**1.46**	**1.44**	**1.44**
8	6.37	3.39	2.65	*2.32*	*2.14*	**1.94**	**1.83**	**1.75**	**1.70**	**1.67**	**1.64**	**1.62**	**1.61**	**1.59**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**
12	7.31	3.72	2.86	2.48	*2.27*	**2.05**	**1.93**	**1.85**	**1.79**	**1.75**	**1.73**	**1.71**	**1.69**	**1.67**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**
16	8.06	3.97	3.01	2.60	*2.37*	*2.13*	**2.01**	**1.91**	**1.85**	**1.81**	**1.79**	**1.76**	**1.75**	**1.72**	**1.70**	**1.69**	**1.68**	**1.67**	**1.66**	**1.65**
20	8.69	4.17	3.13	2.69	2.45	*2.19*	**2.06**	**1.96**	**1.90**	**1.86**	**1.83**	**1.81**	**1.79**	**1.76**	**1.74**	**1.73**	**1.72**	**1.71**	**1.69**	**1.68**
30	9.97	4.55	3.36	2.86	2.59	*2.31*	*2.16*	**2.06**	**1.99**	**1.94**	**1.91**	**1.89**	**1.87**	**1.84**	**1.82**	**1.80**	**1.79**	**1.78**	**1.76**	**1.75**
40	10.98	4.84	3.53	2.99	2.70	*2.39*	*2.24*	*2.12*	**2.05**	**2.00**	**1.97**	**1.94**	**1.92**	**1.89**	**1.87**	**1.85**	**1.84**	**1.83**	**1.81**	**1.80**
50	11.84	5.08	3.66	3.09	2.78	2.46	*2.29*	*2.17*	**2.10**	**2.05**	**2.01**	**1.98**	**1.96**	**1.93**	**1.91**	**1.89**	**1.88**	**1.87**	**1.85**	**1.84**
60	12.58	5.28	3.77	3.17	2.84	2.51	*2.34*	*2.21*	*2.14*	**2.08**	**2.05**	**2.02**	**1.99**	**1.96**	**1.94**	**1.92**	**1.91**	**1.90**	**1.88**	**1.87**
75	13.55	5.54	3.92	3.27	2.93	2.57	*2.39*	*2.26*	*2.18*	*2.13*	**2.09**	**2.06**	**2.04**	**2.00**	**1.98**	**1.96**	**1.95**	**1.93**	**1.92**	**1.90**
100	14.92	5.88	4.11	3.41	3.04	2.66	2.47	*2.33*	*2.24*	*2.19*	*2.14*	*2.11*	**2.09**	**2.05**	**2.03**	**2.01**	**1.99**	**1.98**	**1.96**	**1.94**
125	16.09	6.17	4.26	3.52	3.12	2.72	2.52	*2.38*	*2.29*	*2.23*	*2.19*	*2.15*	*2.13*	**2.09**	**2.06**	**2.04**	**2.03**	**2.02**	**1.99**	**1.98**
150	17.11	6.41	4.38	3.60	3.19	2.78	2.57	*2.42*	*2.33*	*2.27*	*2.22*	*2.19*	*2.16*	*2.12*	**2.09**	**2.07**	**2.06**	**2.05**	**2.03**	**2.01**
175	17.97	6.60	4.49	3.67	3.25	2.82	2.61	2.46	*2.36*	*2.29*	*2.25*	*2.22*	*2.19*	*2.15*	*2.12*	**2.10**	**2.08**	**2.07**	**2.05**	**2.04**
200	18.75	6.80	4.59	3.75	3.30	2.86	2.65	2.49	*2.39*	*2.32*	*2.28*	*2.24*	*2.21*	*2.17*	*2.14*	*2.12*	**2.10**	**2.09**	**2.09**	**2.06**

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Table 19-11. κ-Multipliers for 1-of-3 Intrawell Prediction Limits on Observations (40 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.84	**2.41**	**1.99**	**1.79**	**1.68**	**1.55**	**1.47**	**1.42**	**1.39**	**1.36**	**1.34**	**1.33**	**1.32**	**1.30**	**1.29**	**1.28**	**1.28**	**1.27**	**1.26**	**1.26**
2	4.91	2.87	**2.31**	**2.05**	**1.90**	**1.74**	**1.65**	**1.59**	**1.55**	**1.52**	**1.50**	**1.48**	**1.47**	**1.45**	**1.44**	**1.43**	**1.42**	**1.41**	**1.40**	**1.39**
3	5.65	3.16	*2.50*	**2.20**	**2.04**	**1.85**	**1.76**	**1.68**	**1.64**	**1.61**	**1.58**	**1.57**	**1.55**	**1.53**	**1.52**	**1.51**	**1.50**	**1.49**	**1.48**	**1.47**
4	6.24	3.37	*2.64*	**2.32**	**2.13**	**1.94**	**1.83**	**1.75**	**1.70**	**1.67**	**1.64**	**1.62**	**1.61**	**1.59**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**
5	6.73	3.55	2.75	**2.40**	**2.21**	**2.00**	**1.89**	**1.80**	**1.75**	**1.72**	**1.69**	**1.67**	**1.65**	**1.63**	**1.61**	**1.60**	**1.59**	**1.59**	**1.57**	**1.56**
8	7.90	3.94	3.00	*2.59*	**2.37**	**2.13**	**2.00**	**1.91**	**1.85**	**1.81**	**1.79**	**1.76**	**1.75**	**1.72**	**1.70**	**1.69**	**1.68**	**1.67**	**1.66**	**1.65**
12	9.06	4.31	3.22	2.76	*2.51*	**2.25**	**2.11**	**2.01**	**1.94**	**1.90**	**1.87**	**1.84**	**1.82**	**1.80**	**1.78**	**1.76**	**1.75**	**1.74**	**1.73**	**1.72**
16	9.98	4.59	3.39	2.89	*2.61*	**2.33**	**2.18**	**2.07**	**2.00**	**1.96**	**1.92**	**1.90**	**1.88**	**1.85**	**1.83**	**1.81**	**1.80**	**1.79**	**1.78**	**1.76**
20	10.76	4.82	3.52	2.98	*2.69*	**2.39**	**2.24**	**2.12**	**2.05**	**2.00**	**1.97**	**1.94**	**1.92**	**1.89**	**1.87**	**1.85**	**1.84**	**1.83**	**1.81**	**1.80**
30	12.33	5.25	3.77	3.17	2.84	*2.51*	**2.34**	**2.21**	**2.14**	**2.08**	**2.05**	**2.02**	**1.99**	**1.96**	**1.94**	**1.92**	**1.91**	**1.90**	**1.88**	**1.87**
40	13.59	5.59	3.95	3.30	2.95	*2.59*	**2.41**	**2.28**	**2.20**	**2.14**	**2.10**	**2.07**	**2.05**	**2.01**	**1.99**	**1.97**	**1.96**	**1.95**	**1.93**	**1.91**
50	14.65	5.85	4.10	3.40	3.03	*2.66*	*2.47*	**2.33**	**2.24**	**2.19**	**2.14**	**2.11**	**2.09**	**2.05**	**2.03**	**2.01**	**1.99**	**1.98**	**1.96**	**1.95**
60	15.55	6.08	4.22	3.49	3.11	*2.71*	*2.51*	**2.37**	**2.28**	**2.22**	**2.18**	**2.15**	**2.12**	**2.08**	**2.06**	**2.04**	**2.02**	**2.01**	**1.99**	**1.97**
75	16.80	6.37	4.38	3.60	3.19	2.78	*2.57*	**2.42**	**2.33**	**2.27**	**2.22**	**2.19**	**2.16**	**2.12**	**2.09**	**2.07**	**2.06**	**2.04**	**2.02**	**2.00**
100	18.44	6.76	4.58	3.74	3.31	2.87	*2.64*	*2.49*	**2.39**	**2.32**	**2.28**	**2.24**	**2.21**	**2.17**	**2.14**	**2.12**	**2.10**	**2.09**	**2.06**	**2.04**
125	19.84	7.09	4.75	3.86	3.40	2.93	*2.70*	*2.53*	**2.44**	**2.37**	**2.32**	**2.28**	**2.25**	**2.21**	**2.18**	**2.16**	**2.14**	**2.12**	**2.10**	**2.08**
150	21.09	7.34	4.88	3.95	3.47	2.99	*2.74*	*2.58*	*2.47*	**2.40**	**2.35**	**2.31**	**2.29**	**2.24**	**2.21**	**2.19**	**2.17**	**2.16**	**2.13**	**2.12**
175	22.19	7.58	5.00	4.03	3.54	3.04	*2.79*	*2.61*	*2.50*	**2.43**	**2.38**	**2.34**	**2.31**	**2.27**	**2.24**	**2.21**	**2.19**	**2.18**	**2.16**	**2.14**
200	23.28	7.81	5.12	4.10	3.59	3.08	2.82	*2.64*	*2.53*	*2.46*	**2.41**	**2.36**	**2.33**	**2.29**	**2.26**	**2.24**	**2.22**	**2.20**	**2.18**	**2.16**

Table 19-11. κ-Multipliers for 1-of-3 Intrawell Prediction Limits on Observations (40 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	4.74	*2.83*	**2.29**	**2.04**	**1.90**	**1.74**	**1.65**	**1.59**	**1.55**	**1.52**	**1.50**	**1.48**	**1.47**	**1.45**	**1.44**	**1.43**	**1.42**	**1.41**	**1.40**	**1.39**
2	6.02	3.34	**2.63**	**2.31**	**2.13**	**1.93**	**1.83**	**1.75**	**1.70**	**1.67**	**1.64**	**1.62**	**1.61**	**1.59**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**
3	6.92	3.66	*2.84*	**2.47**	**2.27**	**2.05**	**1.93**	**1.85**	**1.79**	**1.75**	**1.73**	**1.71**	**1.69**	**1.67**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**
4	7.63	3.91	2.99	**2.59**	**2.37**	**2.13**	**2.00**	**1.91**	**1.85**	**1.81**	**1.78**	**1.76**	**1.75**	**1.72**	**1.70**	**1.69**	**1.68**	**1.67**	**1.66**	**1.65**
5	8.23	4.10	3.11	**2.68**	**2.44**	**2.19**	**2.06**	**1.96**	**1.90**	**1.86**	**1.83**	**1.81**	**1.79**	**1.76**	**1.74**	**1.73**	**1.72**	**1.71**	**1.69**	**1.68**
8	9.65	4.55	3.38	*2.88*	**2.61**	**2.33**	**2.18**	**2.07**	**2.00**	**1.96**	**1.92**	**1.90**	**1.88**	**1.85**	**1.83**	**1.81**	**1.80**	**1.79**	**1.78**	**1.76**
12	11.06	4.96	3.62	3.06	**2.76**	**2.44**	**2.28**	**2.16**	**2.09**	**2.04**	**2.00**	**1.98**	**1.95**	**1.92**	**1.90**	**1.88**	**1.87**	**1.86**	**1.84**	**1.83**
16	12.19	5.28	3.80	3.19	*2.86*	**2.53**	**2.35**	**2.23**	**2.15**	**2.10**	**2.06**	**2.03**	**2.01**	**1.97**	**1.95**	**1.93**	**1.92**	**1.91**	**1.89**	**1.88**
20	13.13	5.53	3.94	3.29	*2.95*	**2.59**	**2.41**	**2.28**	**2.20**	**2.14**	**2.10**	**2.07**	**2.05**	**2.01**	**1.99**	**1.97**	**1.96**	**1.95**	**1.93**	**1.91**
30	15.04	6.03	4.21	3.48	3.10	**2.71**	**2.51**	**2.37**	**2.28**	**2.22**	**2.18**	**2.15**	**2.12**	**2.08**	**2.06**	**2.04**	**2.02**	**2.01**	**1.99**	**1.98**
40	16.56	6.40	4.41	3.63	3.22	*2.80*	**2.59**	**2.44**	**2.34**	**2.28**	**2.23**	**2.20**	**2.17**	**2.13**	**2.10**	**2.08**	**2.07**	**2.05**	**2.03**	**2.01**
50	17.85	6.71	4.57	3.74	3.30	*2.86*	**2.64**	**2.49**	**2.39**	**2.32**	**2.28**	**2.24**	**2.21**	**2.17**	**2.14**	**2.12**	**2.10**	**2.09**	**2.06**	**2.04**
60	18.98	6.96	4.70	3.83	3.38	*2.92*	**2.69**	**2.53**	**2.43**	**2.36**	**2.31**	**2.27**	**2.24**	**2.20**	**2.17**	**2.15**	**2.13**	**2.12**	**2.10**	**2.08**
75	20.47	7.29	4.87	3.95	3.47	*2.99*	**2.75**	**2.58**	**2.47**	**2.40**	**2.35**	**2.31**	**2.28**	**2.24**	**2.21**	**2.19**	**2.17**	**2.16**	**2.13**	**2.12**
100	22.50	7.73	5.10	4.10	3.58	*3.08*	*2.82*	**2.64**	**2.53**	**2.46**	**2.40**	**2.37**	**2.33**	**2.29**	**2.26**	**2.23**	**2.22**	**2.20**	**2.18**	**2.16**
125	24.22	8.11	5.27	4.22	3.68	3.14	*2.88*	**2.69**	**2.58**	**2.50**	**2.45**	**2.41**	**2.37**	**2.33**	**2.29**	**2.27**	**2.25**	**2.24**	**2.21**	**2.19**
150	25.78	8.40	5.43	4.32	3.76	3.20	*2.92*	**2.73**	**2.62**	**2.54**	**2.48**	**2.44**	**2.40**	**2.36**	**2.32**	**2.30**	**2.28**	**2.26**	**2.24**	**2.22**
175	27.19	8.67	5.55	4.40	3.83	3.25	*2.97*	*2.77*	**2.65**	**2.57**	**2.51**	**2.47**	**2.43**	**2.38**	**2.35**	**2.32**	**2.31**	**2.29**	**2.26**	**2.24**
200	28.44	8.91	5.66	4.47	3.89	3.29	*3.00*	*2.80*	**2.68**	**2.59**	**2.53**	**2.49**	**2.46**	**2.41**	**2.37**	**2.35**	**2.33**	**2.31**	**2.28**	**2.26**

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Table 19-12. κ-Multipliers for 1-of-4 Intrawell Prediction Limits on Observations (1 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	0.06	-0.01	-0.04	-0.07	-0.08	-0.10	-0.11	-0.12	-0.13	-0.13	-0.13	-0.14	-0.14	-0.14	-0.14	-0.15	-0.15	-0.15	-0.15	-0.15
2	0.39	0.28	0.22	0.19	0.17	0.14	0.12	0.11	0.10	0.10	0.09	0.09	0.09	0.08	0.08	0.08	0.07	0.07	0.07	0.07
3	0.59	0.44	0.37	0.33	0.30	0.27	0.25	0.23	0.22	0.22	0.21	0.21	0.20	0.20	0.20	0.19	0.19	0.19	0.19	0.18
4	0.74	0.55	0.47	0.42	0.39	0.36	0.33	0.32	0.31	0.30	0.29	0.29	0.28	0.28	0.27	0.27	0.27	0.27	0.26	0.26
5	0.85	0.63	0.54	0.49	0.46	0.42	0.40	0.38	0.37	0.36	0.35	0.35	0.34	0.34	0.33	0.33	0.33	0.32	0.32	0.32
8	1.11	0.82	0.70	0.64	0.60	0.55	0.52	0.50	0.49	0.48	0.47	0.46	0.46	0.45	0.45	0.44	0.44	0.44	0.43	0.43
12	1.36	0.98	0.84	0.76	0.72	0.66	0.63	0.60	0.59	0.58	0.57	0.56	0.56	0.55	0.54	0.54	0.53	0.53	0.53	0.52
16	1.54	1.10	0.94	0.85	0.80	0.74	0.70	0.67	0.66	0.64	0.63	0.63	0.62	0.61	0.61	0.60	0.60	0.59	0.59	0.59
20	1.70	1.19	1.01	0.92	0.86	0.80	0.76	0.73	0.71	0.69	0.68	0.68	0.67	0.66	0.65	0.65	0.65	0.64	0.64	0.63
30	2.01	1.37	1.15	1.04	0.98	0.90	0.86	0.82	0.80	0.78	0.77	0.76	0.76	0.75	0.74	0.73	0.73	0.73	0.72	0.72
40	2.25	1.49	1.25	1.13	1.06	0.97	0.92	0.89	0.86	0.85	0.83	0.82	0.82	0.81	0.80	0.79	0.79	0.78	0.78	0.77
50	2.45	1.60	1.33	1.20	1.12	1.03	0.98	0.94	0.91	0.89	0.88	0.87	0.86	0.85	0.84	0.84	0.83	0.83	0.82	0.81
60	2.62	1.68	1.39	1.25	1.17	1.07	1.02	0.98	0.95	0.93	0.92	0.91	0.90	0.89	0.88	0.87	0.87	0.86	0.85	0.85
75	2.85	1.79	1.47	1.32	1.23	1.13	1.07	1.02	1.00	0.98	0.96	0.95	0.94	0.93	0.92	0.91	0.91	0.90	0.90	0.89
100	3.16	1.94	1.58	1.41	1.31	1.20	1.13	1.09	1.06	1.03	1.02	1.01	1.00	0.98	0.97	0.97	0.96	0.96	0.95	0.94
125	3.42	*2.05*	1.66	1.48	1.37	1.25	1.18	1.13	1.10	1.08	1.06	1.05	1.04	1.02	1.01	1.01	1.00	1.00	0.99	0.98
150	3.65	*2.15*	1.73	1.54	1.42	1.29	1.22	1.17	1.14	1.11	1.10	1.08	1.07	1.06	1.05	1.04	1.03	1.03	1.02	1.01
175	3.85	2.24	1.79	1.58	1.46	1.33	1.26	1.20	1.17	1.14	1.13	1.11	1.10	1.09	1.07	1.07	1.06	1.05	1.04	1.04
200	4.04	2.31	1.84	1.63	1.50	1.36	1.29	1.23	1.20	1.17	1.15	1.14	1.13	1.11	1.10	1.09	1.08	1.08	1.07	1.06

Table 19-12. κ-Multipliers for 1-of-4 Intrawell Prediction Limits on Observations (1 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	0.36	0.25	0.21	0.18	0.16	0.13	0.12	0.11	0.10	0.09	0.09	0.09	0.08	0.08	0.08	0.08	0.07	0.07	0.07	0.07
2	0.70	0.53	0.46	0.41	0.39	0.35	0.33	0.31	0.30	0.30	0.29	0.29	0.28	0.28	0.27	0.27	0.27	0.27	0.26	0.26
3	0.91	0.69	0.60	0.54	0.51	0.47	0.44	0.43	0.41	0.40	0.40	0.39	0.39	0.38	0.38	0.37	0.37	0.37	0.36	0.36
4	1.07	0.80	0.69	0.63	0.60	0.55	0.52	0.50	0.49	0.48	0.47	0.46	0.46	0.45	0.45	0.44	0.44	0.44	0.43	0.43
5	1.21	0.89	0.77	0.70	0.66	0.61	0.58	0.56	0.54	0.53	0.52	0.52	0.51	0.50	0.50	0.50	0.49	0.49	0.49	0.48
8	1.50	1.08	0.93	0.85	0.80	0.74	0.70	0.67	0.66	0.64	0.63	0.63	0.62	0.61	0.61	0.60	0.60	0.59	0.59	0.59
12	1.79	1.26	1.07	0.97	0.91	0.84	0.80	0.77	0.75	0.73	0.72	0.72	0.71	0.70	0.69	0.69	0.68	0.68	0.67	0.67
16	2.01	1.38	1.17	1.06	0.99	0.91	0.87	0.84	0.81	0.80	0.79	0.78	0.77	0.76	0.75	0.75	0.74	0.74	0.73	0.73
20	2.20	1.48	1.24	1.13	1.05	0.97	0.92	0.89	0.86	0.85	0.83	0.82	0.82	0.81	0.80	0.79	0.79	0.78	0.78	0.77
30	2.56	1.67	1.39	1.25	1.17	1.07	1.02	0.98	0.95	0.93	0.92	0.91	0.90	0.89	0.88	0.87	0.86	0.86	0.85	0.85
40	2.85	1.81	1.49	1.34	1.25	1.14	1.08	1.04	1.01	0.99	0.97	0.96	0.95	0.94	0.93	0.92	0.92	0.91	0.91	0.90
50	3.10	1.92	1.57	1.41	1.31	1.19	1.13	1.09	1.06	1.03	1.02	1.01	1.00	0.98	0.97	0.97	0.96	0.96	0.95	0.94
60	3.31	2.02	1.64	1.46	1.36	1.24	1.17	1.12	1.09	1.07	1.05	1.04	1.03	1.02	1.01	1.00	0.99	0.99	0.98	0.97
75	3.58	2.14	1.73	1.53	1.42	1.29	1.22	1.17	1.14	1.11	1.10	1.08	1.07	1.06	1.05	1.04	1.03	1.03	1.02	1.01
100	3.96	*2.30*	1.84	1.62	1.50	1.36	1.29	1.23	1.19	1.17	1.15	1.14	1.13	1.11	1.10	1.09	1.08	1.08	1.07	1.06
125	4.28	*2.43*	1.93	1.70	1.56	1.42	1.34	1.28	1.24	1.21	1.19	1.18	1.17	1.15	1.14	1.13	1.12	1.11	1.10	1.10
150	4.57	2.54	2.00	1.75	1.61	1.46	1.38	1.31	1.27	1.25	1.23	1.21	1.20	1.18	1.17	1.16	1.15	1.15	1.14	1.13
175	4.82	2.63	2.06	1.80	1.66	1.50	1.41	1.35	1.30	1.28	1.25	1.24	1.23	1.21	1.19	1.18	1.18	1.17	1.16	1.15
200	5.04	2.72	2.12	1.85	1.70	1.53	1.44	1.37	1.33	1.30	1.28	1.26	1.25	1.23	1.22	1.21	1.20	1.19	1.18	1.17

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Table 19-12. κ-Multipliers for 1-of-4 Intrawell Prediction Limits on Observations (1 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**0.64**	**0.50**	**0.44**	**0.40**	**0.37**	**0.34**	**0.32**	**0.31**	**0.30**	**0.29**	**0.29**	**0.28**	**0.28**	**0.27**	**0.27**	**0.27**	**0.27**	**0.26**	**0.26**	**0.26**
2	**1.01**	**0.78**	**0.68**	**0.62**	**0.59**	**0.54**	**0.52**	**0.50**	**0.48**	**0.47**	**0.47**	**0.46**	**0.46**	**0.45**	**0.45**	**0.44**	**0.44**	**0.44**	**0.43**	**0.43**
3	**1.25**	**0.94**	**0.82**	**0.75**	**0.71**	**0.65**	**0.62**	**0.60**	**0.58**	**0.57**	**0.57**	**0.56**	**0.55**	**0.55**	**0.54**	**0.54**	**0.53**	**0.53**	**0.53**	**0.52**
4	**1.44**	**1.06**	**0.92**	**0.84**	**0.79**	**0.73**	**0.70**	**0.67**	**0.65**	**0.64**	**0.63**	**0.63**	**0.62**	**0.61**	**0.61**	**0.60**	**0.60**	**0.59**	**0.59**	**0.59**
5	**1.59**	**1.15**	**0.99**	**0.91**	**0.85**	**0.79**	**0.75**	**0.72**	**0.71**	**0.69**	**0.68**	**0.68**	**0.67**	**0.66**	**0.65**	**0.65**	**0.64**	**0.64**	**0.64**	**0.63**
8	**1.93**	**1.36**	**1.16**	**1.05**	**0.99**	**0.91**	**0.87**	**0.83**	**0.81**	**0.80**	**0.79**	**0.78**	**0.77**	**0.76**	**0.75**	**0.75**	**0.74**	**0.74**	**0.73**	**0.73**
12	**2.27**	**1.54**	**1.30**	**1.17**	**1.10**	**1.01**	**0.96**	**0.93**	**0.90**	**0.88**	**0.87**	**0.86**	**0.85**	**0.84**	**0.83**	**0.83**	**0.82**	**0.82**	**0.81**	**0.81**
16	**2.53**	**1.68**	**1.40**	**1.26**	**1.18**	**1.08**	**1.03**	**0.99**	**0.96**	**0.94**	**0.93**	**0.92**	**0.91**	**0.90**	**0.89**	**0.88**	**0.88**	**0.87**	**0.87**	**0.86**
20	2.75	**1.79**	**1.48**	**1.33**	**1.24**	**1.14**	**1.08**	**1.04**	**1.01**	**0.99**	**0.97**	**0.96**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.91**	**0.90**
30	3.20	**2.00**	**1.63**	**1.46**	**1.35**	**1.24**	**1.17**	**1.12**	**1.09**	**1.07**	**1.05**	**1.04**	**1.03**	**1.02**	**1.01**	**1.00**	**0.99**	**0.99**	**0.98**	**0.97**
40	3.54	**2.15**	**1.74**	**1.55**	**1.43**	**1.31**	**1.24**	**1.18**	**1.15**	**1.13**	**1.11**	**1.10**	**1.08**	**1.07**	**1.06**	**1.05**	**1.04**	**1.04**	**1.03**	**1.02**
50	3.83	**2.27**	**1.83**	**1.62**	**1.50**	**1.36**	**1.29**	**1.23**	**1.19**	**1.17**	**1.15**	**1.14**	**1.13**	**1.11**	**1.10**	**1.09**	**1.08**	**1.08**	**1.07**	**1.06**
60	4.09	**2.38**	**1.90**	**1.68**	**1.55**	**1.40**	**1.33**	**1.27**	**1.23**	**1.20**	**1.19**	**1.17**	**1.16**	**1.14**	**1.13**	**1.12**	**1.11**	**1.11**	**1.10**	**1.09**
75	4.42	**2.51**	**1.99**	**1.75**	**1.61**	**1.46**	**1.38**	**1.31**	**1.27**	**1.25**	**1.23**	**1.21**	**1.20**	**1.18**	**1.17**	**1.16**	**1.15**	**1.15**	**1.14**	**1.13**
100	4.89	2.69	**2.11**	**1.84**	**1.69**	**1.53**	**1.44**	**1.37**	**1.33**	**1.30**	**1.28**	**1.26**	**1.25**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**
125	5.27	2.84	**2.20**	**1.92**	**1.76**	**1.58**	**1.49**	**1.42**	**1.37**	**1.34**	**1.32**	**1.30**	**1.29**	**1.27**	**1.25**	**1.24**	**1.24**	**1.23**	**1.22**	**1.21**
150	5.62	2.96	**2.28**	**1.98**	**1.81**	**1.63**	**1.53**	**1.45**	**1.41**	**1.38**	**1.35**	**1.33**	**1.32**	**1.30**	**1.28**	**1.27**	**1.26**	**1.26**	**1.25**	**1.24**
175	5.92	3.06	**2.35**	**2.03**	**1.86**	**1.66**	**1.56**	**1.48**	**1.44**	**1.40**	**1.38**	**1.36**	**1.35**	**1.32**	**1.31**	**1.30**	**1.29**	**1.28**	**1.27**	**1.26**
200	6.19	3.16	**2.41**	**2.08**	**1.89**	**1.70**	**1.59**	**1.51**	**1.46**	**1.43**	**1.40**	**1.38**	**1.37**	**1.35**	**1.33**	**1.32**	**1.31**	**1.30**	**1.29**	**1.28**

Table 19-12. κ-Multipliers for 1-of-4 Intrawell Prediction Limits on Observations (2 COC, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**0.39**	**0.28**	**0.22**	**0.19**	**0.17**	**0.14**	**0.12**	**0.11**	**0.10**	**0.10**	**0.09**	**0.09**	**0.09**	**0.08**	**0.08**	**0.08**	**0.07**	**0.07**	**0.07**	**0.07**
2	**0.74**	**0.55**	**0.47**	**0.42**	**0.39**	**0.36**	**0.33**	**0.32**	**0.31**	**0.30**	**0.29**	**0.29**	**0.28**	**0.28**	**0.27**	**0.27**	**0.27**	**0.27**	**0.26**	**0.26**
3	**0.95**	**0.70**	**0.61**	**0.55**	**0.51**	**0.47**	**0.45**	**0.43**	**0.41**	**0.41**	**0.40**	**0.39**	**0.39**	**0.38**	**0.38**	**0.37**	**0.37**	**0.37**	**0.37**	**0.36**
4	**1.11**	**0.82**	**0.70**	**0.64**	**0.60**	**0.55**	**0.52**	**0.50**	**0.49**	**0.48**	**0.47**	**0.46**	**0.46**	**0.45**	**0.45**	**0.44**	**0.44**	**0.44**	**0.43**	**0.43**
5	**1.24**	**0.91**	**0.78**	**0.71**	**0.67**	**0.61**	**0.58**	**0.56**	**0.54**	**0.53**	**0.52**	**0.52**	**0.51**	**0.51**	**0.50**	**0.50**	**0.49**	**0.49**	**0.49**	**0.48**
8	**1.54**	**1.10**	**0.94**	**0.85**	**0.80**	**0.74**	**0.70**	**0.67**	**0.66**	**0.64**	**0.63**	**0.63**	**0.62**	**0.61**	**0.61**	**0.60**	**0.60**	**0.59**	**0.59**	**0.59**
12	**1.83**	**1.27**	**1.07**	**0.97**	**0.91**	**0.84**	**0.80**	**0.77**	**0.75**	**0.74**	**0.72**	**0.72**	**0.71**	**0.70**	**0.69**	**0.69**	**0.68**	**0.68**	**0.67**	**0.67**
16	*2.06*	**1.39**	**1.17**	**1.06**	**0.99**	**0.92**	**0.87**	**0.84**	**0.81**	**0.80**	**0.79**	**0.78**	**0.77**	**0.76**	**0.75**	**0.75**	**0.74**	**0.74**	**0.73**	**0.73**
20	2.25	**1.49**	**1.25**	**1.13**	**1.06**	**0.97**	**0.92**	**0.89**	**0.86**	**0.85**	**0.83**	**0.82**	**0.82**	**0.81**	**0.80**	**0.79**	**0.79**	**0.78**	**0.78**	**0.77**
30	2.62	**1.68**	**1.39**	**1.25**	**1.17**	**1.07**	**1.02**	**0.98**	**0.95**	**0.93**	**0.92**	**0.91**	**0.90**	**0.89**	**0.88**	**0.87**	**0.87**	**0.86**	**0.85**	**0.85**
40	2.91	**1.82**	**1.50**	**1.34**	**1.25**	**1.14**	**1.08**	**1.04**	**1.01**	**0.99**	**0.97**	**0.96**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.91**	**0.90**
50	3.16	**1.94**	**1.58**	**1.41**	**1.31**	**1.20**	**1.13**	**1.09**	**1.06**	**1.03**	**1.02**	**1.01**	**1.00**	**0.98**	**0.97**	**0.97**	**0.96**	**0.96**	**0.95**	**0.94**
60	3.37	*2.03*	**1.65**	**1.47**	**1.36**	**1.24**	**1.17**	**1.12**	**1.09**	**1.07**	**1.05**	**1.04**	**1.03**	**1.02**	**1.01**	**1.00**	**0.99**	**0.99**	**0.98**	**0.97**
75	3.65	*2.15*	**1.73**	**1.54**	**1.42**	**1.29**	**1.22**	**1.17**	**1.14**	**1.11**	**1.10**	**1.08**	**1.07**	**1.06**	**1.05**	**1.04**	**1.03**	**1.03**	**1.02**	**1.01**
100	4.04	2.31	**1.84**	**1.63**	**1.50**	**1.36**	**1.29**	**1.23**	**1.19**	**1.17**	**1.15**	**1.14**	**1.13**	**1.11**	**1.10**	**1.09**	**1.08**	**1.08**	**1.07**	**1.06**
125	4.37	2.44	**1.93**	**1.70**	**1.56**	**1.42**	**1.34**	**1.28**	**1.24**	**1.21**	**1.19**	**1.18**	**1.17**	**1.15**	**1.14**	**1.13**	**1.12**	**1.11**	**1.11**	**1.10**
150	4.65	2.55	*2.01*	**1.76**	**1.62**	**1.46**	**1.38**	**1.31**	**1.27**	**1.25**	**1.23**	**1.21**	**1.20**	**1.18**	**1.17**	**1.16**	**1.15**	**1.15**	**1.14**	**1.13**
175	4.91	2.65	*2.07*	**1.81**	**1.66**	**1.50**	**1.41**	**1.35**	**1.30**	**1.28**	**1.25**	**1.24**	**1.23**	**1.21**	**1.19**	**1.18**	**1.18**	**1.17**	**1.16**	**1.15**
200	5.14	2.73	*2.12*	**1.85**	**1.70**	**1.53**	**1.44**	**1.37**	**1.33**	**1.30**	**1.28**	**1.26**	**1.25**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**

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Table 19-12. κ-Multipliers for 1-of-4 Intrawell Prediction Limits on Observations (2 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	0.70	0.53	0.46	0.41	0.39	0.35	0.33	0.31	0.30	0.30	0.29	0.29	0.28	0.28	0.27	0.27	0.27	0.27	0.26	0.26
2	1.07	0.80	0.69	0.63	0.60	0.55	0.52	0.50	0.49	0.48	0.47	0.46	0.46	0.45	0.45	0.44	0.44	0.44	0.43	0.43
3	1.32	0.97	0.83	0.76	0.71	0.66	0.63	0.60	0.59	0.58	0.57	0.56	0.55	0.55	0.54	0.54	0.53	0.53	0.53	0.52
4	1.50	1.08	0.93	0.85	0.80	0.74	0.70	0.67	0.66	0.64	0.63	0.63	0.62	0.61	0.61	0.60	0.60	0.59	0.59	0.59
5	1.66	1.18	1.01	0.92	0.86	0.79	0.76	0.73	0.71	0.69	0.68	0.68	0.67	0.66	0.65	0.65	0.65	0.64	0.64	0.63
8	2.01	1.38	1.17	1.06	0.99	0.91	0.87	0.84	0.81	0.80	0.79	0.78	0.77	0.76	0.75	0.75	0.74	0.74	0.73	0.73
12	2.36	1.57	1.31	1.18	1.10	1.01	0.96	0.93	0.90	0.88	0.87	0.86	0.85	0.84	0.83	0.83	0.82	0.82	0.81	0.81
16	2.63	1.70	1.41	1.27	1.18	1.09	1.03	0.99	0.96	0.94	0.93	0.92	0.91	0.90	0.89	0.88	0.88	0.87	0.87	0.86
20	2.85	1.81	1.49	1.34	1.25	1.14	1.08	1.04	1.01	0.99	0.97	0.96	0.95	0.94	0.93	0.92	0.92	0.91	0.91	0.90
30	3.31	2.02	1.64	1.46	1.36	1.24	1.17	1.12	1.09	1.07	1.05	1.04	1.03	1.02	1.01	1.00	0.99	0.99	0.98	0.97
40	3.66	2.17	1.75	1.55	1.44	1.31	1.24	1.18	1.15	1.13	1.11	1.10	1.09	1.07	1.06	1.05	1.04	1.04	1.03	1.02
50	3.96	*2.30*	1.84	1.62	1.50	1.36	1.29	1.23	1.19	1.17	1.15	1.14	1.13	1.11	1.10	1.09	1.08	1.08	1.07	1.06
60	4.22	*2.41*	1.91	1.68	1.55	1.41	1.33	1.27	1.23	1.20	1.19	1.17	1.16	1.14	1.13	1.12	1.11	1.11	1.10	1.09
75	4.56	2.54	2.00	1.75	1.61	1.46	1.38	1.31	1.27	1.25	1.23	1.21	1.20	1.18	1.17	1.16	1.15	1.15	1.14	1.13
100	5.04	2.72	2.12	1.85	1.70	1.53	1.44	1.37	1.33	1.30	1.28	1.26	1.25	1.23	1.22	1.21	1.20	1.19	1.18	1.17
125	5.45	2.86	2.21	1.92	1.76	1.58	1.49	1.42	1.37	1.34	1.32	1.30	1.29	1.27	1.25	1.24	1.24	1.23	1.22	1.21
150	5.79	2.99	*2.29*	1.98	1.81	1.63	1.53	1.45	1.41	1.38	1.35	1.33	1.32	1.30	1.28	1.27	1.26	1.26	1.25	1.24
175	6.11	3.09	*2.36*	2.04	1.86	1.66	1.56	1.48	1.44	1.40	1.38	1.36	1.35	1.32	1.31	1.30	1.29	1.28	1.27	1.26
200	6.39	3.19	*2.42*	2.08	1.90	1.70	1.59	1.51	1.46	1.43	1.40	1.38	1.37	1.35	1.33	1.32	1.31	1.30	1.29	1.28

Table 19-12. κ-Multipliers for 1-of-4 Intrawell Prediction Limits on Observations (2 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	1.01	0.78	0.68	0.62	0.59	0.54	0.52	0.50	0.48	0.47	0.47	0.46	0.46	0.45	0.45	0.44	0.44	0.44	0.43	0.43
2	1.44	1.06	0.92	0.84	0.79	0.73	0.70	0.67	0.65	0.64	0.63	0.63	0.62	0.61	0.61	0.60	0.60	0.59	0.59	0.59
3	1.72	1.23	1.06	0.96	0.91	0.84	0.80	0.77	0.75	0.73	0.72	0.72	0.71	0.70	0.69	0.69	0.68	0.68	0.67	0.67
4	1.93	1.36	1.16	1.05	0.99	0.91	0.87	0.83	0.81	0.80	0.79	0.78	0.77	0.76	0.75	0.75	0.74	0.74	0.73	0.73
5	2.11	1.46	1.23	1.12	1.05	0.97	0.92	0.88	0.86	0.84	0.83	0.82	0.82	0.80	0.80	0.79	0.79	0.78	0.78	0.77
8	2.53	1.68	1.40	1.26	1.18	1.08	1.03	0.99	0.96	0.94	0.93	0.92	0.91	0.90	0.89	0.88	0.88	0.87	0.87	0.86
12	2.95	1.88	1.55	1.39	1.29	1.18	1.12	1.08	1.05	1.03	1.01	1.00	0.99	0.98	0.97	0.96	0.95	0.95	0.94	0.93
16	3.27	2.03	1.66	1.48	1.37	1.25	1.19	1.14	1.11	1.08	1.07	1.05	1.04	1.03	1.02	1.01	1.00	1.00	0.99	0.98
20	3.54	2.15	1.74	1.55	1.43	1.31	1.24	1.18	1.15	1.13	1.11	1.10	1.08	1.07	1.06	1.05	1.04	1.04	1.03	1.02
30	4.09	2.38	1.90	1.68	1.55	1.40	1.33	1.27	1.23	1.20	1.19	1.17	1.16	1.14	1.13	1.12	1.11	1.11	1.10	1.09
40	4.52	2.55	2.02	1.77	1.63	1.47	1.39	1.33	1.29	1.26	1.24	1.22	1.21	1.19	1.18	1.17	1.16	1.16	1.15	1.14
50	4.89	2.69	2.11	1.84	1.69	1.53	1.44	1.37	1.33	1.30	1.28	1.26	1.25	1.23	1.22	1.21	1.20	1.19	1.18	1.17
60	5.20	2.81	2.19	1.90	1.75	1.57	1.48	1.41	1.36	1.33	1.31	1.29	1.28	1.26	1.25	1.24	1.23	1.22	1.21	1.20
75	5.62	2.96	2.28	1.98	1.81	1.63	1.53	1.45	1.41	1.38	1.35	1.33	1.32	1.30	1.28	1.27	1.26	1.26	1.25	1.24
100	6.20	3.16	2.41	2.08	1.89	1.69	1.59	1.51	1.46	1.43	1.40	1.38	1.37	1.35	1.33	1.32	1.31	1.30	1.29	1.28
125	6.69	3.32	2.51	2.16	1.96	1.75	1.64	1.56	1.50	1.47	1.44	1.42	1.41	1.38	1.37	1.35	1.35	1.34	1.33	1.32
150	7.11	3.46	*2.59*	2.22	2.01	1.79	1.68	1.59	1.54	1.50	1.47	1.45	1.44	1.41	1.40	1.38	1.37	1.37	1.35	1.34
175	7.49	3.58	*2.67*	2.28	2.06	1.83	1.71	1.62	1.57	1.53	1.50	1.48	1.46	1.44	1.42	1.41	1.40	1.39	1.38	1.37
200	7.84	3.69	*2.73*	2.32	2.10	1.86	1.74	1.65	1.59	1.55	1.52	1.50	1.48	1.46	1.44	1.43	1.42	1.41	1.40	1.39

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Table 19-12. κ-Multipliers for 1-of-4 Intrawell Prediction Limits on Observations (5 COC, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**0.85**	**0.63**	**0.54**	**0.49**	**0.46**	**0.42**	**0.40**	**0.38**	**0.37**	**0.36**	**0.35**	**0.35**	**0.34**	**0.34**	**0.33**	**0.33**	**0.33**	**0.32**	**0.32**	**0.32**
2	**1.24**	**0.91**	**0.78**	**0.71**	**0.67**	**0.61**	**0.58**	**0.56**	**0.54**	**0.53**	**0.52**	**0.52**	**0.51**	**0.51**	**0.50**	**0.50**	**0.49**	**0.49**	**0.49**	**0.48**
3	**1.50**	**1.07**	**0.91**	**0.83**	**0.78**	**0.72**	**0.69**	**0.66**	**0.64**	**0.63**	**0.62**	**0.61**	**0.61**	**0.60**	**0.59**	**0.59**	**0.58**	**0.58**	**0.58**	**0.57**
4	**1.70**	**1.19**	**1.01**	**0.92**	**0.86**	**0.80**	**0.76**	**0.73**	**0.71**	**0.69**	**0.68**	**0.68**	**0.67**	**0.66**	**0.65**	**0.65**	**0.65**	**0.64**	**0.64**	**0.63**
5	**1.86**	**1.29**	**1.09**	**0.99**	**0.92**	**0.85**	**0.81**	**0.78**	**0.76**	**0.74**	**0.73**	**0.73**	**0.72**	**0.71**	**0.70**	**0.70**	**0.69**	**0.69**	**0.68**	**0.68**
8	2.25	**1.49**	**1.25**	**1.13**	**1.06**	**0.97**	**0.92**	**0.89**	**0.86**	**0.85**	**0.83**	**0.82**	**0.82**	**0.81**	**0.80**	**0.79**	**0.79**	**0.78**	**0.78**	**0.77**
12	2.62	**1.68**	**1.39**	**1.25**	**1.17**	**1.07**	**1.02**	**0.98**	**0.95**	**0.93**	**0.92**	**0.91**	**0.90**	**0.89**	**0.88**	**0.87**	**0.87**	**0.86**	**0.85**	**0.85**
16	2.91	**1.82**	**1.50**	**1.34**	**1.25**	**1.14**	**1.08**	**1.04**	**1.01**	**0.99**	**0.97**	**0.96**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.91**	**0.90**
20	3.16	**1.94**	**1.58**	**1.41**	**1.31**	**1.20**	**1.13**	**1.09**	**1.06**	**1.03**	**1.02**	**1.01**	**1.00**	**0.98**	**0.97**	**0.97**	**0.96**	**0.96**	**0.95**	**0.94**
30	3.65	*2.15*	**1.73**	**1.54**	**1.42**	**1.29**	**1.22**	**1.17**	**1.14**	**1.11**	**1.10**	**1.08**	**1.07**	**1.06**	**1.05**	**1.04**	**1.03**	**1.03**	**1.02**	**1.01**
40	4.04	2.31	**1.84**	**1.63**	**1.50**	**1.36**	**1.29**	**1.23**	**1.19**	**1.17**	**1.15**	**1.14**	**1.13**	**1.11**	**1.10**	**1.09**	**1.08**	**1.08**	**1.07**	**1.06**
50	4.37	2.44	**1.93**	**1.70**	**1.56**	**1.42**	**1.34**	**1.28**	**1.24**	**1.21**	**1.19**	**1.18**	**1.17**	**1.15**	**1.14**	**1.13**	**1.12**	**1.11**	**1.11**	**1.10**
60	4.65	2.55	*2.01*	**1.76**	**1.62**	**1.46**	**1.38**	**1.31**	**1.27**	**1.25**	**1.23**	**1.21**	**1.20**	**1.18**	**1.17**	**1.16**	**1.15**	**1.15**	**1.14**	**1.13**
75	5.02	2.69	*2.10*	**1.83**	**1.68**	**1.51**	**1.43**	**1.36**	**1.32**	**1.29**	**1.27**	**1.25**	**1.24**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**	**1.16**
100	5.55	2.88	2.22	**1.92**	**1.76**	**1.58**	**1.49**	**1.42**	**1.37**	**1.34**	**1.32**	**1.30**	**1.29**	**1.27**	**1.25**	**1.24**	**1.24**	**1.23**	**1.22**	**1.21**
125	5.99	3.03	2.31	*2.00*	**1.83**	**1.64**	**1.54**	**1.46**	**1.42**	**1.38**	**1.36**	**1.34**	**1.33**	**1.31**	**1.29**	**1.28**	**1.27**	**1.26**	**1.25**	**1.25**
150	6.37	3.16	2.40	*2.06*	**1.88**	**1.68**	**1.58**	**1.50**	**1.45**	**1.42**	**1.39**	**1.37**	**1.36**	**1.34**	**1.32**	**1.31**	**1.30**	**1.29**	**1.28**	**1.27**
175	6.71	3.27	2.46	*2.12*	**1.92**	**1.72**	**1.61**	**1.53**	**1.48**	**1.44**	**1.42**	**1.40**	**1.38**	**1.36**	**1.35**	**1.33**	**1.32**	**1.32**	**1.30**	**1.30**
200	7.03	3.37	2.52	*2.16*	*1.96*	**1.75**	**1.64**	**1.56**	**1.50**	**1.47**	**1.44**	**1.42**	**1.41**	**1.38**	**1.37**	**1.35**	**1.35**	**1.34**	**1.33**	**1.32**

Table 19-12. κ-Multipliers for 1-of-4 Intrawell Prediction Limits on Observations (5 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.21**	**0.89**	**0.77**	**0.70**	**0.66**	**0.61**	**0.58**	**0.56**	**0.54**	**0.53**	**0.52**	**0.52**	**0.51**	**0.50**	**0.50**	**0.50**	**0.49**	**0.49**	**0.49**	**0.48**
2	**1.66**	**1.18**	**1.01**	**0.92**	**0.86**	**0.79**	**0.76**	**0.73**	**0.71**	**0.69**	**0.68**	**0.68**	**0.67**	**0.66**	**0.65**	**0.65**	**0.65**	**0.64**	**0.64**	**0.63**
3	**1.96**	**1.35**	**1.14**	**1.04**	**0.97**	**0.90**	**0.85**	**0.82**	**0.80**	**0.78**	**0.77**	**0.76**	**0.76**	**0.75**	**0.74**	**0.73**	**0.73**	**0.73**	**0.72**	**0.72**
4	**2.20**	**1.48**	**1.24**	**1.13**	**1.05**	**0.97**	**0.92**	**0.89**	**0.86**	**0.85**	**0.83**	**0.82**	**0.82**	**0.81**	**0.80**	**0.79**	**0.79**	**0.78**	**0.78**	**0.77**
5	2.39	**1.58**	**1.32**	**1.19**	**1.11**	**1.02**	**0.97**	**0.94**	**0.91**	**0.89**	**0.88**	**0.87**	**0.86**	**0.85**	**0.84**	**0.84**	**0.83**	**0.83**	**0.82**	**0.81**
8	2.85	**1.81**	**1.49**	**1.34**	**1.25**	**1.14**	**1.08**	**1.04**	**1.01**	**0.99**	**0.97**	**0.96**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.91**	**0.90**
12	3.31	**2.02**	**1.64**	**1.46**	**1.36**	**1.24**	**1.17**	**1.12**	**1.09**	**1.07**	**1.05**	**1.04**	**1.03**	**1.02**	**1.01**	**1.00**	**0.99**	**0.99**	**0.98**	**0.97**
16	3.66	**2.17**	**1.75**	**1.55**	**1.44**	**1.31**	**1.24**	**1.18**	**1.15**	**1.13**	**1.11**	**1.10**	**1.09**	**1.07**	**1.06**	**1.05**	**1.04**	**1.04**	**1.03**	**1.02**
20	3.96	*2.30*	**1.84**	**1.62**	**1.50**	**1.36**	**1.29**	**1.23**	**1.19**	**1.17**	**1.15**	**1.14**	**1.13**	**1.11**	**1.10**	**1.09**	**1.08**	**1.08**	**1.07**	**1.06**
30	4.56	2.54	**2.00**	**1.75**	**1.61**	**1.46**	**1.38**	**1.31**	**1.27**	**1.25**	**1.23**	**1.21**	**1.20**	**1.18**	**1.17**	**1.16**	**1.15**	**1.15**	**1.14**	**1.13**
40	5.04	2.72	**2.12**	**1.85**	**1.70**	**1.53**	**1.44**	**1.37**	**1.33**	**1.30**	**1.28**	**1.26**	**1.25**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**
50	5.45	2.86	**2.21**	**1.92**	**1.76**	**1.58**	**1.49**	**1.42**	**1.37**	**1.34**	**1.32**	**1.30**	**1.29**	**1.27**	**1.25**	**1.24**	**1.24**	**1.23**	**1.22**	**1.21**
60	5.79	2.99	*2.29*	**1.98**	**1.81**	**1.63**	**1.53**	**1.45**	**1.41**	**1.38**	**1.35**	**1.33**	**1.32**	**1.30**	**1.28**	**1.27**	**1.26**	**1.26**	**1.25**	**1.24**
75	6.25	3.14	*2.39*	**2.06**	**1.88**	**1.68**	**1.58**	**1.50**	**1.45**	**1.42**	**1.39**	**1.37**	**1.36**	**1.34**	**1.32**	**1.31**	**1.30**	**1.29**	**1.28**	**1.27**
100	6.90	3.35	2.52	**2.16**	**1.96**	**1.75**	**1.64**	**1.56**	**1.50**	**1.47**	**1.44**	**1.42**	**1.41**	**1.38**	**1.37**	**1.35**	**1.35**	**1.34**	**1.32**	**1.32**
125	7.44	3.52	2.62	**2.24**	**2.03**	**1.80**	**1.69**	**1.60**	**1.55**	**1.51**	**1.48**	**1.46**	**1.44**	**1.42**	**1.40**	**1.39**	**1.38**	**1.37**	**1.36**	**1.35**
150	7.91	3.67	2.71	*2.30*	**2.08**	**1.85**	**1.72**	**1.64**	**1.58**	**1.54**	**1.51**	**1.49**	**1.47**	**1.45**	**1.43**	**1.42**	**1.41**	**1.40**	**1.39**	**1.38**
175	8.33	3.79	2.78	*2.36*	**2.13**	**1.89**	**1.76**	**1.67**	**1.61**	**1.57**	**1.54**	**1.52**	**1.50**	**1.47**	**1.45**	**1.44**	**1.43**	**1.42**	**1.41**	**1.40**
200	8.73	3.90	2.85	*2.41*	**2.17**	**1.92**	**1.79**	**1.69**	**1.63**	**1.59**	**1.56**	**1.54**	**1.52**	**1.49**	**1.48**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**

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Table 19-12. κ-Multipliers for 1-of-4 Intrawell Prediction Limits on Observations (5 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.59**	**1.15**	**0.99**	**0.91**	**0.85**	**0.79**	**0.75**	**0.72**	**0.71**	**0.69**	**0.68**	**0.68**	**0.67**	**0.66**	**0.65**	**0.65**	**0.64**	**0.64**	**0.64**	**0.63**
2	**2.11**	**1.46**	**1.23**	**1.12**	**1.05**	**0.97**	**0.92**	**0.88**	**0.86**	**0.84**	**0.83**	**0.82**	**0.82**	**0.80**	**0.80**	**0.79**	**0.79**	**0.78**	**0.78**	**0.77**
3	**2.47**	**1.65**	**1.38**	**1.24**	**1.16**	**1.07**	**1.01**	**0.97**	**0.95**	**0.93**	**0.92**	**0.91**	**0.90**	**0.89**	**0.88**	**0.87**	**0.86**	**0.86**	**0.85**	**0.85**
4	2.75	**1.79**	**1.48**	**1.33**	**1.24**	**1.14**	**1.08**	**1.04**	**1.01**	**0.99**	**0.97**	**0.96**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.91**	**0.90**
5	2.99	**1.90**	**1.56**	**1.40**	**1.30**	**1.19**	**1.13**	**1.08**	**1.05**	**1.03**	**1.02**	**1.01**	**1.00**	**0.98**	**0.97**	**0.97**	**0.96**	**0.96**	**0.95**	**0.94**
8	3.54	**2.15**	**1.74**	**1.55**	**1.43**	**1.31**	**1.24**	**1.18**	**1.15**	**1.13**	**1.11**	**1.10**	**1.08**	**1.07**	**1.06**	**1.05**	**1.04**	**1.04**	**1.03**	**1.02**
12	4.09	**2.38**	**1.90**	**1.68**	**1.55**	**1.40**	**1.33**	**1.27**	**1.23**	**1.20**	**1.19**	**1.17**	**1.16**	**1.14**	**1.13**	**1.12**	**1.11**	**1.11**	**1.10**	**1.09**
16	4.52	**2.55**	**2.02**	**1.77**	**1.63**	**1.47**	**1.39**	**1.33**	**1.29**	**1.26**	**1.24**	**1.22**	**1.21**	**1.19**	**1.18**	**1.17**	**1.16**	**1.16**	**1.15**	**1.14**
20	4.89	2.69	**2.11**	**1.84**	**1.69**	**1.53**	**1.44**	**1.37**	**1.33**	**1.30**	**1.28**	**1.26**	**1.25**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**
30	5.62	2.96	**2.28**	**1.98**	**1.81**	**1.63**	**1.53**	**1.45**	**1.41**	**1.38**	**1.35**	**1.33**	**1.32**	**1.30**	**1.28**	**1.27**	**1.26**	**1.26**	**1.25**	**1.24**
40	6.20	3.16	**2.41**	**2.08**	**1.89**	**1.69**	**1.59**	**1.51**	**1.46**	**1.43**	**1.40**	**1.38**	**1.37**	**1.35**	**1.33**	**1.32**	**1.31**	**1.30**	**1.29**	**1.28**
50	6.69	3.32	**2.51**	**2.16**	**1.96**	**1.75**	**1.64**	**1.56**	**1.50**	**1.47**	**1.44**	**1.42**	**1.41**	**1.38**	**1.37**	**1.35**	**1.35**	**1.34**	**1.33**	**1.32**
60	7.11	3.46	*2.59*	**2.22**	**2.01**	**1.79**	**1.68**	**1.59**	**1.54**	**1.50**	**1.47**	**1.45**	**1.44**	**1.41**	**1.40**	**1.38**	**1.37**	**1.37**	**1.35**	**1.34**
75	7.68	3.64	*2.70*	**2.30**	**2.08**	**1.85**	**1.72**	**1.64**	**1.58**	**1.54**	**1.51**	**1.49**	**1.47**	**1.45**	**1.43**	**1.42**	**1.41**	**1.40**	**1.39**	**1.38**
100	8.45	3.87	2.84	**2.41**	**2.17**	**1.92**	**1.79**	**1.69**	**1.63**	**1.59**	**1.56**	**1.54**	**1.52**	**1.49**	**1.48**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**
125	9.11	4.06	2.95	**2.49**	**2.24**	**1.97**	**1.83**	**1.73**	**1.67**	**1.63**	**1.60**	**1.57**	**1.56**	**1.53**	**1.51**	**1.50**	**1.48**	**1.48**	**1.46**	**1.45**
150	9.70	4.23	3.05	*2.56*	**2.29**	**2.02**	**1.88**	**1.77**	**1.71**	**1.66**	**1.63**	**1.60**	**1.59**	**1.56**	**1.54**	**1.52**	**1.51**	**1.50**	**1.49**	**1.48**
175	10.20	4.37	3.13	*2.61*	**2.34**	**2.05**	**1.91**	**1.80**	**1.73**	**1.69**	**1.66**	**1.63**	**1.61**	**1.58**	**1.56**	**1.55**	**1.53**	**1.53**	**1.51**	**1.50**
200	10.66	4.50	3.20	*2.67*	**2.38**	**2.09**	**1.94**	**1.83**	**1.76**	**1.71**	**1.68**	**1.65**	**1.63**	**1.60**	**1.58**	**1.57**	**1.55**	**1.54**	**1.53**	**1.52**

Table 19-12. κ-Multipliers for 1-of-4 Intrawell Prediction Limits on Observations (10 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.24**	**0.91**	**0.78**	**0.71**	**0.67**	**0.61**	**0.58**	**0.56**	**0.54**	**0.53**	**0.52**	**0.52**	**0.51**	**0.51**	**0.50**	**0.50**	**0.49**	**0.49**	**0.49**	**0.48**
2	**1.70**	**1.19**	**1.01**	**0.92**	**0.86**	**0.80**	**0.76**	**0.73**	**0.71**	**0.69**	**0.68**	**0.68**	**0.67**	**0.66**	**0.65**	**0.65**	**0.65**	**0.64**	**0.64**	**0.63**
3	**2.01**	**1.37**	**1.15**	**1.04**	**0.98**	**0.90**	**0.86**	**0.82**	**0.80**	**0.78**	**0.77**	**0.76**	**0.76**	**0.75**	**0.74**	**0.73**	**0.73**	**0.73**	**0.72**	**0.72**
4	2.25	**1.49**	**1.25**	**1.13**	**1.06**	**0.97**	**0.92**	**0.89**	**0.86**	**0.85**	**0.83**	**0.82**	**0.82**	**0.81**	**0.80**	**0.79**	**0.79**	**0.78**	**0.78**	**0.77**
5	2.45	**1.60**	**1.33**	**1.20**	**1.12**	**1.03**	**0.98**	**0.94**	**0.91**	**0.89**	**0.88**	**0.87**	**0.86**	**0.85**	**0.84**	**0.84**	**0.83**	**0.83**	**0.82**	**0.81**
8	2.91	**1.82**	**1.50**	**1.34**	**1.25**	**1.14**	**1.08**	**1.04**	**1.01**	**0.99**	**0.97**	**0.96**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.91**	**0.90**
12	3.37	*2.03*	**1.65**	**1.47**	**1.36**	**1.24**	**1.17**	**1.12**	**1.09**	**1.07**	**1.05**	**1.04**	**1.03**	**1.02**	**1.01**	**1.00**	**0.99**	**0.99**	**0.98**	**0.97**
16	3.74	2.19	**1.76**	**1.56**	**1.44**	**1.31**	**1.24**	**1.18**	**1.15**	**1.13**	**1.11**	**1.10**	**1.09**	**1.07**	**1.06**	**1.05**	**1.04**	**1.04**	**1.03**	**1.02**
20	4.04	2.31	**1.84**	**1.63**	**1.50**	**1.36**	**1.29**	**1.23**	**1.19**	**1.17**	**1.15**	**1.14**	**1.13**	**1.11**	**1.10**	**1.09**	**1.08**	**1.08**	**1.07**	**1.06**
30	4.65	2.55	*2.00*	**1.76**	**1.62**	**1.46**	**1.38**	**1.31**	**1.27**	**1.25**	**1.23**	**1.21**	**1.20**	**1.18**	**1.17**	**1.16**	**1.15**	**1.15**	**1.14**	**1.13**
40	5.14	2.73	*2.12*	**1.85**	**1.70**	**1.53**	**1.44**	**1.37**	**1.33**	**1.30**	**1.28**	**1.26**	**1.25**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**
50	5.55	2.88	2.22	**1.92**	**1.76**	**1.58**	**1.49**	**1.42**	**1.37**	**1.34**	**1.32**	**1.30**	**1.29**	**1.27**	**1.25**	**1.24**	**1.24**	**1.23**	**1.22**	**1.21**
60	5.90	3.00	2.30	*1.99*	**1.81**	**1.63**	**1.53**	**1.45**	**1.41**	**1.38**	**1.35**	**1.33**	**1.32**	**1.30**	**1.28**	**1.27**	**1.26**	**1.26**	**1.25**	**1.24**
75	6.37	3.16	2.39	*2.06*	**1.88**	**1.68**	**1.58**	**1.50**	**1.45**	**1.42**	**1.39**	**1.37**	**1.36**	**1.34**	**1.32**	**1.31**	**1.30**	**1.29**	**1.28**	**1.27**
100	7.03	3.37	2.52	*2.16*	*1.96*	**1.75**	**1.64**	**1.56**	**1.50**	**1.47**	**1.44**	**1.42**	**1.41**	**1.38**	**1.37**	**1.35**	**1.35**	**1.34**	**1.32**	**1.32**
125	7.59	3.54	2.63	2.24	*2.03*	**1.80**	**1.69**	**1.60**	**1.55**	**1.51**	**1.48**	**1.46**	**1.44**	**1.42**	**1.40**	**1.39**	**1.38**	**1.37**	**1.36**	**1.35**
150	8.06	3.68	2.71	2.31	*2.08*	**1.85**	**1.72**	**1.64**	**1.58**	**1.54**	**1.51**	**1.49**	**1.47**	**1.45**	**1.43**	**1.42**	**1.41**	**1.40**	**1.38**	**1.38**
175	8.50	3.81	2.79	2.36	*2.13*	**1.89**	**1.76**	**1.67**	**1.61**	**1.57**	**1.54**	**1.52**	**1.50**	**1.47**	**1.45**	**1.44**	**1.43**	**1.42**	**1.41**	**1.40**
200	8.88	3.93	2.86	2.41	*2.17*	**1.92**	**1.79**	**1.69**	**1.63**	**1.59**	**1.56**	**1.54**	**1.52**	**1.49**	**1.48**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**

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Table 19-12. κ-Multipliers for 1-of-4 Intrawell Prediction Limits on Observations (10 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.66**	**1.18**	**1.01**	**0.92**	**0.86**	**0.79**	**0.76**	**0.73**	**0.71**	**0.69**	**0.68**	**0.68**	**0.67**	**0.66**	**0.65**	**0.65**	**0.65**	**0.64**	**0.64**	**0.63**
2	**2.20**	**1.48**	**1.24**	**1.13**	**1.05**	**0.97**	**0.92**	**0.89**	**0.86**	**0.85**	**0.83**	**0.82**	**0.82**	**0.81**	**0.80**	**0.79**	**0.79**	**0.78**	**0.78**	**0.77**
3	2.56	**1.67**	**1.39**	**1.25**	**1.17**	**1.07**	**1.02**	**0.98**	**0.95**	**0.93**	**0.92**	**0.91**	**0.90**	**0.89**	**0.88**	**0.87**	**0.86**	**0.86**	**0.85**	**0.85**
4	2.85	**1.81**	**1.49**	**1.34**	**1.25**	**1.14**	**1.08**	**1.04**	**1.01**	**0.99**	**0.97**	**0.96**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.91**	**0.90**
5	3.10	**1.92**	**1.57**	**1.41**	**1.31**	**1.19**	**1.13**	**1.09**	**1.06**	**1.03**	**1.02**	**1.01**	**1.00**	**0.98**	**0.97**	**0.97**	**0.96**	**0.96**	**0.95**	**0.94**
8	3.66	**2.17**	**1.75**	**1.55**	**1.44**	**1.31**	**1.24**	**1.18**	**1.15**	**1.13**	**1.11**	**1.10**	**1.09**	**1.07**	**1.06**	**1.05**	**1.04**	**1.04**	**1.03**	**1.02**
12	4.22	*2.41*	**1.91**	**1.68**	**1.55**	**1.41**	**1.33**	**1.27**	**1.23**	**1.20**	**1.19**	**1.17**	**1.16**	**1.14**	**1.13**	**1.12**	**1.11**	**1.11**	**1.10**	**1.09**
16	4.67	2.58	**2.03**	**1.78**	**1.63**	**1.48**	**1.39**	**1.33**	**1.29**	**1.26**	**1.24**	**1.22**	**1.21**	**1.19**	**1.18**	**1.17**	**1.16**	**1.16**	**1.15**	**1.14**
20	5.04	2.72	**2.12**	**1.85**	**1.70**	**1.53**	**1.44**	**1.37**	**1.33**	**1.30**	**1.28**	**1.26**	**1.25**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**
30	5.79	2.99	*2.29*	**1.98**	**1.81**	**1.63**	**1.53**	**1.45**	**1.41**	**1.38**	**1.35**	**1.33**	**1.32**	**1.30**	**1.28**	**1.27**	**1.26**	**1.26**	**1.25**	**1.24**
40	6.39	3.19	*2.42*	**2.08**	**1.90**	**1.70**	**1.59**	**1.51**	**1.46**	**1.43**	**1.40**	**1.38**	**1.37**	**1.35**	**1.33**	**1.32**	**1.31**	**1.30**	**1.29**	**1.28**
50	6.90	3.35	2.52	**2.16**	**1.96**	**1.75**	**1.64**	**1.56**	**1.50**	**1.47**	**1.44**	**1.42**	**1.41**	**1.38**	**1.37**	**1.35**	**1.35**	**1.34**	**1.32**	**1.32**
60	7.34	3.49	2.60	**2.22**	**2.02**	**1.79**	**1.68**	**1.59**	**1.54**	**1.50**	**1.47**	**1.45**	**1.44**	**1.41**	**1.40**	**1.38**	**1.37**	**1.37**	**1.35**	**1.34**
75	7.91	3.67	2.71	*2.30*	**2.08**	**1.85**	**1.72**	**1.64**	**1.58**	**1.54**	**1.51**	**1.49**	**1.47**	**1.45**	**1.43**	**1.42**	**1.41**	**1.40**	**1.39**	**1.38**
100	8.72	3.90	2.85	*2.41*	**2.17**	**1.92**	**1.79**	**1.69**	**1.63**	**1.59**	**1.56**	**1.54**	**1.52**	**1.49**	**1.48**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**
125	9.40	4.10	2.96	*2.49*	**2.24**	**1.97**	**1.83**	**1.74**	**1.67**	**1.63**	**1.60**	**1.57**	**1.56**	**1.53**	**1.51**	**1.50**	**1.48**	**1.48**	**1.46**	**1.45**
150	9.99	4.26	3.05	2.56	*2.30*	**2.02**	**1.88**	**1.77**	**1.71**	**1.66**	**1.63**	**1.60**	**1.59**	**1.56**	**1.54**	**1.52**	**1.51**	**1.50**	**1.49**	**1.48**
175	10.55	4.41	3.13	2.62	*2.34*	**2.05**	**1.91**	**1.80**	**1.73**	**1.69**	**1.66**	**1.63**	**1.61**	**1.58**	**1.56**	**1.55**	**1.53**	**1.53**	**1.51**	**1.50**
200	11.02	4.54	3.21	2.67	*2.39*	**2.09**	**1.94**	**1.83**	**1.76**	**1.71**	**1.68**	**1.65**	**1.63**	**1.60**	**1.58**	**1.57**	**1.55**	**1.55**	**1.53**	**1.52**

Table 19-12. κ-Multipliers for 1-of-4 Intrawell Prediction Limits on Observations (10 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.11**	**1.46**	**1.23**	**1.12**	**1.05**	**0.97**	**0.92**	**0.88**	**0.86**	**0.84**	**0.83**	**0.82**	**0.82**	**0.80**	**0.80**	**0.79**	**0.79**	**0.78**	**0.78**	**0.77**
2	2.75	**1.79**	**1.48**	**1.33**	**1.24**	**1.14**	**1.08**	**1.04**	**1.01**	**0.99**	**0.97**	**0.96**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.91**	**0.90**
3	3.20	**2.00**	**1.63**	**1.46**	**1.35**	**1.24**	**1.17**	**1.12**	**1.09**	**1.07**	**1.05**	**1.04**	**1.03**	**1.02**	**1.01**	**1.00**	**0.99**	**0.99**	**0.98**	**0.97**
4	3.54	**2.15**	**1.74**	**1.55**	**1.43**	**1.31**	**1.24**	**1.18**	**1.15**	**1.13**	**1.11**	**1.10**	**1.08**	**1.07**	**1.06**	**1.05**	**1.04**	**1.04**	**1.03**	**1.02**
5	3.83	**2.27**	**1.83**	**1.62**	**1.50**	**1.36**	**1.29**	**1.23**	**1.19**	**1.17**	**1.15**	**1.14**	**1.13**	**1.11**	**1.10**	**1.09**	**1.08**	**1.08**	**1.07**	**1.06**
8	4.52	**2.55**	**2.02**	**1.77**	**1.63**	**1.47**	**1.39**	**1.33**	**1.29**	**1.26**	**1.24**	**1.22**	**1.21**	**1.19**	**1.18**	**1.17**	**1.16**	**1.16**	**1.15**	**1.14**
12	5.20	2.81	**2.19**	**1.90**	**1.75**	**1.57**	**1.48**	**1.41**	**1.36**	**1.33**	**1.31**	**1.29**	**1.28**	**1.26**	**1.25**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**
16	5.74	3.00	**2.31**	**2.00**	**1.83**	**1.64**	**1.54**	**1.47**	**1.42**	**1.39**	**1.36**	**1.34**	**1.33**	**1.31**	**1.29**	**1.28**	**1.28**	**1.27**	**1.26**	**1.25**
20	6.20	3.16	**2.41**	**2.08**	**1.89**	**1.69**	**1.59**	**1.51**	**1.46**	**1.43**	**1.40**	**1.38**	**1.37**	**1.35**	**1.33**	**1.32**	**1.31**	**1.30**	**1.29**	**1.28**
30	7.11	3.46	*2.59*	**2.22**	**2.01**	**1.79**	**1.68**	**1.59**	**1.54**	**1.50**	**1.47**	**1.45**	**1.44**	**1.41**	**1.40**	**1.38**	**1.37**	**1.37**	**1.35**	**1.34**
40	7.84	3.69	*2.73*	**2.32**	**2.10**	**1.86**	**1.74**	**1.65**	**1.59**	**1.55**	**1.52**	**1.50**	**1.48**	**1.46**	**1.44**	**1.43**	**1.42**	**1.41**	**1.40**	**1.39**
50	8.45	3.87	2.84	**2.41**	**2.17**	**1.92**	**1.79**	**1.69**	**1.63**	**1.59**	**1.56**	**1.54**	**1.52**	**1.49**	**1.48**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**
60	8.99	4.03	2.93	**2.47**	**2.22**	**1.96**	**1.83**	**1.73**	**1.66**	**1.62**	**1.59**	**1.57**	**1.55**	**1.52**	**1.50**	**1.49**	**1.48**	**1.47**	**1.45**	**1.44**
75	9.70	4.23	3.05	*2.56*	**2.29**	**2.02**	**1.87**	**1.77**	**1.71**	**1.66**	**1.63**	**1.60**	**1.59**	**1.56**	**1.54**	**1.52**	**1.51**	**1.50**	**1.49**	**1.48**
100	10.66	4.50	3.20	*2.67*	**2.38**	**2.09**	**1.94**	**1.83**	**1.76**	**1.71**	**1.68**	**1.65**	**1.63**	**1.60**	**1.58**	**1.57**	**1.55**	**1.54**	**1.53**	**1.52**
125	11.51	4.72	3.32	*2.75*	**2.45**	**2.14**	**1.98**	**1.87**	**1.80**	**1.75**	**1.71**	**1.69**	**1.67**	**1.64**	**1.61**	**1.60**	**1.59**	**1.58**	**1.56**	**1.55**
150	12.25	4.91	3.42	2.83	**2.51**	**2.19**	**2.03**	**1.90**	**1.83**	**1.78**	**1.74**	**1.72**	**1.70**	**1.66**	**1.64**	**1.62**	**1.61**	**1.60**	**1.58**	**1.57**
175	12.89	5.07	3.51	2.89	*2.56*	**2.23**	**2.06**	**1.94**	**1.86**	**1.81**	**1.77**	**1.74**	**1.72**	**1.69**	**1.66**	**1.65**	**1.64**	**1.62**	**1.61**	**1.59**
200	13.48	5.21	3.59	2.94	*2.61*	**2.26**	**2.09**	**1.96**	**1.88**	**1.83**	**1.79**	**1.76**	**1.74**	**1.71**	**1.68**	**1.67**	**1.65**	**1.64**	**1.62**	**1.61**

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Table 19-12. κ-Multipliers for 1-of-4 Intrawell Prediction Limits on Observations (20 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.70**	**1.19**	**1.01**	**0.92**	**0.86**	**0.80**	**0.76**	**0.73**	**0.71**	**0.69**	**0.68**	**0.68**	**0.67**	**0.66**	**0.65**	**0.65**	**0.65**	**0.64**	**0.64**	**0.63**
2	2.25	**1.49**	**1.25**	**1.13**	**1.06**	**0.97**	**0.92**	**0.89**	**0.86**	**0.85**	**0.83**	**0.82**	**0.82**	**0.81**	**0.80**	**0.79**	**0.79**	**0.78**	**0.78**	**0.77**
3	2.62	**1.68**	**1.39**	**1.25**	**1.17**	**1.07**	**1.02**	**0.98**	**0.95**	**0.93**	**0.92**	**0.91**	**0.90**	**0.89**	**0.88**	**0.87**	**0.87**	**0.86**	**0.85**	**0.85**
4	2.91	**1.82**	**1.50**	**1.34**	**1.25**	**1.14**	**1.08**	**1.04**	**1.01**	**0.99**	**0.97**	**0.96**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.91**	**0.90**
5	3.16	**1.94**	**1.58**	**1.41**	**1.31**	**1.20**	**1.13**	**1.09**	**1.06**	**1.03**	**1.02**	**1.01**	**1.00**	**0.98**	**0.97**	**0.97**	**0.96**	**0.96**	**0.95**	**0.94**
8	3.74	2.19	**1.76**	**1.56**	**1.44**	**1.31**	**1.24**	**1.18**	**1.15**	**1.13**	**1.11**	**1.10**	**1.09**	**1.07**	**1.06**	**1.05**	**1.04**	**1.04**	**1.03**	**1.02**
12	4.31	2.42	**1.91**	**1.68**	**1.55**	**1.41**	**1.33**	**1.27**	**1.23**	**1.20**	**1.19**	**1.17**	**1.16**	**1.14**	**1.13**	**1.12**	**1.11**	**1.11**	**1.10**	**1.09**
16	4.76	2.59	*2.03*	**1.78**	**1.63**	**1.48**	**1.39**	**1.33**	**1.29**	**1.26**	**1.24**	**1.22**	**1.21**	**1.19**	**1.18**	**1.17**	**1.16**	**1.16**	**1.15**	**1.14**
20	5.14	2.73	*2.12*	**1.85**	**1.70**	**1.53**	**1.44**	**1.37**	**1.33**	**1.30**	**1.28**	**1.26**	**1.25**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**
30	5.90	3.00	2.30	*1.99*	**1.81**	**1.63**	**1.53**	**1.45**	**1.41**	**1.38**	**1.35**	**1.33**	**1.32**	**1.30**	**1.28**	**1.27**	**1.26**	**1.26**	**1.25**	**1.24**
40	6.51	3.20	2.42	*2.08*	**1.90**	**1.70**	**1.59**	**1.51**	**1.46**	**1.43**	**1.40**	**1.38**	**1.37**	**1.35**	**1.33**	**1.32**	**1.31**	**1.30**	**1.29**	**1.28**
50	7.02	3.37	2.52	*2.16*	*1.96*	**1.75**	**1.64**	**1.56**	**1.50**	**1.47**	**1.44**	**1.42**	**1.41**	**1.38**	**1.37**	**1.35**	**1.35**	**1.34**	**1.32**	**1.32**
60	7.47	3.51	2.61	2.23	*2.02*	**1.79**	**1.68**	**1.59**	**1.54**	**1.50**	**1.47**	**1.45**	**1.44**	**1.41**	**1.40**	**1.38**	**1.37**	**1.37**	**1.35**	**1.34**
75	8.06	3.68	2.71	2.31	*2.08*	**1.85**	**1.72**	**1.64**	**1.58**	**1.54**	**1.51**	**1.49**	**1.47**	**1.45**	**1.43**	**1.42**	**1.41**	**1.40**	**1.39**	**1.37**
100	8.88	3.93	2.85	2.41	*2.17*	**1.92**	**1.79**	**1.69**	**1.63**	**1.59**	**1.56**	**1.54**	**1.52**	**1.49**	**1.48**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**
125	9.58	4.12	2.97	2.49	*2.24*	*1.97*	**1.83**	**1.74**	**1.67**	**1.63**	**1.60**	**1.57**	**1.56**	**1.53**	**1.51**	**1.50**	**1.48**	**1.48**	**1.46**	**1.45**
150	10.20	4.28	3.06	2.56	2.30	*2.02*	**1.88**	**1.77**	**1.71**	**1.66**	**1.63**	**1.60**	**1.59**	**1.56**	**1.54**	**1.52**	**1.51**	**1.50**	**1.49**	**1.48**
175	10.72	4.42	3.14	2.62	2.34	*2.06*	**1.91**	**1.80**	**1.73**	**1.69**	**1.66**	**1.63**	**1.61**	**1.58**	**1.56**	**1.55**	**1.53**	**1.53**	**1.51**	**1.50**
200	11.19	4.56	3.21	2.67	2.39	*2.09*	**1.94**	**1.83**	**1.76**	**1.71**	**1.68**	**1.65**	**1.63**	**1.60**	**1.58**	**1.57**	**1.55**	**1.55**	**1.53**	**1.52**

Table 19-12. κ-Multipliers for 1-of-4 Intrawell Prediction Limits on Observations (20 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.20**	**1.48**	**1.24**	**1.13**	**1.05**	**0.97**	**0.92**	**0.89**	**0.86**	**0.85**	**0.83**	**0.82**	**0.82**	**0.81**	**0.80**	**0.79**	**0.79**	**0.78**	**0.78**	**0.77**
2	2.85	**1.81**	**1.49**	**1.34**	**1.25**	**1.14**	**1.08**	**1.04**	**1.01**	**0.99**	**0.97**	**0.96**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.91**	**0.90**
3	3.31	**2.02**	**1.64**	**1.46**	**1.36**	**1.24**	**1.17**	**1.12**	**1.09**	**1.07**	**1.05**	**1.04**	**1.03**	**1.02**	**1.01**	**1.00**	**0.99**	**0.99**	**0.98**	**0.97**
4	3.66	**2.17**	**1.75**	**1.55**	**1.44**	**1.31**	**1.24**	**1.18**	**1.15**	**1.13**	**1.11**	**1.10**	**1.09**	**1.07**	**1.06**	**1.05**	**1.04**	**1.04**	**1.03**	**1.02**
5	3.96	*2.30*	**1.84**	**1.62**	**1.50**	**1.36**	**1.29**	**1.23**	**1.19**	**1.17**	**1.15**	**1.14**	**1.13**	**1.11**	**1.10**	**1.09**	**1.08**	**1.08**	**1.07**	**1.06**
8	4.67	2.58	**2.03**	**1.78**	**1.63**	**1.48**	**1.39**	**1.33**	**1.29**	**1.26**	**1.24**	**1.22**	**1.21**	**1.19**	**1.18**	**1.17**	**1.16**	**1.16**	**1.15**	**1.14**
12	5.37	2.84	**2.19**	**1.91**	**1.75**	**1.57**	**1.48**	**1.41**	**1.36**	**1.33**	**1.31**	**1.29**	**1.28**	**1.26**	**1.25**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**
16	5.93	3.03	*2.32*	**2.01**	**1.83**	**1.64**	**1.54**	**1.47**	**1.42**	**1.39**	**1.36**	**1.34**	**1.33**	**1.31**	**1.29**	**1.28**	**1.28**	**1.27**	**1.26**	**1.25**
20	6.39	3.19	*2.42*	**2.08**	**1.90**	**1.70**	**1.59**	**1.51**	**1.46**	**1.43**	**1.40**	**1.38**	**1.37**	**1.35**	**1.33**	**1.32**	**1.31**	**1.30**	**1.29**	**1.28**
30	7.34	3.49	2.60	**2.22**	**2.02**	**1.79**	**1.68**	**1.59**	**1.54**	**1.50**	**1.47**	**1.45**	**1.44**	**1.41**	**1.40**	**1.38**	**1.37**	**1.37**	**1.35**	**1.34**
40	8.09	3.72	2.74	*2.33*	**2.10**	**1.86**	**1.74**	**1.65**	**1.59**	**1.55**	**1.52**	**1.50**	**1.48**	**1.46**	**1.44**	**1.43**	**1.42**	**1.41**	**1.40**	**1.39**
50	8.72	3.91	2.85	*2.41*	**2.17**	**1.92**	**1.79**	**1.69**	**1.63**	**1.59**	**1.56**	**1.54**	**1.52**	**1.49**	**1.48**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**
60	9.27	4.06	2.94	*2.48*	**2.23**	**1.96**	**1.83**	**1.73**	**1.67**	**1.62**	**1.59**	**1.57**	**1.55**	**1.52**	**1.50**	**1.49**	**1.48**	**1.47**	**1.45**	**1.44**
75	9.99	4.26	3.05	2.56	*2.29*	**2.02**	**1.88**	**1.77**	**1.71**	**1.66**	**1.63**	**1.60**	**1.59**	**1.56**	**1.54**	**1.52**	**1.51**	**1.50**	**1.49**	**1.48**
100	11.02	4.53	3.21	2.67	*2.39*	**2.09**	**1.94**	**1.83**	**1.76**	**1.71**	**1.68**	**1.65**	**1.63**	**1.60**	**1.58**	**1.57**	**1.55**	**1.54**	**1.53**	**1.52**
125	11.87	4.75	3.33	2.76	*2.46*	**2.14**	**1.98**	**1.87**	**1.80**	**1.75**	**1.71**	**1.69**	**1.67**	**1.64**	**1.61**	**1.60**	**1.59**	**1.58**	**1.56**	**1.55**
150	12.60	4.94	3.43	2.83	*2.52*	**2.19**	**2.03**	**1.90**	**1.83**	**1.78**	**1.74**	**1.72**	**1.70**	**1.66**	**1.64**	**1.62**	**1.61**	**1.60**	**1.58**	**1.57**
175	13.30	5.10	3.52	2.89	*2.56*	**2.23**	**2.06**	**1.94**	**1.86**	**1.81**	**1.77**	**1.74**	**1.72**	**1.69**	**1.66**	**1.65**	**1.63**	**1.62**	**1.61**	**1.59**
200	13.89	5.24	3.60	2.95	2.61	*2.26*	**2.09**	**1.96**	**1.88**	**1.83**	**1.79**	**1.76**	**1.74**	**1.71**	**1.68**	**1.67**	**1.65**	**1.64**	**1.62**	**1.61**

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Table 19-12. κ-Multipliers for 1-of-4 Intrawell Prediction Limits on Observations (20 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	2.75	**1.79**	**1.48**	**1.33**	**1.24**	**1.14**	**1.08**	**1.04**	**1.01**	**0.99**	**0.97**	**0.96**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.91**	**0.90**
2	3.54	**2.15**	**1.74**	**1.55**	**1.43**	**1.31**	**1.24**	**1.18**	**1.15**	**1.13**	**1.11**	**1.10**	**1.08**	**1.07**	**1.06**	**1.05**	**1.04**	**1.04**	**1.03**	**1.02**
3	4.09	**2.38**	**1.90**	**1.68**	**1.55**	**1.40**	**1.33**	**1.27**	**1.23**	**1.20**	**1.19**	**1.17**	**1.16**	**1.14**	**1.13**	**1.12**	**1.11**	**1.11**	**1.10**	**1.09**
4	4.52	**2.55**	**2.02**	**1.77**	**1.63**	**1.47**	**1.39**	**1.33**	**1.29**	**1.26**	**1.24**	**1.22**	**1.21**	**1.19**	**1.18**	**1.17**	**1.16**	**1.16**	**1.15**	**1.14**
5	4.88	2.69	**2.11**	**1.84**	**1.69**	**1.53**	**1.44**	**1.37**	**1.33**	**1.30**	**1.28**	**1.26**	**1.25**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**
8	5.74	3.00	**2.31**	**2.00**	**1.83**	**1.64**	**1.54**	**1.47**	**1.42**	**1.39**	**1.36**	**1.34**	**1.33**	**1.31**	**1.29**	**1.28**	**1.28**	**1.27**	**1.26**	**1.25**
12	6.59	3.29	**2.49**	**2.14**	**1.95**	**1.74**	**1.63**	**1.55**	**1.50**	**1.46**	**1.43**	**1.41**	**1.40**	**1.38**	**1.36**	**1.35**	**1.34**	**1.33**	**1.32**	**1.31**
16	7.27	3.51	*2.62*	**2.24**	**2.03**	**1.81**	**1.69**	**1.60**	**1.55**	**1.51**	**1.48**	**1.46**	**1.45**	**1.42**	**1.41**	**1.39**	**1.38**	**1.38**	**1.36**	**1.35**
20	7.84	3.69	*2.73*	**2.32**	**2.10**	**1.86**	**1.74**	**1.65**	**1.59**	**1.55**	**1.52**	**1.50**	**1.48**	**1.46**	**1.44**	**1.43**	**1.42**	**1.41**	**1.40**	**1.39**
30	8.99	4.03	2.93	**2.47**	**2.22**	**1.96**	**1.83**	**1.73**	**1.66**	**1.62**	**1.59**	**1.57**	**1.55**	**1.52**	**1.50**	**1.49**	**1.48**	**1.47**	**1.45**	**1.44**
40	9.90	4.29	3.08	*2.58*	**2.31**	**2.03**	**1.89**	**1.78**	**1.72**	**1.67**	**1.64**	**1.62**	**1.60**	**1.57**	**1.55**	**1.53**	**1.52**	**1.51**	**1.50**	**1.49**
50	10.68	4.50	3.20	*2.67*	**2.38**	**2.09**	**1.94**	**1.83**	**1.76**	**1.71**	**1.68**	**1.65**	**1.63**	**1.60**	**1.58**	**1.57**	**1.55**	**1.54**	**1.53**	**1.52**
60	11.35	4.68	3.30	*2.74*	**2.44**	**2.13**	**1.98**	**1.86**	**1.79**	**1.74**	**1.71**	**1.68**	**1.66**	**1.63**	**1.61**	**1.59**	**1.58**	**1.57**	**1.55**	**1.54**
75	12.23	4.90	3.42	2.83	**2.51**	**2.19**	**2.02**	**1.91**	**1.83**	**1.78**	**1.74**	**1.72**	**1.70**	**1.66**	**1.64**	**1.63**	**1.61**	**1.60**	**1.58**	**1.57**
100	13.48	5.21	3.59	2.94	*2.61*	**2.26**	**2.09**	**1.96**	**1.88**	**1.83**	**1.79**	**1.76**	**1.74**	**1.71**	**1.68**	**1.67**	**1.65**	**1.64**	**1.62**	**1.61**
125	14.53	5.46	3.72	3.04	*2.68*	**2.32**	**2.14**	**2.00**	**1.92**	**1.87**	**1.83**	**1.80**	**1.77**	**1.74**	**1.72**	**1.70**	**1.68**	**1.67**	**1.65**	**1.64**
150	15.41	5.67	3.83	3.11	*2.74*	**2.37**	**2.18**	**2.04**	**1.96**	**1.90**	**1.86**	**1.83**	**1.80**	**1.77**	**1.74**	**1.72**	**1.71**	**1.70**	**1.68**	**1.67**
175	16.23	5.86	3.93	3.18	*2.79*	**2.41**	**2.21**	**2.07**	**1.98**	**1.92**	**1.88**	**1.85**	**1.83**	**1.79**	**1.76**	**1.74**	**1.73**	**1.72**	**1.70**	**1.69**
200	16.99	6.02	4.01	3.24	*2.84*	**2.44**	**2.24**	**2.09**	**2.01**	**1.95**	**1.90**	**1.87**	**1.85**	**1.81**	**1.78**	**1.76**	**1.75**	**1.74**	**1.72**	**1.70**

Table 19-12. κ-Multipliers for 1-of-4 Intrawell Prediction Limits on Observations (40 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	2.25	**1.49**	**1.25**	**1.13**	**1.06**	**0.97**	**0.92**	**0.89**	**0.86**	**0.85**	**0.83**	**0.82**	**0.82**	**0.81**	**0.80**	**0.79**	**0.79**	**0.78**	**0.78**	**0.77**
2	2.91	**1.82**	**1.50**	**1.34**	**1.25**	**1.14**	**1.08**	**1.04**	**1.01**	**0.99**	**0.97**	**0.96**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.91**	**0.90**
3	3.37	*2.03*	**1.65**	**1.47**	**1.36**	**1.24**	**1.17**	**1.12**	**1.09**	**1.07**	**1.05**	**1.04**	**1.03**	**1.02**	**1.01**	**1.00**	**0.99**	**0.99**	**0.98**	**0.97**
4	3.74	2.19	**1.76**	**1.56**	**1.44**	**1.31**	**1.24**	**1.18**	**1.15**	**1.13**	**1.11**	**1.10**	**1.09**	**1.07**	**1.06**	**1.05**	**1.04**	**1.04**	**1.03**	**1.02**
5	4.04	2.31	**1.84**	**1.63**	**1.50**	**1.36**	**1.29**	**1.23**	**1.19**	**1.17**	**1.15**	**1.14**	**1.13**	**1.11**	**1.10**	**1.09**	**1.08**	**1.08**	**1.07**	**1.06**
8	4.76	2.59	*2.03*	**1.78**	**1.63**	**1.48**	**1.39**	**1.33**	**1.29**	**1.26**	**1.24**	**1.22**	**1.21**	**1.19**	**1.18**	**1.17**	**1.16**	**1.16**	**1.15**	**1.14**
12	5.47	2.85	*2.20*	**1.91**	**1.75**	**1.57**	**1.48**	**1.41**	**1.37**	**1.33**	**1.31**	**1.29**	**1.28**	**1.26**	**1.25**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**
16	6.04	3.05	2.32	*2.01*	**1.83**	**1.64**	**1.54**	**1.47**	**1.42**	**1.39**	**1.36**	**1.34**	**1.33**	**1.31**	**1.29**	**1.28**	**1.28**	**1.27**	**1.26**	**1.25**
20	6.51	3.20	2.42	*2.08*	**1.90**	**1.70**	**1.59**	**1.51**	**1.46**	**1.43**	**1.40**	**1.38**	**1.37**	**1.35**	**1.33**	**1.32**	**1.31**	**1.30**	**1.29**	**1.28**
30	7.47	3.51	2.61	2.23	*2.02*	**1.79**	**1.68**	**1.59**	**1.54**	**1.50**	**1.47**	**1.45**	**1.44**	**1.41**	**1.40**	**1.38**	**1.37**	**1.37**	**1.35**	**1.34**
40	8.23	3.74	2.74	2.33	*2.10*	**1.86**	**1.74**	**1.65**	**1.59**	**1.55**	**1.52**	**1.50**	**1.48**	**1.46**	**1.44**	**1.43**	**1.42**	**1.41**	**1.39**	**1.38**
50	8.88	3.93	2.85	2.41	*2.17*	**1.92**	**1.79**	**1.69**	**1.63**	**1.59**	**1.56**	**1.54**	**1.52**	**1.49**	**1.48**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**
60	9.43	4.08	2.94	2.48	*2.23*	*1.96*	**1.83**	**1.73**	**1.66**	**1.62**	**1.59**	**1.57**	**1.55**	**1.52**	**1.50**	**1.49**	**1.48**	**1.47**	**1.45**	**1.44**
75	10.20	4.28	3.06	2.56	2.30	*2.02*	**1.88**	**1.77**	**1.71**	**1.66**	**1.63**	**1.60**	**1.59**	**1.56**	**1.54**	**1.52**	**1.51**	**1.50**	**1.49**	**1.48**
100	11.19	4.56	3.21	2.67	2.39	*2.09*	**1.94**	**1.83**	**1.76**	**1.71**	**1.68**	**1.65**	**1.63**	**1.60**	**1.58**	**1.57**	**1.55**	**1.55**	**1.53**	**1.52**
125	12.07	4.78	3.33	2.76	2.46	*2.15*	*1.98*	**1.87**	**1.80**	**1.75**	**1.71**	**1.69**	**1.67**	**1.64**	**1.61**	**1.60**	**1.59**	**1.58**	**1.56**	**1.55**
150	12.89	4.95	3.44	2.83	2.52	*2.19*	*2.03*	**1.90**	**1.83**	**1.78**	**1.74**	**1.72**	**1.70**	**1.66**	**1.64**	**1.63**	**1.61**	**1.60**	**1.59**	**1.57**
175	13.48	5.13	3.52	2.90	2.56	*2.23*	*2.06*	**1.93**	**1.86**	**1.81**	**1.77**	**1.74**	**1.72**	**1.69**	**1.66**	**1.65**	**1.63**	**1.62**	**1.60**	**1.59**
200	14.18	5.27	3.60	2.94	2.61	*2.26*	*2.09*	*1.96*	**1.88**	**1.83**	**1.79**	**1.77**	**1.74**	**1.71**	**1.68**	**1.67**	**1.65**	**1.64**	**1.62**	**1.61**

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Table 19-12. κ-Multipliers for 1-of-4 Intrawell Prediction Limits on Observations (40 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	2.85	**1.81**	**1.49**	**1.34**	**1.25**	**1.14**	**1.08**	**1.04**	**1.01**	**0.99**	**0.97**	**0.96**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.91**	**0.90**
2	3.66	**2.17**	**1.75**	**1.55**	**1.44**	**1.31**	**1.24**	**1.18**	**1.15**	**1.13**	**1.11**	**1.10**	**1.09**	**1.07**	**1.06**	**1.05**	**1.04**	**1.04**	**1.03**	**1.02**
3	4.22	*2.41*	**1.91**	**1.68**	**1.55**	**1.41**	**1.33**	**1.27**	**1.23**	**1.20**	**1.19**	**1.17**	**1.16**	**1.14**	**1.13**	**1.12**	**1.11**	**1.11**	**1.10**	**1.09**
4	4.67	2.58	**2.03**	**1.78**	**1.63**	**1.48**	**1.39**	**1.33**	**1.29**	**1.26**	**1.24**	**1.22**	**1.21**	**1.19**	**1.18**	**1.17**	**1.16**	**1.16**	**1.15**	**1.14**
5	5.04	2.72	**2.12**	**1.85**	**1.70**	**1.53**	**1.44**	**1.37**	**1.33**	**1.30**	**1.28**	**1.26**	**1.25**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**
8	5.93	3.03	*2.32*	**2.01**	**1.83**	**1.64**	**1.54**	**1.47**	**1.42**	**1.39**	**1.36**	**1.34**	**1.33**	**1.31**	**1.29**	**1.28**	**1.28**	**1.27**	**1.26**	**1.25**
12	6.80	3.32	2.50	**2.15**	**1.95**	**1.74**	**1.63**	**1.55**	**1.50**	**1.46**	**1.43**	**1.41**	**1.40**	**1.38**	**1.36**	**1.35**	**1.34**	**1.33**	**1.32**	**1.31**
16	7.50	3.54	2.63	**2.25**	**2.04**	**1.81**	**1.69**	**1.60**	**1.55**	**1.51**	**1.48**	**1.46**	**1.45**	**1.42**	**1.41**	**1.39**	**1.38**	**1.38**	**1.36**	**1.35**
20	8.09	3.72	2.74	*2.33*	**2.10**	**1.86**	**1.74**	**1.65**	**1.59**	**1.55**	**1.52**	**1.50**	**1.48**	**1.46**	**1.44**	**1.43**	**1.42**	**1.41**	**1.40**	**1.39**
30	9.27	4.06	2.94	*2.48*	**2.23**	**1.96**	**1.83**	**1.73**	**1.67**	**1.62**	**1.59**	**1.57**	**1.55**	**1.52**	**1.50**	**1.49**	**1.48**	**1.47**	**1.45**	**1.44**
40	10.21	4.32	3.09	2.59	*2.31*	**2.03**	**1.89**	**1.78**	**1.72**	**1.67**	**1.64**	**1.61**	**1.60**	**1.57**	**1.55**	**1.53**	**1.52**	**1.51**	**1.50**	**1.49**
50	11.02	4.53	3.21	2.67	*2.39*	**2.09**	**1.94**	**1.83**	**1.76**	**1.71**	**1.68**	**1.65**	**1.63**	**1.60**	**1.58**	**1.57**	**1.55**	**1.54**	**1.53**	**1.52**
60	11.72	4.72	3.31	2.74	*2.44*	**2.14**	**1.98**	**1.86**	**1.79**	**1.74**	**1.71**	**1.68**	**1.66**	**1.63**	**1.61**	**1.59**	**1.58**	**1.57**	**1.55**	**1.54**
75	12.60	4.94	3.43	2.83	*2.52*	**2.19**	**2.03**	**1.90**	**1.83**	**1.78**	**1.74**	**1.72**	**1.70**	**1.66**	**1.64**	**1.62**	**1.61**	**1.60**	**1.58**	**1.57**
100	13.89	5.24	3.60	2.95	2.61	*2.26*	**2.09**	**1.96**	**1.88**	**1.83**	**1.79**	**1.76**	**1.74**	**1.71**	**1.68**	**1.67**	**1.65**	**1.64**	**1.62**	**1.61**
125	15.00	5.51	3.73	3.04	2.68	*2.32*	**2.14**	**2.00**	**1.92**	**1.87**	**1.83**	**1.80**	**1.77**	**1.74**	**1.72**	**1.70**	**1.68**	**1.67**	**1.65**	**1.64**
150	15.94	5.71	3.84	3.12	2.75	*2.37*	**2.18**	**2.04**	**1.96**	**1.90**	**1.86**	**1.83**	**1.80**	**1.77**	**1.74**	**1.72**	**1.71**	**1.70**	**1.68**	**1.67**
175	16.76	5.89	3.94	3.18	2.80	*2.40*	**2.21**	**2.07**	**1.98**	**1.93**	**1.88**	**1.85**	**1.83**	**1.79**	**1.77**	**1.75**	**1.73**	**1.72**	**1.70**	**1.69**
200	17.58	6.06	4.01	3.24	2.84	*2.44*	**2.24**	**2.09**	**2.01**	**1.95**	**1.90**	**1.87**	**1.85**	**1.81**	**1.78**	**1.77**	**1.75**	**1.74**	**1.72**	**1.70**

Table 19-12. κ-Multipliers for 1-of-4 Intrawell Prediction Limits on Observations (40 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.54	**2.15**	**1.74**	**1.55**	**1.43**	**1.31**	**1.24**	**1.18**	**1.15**	**1.13**	**1.11**	**1.10**	**1.08**	**1.07**	**1.06**	**1.05**	**1.04**	**1.04**	**1.03**	**1.02**
2	4.52	**2.55**	**2.02**	**1.77**	**1.63**	**1.47**	**1.39**	**1.33**	**1.29**	**1.26**	**1.24**	**1.22**	**1.21**	**1.19**	**1.18**	**1.17**	**1.16**	**1.16**	**1.15**	**1.14**
3	5.20	2.81	**2.19**	**1.90**	**1.75**	**1.57**	**1.48**	**1.41**	**1.36**	**1.33**	**1.31**	**1.29**	**1.28**	**1.26**	**1.25**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**
4	5.74	3.00	**2.31**	**2.00**	**1.83**	**1.64**	**1.54**	**1.47**	**1.42**	**1.39**	**1.36**	**1.34**	**1.33**	**1.31**	**1.29**	**1.28**	**1.28**	**1.27**	**1.26**	**1.25**
5	6.20	3.16	**2.41**	**2.08**	**1.89**	**1.69**	**1.59**	**1.51**	**1.46**	**1.43**	**1.40**	**1.38**	**1.37**	**1.35**	**1.33**	**1.32**	**1.31**	**1.30**	**1.29**	**1.28**
8	7.27	3.51	*2.62*	**2.24**	**2.03**	**1.81**	**1.69**	**1.60**	**1.55**	**1.51**	**1.48**	**1.46**	**1.45**	**1.42**	**1.41**	**1.39**	**1.38**	**1.38**	**1.36**	**1.35**
12	8.34	3.84	2.82	**2.39**	**2.16**	**1.91**	**1.78**	**1.68**	**1.62**	**1.58**	**1.55**	**1.53**	**1.51**	**1.49**	**1.47**	**1.46**	**1.45**	**1.44**	**1.42**	**1.41**
16	9.18	4.09	2.96	**2.50**	**2.24**	**1.98**	**1.84**	**1.74**	**1.68**	**1.63**	**1.60**	**1.58**	**1.56**	**1.53**	**1.51**	**1.50**	**1.49**	**1.48**	**1.46**	**1.45**
20	9.90	4.29	3.08	*2.58*	**2.31**	**2.03**	**1.89**	**1.78**	**1.72**	**1.67**	**1.64**	**1.62**	**1.60**	**1.57**	**1.55**	**1.53**	**1.52**	**1.51**	**1.50**	**1.49**
30	11.35	4.68	3.30	*2.74*	**2.44**	**2.13**	**1.98**	**1.86**	**1.79**	**1.74**	**1.71**	**1.68**	**1.66**	**1.63**	**1.61**	**1.59**	**1.58**	**1.57**	**1.55**	**1.54**
40	12.51	4.97	3.46	2.85	**2.53**	**2.21**	**2.04**	**1.92**	**1.84**	**1.79**	**1.76**	**1.73**	**1.71**	**1.67**	**1.65**	**1.63**	**1.62**	**1.61**	**1.59**	**1.58**
50	13.48	5.21	3.59	2.94	*2.61*	**2.26**	**2.09**	**1.96**	**1.88**	**1.83**	**1.79**	**1.76**	**1.74**	**1.71**	**1.68**	**1.67**	**1.65**	**1.64**	**1.62**	**1.61**
60	14.33	5.41	3.69	3.02	*2.67*	**2.31**	**2.13**	**2.00**	**1.92**	**1.86**	**1.82**	**1.79**	**1.77**	**1.73**	**1.71**	**1.69**	**1.68**	**1.67**	**1.65**	**1.63**	**1.63**
75	15.41	5.67	3.83	3.11	*2.74*	**2.37**	**2.18**	**2.04**	**1.96**	**1.90**	**1.86**	**1.83**	**1.80**	**1.77**	**1.74**	**1.72**	**1.71**	**1.70**	**1.68**	**1.66**
100	16.99	6.02	4.01	3.24	*2.84*	**2.44**	**2.24**	**2.09**	**2.01**	**1.95**	**1.90**	**1.87**	**1.85**	**1.81**	**1.78**	**1.76**	**1.75**	**1.74**	**1.72**	**1.70**
125	18.28	6.30	4.15	3.34	2.92	**2.50**	**2.29**	**2.14**	**2.05**	**1.98**	**1.94**	**1.91**	**1.88**	**1.84**	**1.81**	**1.79**	**1.78**	**1.77**	**1.74**	**1.73**
150	19.45	6.56	4.28	3.42	2.98	*2.55*	**2.33**	**2.18**	**2.08**	**2.01**	**1.97**	**1.93**	**1.91**	**1.87**	**1.84**	**1.82**	**1.81**	**1.79**	**1.77**	**1.76**
175	20.51	6.77	4.38	3.49	3.03	*2.59*	**2.36**	**2.20**	**2.11**	**2.04**	**1.99**	**1.96**	**1.93**	**1.89**	**1.86**	**1.84**	**1.83**	**1.81**	**1.79**	**1.78**
200	21.33	6.94	4.47	3.54	3.08	*2.62*	**2.39**	**2.23**	**2.13**	**2.07**	**2.01**	**1.98**	**1.95**	**1.91**	**1.88**	**1.86**	**1.85**	**1.83**	**1.81**	**1.79**

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Table 19-13. κ-Multipliers for Modified Calif. Intrawell Prediction Limits on Observations (1 COC, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**0.71**	**0.59**	**0.53**	**0.50**	**0.48**	**0.45**	**0.44**	**0.43**	**0.42**	**0.41**	**0.41**	**0.41**	**0.40**	**0.40**	**0.40**	**0.40**	**0.39**	**0.39**	**0.39**	**0.39**
2	**1.14**	**0.92**	**0.83**	**0.78**	**0.74**	**0.71**	**0.68**	**0.66**	**0.65**	**0.64**	**0.64**	**0.63**	**0.63**	**0.62**	**0.62**	**0.62**	**0.61**	**0.61**	**0.61**	**0.61**
3	**1.42**	**1.11**	**0.99**	**0.93**	**0.89**	**0.84**	**0.81**	**0.79**	**0.78**	**0.77**	**0.76**	**0.75**	**0.75**	**0.74**	**0.74**	**0.73**	**0.73**	**0.73**	**0.73**	**0.72**
4	**1.63**	**1.25**	**1.11**	**1.04**	**0.99**	**0.94**	**0.90**	**0.88**	**0.86**	**0.85**	**0.84**	**0.84**	**0.83**	**0.82**	**0.82**	**0.81**	**0.81**	**0.81**	**0.80**	**0.80**
5	**1.80**	**1.36**	**1.20**	**1.12**	**1.07**	**1.01**	**0.97**	**0.94**	**0.93**	**0.91**	**0.90**	**0.90**	**0.89**	**0.88**	**0.88**	**0.87**	**0.87**	**0.87**	**0.86**	**0.86**
8	**2.19**	**1.60**	**1.40**	**1.29**	**1.23**	**1.15**	**1.11**	**1.08**	**1.05**	**1.04**	**1.03**	**1.02**	**1.01**	**1.00**	**1.00**	**0.99**	**0.99**	**0.98**	**0.98**	**0.97**
12	2.58	**1.82**	**1.57**	**1.44**	**1.36**	**1.27**	**1.22**	**1.19**	**1.16**	**1.14**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.09**	**1.08**	**1.08**	**1.07**	**1.07**
16	2.88	**1.98**	**1.69**	**1.54**	**1.46**	**1.36**	**1.30**	**1.26**	**1.23**	**1.22**	**1.20**	**1.19**	**1.18**	**1.17**	**1.16**	**1.15**	**1.15**	**1.14**	**1.14**	**1.13**
20	3.13	**2.11**	**1.78**	**1.63**	**1.53**	**1.42**	**1.37**	**1.32**	**1.29**	**1.27**	**1.26**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**	**1.20**	**1.19**	**1.19**	**1.18**
30	3.63	**2.35**	**1.96**	**1.78**	**1.67**	**1.54**	**1.47**	**1.42**	**1.39**	**1.37**	**1.35**	**1.34**	**1.33**	**1.31**	**1.30**	**1.29**	**1.29**	**1.28**	**1.27**	**1.27**
40	4.02	**2.53**	**2.09**	**1.88**	**1.76**	**1.63**	**1.55**	**1.49**	**1.46**	**1.43**	**1.41**	**1.40**	**1.39**	**1.37**	**1.36**	**1.35**	**1.35**	**1.34**	**1.33**	**1.32**
50	4.36	2.68	**2.20**	**1.97**	**1.84**	**1.69**	**1.61**	**1.55**	**1.51**	**1.48**	**1.46**	**1.45**	**1.44**	**1.42**	**1.41**	**1.40**	**1.39**	**1.39**	**1.38**	**1.37**
60	4.65	2.80	**2.28**	**2.04**	**1.90**	**1.74**	**1.66**	**1.59**	**1.55**	**1.53**	**1.50**	**1.49**	**1.48**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**	**1.41**	**1.40**
75	5.02	2.96	**2.39**	**2.12**	**1.97**	**1.81**	**1.72**	**1.65**	**1.60**	**1.58**	**1.55**	**1.54**	**1.52**	**1.50**	**1.49**	**1.48**	**1.47**	**1.47**	**1.46**	**1.45**
100	5.55	3.17	**2.53**	**2.24**	**2.07**	**1.89**	**1.79**	**1.72**	**1.67**	**1.64**	**1.62**	**1.60**	**1.58**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**	**1.51**	**1.50**
125	5.99	3.34	*2.64*	**2.32**	**2.15**	**1.95**	**1.85**	**1.77**	**1.72**	**1.69**	**1.66**	**1.64**	**1.63**	**1.61**	**1.59**	**1.58**	**1.57**	**1.56**	**1.55**	**1.54**
150	6.38	3.48	2.73	**2.40**	**2.21**	**2.00**	**1.89**	**1.81**	**1.76**	**1.73**	**1.70**	**1.68**	**1.67**	**1.64**	**1.63**	**1.61**	**1.61**	**1.60**	**1.58**	**1.58**
175	6.72	3.60	2.81	**2.46**	**2.26**	**2.05**	**1.93**	**1.85**	**1.80**	**1.76**	**1.73**	**1.71**	**1.70**	**1.67**	**1.66**	**1.64**	**1.63**	**1.63**	**1.61**	**1.60**
200	7.04	3.72	2.88	**2.51**	**2.31**	**2.09**	**1.97**	**1.88**	**1.83**	**1.79**	**1.76**	**1.74**	**1.72**	**1.70**	**1.68**	**1.67**	**1.66**	**1.65**	**1.64**	**1.63**

Table 19-13. κ-Multipliers for Modified Calif. Intrawell Prediction Limits on Observations (1 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.07**	**0.88**	**0.81**	**0.76**	**0.73**	**0.70**	**0.68**	**0.66**	**0.65**	**0.64**	**0.64**	**0.63**	**0.63**	**0.62**	**0.62**	**0.62**	**0.61**	**0.61**	**0.61**	**0.61**
2	**1.55**	**1.22**	**1.09**	**1.02**	**0.98**	**0.93**	**0.90**	**0.88**	**0.86**	**0.85**	**0.84**	**0.83**	**0.83**	**0.82**	**0.82**	**0.81**	**0.81**	**0.81**	**0.80**	**0.80**
3	**1.86**	**1.42**	**1.26**	**1.18**	**1.12**	**1.06**	**1.02**	**0.99**	**0.97**	**0.96**	**0.95**	**0.94**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.91**	**0.91**	**0.90**
4	**2.10**	**1.57**	**1.38**	**1.28**	**1.22**	**1.15**	**1.11**	**1.07**	**1.05**	**1.04**	**1.03**	**1.02**	**1.01**	**1.00**	**1.00**	**0.99**	**0.99**	**0.98**	**0.98**	**0.97**
5	**2.30**	**1.69**	**1.47**	**1.36**	**1.29**	**1.21**	**1.17**	**1.13**	**1.11**	**1.10**	**1.08**	**1.08**	**1.07**	**1.06**	**1.05**	**1.04**	**1.04**	**1.04**	**1.03**	**1.03**
8	**2.77**	**1.95**	**1.67**	**1.54**	**1.45**	**1.36**	**1.30**	**1.26**	**1.23**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**	**1.16**	**1.15**	**1.15**	**1.14**	**1.14**	**1.13**
12	3.23	**2.18**	**1.85**	**1.69**	**1.59**	**1.47**	**1.41**	**1.36**	**1.33**	**1.31**	**1.30**	**1.29**	**1.28**	**1.26**	**1.25**	**1.24**	**1.24**	**1.23**	**1.22**	**1.22**
16	3.59	**2.36**	**1.98**	**1.79**	**1.68**	**1.56**	**1.49**	**1.44**	**1.40**	**1.38**	**1.36**	**1.35**	**1.34**	**1.32**	**1.31**	**1.31**	**1.30**	**1.29**	**1.29**	**1.28**
20	3.89	**2.50**	**2.08**	**1.88**	**1.76**	**1.62**	**1.55**	**1.49**	**1.46**	**1.43**	**1.41**	**1.40**	**1.39**	**1.37**	**1.36**	**1.35**	**1.35**	**1.34**	**1.33**	**1.32**
30	4.49	**2.77**	**2.27**	**2.03**	**1.89**	**1.74**	**1.66**	**1.59**	**1.55**	**1.53**	**1.50**	**1.49**	**1.48**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**	**1.41**	**1.40**
40	4.97	2.97	**2.40**	**2.14**	**1.99**	**1.82**	**1.73**	**1.66**	**1.62**	**1.59**	**1.57**	**1.55**	**1.54**	**1.52**	**1.50**	**1.49**	**1.48**	**1.48**	**1.47**	**1.46**
50	5.37	3.13	**2.51**	**2.23**	**2.07**	**1.89**	**1.79**	**1.72**	**1.67**	**1.64**	**1.61**	**1.60**	**1.58**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**	**1.51**	**1.50**
60	5.72	3.27	**2.60**	**2.30**	**2.13**	**1.94**	**1.84**	**1.76**	**1.71**	**1.68**	**1.65**	**1.63**	**1.62**	**1.60**	**1.58**	**1.57**	**1.56**	**1.56**	**1.54**	**1.54**
75	6.17	3.44	**2.72**	**2.39**	**2.20**	**2.00**	**1.89**	**1.81**	**1.76**	**1.73**	**1.70**	**1.68**	**1.67**	**1.64**	**1.63**	**1.61**	**1.61**	**1.60**	**1.58**	**1.58**
100	6.81	3.68	*2.87*	**2.51**	**2.30**	**2.08**	**1.97**	**1.88**	**1.83**	**1.79**	**1.76**	**1.74**	**1.72**	**1.70**	**1.68**	**1.67**	**1.66**	**1.65**	**1.64**	**1.63**
125	7.35	3.87	2.99	**2.60**	**2.38**	**2.15**	**2.02**	**1.93**	**1.87**	**1.83**	**1.81**	**1.78**	**1.77**	**1.74**	**1.72**	**1.71**	**1.70**	**1.69**	**1.68**	**1.67**
150	7.82	4.03	3.09	**2.68**	**2.45**	**2.20**	**2.07**	**1.97**	**1.91**	**1.87**	**1.84**	**1.82**	**1.80**	**1.78**	**1.76**	**1.74**	**1.73**	**1.72**	**1.71**	**1.70**
175	8.25	4.17	3.17	**2.74**	**2.50**	**2.24**	**2.11**	**2.01**	**1.95**	**1.91**	**1.87**	**1.85**	**1.83**	**1.80**	**1.78**	**1.77**	**1.76**	**1.75**	**1.74**	**1.72**
200	8.63	4.29	3.25	**2.80**	**2.55**	**2.28**	**2.14**	**2.04**	**1.98**	**1.93**	**1.90**	**1.88**	**1.86**	**1.83**	**1.81**	**1.79**	**1.78**	**1.77**	**1.76**	**1.75**

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Table 19-13. κ-Multipliers for Modified Calif. Intrawell Prediction Limits on Observations (1 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.43**	**1.17**	**1.06**	**1.00**	**0.96**	**0.92**	**0.89**	**0.87**	**0.85**	**0.84**	**0.84**	**0.83**	**0.83**	**0.82**	**0.81**	**0.81**	**0.81**	**0.81**	**0.80**	**0.80**
2	**1.97**	**1.52**	**1.35**	**1.26**	**1.20**	**1.14**	**1.10**	**1.07**	**1.05**	**1.04**	**1.02**	**1.02**	**1.01**	**1.00**	**0.99**	**0.99**	**0.99**	**0.98**	**0.98**	**0.97**
3	**2.33**	**1.74**	**1.52**	**1.41**	**1.34**	**1.26**	**1.22**	**1.18**	**1.16**	**1.14**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.09**	**1.08**	**1.08**	**1.07**	**1.07**
4	**2.61**	**1.90**	**1.65**	**1.52**	**1.44**	**1.35**	**1.30**	**1.26**	**1.23**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**	**1.16**	**1.15**	**1.15**	**1.14**	**1.14**	**1.13**
5	**2.84**	**2.02**	**1.74**	**1.60**	**1.52**	**1.41**	**1.36**	**1.32**	**1.29**	**1.27**	**1.25**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**	**1.20**	**1.19**	**1.19**	**1.18**
8	3.39	**2.31**	**1.95**	**1.78**	**1.67**	**1.55**	**1.49**	**1.44**	**1.40**	**1.38**	**1.36**	**1.35**	**1.34**	**1.32**	**1.31**	**1.31**	**1.30**	**1.29**	**1.28**	**1.28**
12	3.93	**2.56**	**2.14**	**1.93**	**1.81**	**1.67**	**1.59**	**1.54**	**1.50**	**1.47**	**1.45**	**1.44**	**1.43**	**1.41**	**1.40**	**1.39**	**1.38**	**1.38**	**1.37**	**1.36**
16	4.35	**2.76**	**2.27**	**2.04**	**1.91**	**1.75**	**1.67**	**1.61**	**1.57**	**1.54**	**1.52**	**1.50**	**1.49**	**1.47**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**	**1.42**
20	4.71	**2.91**	**2.38**	**2.13**	**1.98**	**1.82**	**1.73**	**1.66**	**1.62**	**1.59**	**1.57**	**1.55**	**1.54**	**1.52**	**1.50**	**1.49**	**1.48**	**1.48**	**1.47**	**1.46**
30	5.42	3.21	**2.58**	**2.29**	**2.12**	**1.93**	**1.83**	**1.76**	**1.71**	**1.68**	**1.65**	**1.63**	**1.62**	**1.60**	**1.58**	**1.57**	**1.56**	**1.56**	**1.54**	**1.54**
40	5.99	3.43	**2.73**	**2.40**	**2.22**	**2.02**	**1.91**	**1.83**	**1.77**	**1.74**	**1.71**	**1.69**	**1.68**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**	**1.59**
50	6.47	3.61	**2.84**	**2.50**	**2.30**	**2.08**	**1.96**	**1.88**	**1.82**	**1.79**	**1.76**	**1.74**	**1.72**	**1.70**	**1.68**	**1.67**	**1.66**	**1.65**	**1.64**	**1.63**
60	6.89	3.77	**2.94**	**2.57**	**2.36**	**2.13**	**2.01**	**1.92**	**1.86**	**1.83**	**1.80**	**1.78**	**1.76**	**1.73**	**1.72**	**1.70**	**1.69**	**1.68**	**1.67**	**1.66**
75	7.43	3.96	**3.06**	**2.66**	**2.44**	**2.20**	**2.07**	**1.97**	**1.91**	**1.87**	**1.84**	**1.82**	**1.80**	**1.77**	**1.76**	**1.74**	**1.73**	**1.72**	**1.71**	**1.70**
100	8.20	4.22	3.23	**2.79**	**2.54**	**2.28**	**2.14**	**2.04**	**1.98**	**1.93**	**1.90**	**1.88**	**1.86**	**1.83**	**1.81**	**1.79**	**1.78**	**1.77**	**1.76**	**1.75**
125	8.84	4.43	3.35	**2.88**	**2.62**	**2.35**	**2.20**	**2.09**	**2.02**	**1.98**	**1.95**	**1.92**	**1.90**	**1.87**	**1.85**	**1.83**	**1.82**	**1.81**	**1.80**	**1.79**
150	9.40	4.62	3.46	**2.96**	**2.69**	**2.40**	**2.25**	**2.13**	**2.06**	**2.02**	**1.98**	**1.95**	**1.93**	**1.90**	**1.88**	**1.87**	**1.85**	**1.84**	**1.83**	**1.82**
175	9.90	4.77	3.55	**3.03**	**2.75**	**2.44**	**2.29**	**2.17**	**2.10**	**2.05**	**2.01**	**1.98**	**1.96**	**1.93**	**1.91**	**1.89**	**1.88**	**1.87**	**1.85**	**1.84**
200	10.36	4.91	3.64	*3.09*	**2.80**	**2.48**	**2.32**	**2.20**	**2.13**	**2.07**	**2.04**	**2.01**	**1.99**	**1.96**	**1.93**	**1.92**	**1.90**	**1.89**	**1.88**	**1.86**

Table 19-13. κ-Multipliers for Modified Calif. Intrawell Prediction Limits on Observations (2 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.14**	**0.92**	**0.83**	**0.78**	**0.74**	**0.71**	**0.68**	**0.66**	**0.65**	**0.64**	**0.64**	**0.63**	**0.63**	**0.62**	**0.62**	**0.62**	**0.61**	**0.61**	**0.61**	**0.61**
2	**1.63**	**1.25**	**1.11**	**1.04**	**0.99**	**0.94**	**0.90**	**0.88**	**0.86**	**0.85**	**0.84**	**0.84**	**0.83**	**0.82**	**0.82**	**0.81**	**0.81**	**0.81**	**0.80**	**0.80**
3	**1.95**	**1.46**	**1.28**	**1.19**	**1.13**	**1.06**	**1.03**	**1.00**	**0.98**	**0.96**	**0.95**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.92**	**0.91**	**0.91**	**0.90**
4	**2.19**	**1.60**	**1.40**	**1.29**	**1.23**	**1.15**	**1.11**	**1.08**	**1.05**	**1.04**	**1.03**	**1.02**	**1.01**	**1.00**	**1.00**	**0.99**	**0.99**	**0.98**	**0.98**	**0.97**
5	**2.40**	**1.72**	**1.49**	**1.37**	**1.30**	**1.22**	**1.17**	**1.14**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**	**1.06**	**1.05**	**1.04**	**1.04**	**1.04**	**1.03**	**1.03**
8	2.88	**1.98**	**1.69**	**1.54**	**1.46**	**1.36**	**1.30**	**1.26**	**1.23**	**1.22**	**1.20**	**1.19**	**1.18**	**1.17**	**1.16**	**1.15**	**1.15**	**1.14**	**1.14**	**1.13**
12	3.35	**2.22**	**1.86**	**1.69**	**1.59**	**1.48**	**1.41**	**1.37**	**1.34**	**1.31**	**1.30**	**1.29**	**1.28**	**1.26**	**1.25**	**1.24**	**1.24**	**1.23**	**1.23**	**1.22**
16	3.72	**2.39**	**1.99**	**1.80**	**1.69**	**1.56**	**1.49**	**1.44**	**1.41**	**1.38**	**1.36**	**1.35**	**1.34**	**1.32**	**1.31**	**1.31**	**1.30**	**1.29**	**1.29**	**1.28**
20	4.02	**2.53**	**2.09**	**1.88**	**1.76**	**1.63**	**1.55**	**1.49**	**1.46**	**1.43**	**1.41**	**1.40**	**1.39**	**1.37**	**1.36**	**1.35**	**1.35**	**1.34**	**1.33**	**1.32**
30	4.65	2.80	**2.28**	**2.04**	**1.90**	**1.74**	**1.66**	**1.59**	**1.55**	**1.53**	**1.50**	**1.49**	**1.48**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**	**1.41**	**1.40**
40	5.14	3.00	**2.42**	**2.15**	**1.99**	**1.82**	**1.73**	**1.66**	**1.62**	**1.59**	**1.57**	**1.55**	**1.54**	**1.52**	**1.50**	**1.49**	**1.48**	**1.48**	**1.47**	**1.46**
50	5.55	3.17	**2.53**	**2.24**	**2.07**	**1.89**	**1.79**	**1.72**	**1.67**	**1.64**	**1.62**	**1.60**	**1.58**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**	**1.51**	**1.50**
60	5.91	3.31	*2.62*	**2.31**	**2.13**	**1.94**	**1.84**	**1.76**	**1.71**	**1.68**	**1.65**	**1.64**	**1.62**	**1.60**	**1.58**	**1.57**	**1.56**	**1.56**	**1.54**	**1.54**
75	6.38	3.48	2.73	**2.40**	**2.21**	**2.00**	**1.89**	**1.81**	**1.76**	**1.73**	**1.70**	**1.68**	**1.67**	**1.64**	**1.63**	**1.61**	**1.61**	**1.60**	**1.58**	**1.58**
100	7.04	3.72	2.88	**2.51**	**2.31**	**2.09**	**1.97**	**1.88**	**1.83**	**1.79**	**1.76**	**1.74**	**1.72**	**1.70**	**1.68**	**1.67**	**1.66**	**1.65**	**1.64**	**1.63**
125	7.60	3.91	3.00	*2.61*	**2.39**	**2.15**	**2.03**	**1.93**	**1.88**	**1.83**	**1.81**	**1.78**	**1.77**	**1.74**	**1.72**	**1.71**	**1.70**	**1.69**	**1.68**	**1.67**
150	8.09	4.07	3.10	*2.68*	**2.45**	**2.20**	**2.07**	**1.98**	**1.92**	**1.87**	**1.84**	**1.82**	**1.80**	**1.78**	**1.76**	**1.74**	**1.73**	**1.72**	**1.71**	**1.70**
175	8.51	4.21	3.19	2.75	**2.50**	**2.25**	**2.11**	**2.01**	**1.95**	**1.91**	**1.87**	**1.85**	**1.83**	**1.80**	**1.79**	**1.77**	**1.76**	**1.75**	**1.74**	**1.72**
200	8.91	4.34	3.26	2.81	*2.55*	**2.29**	**2.14**	**2.04**	**1.98**	**1.93**	**1.90**	**1.88**	**1.86**	**1.83**	**1.81**	**1.79**	**1.78**	**1.77**	**1.76**	**1.75**

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Table 19-13. κ-Multipliers for Modified Calif. Intrawell Prediction Limits on Observations (2 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.55**	**1.22**	**1.09**	**1.02**	**0.98**	**0.93**	**0.90**	**0.88**	**0.86**	**0.85**	**0.84**	**0.83**	**0.83**	**0.82**	**0.82**	**0.81**	**0.81**	**0.81**	**0.80**	**0.80**
2	**2.10**	**1.57**	**1.38**	**1.28**	**1.22**	**1.15**	**1.11**	**1.07**	**1.05**	**1.04**	**1.03**	**1.02**	**1.01**	**1.00**	**1.00**	**0.99**	**0.99**	**0.98**	**0.98**	**0.97**
3	**2.48**	**1.79**	**1.55**	**1.43**	**1.36**	**1.27**	**1.22**	**1.18**	**1.16**	**1.14**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.09**	**1.08**	**1.08**	**1.07**	**1.07**
4	**2.77**	**1.95**	**1.67**	**1.54**	**1.45**	**1.36**	**1.30**	**1.26**	**1.23**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**	**1.16**	**1.15**	**1.15**	**1.14**	**1.14**	**1.13**
5	3.01	**2.08**	**1.77**	**1.62**	**1.53**	**1.42**	**1.36**	**1.32**	**1.29**	**1.27**	**1.25**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**	**1.20**	**1.19**	**1.19**	**1.18**
8	3.59	**2.36**	**1.98**	**1.79**	**1.68**	**1.56**	**1.49**	**1.44**	**1.40**	**1.38**	**1.36**	**1.35**	**1.34**	**1.32**	**1.31**	**1.31**	**1.30**	**1.29**	**1.29**	**1.28**
12	4.15	**2.62**	**2.16**	**1.95**	**1.82**	**1.68**	**1.60**	**1.54**	**1.50**	**1.47**	**1.46**	**1.44**	**1.43**	**1.41**	**1.40**	**1.39**	**1.38**	**1.38**	**1.37**	**1.36**
16	4.59	**2.81**	**2.30**	**2.06**	**1.91**	**1.76**	**1.67**	**1.61**	**1.57**	**1.54**	**1.52**	**1.50**	**1.49**	**1.47**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**	**1.42**
20	4.97	2.97	**2.40**	**2.14**	**1.99**	**1.82**	**1.73**	**1.66**	**1.62**	**1.59**	**1.57**	**1.55**	**1.54**	**1.52**	**1.50**	**1.49**	**1.48**	**1.48**	**1.47**	**1.46**
30	5.72	3.27	**2.60**	**2.30**	**2.13**	**1.94**	**1.84**	**1.76**	**1.71**	**1.68**	**1.65**	**1.63**	**1.62**	**1.60**	**1.58**	**1.57**	**1.56**	**1.56**	**1.54**	**1.54**
40	6.31	3.50	**2.75**	**2.42**	**2.23**	**2.02**	**1.91**	**1.83**	**1.78**	**1.74**	**1.71**	**1.69**	**1.68**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**	**1.59**
50	6.81	3.68	*2.87*	**2.51**	**2.30**	**2.08**	**1.97**	**1.88**	**1.83**	**1.79**	**1.76**	**1.74**	**1.72**	**1.70**	**1.68**	**1.67**	**1.66**	**1.65**	**1.64**	**1.63**
60	7.25	3.83	*2.97*	**2.58**	**2.37**	**2.14**	**2.01**	**1.92**	**1.87**	**1.83**	**1.80**	**1.78**	**1.76**	**1.73**	**1.72**	**1.70**	**1.69**	**1.68**	**1.67**	**1.66**
75	7.82	4.03	3.09	**2.68**	**2.45**	**2.20**	**2.07**	**1.97**	**1.91**	**1.87**	**1.84**	**1.82**	**1.80**	**1.78**	**1.76**	**1.74**	**1.73**	**1.72**	**1.71**	**1.70**
100	8.63	4.29	3.25	**2.80**	**2.55**	**2.28**	**2.14**	**2.04**	**1.98**	**1.93**	**1.90**	**1.88**	**1.86**	**1.83**	**1.81**	**1.79**	**1.78**	**1.77**	**1.76**	**1.75**
125	9.30	4.51	3.38	*2.89*	**2.63**	**2.35**	**2.20**	**2.09**	**2.03**	**1.98**	**1.95**	**1.92**	**1.90**	**1.87**	**1.85**	**1.83**	**1.82**	**1.81**	**1.80**	**1.79**
150	9.89	4.69	3.49	*2.98*	**2.70**	**2.40**	**2.25**	**2.14**	**2.06**	**2.02**	**1.98**	**1.95**	**1.93**	**1.90**	**1.88**	**1.87**	**1.85**	**1.84**	**1.83**	**1.82**
175	10.43	4.85	3.58	3.04	**2.75**	**2.45**	**2.29**	**2.17**	**2.10**	**2.05**	**2.01**	**1.98**	**1.96**	**1.93**	**1.91**	**1.89**	**1.88**	**1.87**	**1.85**	**1.84**
200	10.90	5.00	3.66	3.11	*2.80*	**2.48**	**2.32**	**2.20**	**2.13**	**2.07**	**2.04**	**2.01**	**1.99**	**1.96**	**1.93**	**1.92**	**1.90**	**1.89**	**1.88**	**1.86**

Table 19-13. κ-Multipliers for Modified Calif. Intrawell Prediction Limits on Observations (2 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.97**	**1.52**	**1.35**	**1.26**	**1.20**	**1.14**	**1.10**	**1.07**	**1.05**	**1.04**	**1.02**	**1.02**	**1.01**	**1.00**	**0.99**	**0.99**	**0.99**	**0.98**	**0.98**	**0.97**
2	**2.61**	**1.90**	**1.65**	**1.52**	**1.44**	**1.35**	**1.30**	**1.26**	**1.23**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**	**1.16**	**1.15**	**1.15**	**1.14**	**1.14**	**1.13**
3	3.04	**2.13**	**1.82**	**1.67**	**1.58**	**1.47**	**1.41**	**1.36**	**1.33**	**1.31**	**1.30**	**1.28**	**1.27**	**1.26**	**1.25**	**1.24**	**1.24**	**1.23**	**1.22**	**1.22**
4	3.39	**2.31**	**1.95**	**1.78**	**1.67**	**1.55**	**1.49**	**1.44**	**1.40**	**1.38**	**1.36**	**1.35**	**1.34**	**1.32**	**1.31**	**1.31**	**1.30**	**1.29**	**1.28**	**1.28**
5	3.68	**2.45**	**2.05**	**1.86**	**1.75**	**1.62**	**1.55**	**1.49**	**1.46**	**1.43**	**1.41**	**1.40**	**1.39**	**1.37**	**1.36**	**1.35**	**1.35**	**1.34**	**1.33**	**1.32**
8	4.35	**2.76**	**2.27**	**2.04**	**1.91**	**1.75**	**1.67**	**1.61**	**1.57**	**1.54**	**1.52**	**1.50**	**1.49**	**1.47**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**	**1.42**
12	5.02	**3.04**	**2.47**	**2.20**	**2.04**	**1.87**	**1.78**	**1.70**	**1.66**	**1.63**	**1.61**	**1.59**	**1.57**	**1.55**	**1.54**	**1.53**	**1.52**	**1.51**	**1.50**	**1.49**
16	5.55	3.26	**2.61**	**2.31**	**2.14**	**1.95**	**1.85**	**1.77**	**1.72**	**1.69**	**1.67**	**1.65**	**1.63**	**1.61**	**1.60**	**1.58**	**1.58**	**1.57**	**1.56**	**1.55**
20	5.99	3.43	**2.73**	**2.40**	**2.22**	**2.02**	**1.91**	**1.83**	**1.77**	**1.74**	**1.71**	**1.69**	**1.68**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**	**1.59**
30	6.89	3.77	**2.94**	**2.57**	**2.36**	**2.13**	**2.01**	**1.92**	**1.86**	**1.83**	**1.80**	**1.78**	**1.76**	**1.73**	**1.72**	**1.70**	**1.69**	**1.68**	**1.67**	**1.66**
40	7.60	4.02	*3.10*	**2.69**	**2.46**	**2.22**	**2.09**	**1.99**	**1.93**	**1.89**	**1.86**	**1.83**	**1.81**	**1.79**	**1.77**	**1.75**	**1.74**	**1.73**	**1.72**	**1.71**
50	8.20	4.22	3.23	**2.79**	**2.54**	**2.28**	**2.14**	**2.04**	**1.98**	**1.93**	**1.90**	**1.88**	**1.86**	**1.83**	**1.81**	**1.79**	**1.78**	**1.77**	**1.76**	**1.75**
60	8.72	4.40	3.33	**2.87**	**2.61**	**2.33**	**2.19**	**2.08**	**2.02**	**1.97**	**1.94**	**1.91**	**1.89**	**1.86**	**1.84**	**1.83**	**1.82**	**1.81**	**1.79**	**1.78**
75	9.40	4.62	3.46	**2.96**	**2.69**	**2.40**	**2.25**	**2.13**	**2.06**	**2.02**	**1.98**	**1.95**	**1.93**	**1.90**	**1.88**	**1.87**	**1.85**	**1.84**	**1.83**	**1.82**
100	10.36	4.91	3.64	*3.09*	**2.80**	**2.48**	**2.32**	**2.20**	**2.13**	**2.07**	**2.04**	**2.01**	**1.99**	**1.96**	**1.93**	**1.92**	**1.90**	**1.89**	**1.88**	**1.86**
125	11.18	5.16	3.78	*3.20*	**2.88**	**2.55**	**2.38**	**2.25**	**2.17**	**2.12**	**2.08**	**2.05**	**2.03**	**1.99**	**1.97**	**1.95**	**1.94**	**1.93**	**1.91**	**1.90**
150	11.88	5.36	3.89	*3.28*	**2.95**	**2.60**	**2.42**	**2.29**	**2.21**	**2.16**	**2.12**	**2.09**	**2.06**	**2.03**	**2.00**	**1.98**	**1.97**	**1.96**	**1.94**	**1.93**
175	12.51	5.54	4.00	3.35	**3.01**	**2.65**	**2.46**	**2.33**	**2.24**	**2.19**	**2.15**	**2.11**	**2.09**	**2.05**	**2.03**	**2.01**	**2.00**	**1.99**	**1.97**	**1.95**
200	13.10	5.70	4.08	3.42	**3.06**	**2.69**	**2.50**	**2.36**	**2.27**	**2.21**	**2.17**	**2.14**	**2.11**	**2.08**	**2.05**	**2.03**	**2.02**	**2.01**	**1.99**	**1.97**

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Table 19-13. κ-Multipliers for Modified Calif. Intrawell Prediction Limits on Observations (5 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.80**	**1.36**	**1.20**	**1.12**	**1.07**	**1.01**	**0.97**	**0.94**	**0.93**	**0.91**	**0.90**	**0.90**	**0.89**	**0.88**	**0.88**	**0.87**	**0.87**	**0.87**	**0.86**	**0.86**
2	**2.40**	**1.72**	**1.49**	**1.37**	**1.30**	**1.22**	**1.17**	**1.14**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**	**1.06**	**1.05**	**1.04**	**1.04**	**1.04**	**1.03**	**1.03**
3	2.81	**1.94**	**1.66**	**1.52**	**1.44**	**1.34**	**1.29**	**1.25**	**1.22**	**1.20**	**1.19**	**1.18**	**1.17**	**1.15**	**1.15**	**1.14**	**1.13**	**1.13**	**1.12**	**1.12**
4	3.13	**2.11**	**1.78**	**1.63**	**1.53**	**1.42**	**1.37**	**1.32**	**1.29**	**1.27**	**1.26**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**	**1.20**	**1.19**	**1.19**	**1.18**
5	3.40	**2.24**	**1.88**	**1.71**	**1.61**	**1.49**	**1.43**	**1.38**	**1.35**	**1.32**	**1.31**	**1.30**	**1.29**	**1.27**	**1.26**	**1.25**	**1.25**	**1.24**	**1.23**	**1.23**
8	4.02	**2.53**	**2.09**	**1.88**	**1.76**	**1.63**	**1.55**	**1.49**	**1.46**	**1.43**	**1.41**	**1.40**	**1.39**	**1.37**	**1.36**	**1.35**	**1.35**	**1.34**	**1.33**	**1.32**
12	4.65	2.80	**2.28**	**2.04**	**1.90**	**1.74**	**1.66**	**1.59**	**1.55**	**1.53**	**1.50**	**1.49**	**1.48**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**	**1.41**	**1.40**
16	5.14	3.00	**2.42**	**2.15**	**1.99**	**1.82**	**1.73**	**1.66**	**1.62**	**1.59**	**1.57**	**1.55**	**1.54**	**1.52**	**1.50**	**1.49**	**1.48**	**1.48**	**1.47**	**1.46**
20	5.55	3.17	**2.53**	**2.24**	**2.07**	**1.89**	**1.79**	**1.72**	**1.67**	**1.64**	**1.62**	**1.60**	**1.58**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**	**1.51**	**1.50**
30	6.38	3.48	2.73	**2.40**	**2.21**	**2.00**	**1.89**	**1.81**	**1.76**	**1.73**	**1.70**	**1.68**	**1.67**	**1.64**	**1.63**	**1.61**	**1.61**	**1.60**	**1.59**	**1.58**
40	7.04	3.72	2.88	**2.51**	**2.31**	**2.09**	**1.97**	**1.88**	**1.83**	**1.79**	**1.76**	**1.74**	**1.72**	**1.70**	**1.68**	**1.67**	**1.66**	**1.65**	**1.64**	**1.63**
50	7.60	3.91	3.00	*2.60*	**2.39**	**2.15**	**2.03**	**1.93**	**1.88**	**1.83**	**1.81**	**1.78**	**1.77**	**1.74**	**1.72**	**1.71**	**1.70**	**1.69**	**1.68**	**1.67**
60	8.09	4.07	3.10	*2.68*	**2.45**	**2.20**	**2.07**	**1.98**	**1.91**	**1.87**	**1.84**	**1.82**	**1.80**	**1.77**	**1.76**	**1.74**	**1.73**	**1.72**	**1.71**	**1.70**
75	8.71	4.28	3.23	2.78	*2.53*	**2.27**	**2.13**	**2.03**	**1.96**	**1.92**	**1.89**	**1.86**	**1.84**	**1.82**	**1.80**	**1.78**	**1.77**	**1.76**	**1.75**	**1.74**
100	9.61	4.55	3.39	2.90	*2.63*	**2.35**	**2.20**	**2.09**	**2.03**	**1.98**	**1.95**	**1.92**	**1.90**	**1.87**	**1.85**	**1.83**	**1.82**	**1.81**	**1.80**	**1.78**
125	10.35	4.78	3.53	3.00	*2.71*	**2.41**	**2.26**	**2.14**	**2.07**	**2.02**	**1.99**	**1.96**	**1.94**	**1.91**	**1.89**	**1.87**	**1.86**	**1.85**	**1.83**	**1.82**
150	11.02	4.96	3.63	3.08	2.78	**2.47**	**2.30**	**2.19**	**2.11**	**2.06**	**2.03**	**2.00**	**1.98**	**1.94**	**1.92**	**1.90**	**1.89**	**1.88**	**1.87**	**1.85**
175	11.60	5.14	3.73	3.15	2.84	*2.51*	**2.34**	**2.22**	**2.14**	**2.09**	**2.06**	**2.03**	**2.00**	**1.97**	**1.95**	**1.93**	**1.92**	**1.91**	**1.89**	**1.88**
200	12.11	5.27	3.82	3.21	2.89	*2.55*	**2.38**	**2.25**	**2.17**	**2.12**	**2.08**	**2.05**	**2.03**	**1.99**	**1.97**	**1.95**	**1.94**	**1.93**	**1.91**	**1.90**

Table 19-13. κ-Multipliers for Modified Calif. Intrawell Prediction Limits on Observations (5 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.30**	**1.69**	**1.47**	**1.36**	**1.29**	**1.21**	**1.17**	**1.13**	**1.11**	**1.10**	**1.08**	**1.08**	**1.07**	**1.06**	**1.05**	**1.04**	**1.04**	**1.04**	**1.03**	**1.03**
2	3.01	**2.08**	**1.77**	**1.62**	**1.53**	**1.42**	**1.36**	**1.32**	**1.29**	**1.27**	**1.25**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**	**1.20**	**1.19**	**1.19**	**1.18**
3	3.50	**2.32**	**1.95**	**1.77**	**1.66**	**1.54**	**1.47**	**1.42**	**1.39**	**1.37**	**1.35**	**1.34**	**1.33**	**1.31**	**1.30**	**1.29**	**1.29**	**1.28**	**1.27**	**1.27**
4	3.89	**2.50**	**2.08**	**1.88**	**1.76**	**1.62**	**1.55**	**1.49**	**1.46**	**1.43**	**1.41**	**1.40**	**1.39**	**1.37**	**1.36**	**1.35**	**1.35**	**1.34**	**1.33**	**1.32**
5	4.21	**2.65**	**2.18**	**1.96**	**1.83**	**1.69**	**1.61**	**1.55**	**1.51**	**1.48**	**1.46**	**1.45**	**1.44**	**1.42**	**1.41**	**1.40**	**1.39**	**1.39**	**1.38**	**1.37**
8	4.97	2.97	**2.40**	**2.14**	**1.99**	**1.82**	**1.73**	**1.66**	**1.62**	**1.59**	**1.57**	**1.55**	**1.54**	**1.52**	**1.50**	**1.49**	**1.48**	**1.48**	**1.47**	**1.46**
12	5.72	3.27	**2.60**	**2.30**	**2.13**	**1.94**	**1.84**	**1.76**	**1.71**	**1.68**	**1.65**	**1.63**	**1.62**	**1.60**	**1.58**	**1.57**	**1.56**	**1.56**	**1.54**	**1.54**
16	6.31	3.49	**2.75**	**2.42**	**2.23**	**2.02**	**1.91**	**1.83**	**1.78**	**1.74**	**1.71**	**1.69**	**1.68**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**	**1.59**
20	6.81	3.68	*2.87*	**2.51**	**2.30**	**2.08**	**1.97**	**1.88**	**1.83**	**1.79**	**1.76**	**1.74**	**1.72**	**1.70**	**1.68**	**1.67**	**1.66**	**1.65**	**1.64**	**1.63**
30	7.82	4.03	3.09	**2.68**	**2.45**	**2.20**	**2.07**	**1.97**	**1.91**	**1.87**	**1.84**	**1.82**	**1.80**	**1.77**	**1.76**	**1.74**	**1.73**	**1.72**	**1.71**	**1.70**
40	8.62	4.29	3.25	**2.80**	**2.55**	**2.28**	**2.14**	**2.04**	**1.98**	**1.93**	**1.90**	**1.88**	**1.86**	**1.83**	**1.81**	**1.79**	**1.78**	**1.77**	**1.76**	**1.75**
50	9.30	4.51	3.38	*2.90*	**2.63**	**2.35**	**2.20**	**2.09**	**2.03**	**1.98**	**1.95**	**1.92**	**1.90**	**1.87**	**1.85**	**1.83**	**1.82**	**1.81**	**1.80**	**1.79**
60	9.88	4.69	3.49	*2.98*	**2.70**	**2.40**	**2.25**	**2.14**	**2.06**	**2.02**	**1.98**	**1.95**	**1.93**	**1.90**	**1.88**	**1.87**	**1.85**	**1.84**	**1.83**	**1.82**
75	10.66	4.92	3.62	3.08	**2.78**	**2.47**	**2.30**	**2.19**	**2.11**	**2.06**	**2.03**	**2.00**	**1.98**	**1.94**	**1.92**	**1.90**	**1.89**	**1.88**	**1.86**	**1.85**
100	11.76	5.23	3.80	3.21	*2.89*	**2.55**	**2.38**	**2.25**	**2.17**	**2.12**	**2.08**	**2.05**	**2.03**	**1.99**	**1.97**	**1.95**	**1.94**	**1.93**	**1.91**	**1.90**
125	12.66	5.49	3.95	3.31	*2.97*	**2.62**	**2.43**	**2.30**	**2.22**	**2.17**	**2.12**	**2.09**	**2.07**	**2.03**	**2.01**	**1.99**	**1.98**	**1.97**	**1.95**	**1.93**
150	13.44	5.70	4.06	3.40	*3.04*	**2.67**	**2.48**	**2.34**	**2.26**	**2.20**	**2.16**	**2.13**	**2.10**	**2.07**	**2.04**	**2.02**	**2.01**	**2.00**	**1.98**	**1.96**
175	14.14	5.90	4.17	3.47	3.10	**2.71**	**2.52**	**2.38**	**2.29**	**2.23**	**2.19**	**2.16**	**2.13**	**2.09**	**2.07**	**2.05**	**2.03**	**2.02**	**2.00**	**1.99**
200	14.84	6.05	4.26	3.54	3.15	**2.75**	**2.55**	**2.41**	**2.32**	**2.26**	**2.21**	**2.18**	**2.16**	**2.12**	**2.09**	**2.07**	**2.06**	**2.04**	**2.02**	**2.01**

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Table 19-13. κ-Multipliers for Modified Calif. Intrawell Prediction Limits on Observations (5 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.84**	**2.02**	**1.74**	**1.60**	**1.52**	**1.41**	**1.36**	**1.32**	**1.29**	**1.27**	**1.25**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**	**1.20**	**1.19**	**1.19**	**1.18**
2	3.68	**2.45**	**2.05**	**1.86**	**1.75**	**1.62**	**1.55**	**1.49**	**1.46**	**1.43**	**1.41**	**1.40**	**1.39**	**1.37**	**1.36**	**1.35**	**1.35**	**1.34**	**1.33**	**1.32**
3	4.25	**2.71**	**2.24**	**2.02**	**1.88**	**1.74**	**1.65**	**1.59**	**1.55**	**1.52**	**1.50**	**1.49**	**1.48**	**1.46**	**1.44**	**1.44**	**1.43**	**1.42**	**1.41**	**1.40**
4	4.71	**2.91**	**2.38**	**2.13**	**1.98**	**1.82**	**1.73**	**1.66**	**1.62**	**1.59**	**1.57**	**1.55**	**1.54**	**1.52**	**1.50**	**1.49**	**1.48**	**1.48**	**1.47**	**1.46**
5	5.09	**3.07**	**2.49**	**2.22**	**2.06**	**1.88**	**1.79**	**1.71**	**1.67**	**1.64**	**1.61**	**1.60**	**1.58**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**	**1.51**	**1.50**
8	5.99	3.43	**2.73**	**2.40**	**2.22**	**2.02**	**1.91**	**1.83**	**1.77**	**1.74**	**1.71**	**1.69**	**1.68**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**	**1.59**
12	6.89	3.77	**2.94**	**2.57**	**2.36**	**2.13**	**2.01**	**1.92**	**1.86**	**1.83**	**1.80**	**1.78**	**1.76**	**1.73**	**1.71**	**1.70**	**1.69**	**1.68**	**1.67**	**1.66**
16	7.60	4.02	*3.10*	**2.69**	**2.46**	**2.22**	**2.09**	**1.99**	**1.93**	**1.89**	**1.86**	**1.83**	**1.81**	**1.79**	**1.77**	**1.75**	**1.74**	**1.73**	**1.72**	**1.71**
20	8.20	4.22	3.23	**2.79**	**2.54**	**2.28**	**2.14**	**2.04**	**1.98**	**1.93**	**1.90**	**1.88**	**1.86**	**1.83**	**1.81**	**1.79**	**1.78**	**1.77**	**1.76**	**1.75**
30	9.40	4.62	3.46	**2.97**	**2.69**	**2.40**	**2.25**	**2.13**	**2.06**	**2.02**	**1.98**	**1.95**	**1.93**	**1.90**	**1.88**	**1.87**	**1.85**	**1.84**	**1.83**	**1.82**
40	10.36	4.91	3.64	*3.09*	**2.80**	**2.48**	**2.32**	**2.20**	**2.13**	**2.07**	**2.04**	**2.01**	**1.99**	**1.96**	**1.93**	**1.92**	**1.90**	**1.89**	**1.88**	**1.86**
50	11.17	5.16	3.78	*3.20*	**2.88**	**2.55**	**2.38**	**2.25**	**2.17**	**2.12**	**2.08**	**2.05**	**2.03**	**2.00**	**1.97**	**1.95**	**1.94**	**1.93**	**1.91**	**1.90**
60	11.88	5.36	3.89	*3.28*	**2.95**	**2.60**	**2.42**	**2.29**	**2.21**	**2.16**	**2.12**	**2.09**	**2.06**	**2.03**	**2.00**	**1.98**	**1.97**	**1.96**	**1.94**	**1.93**
75	12.81	5.62	4.04	3.39	**3.03**	**2.67**	**2.48**	**2.34**	**2.26**	**2.20**	**2.16**	**2.13**	**2.10**	**2.07**	**2.04**	**2.02**	**2.01**	**2.00**	**1.98**	**1.96**
100	14.10	5.98	4.23	3.53	*3.15*	**2.75**	**2.55**	**2.41**	**2.32**	**2.26**	**2.21**	**2.18**	**2.16**	**2.12**	**2.09**	**2.07**	**2.06**	**2.04**	**2.02**	**2.00**
125	15.20	6.26	4.39	3.63	*3.23*	**2.82**	**2.61**	**2.46**	**2.37**	**2.30**	**2.26**	**2.22**	**2.19**	**2.16**	**2.13**	**2.11**	**2.09**	**2.08**	**2.05**	**2.04**
150	16.17	6.50	4.52	3.73	*3.31*	**2.88**	**2.66**	**2.50**	**2.40**	**2.34**	**2.29**	**2.26**	**2.23**	**2.19**	**2.16**	**2.14**	**2.12**	**2.11**	**2.08**	**2.07**
175	17.03	6.72	4.63	3.81	3.37	**2.92**	**2.70**	**2.54**	**2.44**	**2.37**	**2.32**	**2.29**	**2.26**	**2.21**	**2.18**	**2.16**	**2.15**	**2.13**	**2.11**	**2.09**
200	17.81	6.91	4.74	3.88	3.43	**2.96**	**2.73**	**2.57**	**2.47**	**2.40**	**2.35**	**2.31**	**2.28**	**2.24**	**2.21**	**2.18**	**2.17**	**2.15**	**2.13**	**2.11**

Table 19-13. κ-Multipliers for Modified Calif. Intrawell Prediction Limits on Observations (10 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.40**	**1.72**	**1.49**	**1.37**	**1.30**	**1.22**	**1.17**	**1.14**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**	**1.06**	**1.05**	**1.04**	**1.04**	**1.04**	**1.03**	**1.03**
2	3.13	**2.11**	**1.78**	**1.63**	**1.53**	**1.42**	**1.37**	**1.32**	**1.29**	**1.27**	**1.26**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**	**1.20**	**1.19**	**1.19**	**1.18**
3	3.63	**2.35**	**1.96**	**1.78**	**1.67**	**1.54**	**1.47**	**1.42**	**1.39**	**1.37**	**1.35**	**1.34**	**1.33**	**1.31**	**1.30**	**1.29**	**1.29**	**1.28**	**1.27**	**1.27**
4	4.02	**2.53**	**2.09**	**1.88**	**1.76**	**1.63**	**1.55**	**1.49**	**1.46**	**1.43**	**1.41**	**1.40**	**1.39**	**1.37**	**1.36**	**1.35**	**1.35**	**1.34**	**1.33**	**1.32**
5	4.36	2.68	**2.20**	**1.97**	**1.84**	**1.69**	**1.61**	**1.55**	**1.51**	**1.48**	**1.46**	**1.45**	**1.44**	**1.42**	**1.41**	**1.40**	**1.39**	**1.39**	**1.38**	**1.37**
8	5.14	3.00	**2.42**	**2.15**	**1.99**	**1.82**	**1.73**	**1.66**	**1.62**	**1.59**	**1.57**	**1.55**	**1.54**	**1.52**	**1.50**	**1.49**	**1.49**	**1.48**	**1.47**	**1.46**
12	5.91	3.31	*2.62*	**2.31**	**2.13**	**1.94**	**1.84**	**1.76**	**1.71**	**1.68**	**1.65**	**1.63**	**1.62**	**1.60**	**1.58**	**1.57**	**1.56**	**1.56**	**1.54**	**1.54**
16	6.52	3.53	2.76	**2.42**	**2.23**	**2.02**	**1.91**	**1.83**	**1.78**	**1.74**	**1.71**	**1.69**	**1.68**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**	**1.59**
20	7.04	3.72	2.88	**2.51**	**2.31**	**2.09**	**1.97**	**1.88**	**1.83**	**1.79**	**1.76**	**1.74**	**1.72**	**1.70**	**1.68**	**1.67**	**1.66**	**1.65**	**1.64**	**1.63**
30	8.08	4.07	3.10	*2.68*	**2.45**	**2.20**	**2.07**	**1.97**	**1.91**	**1.87**	**1.84**	**1.82**	**1.80**	**1.78**	**1.76**	**1.74**	**1.73**	**1.72**	**1.71**	**1.70**
40	8.91	4.33	3.26	2.80	*2.55*	**2.29**	**2.15**	**2.04**	**1.98**	**1.93**	**1.90**	**1.88**	**1.86**	**1.83**	**1.81**	**1.79**	**1.78**	**1.77**	**1.76**	**1.75**
50	9.62	4.55	3.39	2.90	*2.63*	**2.35**	**2.20**	**2.09**	**2.02**	**1.98**	**1.95**	**1.92**	**1.90**	**1.87**	**1.85**	**1.83**	**1.82**	**1.81**	**1.80**	**1.79**
60	10.21	4.74	3.50	2.98	*2.70*	**2.40**	**2.25**	**2.13**	**2.06**	**2.02**	**1.98**	**1.95**	**1.93**	**1.90**	**1.88**	**1.87**	**1.85**	**1.84**	**1.83**	**1.82**
75	11.04	4.97	3.64	3.08	2.78	**2.47**	**2.30**	**2.19**	**2.11**	**2.06**	**2.03**	**2.00**	**1.97**	**1.94**	**1.92**	**1.90**	**1.89**	**1.88**	**1.86**	**1.85**
100	12.11	5.27	3.82	3.21	2.89	*2.55*	**2.38**	**2.25**	**2.17**	**2.12**	**2.08**	**2.05**	**2.03**	**2.00**	**1.97**	**1.95**	**1.94**	**1.93**	**1.91**	**1.90**
125	13.09	5.54	3.96	3.32	2.97	*2.62*	**2.44**	**2.30**	**2.22**	**2.17**	**2.12**	**2.09**	**2.07**	**2.04**	**2.01**	**1.99**	**1.98**	**1.97**	**1.95**	**1.93**
150	13.87	5.76	4.08	3.41	3.04	*2.67*	**2.48**	**2.34**	**2.26**	**2.20**	**2.16**	**2.13**	**2.11**	**2.07**	**2.04**	**2.02**	**2.01**	**2.00**	**1.98**	**1.96**
175	14.65	5.96	4.17	3.48	3.10	*2.72*	*2.52*	**2.38**	**2.29**	**2.23**	**2.19**	**2.15**	**2.13**	**2.09**	**2.07**	**2.05**	**2.03**	**2.02**	**2.00**	**1.99**
200	15.23	6.10	4.27	3.54	3.15	*2.76*	*2.55*	**2.41**	**2.32**	**2.26**	**2.22**	**2.18**	**2.15**	**2.12**	**2.09**	**2.07**	**2.05**	**2.04**	**2.02**	**2.01**

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Table 19-13. κ-Multipliers for Modified Calif. Intrawell Prediction Limits on Observations (10 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.01	**2.08**	**1.77**	**1.62**	**1.53**	**1.42**	**1.36**	**1.32**	**1.29**	**1.27**	**1.25**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**	**1.20**	**1.19**	**1.19**	**1.18**
2	3.89	**2.50**	**2.08**	**1.88**	**1.76**	**1.62**	**1.55**	**1.49**	**1.46**	**1.43**	**1.41**	**1.40**	**1.39**	**1.37**	**1.36**	**1.35**	**1.35**	**1.34**	**1.33**	**1.32**
3	4.49	**2.77**	**2.27**	**2.03**	**1.89**	**1.74**	**1.66**	**1.59**	**1.55**	**1.53**	**1.50**	**1.49**	**1.48**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**	**1.41**	**1.40**
4	4.97	2.97	**2.40**	**2.14**	**1.99**	**1.82**	**1.73**	**1.66**	**1.62**	**1.59**	**1.57**	**1.55**	**1.54**	**1.52**	**1.50**	**1.49**	**1.48**	**1.48**	**1.47**	**1.46**
5	5.37	3.13	**2.51**	**2.23**	**2.07**	**1.89**	**1.79**	**1.72**	**1.67**	**1.64**	**1.61**	**1.60**	**1.58**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**	**1.51**	**1.50**
8	6.31	3.50	**2.75**	**2.42**	**2.23**	**2.02**	**1.91**	**1.83**	**1.78**	**1.74**	**1.71**	**1.69**	**1.68**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**	**1.59**
12	7.25	3.83	*2.97*	**2.58**	**2.37**	**2.14**	**2.01**	**1.92**	**1.87**	**1.83**	**1.80**	**1.78**	**1.76**	**1.73**	**1.72**	**1.70**	**1.69**	**1.68**	**1.67**	**1.66**
16	8.00	4.09	3.12	**2.70**	**2.47**	**2.22**	**2.09**	**1.99**	**1.93**	**1.89**	**1.86**	**1.83**	**1.81**	**1.79**	**1.77**	**1.75**	**1.74**	**1.73**	**1.72**	**1.71**
20	8.63	4.29	3.25	**2.80**	**2.55**	**2.28**	**2.14**	**2.04**	**1.98**	**1.93**	**1.90**	**1.88**	**1.86**	**1.83**	**1.81**	**1.79**	**1.78**	**1.77**	**1.76**	**1.75**
30	9.89	4.69	3.49	*2.98*	**2.70**	**2.40**	**2.25**	**2.13**	**2.06**	**2.02**	**1.98**	**1.95**	**1.93**	**1.90**	**1.88**	**1.87**	**1.85**	**1.84**	**1.83**	**1.82**
40	10.89	4.99	3.66	3.10	*2.80*	**2.48**	**2.32**	**2.20**	**2.13**	**2.08**	**2.04**	**2.01**	**1.99**	**1.96**	**1.93**	**1.92**	**1.90**	**1.89**	**1.88**	**1.86**
50	11.77	5.24	3.80	3.21	*2.89*	**2.55**	**2.38**	**2.25**	**2.17**	**2.12**	**2.08**	**2.05**	**2.03**	**2.00**	**1.97**	**1.95**	**1.94**	**1.93**	**1.91**	**1.90**
60	12.50	5.44	3.92	3.29	*2.95*	**2.60**	**2.42**	**2.29**	**2.21**	**2.16**	**2.12**	**2.09**	**2.06**	**2.03**	**2.00**	**1.99**	**1.97**	**1.96**	**1.94**	**1.93**
75	13.48	5.71	4.06	3.40	*3.04*	**2.67**	**2.48**	**2.34**	**2.26**	**2.20**	**2.16**	**2.13**	**2.10**	**2.07**	**2.04**	**2.02**	**2.01**	**2.00**	**1.98**	**1.96**
100	14.84	6.05	4.26	3.54	3.15	**2.76**	**2.55**	**2.41**	**2.32**	**2.26**	**2.22**	**2.18**	**2.15**	**2.12**	**2.09**	**2.07**	**2.06**	**2.04**	**2.02**	**2.00**
125	16.02	6.35	4.42	3.65	3.24	*2.82*	**2.61**	**2.46**	**2.37**	**2.30**	**2.26**	**2.22**	**2.20**	**2.15**	**2.13**	**2.11**	**2.09**	**2.08**	**2.05**	**2.04**
150	16.99	6.59	4.54	3.74	3.31	*2.88*	**2.66**	**2.50**	**2.40**	**2.34**	**2.29**	**2.26**	**2.23**	**2.19**	**2.16**	**2.14**	**2.12**	**2.11**	**2.09**	**2.07**
175	17.97	6.84	4.66	3.81	3.37	*2.93*	**2.70**	**2.54**	**2.44**	**2.37**	**2.32**	**2.28**	**2.26**	**2.22**	**2.19**	**2.16**	**2.15**	**2.13**	**2.11**	**2.09**
200	18.75	7.03	4.76	3.88	3.43	*2.97*	**2.73**	**2.56**	**2.47**	**2.39**	**2.34**	**2.31**	**2.28**	**2.23**	**2.20**	**2.19**	**2.17**	**2.15**	**2.13**	**2.11**

Table 19-13. κ-Multipliers for Modified Calif. Intrawell Prediction Limits on Observations (10 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.68	**2.45**	**2.05**	**1.86**	**1.75**	**1.62**	**1.55**	**1.49**	**1.46**	**1.43**	**1.41**	**1.40**	**1.39**	**1.37**	**1.36**	**1.35**	**1.35**	**1.34**	**1.33**	**1.32**
2	4.71	**2.91**	**2.38**	**2.13**	**1.98**	**1.82**	**1.73**	**1.66**	**1.62**	**1.59**	**1.57**	**1.55**	**1.54**	**1.52**	**1.50**	**1.49**	**1.48**	**1.48**	**1.47**	**1.46**
3	5.42	3.21	**2.58**	**2.29**	**2.12**	**1.93**	**1.83**	**1.76**	**1.71**	**1.68**	**1.65**	**1.63**	**1.62**	**1.60**	**1.58**	**1.57**	**1.56**	**1.56**	**1.54**	**1.54**
4	5.99	3.43	**2.73**	**2.40**	**2.22**	**2.02**	**1.91**	**1.83**	**1.77**	**1.74**	**1.71**	**1.69**	**1.68**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**	**1.59**
5	6.47	3.61	**2.84**	**2.50**	**2.30**	**2.08**	**1.96**	**1.88**	**1.82**	**1.79**	**1.76**	**1.74**	**1.72**	**1.70**	**1.68**	**1.67**	**1.66**	**1.65**	**1.64**	**1.63**
8	7.60	4.02	*3.10*	**2.69**	**2.46**	**2.22**	**2.09**	**1.99**	**1.93**	**1.89**	**1.86**	**1.83**	**1.81**	**1.79**	**1.77**	**1.75**	**1.74**	**1.73**	**1.72**	**1.71**
12	8.72	4.40	3.33	**2.87**	**2.61**	**2.33**	**2.19**	**2.08**	**2.02**	**1.97**	**1.94**	**1.91**	**1.89**	**1.86**	**1.84**	**1.83**	**1.82**	**1.81**	**1.79**	**1.78**
16	9.61	4.68	3.50	**2.99**	**2.71**	**2.42**	**2.26**	**2.15**	**2.08**	**2.03**	**1.99**	**1.97**	**1.95**	**1.91**	**1.89**	**1.88**	**1.87**	**1.86**	**1.84**	**1.83**
20	10.36	4.91	3.64	*3.09*	**2.80**	**2.48**	**2.32**	**2.20**	**2.13**	**2.07**	**2.04**	**2.01**	**1.99**	**1.96**	**1.93**	**1.92**	**1.90**	**1.89**	**1.87**	**1.86**
30	11.89	5.36	3.89	*3.28*	**2.95**	**2.60**	**2.42**	**2.29**	**2.21**	**2.16**	**2.12**	**2.09**	**2.06**	**2.03**	**2.00**	**1.99**	**1.97**	**1.96**	**1.94**	**1.93**
40	13.09	5.70	4.08	3.42	**3.06**	**2.69**	**2.50**	**2.36**	**2.27**	**2.21**	**2.17**	**2.14**	**2.11**	**2.08**	**2.05**	**2.03**	**2.02**	**2.01**	**1.99**	**1.97**
50	14.11	5.97	4.24	3.52	*3.15*	**2.75**	**2.55**	**2.41**	**2.32**	**2.26**	**2.21**	**2.18**	**2.15**	**2.12**	**2.09**	**2.07**	**2.06**	**2.04**	**2.02**	**2.00**
60	14.99	6.20	4.36	3.61	*3.22*	**2.81**	**2.60**	**2.45**	**2.36**	**2.29**	**2.25**	**2.22**	**2.19**	**2.15**	**2.12**	**2.10**	**2.08**	**2.07**	**2.04**	**2.04**
75	16.16	6.49	4.52	3.73	*3.31*	**2.87**	**2.66**	**2.50**	**2.40**	**2.34**	**2.29**	**2.26**	**2.23**	**2.19**	**2.16**	**2.14**	**2.12**	**2.11**	**2.09**	**2.07**
100	17.77	6.91	4.74	3.88	3.42	**2.97**	**2.73**	**2.57**	**2.47**	**2.40**	**2.35**	**2.31**	**2.28**	**2.24**	**2.21**	**2.19**	**2.17**	**2.15**	**2.13**	**2.11**
125	19.14	7.23	4.91	3.99	3.52	**3.03**	**2.79**	**2.62**	**2.51**	**2.44**	**2.39**	**2.35**	**2.32**	**2.27**	**2.24**	**2.22**	**2.20**	**2.19**	**2.16**	**2.15**
150	20.31	7.52	5.05	4.09	3.59	*3.09*	**2.84**	**2.66**	**2.55**	**2.48**	**2.42**	**2.38**	**2.35**	**2.30**	**2.27**	**2.25**	**2.23**	**2.22**	**2.19**	**2.17**
175	21.48	7.76	5.18	4.17	3.66	*3.14*	**2.88**	**2.69**	**2.58**	**2.50**	**2.45**	**2.41**	**2.38**	**2.33**	**2.29**	**2.27**	**2.26**	**2.24**	**2.22**	**2.20**
200	22.46	7.96	5.27	4.25	3.71	*3.17*	**2.92**	**2.72**	**2.61**	**2.53**	**2.48**	**2.44**	**2.40**	**2.35**	**2.32**	**2.29**	**2.28**	**2.26**	**2.23**	**2.22**

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Table 19-13. κ-Multipliers for Modified Calif. Intrawell Prediction Limits on Observations (20 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.13	**2.11**	**1.78**	**1.63**	**1.53**	**1.42**	**1.37**	**1.32**	**1.29**	**1.27**	**1.26**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**	**1.20**	**1.19**	**1.19**	**1.18**
2	4.02	**2.53**	**2.09**	**1.88**	**1.76**	**1.63**	**1.55**	**1.49**	**1.46**	**1.43**	**1.41**	**1.40**	**1.39**	**1.37**	**1.36**	**1.35**	**1.35**	**1.34**	**1.33**	**1.32**
3	4.65	2.80	**2.28**	**2.04**	**1.90**	**1.74**	**1.66**	**1.59**	**1.55**	**1.53**	**1.50**	**1.49**	**1.48**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**	**1.41**	**1.40**
4	5.14	3.00	**2.42**	**2.15**	**1.99**	**1.82**	**1.73**	**1.66**	**1.62**	**1.59**	**1.57**	**1.55**	**1.54**	**1.52**	**1.50**	**1.49**	**1.49**	**1.48**	**1.47**	**1.46**
5	5.55	3.17	**2.53**	**2.24**	**2.07**	**1.89**	**1.79**	**1.72**	**1.67**	**1.64**	**1.62**	**1.60**	**1.58**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**	**1.51**	**1.50**
8	6.52	3.53	2.76	**2.42**	**2.23**	**2.02**	**1.91**	**1.83**	**1.78**	**1.74**	**1.71**	**1.69**	**1.68**	**1.66**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**	**1.59**
12	7.49	3.87	2.98	*2.59*	**2.37**	**2.14**	**2.01**	**1.92**	**1.87**	**1.83**	**1.80**	**1.78**	**1.76**	**1.73**	**1.72**	**1.70**	**1.69**	**1.68**	**1.67**	**1.66**
16	8.26	4.13	3.14	*2.71*	**2.47**	**2.22**	**2.09**	**1.99**	**1.93**	**1.89**	**1.86**	**1.83**	**1.81**	**1.79**	**1.77**	**1.75**	**1.74**	**1.73**	**1.72**	**1.71**
20	8.91	4.34	3.26	2.81	*2.55*	**2.29**	**2.14**	**2.04**	**1.98**	**1.93**	**1.90**	**1.88**	**1.86**	**1.83**	**1.81**	**1.79**	**1.78**	**1.77**	**1.76**	**1.75**
30	10.22	4.74	3.50	2.98	*2.70*	**2.40**	**2.25**	**2.14**	**2.06**	**2.02**	**1.98**	**1.95**	**1.93**	**1.90**	**1.88**	**1.87**	**1.85**	**1.84**	**1.83**	**1.82**
40	11.25	5.04	3.68	3.11	2.81	**2.49**	**2.32**	**2.20**	**2.13**	**2.07**	**2.04**	**2.01**	**1.99**	**1.96**	**1.93**	**1.92**	**1.90**	**1.89**	**1.88**	**1.86**
50	12.13	5.29	3.82	3.21	2.89	*2.55*	**2.38**	**2.25**	**2.17**	**2.12**	**2.08**	**2.05**	**2.03**	**2.00**	**1.97**	**1.95**	**1.94**	**1.93**	**1.91**	**1.90**
60	12.89	5.49	3.93	3.30	2.96	*2.60*	**2.42**	**2.29**	**2.21**	**2.16**	**2.12**	**2.09**	**2.06**	**2.03**	**2.00**	**1.98**	**1.97**	**1.96**	**1.94**	**1.93**
75	13.89	5.76	4.08	3.41	3.04	*2.67*	**2.48**	**2.34**	**2.26**	**2.20**	**2.16**	**2.13**	**2.10**	**2.07**	**2.04**	**2.02**	**2.01**	**2.00**	**1.98**	**1.96**
100	15.35	6.12	4.28	3.54	3.16	*2.76*	*2.56*	**2.41**	**2.32**	**2.26**	**2.22**	**2.18**	**2.16**	**2.12**	**2.09**	**2.07**	**2.05**	**2.04**	**2.02**	**2.00**
125	16.52	6.42	4.42	3.65	3.24	2.83	*2.61*	**2.46**	**2.37**	**2.30**	**2.26**	**2.22**	**2.20**	**2.15**	**2.13**	**2.11**	**2.09**	**2.08**	**2.05**	**2.03**
150	17.58	6.65	4.57	3.75	3.31	2.88	*2.66*	*2.50*	**2.40**	**2.34**	**2.29**	**2.26**	**2.23**	**2.19**	**2.16**	**2.14**	**2.12**	**2.11**	**2.08**	**2.07**
175	18.52	6.86	4.69	3.82	3.38	2.93	*2.70*	*2.53*	**2.44**	**2.37**	**2.32**	**2.29**	**2.26**	**2.21**	**2.18**	**2.16**	**2.15**	**2.13**	**2.11**	**2.09**
200	19.22	7.09	4.78	3.90	3.43	2.97	*2.73*	*2.56*	**2.47**	**2.40**	**2.34**	**2.31**	**2.28**	**2.23**	**2.20**	**2.18**	**2.17**	**2.15**	**2.13**	**2.12**

Table 19-13. κ-Multipliers for Modified Calif. Intrawell Prediction Limits on Observations (20 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.89	**2.50**	**2.08**	**1.88**	**1.76**	**1.62**	**1.55**	**1.49**	**1.46**	**1.43**	**1.41**	**1.40**	**1.39**	**1.37**	**1.36**	**1.35**	**1.35**	**1.34**	**1.33**	**1.32**
2	4.97	2.97	**2.40**	**2.14**	**1.99**	**1.82**	**1.73**	**1.66**	**1.62**	**1.59**	**1.57**	**1.55**	**1.54**	**1.52**	**1.50**	**1.49**	**1.48**	**1.48**	**1.47**	**1.46**
3	5.72	3.27	**2.60**	**2.30**	**2.13**	**1.94**	**1.84**	**1.76**	**1.71**	**1.68**	**1.65**	**1.63**	**1.62**	**1.60**	**1.58**	**1.57**	**1.56**	**1.56**	**1.54**	**1.54**
4	6.31	3.50	**2.75**	**2.42**	**2.23**	**2.02**	**1.91**	**1.83**	**1.78**	**1.74**	**1.71**	**1.69**	**1.68**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**	**1.59**
5	6.81	3.68	*2.87*	**2.51**	**2.30**	**2.08**	**1.97**	**1.88**	**1.83**	**1.79**	**1.76**	**1.74**	**1.72**	**1.70**	**1.68**	**1.67**	**1.66**	**1.65**	**1.64**	**1.63**
8	8.00	4.09	3.12	**2.70**	**2.47**	**2.22**	**2.09**	**1.99**	**1.93**	**1.89**	**1.86**	**1.83**	**1.81**	**1.79**	**1.77**	**1.75**	**1.74**	**1.73**	**1.72**	**1.71**
12	9.18	4.47	3.35	*2.88*	**2.61**	**2.34**	**2.19**	**2.08**	**2.02**	**1.97**	**1.94**	**1.91**	**1.89**	**1.86**	**1.84**	**1.83**	**1.82**	**1.81**	**1.79**	**1.78**
16	10.11	4.76	3.52	*3.00*	**2.72**	**2.42**	**2.26**	**2.15**	**2.08**	**2.03**	**1.99**	**1.97**	**1.95**	**1.92**	**1.89**	**1.88**	**1.86**	**1.86**	**1.84**	**1.83**
20	10.90	4.99	3.66	3.10	*2.80*	**2.48**	**2.32**	**2.20**	**2.13**	**2.07**	**2.04**	**2.01**	**1.99**	**1.96**	**1.93**	**1.92**	**1.90**	**1.89**	**1.88**	**1.86**
30	12.48	5.44	3.92	3.29	*2.96*	**2.60**	**2.42**	**2.29**	**2.21**	**2.16**	**2.12**	**2.09**	**2.06**	**2.03**	**2.00**	**1.98**	**1.97**	**1.96**	**1.94**	**1.93**
40	13.77	5.79	4.11	3.43	3.07	**2.69**	**2.50**	**2.36**	**2.27**	**2.21**	**2.17**	**2.14**	**2.11**	**2.08**	**2.05**	**2.03**	**2.02**	**2.01**	**1.99**	**1.97**
50	14.82	6.06	4.26	3.54	3.15	**2.76**	**2.55**	**2.41**	**2.32**	**2.26**	**2.22**	**2.18**	**2.16**	**2.12**	**2.09**	**2.07**	**2.06**	**2.04**	**2.02**	**2.00**
60	15.76	6.30	4.39	3.63	3.22	*2.81*	**2.60**	**2.45**	**2.36**	**2.30**	**2.25**	**2.22**	**2.19**	**2.15**	**2.12**	**2.10**	**2.08**	**2.07**	**2.04**	**2.04**
75	16.99	6.59	4.55	3.74	3.31	*2.88*	**2.66**	**2.50**	**2.41**	**2.34**	**2.29**	**2.26**	**2.23**	**2.19**	**2.16**	**2.14**	**2.12**	**2.11**	**2.09**	**2.07**
100	18.75	7.00	4.76	3.88	3.43	*2.97*	**2.73**	**2.57**	**2.46**	**2.40**	**2.35**	**2.31**	**2.28**	**2.24**	**2.20**	**2.18**	**2.17**	**2.15**	**2.13**	**2.11**
125	20.16	7.32	4.94	4.00	3.52	*3.03*	*2.79*	**2.62**	**2.51**	**2.44**	**2.39**	**2.35**	**2.32**	**2.27**	**2.24**	**2.22**	**2.20**	**2.19**	**2.16**	**2.15**
150	21.33	7.62	5.07	4.10	3.60	*3.09*	*2.84*	**2.66**	**2.55**	**2.48**	**2.42**	**2.38**	**2.35**	**2.31**	**2.27**	**2.25**	**2.23**	**2.22**	**2.19**	**2.18**
175	22.50	7.85	5.20	4.19	3.66	3.13	*2.88*	**2.70**	**2.58**	**2.50**	**2.45**	**2.41**	**2.38**	**2.33**	**2.30**	**2.27**	**2.26**	**2.24**	**2.22**	**2.20**
200	23.44	8.09	5.30	4.25	3.72	3.18	*2.92*	**2.72**	**2.61**	**2.53**	**2.48**	**2.43**	**2.40**	**2.35**	**2.32**	**2.29**	**2.28**	**2.26**	**2.23**	**2.22**

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Table 19-13. κ-Multipliers for Modified Calif. Intrawell Prediction Limits on Observations (20 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	4.71	**2.91**	**2.38**	**2.13**	**1.98**	**1.82**	**1.73**	**1.66**	**1.62**	**1.59**	**1.57**	**1.55**	**1.54**	**1.52**	**1.50**	**1.49**	**1.48**	**1.48**	**1.47**	**1.46**
2	5.99	3.43	**2.73**	**2.40**	**2.22**	**2.02**	**1.91**	**1.83**	**1.77**	**1.74**	**1.71**	**1.69**	**1.68**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**	**1.59**
3	6.89	3.77	**2.94**	**2.57**	**2.36**	**2.13**	**2.01**	**1.92**	**1.86**	**1.83**	**1.80**	**1.78**	**1.76**	**1.73**	**1.71**	**1.70**	**1.69**	**1.68**	**1.67**	**1.66**
4	7.60	4.02	*3.10*	**2.69**	**2.46**	**2.22**	**2.09**	**1.99**	**1.93**	**1.89**	**1.86**	**1.83**	**1.81**	**1.79**	**1.77**	**1.75**	**1.74**	**1.73**	**1.72**	**1.71**
5	8.20	4.22	3.23	**2.79**	**2.54**	**2.28**	**2.14**	**2.04**	**1.98**	**1.93**	**1.90**	**1.88**	**1.86**	**1.83**	**1.81**	**1.79**	**1.78**	**1.77**	**1.76**	**1.75**
8	9.61	4.68	3.50	**2.99**	**2.71**	**2.42**	**2.26**	**2.15**	**2.08**	**2.03**	**1.99**	**1.97**	**1.95**	**1.91**	**1.89**	**1.88**	**1.86**	**1.86**	**1.84**	**1.83**
12	11.02	5.11	3.75	*3.18*	**2.86**	**2.54**	**2.37**	**2.24**	**2.16**	**2.11**	**2.07**	**2.04**	**2.02**	**1.99**	**1.96**	**1.95**	**1.93**	**1.92**	**1.90**	**1.89**
16	12.14	5.43	3.93	3.31	**2.97**	**2.62**	**2.44**	**2.31**	**2.23**	**2.17**	**2.13**	**2.10**	**2.07**	**2.04**	**2.01**	**2.00**	**1.98**	**1.97**	**1.95**	**1.94**
20	13.08	5.70	4.08	3.42	**3.06**	**2.69**	**2.50**	**2.36**	**2.27**	**2.21**	**2.17**	**2.14**	**2.11**	**2.08**	**2.05**	**2.03**	**2.02**	**2.01**	**1.99**	**1.97**
30	15.00	6.20	4.36	3.61	*3.22*	**2.81**	**2.60**	**2.45**	**2.36**	**2.30**	**2.25**	**2.21**	**2.19**	**2.15**	**2.12**	**2.10**	**2.08**	**2.07**	**2.04**	**2.04**
40	16.52	6.59	4.57	3.76	*3.33*	**2.90**	**2.68**	**2.52**	**2.42**	**2.35**	**2.30**	**2.27**	**2.24**	**2.20**	**2.17**	**2.15**	**2.13**	**2.12**	**2.10**	**2.08**
50	17.81	6.90	4.73	3.87	3.42	**2.96**	**2.73**	**2.57**	**2.46**	**2.40**	**2.35**	**2.31**	**2.28**	**2.24**	**2.21**	**2.18**	**2.17**	**2.15**	**2.13**	**2.11**
60	18.93	7.18	4.87	3.97	3.50	**3.02**	**2.78**	**2.61**	**2.50**	**2.43**	**2.38**	**2.34**	**2.31**	**2.27**	**2.24**	**2.21**	**2.20**	**2.18**	**2.16**	**2.14**
75	20.39	7.50	5.05	4.09	3.59	*3.09*	**2.84**	**2.66**	**2.55**	**2.48**	**2.42**	**2.38**	**2.35**	**2.30**	**2.27**	**2.25**	**2.23**	**2.22**	**2.19**	**2.18**
100	22.50	7.97	5.27	4.25	3.71	*3.18*	**2.92**	**2.72**	**2.61**	**2.53**	**2.48**	**2.44**	**2.40**	**2.35**	**2.32**	**2.29**	**2.27**	**2.26**	**2.23**	**2.22**
125	24.14	8.35	5.46	4.37	3.81	*3.25*	**2.97**	**2.78**	**2.66**	**2.57**	**2.52**	**2.48**	**2.44**	**2.39**	**2.35**	**2.33**	**2.31**	**2.30**	**2.27**	**2.25**
150	25.78	8.67	5.62	4.48	3.90	*3.31*	**3.02**	**2.82**	**2.70**	**2.61**	**2.55**	**2.50**	**2.47**	**2.42**	**2.38**	**2.36**	**2.34**	**2.32**	**2.29**	**2.27**
175	27.19	8.96	5.77	4.57	3.96	*3.35*	**3.06**	**2.85**	**2.72**	**2.64**	**2.58**	**2.53**	**2.50**	**2.45**	**2.41**	**2.38**	**2.36**	**2.34**	**2.32**	**2.30**
200	28.12	9.20	5.86	4.64	4.01	*3.40*	*3.10*	**2.89**	**2.75**	**2.67**	**2.60**	**2.56**	**2.52**	**2.47**	**2.43**	**2.40**	**2.38**	**2.37**	**2.34**	**2.32**

Table 19-13. κ-Multipliers for Modified Calif. Intrawell Prediction Limits on Observations (40 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	4.02	**2.53**	**2.09**	**1.88**	**1.76**	**1.63**	**1.55**	**1.49**	**1.46**	**1.43**	**1.41**	**1.40**	**1.39**	**1.37**	**1.36**	**1.35**	**1.35**	**1.34**	**1.33**	**1.32**
2	5.14	3.00	**2.42**	**2.15**	**1.99**	**1.82**	**1.73**	**1.66**	**1.62**	**1.59**	**1.57**	**1.55**	**1.54**	**1.52**	**1.50**	**1.49**	**1.49**	**1.48**	**1.47**	**1.46**
3	5.91	3.31	*2.62*	**2.31**	**2.13**	**1.94**	**1.84**	**1.76**	**1.71**	**1.68**	**1.65**	**1.64**	**1.62**	**1.60**	**1.58**	**1.57**	**1.56**	**1.56**	**1.54**	**1.54**
4	6.52	3.53	2.76	**2.42**	**2.23**	**2.02**	**1.91**	**1.83**	**1.78**	**1.74**	**1.71**	**1.69**	**1.68**	**1.66**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**	**1.59**
5	7.04	3.72	2.88	**2.51**	**2.31**	**2.09**	**1.97**	**1.88**	**1.83**	**1.79**	**1.76**	**1.74**	**1.72**	**1.70**	**1.68**	**1.67**	**1.66**	**1.65**	**1.64**	**1.63**
8	8.26	4.13	3.14	*2.71*	**2.47**	**2.22**	**2.09**	**1.99**	**1.93**	**1.89**	**1.86**	**1.83**	**1.81**	**1.79**	**1.77**	**1.75**	**1.74**	**1.74**	**1.72**	**1.71**
12	9.48	4.51	3.37	2.88	*2.62*	**2.34**	**2.19**	**2.08**	**2.02**	**1.97**	**1.94**	**1.91**	**1.89**	**1.86**	**1.84**	**1.83**	**1.82**	**1.81**	**1.79**	**1.78**
16	10.44	4.80	3.54	3.01	*2.72*	**2.42**	**2.26**	**2.15**	**2.08**	**2.03**	**1.99**	**1.97**	**1.95**	**1.92**	**1.89**	**1.88**	**1.86**	**1.86**	**1.84**	**1.83**
20	11.25	5.04	3.68	3.11	2.81	**2.49**	**2.32**	**2.20**	**2.13**	**2.07**	**2.04**	**2.01**	**1.99**	**1.96**	**1.93**	**1.92**	**1.90**	**1.89**	**1.87**	**1.86**
30	12.90	5.49	3.93	3.30	2.96	*2.60*	**2.42**	**2.29**	**2.21**	**2.16**	**2.12**	**2.09**	**2.06**	**2.03**	**2.00**	**1.99**	**1.97**	**1.96**	**1.94**	**1.93**
40	14.20	5.84	4.12	3.43	3.07	*2.69*	**2.50**	**2.36**	**2.27**	**2.21**	**2.17**	**2.14**	**2.11**	**2.08**	**2.05**	**2.03**	**2.02**	**2.01**	**1.99**	**1.97**
50	15.31	6.12	4.27	3.54	3.15	*2.76*	*2.55*	**2.41**	**2.32**	**2.26**	**2.21**	**2.18**	**2.16**	**2.12**	**2.09**	**2.07**	**2.05**	**2.04**	**2.02**	**2.00**
60	16.27	6.36	4.40	3.63	3.23	2.81	*2.60*	**2.45**	**2.36**	**2.29**	**2.25**	**2.21**	**2.19**	**2.15**	**2.12**	**2.10**	**2.08**	**2.07**	**2.04**	**2.02**
75	17.54	6.66	4.57	3.74	3.32	2.88	*2.66*	*2.50*	**2.40**	**2.34**	**2.29**	**2.26**	**2.23**	**2.19**	**2.16**	**2.14**	**2.12**	**2.11**	**2.08**	**2.07**
100	19.30	7.07	4.78	3.89	3.43	2.97	*2.73*	*2.57*	**2.46**	**2.40**	**2.35**	**2.31**	**2.28**	**2.24**	**2.21**	**2.18**	**2.17**	**2.15**	**2.13**	**2.11**
125	20.78	7.40	4.95	4.01	3.53	3.03	*2.79*	*2.62*	*2.51*	**2.44**	**2.39**	**2.35**	**2.32**	**2.27**	**2.24**	**2.22**	**2.20**	**2.19**	**2.16**	**2.15**
150	22.11	7.70	5.09	4.11	3.60	3.09	2.84	*2.66*	*2.55*	**2.48**	**2.42**	**2.38**	**2.35**	**2.30**	**2.27**	**2.25**	**2.23**	**2.22**	**2.19**	**2.18**
175	23.28	7.93	5.21	4.19	3.66	3.14	2.88	*2.70*	*2.58*	*2.50*	**2.45**	**2.41**	**2.38**	**2.33**	**2.30**	**2.28**	**2.26**	**2.25**	**2.21**	**2.20**
200	24.38	8.16	5.32	4.26	3.72	3.18	2.92	*2.72*	*2.61*	*2.53*	**2.48**	**2.43**	**2.40**	**2.35**	**2.32**	**2.30**	**2.28**	**2.27**	**2.23**	**2.22**

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Table 19-13. κ-Multipliers for Modified Calif. Intrawell Prediction Limits on Observations (40 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	4.97	2.97	**2.40**	**2.14**	**1.99**	**1.82**	**1.73**	**1.66**	**1.62**	**1.59**	**1.57**	**1.55**	**1.54**	**1.52**	**1.50**	**1.49**	**1.48**	**1.48**	**1.47**	**1.46**
2	6.31	3.49	**2.75**	**2.42**	**2.23**	**2.02**	**1.91**	**1.83**	**1.78**	**1.74**	**1.71**	**1.69**	**1.68**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**	**1.59**
3	7.25	3.83	*2.97*	**2.58**	**2.37**	**2.14**	**2.01**	**1.92**	**1.87**	**1.83**	**1.80**	**1.78**	**1.76**	**1.73**	**1.72**	**1.70**	**1.69**	**1.68**	**1.67**	**1.66**
4	8.00	4.09	3.12	**2.70**	**2.47**	**2.22**	**2.09**	**1.99**	**1.93**	**1.89**	**1.86**	**1.83**	**1.81**	**1.79**	**1.77**	**1.75**	**1.74**	**1.73**	**1.72**	**1.71**
5	8.63	4.29	3.25	**2.80**	**2.55**	**2.28**	**2.14**	**2.04**	**1.98**	**1.93**	**1.90**	**1.88**	**1.86**	**1.83**	**1.81**	**1.79**	**1.78**	**1.77**	**1.76**	**1.75**
8	10.11	4.76	3.53	*3.00*	**2.72**	**2.42**	**2.26**	**2.15**	**2.08**	**2.03**	**1.99**	**1.97**	**1.95**	**1.91**	**1.89**	**1.88**	**1.86**	**1.86**	**1.84**	**1.83**
12	11.59	5.19	3.78	3.19	*2.87*	**2.54**	**2.37**	**2.24**	**2.16**	**2.11**	**2.07**	**2.04**	**2.02**	**1.99**	**1.96**	**1.95**	**1.93**	**1.92**	**1.90**	**1.89**
16	12.76	5.52	3.96	3.32	*2.98*	**2.62**	**2.44**	**2.31**	**2.23**	**2.17**	**2.13**	**2.10**	**2.07**	**2.04**	**2.01**	**2.00**	**1.98**	**1.97**	**1.95**	**1.94**
20	13.76	5.79	4.11	3.43	3.07	**2.69**	**2.50**	**2.36**	**2.27**	**2.21**	**2.17**	**2.14**	**2.11**	**2.08**	**2.05**	**2.03**	**2.02**	**2.01**	**1.99**	**1.97**
30	15.76	6.30	4.39	3.63	3.22	*2.81*	**2.60**	**2.45**	**2.36**	**2.29**	**2.25**	**2.21**	**2.19**	**2.15**	**2.12**	**2.10**	**2.08**	**2.07**	**2.04**	**2.02**
40	17.34	6.69	4.59	3.77	3.34	*2.90*	**2.68**	**2.52**	**2.42**	**2.35**	**2.30**	**2.27**	**2.24**	**2.20**	**2.17**	**2.15**	**2.13**	**2.12**	**2.10**	**2.08**
50	18.71	7.01	4.76	3.89	3.43	*2.97*	**2.73**	**2.57**	**2.46**	**2.40**	**2.35**	**2.31**	**2.28**	**2.24**	**2.21**	**2.18**	**2.17**	**2.15**	**2.13**	**2.11**
60	19.88	7.28	4.90	3.98	3.51	*3.02*	**2.78**	**2.61**	**2.50**	**2.43**	**2.38**	**2.34**	**2.31**	**2.27**	**2.24**	**2.21**	**2.20**	**2.18**	**2.16**	**2.14**
75	21.41	7.62	5.08	4.10	3.60	*3.09*	*2.84*	**2.66**	**2.55**	**2.48**	**2.42**	**2.38**	**2.35**	**2.30**	**2.27**	**2.25**	**2.23**	**2.22**	**2.19**	**2.18**
100	23.59	8.09	5.31	4.26	3.72	3.18	*2.92*	**2.72**	**2.61**	**2.53**	**2.48**	**2.43**	**2.40**	**2.35**	**2.32**	**2.29**	**2.28**	**2.26**	**2.23**	**2.22**
125	25.47	8.48	5.49	4.38	3.82	3.25	*2.97*	**2.77**	**2.66**	**2.57**	**2.52**	**2.47**	**2.44**	**2.39**	**2.36**	**2.33**	**2.31**	**2.29**	**2.27**	**2.25**
150	27.03	8.79	5.64	4.49	3.90	3.31	*3.02*	*2.82*	**2.70**	**2.61**	**2.55**	**2.50**	**2.47**	**2.42**	**2.39**	**2.36**	**2.34**	**2.32**	**2.29**	**2.28**
175	28.44	9.06	5.78	4.57	3.96	3.36	*3.06*	*2.85*	**2.72**	**2.64**	**2.58**	**2.53**	**2.50**	**2.45**	**2.41**	**2.39**	**2.36**	**2.34**	**2.32**	**2.30**
200	29.69	9.30	5.90	4.65	4.02	3.40	*3.10*	*2.88*	**2.75**	**2.67**	**2.60**	**2.56**	**2.52**	**2.47**	**2.43**	**2.41**	**2.39**	**2.36**	**2.34**	**2.32**

Table 19-13. κ-Multipliers for Modified Calif. Intrawell Prediction Limits on Observations (40 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	5.99	3.43	**2.73**	**2.40**	**2.22**	**2.02**	**1.91**	**1.83**	**1.77**	**1.74**	**1.71**	**1.69**	**1.68**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**	**1.59**
2	7.60	4.02	*3.10*	**2.69**	**2.46**	**2.22**	**2.09**	**1.99**	**1.93**	**1.89**	**1.86**	**1.83**	**1.81**	**1.79**	**1.77**	**1.75**	**1.74**	**1.73**	**1.72**	**1.71**
3	8.72	4.40	3.33	**2.87**	**2.61**	**2.33**	**2.19**	**2.08**	**2.02**	**1.97**	**1.94**	**1.91**	**1.89**	**1.86**	**1.84**	**1.83**	**1.82**	**1.81**	**1.79**	**1.78**
4	9.61	4.68	3.50	**2.99**	**2.71**	**2.42**	**2.26**	**2.15**	**2.08**	**2.03**	**1.99**	**1.97**	**1.95**	**1.91**	**1.89**	**1.88**	**1.86**	**1.86**	**1.84**	**1.83**
5	10.36	4.91	3.64	*3.09*	**2.80**	**2.48**	**2.32**	**2.20**	**2.13**	**2.07**	**2.04**	**2.01**	**1.99**	**1.96**	**1.93**	**1.92**	**1.90**	**1.89**	**1.87**	**1.86**
8	12.14	5.43	3.93	3.31	**2.97**	**2.62**	**2.44**	**2.31**	**2.23**	**2.17**	**2.13**	**2.10**	**2.07**	**2.04**	**2.01**	**2.00**	**1.98**	**1.97**	**1.95**	**1.94**
12	13.91	5.92	4.21	3.51	*3.13*	**2.74**	**2.54**	**2.40**	**2.31**	**2.25**	**2.21**	**2.17**	**2.15**	**2.11**	**2.08**	**2.06**	**2.05**	**2.04**	**2.02**	**2.00**
16	15.32	6.29	4.41	3.65	*3.24*	**2.83**	**2.62**	**2.47**	**2.37**	**2.31**	**2.26**	**2.23**	**2.20**	**2.16**	**2.13**	**2.11**	**2.09**	**2.08**	**2.06**	**2.05**
20	16.50	6.59	4.57	3.76	*3.33*	**2.90**	**2.67**	**2.52**	**2.42**	**2.35**	**2.30**	**2.27**	**2.24**	**2.20**	**2.17**	**2.15**	**2.13**	**2.12**	**2.10**	**2.08**
30	18.91	7.17	4.87	3.97	3.50	**3.02**	**2.78**	**2.61**	**2.50**	**2.43**	**2.38**	**2.34**	**2.31**	**2.27**	**2.24**	**2.21**	**2.20**	**2.18**	**2.16**	**2.14**
40	20.82	7.61	5.10	4.12	3.62	*3.11*	**2.85**	**2.67**	**2.56**	**2.49**	**2.43**	**2.39**	**2.36**	**2.32**	**2.28**	**2.26**	**2.24**	**2.23**	**2.20**	**2.18**
50	22.42	7.97	5.28	4.25	3.72	*3.18*	**2.91**	**2.72**	**2.61**	**2.53**	**2.48**	**2.43**	**2.40**	**2.35**	**2.32**	**2.29**	**2.28**	**2.26**	**2.23**	**2.22**
60	23.83	8.28	5.43	4.35	3.79	*3.24*	**2.96**	**2.77**	**2.65**	**2.57**	**2.51**	**2.47**	**2.43**	**2.38**	**2.35**	**2.32**	**2.30**	**2.29**	**2.26**	**2.24**
75	25.70	8.67	5.62	4.47	3.89	*3.31*	**3.02**	**2.82**	**2.69**	**2.61**	**2.55**	**2.51**	**2.47**	**2.42**	**2.38**	**2.36**	**2.34**	**2.32**	**2.29**	**2.27**
100	28.28	9.18	5.88	4.64	4.02	*3.40*	*3.10*	**2.88**	**2.75**	**2.67**	**2.60**	**2.56**	**2.52**	**2.47**	**2.43**	**2.40**	**2.38**	**2.36**	**2.33**	**2.31**
125	30.47	9.61	6.07	4.78	4.12	3.47	*3.15*	**2.93**	**2.80**	**2.71**	**2.64**	**2.60**	**2.56**	**2.50**	**2.47**	**2.44**	**2.41**	**2.40**	**2.37**	**2.34**
150	32.34	10.00	6.25	4.88	4.20	3.54	*3.20*	**2.97**	**2.84**	**2.74**	**2.68**	**2.63**	**2.59**	**2.53**	**2.50**	**2.47**	**2.44**	**2.42**	**2.39**	**2.37**
175	34.06	10.31	6.41	4.98	4.28	3.58	*3.25*	**3.01**	**2.87**	**2.77**	**2.71**	**2.66**	**2.62**	**2.56**	**2.52**	**2.49**	**2.47**	**2.45**	**2.42**	**2.40**
200	35.62	10.59	6.52	5.06	4.34	3.62	*3.28*	**3.04**	**2.90**	**2.80**	**2.73**	**2.68**	**2.64**	**2.58**	**2.54**	**2.51**	**2.49**	**2.47**	**2.44**	**2.41**

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D STATISTICAL TABLES

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Table 19-14. κ-Multipliers for 1-of-1 Intrawell Prediction Limits on Means of Order 2 (1 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.42**	**1.20**	**1.12**	**1.07**	**1.04**	**1.01**	**0.98**	**0.97**	**0.96**	**0.95**	**0.94**	**0.94**	**0.94**	**0.93**	**0.93**	**0.93**	**0.92**	**0.92**	**0.92**	**0.92**
2	**2.01**	**1.63**	**1.48**	**1.41**	**1.36**	**1.30**	**1.27**	**1.25**	**1.23**	**1.22**	**1.21**	**1.20**	**1.20**	**1.19**	**1.19**	**1.18**	**1.18**	**1.18**	**1.17**	**1.17**
3	**2.41**	**1.88**	**1.70**	**1.60**	**1.54**	**1.47**	**1.43**	**1.40**	**1.38**	**1.37**	**1.35**	**1.35**	**1.34**	**1.33**	**1.32**	**1.32**	**1.32**	**1.31**	**1.31**	**1.30**
4	**2.71**	**2.07**	**1.85**	**1.73**	**1.66**	**1.58**	**1.54**	**1.50**	**1.48**	**1.46**	**1.45**	**1.44**	**1.44**	**1.43**	**1.42**	**1.41**	**1.41**	**1.40**	**1.40**	**1.39**
5	**2.97**	**2.22**	**1.97**	**1.84**	**1.76**	**1.67**	**1.62**	**1.58**	**1.56**	**1.54**	**1.53**	**1.52**	**1.51**	**1.50**	**1.49**	**1.48**	**1.48**	**1.47**	**1.47**	**1.46**
8	3.55	**2.55**	**2.22**	**2.06**	**1.96**	**1.85**	**1.79**	**1.74**	**1.71**	**1.69**	**1.67**	**1.66**	**1.65**	**1.64**	**1.63**	**1.62**	**1.62**	**1.61**	**1.60**	**1.60**
12	4.13	**2.85**	**2.45**	**2.25**	**2.13**	**2.00**	**1.93**	**1.88**	**1.84**	**1.82**	**1.80**	**1.78**	**1.77**	**1.76**	**1.75**	**1.74**	**1.73**	**1.73**	**1.72**	**1.71**
16	4.59	3.07	**2.61**	**2.39**	**2.26**	**2.11**	**2.03**	**1.97**	**1.93**	**1.90**	**1.88**	**1.87**	**1.86**	**1.84**	**1.83**	**1.82**	**1.81**	**1.80**	**1.79**	**1.79**
20	4.97	3.25	**2.74**	**2.49**	**2.35**	**2.19**	**2.10**	**2.04**	**2.00**	**1.97**	**1.95**	**1.93**	**1.92**	**1.90**	**1.89**	**1.88**	**1.87**	**1.86**	**1.85**	**1.84**
30	5.74	3.59	**2.98**	**2.69**	**2.52**	**2.34**	**2.24**	**2.17**	**2.12**	**2.09**	**2.06**	**2.04**	**2.03**	**2.01**	**1.99**	**1.98**	**1.97**	**1.97**	**1.95**	**1.95**
40	6.34	3.85	3.15	**2.83**	**2.65**	**2.45**	**2.34**	**2.26**	**2.20**	**2.17**	**2.14**	**2.12**	**2.11**	**2.08**	**2.07**	**2.05**	**2.05**	**2.04**	**2.02**	**2.02**
50	6.85	4.06	3.29	**2.94**	**2.75**	**2.53**	**2.41**	**2.32**	**2.27**	**2.23**	**2.20**	**2.18**	**2.16**	**2.14**	**2.12**	**2.11**	**2.10**	**2.09**	**2.08**	**2.07**
60	7.30	4.23	3.41	*3.04*	**2.83**	**2.59**	**2.47**	**2.38**	**2.32**	**2.28**	**2.25**	**2.23**	**2.21**	**2.19**	**2.17**	**2.15**	**2.14**	**2.14**	**2.12**	**2.11**
75	7.88	4.46	3.56	*3.15*	**2.92**	**2.68**	**2.54**	**2.45**	**2.38**	**2.34**	**2.31**	**2.29**	**2.27**	**2.24**	**2.22**	**2.21**	**2.20**	**2.19**	**2.17**	**2.16**
100	8.69	4.76	3.75	3.30	*3.05*	**2.78**	**2.64**	**2.53**	**2.47**	**2.42**	**2.39**	**2.36**	**2.34**	**2.31**	**2.29**	**2.28**	**2.26**	**2.26**	**2.24**	**2.23**
125	9.38	5.00	3.90	3.42	*3.15*	**2.86**	**2.71**	**2.60**	**2.53**	**2.48**	**2.44**	**2.42**	**2.40**	**2.37**	**2.34**	**2.33**	**2.32**	**2.31**	**2.29**	**2.28**
150	9.98	5.21	4.03	3.52	3.23	**2.93**	**2.77**	**2.65**	**2.58**	**2.53**	**2.49**	**2.46**	**2.44**	**2.41**	**2.39**	**2.37**	**2.36**	**2.35**	**2.33**	**2.32**
175	10.51	5.39	4.14	3.60	3.30	*2.99*	**2.82**	**2.70**	**2.62**	**2.57**	**2.53**	**2.50**	**2.48**	**2.45**	**2.42**	**2.41**	**2.39**	**2.38**	**2.36**	**2.35**
200	11.00	5.54	4.24	3.67	3.36	*3.04*	**2.86**	**2.74**	**2.66**	**2.60**	**2.56**	**2.53**	**2.51**	**2.48**	**2.45**	**2.44**	**2.42**	**2.41**	**2.39**	**2.38**

Table 19-14. κ-Multipliers for 1-of-1 Intrawell Prediction Limits on Means of Order 2 (1 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.89**	**1.58**	**1.45**	**1.38**	**1.34**	**1.29**	**1.26**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**	**1.20**	**1.19**	**1.18**	**1.18**	**1.18**	**1.18**	**1.17**	**1.17**
2	**2.57**	**2.02**	**1.82**	**1.71**	**1.65**	**1.57**	**1.53**	**1.50**	**1.48**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**	**1.42**	**1.41**	**1.41**	**1.40**	**1.40**	**1.39**
3	**3.03**	**2.29**	**2.04**	**1.91**	**1.83**	**1.73**	**1.68**	**1.64**	**1.61**	**1.60**	**1.58**	**1.57**	**1.56**	**1.55**	**1.54**	**1.54**	**1.53**	**1.53**	**1.52**	**1.52**
4	3.39	**2.50**	**2.19**	**2.04**	**1.95**	**1.84**	**1.78**	**1.74**	**1.71**	**1.69**	**1.67**	**1.66**	**1.65**	**1.64**	**1.63**	**1.62**	**1.62**	**1.61**	**1.60**	**1.60**
5	3.68	**2.66**	**2.32**	**2.15**	**2.04**	**1.93**	**1.86**	**1.81**	**1.78**	**1.76**	**1.74**	**1.73**	**1.72**	**1.70**	**1.69**	**1.69**	**1.68**	**1.67**	**1.67**	**1.66**
8	4.38	**3.02**	**2.58**	**2.37**	**2.25**	**2.10**	**2.03**	**1.97**	**1.93**	**1.90**	**1.88**	**1.87**	**1.86**	**1.84**	**1.83**	**1.82**	**1.81**	**1.80**	**1.79**	**1.79**
12	5.07	3.35	**2.82**	**2.57**	**2.42**	**2.25**	**2.16**	**2.09**	**2.05**	**2.02**	**2.00**	**1.98**	**1.97**	**1.95**	**1.93**	**1.92**	**1.92**	**1.91**	**1.90**	**1.89**
16	5.61	3.59	**2.99**	**2.71**	**2.54**	**2.36**	**2.26**	**2.18**	**2.14**	**2.10**	**2.08**	**2.06**	**2.05**	**2.02**	**2.01**	**2.00**	**1.99**	**1.98**	**1.97**	**1.96**
20	6.07	3.79	**3.13**	**2.82**	**2.64**	**2.44**	**2.33**	**2.25**	**2.20**	**2.17**	**2.14**	**2.12**	**2.11**	**2.08**	**2.07**	**2.05**	**2.05**	**2.04**	**2.02**	**2.02**
30	6.99	4.17	3.39	**3.02**	**2.82**	**2.59**	**2.47**	**2.38**	**2.32**	**2.28**	**2.25**	**2.23**	**2.21**	**2.19**	**2.17**	**2.15**	**2.14**	**2.14**	**2.12**	**2.11**
40	7.72	4.46	3.57	**3.17**	**2.94**	**2.70**	**2.56**	**2.46**	**2.40**	**2.36**	**2.33**	**2.30**	**2.28**	**2.26**	**2.24**	**2.22**	**2.21**	**2.20**	**2.19**	**2.18**
50	8.33	4.69	3.72	*3.29*	**3.04**	**2.78**	**2.64**	**2.53**	**2.46**	**2.42**	**2.39**	**2.36**	**2.34**	**2.31**	**2.29**	**2.28**	**2.26**	**2.26**	**2.24**	**2.23**
60	8.87	4.89	3.85	*3.39*	**3.13**	**2.84**	**2.70**	**2.59**	**2.52**	**2.47**	**2.43**	**2.41**	**2.39**	**2.36**	**2.33**	**2.32**	**2.31**	**2.30**	**2.28**	**2.27**
75	9.57	5.14	4.01	3.51	**3.23**	**2.93**	**2.77**	**2.65**	**2.58**	**2.53**	**2.49**	**2.46**	**2.44**	**2.41**	**2.39**	**2.37**	**2.36**	**2.35**	**2.33**	**2.32**
100	10.55	5.47	4.21	3.66	*3.36*	**3.03**	**2.86**	**2.74**	**2.66**	**2.60**	**2.56**	**2.53**	**2.51**	**2.48**	**2.45**	**2.44**	**2.42**	**2.41**	**2.39**	**2.38**
125	11.38	5.75	4.38	3.79	*3.46*	**3.12**	**2.93**	**2.80**	**2.72**	**2.66**	**2.62**	**2.59**	**2.57**	**2.53**	**2.50**	**2.48**	**2.47**	**2.46**	**2.44**	**2.43**
150	12.10	5.98	4.52	3.89	3.55	**3.18**	**2.99**	**2.85**	**2.77**	**2.71**	**2.67**	**2.63**	**2.61**	**2.57**	**2.54**	**2.53**	**2.51**	**2.50**	**2.48**	**2.46**
175	12.74	6.18	4.64	3.98	3.62	**3.24**	**3.04**	**2.90**	**2.81**	**2.75**	**2.70**	**2.67**	**2.64**	**2.61**	**2.58**	**2.56**	**2.54**	**2.53**	**2.51**	**2.50**
200	13.33	6.36	4.74	4.06	3.68	*3.29*	**3.09**	**2.94**	**2.85**	**2.78**	**2.74**	**2.70**	**2.68**	**2.64**	**2.61**	**2.59**	**2.57**	**2.56**	**2.54**	**2.52**

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Table 19-14. κ-Multipliers for 1-of-1 Intrawell Prediction Limits on Means of Order 2 (1 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.37**	**1.94**	**1.77**	**1.68**	**1.62**	**1.56**	**1.52**	**1.49**	**1.47**	**1.45**	**1.44**	**1.44**	**1.43**	**1.42**	**1.41**	**1.41**	**1.40**	**1.40**	**1.40**	**1.39**
2	**3.14**	**2.41**	**2.15**	**2.01**	**1.93**	**1.83**	**1.77**	**1.73**	**1.70**	**1.68**	**1.67**	**1.66**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.61**	**1.60**	**1.60**
3	3.67	**2.71**	**2.37**	**2.21**	**2.10**	**1.98**	**1.92**	**1.87**	**1.83**	**1.81**	**1.79**	**1.78**	**1.77**	**1.75**	**1.74**	**1.74**	**1.73**	**1.72**	**1.72**	**1.71**
4	4.09	**2.93**	**2.54**	**2.34**	**2.23**	**2.09**	**2.02**	**1.96**	**1.92**	**1.90**	**1.88**	**1.86**	**1.85**	**1.84**	**1.82**	**1.82**	**1.81**	**1.80**	**1.79**	**1.79**
5	4.43	**3.10**	**2.67**	**2.45**	**2.32**	**2.18**	**2.09**	**2.03**	**1.99**	**1.96**	**1.94**	**1.93**	**1.92**	**1.90**	**1.88**	**1.88**	**1.87**	**1.86**	**1.85**	**1.84**
8	5.25	**3.50**	**2.95**	**2.68**	**2.53**	**2.35**	**2.25**	**2.18**	**2.13**	**2.10**	**2.08**	**2.06**	**2.05**	**2.02**	**2.01**	**2.00**	**1.99**	**1.98**	**1.97**	**1.96**
12	6.06	3.86	**3.20**	**2.89**	**2.70**	**2.50**	**2.39**	**2.31**	**2.25**	**2.22**	**2.19**	**2.17**	**2.15**	**2.13**	**2.11**	**2.10**	**2.09**	**2.08**	**2.07**	**2.06**
16	6.70	4.13	**3.39**	**3.03**	**2.83**	**2.61**	**2.48**	**2.39**	**2.34**	**2.30**	**2.27**	**2.24**	**2.23**	**2.20**	**2.18**	**2.17**	**2.16**	**2.15**	**2.14**	**2.13**
20	7.24	4.35	**3.53**	**3.15**	**2.93**	**2.69**	**2.56**	**2.46**	**2.40**	**2.36**	**2.33**	**2.30**	**2.28**	**2.26**	**2.24**	**2.22**	**2.21**	**2.20**	**2.19**	**2.18**
30	8.32	4.78	3.81	**3.36**	**3.11**	**2.84**	**2.69**	**2.58**	**2.51**	**2.47**	**2.43**	**2.41**	**2.39**	**2.36**	**2.33**	**2.32**	**2.31**	**2.30**	**2.28**	**2.27**
40	9.18	5.10	4.01	**3.52**	**3.24**	**2.94**	**2.79**	**2.67**	**2.59**	**2.54**	**2.51**	**2.48**	**2.46**	**2.42**	**2.40**	**2.38**	**2.37**	**2.36**	**2.34**	**2.33**
50	9.90	5.35	4.17	*3.64*	**3.35**	**3.03**	**2.86**	**2.73**	**2.66**	**2.60**	**2.56**	**2.53**	**2.51**	**2.48**	**2.45**	**2.43**	**2.42**	**2.41**	**2.39**	**2.38**
60	10.54	5.57	4.30	3.74	**3.43**	**3.09**	**2.92**	**2.79**	**2.71**	**2.65**	**2.61**	**2.58**	**2.55**	**2.52**	**2.49**	**2.48**	**2.46**	**2.45**	**2.43**	**2.42**
75	11.36	5.85	4.47	3.87	**3.54**	**3.18**	**2.99**	**2.85**	**2.77**	**2.71**	**2.67**	**2.63**	**2.61**	**2.57**	**2.54**	**2.53**	**2.51**	**2.50**	**2.48**	**2.46**
100	12.52	6.23	4.70	4.04	*3.67*	**3.29**	**3.08**	**2.94**	**2.85**	**2.78**	**2.74**	**2.70**	**2.68**	**2.64**	**2.61**	**2.59**	**2.57**	**2.56**	**2.54**	**2.52**
125	13.50	6.53	4.88	4.17	3.78	**3.37**	**3.16**	**3.00**	**2.91**	**2.84**	**2.79**	**2.76**	**2.73**	**2.69**	**2.66**	**2.64**	**2.62**	**2.61**	**2.58**	**2.57**
150	14.35	6.79	5.03	4.28	3.87	**3.44**	**3.22**	**3.06**	**2.96**	**2.89**	**2.84**	**2.80**	**2.77**	**2.73**	**2.70**	**2.67**	**2.66**	**2.65**	**2.62**	**2.60**
175	15.11	7.02	5.16	4.37	3.94	**3.50**	**3.27**	**3.10**	**3.00**	**2.93**	**2.87**	**2.84**	**2.81**	**2.76**	**2.73**	**2.71**	**2.69**	**2.68**	**2.65**	**2.63**
200	15.80	7.22	5.27	4.45	4.01	**3.55**	**3.31**	**3.14**	**3.03**	**2.96**	**2.91**	**2.87**	**2.84**	**2.79**	**2.76**	**2.74**	**2.72**	**2.70**	**2.68**	**2.66**

Table 19-14. κ-Multipliers for 1-of-1 Intrawell Prediction Limits on Means of Order 2 (2 COC, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.01**	**1.63**	**1.48**	**1.41**	**1.36**	**1.30**	**1.27**	**1.25**	**1.23**	**1.22**	**1.21**	**1.20**	**1.20**	**1.19**	**1.19**	**1.18**	**1.18**	**1.18**	**1.17**	**1.17**
2	**2.71**	**2.07**	**1.85**	**1.73**	**1.66**	**1.58**	**1.54**	**1.50**	**1.48**	**1.46**	**1.45**	**1.44**	**1.44**	**1.43**	**1.42**	**1.41**	**1.41**	**1.40**	**1.40**	**1.39**
3	3.18	**2.35**	**2.06**	**1.92**	**1.84**	**1.74**	**1.69**	**1.64**	**1.62**	**1.60**	**1.58**	**1.57**	**1.57**	**1.55**	**1.54**	**1.54**	**1.53**	**1.53**	**1.52**	**1.52**
4	3.55	**2.55**	**2.22**	**2.06**	**1.96**	**1.85**	**1.79**	**1.74**	**1.71**	**1.69**	**1.67**	**1.66**	**1.65**	**1.64**	**1.63**	**1.62**	**1.62**	**1.61**	**1.60**	**1.60**
5	3.86	**2.71**	**2.34**	**2.16**	**2.06**	**1.93**	**1.87**	**1.82**	**1.78**	**1.76**	**1.74**	**1.73**	**1.72**	**1.71**	**1.69**	**1.69**	**1.68**	**1.68**	**1.67**	**1.66**
8	4.59	3.07	**2.61**	**2.39**	**2.26**	**2.11**	**2.03**	**1.97**	**1.93**	**1.90**	**1.88**	**1.87**	**1.86**	**1.84**	**1.83**	**1.82**	**1.81**	**1.80**	**1.79**	**1.79**
12	5.30	3.40	**2.84**	**2.58**	**2.43**	**2.26**	**2.17**	**2.10**	**2.05**	**2.02**	**2.00**	**1.98**	**1.97**	**1.95**	**1.93**	**1.92**	**1.92**	**1.91**	**1.90**	**1.89**
16	5.87	3.65	*3.02*	**2.72**	**2.55**	**2.36**	**2.26**	**2.19**	**2.14**	**2.11**	**2.08**	**2.06**	**2.05**	**2.03**	**2.01**	**2.00**	**1.99**	**1.98**	**1.97**	**1.96**
20	6.34	3.85	3.15	**2.83**	**2.65**	**2.45**	**2.34**	**2.26**	**2.20**	**2.17**	**2.14**	**2.12**	**2.11**	**2.08**	**2.07**	**2.05**	**2.05**	**2.04**	**2.02**	**2.02**
30	7.30	4.23	3.41	*3.04*	**2.83**	**2.59**	**2.47**	**2.38**	**2.32**	**2.28**	**2.25**	**2.23**	**2.21**	**2.19**	**2.17**	**2.15**	**2.14**	**2.14**	**2.12**	**2.11**
40	8.05	4.52	3.60	3.18	**2.95**	**2.70**	**2.56**	**2.47**	**2.40**	**2.36**	**2.33**	**2.30**	**2.29**	**2.26**	**2.24**	**2.22**	**2.21**	**2.20**	**2.19**	**2.18**
50	8.69	4.76	3.75	3.30	*3.05*	**2.78**	**2.64**	**2.53**	**2.47**	**2.42**	**2.39**	**2.36**	**2.34**	**2.31**	**2.29**	**2.28**	**2.26**	**2.26**	**2.24**	**2.23**
60	9.25	4.95	3.87	3.40	*3.13*	**2.85**	**2.70**	**2.59**	**2.52**	**2.47**	**2.43**	**2.41**	**2.39**	**2.36**	**2.33**	**2.32**	**2.31**	**2.30**	**2.28**	**2.27**
75	9.98	5.21	4.03	3.52	3.23	**2.93**	**2.77**	**2.65**	**2.58**	**2.53**	**2.49**	**2.46**	**2.44**	**2.41**	**2.39**	**2.37**	**2.36**	**2.35**	**2.33**	**2.32**
100	11.00	5.54	4.24	3.67	3.36	*3.04*	**2.86**	**2.74**	**2.66**	**2.60**	**2.56**	**2.53**	**2.51**	**2.48**	**2.45**	**2.44**	**2.42**	**2.41**	**2.39**	**2.38**
125	11.86	5.82	4.40	3.80	3.47	*3.12*	**2.94**	**2.80**	**2.72**	**2.66**	**2.62**	**2.59**	**2.57**	**2.53**	**2.50**	**2.48**	**2.47**	**2.46**	**2.44**	**2.43**
150	12.61	6.05	4.54	3.90	3.55	*3.19*	*2.99*	**2.86**	**2.77**	**2.71**	**2.67**	**2.63**	**2.61**	**2.57**	**2.55**	**2.53**	**2.51**	**2.50**	**2.48**	**2.46**
175	13.28	6.26	4.66	3.99	3.63	3.24	*3.04*	**2.90**	**2.81**	**2.75**	**2.70**	**2.67**	**2.65**	**2.61**	**2.58**	**2.56**	**2.54**	**2.53**	**2.51**	**2.50**
200	13.89	6.44	4.77	4.07	3.69	3.29	*3.09*	**2.94**	**2.85**	**2.78**	**2.74**	**2.70**	**2.68**	**2.64**	**2.61**	**2.59**	**2.57**	**2.56**	**2.54**	**2.51**

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Table 19-14. κ-Multipliers for 1-of-1 Intrawell Prediction Limits on Means of Order 2 (2 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.57**	**2.02**	**1.82**	**1.71**	**1.65**	**1.57**	**1.53**	**1.50**	**1.48**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**	**1.42**	**1.41**	**1.41**	**1.40**	**1.40**	**1.39**
2	3.39	**2.50**	**2.19**	**2.04**	**1.95**	**1.84**	**1.78**	**1.74**	**1.71**	**1.69**	**1.67**	**1.66**	**1.65**	**1.64**	**1.63**	**1.62**	**1.62**	**1.61**	**1.60**	**1.60**
3	3.94	**2.80**	**2.42**	**2.23**	**2.12**	**2.00**	**1.93**	**1.87**	**1.84**	**1.81**	**1.80**	**1.78**	**1.77**	**1.76**	**1.75**	**1.74**	**1.73**	**1.73**	**1.72**	**1.71**
4	4.38	**3.02**	**2.58**	**2.37**	**2.25**	**2.10**	**2.03**	**1.97**	**1.93**	**1.90**	**1.88**	**1.87**	**1.86**	**1.84**	**1.83**	**1.82**	**1.81**	**1.80**	**1.79**	**1.79**
5	4.75	**3.20**	**2.71**	**2.48**	**2.34**	**2.19**	**2.10**	**2.04**	**2.00**	**1.97**	**1.95**	**1.93**	**1.92**	**1.90**	**1.89**	**1.88**	**1.87**	**1.86**	**1.85**	**1.84**
8	5.61	3.59	**2.99**	**2.71**	**2.54**	**2.36**	**2.26**	**2.18**	**2.14**	**2.10**	**2.08**	**2.06**	**2.05**	**2.02**	**2.01**	**2.00**	**1.99**	**1.98**	**1.97**	**1.96**
12	6.47	3.96	**3.24**	**2.91**	**2.72**	**2.51**	**2.39**	**2.31**	**2.26**	**2.22**	**2.19**	**2.17**	**2.15**	**2.13**	**2.11**	**2.10**	**2.09**	**2.08**	**2.07**	**2.06**
16	7.15	4.24	3.43	**3.06**	**2.85**	**2.61**	**2.49**	**2.40**	**2.34**	**2.30**	**2.27**	**2.25**	**2.23**	**2.20**	**2.18**	**2.17**	**2.16**	**2.15**	**2.14**	**2.13**
20	7.72	4.46	3.57	**3.17**	**2.94**	**2.70**	**2.56**	**2.46**	**2.40**	**2.36**	**2.33**	**2.30**	**2.28**	**2.26**	**2.24**	**2.22**	**2.21**	**2.20**	**2.19**	**2.18**
30	8.87	4.89	3.85	*3.39*	**3.13**	**2.84**	**2.70**	**2.59**	**2.52**	**2.47**	**2.43**	**2.41**	**2.39**	**2.36**	**2.33**	**2.32**	**2.31**	**2.30**	**2.28**	**2.27**
40	9.78	5.21	4.05	3.54	**3.26**	**2.95**	**2.79**	**2.67**	**2.60**	**2.54**	**2.51**	**2.48**	**2.46**	**2.42**	**2.40**	**2.38**	**2.37**	**2.36**	**2.34**	**2.33**
50	10.55	5.47	4.21	3.66	*3.36*	**3.03**	**2.86**	**2.74**	**2.66**	**2.60**	**2.56**	**2.53**	**2.51**	**2.48**	**2.45**	**2.44**	**2.42**	**2.41**	**2.39**	**2.38**
60	11.22	5.70	4.35	3.76	*3.44*	**3.10**	**2.92**	**2.79**	**2.71**	**2.65**	**2.61**	**2.58**	**2.56**	**2.52**	**2.49**	**2.48**	**2.46**	**2.45**	**2.43**	**2.42**
75	12.10	5.98	4.52	3.89	3.55	**3.18**	**2.99**	**2.85**	**2.77**	**2.71**	**2.67**	**2.63**	**2.61**	**2.57**	**2.54**	**2.53**	**2.51**	**2.50**	**2.48**	**2.46**
100	13.33	6.36	4.74	4.06	3.68	*3.29*	**3.09**	**2.94**	**2.85**	**2.78**	**2.74**	**2.70**	**2.68**	**2.64**	**2.61**	**2.59**	**2.57**	**2.56**	**2.54**	**2.52**
125	14.36	6.67	4.92	4.19	3.79	*3.37*	**3.16**	**3.00**	**2.91**	**2.84**	**2.79**	**2.76**	**2.73**	**2.69**	**2.66**	**2.64**	**2.62**	**2.61**	**2.58**	**2.57**
150	15.25	6.93	5.07	4.30	3.88	*3.44*	**3.22**	**3.06**	**2.96**	**2.89**	**2.84**	**2.80**	**2.77**	**2.73**	**2.70**	**2.68**	**2.66**	**2.65**	**2.62**	**2.60**
175	16.05	7.16	5.20	4.39	3.96	*3.50*	**3.27**	**3.10**	**3.00**	**2.93**	**2.87**	**2.84**	**2.81**	**2.76**	**2.73**	**2.71**	**2.69**	**2.68**	**2.65**	**2.63**
200	16.80	7.37	5.31	4.47	4.02	3.55	*3.31*	**3.14**	**3.03**	**2.96**	**2.91**	**2.87**	**2.84**	**2.79**	**2.76**	**2.74**	**2.72**	**2.70**	**2.68**	**2.66**

Table 19-14. κ-Multipliers for 1-of-1 Intrawell Prediction Limits on Means of Order 2 (2 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**3.14**	**2.41**	**2.15**	**2.01**	**1.93**	**1.83**	**1.77**	**1.73**	**1.70**	**1.68**	**1.67**	**1.66**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.61**	**1.60**	**1.60**
2	4.09	**2.93**	**2.54**	**2.34**	**2.23**	**2.09**	**2.02**	**1.96**	**1.92**	**1.90**	**1.88**	**1.86**	**1.85**	**1.84**	**1.82**	**1.82**	**1.81**	**1.80**	**1.79**	**1.79**
3	4.74	**3.25**	**2.78**	**2.54**	**2.40**	**2.24**	**2.16**	**2.09**	**2.05**	**2.02**	**2.00**	**1.98**	**1.97**	**1.95**	**1.93**	**1.92**	**1.92**	**1.91**	**1.90**	**1.89**
4	5.25	**3.50**	**2.95**	**2.68**	**2.53**	**2.35**	**2.25**	**2.18**	**2.13**	**2.10**	**2.08**	**2.06**	**2.05**	**2.02**	**2.01**	**2.00**	**1.99**	**1.98**	**1.97**	**1.96**
5	5.68	3.69	**3.09**	**2.80**	**2.62**	**2.43**	**2.33**	**2.25**	**2.20**	**2.17**	**2.14**	**2.12**	**2.10**	**2.08**	**2.07**	**2.05**	**2.04**	**2.04**	**2.02**	**2.02**
8	6.70	4.13	**3.39**	**3.03**	**2.83**	**2.61**	**2.48**	**2.39**	**2.34**	**2.30**	**2.27**	**2.24**	**2.23**	**2.20**	**2.18**	**2.17**	**2.16**	**2.15**	**2.14**	**2.13**
12	7.71	4.54	3.65	**3.25**	**3.01**	**2.76**	**2.62**	**2.52**	**2.45**	**2.41**	**2.37**	**2.35**	**2.33**	**2.30**	**2.28**	**2.27**	**2.25**	**2.25**	**2.23**	**2.22**
16	8.51	4.85	3.85	**3.40**	**3.14**	**2.86**	**2.71**	**2.60**	**2.53**	**2.48**	**2.45**	**2.42**	**2.40**	**2.37**	**2.35**	**2.33**	**2.32**	**2.31**	**2.29**	**2.28**
20	9.18	5.10	4.01	**3.52**	**3.24**	**2.94**	**2.79**	**2.67**	**2.59**	**2.54**	**2.51**	**2.48**	**2.46**	**2.42**	**2.40**	**2.38**	**2.37**	**2.36**	**2.34**	**2.33**
30	10.54	5.57	4.30	3.74	**3.43**	**3.09**	**2.92**	**2.79**	**2.71**	**2.65**	**2.61**	**2.58**	**2.55**	**2.52**	**2.49**	**2.48**	**2.46**	**2.45**	**2.43**	**2.42**
40	11.61	5.93	4.52	3.91	**3.57**	**3.20**	**3.01**	**2.87**	**2.79**	**2.73**	**2.68**	**2.65**	**2.62**	**2.59**	**2.56**	**2.54**	**2.52**	**2.51**	**2.49**	**2.48**
50	12.52	6.23	4.70	4.04	*3.67*	**3.29**	**3.08**	**2.94**	**2.85**	**2.78**	**2.74**	**2.70**	**2.68**	**2.64**	**2.61**	**2.59**	**2.57**	**2.56**	**2.54**	**2.52**
60	13.32	6.48	4.84	4.14	3.76	**3.35**	**3.14**	**2.99**	**2.90**	**2.83**	**2.78**	**2.75**	**2.72**	**2.68**	**2.65**	**2.63**	**2.61**	**2.60**	**2.57**	**2.56**
75	14.35	6.79	5.03	4.28	3.87	**3.44**	**3.22**	**3.06**	**2.96**	**2.89**	**2.84**	**2.80**	**2.77**	**2.73**	**2.70**	**2.67**	**2.66**	**2.65**	**2.62**	**2.60**
100	15.80	7.22	5.27	4.45	4.01	**3.55**	**3.31**	**3.14**	**3.03**	**2.96**	**2.91**	**2.87**	**2.84**	**2.79**	**2.76**	**2.74**	**2.72**	**2.70**	**2.68**	**2.66**
125	17.02	7.57	5.46	4.59	4.12	*3.63*	**3.38**	**3.20**	**3.09**	**3.02**	**2.96**	**2.92**	**2.89**	**2.84**	**2.81**	**2.78**	**2.76**	**2.75**	**2.72**	**2.70**
150	18.10	7.87	5.63	4.71	4.22	*3.70*	**3.44**	**3.26**	**3.14**	**3.06**	**3.01**	**2.96**	**2.93**	**2.88**	**2.84**	**2.82**	**2.80**	**2.78**	**2.76**	**2.74**
175	19.02	8.12	5.77	4.81	4.29	*3.76*	**3.49**	**3.30**	**3.18**	**3.10**	**3.04**	**3.00**	**2.96**	**2.91**	**2.88**	**2.85**	**2.83**	**2.82**	**2.79**	**2.77**
200	19.90	8.35	5.89	4.89	4.36	*3.82*	**3.54**	**3.34**	**3.22**	**3.13**	**3.07**	**3.03**	**2.99**	**2.94**	**2.91**	**2.88**	**2.85**	**2.84**	**2.81**	**2.79**

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Table 19-14. κ-Multipliers for 1-of-1 Intrawell Prediction Limits on Means of Order 2 (5 COC, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.97**	**2.22**	**1.97**	**1.84**	**1.76**	**1.67**	**1.62**	**1.58**	**1.56**	**1.54**	**1.53**	**1.52**	**1.51**	**1.50**	**1.49**	**1.48**	**1.48**	**1.47**	**1.47**	**1.46**
2	3.86	**2.71**	**2.34**	**2.16**	**2.06**	**1.93**	**1.87**	**1.82**	**1.78**	**1.76**	**1.74**	**1.73**	**1.72**	**1.71**	**1.69**	**1.69**	**1.68**	**1.68**	**1.67**	**1.66**
3	4.48	**3.02**	**2.57**	**2.36**	**2.23**	**2.09**	**2.01**	**1.95**	**1.91**	**1.88**	**1.86**	**1.85**	**1.84**	**1.82**	**1.81**	**1.80**	**1.79**	**1.79**	**1.78**	**1.77**
4	4.97	3.25	**2.74**	**2.49**	**2.35**	**2.19**	**2.10**	**2.04**	**2.00**	**1.97**	**1.95**	**1.93**	**1.92**	**1.90**	**1.89**	**1.88**	**1.87**	**1.86**	**1.85**	**1.84**
5	5.38	3.44	**2.87**	**2.60**	**2.45**	**2.27**	**2.18**	**2.11**	**2.07**	**2.03**	**2.01**	**1.99**	**1.98**	**1.96**	**1.95**	**1.94**	**1.93**	**1.92**	**1.91**	**1.90**
8	6.34	3.85	3.15	**2.83**	**2.65**	**2.45**	**2.34**	**2.26**	**2.20**	**2.17**	**2.14**	**2.12**	**2.11**	**2.08**	**2.07**	**2.05**	**2.05**	**2.04**	**2.02**	**2.02**
12	7.30	4.23	3.41	*3.04*	**2.83**	**2.59**	**2.47**	**2.38**	**2.32**	**2.28**	**2.25**	**2.23**	**2.21**	**2.19**	**2.17**	**2.15**	**2.14**	**2.14**	**2.12**	**2.11**
16	8.05	4.52	3.60	3.18	**2.95**	**2.70**	**2.56**	**2.47**	**2.40**	**2.36**	**2.33**	**2.30**	**2.29**	**2.26**	**2.24**	**2.22**	**2.21**	**2.20**	**2.19**	**2.18**
20	8.69	4.76	3.75	3.30	*3.05*	**2.78**	**2.64**	**2.53**	**2.47**	**2.42**	**2.39**	**2.36**	**2.34**	**2.31**	**2.29**	**2.28**	**2.26**	**2.26**	**2.24**	**2.23**
30	9.98	5.21	4.03	3.52	3.23	**2.93**	**2.77**	**2.65**	**2.58**	**2.53**	**2.49**	**2.46**	**2.44**	**2.41**	**2.39**	**2.37**	**2.36**	**2.35**	**2.33**	**2.32**
40	10.99	5.54	4.24	3.67	3.36	*3.04*	**2.86**	**2.74**	**2.66**	**2.60**	**2.56**	**2.54**	**2.51**	**2.48**	**2.45**	**2.44**	**2.42**	**2.41**	**2.39**	**2.38**
50	11.86	5.82	4.40	3.80	3.47	*3.12*	**2.94**	**2.80**	**2.72**	**2.66**	**2.62**	**2.59**	**2.57**	**2.53**	**2.50**	**2.48**	**2.47**	**2.46**	**2.44**	**2.43**
60	12.61	6.05	4.54	3.90	3.55	*3.19*	**2.99**	**2.86**	**2.77**	**2.71**	**2.67**	**2.63**	**2.61**	**2.57**	**2.55**	**2.53**	**2.51**	**2.50**	**2.48**	**2.46**
75	13.59	6.35	4.71	4.03	3.66	3.27	*3.07*	**2.92**	**2.83**	**2.77**	**2.72**	**2.69**	**2.66**	**2.62**	**2.59**	**2.57**	**2.56**	**2.55**	**2.52**	**2.51**
100	14.97	6.75	4.94	4.20	3.80	3.38	*3.16*	*3.00*	**2.91**	**2.84**	**2.79**	**2.76**	**2.73**	**2.69**	**2.66**	**2.64**	**2.62**	**2.60**	**2.58**	**2.57**
125	16.14	7.08	5.13	4.33	3.90	3.46	*3.23*	*3.07*	*2.97*	**2.90**	**2.85**	**2.81**	**2.78**	**2.74**	**2.71**	**2.68**	**2.67**	**2.65**	**2.62**	**2.61**
150	17.14	7.35	5.28	4.44	4.00	3.53	3.29	*3.12*	*3.01*	*2.95*	**2.89**	**2.85**	**2.82**	**2.78**	**2.75**	**2.72**	**2.70**	**2.69**	**2.66**	**2.65**
175	18.05	7.59	5.41	4.53	4.06	3.59	3.34	*3.16*	*3.05*	*2.98*	**2.92**	**2.89**	**2.86**	**2.81**	**2.78**	**2.75**	**2.74**	**2.72**	**2.70**	**2.68**
200	18.87	7.81	5.53	4.61	4.13	3.64	3.39	*3.20*	*3.09*	*3.02*	*2.96*	**2.92**	**2.89**	**2.84**	**2.81**	**2.78**	**2.76**	**2.75**	**2.72**	**2.70**

Table 19-14. κ-Multipliers for 1-of-1 Intrawell Prediction Limits on Means of Order 2 (5 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.68	**2.66**	**2.32**	**2.15**	**2.04**	**1.93**	**1.86**	**1.81**	**1.78**	**1.76**	**1.74**	**1.73**	**1.72**	**1.70**	**1.69**	**1.69**	**1.68**	**1.67**	**1.67**	**1.66**
2	4.75	**3.20**	**2.71**	**2.48**	**2.34**	**2.19**	**2.10**	**2.04**	**2.00**	**1.97**	**1.95**	**1.93**	**1.92**	**1.90**	**1.89**	**1.88**	**1.87**	**1.86**	**1.85**	**1.84**
3	5.49	3.54	**2.95**	**2.68**	**2.52**	**2.34**	**2.24**	**2.16**	**2.12**	**2.09**	**2.06**	**2.04**	**2.03**	**2.01**	**1.99**	**1.98**	**1.97**	**1.97**	**1.95**	**1.95**
4	6.07	3.79	**3.13**	**2.82**	**2.64**	**2.44**	**2.33**	**2.25**	**2.20**	**2.17**	**2.14**	**2.12**	**2.11**	**2.08**	**2.07**	**2.05**	**2.05**	**2.04**	**2.02**	**2.02**
5	6.56	4.00	**3.27**	**2.93**	**2.74**	**2.52**	**2.41**	**2.32**	**2.27**	**2.23**	**2.20**	**2.18**	**2.16**	**2.14**	**2.12**	**2.11**	**2.10**	**2.09**	**2.08**	**2.07**
8	7.72	4.46	3.57	**3.17**	**2.94**	**2.70**	**2.56**	**2.46**	**2.40**	**2.36**	**2.33**	**2.30**	**2.28**	**2.26**	**2.24**	**2.22**	**2.21**	**2.20**	**2.19**	**2.18**
12	8.87	4.89	3.85	*3.39*	**3.13**	**2.84**	**2.70**	**2.59**	**2.52**	**2.47**	**2.43**	**2.41**	**2.39**	**2.36**	**2.33**	**2.32**	**2.31**	**2.30**	**2.28**	**2.27**
16	9.78	5.21	4.05	3.54	**3.26**	**2.95**	**2.79**	**2.67**	**2.60**	**2.54**	**2.51**	**2.48**	**2.46**	**2.42**	**2.40**	**2.38**	**2.37**	**2.36**	**2.34**	**2.33**
20	10.55	5.47	4.21	3.66	*3.36*	**3.03**	**2.86**	**2.74**	**2.66**	**2.60**	**2.56**	**2.53**	**2.51**	**2.48**	**2.45**	**2.44**	**2.42**	**2.41**	**2.39**	**2.38**
30	12.10	5.98	4.52	3.89	3.55	**3.18**	**2.99**	**2.85**	**2.77**	**2.71**	**2.67**	**2.63**	**2.61**	**2.57**	**2.54**	**2.53**	**2.51**	**2.50**	**2.48**	**2.46**
40	13.33	6.36	4.74	4.06	3.68	*3.29*	**3.09**	**2.94**	**2.85**	**2.78**	**2.74**	**2.70**	**2.68**	**2.64**	**2.61**	**2.59**	**2.57**	**2.56**	**2.54**	**2.52**
50	14.36	6.67	4.92	4.19	3.79	*3.37*	**3.16**	**3.00**	**2.91**	**2.84**	**2.79**	**2.76**	**2.73**	**2.69**	**2.66**	**2.64**	**2.62**	**2.61**	**2.58**	**2.57**
60	15.26	6.93	5.07	4.30	3.88	*3.44*	**3.22**	**3.06**	**2.96**	**2.89**	**2.84**	**2.80**	**2.77**	**2.73**	**2.70**	**2.68**	**2.66**	**2.65**	**2.62**	**2.60**
75	16.44	7.27	5.26	4.43	3.99	3.53	*3.29*	**3.12**	**3.02**	**2.94**	**2.89**	**2.85**	**2.82**	**2.78**	**2.75**	**2.72**	**2.70**	**2.68**	**2.66**	**2.65**
100	18.11	7.72	5.51	4.61	4.13	3.64	*3.39*	**3.20**	**3.09**	**3.02**	**2.96**	**2.92**	**2.89**	**2.84**	**2.81**	**2.78**	**2.76**	**2.75**	**2.72**	**2.70**
125	19.51	8.09	5.71	4.75	4.24	3.72	*3.46*	*3.27*	**3.15**	**3.07**	**3.01**	**2.97**	**2.94**	**2.89**	**2.85**	**2.83**	**2.81**	**2.79**	**2.77**	**2.75**
150	20.74	8.41	5.88	4.87	4.34	3.79	*3.52*	*3.32*	**3.20**	**3.12**	**3.06**	**3.01**	**2.98**	**2.93**	**2.89**	**2.87**	**2.85**	**2.83**	**2.80**	**2.78**
175	21.80	8.67	6.03	4.97	4.42	3.85	3.57	*3.36*	**3.24**	**3.15**	**3.09**	**3.05**	**3.01**	**2.96**	**2.92**	**2.90**	**2.88**	**2.86**	**2.83**	**2.81**
200	22.85	8.91	6.15	5.06	4.49	3.91	3.61	*3.40*	*3.28*	**3.19**	**3.13**	**3.08**	**3.04**	**2.99**	**2.95**	**2.92**	**2.90**	**2.89**	**2.86**	**2.84**

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Table 19-14. κ-Multipliers for 1-of-1 Intrawell Prediction Limits on Means of Order 2 (5 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	4.43	**3.10**	**2.67**	**2.45**	**2.32**	**2.18**	**2.09**	**2.03**	**1.99**	**1.96**	**1.94**	**1.93**	**1.92**	**1.90**	**1.88**	**1.88**	**1.87**	**1.86**	**1.85**	**1.84**
2	5.68	3.69	**3.09**	**2.80**	**2.62**	**2.43**	**2.33**	**2.25**	**2.20**	**2.17**	**2.14**	**2.12**	**2.10**	**2.08**	**2.07**	**2.05**	**2.04**	**2.04**	**2.02**	**2.02**
3	6.55	4.07	**3.34**	**3.00**	**2.80**	**2.58**	**2.46**	**2.37**	**2.32**	**2.28**	**2.25**	**2.23**	**2.21**	**2.19**	**2.17**	**2.15**	**2.14**	**2.14**	**2.12**	**2.11**
4	7.24	4.35	**3.53**	**3.15**	**2.93**	**2.69**	**2.56**	**2.46**	**2.40**	**2.36**	**2.33**	**2.30**	**2.28**	**2.26**	**2.24**	**2.22**	**2.21**	**2.20**	**2.19**	**2.18**
5	7.81	4.58	3.68	**3.27**	**3.03**	**2.77**	**2.63**	**2.53**	**2.46**	**2.42**	**2.39**	**2.36**	**2.34**	**2.31**	**2.29**	**2.28**	**2.26**	**2.25**	**2.24**	**2.23**
8	9.18	5.10	4.01	**3.52**	**3.24**	**2.94**	**2.79**	**2.67**	**2.59**	**2.54**	**2.51**	**2.48**	**2.46**	**2.42**	**2.40**	**2.38**	**2.37**	**2.36**	**2.34**	**2.33**
12	10.54	5.57	4.30	3.74	**3.43**	**3.09**	**2.92**	**2.79**	**2.71**	**2.65**	**2.61**	**2.58**	**2.55**	**2.52**	**2.49**	**2.48**	**2.46**	**2.45**	**2.43**	**2.42**
16	11.61	5.93	4.52	3.91	**3.57**	**3.20**	**3.01**	**2.87**	**2.79**	**2.73**	**2.68**	**2.65**	**2.62**	**2.59**	**2.56**	**2.54**	**2.52**	**2.51**	**2.49**	**2.48**
20	12.52	6.23	4.70	4.04	*3.67*	**3.29**	**3.08**	**2.94**	**2.85**	**2.78**	**2.74**	**2.70**	**2.68**	**2.64**	**2.61**	**2.59**	**2.57**	**2.56**	**2.54**	**2.52**
30	14.35	6.79	5.03	4.28	3.87	**3.44**	**3.22**	**3.06**	**2.96**	**2.89**	**2.84**	**2.80**	**2.77**	**2.73**	**2.70**	**2.67**	**2.66**	**2.65**	**2.62**	**2.60**
40	15.81	7.22	5.27	4.45	4.01	**3.55**	**3.31**	**3.14**	**3.03**	**2.96**	**2.91**	**2.87**	**2.84**	**2.79**	**2.76**	**2.74**	**2.72**	**2.70**	**2.68**	**2.66**
50	17.02	7.57	5.46	4.59	4.12	*3.63*	**3.38**	**3.20**	**3.09**	**3.02**	**2.96**	**2.92**	**2.89**	**2.84**	**2.81**	**2.78**	**2.76**	**2.75**	**2.72**	**2.70**
60	18.09	7.87	5.63	4.71	4.22	*3.70*	**3.44**	**3.26**	**3.14**	**3.06**	**3.01**	**2.96**	**2.93**	**2.88**	**2.84**	**2.82**	**2.80**	**2.78**	**2.76**	**2.74**
75	19.48	8.24	5.83	4.85	4.33	*3.79*	**3.52**	**3.32**	**3.20**	**3.12**	**3.06**	**3.01**	**2.98**	**2.93**	**2.89**	**2.87**	**2.85**	**2.83**	**2.80**	**2.78**
100	21.45	8.75	6.10	5.04	4.48	3.90	*3.61*	**3.40**	**3.28**	**3.19**	**3.13**	**3.08**	**3.04**	**2.99**	**2.95**	**2.93**	**2.90**	**2.89**	**2.86**	**2.84**
125	23.09	9.15	6.32	5.19	4.60	3.99	*3.68*	**3.47**	**3.34**	**3.25**	**3.18**	**3.13**	**3.09**	**3.04**	**3.00**	**2.97**	**2.95**	**2.93**	**2.90**	**2.88**
150	24.55	9.49	6.50	5.32	4.69	4.06	*3.74*	**3.52**	**3.39**	**3.29**	**3.22**	**3.18**	**3.13**	**3.07**	**3.03**	**3.00**	**2.98**	**2.96**	**2.93**	**2.91**
175	25.84	9.79	6.67	5.43	4.78	4.12	*3.80*	**3.57**	**3.43**	**3.33**	**3.26**	**3.21**	**3.17**	**3.11**	**3.07**	**3.04**	**3.01**	**2.99**	**2.96**	**2.94**
200	27.07	10.03	6.80	5.52	4.85	4.18	*3.84*	*3.61*	**3.46**	**3.36**	**3.29**	**3.24**	**3.20**	**3.13**	**3.09**	**3.06**	**3.04**	**3.02**	**2.99**	**2.96**

Table 19-14. κ-Multipliers for 1-of-1 Intrawell Prediction Limits on Means of Order 2 (10 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.86	**2.71**	**2.34**	**2.16**	**2.06**	**1.93**	**1.87**	**1.82**	**1.78**	**1.76**	**1.74**	**1.73**	**1.72**	**1.71**	**1.69**	**1.69**	**1.68**	**1.68**	**1.67**	**1.66**
2	4.97	3.25	**2.74**	**2.49**	**2.35**	**2.19**	**2.10**	**2.04**	**2.00**	**1.97**	**1.95**	**1.93**	**1.92**	**1.90**	**1.89**	**1.88**	**1.87**	**1.86**	**1.85**	**1.84**
3	5.74	3.59	**2.98**	**2.69**	**2.52**	**2.34**	**2.24**	**2.17**	**2.12**	**2.09**	**2.06**	**2.04**	**2.03**	**2.01**	**1.99**	**1.98**	**1.97**	**1.97**	**1.95**	**1.95**
4	6.34	3.85	3.15	**2.83**	**2.65**	**2.45**	**2.34**	**2.26**	**2.20**	**2.17**	**2.14**	**2.12**	**2.11**	**2.08**	**2.07**	**2.05**	**2.05**	**2.04**	**2.02**	**2.02**
5	6.85	4.06	3.29	**2.94**	**2.75**	**2.53**	**2.41**	**2.32**	**2.27**	**2.23**	**2.20**	**2.18**	**2.16**	**2.14**	**2.12**	**2.11**	**2.10**	**2.09**	**2.08**	**2.07**
8	8.05	4.52	3.60	3.18	**2.95**	**2.70**	**2.56**	**2.47**	**2.40**	**2.36**	**2.33**	**2.30**	**2.29**	**2.26**	**2.24**	**2.22**	**2.21**	**2.20**	**2.19**	**2.18**
12	9.25	4.95	3.87	3.40	*3.13*	**2.85**	**2.70**	**2.59**	**2.52**	**2.47**	**2.43**	**2.41**	**2.39**	**2.36**	**2.33**	**2.32**	**2.31**	**2.30**	**2.28**	**2.27**
16	10.20	5.28	4.08	3.55	3.26	**2.95**	**2.79**	**2.67**	**2.60**	**2.55**	**2.51**	**2.48**	**2.46**	**2.42**	**2.40**	**2.38**	**2.37**	**2.36**	**2.34**	**2.33**
20	11.00	5.54	4.24	3.67	3.36	*3.04*	**2.86**	**2.74**	**2.66**	**2.60**	**2.56**	**2.53**	**2.51**	**2.48**	**2.45**	**2.44**	**2.42**	**2.41**	**2.39**	**2.38**
30	12.61	6.05	4.54	3.90	3.55	*3.19*	*2.99*	**2.86**	**2.77**	**2.71**	**2.67**	**2.63**	**2.61**	**2.57**	**2.55**	**2.53**	**2.51**	**2.50**	**2.48**	**2.46**
40	13.89	6.44	4.77	4.07	3.69	3.29	*3.09*	**2.94**	**2.85**	**2.78**	**2.74**	**2.70**	**2.68**	**2.64**	**2.61**	**2.59**	**2.57**	**2.56**	**2.54**	**2.52**
50	14.96	6.75	4.94	4.20	3.80	3.38	*3.16*	*3.00*	**2.91**	**2.84**	**2.79**	**2.76**	**2.73**	**2.69**	**2.66**	**2.64**	**2.62**	**2.60**	**2.58**	**2.57**
60	15.90	7.01	5.09	4.31	3.88	3.44	*3.22*	*3.06*	*2.96*	**2.89**	**2.84**	**2.80**	**2.77**	**2.73**	**2.69**	**2.67**	**2.66**	**2.64**	**2.62**	**2.60**
75	17.15	7.35	5.28	4.44	3.99	3.53	3.29	*3.12*	*3.02*	*2.95*	**2.89**	**2.85**	**2.82**	**2.78**	**2.75**	**2.72**	**2.70**	**2.69**	**2.66**	**2.65**
100	18.91	7.82	5.53	4.61	4.13	3.64	3.39	*3.20*	*3.09*	*3.02*	*2.96*	**2.92**	**2.89**	**2.84**	**2.81**	**2.78**	**2.76**	**2.75**	**2.72**	**2.70**
125	20.31	8.19	5.74	4.76	4.25	3.73	3.46	*3.27*	*3.15*	*3.07*	*3.02*	*2.97*	**2.94**	**2.89**	**2.85**	**2.83**	**2.81**	**2.79**	**2.77**	**2.75**
150	21.64	8.51	5.91	4.88	4.35	3.80	3.52	3.32	*3.20*	*3.12*	*3.06*	*3.01*	*2.98*	**2.93**	**2.89**	**2.87**	**2.85**	**2.83**	**2.80**	**2.78**
175	22.81	8.78	6.05	4.98	4.42	3.86	3.57	3.37	*3.24*	*3.16*	*3.10*	*3.05*	*3.01*	*2.96*	**2.91**	**2.90**	**2.88**	**2.86**	**2.83**	**2.81**
200	23.83	9.03	6.18	5.07	4.49	3.91	3.61	3.41	3.28	*3.19*	*3.13*	*3.08*	*3.04*	*2.99*	*2.95*	**2.92**	**2.90**	**2.89**	**2.86**	**2.84**

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Table 19-14. κ-Multipliers for 1-of-1 Intrawell Prediction Limits on Means of Order 2 (10 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	4.75	3.20	2.71	2.48	2.34	2.19	2.10	2.04	2.00	1.97	1.95	1.93	1.92	1.90	1.89	1.88	1.87	1.86	1.85	1.84
2	6.07	3.79	3.13	2.82	2.64	2.44	2.33	2.25	2.20	2.17	2.14	2.12	2.11	2.08	2.07	2.05	2.05	2.04	2.02	2.02
3	6.99	4.17	3.39	3.02	2.82	2.59	2.47	2.38	2.32	2.28	2.25	2.23	2.21	2.19	2.17	2.15	2.14	2.14	2.12	2.11
4	7.72	4.46	3.57	3.17	2.94	2.70	2.56	2.46	2.40	2.36	2.33	2.30	2.28	2.26	2.24	2.22	2.21	2.20	2.19	2.18
5	8.33	4.69	3.72	*3.29*	3.04	2.78	2.64	2.53	2.46	2.42	2.39	2.36	2.34	2.31	2.29	2.28	2.26	2.26	2.24	2.23
8	9.78	5.21	4.05	3.54	3.26	2.95	2.79	2.67	2.60	2.54	2.51	2.48	2.46	2.42	2.40	2.38	2.37	2.36	2.34	2.33
12	11.22	5.70	4.35	3.76	*3.44*	3.10	2.92	2.79	2.71	2.65	2.61	2.58	2.56	2.52	2.49	2.48	2.46	2.45	2.43	2.42
16	12.36	6.06	4.57	3.93	3.58	3.21	3.01	2.87	2.79	2.73	2.68	2.65	2.62	2.59	2.56	2.54	2.52	2.51	2.49	2.48
20	13.33	6.36	4.74	4.06	3.68	*3.29*	3.09	2.94	2.85	2.78	2.74	2.70	2.68	2.64	2.61	2.59	2.57	2.56	2.54	2.52
30	15.25	6.93	5.07	4.30	3.88	*3.44*	3.22	3.06	2.96	2.89	2.84	2.80	2.77	2.73	2.70	2.68	2.66	2.65	2.62	2.60
40	16.80	7.37	5.31	4.47	4.02	3.55	*3.31*	3.14	3.03	2.96	2.91	2.87	2.84	2.79	2.76	2.74	2.72	2.70	2.68	2.66
50	18.09	7.72	5.51	4.61	4.13	3.64	*3.39*	3.20	3.09	3.02	2.96	2.92	2.89	2.84	2.81	2.78	2.76	2.75	2.72	2.70
60	19.22	8.03	5.67	4.73	4.22	3.71	*3.44*	*3.26*	3.14	3.06	3.00	2.96	2.93	2.88	2.85	2.82	2.80	2.78	2.76	2.74
75	20.70	8.40	5.88	4.87	4.34	3.79	*3.52*	*3.32*	3.20	3.12	3.06	3.01	2.98	2.93	2.89	2.87	2.85	2.83	2.80	2.78
100	22.81	8.91	6.15	5.06	4.49	3.91	3.61	*3.40*	*3.28*	3.19	3.12	3.08	3.04	2.99	2.95	2.92	2.90	2.89	2.86	2.84
125	24.61	9.30	6.38	5.21	4.61	3.99	3.69	*3.47*	*3.34*	3.25	3.17	3.13	3.09	3.04	3.00	2.97	2.95	2.93	2.90	2.88
150	26.09	9.65	6.56	5.34	4.71	4.07	3.75	*3.52*	*3.39*	*3.30*	3.22	3.17	3.13	3.07	3.03	3.00	2.98	2.96	2.93	2.91
175	27.50	9.96	6.72	5.45	4.79	4.13	3.80	*3.57*	*3.43*	*3.33*	3.26	3.21	3.17	3.11	3.07	3.04	3.01	2.99	2.96	2.94
200	28.75	10.23	6.86	5.55	4.86	4.18	3.84	3.61	*3.46*	*3.35*	*3.29*	3.24	3.20	3.13	3.09	3.06	3.04	3.02	2.99	2.96

Table 19-14. κ-Multipliers for 1-of-1 Intrawell Prediction Limits on Means of Order 2 (10 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	5.68	3.69	3.09	2.80	2.62	2.43	2.33	2.25	2.20	2.17	2.14	2.12	2.10	2.08	2.07	2.05	2.04	2.04	2.02	2.02
2	7.24	4.35	3.53	3.15	2.93	2.69	2.56	2.46	2.40	2.36	2.33	2.30	2.28	2.26	2.24	2.22	2.21	2.20	2.19	2.18
3	8.32	4.78	3.81	3.36	3.11	2.84	2.69	2.58	2.51	2.47	2.43	2.41	2.39	2.36	2.33	2.32	2.31	2.30	2.28	2.27
4	9.18	5.10	4.01	3.52	3.24	2.94	2.79	2.67	2.59	2.54	2.51	2.48	2.46	2.42	2.40	2.38	2.37	2.36	2.34	2.33
5	9.90	5.35	4.17	*3.64*	3.35	3.03	2.86	2.73	2.66	2.60	2.56	2.53	2.51	2.48	2.45	2.43	2.42	2.41	2.39	2.38
8	11.61	5.93	4.52	3.91	3.57	3.20	3.01	2.87	2.79	2.73	2.68	2.65	2.62	2.59	2.56	2.54	2.52	2.51	2.49	2.48
12	13.32	6.48	4.84	4.14	3.76	3.35	3.14	2.99	2.90	2.83	2.78	2.75	2.72	2.68	2.65	2.63	2.61	2.60	2.57	2.56
16	14.67	6.89	5.08	4.32	3.90	3.46	3.24	3.07	2.97	2.90	2.85	2.81	2.79	2.74	2.71	2.69	2.67	2.66	2.63	2.62
20	15.80	7.22	5.27	4.45	4.01	3.55	3.31	3.14	3.03	2.96	2.91	2.87	2.84	2.79	2.76	2.74	2.72	2.70	2.68	2.66
30	18.10	7.87	5.63	4.71	4.22	*3.70*	3.44	3.26	3.14	3.06	3.01	2.96	2.93	2.88	2.84	2.82	2.80	2.78	2.76	2.74
40	19.90	8.35	5.89	4.89	4.36	*3.82*	3.54	3.34	3.22	3.13	3.07	3.03	2.99	2.94	2.91	2.88	2.86	2.84	2.81	2.79
50	21.45	8.75	6.10	5.04	4.48	3.90	*3.61*	3.40	3.28	3.19	3.13	3.08	3.04	2.99	2.95	2.92	2.90	2.89	2.86	2.84
60	22.81	9.08	6.28	5.16	4.58	3.97	*3.67*	3.46	3.33	3.23	3.17	3.12	3.08	3.03	2.99	2.96	2.94	2.92	2.89	2.87
75	24.53	9.49	6.50	5.32	4.70	4.06	*3.75*	3.52	3.39	3.29	3.22	3.17	3.13	3.07	3.03	3.00	2.98	2.96	2.93	2.91
100	27.03	10.04	6.81	5.52	4.85	4.18	*3.84*	*3.61*	3.46	3.36	3.29	3.24	3.20	3.13	3.09	3.06	3.04	3.02	2.99	2.96
125	29.14	10.51	7.03	5.68	4.98	4.27	3.92	*3.67*	3.52	3.42	3.34	3.29	3.24	3.18	3.14	3.11	3.08	3.06	3.03	3.00
150	30.94	10.90	7.21	5.81	5.08	4.35	3.97	*3.73*	3.57	3.46	3.38	3.33	3.28	3.22	3.17	3.14	3.12	3.10	3.06	3.04
175	32.66	11.25	7.36	5.93	5.17	4.40	4.03	*3.77*	*3.60*	3.50	3.42	3.36	3.32	3.25	3.20	3.17	3.14	3.12	3.09	3.06
200	34.06	11.56	7.46	6.04	5.24	4.46	4.07	*3.81*	*3.64*	3.53	3.45	3.39	3.35	3.28	3.23	3.20	3.17	3.15	3.11	3.09

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Table 19-14. κ-Multipliers for 1-of-1 Intrawell Prediction Limits on Means of Order 2 (20 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	4.97	3.25	2.74	2.49	2.35	2.19	2.10	2.04	2.00	1.97	1.95	1.93	1.92	1.90	1.89	1.88	1.87	1.86	1.85	1.84
2	6.34	3.85	3.15	2.83	2.65	2.45	2.34	2.26	2.20	2.17	2.14	2.12	2.11	2.08	2.07	2.05	2.05	2.04	2.02	2.02
3	7.30	4.23	3.41	3.04	2.82	2.59	2.47	2.38	2.32	2.28	2.25	2.23	2.21	2.19	2.17	2.15	2.14	2.14	2.12	2.11
4	8.05	4.52	3.60	3.18	2.95	2.70	2.56	2.47	2.40	2.36	2.33	2.30	2.29	2.26	2.24	2.22	2.21	2.20	2.19	2.18
5	8.69	4.76	3.75	3.30	3.05	2.78	2.64	2.53	2.47	2.42	2.39	2.36	2.34	2.31	2.29	2.28	2.26	2.26	2.24	2.23
8	10.20	5.28	4.08	3.55	3.26	2.95	2.79	2.67	2.60	2.55	2.51	2.48	2.46	2.42	2.40	2.38	2.37	2.36	2.34	2.33
12	11.69	5.77	4.37	3.78	3.45	3.10	2.92	2.79	2.71	2.65	2.61	2.58	2.56	2.52	2.49	2.48	2.46	2.45	2.43	2.42
16	12.89	6.14	4.59	3.94	3.58	3.21	3.02	2.87	2.79	2.73	2.68	2.65	2.62	2.59	2.56	2.54	2.52	2.51	2.49	2.48
20	13.89	6.44	4.77	4.07	3.69	3.29	3.09	2.94	2.85	2.78	2.74	2.70	2.68	2.64	2.61	2.59	2.57	2.56	2.54	2.52
30	15.92	7.02	5.10	4.31	3.88	3.45	3.22	3.06	2.96	2.89	2.84	2.80	2.77	2.73	2.70	2.67	2.66	2.64	2.62	2.60
40	17.53	7.46	5.34	4.48	4.03	3.56	3.31	3.14	3.03	2.96	2.91	2.87	2.84	2.79	2.76	2.74	2.72	2.70	2.68	2.66
50	18.90	7.81	5.54	4.62	4.14	3.64	3.39	3.20	3.09	3.02	2.96	2.92	2.89	2.84	2.81	2.78	2.76	2.75	2.72	2.70
60	20.12	8.12	5.70	4.74	4.23	3.71	3.45	3.26	3.14	3.06	3.01	2.96	2.93	2.88	2.84	2.82	2.80	2.78	2.76	2.74
75	21.68	8.50	5.91	4.88	4.35	3.80	3.52	3.32	3.20	3.12	3.06	3.02	2.98	2.93	2.89	2.87	2.84	2.83	2.80	2.78
100	23.83	9.03	6.18	5.08	4.49	3.91	3.61	3.41	3.28	3.19	3.12	3.08	3.04	2.99	2.95	2.92	2.90	2.89	2.86	2.84
125	25.59	9.47	6.40	5.22	4.61	4.00	3.69	3.47	3.33	3.25	3.18	3.13	3.09	3.04	3.00	2.97	2.95	2.93	2.90	2.88
150	27.34	9.81	6.59	5.35	4.71	4.06	3.75	3.52	3.38	3.29	3.22	3.17	3.13	3.08	3.03	3.00	2.98	2.97	2.93	2.91
175	28.71	10.16	6.74	5.46	4.80	4.13	3.80	3.56	3.42	3.33	3.26	3.21	3.17	3.11	3.06	3.03	3.02	2.99	2.96	2.94
200	30.08	10.45	6.88	5.54	4.86	4.19	3.85	3.60	3.45	3.36	3.29	3.23	3.20	3.14	3.09	3.06	3.04	3.02	2.99	2.96

Table 19-14. κ-Multipliers for 1-of-1 Intrawell Prediction Limits on Means of Order 2 (20 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	6.07	3.79	3.13	2.82	2.64	2.44	2.33	2.25	2.20	2.17	2.14	2.12	2.11	2.08	2.07	2.05	2.05	2.04	2.02	2.02
2	7.72	4.46	3.57	3.17	2.94	2.70	2.56	2.46	2.40	2.36	2.33	2.30	2.29	2.26	2.24	2.22	2.21	2.20	2.19	2.18
3	8.87	4.89	3.85	3.39	3.13	2.84	2.70	2.59	2.52	2.47	2.43	2.41	2.39	2.36	2.33	2.32	2.31	2.30	2.28	2.27
4	9.78	5.21	4.05	3.54	3.26	2.95	2.79	2.67	2.60	2.54	2.51	2.48	2.46	2.42	2.40	2.38	2.37	2.36	2.34	2.33
5	10.55	5.47	4.21	3.66	3.36	3.03	2.86	2.74	2.66	2.60	2.56	2.53	2.51	2.48	2.45	2.44	2.42	2.41	2.39	2.38
8	12.37	6.06	4.57	3.93	3.58	3.21	3.01	2.87	2.79	2.73	2.68	2.65	2.62	2.59	2.56	2.54	2.52	2.51	2.49	2.48
12	14.17	6.61	4.89	4.16	3.77	3.36	3.15	2.99	2.90	2.83	2.78	2.75	2.72	2.68	2.65	2.63	2.61	2.60	2.57	2.56
16	15.61	7.03	5.12	4.34	3.91	3.47	3.24	3.08	2.97	2.90	2.85	2.82	2.79	2.74	2.71	2.69	2.67	2.66	2.63	2.62
20	16.82	7.37	5.32	4.47	4.02	3.55	3.31	3.14	3.03	2.96	2.91	2.87	2.84	2.79	2.76	2.74	2.72	2.70	2.68	2.66
30	19.29	8.02	5.68	4.73	4.22	3.71	3.45	3.26	3.14	3.06	3.01	2.96	2.93	2.88	2.85	2.82	2.80	2.78	2.76	2.74
40	21.24	8.52	5.94	4.91	4.37	3.82	3.54	3.34	3.22	3.13	3.07	3.03	2.99	2.94	2.91	2.88	2.86	2.84	2.81	2.78
50	22.85	8.92	6.15	5.06	4.49	3.91	3.61	3.41	3.28	3.19	3.13	3.08	3.04	2.99	2.95	2.92	2.90	2.89	2.86	2.84
60	24.32	9.27	6.34	5.19	4.58	3.98	3.67	3.46	3.32	3.23	3.17	3.12	3.08	3.03	2.99	2.96	2.94	2.92	2.89	2.87
75	26.17	9.72	6.56	5.33	4.71	4.06	3.75	3.52	3.38	3.29	3.22	3.17	3.13	3.07	3.03	3.01	2.98	2.96	2.93	2.91
100	28.91	10.30	6.86	5.54	4.86	4.18	3.85	3.61	3.46	3.36	3.29	3.23	3.20	3.13	3.09	3.06	3.04	3.01	2.99	2.96
125	31.05	10.79	7.10	5.70	4.98	4.27	3.92	3.67	3.52	3.42	3.34	3.29	3.24	3.18	3.14	3.11	3.08	3.06	3.03	3.00
150	33.01	11.18	7.30	5.83	5.09	4.35	3.98	3.72	3.56	3.46	3.39	3.33	3.28	3.22	3.17	3.14	3.12	3.10	3.06	3.04
175	34.77	11.52	7.47	5.96	5.18	4.41	4.03	3.77	3.61	3.50	3.42	3.36	3.31	3.25	3.20	3.17	3.14	3.12	3.09	3.06
200	36.33	11.87	7.62	6.05	5.25	4.47	4.08	3.81	3.64	3.53	3.45	3.39	3.34	3.28	3.23	3.20	3.17	3.15	3.11	3.09

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Table 19-14. κ-Multipliers for 1-of-1 Intrawell Prediction Limits on Means of Order 2 (20 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	7.24	4.35	**3.53**	**3.15**	**2.93**	**2.69**	**2.56**	**2.46**	**2.40**	**2.36**	**2.33**	**2.30**	**2.28**	**2.26**	**2.24**	**2.22**	**2.21**	**2.20**	**2.19**	**2.18**
2	9.18	5.10	4.01	**3.52**	**3.24**	**2.94**	**2.79**	**2.67**	**2.59**	**2.54**	**2.51**	**2.48**	**2.46**	**2.42**	**2.40**	**2.38**	**2.37**	**2.36**	**2.34**	**2.33**
3	0.54	5.57	4.30	3.74	**3.43**	**3.09**	**2.92**	**2.79**	**2.71**	**2.65**	**2.61**	**2.58**	**2.55**	**2.52**	**2.49**	**2.48**	**2.46**	**2.45**	**2.43**	**2.42**
4	11.61	5.93	4.52	3.91	**3.57**	**3.20**	**3.01**	**2.87**	**2.79**	**2.73**	**2.68**	**2.65**	**2.62**	**2.59**	**2.56**	**2.54**	**2.52**	**2.51**	**2.49**	**2.48**
5	12.52	6.23	4.70	4.04	*3.67*	**3.29**	**3.08**	**2.94**	**2.85**	**2.78**	**2.74**	**2.70**	**2.68**	**2.64**	**2.61**	**2.59**	**2.57**	**2.56**	**2.54**	**2.52**
8	14.67	6.89	5.08	4.32	3.90	**3.46**	**3.24**	**3.07**	**2.97**	**2.90**	**2.85**	**2.81**	**2.79**	**2.74**	**2.71**	**2.69**	**2.67**	**2.66**	**2.63**	**2.62**
12	16.81	7.50	5.43	4.57	4.10	*3.62*	**3.37**	**3.19**	**3.08**	**3.01**	**2.95**	**2.91**	**2.88**	**2.83**	**2.80**	**2.77**	**2.75**	**2.74**	**2.71**	**2.70**
16	18.52	7.97	5.69	4.75	4.25	*3.73*	**3.47**	**3.27**	**3.16**	**3.08**	**3.02**	**2.98**	**2.94**	**2.89**	**2.86**	**2.83**	**2.81**	**2.80**	**2.77**	**2.75**
20	19.95	8.35	5.89	4.89	4.36	*3.82*	**3.54**	**3.34**	**3.22**	**3.13**	**3.07**	**3.03**	**2.99**	**2.94**	**2.91**	**2.88**	**2.86**	**2.84**	**2.81**	**2.79**
30	22.85	9.09	6.28	5.16	4.57	3.98	*3.67*	**3.46**	**3.32**	**3.23**	**3.17**	**3.12**	**3.08**	**3.03**	**2.99**	**2.96**	**2.94**	**2.92**	**2.89**	**2.87**
40	25.20	9.64	6.57	5.36	4.73	4.09	*3.77*	**3.54**	**3.40**	**3.31**	**3.24**	**3.19**	**3.15**	**3.09**	**3.05**	**3.02**	**3.00**	**2.98**	**2.94**	**2.92**
50	27.15	10.11	6.80	5.52	4.85	4.18	*3.84*	*3.60*	**3.46**	**3.36**	**3.29**	**3.24**	**3.20**	**3.13**	**3.09**	**3.06**	**3.04**	**3.02**	**2.99**	**2.96**
60	28.81	10.47	6.99	5.65	4.96	4.25	3.91	*3.66*	**3.51**	**3.41**	**3.33**	**3.28**	**3.23**	**3.17**	**3.13**	**3.10**	**3.07**	**3.05**	**3.02**	**3.00**
75	31.05	10.99	7.25	5.81	5.08	4.35	3.98	*3.72*	**3.56**	**3.46**	**3.38**	**3.33**	**3.28**	**3.22**	**3.17**	**3.14**	**3.11**	**3.10**	**3.06**	**3.04**
100	34.18	11.62	7.57	6.03	5.25	4.46	4.08	*3.81*	*3.64*	**3.53**	**3.45**	**3.39**	**3.34**	**3.28**	**3.23**	**3.20**	**3.17**	**3.15**	**3.11**	**3.09**
125	36.72	12.21	7.84	6.20	5.37	4.55	4.15	*3.87*	*3.70*	*3.58*	**3.50**	**3.44**	**3.39**	**3.32**	**3.27**	**3.24**	**3.21**	**3.19**	**3.15**	**3.13**
150	39.06	12.65	8.06	6.35	5.48	4.63	4.21	*3.92*	*3.75*	*3.63*	**3.55**	**3.48**	**3.43**	**3.36**	**3.31**	**3.27**	**3.25**	**3.22**	**3.19**	**3.16**
175	41.41	13.09	8.25	6.47	5.57	4.70	4.27	3.97	*3.78*	*3.67*	*3.58*	**3.52**	**3.47**	**3.39**	**3.34**	**3.30**	**3.27**	**3.25**	**3.21**	**3.19**
200	42.97	13.38	8.40	6.59	5.66	4.76	4.32	4.00	*3.82*	*3.70*	*3.61*	**3.55**	**3.49**	**3.42**	**3.37**	**3.33**	**3.30**	**3.28**	**3.24**	**3.21**

Table 19-14. κ-Multipliers for 1-of-1 Intrawell Prediction Limits on Means of Order 2 (40 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	6.34	3.85	3.15	**2.83**	**2.65**	**2.45**	**2.34**	**2.26**	**2.20**	**2.17**	**2.14**	**2.12**	**2.11**	**2.08**	**2.07**	**2.05**	**2.05**	**2.04**	**2.02**	**2.02**
2	8.05	4.52	3.60	3.18	**2.95**	**2.70**	**2.56**	**2.47**	**2.40**	**2.36**	**2.33**	**2.30**	**2.29**	**2.26**	**2.24**	**2.22**	**2.21**	**2.20**	**2.19**	**2.18**
3	9.25	4.95	3.87	3.40	*3.13*	**2.85**	**2.70**	**2.59**	**2.52**	**2.47**	**2.43**	**2.41**	**2.39**	**2.36**	**2.33**	**2.32**	**2.31**	**2.30**	**2.28**	**2.27**
4	10.20	5.28	4.08	3.55	3.26	**2.95**	**2.79**	**2.67**	**2.60**	**2.55**	**2.51**	**2.48**	**2.46**	**2.42**	**2.40**	**2.38**	**2.37**	**2.36**	**2.34**	**2.33**
5	11.00	5.55	4.24	3.67	3.36	*3.04*	**2.86**	**2.74**	**2.66**	**2.60**	**2.56**	**2.54**	**2.51**	**2.48**	**2.45**	**2.44**	**2.42**	**2.41**	**2.39**	**2.38**
8	12.89	6.14	4.59	3.94	3.58	*3.21*	*3.02*	**2.87**	**2.79**	**2.73**	**2.68**	**2.65**	**2.62**	**2.59**	**2.56**	**2.54**	**2.52**	**2.51**	**2.49**	**2.48**
12	14.77	6.70	4.91	4.17	3.78	3.36	*3.15*	*2.99*	**2.90**	**2.83**	**2.78**	**2.75**	**2.72**	**2.68**	**2.65**	**2.63**	**2.61**	**2.60**	**2.57**	**2.56**
16	16.27	7.12	5.15	4.35	3.92	3.47	*3.24*	*3.08*	*2.97*	**2.90**	**2.85**	**2.82**	**2.79**	**2.74**	**2.71**	**2.69**	**2.67**	**2.66**	**2.63**	**2.62**
20	17.53	7.46	5.34	4.48	4.03	3.55	3.31	*3.14*	*3.03*	*2.96*	**2.91**	**2.87**	**2.84**	**2.79**	**2.76**	**2.74**	**2.72**	**2.70**	**2.68**	**2.66**
30	20.08	8.12	5.70	4.74	4.23	3.71	3.45	*3.26*	*3.14*	*3.06*	*3.01*	*2.96*	**2.93**	**2.88**	**2.85**	**2.82**	**2.80**	**2.79**	**2.76**	**2.74**
40	22.12	8.62	5.97	4.92	4.38	3.82	3.54	3.34	*3.22*	*3.13*	*3.07*	*3.03*	*2.99*	*2.94*	**2.90**	**2.88**	**2.86**	**2.84**	**2.81**	**2.79**
50	23.82	9.03	6.18	5.07	4.50	3.91	3.61	3.40	*3.28*	*3.19*	*3.13*	*3.08*	*3.04*	*2.99*	*2.95*	**2.92**	**2.90**	**2.89**	**2.86**	**2.84**
60	25.31	9.38	6.36	5.20	4.59	3.98	3.67	3.46	3.33	*3.23*	*3.17*	*3.12*	*3.08*	*3.03*	*2.99*	*2.96*	*2.94*	**2.92**	**2.89**	**2.87**
75	27.30	9.81	6.58	5.35	4.71	4.07	3.75	3.52	3.38	*3.29*	*3.22*	*3.17*	*3.13*	*3.07*	*3.03*	*3.00*	*2.98*	*2.96*	*2.93*	**2.91**
100	30.06	10.42	6.88	5.55	4.87	4.18	3.85	3.61	3.46	3.36	*3.29*	*3.24*	*3.20*	*3.13*	*3.09*	*3.06*	*3.04*	*3.02*	*2.99*	*2.96*
125	32.34	10.90	7.13	5.71	4.99	4.27	3.92	3.67	3.52	3.42	3.34	*3.29*	*3.24*	*3.18*	*3.14*	*3.11*	*3.08*	*3.06*	*3.03*	*3.00*
150	34.45	11.31	7.32	5.84	5.10	4.35	3.98	3.72	3.57	3.46	3.38	3.33	*3.28*	*3.22*	*3.17*	*3.14*	*3.12*	*3.10*	*3.06*	*3.04*
175	36.21	11.69	7.50	5.96	5.19	4.41	4.04	3.77	3.61	3.50	3.42	3.36	*3.32*	*3.25*	*3.20*	*3.17*	*3.15*	*3.12*	*3.09*	*3.06*
200	37.85	12.01	7.66	6.06	5.26	4.47	4.08	3.81	3.64	3.53	3.45	3.39	3.35	3.28	3.23	3.20	3.17	3.15	3.11	3.09

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Table 19-14. κ-Multipliers for 1-of-1 Intrawell Prediction Limits on Means of Order 2 (40 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	7.72	4.46	3.57	**3.17**	**2.94**	**2.70**	**2.56**	**2.46**	**2.40**	**2.36**	**2.33**	**2.30**	**2.29**	**2.26**	**2.24**	**2.22**	**2.21**	**2.20**	**2.19**	**2.18**
2	9.78	5.21	4.05	3.54	**3.26**	**2.95**	**2.79**	**2.67**	**2.60**	**2.54**	**2.51**	**2.48**	**2.46**	**2.42**	**2.40**	**2.38**	**2.37**	**2.36**	**2.34**	**2.33**
3	11.22	5.70	4.35	3.76	*3.44*	**3.10**	**2.92**	**2.79**	**2.71**	**2.65**	**2.61**	**2.58**	**2.56**	**2.52**	**2.49**	**2.48**	**2.46**	**2.45**	**2.43**	**2.42**
4	12.36	6.06	4.57	3.93	3.58	**3.21**	**3.01**	**2.87**	**2.79**	**2.73**	**2.68**	**2.65**	**2.62**	**2.59**	**2.56**	**2.54**	**2.52**	**2.51**	**2.49**	**2.48**
5	13.33	6.36	4.74	4.06	3.68	*3.29*	**3.09**	**2.94**	**2.85**	**2.78**	**2.74**	**2.70**	**2.68**	**2.64**	**2.61**	**2.59**	**2.57**	**2.56**	**2.54**	**2.52**
8	15.61	7.03	5.13	4.34	3.91	*3.47*	**3.24**	**3.08**	**2.97**	**2.90**	**2.85**	**2.82**	**2.79**	**2.74**	**2.71**	**2.69**	**2.67**	**2.66**	**2.63**	**2.62**
12	17.89	7.66	5.47	4.59	4.11	3.62	*3.37*	**3.19**	**3.08**	**3.01**	**2.95**	**2.91**	**2.88**	**2.83**	**2.80**	**2.77**	**2.75**	**2.74**	**2.71**	**2.70**
16	19.70	8.13	5.73	4.77	4.26	3.73	*3.47*	*3.28*	**3.16**	**3.08**	**3.02**	**2.98**	**2.94**	**2.89**	**2.86**	**2.83**	**2.81**	**2.80**	**2.77**	**2.75**
20	21.23	8.52	5.94	4.91	4.37	3.82	*3.54*	*3.34*	**3.22**	**3.13**	**3.07**	**3.03**	**2.99**	**2.94**	**2.90**	**2.88**	**2.86**	**2.84**	**2.81**	**2.78**
30	24.32	9.27	6.33	5.18	4.59	3.98	3.67	*3.46*	*3.32*	**3.23**	**3.17**	**3.12**	**3.08**	**3.03**	**2.99**	**2.96**	**2.94**	**2.92**	**2.88**	**2.87**
40	26.78	9.83	6.62	5.38	4.74	4.09	3.77	*3.54*	*3.40*	*3.31*	**3.24**	**3.19**	**3.15**	**3.09**	**3.05**	**3.02**	**2.99**	**2.98**	**2.94**	**2.92**
50	28.83	10.30	6.86	5.54	4.86	4.18	3.85	3.61	*3.46*	*3.36*	*3.29*	**3.24**	**3.20**	**3.13**	**3.09**	**3.06**	**3.04**	**3.01**	**2.99**	**2.96**
60	30.64	10.69	7.05	5.67	4.96	4.26	3.91	3.66	*3.51*	*3.41*	*3.33*	*3.28*	**3.23**	**3.17**	**3.13**	**3.10**	**3.07**	**3.05**	**3.02**	**3.00**
75	33.05	11.19	7.30	5.83	5.09	4.35	3.98	3.72	*3.57*	*3.46*	*3.38*	*3.33*	*3.28*	**3.22**	**3.17**	**3.14**	**3.12**	**3.10**	**3.06**	**3.04**
100	36.33	11.87	7.62	6.05	5.26	4.46	4.08	3.81	3.64	*3.53*	*3.45*	*3.39*	*3.35*	*3.28*	**3.23**	**3.20**	**3.17**	**3.15**	**3.11**	**3.09**
125	39.14	12.42	7.90	6.23	5.38	4.56	4.15	3.87	3.70	*3.59*	*3.50*	*3.44*	*3.39*	*3.32*	*3.27*	**3.24**	**3.21**	**3.19**	**3.15**	**3.13**
150	41.60	12.89	8.12	6.36	5.49	4.64	4.22	3.93	3.75	*3.63*	*3.54*	*3.48*	*3.43*	*3.36*	*3.31*	*3.27*	**3.25**	**3.22**	**3.19**	**3.16**
175	43.83	13.30	8.31	6.49	5.59	4.70	4.27	3.97	3.79	3.67	*3.58*	*3.52*	*3.46*	*3.39*	*3.34*	*3.30*	*3.27*	**3.25**	**3.21**	**3.19**
200	45.70	13.65	8.47	6.60	5.67	4.76	4.31	4.01	3.82	3.70	*3.61*	*3.54*	*3.49*	*3.42*	*3.37*	*3.33*	*3.30*	*3.28*	**3.24**	**3.21**

Table 19-14. κ-Multipliers for 1-of-1 Intrawell Prediction Limits on Means of Order 2 (40 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	9.18	5.10	4.01	**3.52**	**3.24**	**2.94**	**2.79**	**2.67**	**2.59**	**2.54**	**2.51**	**2.48**	**2.46**	**2.42**	**2.40**	**2.38**	**2.37**	**2.36**	**2.34**	**2.33**
2	11.61	5.93	4.52	3.91	**3.57**	**3.20**	**3.01**	**2.87**	**2.79**	**2.73**	**2.68**	**2.65**	**2.62**	**2.59**	**2.56**	**2.54**	**2.52**	**2.51**	**2.49**	**2.48**
3	13.32	6.48	4.84	4.14	3.76	**3.35**	**3.14**	**2.99**	**2.89**	**2.83**	**2.78**	**2.75**	**2.72**	**2.68**	**2.65**	**2.63**	**2.61**	**2.60**	**2.57**	**2.56**
4	14.67	6.89	5.08	4.32	3.90	**3.46**	**3.24**	**3.07**	**2.97**	**2.90**	**2.85**	**2.81**	**2.79**	**2.74**	**2.71**	**2.69**	**2.67**	**2.66**	**2.63**	**2.62**
5	15.81	7.22	5.27	4.45	4.01	**3.55**	**3.31**	**3.14**	**3.03**	**2.96**	**2.91**	**2.87**	**2.84**	**2.79**	**2.76**	**2.74**	**2.72**	**2.70**	**2.68**	**2.66**
8	18.52	7.97	5.69	4.75	4.25	*3.73*	**3.47**	**3.27**	**3.16**	**3.08**	**3.02**	**2.98**	**2.94**	**2.89**	**2.86**	**2.83**	**2.81**	**2.80**	**2.77**	**2.75**
12	21.21	8.68	6.07	5.01	4.46	3.89	*3.60*	**3.39**	**3.26**	**3.18**	**3.12**	**3.07**	**3.03**	**2.98**	**2.94**	**2.92**	**2.89**	**2.88**	**2.85**	**2.83**
16	23.36	9.21	6.35	5.21	4.61	4.00	*3.69*	**3.48**	**3.34**	**3.25**	**3.19**	**3.14**	**3.10**	**3.04**	**3.00**	**2.97**	**2.95**	**2.93**	**2.90**	**2.88**
20	25.17	9.65	6.57	5.36	4.73	4.09	*3.77*	**3.54**	**3.40**	**3.31**	**3.24**	**3.19**	**3.15**	**3.09**	**3.05**	**3.02**	**2.99**	**2.98**	**2.94**	**2.92**
30	28.81	10.48	7.00	5.65	4.95	4.25	3.90	*3.66*	**3.51**	**3.41**	**3.33**	**3.28**	**3.24**	**3.17**	**3.13**	**3.10**	**3.07**	**3.04**	**3.02**	**3.00**
40	31.73	11.13	7.32	5.86	5.12	4.37	4.00	*3.74*	*3.58*	**3.48**	**3.40**	**3.34**	**3.30**	**3.23**	**3.19**	**3.15**	**3.12**	**3.11**	**3.07**	**3.05**
50	34.16	11.65	7.57	6.03	5.24	4.46	4.08	*3.81*	*3.64*	**3.53**	**3.45**	**3.39**	**3.35**	**3.28**	**3.23**	**3.20**	**3.17**	**3.15**	**3.11**	**3.09**
60	36.33	12.08	7.79	6.17	5.35	4.54	4.14	*3.86*	*3.69*	**3.58**	**3.49**	**3.43**	**3.38**	**3.32**	**3.27**	**3.23**	**3.20**	**3.18**	**3.15**	**3.12**
75	39.14	12.64	8.05	6.35	5.48	4.63	4.22	*3.92*	*3.75*	*3.63*	**3.54**	**3.48**	**3.43**	**3.36**	**3.31**	**3.27**	**3.25**	**3.22**	**3.19**	**3.16**
100	43.12	13.42	8.41	6.58	5.66	4.75	4.31	4.01	*3.82*	*3.70*	*3.61*	**3.54**	**3.49**	**3.42**	**3.37**	**3.33**	**3.30**	**3.28**	**3.24**	**3.21**
125	46.41	14.03	8.70	6.76	5.79	4.85	4.39	4.07	*3.88*	*3.75*	*3.66*	*3.59*	**3.54**	**3.46**	**3.41**	**3.37**	**3.34**	**3.32**	**3.28**	**3.25**
150	49.34	14.56	8.94	6.91	5.91	4.93	4.46	4.13	*3.93*	*3.80*	*3.70*	*3.63*	*3.58*	**3.50**	**3.44**	**3.40**	**3.37**	**3.35**	**3.31**	**3.28**
175	52.03	15.03	9.14	7.05	6.01	5.00	4.51	4.17	3.97	*3.83*	*3.74*	*3.67*	*3.61*	**3.53**	**3.47**	**3.43**	**3.40**	**3.38**	**3.33**	**3.30**
200	54.38	15.44	9.33	7.16	6.09	5.05	4.56	4.21	4.01	*3.87*	*3.77*	*3.70*	*3.64*	**3.56**	**3.50**	**3.46**	**3.43**	**3.40**	**3.36**	**3.33**

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Table 19-15. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Means of Order 2 (1 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	0.69	0.56	0.50	0.47	0.45	0.42	0.40	0.39	0.38	0.37	0.37	0.37	0.36	0.36	0.36	0.35	0.35	0.35	0.35	0.35
2	1.10	0.87	0.77	0.72	0.69	0.65	0.62	0.60	0.59	0.58	0.58	0.57	0.57	0.56	0.56	0.55	0.55	0.55	0.55	0.54
3	1.36	1.05	0.93	0.86	0.82	0.77	0.74	0.72	0.70	0.69	0.69	0.68	0.68	0.67	0.66	0.66	0.66	0.65	0.65	0.65
4	1.56	1.18	1.04	0.96	0.91	0.86	0.82	0.80	0.78	0.77	0.76	0.75	0.75	0.74	0.73	0.73	0.73	0.72	0.72	0.72
5	1.72	1.28	1.12	1.04	0.98	0.92	0.88	0.86	0.84	0.83	0.82	0.81	0.80	0.79	0.79	0.78	0.78	0.78	0.77	0.77
8	2.10	1.51	1.30	1.19	1.13	1.05	1.01	0.98	0.95	0.94	0.93	0.92	0.91	0.90	0.89	0.89	0.88	0.88	0.88	0.87
12	2.46	1.71	1.46	1.33	1.25	1.16	1.11	1.08	1.05	1.03	1.02	1.01	1.00	0.99	0.98	0.98	0.97	0.97	0.96	0.96
16	2.75	1.86	1.57	1.43	1.34	1.24	1.19	1.14	1.12	1.10	1.08	1.07	1.06	1.05	1.04	1.04	1.03	1.03	1.02	1.01
20	2.99	1.98	1.66	1.50	1.41	1.30	1.24	1.20	1.17	1.15	1.13	1.12	1.11	1.10	1.09	1.08	1.07	1.07	1.06	1.06
30	3.46	2.21	1.82	1.64	1.53	1.41	1.34	1.29	1.26	1.23	1.22	1.20	1.19	1.18	1.17	1.16	1.15	1.15	1.14	1.13
40	3.84	2.38	1.94	1.74	1.62	1.49	1.41	1.36	1.32	1.29	1.28	1.26	1.25	1.23	1.22	1.21	1.21	1.20	1.19	1.19
50	4.16	2.51	2.04	1.82	1.69	1.54	1.46	1.40	1.37	1.34	1.32	1.31	1.29	1.28	1.26	1.25	1.25	1.24	1.23	1.23
60	4.43	2.63	2.12	1.88	1.74	1.59	1.51	1.45	1.41	1.38	1.36	1.34	1.33	1.31	1.30	1.29	1.28	1.27	1.26	1.26
75	4.79	2.77	2.22	1.96	1.81	1.65	1.56	1.49	1.45	1.42	1.40	1.38	1.37	1.35	1.34	1.33	1.32	1.31	1.30	1.30
100	5.29	2.97	2.35	2.06	1.90	1.72	1.63	1.56	1.51	1.48	1.46	1.44	1.42	1.40	1.39	1.38	1.37	1.36	1.35	1.34
125	5.71	3.13	2.45	2.14	1.97	1.78	1.68	1.60	1.56	1.52	1.50	1.48	1.47	1.44	1.43	1.42	1.41	1.40	1.39	1.38
150	6.08	3.26	2.54	2.21	2.03	1.83	1.72	1.64	1.59	1.56	1.53	1.51	1.50	1.48	1.46	1.45	1.44	1.43	1.42	1.41
175	6.42	3.38	2.61	2.27	2.08	1.87	1.76	1.68	1.62	1.59	1.56	1.54	1.53	1.50	1.49	1.47	1.46	1.46	1.44	1.43
200	6.71	3.48	*2.68*	2.32	2.12	1.90	1.79	1.70	1.65	1.61	1.59	1.57	1.55	1.53	1.51	1.50	1.49	1.48	1.46	1.46

Table 19-15. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Means of Order 2 (1 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	1.02	0.83	0.75	0.70	0.67	0.64	0.62	0.60	0.59	0.58	0.57	0.57	0.56	0.56	0.55	0.55	0.55	0.55	0.54	0.54
2	1.47	1.14	1.02	0.95	0.90	0.85	0.82	0.79	0.78	0.77	0.76	0.75	0.75	0.74	0.73	0.73	0.73	0.72	0.72	0.72
3	1.77	1.33	1.17	1.09	1.03	0.97	0.93	0.90	0.88	0.87	0.86	0.85	0.84	0.84	0.83	0.82	0.82	0.82	0.81	0.81
4	2.00	1.47	1.28	1.18	1.12	1.05	1.01	0.97	0.95	0.94	0.93	0.92	0.91	0.90	0.89	0.89	0.88	0.88	0.87	0.87
5	2.19	1.58	1.37	1.26	1.19	1.11	1.06	1.03	1.01	0.99	0.98	0.97	0.96	0.95	0.94	0.94	0.93	0.93	0.92	0.92
8	2.63	1.82	1.55	1.42	1.33	1.24	1.18	1.14	1.12	1.10	1.08	1.07	1.06	1.05	1.04	1.04	1.03	1.03	1.02	1.01
12	3.06	2.04	1.72	1.56	1.46	1.35	1.29	1.24	1.21	1.19	1.17	1.16	1.15	1.13	1.12	1.12	1.11	1.11	1.10	1.09
16	3.40	2.21	1.84	1.65	1.55	1.42	1.36	1.30	1.27	1.25	1.23	1.22	1.21	1.19	1.18	1.17	1.17	1.16	1.15	1.14
20	3.68	2.34	1.93	1.73	1.61	1.48	1.41	1.35	1.32	1.29	1.28	1.26	1.25	1.23	1.22	1.21	1.21	1.20	1.19	1.19
30	4.26	2.59	2.10	1.87	1.74	1.59	1.51	1.44	1.40	1.38	1.36	1.34	1.33	1.31	1.30	1.29	1.28	1.27	1.26	1.26
40	4.71	2.78	2.23	1.98	1.83	1.66	1.57	1.51	1.46	1.43	1.41	1.40	1.38	1.36	1.35	1.34	1.33	1.32	1.31	1.31
50	5.09	*2.93*	2.33	2.06	1.90	1.72	1.63	1.56	1.51	1.48	1.46	1.44	1.42	1.40	1.39	1.38	1.37	1.36	1.35	1.34
60	5.42	3.06	2.42	2.12	1.95	1.77	1.67	1.59	1.55	1.51	1.49	1.47	1.46	1.44	1.42	1.41	1.40	1.39	1.38	1.37
75	5.85	3.22	2.52	2.20	2.02	1.83	1.72	1.64	1.59	1.56	1.53	1.51	1.50	1.48	1.46	1.45	1.44	1.43	1.42	1.41
100	6.46	3.44	2.66	2.31	2.12	1.90	1.79	1.70	1.65	1.61	1.59	1.57	1.55	1.53	1.51	1.50	1.49	1.48	1.46	1.46
125	6.97	3.62	2.77	2.40	2.19	1.96	1.84	1.75	1.69	1.66	1.63	1.61	1.59	1.56	1.55	1.53	1.52	1.51	1.50	1.49
150	7.41	3.77	*2.86*	2.47	2.25	2.01	1.88	1.79	1.73	1.69	1.66	1.64	1.62	1.59	1.58	1.56	1.55	1.54	1.53	1.52
175	7.81	3.90	*2.94*	2.53	2.30	2.05	1.92	1.82	1.76	1.72	1.69	1.67	1.65	1.62	1.60	1.59	1.58	1.57	1.55	1.54
200	8.17	4.02	3.01	2.58	2.34	2.08	1.95	1.85	1.79	1.74	1.71	1.69	1.67	1.64	1.62	1.61	1.60	1.59	1.57	1.56

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Table 19-15. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Means of Order 2 (1 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	1.34	1.09	0.98	0.92	0.88	0.84	0.81	0.79	0.77	0.76	0.75	0.75	0.74	0.74	0.73	0.73	0.72	0.72	0.72	0.71
2	1.85	1.42	1.25	1.16	1.10	1.04	1.00	0.97	0.95	0.93	0.92	0.92	0.91	0.90	0.89	0.89	0.88	0.88	0.87	0.87
3	2.19	1.62	1.41	1.30	1.23	1.15	1.11	1.07	1.05	1.03	1.02	1.01	1.00	0.99	0.98	0.97	0.97	0.97	0.96	0.96
4	2.45	1.77	1.52	1.40	1.32	1.23	1.18	1.14	1.11	1.09	1.08	1.07	1.06	1.05	1.04	1.03	1.03	1.03	1.02	1.01
5	2.67	1.89	1.61	1.48	1.39	1.29	1.24	1.19	1.16	1.14	1.13	1.12	1.11	1.10	1.09	1.08	1.07	1.07	1.06	1.06
8	3.19	2.15	1.81	1.64	1.54	1.42	1.35	1.30	1.27	1.25	1.23	1.22	1.21	1.19	1.18	1.17	1.16	1.16	1.15	1.14
12	3.69	2.39	1.98	1.78	1.66	1.52	1.45	1.39	1.36	1.33	1.31	1.30	1.28	1.27	1.26	1.25	1.24	1.23	1.22	1.22
16	4.09	2.57	2.11	1.88	1.75	1.60	1.52	1.46	1.42	1.39	1.37	1.35	1.34	1.32	1.31	1.30	1.29	1.29	1.28	1.27
20	4.43	2.71	2.20	1.96	1.82	1.66	1.57	1.51	1.46	1.43	1.41	1.40	1.38	1.36	1.35	1.34	1.33	1.32	1.31	1.31
30	5.10	2.99	2.39	2.11	1.95	1.77	1.67	1.59	1.55	1.51	1.49	1.47	1.46	1.44	1.42	1.41	1.40	1.39	1.38	1.37
40	5.64	3.20	2.53	2.22	2.04	1.84	1.73	1.65	1.60	1.57	1.54	1.52	1.51	1.49	1.47	1.46	1.45	1.44	1.43	1.42
50	6.09	3.37	2.63	2.30	2.11	1.90	1.79	1.70	1.65	1.61	1.59	1.57	1.55	1.52	1.51	1.50	1.49	1.48	1.46	1.46
60	6.48	3.51	2.72	2.37	2.17	1.95	1.83	1.74	1.69	1.65	1.62	1.60	1.58	1.56	1.54	1.53	1.52	1.51	1.49	1.48
75	7.00	3.69	2.84	2.45	2.24	2.01	1.88	1.79	1.73	1.69	1.66	1.64	1.62	1.59	1.58	1.56	1.55	1.54	1.53	1.52
100	7.71	3.94	2.99	2.57	2.33	2.08	1.95	1.85	1.79	1.74	1.71	1.69	1.67	1.64	1.62	1.61	1.60	1.59	1.57	1.56
125	8.32	4.14	*3.11*	2.66	2.41	2.14	2.00	1.89	1.83	1.78	1.75	1.73	1.71	1.68	1.66	1.64	1.63	1.62	1.61	1.60
150	8.85	4.31	*3.21*	2.73	2.47	2.19	2.04	1.93	1.86	1.82	1.78	1.76	1.74	1.71	1.69	1.67	1.66	1.65	1.63	1.62
175	9.33	4.45	3.29	2.80	2.52	2.23	2.08	1.96	1.89	1.85	1.81	1.79	1.76	1.73	1.71	1.70	1.68	1.67	1.66	1.65
200	9.76	4.58	3.37	2.85	2.57	2.26	2.11	1.99	1.92	1.87	1.84	1.81	1.79	1.75	1.73	1.72	1.70	1.69	1.68	1.67

Table 19-15. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Means of Order 2 (2 COC, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	1.10	0.87	0.77	0.72	0.69	0.65	0.62	0.60	0.59	0.58	0.58	0.57	0.57	0.56	0.56	0.55	0.55	0.55	0.55	0.54
2	1.56	1.18	1.04	0.96	0.91	0.86	0.82	0.80	0.78	0.77	0.76	0.75	0.75	0.74	0.73	0.73	0.73	0.72	0.72	0.72
3	1.86	1.37	1.19	1.10	1.04	0.97	0.93	0.90	0.88	0.87	0.86	0.85	0.85	0.84	0.83	0.82	0.82	0.82	0.81	0.81
4	2.10	1.51	1.30	1.19	1.13	1.05	1.01	0.98	0.95	0.94	0.93	0.92	0.91	0.90	0.89	0.89	0.88	0.88	0.88	0.87
5	2.29	1.62	1.39	1.27	1.20	1.11	1.07	1.03	1.01	0.99	0.98	0.97	0.96	0.95	0.94	0.94	0.93	0.93	0.92	0.92
8	2.75	1.86	1.57	1.43	1.34	1.24	1.19	1.14	1.12	1.10	1.08	1.07	1.06	1.05	1.04	1.04	1.03	1.03	1.02	1.01
12	3.19	2.08	1.73	1.56	1.46	1.35	1.29	1.24	1.21	1.19	1.17	1.16	1.15	1.13	1.12	1.12	1.11	1.11	1.10	1.09
16	3.54	2.24	1.85	1.66	1.55	1.43	1.36	1.30	1.27	1.25	1.23	1.22	1.21	1.19	1.18	1.17	1.17	1.16	1.15	1.15
20	3.84	2.38	1.94	1.74	1.62	1.49	1.41	1.36	1.32	1.29	1.28	1.26	1.25	1.23	1.22	1.21	1.21	1.20	1.19	1.19
30	4.43	2.63	2.12	1.88	1.74	1.59	1.51	1.45	1.41	1.38	1.36	1.34	1.33	1.31	1.30	1.29	1.28	1.27	1.26	1.26
40	4.90	2.82	2.25	1.98	1.83	1.67	1.58	1.51	1.46	1.44	1.41	1.40	1.38	1.36	1.35	1.34	1.33	1.32	1.31	1.31
50	5.29	2.97	2.35	2.06	1.90	1.72	1.63	1.56	1.51	1.48	1.46	1.44	1.42	1.40	1.39	1.38	1.37	1.36	1.35	1.34
60	5.64	3.10	2.43	2.13	1.96	1.77	1.67	1.60	1.55	1.51	1.49	1.47	1.46	1.44	1.42	1.41	1.40	1.39	1.38	1.37
75	6.09	3.26	2.54	2.21	2.03	1.83	1.72	1.64	1.59	1.56	1.53	1.51	1.50	1.48	1.46	1.45	1.44	1.43	1.42	1.41
100	6.71	3.48	*2.68*	2.32	2.12	1.90	1.79	1.70	1.65	1.61	1.59	1.57	1.55	1.53	1.51	1.50	1.49	1.48	1.46	1.46
125	7.24	3.66	*2.79*	2.40	2.19	1.96	1.84	1.75	1.69	1.66	1.63	1.61	1.59	1.56	1.55	1.53	1.52	1.51	1.50	1.49
150	7.71	3.82	2.88	2.48	2.25	2.01	1.88	1.79	1.73	1.69	1.66	1.64	1.62	1.59	1.58	1.56	1.55	1.54	1.53	1.52
175	8.12	3.95	2.96	2.53	2.30	2.05	1.92	1.82	1.76	1.72	1.69	1.67	1.65	1.62	1.60	1.59	1.58	1.57	1.55	1.54
200	8.50	4.06	3.03	2.59	2.34	2.09	1.95	1.85	1.79	1.74	1.71	1.69	1.67	1.64	1.62	1.61	1.60	1.59	1.57	1.56

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Table 19-15. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Means of Order 2 (2 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	1.47	1.14	1.02	0.95	0.90	0.85	0.82	0.79	0.78	0.77	0.76	0.75	0.75	0.74	0.73	0.73	0.73	0.72	0.72	0.72
2	2.00	1.47	1.28	1.18	1.12	1.05	1.01	0.97	0.95	0.94	0.93	0.92	0.91	0.90	0.89	0.89	0.88	0.88	0.87	0.87
3	2.35	1.68	1.44	1.32	1.25	1.16	1.11	1.07	1.05	1.03	1.02	1.01	1.00	0.99	0.98	0.98	0.97	0.97	0.96	0.96
4	2.63	1.82	1.55	1.42	1.33	1.24	1.18	1.14	1.12	1.10	1.08	1.07	1.06	1.05	1.04	1.04	1.03	1.03	1.02	1.01
5	2.86	1.94	1.64	1.49	1.40	1.30	1.24	1.20	1.17	1.15	1.13	1.12	1.11	1.10	1.09	1.08	1.07	1.07	1.06	1.06
8	3.40	2.21	1.84	1.65	1.55	1.42	1.36	1.30	1.27	1.25	1.23	1.22	1.21	1.19	1.18	1.17	1.17	1.16	1.15	1.14
12	3.93	2.45	2.01	1.79	1.67	1.53	1.45	1.39	1.36	1.33	1.31	1.30	1.29	1.27	1.26	1.25	1.24	1.23	1.22	1.22
16	4.35	2.63	2.13	1.90	1.76	1.61	1.52	1.46	1.42	1.39	1.37	1.35	1.34	1.32	1.31	1.30	1.29	1.29	1.28	1.27
20	4.71	2.78	2.23	1.98	1.83	1.66	1.57	1.51	1.46	1.43	1.41	1.40	1.38	1.36	1.35	1.34	1.33	1.32	1.31	1.31
30	5.42	3.06	2.42	2.12	1.95	1.77	1.67	1.59	1.55	1.51	1.49	1.47	1.46	1.44	1.42	1.41	1.40	1.39	1.38	1.37
40	5.98	3.27	2.55	2.23	2.04	1.84	1.74	1.66	1.61	1.57	1.54	1.52	1.51	1.49	1.47	1.46	1.45	1.44	1.43	1.42
50	6.46	3.44	2.66	2.31	2.12	1.90	1.79	1.70	1.65	1.61	1.59	1.57	1.55	1.53	1.51	1.50	1.49	1.48	1.46	1.46
60	6.87	3.59	2.75	2.38	2.17	1.95	1.83	1.74	1.69	1.65	1.62	1.60	1.58	1.56	1.54	1.53	1.52	1.51	1.49	1.48
75	7.41	3.77	*2.86*	2.47	2.25	2.01	1.88	1.79	1.73	1.69	1.66	1.64	1.62	1.59	1.58	1.56	1.55	1.54	1.53	1.52
100	8.17	4.02	3.01	2.58	2.34	2.08	1.95	1.85	1.79	1.74	1.71	1.69	1.67	1.64	1.62	1.61	1.60	1.59	1.57	1.56
125	8.82	4.22	3.13	2.67	2.42	2.14	2.00	1.90	1.83	1.79	1.75	1.73	1.71	1.68	1.66	1.64	1.63	1.62	1.61	1.60
150	9.38	4.39	3.23	2.74	2.48	2.19	2.04	1.93	1.86	1.82	1.78	1.76	1.74	1.71	1.69	1.67	1.66	1.65	1.63	1.62
175	9.87	4.53	3.32	2.81	2.53	2.23	2.08	1.96	1.90	1.85	1.81	1.79	1.76	1.73	1.71	1.70	1.68	1.67	1.66	1.65
200	10.34	4.67	3.39	*2.86*	2.57	2.27	2.11	1.99	1.92	1.87	1.83	1.81	1.79	1.76	1.73	1.72	1.70	1.69	1.68	1.66

Table 19-15. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Means of Order 2 (2 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	1.85	1.42	1.25	1.16	1.10	1.04	1.00	0.97	0.95	0.93	0.92	0.92	0.91	0.90	0.89	0.89	0.88	0.88	0.87	0.87
2	2.45	1.77	1.52	1.40	1.32	1.23	1.18	1.14	1.11	1.09	1.08	1.07	1.06	1.05	1.04	1.03	1.03	1.02	1.02	1.01
3	2.86	1.99	1.69	1.54	1.45	1.34	1.28	1.23	1.20	1.18	1.17	1.16	1.15	1.13	1.12	1.12	1.11	1.10	1.10	1.09
4	3.19	2.15	1.81	1.64	1.54	1.42	1.35	1.30	1.27	1.25	1.23	1.22	1.21	1.19	1.18	1.17	1.16	1.16	1.15	1.14
5	3.46	2.28	1.90	1.72	1.60	1.48	1.41	1.35	1.32	1.29	1.27	1.26	1.25	1.23	1.22	1.21	1.21	1.20	1.19	1.19
8	4.09	2.57	2.11	1.88	1.75	1.60	1.52	1.46	1.42	1.39	1.37	1.35	1.34	1.32	1.31	1.30	1.29	1.29	1.28	1.27
12	4.72	2.84	2.29	2.03	1.88	1.71	1.61	1.54	1.50	1.47	1.45	1.43	1.42	1.40	1.38	1.37	1.36	1.36	1.34	1.34
16	5.22	3.04	2.42	2.13	1.97	1.78	1.68	1.61	1.56	1.53	1.50	1.48	1.47	1.45	1.43	1.42	1.41	1.40	1.39	1.38
20	5.64	3.20	2.53	2.22	2.04	1.84	1.73	1.65	1.60	1.57	1.54	1.52	1.51	1.49	1.47	1.46	1.45	1.44	1.43	1.42
30	6.48	3.51	2.72	2.37	2.17	1.95	1.83	1.74	1.69	1.65	1.62	1.60	1.58	1.56	1.54	1.53	1.52	1.51	1.49	1.48
40	7.15	3.75	2.87	2.48	2.26	2.02	1.90	1.80	1.74	1.70	1.67	1.65	1.63	1.60	1.59	1.57	1.56	1.55	1.54	1.53
50	7.72	3.94	2.99	2.57	2.33	2.08	1.95	1.85	1.79	1.74	1.71	1.69	1.67	1.64	1.62	1.61	1.60	1.59	1.57	1.56
60	8.21	4.10	*3.08*	2.64	2.39	2.13	1.99	1.89	1.82	1.78	1.74	1.72	1.70	1.67	1.65	1.64	1.63	1.62	1.60	1.59
75	8.85	4.31	*3.21*	2.73	2.47	2.19	2.04	1.93	1.86	1.82	1.78	1.76	1.74	1.71	1.69	1.67	1.66	1.65	1.63	1.62
100	9.76	4.58	3.37	2.85	2.57	2.27	2.11	1.99	1.92	1.87	1.84	1.81	1.79	1.76	1.73	1.72	1.70	1.69	1.68	1.66
125	10.52	4.81	3.50	2.94	2.64	2.32	2.16	2.04	1.96	1.91	1.87	1.85	1.82	1.79	1.77	1.75	1.74	1.73	1.71	1.70
150	11.19	5.00	3.61	3.02	2.71	2.37	2.20	2.08	2.00	1.94	1.91	1.88	1.85	1.82	1.80	1.78	1.77	1.75	1.74	1.72
175	11.78	5.16	3.70	*3.09*	2.76	2.42	2.24	2.11	2.03	1.97	1.93	1.90	1.88	1.84	1.82	1.80	1.79	1.78	1.76	1.74
200	12.30	5.32	3.78	*3.15*	2.81	2.45	2.27	2.14	2.05	2.00	1.96	1.92	1.90	1.86	1.84	1.82	1.81	1.80	1.78	1.76

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Table 19-15. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Means of Order 2 (5 COC, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.72**	**1.28**	**1.12**	**1.04**	**0.98**	**0.92**	**0.88**	**0.86**	**0.84**	**0.83**	**0.82**	**0.81**	**0.80**	**0.79**	**0.79**	**0.78**	**0.78**	**0.78**	**0.77**	**0.77**
2	**2.29**	**1.62**	**1.39**	**1.27**	**1.20**	**1.11**	**1.07**	**1.03**	**1.01**	**0.99**	**0.98**	**0.97**	**0.96**	**0.95**	**0.94**	**0.94**	**0.93**	**0.93**	**0.92**	**0.92**
3	**2.68**	**1.82**	**1.55**	**1.41**	**1.32**	**1.23**	**1.17**	**1.13**	**1.10**	**1.08**	**1.07**	**1.06**	**1.05**	**1.04**	**1.03**	**1.02**	**1.02**	**1.01**	**1.01**	**1.00**
4	2.99	**1.98**	**1.66**	**1.50**	**1.41**	**1.30**	**1.24**	**1.20**	**1.17**	**1.15**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**	**1.07**	**1.06**	**1.06**
5	3.24	**2.10**	**1.75**	**1.58**	**1.48**	**1.36**	**1.30**	**1.25**	**1.22**	**1.20**	**1.18**	**1.17**	**1.16**	**1.14**	**1.13**	**1.12**	**1.12**	**1.11**	**1.10**	**1.10**
8	3.84	**2.38**	**1.94**	**1.74**	**1.62**	**1.49**	**1.41**	**1.36**	**1.32**	**1.29**	**1.28**	**1.26**	**1.25**	**1.23**	**1.22**	**1.21**	**1.21**	**1.20**	**1.19**	**1.19**
12	4.43	**2.63**	**2.12**	**1.88**	**1.74**	**1.59**	**1.51**	**1.45**	**1.41**	**1.38**	**1.36**	**1.34**	**1.33**	**1.31**	**1.30**	**1.29**	**1.28**	**1.27**	**1.26**	**1.26**
16	4.90	2.82	**2.25**	**1.98**	**1.83**	**1.67**	**1.58**	**1.51**	**1.46**	**1.43**	**1.41**	**1.40**	**1.38**	**1.36**	**1.35**	**1.34**	**1.33**	**1.33**	**1.31**	**1.31**
20	5.29	2.97	**2.35**	**2.06**	**1.90**	**1.72**	**1.63**	**1.56**	**1.51**	**1.48**	**1.46**	**1.44**	**1.42**	**1.40**	**1.39**	**1.38**	**1.37**	**1.36**	**1.35**	**1.34**
30	6.08	3.26	**2.54**	**2.21**	**2.03**	**1.83**	**1.72**	**1.64**	**1.59**	**1.56**	**1.53**	**1.51**	**1.50**	**1.48**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**	**1.41**
40	6.71	3.48	*2.68*	**2.32**	**2.12**	**1.90**	**1.79**	**1.70**	**1.65**	**1.61**	**1.59**	**1.57**	**1.55**	**1.53**	**1.51**	**1.50**	**1.49**	**1.48**	**1.46**	**1.46**
50	7.25	3.66	*2.79*	**2.40**	**2.19**	**1.96**	**1.84**	**1.75**	**1.69**	**1.66**	**1.63**	**1.61**	**1.59**	**1.56**	**1.55**	**1.53**	**1.52**	**1.51**	**1.50**	**1.49**
60	7.71	3.81	2.88	**2.48**	**2.25**	**2.01**	**1.88**	**1.79**	**1.73**	**1.69**	**1.66**	**1.64**	**1.62**	**1.59**	**1.58**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**
75	8.30	4.00	3.00	**2.56**	**2.32**	**2.07**	**1.93**	**1.84**	**1.77**	**1.73**	**1.70**	**1.68**	**1.66**	**1.63**	**1.61**	**1.60**	**1.59**	**1.58**	**1.56**	**1.55**
100	9.16	4.27	3.15	*2.68*	**2.42**	**2.14**	**2.00**	**1.90**	**1.83**	**1.78**	**1.75**	**1.73**	**1.71**	**1.68**	**1.66**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**
125	9.88	4.47	3.27	*2.77*	**2.49**	**2.20**	**2.05**	**1.94**	**1.87**	**1.83**	**1.79**	**1.77**	**1.75**	**1.72**	**1.69**	**1.68**	**1.67**	**1.66**	**1.64**	**1.63**
150	10.51	4.66	3.37	*2.84*	**2.55**	**2.25**	**2.09**	**1.98**	**1.91**	**1.86**	**1.82**	**1.80**	**1.77**	**1.75**	**1.72**	**1.71**	**1.69**	**1.68**	**1.67**	**1.66**
175	11.05	4.80	3.47	2.91	*2.61*	**2.29**	**2.13**	**2.01**	**1.94**	**1.89**	**1.85**	**1.82**	**1.80**	**1.77**	**1.75**	**1.73**	**1.72**	**1.71**	**1.69**	**1.68**
200	11.56	4.96	3.54	2.96	*2.65*	**2.33**	**2.16**	**2.04**	**1.96**	**1.91**	**1.88**	**1.85**	**1.82**	**1.79**	**1.77**	**1.75**	**1.74**	**1.73**	**1.71**	**1.70**

Table 19-15. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Means of Order 2 (5 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.19**	**1.58**	**1.37**	**1.26**	**1.19**	**1.11**	**1.06**	**1.03**	**1.01**	**0.99**	**0.98**	**0.97**	**0.96**	**0.95**	**0.94**	**0.94**	**0.93**	**0.93**	**0.92**	**0.92**
2	2.86	**1.94**	**1.64**	**1.49**	**1.40**	**1.30**	**1.24**	**1.20**	**1.17**	**1.15**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**	**1.07**	**1.06**	**1.06**
3	3.32	**2.17**	**1.81**	**1.63**	**1.53**	**1.41**	**1.34**	**1.29**	**1.26**	**1.23**	**1.22**	**1.20**	**1.19**	**1.18**	**1.17**	**1.16**	**1.15**	**1.15**	**1.14**	**1.13**
4	3.68	**2.34**	**1.93**	**1.73**	**1.61**	**1.48**	**1.41**	**1.35**	**1.32**	**1.29**	**1.28**	**1.26**	**1.25**	**1.23**	**1.22**	**1.21**	**1.21**	**1.20**	**1.19**	**1.19**
5	3.99	**2.48**	**2.02**	**1.81**	**1.68**	**1.54**	**1.46**	**1.40**	**1.37**	**1.34**	**1.32**	**1.31**	**1.29**	**1.28**	**1.26**	**1.25**	**1.25**	**1.24**	**1.23**	**1.23**
8	4.71	**2.78**	**2.23**	**1.98**	**1.83**	**1.66**	**1.57**	**1.51**	**1.46**	**1.43**	**1.41**	**1.40**	**1.38**	**1.36**	**1.35**	**1.34**	**1.33**	**1.32**	**1.31**	**1.31**
12	5.42	3.06	**2.42**	**2.12**	**1.95**	**1.77**	**1.67**	**1.59**	**1.55**	**1.51**	**1.49**	**1.47**	**1.46**	**1.44**	**1.42**	**1.41**	**1.40**	**1.39**	**1.38**	**1.37**
16	5.98	3.27	**2.55**	**2.23**	**2.04**	**1.84**	**1.74**	**1.66**	**1.61**	**1.57**	**1.54**	**1.52**	**1.51**	**1.49**	**1.47**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**
20	6.46	3.44	**2.66**	**2.31**	**2.12**	**1.90**	**1.79**	**1.70**	**1.65**	**1.61**	**1.59**	**1.57**	**1.55**	**1.53**	**1.51**	**1.50**	**1.49**	**1.48**	**1.46**	**1.46**
30	7.41	3.77	*2.86*	**2.47**	**2.25**	**2.01**	**1.88**	**1.79**	**1.73**	**1.69**	**1.66**	**1.64**	**1.62**	**1.59**	**1.58**	**1.56**	**1.55**	**1.54**	**1.53**	**1.52**
40	8.17	4.02	3.01	**2.58**	**2.34**	**2.08**	**1.95**	**1.85**	**1.79**	**1.74**	**1.71**	**1.69**	**1.67**	**1.64**	**1.62**	**1.61**	**1.60**	**1.59**	**1.57**	**1.56**
50	8.82	4.22	3.13	**2.67**	**2.41**	**2.14**	**2.00**	**1.90**	**1.83**	**1.78**	**1.75**	**1.73**	**1.71**	**1.68**	**1.66**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**
60	9.38	4.39	3.23	**2.74**	**2.48**	**2.19**	**2.04**	**1.93**	**1.87**	**1.82**	**1.78**	**1.76**	**1.74**	**1.71**	**1.69**	**1.67**	**1.66**	**1.65**	**1.63**	**1.62**
75	10.12	4.60	3.36	*2.84*	**2.55**	**2.25**	**2.09**	**1.98**	**1.91**	**1.86**	**1.82**	**1.80**	**1.78**	**1.74**	**1.72**	**1.71**	**1.69**	**1.68**	**1.67**	**1.66**
100	11.13	4.89	3.53	*2.96*	**2.65**	**2.33**	**2.16**	**2.04**	**1.96**	**1.91**	**1.88**	**1.85**	**1.82**	**1.79**	**1.77**	**1.75**	**1.74**	**1.73**	**1.71**	**1.70**
125	11.99	5.14	3.66	*3.05*	**2.73**	**2.39**	**2.21**	**2.08**	**2.01**	**1.95**	**1.91**	**1.88**	**1.86**	**1.83**	**1.80**	**1.78**	**1.77**	**1.76**	**1.74**	**1.73**
150	12.73	5.33	3.77	3.13	**2.79**	**2.44**	**2.25**	**2.12**	**2.04**	**1.98**	**1.94**	**1.91**	**1.89**	**1.86**	**1.83**	**1.81**	**1.80**	**1.79**	**1.77**	**1.75**
175	13.44	5.51	3.87	3.20	*2.85*	**2.48**	**2.29**	**2.15**	**2.07**	**2.01**	**1.97**	**1.94**	**1.91**	**1.88**	**1.85**	**1.84**	**1.82**	**1.81**	**1.79**	**1.77**
200	14.06	5.66	3.96	3.26	*2.89*	**2.51**	**2.32**	**2.18**	**2.09**	**2.04**	**1.99**	**1.96**	**1.94**	**1.90**	**1.88**	**1.86**	**1.84**	**1.83**	**1.80**	**1.79**

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Table 19-15. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Means of Order 2 (5 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	2.67	1.89	1.61	1.48	1.39	1.29	1.24	1.19	1.16	1.14	1.13	1.12	1.11	1.10	1.09	1.08	1.07	1.07	1.06	1.06
2	3.46	2.28	1.90	1.72	1.60	1.48	1.41	1.35	1.32	1.29	1.27	1.26	1.25	1.23	1.22	1.21	1.21	1.20	1.19	1.19
3	4.00	2.53	2.08	1.86	1.73	1.58	1.50	1.44	1.40	1.38	1.36	1.34	1.33	1.31	1.30	1.29	1.28	1.27	1.26	1.26
4	4.43	2.71	2.20	1.96	1.82	1.66	1.57	1.51	1.46	1.43	1.41	1.40	1.38	1.36	1.35	1.34	1.33	1.32	1.31	1.31
5	4.79	2.87	2.31	2.04	1.89	1.72	1.62	1.55	1.51	1.48	1.46	1.44	1.42	1.40	1.39	1.38	1.37	1.36	1.35	1.34
8	5.64	3.20	2.53	2.22	2.04	1.84	1.73	1.65	1.60	1.57	1.54	1.52	1.51	1.49	1.47	1.46	1.45	1.44	1.43	1.42
12	6.48	3.51	2.72	2.37	2.17	1.95	1.83	1.74	1.69	1.65	1.62	1.60	1.58	1.56	1.54	1.53	1.52	1.51	1.49	1.48
16	7.15	3.75	2.87	2.48	2.26	2.02	1.90	1.80	1.74	1.70	1.67	1.65	1.63	1.60	1.59	1.57	1.56	1.55	1.54	1.53
20	7.71	3.94	2.99	2.57	2.33	2.08	1.95	1.85	1.79	1.74	1.71	1.69	1.67	1.64	1.62	1.61	1.60	1.59	1.57	1.56
30	8.85	4.31	*3.21*	2.73	2.47	2.19	2.04	1.93	1.86	1.82	1.78	1.76	1.74	1.71	1.69	1.67	1.66	1.65	1.63	1.62
40	9.76	4.58	3.37	2.85	2.57	2.26	2.11	1.99	1.92	1.87	1.84	1.81	1.79	1.75	1.73	1.72	1.70	1.69	1.68	1.67
50	10.52	4.81	3.50	2.94	2.64	2.32	2.16	2.04	1.96	1.91	1.87	1.85	1.82	1.79	1.77	1.75	1.74	1.73	1.71	1.70
60	11.19	5.00	3.61	3.02	2.71	2.37	2.20	2.08	2.00	1.94	1.91	1.88	1.85	1.82	1.80	1.78	1.77	1.75	1.74	1.72
75	12.05	5.24	3.74	*3.12*	2.79	2.43	2.25	2.12	2.04	1.98	1.94	1.91	1.89	1.85	1.83	1.81	1.80	1.79	1.77	1.75
100	13.28	5.57	3.92	*3.25*	2.89	2.51	2.32	2.18	2.09	2.04	1.99	1.96	1.94	1.90	1.87	1.85	1.84	1.83	1.80	1.78
125	14.30	5.84	4.07	3.35	2.97	2.57	2.37	2.23	2.14	2.08	2.03	2.00	1.97	1.93	1.91	1.88	1.87	1.85	1.84	1.82
150	15.23	6.07	4.19	3.43	3.04	2.62	2.42	2.26	2.17	2.11	2.06	2.03	2.00	1.96	1.93	1.91	1.90	1.89	1.86	1.85
175	16.02	6.27	4.30	3.51	*3.09*	2.67	2.45	2.30	2.20	2.14	2.09	2.06	2.03	1.99	1.96	1.94	1.92	1.91	1.88	1.87
200	16.72	6.45	4.38	3.57	*3.14*	2.71	2.48	2.32	2.23	2.16	2.11	2.08	2.05	2.01	1.98	1.96	1.94	1.93	1.90	1.89

Table 19-15. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Means of Order 2 (10 COC, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	2.29	1.62	1.39	1.27	1.20	1.11	1.07	1.03	1.01	0.99	0.98	0.97	0.96	0.95	0.94	0.94	0.93	0.93	0.92	0.92
2	2.99	1.98	1.66	1.50	1.41	1.30	1.24	1.20	1.17	1.15	1.13	1.12	1.11	1.10	1.09	1.08	1.07	1.07	1.06	1.06
3	3.46	2.21	1.82	1.64	1.53	1.41	1.34	1.29	1.26	1.23	1.22	1.20	1.19	1.18	1.17	1.16	1.15	1.15	1.14	1.13
4	3.84	2.38	1.94	1.74	1.62	1.49	1.41	1.36	1.32	1.29	1.28	1.26	1.25	1.23	1.22	1.21	1.21	1.20	1.19	1.19
5	4.15	2.51	2.04	1.82	1.69	1.54	1.46	1.40	1.37	1.34	1.32	1.31	1.29	1.28	1.26	1.25	1.25	1.24	1.23	1.23
8	4.90	2.82	2.25	1.98	1.83	1.67	1.58	1.51	1.46	1.44	1.41	1.40	1.38	1.36	1.35	1.34	1.33	1.33	1.31	1.31
12	5.63	3.10	2.43	2.13	1.96	1.77	1.67	1.60	1.55	1.51	1.49	1.47	1.46	1.44	1.42	1.41	1.40	1.39	1.38	1.37
16	6.22	3.31	2.57	2.24	2.05	1.85	1.74	1.66	1.61	1.57	1.54	1.53	1.51	1.49	1.47	1.46	1.45	1.44	1.43	1.42
20	6.71	3.48	*2.68*	2.32	2.12	1.90	1.79	1.70	1.65	1.61	1.59	1.57	1.55	1.53	1.51	1.50	1.49	1.48	1.46	1.46
30	7.70	3.81	2.88	2.47	2.25	2.01	1.88	1.79	1.73	1.69	1.66	1.64	1.62	1.59	1.58	1.56	1.55	1.54	1.53	1.52
40	8.50	4.06	3.03	2.59	2.34	2.09	1.95	1.85	1.79	1.74	1.71	1.69	1.67	1.64	1.62	1.61	1.60	1.59	1.57	1.56
50	9.16	4.27	3.15	*2.68*	2.42	2.15	2.00	1.90	1.83	1.79	1.75	1.73	1.71	1.68	1.66	1.64	1.63	1.62	1.61	1.59
60	9.74	4.44	3.25	*2.75*	2.48	2.19	2.04	1.93	1.86	1.82	1.79	1.76	1.74	1.71	1.69	1.67	1.66	1.65	1.63	1.62
75	10.50	4.66	3.38	*2.84*	2.55	2.25	2.09	1.98	1.91	1.86	1.82	1.80	1.78	1.75	1.72	1.71	1.69	1.68	1.67	1.66
100	11.57	4.96	3.54	2.97	*2.66*	2.33	2.16	2.04	1.96	1.91	1.87	1.85	1.82	1.79	1.77	1.75	1.74	1.73	1.71	1.70
125	12.50	5.20	3.67	3.06	*2.73*	2.39	2.21	2.09	2.01	1.95	1.91	1.88	1.86	1.82	1.80	1.79	1.77	1.76	1.74	1.73
150	13.28	5.40	3.78	3.14	*2.80*	2.44	2.26	2.12	2.04	1.98	1.94	1.91	1.89	1.86	1.83	1.81	1.80	1.79	1.77	1.75
175	13.96	5.57	3.88	3.21	*2.84*	2.48	2.29	2.15	2.07	2.01	1.97	1.94	1.92	1.88	1.86	1.84	1.82	1.81	1.79	1.77
200	14.65	5.71	3.98	3.27	2.89	2.51	2.32	2.19	2.10	2.04	2.00	1.96	1.93	1.90	1.87	1.85	1.84	1.83	1.81	1.79

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Table 19-15. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Means of Order 2 (10 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	2.86	**1.94**	**1.64**	**1.49**	**1.40**	**1.30**	**1.24**	**1.20**	**1.17**	**1.15**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**	**1.07**	**1.06**	**1.06**
2	3.68	**2.34**	**1.93**	**1.73**	**1.61**	**1.48**	**1.41**	**1.35**	**1.32**	**1.29**	**1.28**	**1.26**	**1.25**	**1.23**	**1.22**	**1.21**	**1.21**	**1.20**	**1.19**	**1.19**
3	4.26	**2.59**	**2.10**	**1.87**	**1.74**	**1.59**	**1.51**	**1.44**	**1.40**	**1.38**	**1.36**	**1.34**	**1.33**	**1.31**	**1.30**	**1.29**	**1.28**	**1.27**	**1.26**	**1.26**
4	4.71	**2.78**	**2.23**	**1.98**	**1.83**	**1.66**	**1.57**	**1.51**	**1.46**	**1.43**	**1.41**	**1.40**	**1.38**	**1.36**	**1.35**	**1.34**	**1.33**	**1.32**	**1.31**	**1.31**
5	5.09	*2.93*	**2.33**	**2.06**	**1.90**	**1.72**	**1.63**	**1.56**	**1.51**	**1.48**	**1.46**	**1.44**	**1.42**	**1.40**	**1.39**	**1.38**	**1.37**	**1.36**	**1.35**	**1.34**
8	5.98	3.27	**2.55**	**2.23**	**2.05**	**1.84**	**1.74**	**1.66**	**1.61**	**1.57**	**1.54**	**1.52**	**1.51**	**1.49**	**1.47**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**
12	6.87	3.59	**2.75**	**2.38**	**2.17**	**1.95**	**1.83**	**1.74**	**1.69**	**1.65**	**1.62**	**1.60**	**1.58**	**1.56**	**1.54**	**1.53**	**1.52**	**1.51**	**1.49**	**1.48**
16	7.58	3.82	*2.90*	**2.49**	**2.27**	**2.02**	**1.90**	**1.80**	**1.74**	**1.70**	**1.67**	**1.65**	**1.63**	**1.60**	**1.59**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**
20	8.18	4.02	3.01	**2.58**	**2.34**	**2.08**	**1.95**	**1.85**	**1.79**	**1.74**	**1.71**	**1.69**	**1.67**	**1.64**	**1.62**	**1.61**	**1.60**	**1.59**	**1.57**	**1.56**
30	9.38	4.39	3.23	**2.74**	**2.47**	**2.19**	**2.04**	**1.93**	**1.87**	**1.82**	**1.78**	**1.76**	**1.74**	**1.71**	**1.69**	**1.67**	**1.66**	**1.65**	**1.63**	**1.62**
40	10.33	4.67	3.40	*2.86*	**2.57**	**2.27**	**2.11**	**1.99**	**1.92**	**1.87**	**1.84**	**1.81**	**1.79**	**1.75**	**1.73**	**1.72**	**1.70**	**1.69**	**1.68**	**1.66**
50	11.13	4.90	3.53	*2.96*	**2.65**	**2.33**	**2.16**	**2.04**	**1.96**	**1.91**	**1.87**	**1.85**	**1.82**	**1.79**	**1.77**	**1.75**	**1.74**	**1.73**	**1.71**	**1.70**
60	11.84	5.09	3.63	*3.03*	**2.71**	**2.38**	**2.20**	**2.08**	**2.00**	**1.94**	**1.91**	**1.88**	**1.85**	**1.82**	**1.80**	**1.78**	**1.77**	**1.75**	**1.73**	**1.72**
75	12.74	5.33	3.77	3.13	**2.79**	**2.44**	**2.26**	**2.12**	**2.04**	**1.98**	**1.94**	**1.91**	**1.89**	**1.86**	**1.83**	**1.81**	**1.80**	**1.79**	**1.77**	**1.75**
100	14.06	5.66	3.96	3.26	*2.89*	**2.51**	**2.32**	**2.18**	**2.09**	**2.04**	**1.99**	**1.96**	**1.94**	**1.90**	**1.87**	**1.86**	**1.84**	**1.83**	**1.80**	**1.77**
125	15.14	5.96	4.10	3.36	*2.97*	**2.58**	**2.37**	**2.23**	**2.14**	**2.08**	**2.03**	**2.00**	**1.97**	**1.93**	**1.90**	**1.88**	**1.87**	**1.85**	**1.84**	**1.82**
150	16.11	6.18	4.22	3.44	*3.04*	**2.62**	**2.42**	**2.26**	**2.17**	**2.11**	**2.06**	**2.03**	**2.00**	**1.96**	**1.93**	**1.91**	**1.89**	**1.89**	**1.86**	**1.85**
175	16.99	6.40	4.32	3.52	*3.10*	**2.67**	**2.45**	**2.29**	**2.20**	**2.14**	**2.09**	**2.06**	**2.03**	**1.99**	**1.96**	**1.93**	**1.92**	**1.91**	**1.89**	**1.87**
200	17.77	6.54	4.42	3.59	3.15	**2.71**	**2.48**	**2.33**	**2.23**	**2.16**	**2.11**	**2.08**	**2.05**	**2.01**	**1.98**	**1.95**	**1.94**	**1.93**	**1.90**	**1.89**

Table 19-15. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Means of Order 2 (10 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.46	**2.28**	**1.90**	**1.72**	**1.60**	**1.48**	**1.41**	**1.35**	**1.32**	**1.29**	**1.27**	**1.26**	**1.25**	**1.23**	**1.22**	**1.21**	**1.21**	**1.20**	**1.19**	**1.19**
2	4.43	**2.71**	**2.20**	**1.96**	**1.82**	**1.66**	**1.57**	**1.51**	**1.46**	**1.43**	**1.41**	**1.40**	**1.38**	**1.36**	**1.35**	**1.34**	**1.33**	**1.32**	**1.31**	**1.31**
3	5.11	**2.99**	**2.39**	**2.11**	**1.95**	**1.77**	**1.67**	**1.59**	**1.55**	**1.51**	**1.49**	**1.47**	**1.46**	**1.44**	**1.42**	**1.41**	**1.40**	**1.39**	**1.38**	**1.37**
4	5.64	3.20	**2.53**	**2.22**	**2.04**	**1.84**	**1.73**	**1.65**	**1.60**	**1.57**	**1.54**	**1.52**	**1.51**	**1.49**	**1.47**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**
5	6.09	3.37	**2.63**	**2.30**	**2.11**	**1.90**	**1.79**	**1.70**	**1.65**	**1.61**	**1.59**	**1.56**	**1.55**	**1.52**	**1.51**	**1.50**	**1.49**	**1.48**	**1.46**	**1.46**
8	7.15	3.75	**2.87**	**2.48**	**2.26**	**2.02**	**1.90**	**1.80**	**1.74**	**1.70**	**1.67**	**1.65**	**1.63**	**1.60**	**1.59**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**
12	8.21	4.10	*3.08*	**2.64**	**2.39**	**2.13**	**1.99**	**1.89**	**1.82**	**1.78**	**1.74**	**1.72**	**1.70**	**1.67**	**1.65**	**1.64**	**1.63**	**1.62**	**1.60**	**1.59**
16	9.05	4.37	3.24	**2.76**	**2.49**	**2.20**	**2.06**	**1.95**	**1.88**	**1.83**	**1.80**	**1.77**	**1.75**	**1.72**	**1.70**	**1.68**	**1.67**	**1.66**	**1.64**	**1.63**
20	9.75	4.58	3.37	**2.85**	**2.57**	**2.26**	**2.11**	**1.99**	**1.92**	**1.87**	**1.83**	**1.81**	**1.79**	**1.75**	**1.73**	**1.72**	**1.70**	**1.69**	**1.68**	**1.66**
30	11.18	5.00	3.61	**3.02**	**2.71**	**2.37**	**2.20**	**2.08**	**2.00**	**1.94**	**1.91**	**1.88**	**1.85**	**1.82**	**1.80**	**1.78**	**1.76**	**1.75**	**1.74**	**1.72**
40	12.30	5.32	3.78	*3.15*	**2.81**	**2.45**	**2.27**	**2.13**	**2.05**	**2.00**	**1.96**	**1.92**	**1.90**	**1.86**	**1.84**	**1.82**	**1.81**	**1.80**	**1.78**	**1.76**
50	13.28	5.57	3.92	*3.25*	**2.89**	**2.51**	**2.32**	**2.18**	**2.10**	**2.04**	**1.99**	**1.96**	**1.94**	**1.90**	**1.87**	**1.85**	**1.84**	**1.83**	**1.80**	**1.78**
60	14.11	5.79	4.04	3.33	**2.95**	**2.56**	**2.36**	**2.22**	**2.13**	**2.07**	**2.02**	**1.99**	**1.97**	**1.93**	**1.90**	**1.88**	**1.86**	**1.85**	**1.83**	**1.82**
75	15.23	6.07	4.19	3.44	**3.03**	**2.62**	**2.42**	**2.26**	**2.17**	**2.11**	**2.06**	**2.03**	**2.00**	**1.96**	**1.93**	**1.91**	**1.90**	**1.89**	**1.86**	**1.85**
100	16.80	6.45	4.38	3.57	*3.14*	**2.70**	**2.48**	**2.33**	**2.23**	**2.16**	**2.11**	**2.08**	**2.05**	**2.01**	**1.98**	**1.96**	**1.94**	**1.93**	**1.90**	**1.89**
125	18.07	6.74	4.54	3.67	*3.22*	**2.76**	**2.53**	**2.37**	**2.27**	**2.20**	**2.15**	**2.11**	**2.09**	**2.04**	**2.01**	**1.99**	**1.97**	**1.96**	**1.93**	**1.92**
150	19.14	7.01	4.68	3.77	*3.30*	**2.82**	**2.58**	**2.41**	**2.30**	**2.23**	**2.19**	**2.15**	**2.12**	**2.07**	**2.04**	**2.01**	**2.00**	**1.98**	**1.96**	**1.94**
175	20.12	7.23	4.79	3.85	3.36	**2.86**	**2.61**	**2.44**	**2.33**	**2.26**	**2.21**	**2.17**	**2.14**	**2.09**	**2.06**	**2.03**	**2.02**	**2.00**	**1.98**	**1.96**
200	21.09	7.42	4.88	3.91	3.41	**2.91**	**2.65**	**2.47**	**2.36**	**2.28**	**2.23**	**2.19**	**2.15**	**2.11**	**2.08**	**2.05**	**2.04**	**2.02**	**1.99**	**1.98**

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Table 19-15. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Means of Order 2 (20 COC, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	2.99	**1.98**	**1.66**	**1.50**	**1.41**	**1.30**	**1.24**	**1.20**	**1.17**	**1.15**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**	**1.07**	**1.06**	**1.06**
2	3.84	**2.38**	**1.94**	**1.74**	**1.62**	**1.49**	**1.41**	**1.36**	**1.32**	**1.29**	**1.28**	**1.26**	**1.25**	**1.23**	**1.22**	**1.21**	**1.21**	**1.20**	**1.19**	**1.19**
3	4.43	**2.63**	**2.12**	**1.88**	**1.74**	**1.59**	**1.51**	**1.45**	**1.41**	**1.38**	**1.36**	**1.34**	**1.33**	**1.31**	**1.30**	**1.29**	**1.28**	**1.27**	**1.26**	**1.26**
4	4.90	2.82	**2.25**	**1.98**	**1.83**	**1.67**	**1.58**	**1.51**	**1.46**	**1.44**	**1.41**	**1.40**	**1.38**	**1.36**	**1.35**	**1.34**	**1.33**	**1.32**	**1.31**	**1.31**
5	5.29	2.97	**2.35**	**2.06**	**1.90**	**1.72**	**1.63**	**1.56**	**1.51**	**1.48**	**1.46**	**1.44**	**1.42**	**1.40**	**1.39**	**1.38**	**1.37**	**1.36**	**1.35**	**1.34**
8	6.22	3.31	**2.57**	**2.24**	**2.05**	**1.85**	**1.74**	**1.66**	**1.61**	**1.57**	**1.54**	**1.53**	**1.51**	**1.49**	**1.47**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**
12	7.14	3.63	*2.77*	**2.39**	**2.18**	**1.95**	**1.83**	**1.74**	**1.69**	**1.65**	**1.62**	**1.60**	**1.58**	**1.56**	**1.54**	**1.53**	**1.52**	**1.51**	**1.49**	**1.48**
16	7.88	3.87	2.91	**2.50**	**2.27**	**2.03**	**1.90**	**1.80**	**1.74**	**1.70**	**1.67**	**1.65**	**1.63**	**1.60**	**1.59**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**
20	8.49	4.06	3.03	**2.59**	**2.34**	**2.08**	**1.95**	**1.85**	**1.79**	**1.74**	**1.71**	**1.69**	**1.67**	**1.64**	**1.62**	**1.61**	**1.60**	**1.59**	**1.57**	**1.56**
30	9.74	4.44	3.25	*2.75*	**2.48**	**2.19**	**2.04**	**1.93**	**1.86**	**1.82**	**1.78**	**1.76**	**1.74**	**1.71**	**1.69**	**1.67**	**1.66**	**1.65**	**1.63**	**1.62**
40	10.73	4.72	3.41	2.87	**2.58**	**2.27**	**2.11**	**1.99**	**1.92**	**1.87**	**1.84**	**1.81**	**1.79**	**1.75**	**1.73**	**1.72**	**1.70**	**1.69**	**1.68**	**1.67**
50	11.55	4.96	3.54	2.97	*2.65*	**2.33**	**2.16**	**2.04**	**1.96**	**1.91**	**1.87**	**1.85**	**1.82**	**1.79**	**1.77**	**1.75**	**1.74**	**1.73**	**1.71**	**1.70**
60	12.30	5.14	3.65	3.04	*2.72*	**2.38**	**2.20**	**2.08**	**2.00**	**1.94**	**1.91**	**1.88**	**1.85**	**1.82**	**1.80**	**1.78**	**1.76**	**1.75**	**1.73**	**1.72**
75	13.26	5.40	3.79	3.14	*2.79*	**2.44**	**2.26**	**2.12**	**2.04**	**1.98**	**1.94**	**1.91**	**1.89**	**1.85**	**1.83**	**1.81**	**1.80**	**1.79**	**1.77**	**1.75**
100	14.63	5.74	3.96	3.26	2.90	**2.52**	**2.32**	**2.18**	**2.10**	**2.04**	**2.00**	**1.96**	**1.94**	**1.90**	**1.87**	**1.85**	**1.83**	**1.82**	**1.79**	**1.77**
125	15.72	6.02	4.12	3.37	2.97	**2.58**	**2.38**	**2.23**	**2.14**	**2.08**	**2.03**	**2.00**	**1.97**	**1.93**	**1.91**	**1.88**	**1.87**	**1.85**	**1.82**	**1.80**
150	16.68	6.22	4.24	3.45	3.04	*2.62*	**2.42**	**2.26**	**2.17**	**2.11**	**2.06**	**2.03**	**2.00**	**1.96**	**1.93**	**1.91**	**1.89**	**1.88**	**1.86**	**1.85**
175	17.64	6.43	4.34	3.52	3.10	*2.67*	**2.45**	**2.30**	**2.20**	**2.14**	**2.09**	**2.06**	**2.03**	**1.99**	**1.96**	**1.94**	**1.92**	**1.91**	**1.88**	**1.87**
200	18.32	6.63	4.44	3.59	3.14	*2.71*	**2.49**	**2.32**	**2.23**	**2.16**	**2.11**	**2.08**	**2.05**	**2.01**	**1.98**	**1.96**	**1.94**	**1.93**	**1.91**	**1.89**

Table 19-15. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Means of Order 2 (20 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.68	**2.34**	**1.93**	**1.73**	**1.61**	**1.48**	**1.41**	**1.35**	**1.32**	**1.29**	**1.28**	**1.26**	**1.25**	**1.23**	**1.22**	**1.21**	**1.21**	**1.20**	**1.19**	**1.19**
2	4.71	**2.78**	**2.23**	**1.98**	**1.83**	**1.66**	**1.57**	**1.51**	**1.46**	**1.43**	**1.41**	**1.40**	**1.38**	**1.36**	**1.35**	**1.34**	**1.33**	**1.32**	**1.31**	**1.31**
3	5.42	3.06	**2.42**	**2.12**	**1.95**	**1.77**	**1.67**	**1.59**	**1.55**	**1.51**	**1.49**	**1.47**	**1.46**	**1.44**	**1.42**	**1.41**	**1.40**	**1.39**	**1.38**	**1.37**
4	5.98	3.27	**2.55**	**2.23**	**2.04**	**1.84**	**1.74**	**1.66**	**1.61**	**1.57**	**1.54**	**1.52**	**1.51**	**1.49**	**1.47**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**
5	6.46	3.44	**2.66**	**2.31**	**2.12**	**1.90**	**1.79**	**1.70**	**1.65**	**1.61**	**1.59**	**1.57**	**1.55**	**1.53**	**1.51**	**1.50**	**1.49**	**1.48**	**1.46**	**1.46**
8	7.58	3.82	*2.90*	**2.49**	**2.27**	**2.03**	**1.90**	**1.80**	**1.74**	**1.70**	**1.67**	**1.65**	**1.63**	**1.60**	**1.59**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**
12	8.70	4.18	3.11	**2.65**	**2.40**	**2.13**	**1.99**	**1.89**	**1.82**	**1.78**	**1.75**	**1.72**	**1.70**	**1.67**	**1.65**	**1.64**	**1.63**	**1.62**	**1.60**	**1.59**
16	9.59	4.45	3.27	**2.77**	**2.50**	**2.21**	**2.06**	**1.95**	**1.88**	**1.83**	**1.80**	**1.77**	**1.75**	**1.72**	**1.70**	**1.68**	**1.67**	**1.66**	**1.64**	**1.63**
20	10.33	4.67	3.40	*2.86*	**2.57**	**2.27**	**2.11**	**1.99**	**1.92**	**1.87**	**1.84**	**1.81**	**1.79**	**1.75**	**1.73**	**1.72**	**1.70**	**1.69**	**1.68**	**1.67**
30	11.84	5.09	3.64	*3.04*	**2.71**	**2.38**	**2.20**	**2.08**	**2.00**	**1.95**	**1.91**	**1.88**	**1.85**	**1.82**	**1.80**	**1.78**	**1.77**	**1.75**	**1.74**	**1.72**
40	13.06	5.41	3.81	3.16	**2.81**	**2.45**	**2.27**	**2.14**	**2.05**	**2.00**	**1.96**	**1.92**	**1.90**	**1.86**	**1.84**	**1.82**	**1.81**	**1.80**	**1.78**	**1.76**
50	14.05	5.67	3.95	3.26	*2.89*	**2.51**	**2.32**	**2.18**	**2.10**	**2.04**	**1.99**	**1.96**	**1.94**	**1.90**	**1.87**	**1.85**	**1.84**	**1.83**	**1.80**	**1.77**
60	14.94	5.90	4.07	3.34	*2.96*	**2.56**	**2.36**	**2.22**	**2.13**	**2.07**	**2.03**	**1.99**	**1.97**	**1.93**	**1.90**	**1.88**	**1.86**	**1.85**	**1.82**	**1.82**
75	16.13	6.17	4.22	3.44	*3.04*	**2.63**	**2.42**	**2.26**	**2.17**	**2.11**	**2.06**	**2.03**	**2.00**	**1.96**	**1.93**	**1.91**	**1.89**	**1.89**	**1.86**	**1.85**
100	17.77	6.56	4.41	3.58	3.14	**2.70**	**2.48**	**2.32**	**2.23**	**2.16**	**2.11**	**2.08**	**2.05**	**2.01**	**1.98**	**1.95**	**1.94**	**1.93**	**1.90**	**1.89**
125	19.14	6.87	4.58	3.69	3.23	**2.77**	**2.54**	**2.37**	**2.27**	**2.20**	**2.15**	**2.11**	**2.08**	**2.04**	**2.01**	**1.99**	**1.97**	**1.96**	**1.93**	**1.92**
150	20.23	7.11	4.72	3.78	3.30	*2.82*	**2.58**	**2.41**	**2.31**	**2.23**	**2.18**	**2.14**	**2.11**	**2.07**	**2.03**	**2.01**	**2.00**	**1.98**	**1.96**	**1.94**
175	21.33	7.38	4.82	3.86	3.37	*2.86*	**2.61**	**2.44**	**2.33**	**2.26**	**2.21**	**2.17**	**2.14**	**2.09**	**2.06**	**2.03**	**2.01**	**2.00**	**1.98**	**1.96**
200	22.42	7.59	4.92	3.93	3.42	*2.91*	**2.65**	**2.47**	**2.36**	**2.29**	**2.23**	**2.20**	**2.16**	**2.11**	**2.08**	**2.05**	**2.03**	**2.02**	**1.99**	**1.98**

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Table 19-15. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Means of Order 2 (20 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	4.43	**2.71**	**2.20**	**1.96**	**1.82**	**1.66**	**1.57**	**1.51**	**1.46**	**1.43**	**1.41**	**1.40**	**1.38**	**1.36**	**1.35**	**1.34**	**1.33**	**1.32**	**1.31**	**1.31**
2	5.64	3.20	**2.53**	**2.22**	**2.04**	**1.84**	**1.73**	**1.65**	**1.60**	**1.57**	**1.54**	**1.52**	**1.51**	**1.49**	**1.47**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**
3	6.48	3.51	**2.72**	**2.37**	**2.17**	**1.95**	**1.83**	**1.74**	**1.69**	**1.65**	**1.62**	**1.60**	**1.58**	**1.56**	**1.54**	**1.53**	**1.52**	**1.51**	**1.49**	**1.48**
4	7.15	3.75	**2.87**	**2.48**	**2.26**	**2.02**	**1.90**	**1.80**	**1.74**	**1.70**	**1.67**	**1.65**	**1.63**	**1.60**	**1.59**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**
5	7.72	3.94	**2.99**	**2.57**	**2.33**	**2.08**	**1.95**	**1.85**	**1.79**	**1.74**	**1.71**	**1.69**	**1.67**	**1.64**	**1.62**	**1.61**	**1.60**	**1.59**	**1.57**	**1.56**
8	9.05	4.37	3.24	**2.76**	**2.49**	**2.21**	**2.06**	**1.95**	**1.88**	**1.83**	**1.80**	**1.77**	**1.75**	**1.72**	**1.70**	**1.68**	**1.67**	**1.66**	**1.64**	**1.63**
12	10.37	4.77	3.47	**2.93**	**2.63**	**2.31**	**2.15**	**2.03**	**1.96**	**1.90**	**1.87**	**1.84**	**1.82**	**1.78**	**1.76**	**1.74**	**1.73**	**1.72**	**1.70**	**1.69**
16	11.43	5.07	3.64	**3.05**	**2.73**	**2.39**	**2.22**	**2.09**	**2.01**	**1.96**	**1.92**	**1.89**	**1.86**	**1.83**	**1.81**	**1.79**	**1.77**	**1.76**	**1.74**	**1.73**
20	12.32	5.31	3.78	*3.15*	**2.81**	**2.45**	**2.27**	**2.14**	**2.05**	**2.00**	**1.96**	**1.92**	**1.90**	**1.86**	**1.84**	**1.82**	**1.81**	**1.80**	**1.78**	**1.76**
30	14.12	5.79	4.04	3.33	**2.95**	**2.56**	**2.36**	**2.22**	**2.13**	**2.07**	**2.03**	**1.99**	**1.97**	**1.93**	**1.90**	**1.88**	**1.86**	**1.85**	**1.83**	**1.82**
40	15.55	6.15	4.23	3.46	**3.06**	**2.64**	**2.43**	**2.28**	**2.18**	**2.12**	**2.07**	**2.04**	**2.01**	**1.97**	**1.94**	**1.92**	**1.91**	**1.89**	**1.87**	**1.86**
50	16.75	6.44	4.38	3.57	*3.14*	**2.70**	**2.48**	**2.32**	**2.23**	**2.16**	**2.11**	**2.08**	**2.05**	**2.01**	**1.98**	**1.95**	**1.94**	**1.93**	**1.90**	**1.89**
60	17.77	6.68	4.51	3.66	*3.21*	**2.76**	**2.53**	**2.36**	**2.26**	**2.19**	**2.14**	**2.11**	**2.08**	**2.03**	**2.00**	**1.98**	**1.96**	**1.95**	**1.93**	**1.91**
75	19.14	7.01	4.67	3.77	*3.30*	**2.82**	**2.58**	**2.41**	**2.30**	**2.23**	**2.18**	**2.14**	**2.11**	**2.07**	**2.04**	**2.01**	**2.00**	**1.98**	**1.96**	**1.94**
100	21.05	7.43	4.89	3.91	3.41	**2.90**	**2.65**	**2.47**	**2.36**	**2.29**	**2.23**	**2.19**	**2.16**	**2.11**	**2.08**	**2.05**	**2.04**	**2.02**	**1.99**	**1.98**
125	22.70	7.79	5.06	4.03	3.49	**2.97**	**2.70**	**2.51**	**2.40**	**2.32**	**2.27**	**2.23**	**2.19**	**2.14**	**2.11**	**2.08**	**2.06**	**2.05**	**2.02**	**2.00**
150	24.20	8.07	5.21	4.12	3.57	**3.02**	**2.74**	**2.55**	**2.44**	**2.36**	**2.30**	**2.26**	**2.22**	**2.17**	**2.14**	**2.11**	**2.09**	**2.07**	**2.05**	**2.03**
175	25.43	8.34	5.33	4.20	3.63	**3.06**	**2.79**	**2.58**	**2.47**	**2.38**	**2.33**	**2.29**	**2.24**	**2.19**	**2.16**	**2.13**	**2.11**	**2.10**	**2.07**	**2.05**
200	26.52	8.54	5.43	4.27	3.69	*3.10*	**2.81**	**2.61**	**2.49**	**2.41**	**2.35**	**2.31**	**2.26**	**2.21**	**2.18**	**2.15**	**2.13**	**2.11**	**2.08**	**2.07**

Table 19-15. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Means of Order 2 (40 COC, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.84	**2.38**	**1.94**	**1.74**	**1.62**	**1.49**	**1.41**	**1.36**	**1.32**	**1.29**	**1.28**	**1.26**	**1.25**	**1.23**	**1.22**	**1.21**	**1.21**	**1.20**	**1.19**	**1.19**
2	4.90	2.82	**2.25**	**1.98**	**1.83**	**1.67**	**1.58**	**1.51**	**1.46**	**1.43**	**1.41**	**1.40**	**1.38**	**1.36**	**1.35**	**1.34**	**1.33**	**1.33**	**1.31**	**1.31**
3	5.63	3.10	**2.43**	**2.13**	**1.96**	**1.77**	**1.67**	**1.60**	**1.55**	**1.51**	**1.49**	**1.47**	**1.46**	**1.44**	**1.42**	**1.41**	**1.40**	**1.39**	**1.38**	**1.37**
4	6.22	3.31	**2.57**	**2.24**	**2.05**	**1.85**	**1.74**	**1.66**	**1.61**	**1.57**	**1.54**	**1.53**	**1.51**	**1.49**	**1.47**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**
5	6.71	3.48	*2.68*	**2.32**	**2.12**	**1.90**	**1.79**	**1.70**	**1.65**	**1.61**	**1.59**	**1.57**	**1.55**	**1.53**	**1.51**	**1.50**	**1.49**	**1.48**	**1.46**	**1.46**
8	7.88	3.87	2.91	**2.50**	**2.27**	**2.03**	**1.90**	**1.80**	**1.74**	**1.70**	**1.67**	**1.65**	**1.63**	**1.61**	**1.59**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**
12	9.03	4.23	3.13	*2.66*	**2.40**	**2.13**	**1.99**	**1.89**	**1.82**	**1.78**	**1.74**	**1.72**	**1.70**	**1.67**	**1.65**	**1.64**	**1.63**	**1.62**	**1.60**	**1.59**
16	9.96	4.50	3.29	*2.78*	**2.50**	**2.21**	**2.06**	**1.95**	**1.88**	**1.83**	**1.80**	**1.77**	**1.75**	**1.72**	**1.70**	**1.68**	**1.67**	**1.66**	**1.64**	**1.63**
20	10.74	4.72	3.41	2.87	**2.58**	**2.27**	**2.11**	**1.99**	**1.92**	**1.87**	**1.84**	**1.81**	**1.79**	**1.76**	**1.73**	**1.72**	**1.70**	**1.69**	**1.68**	**1.67**
30	12.30	5.15	3.65	3.04	*2.71*	**2.38**	**2.20**	**2.08**	**2.00**	**1.95**	**1.91**	**1.88**	**1.85**	**1.82**	**1.80**	**1.78**	**1.77**	**1.75**	**1.74**	**1.72**
40	13.52	5.47	3.83	3.16	*2.82*	**2.46**	**2.27**	**2.14**	**2.05**	**2.00**	**1.96**	**1.92**	**1.90**	**1.87**	**1.84**	**1.82**	**1.81**	**1.80**	**1.78**	**1.76**
50	14.61	5.74	3.96	3.27	2.90	**2.51**	**2.32**	**2.18**	**2.09**	**2.04**	**1.99**	**1.96**	**1.94**	**1.90**	**1.88**	**1.86**	**1.84**	**1.83**	**1.81**	**1.79**
60	15.47	5.96	4.08	3.35	2.96	**2.56**	**2.36**	**2.22**	**2.13**	**2.07**	**2.03**	**1.99**	**1.97**	**1.93**	**1.90**	**1.88**	**1.87**	**1.86**	**1.83**	**1.82**
75	16.72	6.25	4.24	3.46	3.05	*2.63*	**2.42**	**2.27**	**2.17**	**2.11**	**2.06**	**2.03**	**2.00**	**1.96**	**1.93**	**1.91**	**1.90**	**1.88**	**1.87**	**1.85**
100	18.44	6.64	4.43	3.59	3.14	*2.71*	**2.48**	**2.32**	**2.23**	**2.16**	**2.11**	**2.08**	**2.05**	**2.01**	**1.98**	**1.95**	**1.94**	**1.92**	**1.90**	**1.89**
125	19.69	6.95	4.59	3.69	3.24	*2.77*	**2.54**	**2.37**	**2.27**	**2.20**	**2.15**	**2.11**	**2.08**	**2.04**	**2.01**	**1.99**	**1.97**	**1.96**	**1.93**	**1.92**
150	21.25	7.19	4.73	3.79	3.30	*2.81*	*2.58*	**2.40**	**2.30**	**2.23**	**2.18**	**2.14**	**2.11**	**2.07**	**2.04**	**2.01**	**1.99**	**1.98**	**1.96**	**1.94**
175	22.19	7.42	4.84	3.87	3.36	*2.87*	*2.62*	**2.44**	**2.32**	**2.26**	**2.21**	**2.17**	**2.14**	**2.09**	**2.06**	**2.03**	**2.02**	**2.00**	**1.98**	**1.96**
200	23.12	7.66	4.92	3.95	3.42	*2.91*	*2.65*	**2.46**	**2.35**	**2.29**	**2.23**	**2.19**	**2.16**	**2.11**	**2.08**	**2.05**	**2.03**	**2.02**	**1.99**	**1.98**

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Table 19-15. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Means of Order 2 (40 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	4.71	**2.78**	**2.23**	**1.98**	**1.83**	**1.66**	**1.57**	**1.51**	**1.46**	**1.43**	**1.41**	**1.40**	**1.38**	**1.36**	**1.35**	**1.34**	**1.33**	**1.32**	**1.31**	**1.31**
2	5.98	3.27	**2.55**	**2.23**	**2.04**	**1.84**	**1.74**	**1.66**	**1.61**	**1.57**	**1.54**	**1.52**	**1.51**	**1.49**	**1.47**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**
3	6.87	3.59	**2.75**	**2.38**	**2.17**	**1.95**	**1.83**	**1.74**	**1.69**	**1.65**	**1.62**	**1.60**	**1.58**	**1.56**	**1.54**	**1.53**	**1.52**	**1.51**	**1.49**	**1.48**
4	7.58	3.82	*2.90*	**2.49**	**2.27**	**2.03**	**1.90**	**1.80**	**1.74**	**1.70**	**1.67**	**1.65**	**1.63**	**1.60**	**1.59**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**
5	8.17	4.02	3.01	**2.58**	**2.34**	**2.08**	**1.95**	**1.85**	**1.79**	**1.74**	**1.71**	**1.69**	**1.67**	**1.64**	**1.62**	**1.61**	**1.60**	**1.59**	**1.57**	**1.56**
8	9.58	4.45	3.27	**2.77**	**2.50**	**2.21**	**2.06**	**1.95**	**1.88**	**1.83**	**1.80**	**1.77**	**1.75**	**1.72**	**1.70**	**1.68**	**1.67**	**1.66**	**1.64**	**1.63**
12	10.98	4.85	3.50	*2.94*	**2.63**	**2.32**	**2.15**	**2.03**	**1.96**	**1.90**	**1.87**	**1.84**	**1.82**	**1.78**	**1.76**	**1.74**	**1.73**	**1.72**	**1.70**	**1.69**
16	12.11	5.16	3.67	*3.06*	**2.73**	**2.39**	**2.22**	**2.09**	**2.01**	**1.96**	**1.92**	**1.89**	**1.86**	**1.83**	**1.81**	**1.79**	**1.77**	**1.76**	**1.74**	**1.73**
20	13.05	5.41	3.81	3.16	**2.81**	**2.45**	**2.27**	**2.14**	**2.05**	**2.00**	**1.96**	**1.93**	**1.90**	**1.87**	**1.84**	**1.82**	**1.81**	**1.80**	**1.78**	**1.76**
30	14.92	5.90	4.07	3.34	*2.96*	**2.56**	**2.36**	**2.22**	**2.13**	**2.07**	**2.02**	**1.99**	**1.97**	**1.93**	**1.90**	**1.88**	**1.87**	**1.85**	**1.83**	**1.82**
40	16.48	6.25	4.26	3.48	*3.07*	**2.64**	**2.43**	**2.28**	**2.18**	**2.12**	**2.07**	**2.04**	**2.01**	**1.97**	**1.94**	**1.92**	**1.91**	**1.89**	**1.87**	**1.86**
50	17.73	6.56	4.41	3.58	3.14	**2.71**	**2.48**	**2.32**	**2.23**	**2.16**	**2.11**	**2.08**	**2.05**	**2.00**	**1.98**	**1.96**	**1.94**	**1.93**	**1.90**	**1.89**
60	18.91	6.80	4.55	3.67	3.21	**2.75**	**2.52**	**2.36**	**2.26**	**2.19**	**2.14**	**2.10**	**2.08**	**2.03**	**2.00**	**1.98**	**1.97**	**1.95**	**1.93**	**1.91**
75	20.31	7.11	4.71	3.78	3.30	*2.82*	**2.58**	**2.41**	**2.30**	**2.23**	**2.18**	**2.14**	**2.11**	**2.07**	**2.04**	**2.01**	**2.00**	**1.98**	**1.96**	**1.94**
100	22.34	7.58	4.92	3.93	3.42	*2.90*	**2.65**	**2.47**	**2.36**	**2.28**	**2.23**	**2.19**	**2.15**	**2.11**	**2.08**	**2.05**	**2.04**	**2.02**	**2.00**	**1.98**
125	24.06	7.89	5.08	4.04	3.50	*2.97*	**2.70**	**2.51**	**2.39**	**2.32**	**2.27**	**2.22**	**2.19**	**2.14**	**2.11**	**2.08**	**2.07**	**2.05**	**2.03**	**2.01**
150	25.62	8.20	5.23	4.14	3.57	*3.02*	**2.74**	**2.55**	**2.43**	**2.35**	**2.29**	**2.25**	**2.22**	**2.17**	**2.14**	**2.11**	**2.09**	**2.08**	**2.05**	**2.03**
175	26.88	8.44	5.39	4.22	3.63	*3.07*	**2.77**	**2.58**	**2.46**	**2.38**	**2.32**	**2.28**	**2.25**	**2.19**	**2.16**	**2.13**	**2.11**	**2.10**	**2.07**	**2.05**
200	28.12	8.75	5.47	4.30	3.69	*3.11*	**2.81**	**2.61**	**2.48**	**2.40**	**2.34**	**2.29**	**2.27**	**2.21**	**2.18**	**2.15**	**2.13**	**2.11**	**2.09**	**2.07**

Table 19-15. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Means of Order 2 (40 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	5.64	3.20	**2.53**	**2.22**	**2.04**	**1.84**	**1.73**	**1.65**	**1.60**	**1.57**	**1.54**	**1.52**	**1.51**	**1.49**	**1.47**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**
2	7.15	3.75	**2.87**	**2.48**	**2.26**	**2.02**	**1.90**	**1.80**	**1.74**	**1.70**	**1.67**	**1.65**	**1.63**	**1.60**	**1.59**	**1.57**	**1.56**	**1.55**	**1.54**	**1.53**
3	8.21	4.10	*3.08*	**2.64**	**2.39**	**2.13**	**1.99**	**1.89**	**1.82**	**1.78**	**1.74**	**1.72**	**1.70**	**1.67**	**1.65**	**1.64**	**1.63**	**1.62**	**1.60**	**1.59**
4	9.05	4.37	3.24	**2.76**	**2.49**	**2.21**	**2.06**	**1.95**	**1.88**	**1.83**	**1.80**	**1.77**	**1.75**	**1.72**	**1.70**	**1.68**	**1.67**	**1.66**	**1.64**	**1.63**
5	9.76	4.58	3.37	**2.85**	**2.57**	**2.26**	**2.11**	**1.99**	**1.92**	**1.87**	**1.84**	**1.81**	**1.79**	**1.76**	**1.73**	**1.72**	**1.70**	**1.69**	**1.68**	**1.67**
8	11.43	5.07	3.65	**3.05**	**2.73**	**2.39**	**2.22**	**2.09**	**2.01**	**1.96**	**1.92**	**1.89**	**1.86**	**1.83**	**1.81**	**1.79**	**1.77**	**1.76**	**1.74**	**1.73**
12	13.11	5.52	3.90	*3.23*	**2.87**	**2.50**	**2.31**	**2.17**	**2.09**	**2.03**	**1.99**	**1.95**	**1.93**	**1.89**	**1.87**	**1.85**	**1.83**	**1.82**	**1.80**	**1.79**
16	14.41	5.87	4.08	3.36	**2.98**	**2.58**	**2.38**	**2.23**	**2.14**	**2.08**	**2.04**	**2.00**	**1.98**	**1.94**	**1.91**	**1.89**	**1.88**	**1.86**	**1.84**	**1.83**
20	15.55	6.15	4.23	3.46	**3.06**	**2.64**	**2.43**	**2.28**	**2.18**	**2.12**	**2.07**	**2.04**	**2.01**	**1.97**	**1.94**	**1.92**	**1.91**	**1.89**	**1.87**	**1.86**
30	17.81	6.69	4.51	3.66	*3.21*	**2.75**	**2.52**	**2.36**	**2.26**	**2.19**	**2.14**	**2.10**	**2.08**	**2.03**	**2.00**	**1.98**	**1.96**	**1.95**	**1.93**	**1.91**
40	19.61	7.11	4.73	3.80	*3.32*	**2.84**	**2.59**	**2.42**	**2.31**	**2.24**	**2.19**	**2.15**	**2.12**	**2.08**	**2.05**	**2.02**	**2.00**	**1.99**	**1.97**	**1.95**
50	21.09	7.42	4.88	3.92	3.41	**2.90**	**2.65**	**2.47**	**2.36**	**2.28**	**2.23**	**2.19**	**2.16**	**2.11**	**2.08**	**2.05**	**2.04**	**2.02**	**1.99**	**1.98**
60	22.50	7.73	5.03	4.00	3.48	**2.95**	**2.69**	**2.50**	**2.39**	**2.31**	**2.26**	**2.22**	**2.18**	**2.14**	**2.10**	**2.08**	**2.06**	**2.05**	**2.02**	**2.00**
75	24.22	8.09	5.21	4.12	3.56	**3.02**	**2.74**	**2.55**	**2.43**	**2.35**	**2.29**	**2.25**	**2.22**	**2.17**	**2.13**	**2.11**	**2.09**	**2.08**	**2.05**	**2.03**
100	26.56	8.59	5.43	4.28	3.69	*3.10*	**2.81**	**2.61**	**2.49**	**2.40**	**2.34**	**2.29**	**2.26**	**2.21**	**2.18**	**2.15**	**2.13**	**2.11**	**2.08**	**2.07**
125	28.75	8.98	5.62	4.39	3.77	*3.16*	**2.86**	**2.66**	**2.53**	**2.44**	**2.38**	**2.33**	**2.29**	**2.25**	**2.21**	**2.18**	**2.16**	**2.14**	**2.11**	**2.09**
150	30.62	9.30	5.78	4.49	3.87	*3.22*	**2.91**	**2.70**	**2.56**	**2.47**	**2.41**	**2.36**	**2.32**	**2.27**	**2.23**	**2.21**	**2.18**	**2.17**	**2.14**	**2.12**
175	31.88	9.61	5.94	4.59	3.93	*3.26*	**2.95**	**2.72**	**2.59**	**2.50**	**2.43**	**2.38**	**2.34**	**2.29**	**2.26**	**2.23**	**2.21**	**2.19**	**2.16**	**2.14**
200	33.75	9.84	6.02	4.69	3.98	*3.30*	**2.99**	**2.75**	**2.62**	**2.52**	**2.46**	**2.40**	**2.36**	**2.31**	**2.28**	**2.25**	**2.22**	**2.21**	**2.18**	**2.15**

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Table 19-16. κ-Multipliers for 1-of-3 Intrawell Prediction Limits on Means of Order 2 (1 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**0.37**	**0.27**	**0.22**	**0.19**	**0.17**	**0.14**	**0.13**	**0.11**	**0.11**	**0.10**	**0.10**	**0.09**	**0.09**	**0.08**	**0.08**	**0.08**	**0.08**	**0.08**	**0.07**	**0.07**
2	**0.71**	**0.53**	**0.45**	**0.41**	**0.38**	**0.34**	**0.32**	**0.30**	**0.29**	**0.28**	**0.28**	**0.27**	**0.27**	**0.26**	**0.26**	**0.25**	**0.25**	**0.25**	**0.25**	**0.24**
3	**0.92**	**0.68**	**0.58**	**0.53**	**0.49**	**0.45**	**0.42**	**0.40**	**0.39**	**0.38**	**0.37**	**0.37**	**0.36**	**0.35**	**0.35**	**0.35**	**0.34**	**0.34**	**0.34**	**0.33**
4	**1.07**	**0.79**	**0.67**	**0.61**	**0.57**	**0.52**	**0.49**	**0.47**	**0.45**	**0.44**	**0.44**	**0.43**	**0.42**	**0.42**	**0.41**	**0.41**	**0.40**	**0.40**	**0.40**	**0.39**
5	**1.20**	**0.87**	**0.74**	**0.67**	**0.63**	**0.58**	**0.54**	**0.52**	**0.50**	**0.49**	**0.48**	**0.48**	**0.47**	**0.46**	**0.46**	**0.45**	**0.45**	**0.45**	**0.44**	**0.44**
8	**1.49**	**1.05**	**0.89**	**0.81**	**0.75**	**0.69**	**0.65**	**0.62**	**0.60**	**0.59**	**0.58**	**0.57**	**0.57**	**0.56**	**0.55**	**0.54**	**0.54**	**0.54**	**0.53**	**0.53**
12	**1.77**	**1.22**	**1.02**	**0.92**	**0.86**	**0.78**	**0.74**	**0.71**	**0.69**	**0.67**	**0.66**	**0.65**	**0.64**	**0.63**	**0.62**	**0.62**	**0.61**	**0.61**	**0.61**	**0.60**
16	**1.98**	**1.34**	**1.11**	**1.00**	**0.93**	**0.85**	**0.80**	**0.77**	**0.74**	**0.73**	**0.71**	**0.70**	**0.70**	**0.68**	**0.68**	**0.67**	**0.67**	**0.66**	**0.65**	**0.65**
20	**2.17**	**1.43**	**1.19**	**1.06**	**0.99**	**0.90**	**0.85**	**0.81**	**0.78**	**0.77**	**0.75**	**0.74**	**0.74**	**0.72**	**0.72**	**0.71**	**0.70**	**0.70**	**0.69**	**0.69**
30	**2.52**	**1.61**	**1.32**	**1.18**	**1.09**	**0.99**	**0.93**	**0.89**	**0.86**	**0.84**	**0.83**	**0.81**	**0.81**	**0.79**	**0.78**	**0.78**	**0.77**	**0.77**	**0.76**	**0.75**
40	2.81	**1.74**	**1.42**	**1.26**	**1.16**	**1.05**	**0.99**	**0.94**	**0.91**	**0.89**	**0.88**	**0.86**	**0.85**	**0.84**	**0.83**	**0.82**	**0.82**	**0.81**	**0.80**	**0.80**
50	3.04	**1.85**	**1.49**	**1.32**	**1.22**	**1.10**	**1.04**	**0.99**	**0.95**	**0.93**	**0.91**	**0.90**	**0.89**	**0.88**	**0.87**	**0.86**	**0.85**	**0.85**	**0.84**	**0.83**
60	3.25	**1.94**	**1.56**	**1.37**	**1.26**	**1.14**	**1.07**	**1.02**	**0.99**	**0.96**	**0.94**	**0.93**	**0.92**	**0.91**	**0.89**	**0.89**	**0.88**	**0.87**	**0.86**	**0.86**
75	3.52	**2.06**	**1.63**	**1.44**	**1.32**	**1.19**	**1.12**	**1.06**	**1.02**	**1.00**	**0.98**	**0.97**	**0.96**	**0.94**	**0.93**	**0.92**	**0.91**	**0.91**	**0.90**	**0.89**
100	3.89	**2.21**	**1.74**	**1.52**	**1.39**	**1.25**	**1.17**	**1.11**	**1.07**	**1.05**	**1.03**	**1.01**	**1.00**	**0.98**	**0.97**	**0.96**	**0.96**	**0.95**	**0.94**	**0.93**
125	4.21	**2.33**	**1.82**	**1.58**	**1.45**	**1.30**	**1.21**	**1.15**	**1.11**	**1.08**	**1.06**	**1.05**	**1.04**	**1.02**	**1.00**	**0.99**	**0.99**	**0.98**	**0.97**	**0.96**
150	4.49	**2.43**	**1.89**	**1.64**	**1.49**	**1.34**	**1.25**	**1.18**	**1.14**	**1.11**	**1.09**	**1.08**	**1.06**	**1.04**	**1.03**	**1.02**	**1.01**	**1.01**	**1.00**	**0.99**
175	4.73	*2.52*	**1.94**	**1.68**	**1.53**	**1.37**	**1.28**	**1.21**	**1.17**	**1.14**	**1.12**	**1.10**	**1.09**	**1.07**	**1.05**	**1.04**	**1.04**	**1.03**	**1.02**	**1.01**
200	4.96	*2.61*	**2.00**	**1.72**	**1.57**	**1.40**	**1.30**	**1.24**	**1.19**	**1.16**	**1.14**	**1.12**	**1.11**	**1.09**	**1.07**	**1.06**	**1.05**	**1.05**	**1.04**	**1.03**

Table 19-16. κ-Multipliers for 1-of-3 Intrawell Prediction Limits on Means of Order 2 (1 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**0.64**	**0.50**	**0.43**	**0.39**	**0.36**	**0.33**	**0.31**	**0.30**	**0.29**	**0.28**	**0.27**	**0.27**	**0.26**	**0.26**	**0.25**	**0.25**	**0.25**	**0.25**	**0.24**	**0.24**
2	**1.00**	**0.76**	**0.66**	**0.60**	**0.56**	**0.51**	**0.49**	**0.47**	**0.45**	**0.44**	**0.43**	**0.43**	**0.42**	**0.41**	**0.41**	**0.41**	**0.40**	**0.40**	**0.40**	**0.39**
3	**1.23**	**0.91**	**0.79**	**0.72**	**0.67**	**0.62**	**0.58**	**0.56**	**0.54**	**0.53**	**0.52**	**0.51**	**0.51**	**0.50**	**0.49**	**0.49**	**0.48**	**0.48**	**0.48**	**0.47**
4	**1.41**	**1.03**	**0.88**	**0.80**	**0.75**	**0.68**	**0.65**	**0.62**	**0.60**	**0.59**	**0.58**	**0.57**	**0.56**	**0.56**	**0.55**	**0.54**	**0.54**	**0.54**	**0.53**	**0.53**
5	**1.56**	**1.11**	**0.95**	**0.86**	**0.80**	**0.74**	**0.70**	**0.67**	**0.65**	**0.63**	**0.62**	**0.61**	**0.61**	**0.60**	**0.59**	**0.59**	**0.58**	**0.58**	**0.57**	**0.57**
8	**1.89**	**1.31**	**1.10**	**0.99**	**0.92**	**0.85**	**0.80**	**0.76**	**0.74**	**0.72**	**0.71**	**0.70**	**0.70**	**0.68**	**0.68**	**0.67**	**0.67**	**0.66**	**0.65**	**0.65**
12	**2.22**	**1.48**	**1.23**	**1.11**	**1.03**	**0.94**	**0.88**	**0.84**	**0.82**	**0.80**	**0.79**	**0.78**	**0.77**	**0.75**	**0.75**	**0.74**	**0.73**	**0.73**	**0.72**	**0.72**
16	**2.48**	**1.61**	**1.33**	**1.19**	**1.10**	**1.00**	**0.94**	**0.90**	**0.87**	**0.85**	**0.84**	**0.83**	**0.82**	**0.80**	**0.79**	**0.79**	**0.78**	**0.78**	**0.77**	**0.76**
20	2.69	**1.72**	**1.40**	**1.25**	**1.16**	**1.05**	**0.99**	**0.94**	**0.91**	**0.89**	**0.88**	**0.86**	**0.85**	**0.84**	**0.83**	**0.82**	**0.82**	**0.81**	**0.80**	**0.80**
30	3.12	**1.91**	**1.54**	**1.36**	**1.26**	**1.14**	**1.07**	**1.02**	**0.99**	**0.96**	**0.94**	**0.93**	**0.92**	**0.90**	**0.89**	**0.89**	**0.88**	**0.87**	**0.86**	**0.86**
40	3.46	**2.06**	**1.65**	**1.45**	**1.33**	**1.20**	**1.13**	**1.07**	**1.04**	**1.01**	**0.99**	**0.98**	**0.97**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.90**
50	3.75	**2.18**	**1.73**	**1.51**	**1.39**	**1.25**	**1.17**	**1.11**	**1.07**	**1.05**	**1.03**	**1.01**	**1.00**	**0.98**	**0.97**	**0.96**	**0.96**	**0.95**	**0.94**	**0.93**
60	3.99	**2.28**	**1.79**	**1.57**	**1.43**	**1.29**	**1.21**	**1.14**	**1.10**	**1.08**	**1.06**	**1.04**	**1.03**	**1.01**	**1.00**	**0.99**	**0.98**	**0.98**	**0.96**	**0.96**
75	4.32	**2.40**	**1.88**	**1.63**	**1.49**	**1.33**	**1.25**	**1.18**	**1.14**	**1.11**	**1.09**	**1.08**	**1.06**	**1.04**	**1.03**	**1.02**	**1.01**	**1.01**	**1.00**	**0.99**
100	4.77	**2.57**	**1.99**	**1.72**	**1.56**	**1.40**	**1.30**	**1.24**	**1.19**	**1.16**	**1.14**	**1.12**	**1.11**	**1.09**	**1.07**	**1.06**	**1.05**	**1.05**	**1.04**	**1.03**
125	5.16	*2.71*	**2.08**	**1.79**	**1.62**	**1.44**	**1.35**	**1.27**	**1.23**	**1.20**	**1.17**	**1.15**	**1.14**	**1.12**	**1.10**	**1.09**	**1.08**	**1.08**	**1.07**	**1.06**
150	5.47	2.82	**2.15**	**1.84**	**1.67**	**1.48**	**1.38**	**1.31**	**1.26**	**1.23**	**1.20**	**1.18**	**1.17**	**1.15**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.08**
175	5.78	2.93	**2.21**	**1.89**	**1.71**	**1.52**	**1.41**	**1.33**	**1.28**	**1.25**	**1.22**	**1.20**	**1.19**	**1.17**	**1.15**	**1.14**	**1.13**	**1.12**	**1.11**	**1.10**
200	6.05	3.02	**2.27**	**1.93**	**1.75**	**1.54**	**1.44**	**1.36**	**1.30**	**1.27**	**1.25**	**1.22**	**1.21**	**1.19**	**1.17**	**1.16**	**1.15**	**1.14**	**1.13**	**1.12**

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Table 19-16. κ-Multipliers for 1-of-3 Intrawell Prediction Limits on Means of Order 2 (1 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	0.90	0.71	0.62	0.57	0.54	0.50	0.48	0.46	0.45	0.44	0.43	0.42	0.42	0.41	0.41	0.40	0.40	0.40	0.39	0.39
2	1.30	0.98	0.85	0.78	0.73	0.68	0.64	0.62	0.60	0.59	0.58	0.57	0.56	0.55	0.55	0.54	0.54	0.54	0.53	0.53
3	1.56	1.14	0.98	0.89	0.84	0.77	0.73	0.70	0.68	0.67	0.66	0.65	0.64	0.63	0.62	0.62	0.61	0.61	0.60	0.60
4	1.76	1.26	1.08	0.98	0.91	0.84	0.79	0.76	0.74	0.72	0.71	0.70	0.69	0.68	0.67	0.67	0.66	0.66	0.65	0.65
5	1.93	1.36	1.15	1.04	0.97	0.89	0.84	0.81	0.78	0.76	0.75	0.74	0.73	0.72	0.71	0.71	0.70	0.70	0.69	0.69
8	2.32	1.57	1.31	1.17	1.09	0.99	0.94	0.90	0.87	0.85	0.84	0.82	0.82	0.80	0.79	0.79	0.78	0.78	0.77	0.76
12	2.71	1.76	1.44	1.29	1.19	1.08	1.02	0.97	0.94	0.92	0.91	0.89	0.88	0.87	0.86	0.85	0.84	0.84	0.83	0.83
16	3.01	1.90	1.54	1.37	1.27	1.15	1.08	1.03	1.00	0.97	0.95	0.94	0.93	0.91	0.90	0.90	0.89	0.88	0.87	0.87
20	3.26	2.01	1.62	1.44	1.32	1.20	1.12	1.07	1.03	1.01	0.99	0.98	0.97	0.95	0.94	0.93	0.92	0.92	0.91	0.90
30	3.76	2.23	1.77	1.56	1.43	1.28	1.20	1.14	1.10	1.08	1.06	1.04	1.03	1.01	1.00	0.99	0.98	0.98	0.96	0.96
40	4.17	2.39	1.88	1.64	1.50	1.35	1.26	1.19	1.15	1.12	1.10	1.09	1.07	1.05	1.04	1.03	1.02	1.02	1.01	1.00
50	4.50	2.52	1.97	1.71	1.56	1.39	1.30	1.23	1.19	1.16	1.14	1.12	1.11	1.09	1.07	1.06	1.05	1.05	1.04	1.03
60	4.79	2.63	2.04	1.76	1.61	1.43	1.34	1.27	1.22	1.19	1.17	1.15	1.13	1.11	1.10	1.09	1.08	1.07	1.06	1.05
75	5.18	2.77	2.13	1.83	1.67	1.48	1.38	1.30	1.26	1.22	1.20	1.18	1.17	1.15	1.13	1.12	1.11	1.10	1.09	1.08
100	5.72	2.96	2.25	1.92	1.74	1.54	1.44	1.35	1.30	1.27	1.24	1.22	1.21	1.19	1.17	1.16	1.15	1.14	1.13	1.12
125	6.17	3.12	2.34	1.99	1.80	1.59	1.48	1.39	1.34	1.30	1.28	1.26	1.24	1.22	1.20	1.19	1.18	1.17	1.16	1.15
150	6.56	3.24	2.42	2.06	1.85	1.63	1.51	1.43	1.37	1.33	1.30	1.28	1.27	1.24	1.22	1.21	1.20	1.19	1.18	1.17
175	6.91	3.36	2.49	2.10	1.89	1.66	1.54	1.45	1.39	1.35	1.33	1.31	1.29	1.26	1.25	1.23	1.22	1.21	1.20	1.19
200	7.23	3.46	2.54	2.15	1.93	1.69	1.57	1.47	1.42	1.38	1.35	1.32	1.31	1.28	1.26	1.25	1.24	1.23	1.22	1.21

Table 19-16. κ-Multipliers for 1-of-3 Intrawell Prediction Limits on Means of Order 2 (2 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	0.71	0.53	0.45	0.41	0.38	0.34	0.32	0.30	0.29	0.28	0.28	0.27	0.27	0.26	0.26	0.25	0.25	0.25	0.25	0.24
2	1.07	0.79	0.67	0.61	0.57	0.52	0.49	0.47	0.45	0.44	0.44	0.43	0.42	0.42	0.41	0.41	0.40	0.40	0.40	0.39
3	1.31	0.94	0.80	0.73	0.68	0.62	0.59	0.56	0.54	0.53	0.52	0.51	0.51	0.50	0.49	0.49	0.49	0.48	0.48	0.47
4	1.49	1.05	0.89	0.81	0.75	0.69	0.65	0.62	0.60	0.59	0.58	0.57	0.57	0.56	0.55	0.54	0.54	0.54	0.53	0.53
5	1.64	1.14	0.96	0.87	0.81	0.74	0.70	0.67	0.65	0.63	0.62	0.62	0.61	0.60	0.59	0.59	0.58	0.58	0.57	0.57
8	1.98	1.34	1.11	1.00	0.93	0.85	0.80	0.77	0.74	0.73	0.71	0.70	0.70	0.68	0.68	0.67	0.67	0.66	0.65	0.65
12	2.32	1.51	1.25	1.11	1.03	0.94	0.89	0.85	0.82	0.80	0.79	0.78	0.77	0.76	0.75	0.74	0.73	0.73	0.72	0.72
16	2.59	1.64	1.34	1.19	1.10	1.00	0.95	0.90	0.87	0.85	0.84	0.83	0.82	0.80	0.79	0.79	0.78	0.78	0.77	0.76
20	2.81	1.74	1.42	1.26	1.16	1.05	0.99	0.94	0.91	0.89	0.88	0.86	0.85	0.84	0.83	0.82	0.82	0.81	0.80	0.80
30	3.25	1.94	1.56	1.37	1.26	1.14	1.07	1.02	0.99	0.96	0.94	0.93	0.92	0.91	0.89	0.89	0.88	0.87	0.86	0.86
40	3.60	2.09	1.66	1.45	1.34	1.20	1.13	1.07	1.04	1.01	0.99	0.98	0.97	0.95	0.94	0.93	0.92	0.92	0.91	0.90
50	3.89	2.21	1.74	1.52	1.39	1.25	1.17	1.11	1.07	1.05	1.03	1.01	1.00	0.98	0.97	0.96	0.96	0.95	0.94	0.93
60	4.15	2.30	1.80	1.57	1.44	1.29	1.21	1.15	1.11	1.08	1.06	1.04	1.03	1.01	1.00	0.99	0.98	0.98	0.97	0.96
75	4.49	2.43	1.89	1.64	1.49	1.34	1.25	1.18	1.14	1.11	1.09	1.08	1.06	1.04	1.03	1.02	1.01	1.01	1.00	0.99
100	4.96	*2.61*	2.00	1.72	1.57	1.40	1.30	1.24	1.19	1.16	1.14	1.12	1.11	1.09	1.07	1.06	1.05	1.05	1.04	1.03
125	5.35	2.74	2.09	1.79	1.63	1.45	1.35	1.27	1.23	1.20	1.17	1.15	1.14	1.12	1.10	1.09	1.08	1.08	1.06	1.06
150	5.70	2.85	2.16	1.85	1.67	1.48	1.38	1.31	1.26	1.23	1.20	1.18	1.17	1.15	1.13	1.12	1.11	1.10	1.09	1.08
175	6.02	2.97	2.23	1.89	1.72	1.52	1.41	1.33	1.28	1.25	1.23	1.21	1.19	1.17	1.15	1.14	1.13	1.12	1.11	1.10
200	6.25	3.05	2.28	1.93	1.75	1.54	1.44	1.36	1.30	1.27	1.25	1.23	1.21	1.19	1.17	1.16	1.15	1.14	1.13	1.12

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Table 19-16. κ-Multipliers for 1-of-3 Intrawell Prediction Limits on Means of Order 2 (2 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	1.00	0.76	0.66	0.60	0.56	0.51	0.49	0.47	0.45	0.44	0.43	0.43	0.42	0.41	0.41	0.41	0.40	0.40	0.40	0.39
2	1.41	1.03	0.88	0.80	0.75	0.68	0.65	0.62	0.60	0.59	0.58	0.57	0.56	0.56	0.55	0.54	0.54	0.54	0.53	0.53
3	1.68	1.19	1.01	0.91	0.85	0.78	0.74	0.71	0.68	0.67	0.66	0.65	0.64	0.63	0.62	0.62	0.61	0.61	0.60	0.60
4	1.89	1.31	1.10	0.99	0.92	0.85	0.80	0.76	0.74	0.72	0.71	0.70	0.70	0.68	0.68	0.67	0.67	0.66	0.65	0.65
5	2.07	1.40	1.17	1.05	0.98	0.90	0.85	0.81	0.78	0.77	0.75	0.74	0.74	0.72	0.71	0.71	0.70	0.70	0.69	0.69
8	2.48	1.61	1.33	1.19	1.10	1.00	0.94	0.90	0.87	0.85	0.84	0.83	0.82	0.80	0.79	0.79	0.78	0.78	0.77	0.76
12	2.88	1.80	1.47	1.30	1.20	1.09	1.03	0.98	0.95	0.92	0.91	0.89	0.88	0.87	0.86	0.85	0.84	0.84	0.83	0.83
16	3.20	1.94	1.57	1.38	1.27	1.15	1.08	1.03	1.00	0.97	0.96	0.94	0.93	0.91	0.90	0.90	0.89	0.88	0.87	0.87
20	3.46	2.06	1.65	1.45	1.33	1.20	1.13	1.07	1.04	1.01	0.99	0.98	0.97	0.95	0.94	0.93	0.92	0.92	0.91	0.90
30	3.99	2.28	1.79	1.57	1.43	1.29	1.21	1.14	1.10	1.08	1.06	1.04	1.03	1.01	1.00	0.99	0.98	0.98	0.96	0.96
40	4.41	2.44	1.90	1.65	1.51	1.35	1.26	1.20	1.15	1.12	1.10	1.09	1.07	1.05	1.04	1.03	1.02	1.02	1.01	1.00
50	4.77	2.57	1.99	1.72	1.56	1.40	1.30	1.24	1.19	1.16	1.14	1.12	1.11	1.09	1.07	1.06	1.05	1.05	1.04	1.03
60	5.08	*2.69*	2.06	1.77	1.61	1.44	1.34	1.27	1.22	1.19	1.17	1.15	1.13	1.11	1.10	1.09	1.08	1.07	1.06	1.05
75	5.47	2.82	2.15	1.84	1.67	1.48	1.38	1.31	1.26	1.23	1.20	1.18	1.17	1.15	1.13	1.12	1.11	1.10	1.09	1.08
100	6.05	3.02	2.27	1.93	1.75	1.54	1.44	1.36	1.30	1.27	1.25	1.22	1.21	1.19	1.17	1.16	1.15	1.14	1.13	1.12
125	6.52	3.16	2.36	2.00	1.81	1.59	1.48	1.40	1.34	1.30	1.28	1.26	1.24	1.22	1.20	1.19	1.18	1.17	1.16	1.15
150	6.95	3.30	2.44	2.06	1.86	1.63	1.51	1.43	1.37	1.33	1.30	1.28	1.26	1.24	1.23	1.21	1.20	1.19	1.18	1.17
175	7.34	3.42	2.50	2.11	1.89	1.67	1.54	1.45	1.40	1.36	1.33	1.30	1.29	1.26	1.25	1.23	1.22	1.21	1.20	1.19
200	7.66	3.52	2.56	2.16	1.93	1.69	1.57	1.47	1.42	1.38	1.35	1.32	1.31	1.28	1.26	1.25	1.24	1.23	1.22	1.21

Table 19-16. κ-Multipliers for 1-of-3 Intrawell Prediction Limits on Means of Order 2 (2 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	1.30	0.98	0.85	0.78	0.73	0.68	0.64	0.62	0.60	0.59	0.58	0.57	0.56	0.55	0.55	0.54	0.54	0.54	0.53	0.53
2	1.76	1.26	1.08	0.98	0.91	0.84	0.79	0.76	0.74	0.72	0.71	0.70	0.69	0.68	0.67	0.67	0.66	0.66	0.65	0.65
3	2.08	1.44	1.21	1.09	1.02	0.93	0.88	0.84	0.82	0.80	0.78	0.77	0.77	0.75	0.74	0.74	0.73	0.73	0.72	0.72
4	2.32	1.57	1.31	1.17	1.09	0.99	0.94	0.90	0.87	0.85	0.84	0.82	0.82	0.80	0.79	0.79	0.78	0.78	0.77	0.76
5	2.53	1.67	1.38	1.24	1.15	1.04	0.99	0.94	0.91	0.89	0.87	0.86	0.85	0.84	0.83	0.82	0.82	0.81	0.80	0.80
8	3.01	1.90	1.54	1.37	1.27	1.15	1.08	1.03	1.00	0.97	0.95	0.94	0.93	0.91	0.90	0.90	0.89	0.88	0.87	0.87
12	3.48	2.11	1.69	1.49	1.37	1.24	1.16	1.10	1.07	1.04	1.02	1.01	0.99	0.98	0.97	0.96	0.95	0.94	0.93	0.93
16	3.85	2.26	1.80	1.57	1.44	1.30	1.22	1.15	1.12	1.09	1.07	1.05	1.04	1.02	1.01	1.00	0.99	0.98	0.97	0.97
20	4.17	2.39	1.88	1.64	1.50	1.35	1.26	1.19	1.15	1.12	1.10	1.09	1.07	1.05	1.04	1.03	1.02	1.02	1.01	1.00
30	4.79	2.63	2.04	1.76	1.61	1.43	1.34	1.27	1.22	1.19	1.17	1.15	1.13	1.11	1.10	1.09	1.08	1.07	1.06	1.05
40	5.29	2.81	2.15	1.85	1.68	1.49	1.39	1.32	1.27	1.23	1.21	1.19	1.18	1.15	1.14	1.13	1.12	1.11	1.10	1.09
50	5.72	2.96	2.25	1.92	1.74	1.54	1.44	1.35	1.30	1.27	1.24	1.22	1.21	1.19	1.17	1.16	1.15	1.14	1.13	1.12
60	6.09	3.09	2.32	1.98	1.79	1.58	1.47	1.39	1.33	1.30	1.27	1.25	1.23	1.21	1.19	1.18	1.17	1.16	1.15	1.14
75	6.56	3.24	2.42	2.06	1.85	1.63	1.51	1.43	1.37	1.33	1.30	1.28	1.27	1.24	1.22	1.21	1.20	1.19	1.18	1.17
100	7.23	3.46	2.54	2.15	1.93	1.69	1.57	1.47	1.42	1.38	1.35	1.32	1.31	1.28	1.26	1.25	1.24	1.23	1.22	1.21
125	7.81	3.63	2.65	2.23	1.99	1.74	1.61	1.51	1.45	1.41	1.38	1.35	1.34	1.31	1.29	1.28	1.27	1.26	1.24	1.23
150	8.28	3.77	2.73	2.29	2.04	1.78	1.65	1.54	1.48	1.44	1.41	1.38	1.36	1.33	1.31	1.30	1.29	1.28	1.26	1.25
175	8.75	3.91	2.80	2.34	2.08	1.82	1.67	1.57	1.50	1.46	1.43	1.40	1.38	1.35	1.33	1.32	1.31	1.30	1.28	1.27
200	9.14	4.02	*2.87*	2.38	2.12	1.85	1.70	1.59	1.52	1.48	1.45	1.42	1.40	1.37	1.35	1.34	1.32	1.31	1.30	1.29

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Table 19-16. κ-Multipliers for 1-of-3 Intrawell Prediction Limits on Means of Order 2 (5 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.20**	**0.87**	**0.74**	**0.67**	**0.63**	**0.58**	**0.54**	**0.52**	**0.50**	**0.49**	**0.48**	**0.48**	**0.47**	**0.46**	**0.46**	**0.45**	**0.45**	**0.45**	**0.44**	**0.44**
2	**1.64**	**1.14**	**0.96**	**0.87**	**0.81**	**0.74**	**0.70**	**0.67**	**0.65**	**0.63**	**0.62**	**0.62**	**0.61**	**0.60**	**0.59**	**0.59**	**0.58**	**0.58**	**0.57**	**0.57**
3	**1.93**	**1.31**	**1.09**	**0.98**	**0.91**	**0.83**	**0.79**	**0.75**	**0.73**	**0.71**	**0.70**	**0.69**	**0.68**	**0.67**	**0.66**	**0.66**	**0.65**	**0.65**	**0.64**	**0.64**
4	**2.16**	**1.43**	**1.19**	**1.06**	**0.99**	**0.90**	**0.85**	**0.81**	**0.78**	**0.77**	**0.75**	**0.74**	**0.74**	**0.72**	**0.71**	**0.71**	**0.70**	**0.70**	**0.69**	**0.69**
5	**2.36**	**1.53**	**1.26**	**1.12**	**1.04**	**0.95**	**0.90**	**0.85**	**0.83**	**0.81**	**0.79**	**0.78**	**0.77**	**0.76**	**0.75**	**0.75**	**0.74**	**0.74**	**0.73**	**0.72**
8	2.81	**1.74**	**1.42**	**1.26**	**1.16**	**1.05**	**0.99**	**0.94**	**0.91**	**0.89**	**0.88**	**0.86**	**0.85**	**0.84**	**0.83**	**0.82**	**0.82**	**0.81**	**0.80**	**0.80**
12	3.25	**1.94**	**1.56**	**1.37**	**1.26**	**1.14**	**1.07**	**1.02**	**0.99**	**0.96**	**0.94**	**0.93**	**0.92**	**0.91**	**0.89**	**0.89**	**0.88**	**0.87**	**0.86**	**0.86**
16	3.60	**2.09**	**1.66**	**1.45**	**1.34**	**1.20**	**1.13**	**1.07**	**1.04**	**1.01**	**0.99**	**0.98**	**0.97**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.90**
20	3.89	**2.21**	**1.74**	**1.52**	**1.39**	**1.25**	**1.17**	**1.11**	**1.07**	**1.05**	**1.03**	**1.01**	**1.00**	**0.98**	**0.97**	**0.96**	**0.96**	**0.95**	**0.94**	**0.93**
30	4.48	**2.43**	**1.89**	**1.64**	**1.49**	**1.34**	**1.25**	**1.18**	**1.14**	**1.11**	**1.09**	**1.08**	**1.06**	**1.04**	**1.03**	**1.02**	**1.01**	**1.01**	**1.00**	**0.99**
40	4.95	*2.60*	**2.00**	**1.72**	**1.57**	**1.40**	**1.30**	**1.24**	**1.19**	**1.16**	**1.14**	**1.12**	**1.11**	**1.09**	**1.07**	**1.06**	**1.05**	**1.05**	**1.04**	**1.03**
50	5.34	2.74	**2.08**	**1.79**	**1.63**	**1.45**	**1.35**	**1.27**	**1.23**	**1.20**	**1.17**	**1.15**	**1.14**	**1.12**	**1.10**	**1.09**	**1.08**	**1.08**	**1.07**	**1.06**
60	5.68	2.86	**2.16**	**1.85**	**1.67**	**1.48**	**1.38**	**1.31**	**1.26**	**1.22**	**1.20**	**1.18**	**1.17**	**1.15**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.08**
75	6.13	3.01	**2.25**	**1.92**	**1.73**	**1.53**	**1.42**	**1.35**	**1.30**	**1.26**	**1.23**	**1.21**	**1.20**	**1.18**	**1.16**	**1.15**	**1.14**	**1.13**	**1.12**	**1.11**
100	6.76	3.21	**2.37**	**2.01**	**1.81**	**1.59**	**1.48**	**1.39**	**1.34**	**1.30**	**1.28**	**1.26**	**1.24**	**1.22**	**1.20**	**1.19**	**1.18**	**1.17**	**1.16**	**1.15**
125	7.30	3.37	*2.47*	**2.08**	**1.87**	**1.64**	**1.52**	**1.43**	**1.38**	**1.34**	**1.31**	**1.29**	**1.27**	**1.25**	**1.23**	**1.22**	**1.21**	**1.20**	**1.18**	**1.17**
150	7.77	3.51	*2.55*	**2.14**	**1.92**	**1.68**	**1.56**	**1.46**	**1.41**	**1.37**	**1.34**	**1.32**	**1.30**	**1.27**	**1.25**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**
175	8.16	3.63	*2.62*	**2.19**	**1.96**	**1.71**	**1.59**	**1.49**	**1.43**	**1.39**	**1.36**	**1.34**	**1.32**	**1.29**	**1.27**	**1.26**	**1.25**	**1.24**	**1.23**	**1.22**
200	8.55	3.73	2.68	**2.24**	**2.00**	**1.74**	**1.61**	**1.51**	**1.45**	**1.41**	**1.38**	**1.35**	**1.34**	**1.31**	**1.29**	**1.28**	**1.27**	**1.26**	**1.24**	**1.23**

Table 19-16. κ-Multipliers for 1-of-3 Intrawell Prediction Limits on Means of Order 2 (5 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.56**	**1.11**	**0.95**	**0.86**	**0.80**	**0.74**	**0.70**	**0.67**	**0.65**	**0.63**	**0.62**	**0.61**	**0.61**	**0.60**	**0.59**	**0.59**	**0.58**	**0.58**	**0.57**	**0.57**
2	**2.07**	**1.40**	**1.17**	**1.05**	**0.98**	**0.90**	**0.85**	**0.81**	**0.78**	**0.77**	**0.75**	**0.74**	**0.74**	**0.72**	**0.71**	**0.71**	**0.70**	**0.70**	**0.69**	**0.69**
3	**2.42**	**1.58**	**1.31**	**1.17**	**1.08**	**0.99**	**0.93**	**0.89**	**0.86**	**0.84**	**0.83**	**0.81**	**0.81**	**0.79**	**0.78**	**0.78**	**0.77**	**0.77**	**0.76**	**0.75**
4	2.69	**1.72**	**1.40**	**1.25**	**1.16**	**1.05**	**0.99**	**0.94**	**0.91**	**0.89**	**0.88**	**0.86**	**0.85**	**0.84**	**0.83**	**0.82**	**0.82**	**0.81**	**0.80**	**0.80**
5	2.92	**1.82**	**1.48**	**1.31**	**1.21**	**1.10**	**1.03**	**0.98**	**0.95**	**0.93**	**0.91**	**0.90**	**0.89**	**0.88**	**0.87**	**0.86**	**0.85**	**0.85**	**0.84**	**0.83**
8	3.46	**2.06**	**1.65**	**1.45**	**1.33**	**1.20**	**1.13**	**1.07**	**1.04**	**1.01**	**0.99**	**0.98**	**0.97**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.90**
12	3.99	**2.28**	**1.79**	**1.57**	**1.43**	**1.29**	**1.21**	**1.14**	**1.11**	**1.08**	**1.06**	**1.04**	**1.03**	**1.01**	**1.00**	**0.99**	**0.98**	**0.98**	**0.97**	**0.96**
16	4.41	**2.44**	**1.90**	**1.65**	**1.51**	**1.35**	**1.26**	**1.20**	**1.15**	**1.12**	**1.10**	**1.09**	**1.07**	**1.05**	**1.04**	**1.03**	**1.02**	**1.02**	**1.01**	**1.00**
20	4.77	**2.57**	**1.99**	**1.72**	**1.57**	**1.40**	**1.30**	**1.24**	**1.19**	**1.16**	**1.14**	**1.12**	**1.11**	**1.09**	**1.07**	**1.06**	**1.05**	**1.05**	**1.04**	**1.03**
30	5.48	2.83	**2.15**	**1.84**	**1.67**	**1.48**	**1.38**	**1.31**	**1.26**	**1.22**	**1.20**	**1.18**	**1.17**	**1.15**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.08**
40	6.04	3.02	**2.27**	**1.93**	**1.75**	**1.54**	**1.44**	**1.36**	**1.30**	**1.27**	**1.24**	**1.22**	**1.21**	**1.19**	**1.17**	**1.16**	**1.15**	**1.14**	**1.13**	**1.12**
50	6.52	3.17	**2.36**	**2.00**	**1.81**	**1.59**	**1.48**	**1.39**	**1.34**	**1.30**	**1.28**	**1.26**	**1.24**	**1.22**	**1.20**	**1.19**	**1.18**	**1.17**	**1.16**	**1.15**
60	6.93	3.30	**2.44**	**2.06**	**1.86**	**1.63**	**1.51**	**1.43**	**1.37**	**1.33**	**1.30**	**1.28**	**1.27**	**1.24**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**
75	7.48	3.47	**2.54**	**2.14**	**1.92**	**1.68**	**1.56**	**1.46**	**1.41**	**1.37**	**1.34**	**1.31**	**1.30**	**1.27**	**1.25**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**
100	8.24	3.69	*2.67*	**2.23**	**1.99**	**1.74**	**1.61**	**1.51**	**1.45**	**1.41**	**1.38**	**1.36**	**1.34**	**1.31**	**1.29**	**1.28**	**1.27**	**1.26**	**1.24**	**1.23**
125	8.91	3.88	*2.77*	**2.31**	**2.06**	**1.79**	**1.65**	**1.55**	**1.49**	**1.44**	**1.41**	**1.39**	**1.37**	**1.34**	**1.32**	**1.31**	**1.29**	**1.29**	**1.27**	**1.26**
150	9.45	4.03	2.86	**2.37**	**2.11**	**1.83**	**1.69**	**1.58**	**1.52**	**1.47**	**1.44**	**1.41**	**1.39**	**1.36**	**1.34**	**1.33**	**1.32**	**1.31**	**1.29**	**1.28**
175	9.96	4.17	2.93	**2.43**	**2.15**	**1.87**	**1.72**	**1.61**	**1.54**	**1.49**	**1.46**	**1.43**	**1.41**	**1.38**	**1.36**	**1.35**	**1.34**	**1.33**	**1.31**	**1.30**
200	10.39	4.30	3.00	**2.47**	**2.19**	**1.89**	**1.74**	**1.63**	**1.56**	**1.51**	**1.48**	**1.45**	**1.43**	**1.40**	**1.38**	**1.36**	**1.35**	**1.34**	**1.33**	**1.31**

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Table 19-16. κ-Multipliers for 1-of-3 Intrawell Prediction Limits on Means of Order 2 (5 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.93**	**1.36**	**1.15**	**1.04**	**0.97**	**0.89**	**0.84**	**0.81**	**0.78**	**0.76**	**0.75**	**0.74**	**0.73**	**0.72**	**0.71**	**0.71**	**0.70**	**0.70**	**0.69**	**0.69**
2	**2.53**	**1.67**	**1.38**	**1.24**	**1.15**	**1.04**	**0.99**	**0.94**	**0.91**	**0.89**	**0.87**	**0.86**	**0.85**	**0.84**	**0.83**	**0.82**	**0.82**	**0.81**	**0.80**	**0.80**
3	2.94	**1.86**	**1.52**	**1.35**	**1.25**	**1.13**	**1.07**	**1.02**	**0.98**	**0.96**	**0.94**	**0.93**	**0.92**	**0.90**	**0.89**	**0.89**	**0.88**	**0.87**	**0.86**	**0.86**
4	3.26	**2.01**	**1.62**	**1.44**	**1.32**	**1.20**	**1.12**	**1.07**	**1.03**	**1.01**	**0.99**	**0.98**	**0.97**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.90**
5	3.53	**2.13**	**1.71**	**1.50**	**1.38**	**1.24**	**1.17**	**1.11**	**1.07**	**1.05**	**1.03**	**1.01**	**1.00**	**0.98**	**0.97**	**0.96**	**0.96**	**0.95**	**0.94**	**0.93**
8	4.17	**2.39**	**1.88**	**1.64**	**1.50**	**1.35**	**1.26**	**1.19**	**1.15**	**1.12**	**1.10**	**1.09**	**1.07**	**1.05**	**1.04**	**1.03**	**1.02**	**1.02**	**1.01**	**1.00**
12	4.79	**2.63**	**2.04**	**1.76**	**1.61**	**1.43**	**1.34**	**1.27**	**1.22**	**1.19**	**1.17**	**1.15**	**1.13**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**	**1.06**	**1.05**
16	5.30	**2.81**	**2.15**	**1.85**	**1.68**	**1.49**	**1.39**	**1.32**	**1.27**	**1.23**	**1.21**	**1.19**	**1.18**	**1.15**	**1.14**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**
20	5.72	2.96	**2.24**	**1.92**	**1.74**	**1.54**	**1.44**	**1.36**	**1.30**	**1.27**	**1.24**	**1.22**	**1.21**	**1.19**	**1.17**	**1.16**	**1.15**	**1.14**	**1.13**	**1.12**
30	6.56	3.24	**2.42**	**2.05**	**1.85**	**1.63**	**1.51**	**1.43**	**1.37**	**1.33**	**1.30**	**1.28**	**1.27**	**1.24**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**
40	7.24	3.45	**2.54**	**2.15**	**1.93**	**1.69**	**1.57**	**1.47**	**1.42**	**1.38**	**1.35**	**1.32**	**1.31**	**1.28**	**1.26**	**1.25**	**1.24**	**1.23**	**1.21**	**1.21**
50	7.80	3.63	**2.65**	**2.22**	**1.99**	**1.74**	**1.61**	**1.51**	**1.45**	**1.41**	**1.38**	**1.36**	**1.34**	**1.31**	**1.29**	**1.28**	**1.27**	**1.26**	**1.24**	**1.23**
60	8.30	3.77	**2.73**	**2.29**	**2.04**	**1.78**	**1.64**	**1.54**	**1.48**	**1.44**	**1.41**	**1.38**	**1.36**	**1.33**	**1.31**	**1.30**	**1.29**	**1.28**	**1.26**	**1.25**
75	8.95	3.96	*2.84*	**2.36**	**2.10**	**1.83**	**1.69**	**1.58**	**1.52**	**1.47**	**1.44**	**1.41**	**1.39**	**1.36**	**1.34**	**1.33**	**1.32**	**1.31**	**1.29**	**1.28**
100	9.84	4.22	*2.98*	**2.46**	**2.19**	**1.89**	**1.74**	**1.63**	**1.56**	**1.51**	**1.48**	**1.45**	**1.43**	**1.40**	**1.38**	**1.36**	**1.35**	**1.34**	**1.33**	**1.31**
125	10.62	4.42	3.09	**2.54**	**2.25**	**1.94**	**1.78**	**1.67**	**1.60**	**1.55**	**1.51**	**1.48**	**1.46**	**1.43**	**1.41**	**1.39**	**1.38**	**1.37**	**1.35**	**1.34**
150	11.29	4.59	3.18	**2.61**	**2.30**	**1.98**	**1.82**	**1.70**	**1.62**	**1.57**	**1.54**	**1.51**	**1.49**	**1.45**	**1.43**	**1.41**	**1.40**	**1.39**	**1.37**	**1.36**
175	11.88	4.75	3.27	**2.67**	**2.35**	**2.02**	**1.85**	**1.72**	**1.65**	**1.60**	**1.56**	**1.53**	**1.51**	**1.47**	**1.45**	**1.43**	**1.42**	**1.41**	**1.39**	**1.38**
200	12.42	4.88	3.34	**2.71**	**2.39**	**2.05**	**1.87**	**1.75**	**1.67**	**1.62**	**1.58**	**1.55**	**1.52**	**1.49**	**1.47**	**1.45**	**1.44**	**1.43**	**1.41**	**1.39**

Table 19-16. κ-Multipliers for 1-of-3 Intrawell Prediction Limits on Means of Order 2 (10 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.64**	**1.14**	**0.96**	**0.87**	**0.81**	**0.74**	**0.70**	**0.67**	**0.65**	**0.63**	**0.62**	**0.62**	**0.61**	**0.60**	**0.59**	**0.59**	**0.58**	**0.58**	**0.57**	**0.57**
2	**2.16**	**1.43**	**1.19**	**1.06**	**0.99**	**0.90**	**0.85**	**0.81**	**0.78**	**0.77**	**0.75**	**0.74**	**0.74**	**0.72**	**0.71**	**0.71**	**0.70**	**0.70**	**0.69**	**0.69**
3	**2.52**	**1.61**	**1.32**	**1.18**	**1.09**	**0.99**	**0.93**	**0.89**	**0.86**	**0.84**	**0.83**	**0.82**	**0.81**	**0.79**	**0.78**	**0.78**	**0.77**	**0.77**	**0.76**	**0.75**
4	2.81	**1.74**	**1.42**	**1.26**	**1.16**	**1.05**	**0.99**	**0.94**	**0.91**	**0.89**	**0.88**	**0.86**	**0.85**	**0.84**	**0.83**	**0.82**	**0.82**	**0.81**	**0.80**	**0.80**
5	3.04	**1.85**	**1.49**	**1.32**	**1.22**	**1.10**	**1.04**	**0.99**	**0.95**	**0.93**	**0.91**	**0.90**	**0.89**	**0.88**	**0.87**	**0.86**	**0.85**	**0.85**	**0.84**	**0.83**
8	3.60	**2.09**	**1.66**	**1.45**	**1.34**	**1.20**	**1.13**	**1.07**	**1.04**	**1.01**	**0.99**	**0.98**	**0.97**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.90**
12	4.15	**2.31**	**1.80**	**1.57**	**1.44**	**1.29**	**1.21**	**1.15**	**1.11**	**1.08**	**1.06**	**1.04**	**1.03**	**1.01**	**1.00**	**0.99**	**0.98**	**0.98**	**0.97**	**0.96**
16	4.58	*2.47*	**1.91**	**1.66**	**1.51**	**1.35**	**1.26**	**1.20**	**1.15**	**1.12**	**1.10**	**1.09**	**1.07**	**1.05**	**1.04**	**1.03**	**1.02**	**1.02**	**1.01**	**1.00**
20	4.95	*2.60*	**2.00**	**1.72**	**1.57**	**1.40**	**1.30**	**1.24**	**1.19**	**1.16**	**1.14**	**1.12**	**1.11**	**1.09**	**1.07**	**1.06**	**1.05**	**1.05**	**1.04**	**1.03**
30	5.68	2.86	**2.16**	**1.85**	**1.67**	**1.48**	**1.38**	**1.31**	**1.26**	**1.22**	**1.20**	**1.18**	**1.17**	**1.15**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.08**
40	6.27	3.05	**2.28**	**1.94**	**1.75**	**1.55**	**1.44**	**1.36**	**1.30**	**1.27**	**1.24**	**1.22**	**1.21**	**1.19**	**1.17**	**1.16**	**1.15**	**1.14**	**1.13**	**1.12**
50	6.76	3.21	**2.37**	**2.01**	**1.81**	**1.59**	**1.48**	**1.39**	**1.34**	**1.30**	**1.28**	**1.26**	**1.24**	**1.22**	**1.20**	**1.19**	**1.18**	**1.17**	**1.16**	**1.15**
60	7.19	3.34	*2.45*	**2.07**	**1.86**	**1.63**	**1.51**	**1.43**	**1.37**	**1.33**	**1.30**	**1.28**	**1.27**	**1.24**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**
75	7.77	3.51	*2.55*	**2.14**	**1.92**	**1.68**	**1.56**	**1.46**	**1.41**	**1.37**	**1.34**	**1.32**	**1.30**	**1.27**	**1.25**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**
100	8.55	3.73	2.68	**2.24**	**2.00**	**1.74**	**1.61**	**1.51**	**1.45**	**1.41**	**1.38**	**1.35**	**1.34**	**1.31**	**1.29**	**1.28**	**1.27**	**1.26**	**1.24**	**1.23**
125	9.22	3.93	2.78	**2.31**	**2.06**	**1.79**	**1.66**	**1.55**	**1.49**	**1.44**	**1.41**	**1.39**	**1.37**	**1.34**	**1.32**	**1.31**	**1.29**	**1.28**	**1.27**	**1.26**
150	9.84	4.08	2.87	**2.37**	**2.11**	**1.83**	**1.69**	**1.58**	**1.52**	**1.47**	**1.44**	**1.41**	**1.39**	**1.36**	**1.34**	**1.33**	**1.32**	**1.31**	**1.29**	**1.28**
175	10.31	4.22	2.95	*2.43*	**2.16**	**1.87**	**1.72**	**1.61**	**1.54**	**1.49**	**1.46**	**1.44**	**1.42**	**1.38**	**1.36**	**1.35**	**1.34**	**1.33**	**1.31**	**1.30**
200	10.78	4.34	3.01	*2.48*	**2.19**	**1.89**	**1.74**	**1.63**	**1.56**	**1.51**	**1.48**	**1.46**	**1.43**	**1.40**	**1.38**	**1.36**	**1.35**	**1.34**	**1.33**	**1.31**

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Table 19-16. κ-Multipliers for 1-of-3 Intrawell Prediction Limits on Means of Order 2 (10 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.07**	**1.40**	**1.17**	**1.05**	**0.98**	**0.90**	**0.85**	**0.81**	**0.78**	**0.77**	**0.75**	**0.74**	**0.74**	**0.72**	**0.71**	**0.71**	**0.70**	**0.70**	**0.69**	**0.69**
2	2.69	**1.72**	**1.40**	**1.25**	**1.16**	**1.05**	**0.99**	**0.94**	**0.91**	**0.89**	**0.88**	**0.86**	**0.85**	**0.84**	**0.83**	**0.82**	**0.82**	**0.81**	**0.80**	**0.80**
3	3.12	**1.91**	**1.54**	**1.36**	**1.26**	**1.14**	**1.07**	**1.02**	**0.98**	**0.96**	**0.94**	**0.93**	**0.92**	**0.90**	**0.89**	**0.89**	**0.88**	**0.87**	**0.86**	**0.86**
4	3.46	**2.06**	**1.65**	**1.45**	**1.33**	**1.20**	**1.13**	**1.07**	**1.04**	**1.01**	**0.99**	**0.98**	**0.97**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.90**
5	3.75	**2.18**	**1.73**	**1.51**	**1.39**	**1.25**	**1.17**	**1.11**	**1.07**	**1.05**	**1.03**	**1.01**	**1.00**	**0.98**	**0.97**	**0.96**	**0.96**	**0.95**	**0.94**	**0.93**
8	4.41	**2.44**	**1.90**	**1.65**	**1.51**	**1.35**	**1.26**	**1.20**	**1.15**	**1.12**	**1.10**	**1.09**	**1.07**	**1.05**	**1.04**	**1.03**	**1.02**	**1.02**	**1.01**	**1.00**
12	5.08	*2.68*	**2.06**	**1.77**	**1.61**	**1.43**	**1.34**	**1.27**	**1.22**	**1.19**	**1.17**	**1.15**	**1.13**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**	**1.06**	**1.05**
16	5.60	2.87	**2.17**	**1.86**	**1.69**	**1.50**	**1.39**	**1.32**	**1.27**	**1.23**	**1.21**	**1.19**	**1.18**	**1.15**	**1.14**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**
20	6.04	3.02	**2.27**	**1.93**	**1.75**	**1.54**	**1.44**	**1.36**	**1.30**	**1.27**	**1.24**	**1.22**	**1.21**	**1.19**	**1.17**	**1.16**	**1.15**	**1.14**	**1.13**	**1.12**
30	6.93	3.30	**2.44**	**2.06**	**1.86**	**1.63**	**1.51**	**1.43**	**1.37**	**1.33**	**1.30**	**1.28**	**1.27**	**1.24**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**
40	7.66	3.52	**2.56**	**2.16**	**1.93**	**1.69**	**1.57**	**1.47**	**1.42**	**1.38**	**1.35**	**1.32**	**1.31**	**1.28**	**1.26**	**1.25**	**1.24**	**1.23**	**1.21**	**1.20**
50	8.24	3.69	*2.67*	**2.23**	**1.99**	**1.74**	**1.61**	**1.51**	**1.45**	**1.41**	**1.38**	**1.36**	**1.34**	**1.31**	**1.29**	**1.28**	**1.27**	**1.26**	**1.24**	**1.23**
60	8.77	3.85	*2.75*	**2.29**	**2.05**	**1.78**	**1.65**	**1.54**	**1.48**	**1.44**	**1.41**	**1.38**	**1.36**	**1.33**	**1.31**	**1.30**	**1.29**	**1.28**	**1.26**	**1.25**
75	9.45	4.03	2.86	**2.37**	**2.11**	**1.83**	**1.69**	**1.58**	**1.52**	**1.47**	**1.44**	**1.41**	**1.39**	**1.36**	**1.34**	**1.33**	**1.32**	**1.31**	**1.29**	**1.28**
100	10.39	4.30	3.00	**2.47**	**2.19**	**1.89**	**1.74**	**1.63**	**1.56**	**1.51**	**1.48**	**1.45**	**1.43**	**1.40**	**1.38**	**1.36**	**1.35**	**1.34**	**1.33**	**1.31**
125	11.25	4.49	3.12	**2.55**	**2.26**	**1.94**	**1.78**	**1.67**	**1.60**	**1.55**	**1.51**	**1.48**	**1.46**	**1.43**	**1.41**	**1.39**	**1.38**	**1.37**	**1.35**	**1.34**
150	11.88	4.67	3.20	*2.62*	**2.30**	**1.98**	**1.82**	**1.70**	**1.63**	**1.57**	**1.54**	**1.51**	**1.48**	**1.46**	**1.43**	**1.41**	**1.40**	**1.39**	**1.37**	**1.36**
175	12.50	4.84	3.28	*2.68*	**2.35**	**2.02**	**1.85**	**1.72**	**1.65**	**1.60**	**1.56**	**1.53**	**1.51**	**1.47**	**1.45**	**1.43**	**1.42**	**1.41**	**1.39**	**1.38**
200	13.12	4.96	3.36	*2.73*	**2.39**	**2.05**	**1.88**	**1.75**	**1.67**	**1.62**	**1.58**	**1.55**	**1.52**	**1.49**	**1.46**	**1.45**	**1.44**	**1.43**	**1.41**	**1.39**

Table 19-16. κ-Multipliers for 1-of-3 Intrawell Prediction Limits on Means of Order 2 (10 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.53**	**1.67**	**1.38**	**1.24**	**1.15**	**1.04**	**0.99**	**0.94**	**0.91**	**0.89**	**0.87**	**0.86**	**0.85**	**0.84**	**0.83**	**0.82**	**0.82**	**0.81**	**0.80**	**0.80**
2	3.26	**2.01**	**1.62**	**1.44**	**1.32**	**1.20**	**1.12**	**1.07**	**1.03**	**1.01**	**0.99**	**0.98**	**0.97**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.90**
3	3.77	**2.23**	**1.77**	**1.56**	**1.43**	**1.28**	**1.20**	**1.14**	**1.10**	**1.08**	**1.06**	**1.04**	**1.03**	**1.01**	**1.00**	**0.99**	**0.98**	**0.98**	**0.97**	**0.96**
4	4.17	**2.39**	**1.88**	**1.64**	**1.50**	**1.35**	**1.26**	**1.19**	**1.15**	**1.12**	**1.10**	**1.09**	**1.07**	**1.05**	**1.04**	**1.03**	**1.02**	**1.02**	**1.01**	**1.00**
5	4.50	**2.52**	**1.97**	**1.71**	**1.56**	**1.39**	**1.30**	**1.23**	**1.19**	**1.16**	**1.14**	**1.12**	**1.11**	**1.09**	**1.07**	**1.06**	**1.05**	**1.05**	**1.04**	**1.03**
8	5.30	**2.81**	**2.15**	**1.85**	**1.68**	**1.49**	**1.39**	**1.32**	**1.27**	**1.23**	**1.21**	**1.19**	**1.18**	**1.15**	**1.14**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**
12	6.08	3.08	**2.32**	**1.98**	**1.79**	**1.58**	**1.47**	**1.39**	**1.33**	**1.30**	**1.27**	**1.25**	**1.23**	**1.21**	**1.19**	**1.18**	**1.17**	**1.16**	**1.15**	**1.14**
16	6.71	3.29	**2.45**	**2.08**	**1.87**	**1.64**	**1.52**	**1.44**	**1.38**	**1.34**	**1.31**	**1.29**	**1.28**	**1.25**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**
20	7.24	3.45	**2.54**	**2.15**	**1.93**	**1.69**	**1.57**	**1.47**	**1.42**	**1.38**	**1.35**	**1.32**	**1.31**	**1.28**	**1.26**	**1.25**	**1.24**	**1.23**	**1.21**	**1.21**
30	8.30	3.77	**2.73**	**2.29**	**2.04**	**1.78**	**1.64**	**1.54**	**1.48**	**1.44**	**1.41**	**1.38**	**1.36**	**1.33**	**1.31**	**1.30**	**1.29**	**1.28**	**1.26**	**1.25**
40	9.14	4.02	*2.87*	**2.39**	**2.12**	**1.84**	**1.70**	**1.59**	**1.53**	**1.48**	**1.45**	**1.42**	**1.40**	**1.37**	**1.35**	**1.34**	**1.32**	**1.32**	**1.30**	**1.29**
50	9.84	4.22	*2.98*	**2.46**	**2.19**	**1.89**	**1.74**	**1.63**	**1.56**	**1.51**	**1.48**	**1.45**	**1.43**	**1.40**	**1.38**	**1.36**	**1.35**	**1.34**	**1.33**	**1.31**
60	10.47	4.38	3.07	**2.53**	**2.24**	**1.93**	**1.77**	**1.66**	**1.59**	**1.54**	**1.50**	**1.48**	**1.46**	**1.42**	**1.40**	**1.39**	**1.37**	**1.36**	**1.35**	**1.34**
75	11.29	4.59	3.18	**2.61**	**2.30**	**1.98**	**1.82**	**1.70**	**1.62**	**1.57**	**1.54**	**1.51**	**1.49**	**1.45**	**1.43**	**1.41**	**1.40**	**1.39**	**1.37**	**1.36**
100	12.42	4.88	3.34	**2.71**	**2.39**	**2.05**	**1.87**	**1.75**	**1.67**	**1.62**	**1.58**	**1.55**	**1.52**	**1.49**	**1.47**	**1.45**	**1.44**	**1.43**	**1.41**	**1.39**
125	13.44	5.12	3.46	**2.80**	**2.46**	**2.10**	**1.91**	**1.78**	**1.70**	**1.65**	**1.61**	**1.58**	**1.55**	**1.52**	**1.49**	**1.47**	**1.46**	**1.45**	**1.43**	**1.42**
150	14.22	5.31	3.56	*2.87*	**2.51**	**2.14**	**1.95**	**1.82**	**1.73**	**1.67**	**1.63**	**1.60**	**1.58**	**1.54**	**1.52**	**1.50**	**1.48**	**1.47**	**1.45**	**1.44**
175	15.00	5.49	3.65	*2.93*	**2.56**	**2.18**	**1.98**	**1.84**	**1.75**	**1.69**	**1.66**	**1.62**	**1.60**	**1.56**	**1.53**	**1.51**	**1.50**	**1.49**	**1.46**	**1.45**
200	15.62	5.62	3.73	*2.99*	**2.60**	**2.21**	**2.01**	**1.87**	**1.78**	**1.71**	**1.67**	**1.64**	**1.62**	**1.58**	**1.55**	**1.53**	**1.51**	**1.50**	**1.48**	**1.47**

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Table 19-16. κ-Multipliers for 1-of-3 Intrawell Prediction Limits on Means of Order 2 (20 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	2.16	1.43	1.19	1.06	0.99	0.90	0.85	0.81	0.78	0.77	0.75	0.74	0.74	0.72	0.71	0.71	0.70	0.70	0.69	0.69
2	2.81	1.74	1.42	1.26	1.16	1.05	0.99	0.94	0.91	0.89	0.88	0.86	0.85	0.84	0.83	0.82	0.82	0.81	0.80	0.80
3	3.25	1.94	1.56	1.37	1.26	1.14	1.07	1.02	0.99	0.96	0.94	0.93	0.92	0.91	0.89	0.89	0.88	0.87	0.86	0.86
4	3.60	2.09	1.66	1.45	1.34	1.20	1.13	1.07	1.04	1.01	0.99	0.98	0.97	0.95	0.94	0.93	0.92	0.92	0.91	0.90
5	3.89	2.21	1.74	1.52	1.39	1.25	1.17	1.11	1.07	1.05	1.03	1.01	1.00	0.98	0.97	0.96	0.96	0.95	0.94	0.93
8	4.58	*2.47*	1.91	1.66	1.51	1.35	1.26	1.20	1.15	1.12	1.10	1.09	1.07	1.05	1.04	1.03	1.02	1.02	1.01	1.00
12	5.27	2.72	2.07	1.78	1.62	1.44	1.34	1.27	1.22	1.19	1.17	1.15	1.13	1.11	1.10	1.09	1.08	1.07	1.06	1.05
16	5.82	2.90	2.19	1.87	1.69	1.50	1.39	1.32	1.27	1.24	1.21	1.19	1.18	1.15	1.14	1.13	1.12	1.11	1.10	1.09
20	6.27	3.05	2.28	1.94	1.75	1.55	1.44	1.36	1.31	1.27	1.24	1.22	1.21	1.19	1.17	1.16	1.15	1.14	1.13	1.12
30	7.20	3.34	*2.45*	2.07	1.86	1.63	1.51	1.43	1.37	1.33	1.30	1.28	1.27	1.24	1.22	1.21	1.20	1.19	1.18	1.17
40	7.93	3.56	*2.58*	2.16	1.94	1.70	1.57	1.48	1.42	1.38	1.35	1.32	1.31	1.28	1.26	1.25	1.24	1.23	1.21	1.21
50	8.54	3.74	2.68	2.24	2.00	1.74	1.61	1.51	1.45	1.41	1.38	1.36	1.34	1.31	1.29	1.28	1.27	1.26	1.24	1.23
60	9.08	3.88	2.76	2.30	2.05	1.78	1.64	1.54	1.48	1.44	1.41	1.38	1.36	1.34	1.32	1.30	1.29	1.28	1.26	1.25
75	9.81	4.08	2.87	2.37	2.11	1.83	1.69	1.58	1.52	1.47	1.44	1.41	1.39	1.36	1.34	1.33	1.32	1.31	1.29	1.28
100	10.79	4.33	3.02	*2.48*	2.19	1.90	1.74	1.63	1.56	1.51	1.48	1.45	1.43	1.40	1.38	1.36	1.35	1.34	1.32	1.32
125	11.62	4.54	3.12	*2.56*	2.26	1.95	1.79	1.67	1.60	1.55	1.51	1.48	1.46	1.43	1.41	1.39	1.38	1.37	1.35	1.34
150	12.40	4.71	3.22	*2.62*	2.31	1.98	1.82	1.70	1.62	1.57	1.54	1.51	1.49	1.45	1.43	1.41	1.40	1.39	1.37	1.36
175	13.09	4.88	3.30	*2.69*	2.36	2.02	1.85	1.73	1.65	1.60	1.56	1.53	1.51	1.47	1.45	1.43	1.42	1.41	1.39	1.38
200	13.67	5.03	3.37	2.73	2.39	2.05	1.87	1.75	1.67	1.62	1.57	1.55	1.53	1.49	1.46	1.45	1.43	1.42	1.41	1.39

Table 19-16. κ-Multipliers for 1-of-3 Intrawell Prediction Limits on Means of Order 2 (20 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	2.69	1.72	1.40	1.25	1.16	1.05	0.99	0.94	0.91	0.89	0.88	0.86	0.85	0.84	0.83	0.82	0.82	0.81	0.80	0.80
2	3.46	2.06	1.65	1.45	1.33	1.20	1.13	1.07	1.04	1.01	0.99	0.98	0.97	0.95	0.94	0.93	0.92	0.92	0.91	0.90
3	3.99	2.28	1.79	1.57	1.43	1.29	1.21	1.14	1.11	1.08	1.06	1.04	1.03	1.01	1.00	0.99	0.98	0.98	0.97	0.96
4	4.41	2.44	1.90	1.65	1.51	1.35	1.26	1.20	1.15	1.12	1.10	1.09	1.07	1.05	1.04	1.03	1.02	1.02	1.01	1.00
5	4.77	2.57	1.99	1.72	1.57	1.40	1.30	1.24	1.19	1.16	1.14	1.12	1.11	1.09	1.07	1.06	1.05	1.05	1.04	1.03
8	5.60	2.87	2.17	1.86	1.69	1.50	1.39	1.32	1.27	1.23	1.21	1.19	1.18	1.15	1.14	1.13	1.12	1.11	1.10	1.09
12	6.43	3.14	2.34	1.99	1.80	1.58	1.47	1.39	1.33	1.30	1.27	1.25	1.23	1.21	1.19	1.18	1.17	1.16	1.15	1.14
16	7.09	3.35	2.47	2.08	1.87	1.65	1.53	1.44	1.38	1.34	1.31	1.29	1.28	1.25	1.23	1.22	1.21	1.20	1.19	1.18
20	7.65	3.52	2.57	2.16	1.93	1.69	1.57	1.47	1.42	1.38	1.35	1.32	1.31	1.28	1.26	1.25	1.24	1.23	1.21	1.21
30	8.76	3.85	*2.75*	2.29	2.05	1.78	1.64	1.54	1.48	1.44	1.41	1.38	1.36	1.33	1.32	1.30	1.29	1.28	1.26	1.25
40	9.67	4.09	2.89	2.39	2.13	1.84	1.70	1.59	1.53	1.48	1.45	1.42	1.40	1.37	1.35	1.34	1.32	1.32	1.30	1.29
50	10.40	4.28	3.00	2.47	2.19	1.90	1.74	1.63	1.56	1.51	1.48	1.45	1.43	1.40	1.38	1.36	1.35	1.34	1.33	1.31
60	11.08	4.46	3.09	2.54	2.24	1.93	1.78	1.66	1.59	1.54	1.50	1.48	1.46	1.43	1.40	1.39	1.37	1.36	1.35	1.34
75	11.91	4.68	3.21	*2.62*	2.31	1.98	1.82	1.70	1.62	1.57	1.54	1.51	1.49	1.45	1.43	1.41	1.40	1.39	1.37	1.36
100	13.13	4.96	3.36	*2.73*	2.39	2.05	1.87	1.75	1.67	1.61	1.58	1.55	1.52	1.49	1.47	1.45	1.43	1.43	1.41	1.39
125	14.16	5.20	3.49	*2.81*	2.46	2.10	1.92	1.79	1.70	1.65	1.61	1.58	1.55	1.52	1.49	1.47	1.46	1.45	1.43	1.42
150	15.04	5.40	3.59	*2.88*	2.51	2.14	1.95	1.82	1.73	1.67	1.63	1.60	1.58	1.54	1.52	1.50	1.48	1.47	1.45	1.44
175	15.82	5.57	3.69	2.94	2.56	2.17	1.98	1.84	1.75	1.70	1.65	1.62	1.60	1.56	1.54	1.51	1.50	1.49	1.47	1.45
200	16.60	5.74	3.76	3.00	*2.60*	2.21	2.01	1.86	1.78	1.72	1.67	1.64	1.61	1.57	1.55	1.53	1.51	1.50	1.48	1.47

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Table 19-16. κ-Multipliers for 1-of-3 Intrawell Prediction Limits on Means of Order 2 (20 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.26	**2.01**	**1.62**	**1.44**	**1.32**	**1.20**	**1.12**	**1.07**	**1.03**	**1.01**	**0.99**	**0.98**	**0.97**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.90**
2	4.17	**2.39**	**1.88**	**1.64**	**1.50**	**1.35**	**1.26**	**1.19**	**1.15**	**1.12**	**1.10**	**1.09**	**1.07**	**1.05**	**1.04**	**1.03**	**1.02**	**1.02**	**1.01**	**1.00**
3	4.80	**2.63**	**2.04**	**1.76**	**1.61**	**1.43**	**1.34**	**1.27**	**1.22**	**1.19**	**1.17**	**1.15**	**1.13**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**	**1.06**	**1.05**
4	5.29	**2.81**	**2.15**	**1.85**	**1.68**	**1.49**	**1.39**	**1.32**	**1.27**	**1.23**	**1.21**	**1.19**	**1.18**	**1.15**	**1.14**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**
5	5.72	2.96	**2.24**	**1.92**	**1.74**	**1.54**	**1.44**	**1.36**	**1.30**	**1.27**	**1.24**	**1.22**	**1.21**	**1.19**	**1.17**	**1.16**	**1.15**	**1.14**	**1.13**	**1.12**
8	6.71	3.29	**2.45**	**2.08**	**1.87**	**1.64**	**1.52**	**1.44**	**1.38**	**1.34**	**1.31**	**1.29**	**1.28**	**1.25**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**
12	7.70	3.60	**2.63**	**2.21**	**1.98**	**1.73**	**1.60**	**1.51**	**1.45**	**1.40**	**1.37**	**1.35**	**1.33**	**1.30**	**1.29**	**1.27**	**1.26**	**1.25**	**1.24**	**1.23**
16	8.48	3.83	**2.76**	**2.31**	**2.06**	**1.79**	**1.66**	**1.55**	**1.49**	**1.45**	**1.41**	**1.39**	**1.37**	**1.34**	**1.32**	**1.31**	**1.30**	**1.29**	**1.27**	**1.26**
20	9.14	4.02	*2.87*	**2.38**	**2.12**	**1.84**	**1.70**	**1.59**	**1.53**	**1.48**	**1.45**	**1.42**	**1.40**	**1.37**	**1.35**	**1.34**	**1.32**	**1.32**	**1.30**	**1.29**
30	10.47	4.38	3.07	**2.53**	**2.24**	**1.93**	**1.78**	**1.66**	**1.59**	**1.54**	**1.50**	**1.48**	**1.46**	**1.43**	**1.40**	**1.39**	**1.37**	**1.36**	**1.35**	**1.34**
40	11.55	4.66	3.22	**2.63**	**2.32**	**2.00**	**1.83**	**1.71**	**1.63**	**1.58**	**1.54**	**1.52**	**1.49**	**1.46**	**1.44**	**1.42**	**1.41**	**1.40**	**1.38**	**1.37**
50	12.45	4.88	3.34	**2.72**	**2.39**	**2.05**	**1.87**	**1.75**	**1.67**	**1.61**	**1.58**	**1.55**	**1.52**	**1.49**	**1.47**	**1.45**	**1.44**	**1.43**	**1.41**	**1.39**
60	13.23	5.07	3.44	**2.79**	**2.44**	**2.09**	**1.91**	**1.78**	**1.70**	**1.64**	**1.60**	**1.57**	**1.55**	**1.51**	**1.49**	**1.47**	**1.46**	**1.45**	**1.43**	**1.41**
75	14.26	5.31	3.56	*2.87*	**2.51**	**2.14**	**1.95**	**1.82**	**1.73**	**1.67**	**1.63**	**1.60**	**1.58**	**1.54**	**1.52**	**1.50**	**1.48**	**1.47**	**1.45**	**1.43**
100	15.72	5.64	3.74	*2.99*	**2.60**	**2.20**	**2.01**	**1.86**	**1.78**	**1.72**	**1.67**	**1.64**	**1.61**	**1.58**	**1.55**	**1.53**	**1.52**	**1.50**	**1.48**	**1.46**
125	16.89	5.91	3.87	*3.08*	**2.67**	**2.26**	**2.05**	**1.90**	**1.81**	**1.75**	**1.70**	**1.67**	**1.64**	**1.61**	**1.58**	**1.56**	**1.54**	**1.53**	**1.51**	**1.49**
150	17.97	6.15	3.98	3.15	**2.73**	**2.30**	**2.08**	**1.93**	**1.84**	**1.77**	**1.73**	**1.69**	**1.67**	**1.63**	**1.60**	**1.58**	**1.56**	**1.55**	**1.53**	**1.51**
175	18.95	6.35	4.08	3.22	**2.78**	**2.33**	**2.11**	**1.96**	**1.86**	**1.79**	**1.75**	**1.72**	**1.68**	**1.64**	**1.62**	**1.60**	**1.58**	**1.57**	**1.54**	**1.53**
200	19.73	6.49	4.15	3.27	**2.82**	**2.37**	**2.14**	**1.98**	**1.88**	**1.81**	**1.77**	**1.73**	**1.70**	**1.66**	**1.63**	**1.61**	**1.60**	**1.58**	**1.56**	**1.54**

Table 19-16. κ-Multipliers for 1-of-3 Intrawell Prediction Limits on Means of Order 2 (40 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	2.81	**1.74**	**1.42**	**1.26**	**1.16**	**1.05**	**0.99**	**0.94**	**0.91**	**0.89**	**0.88**	**0.86**	**0.85**	**0.84**	**0.83**	**0.82**	**0.82**	**0.81**	**0.80**	**0.80**
2	3.60	**2.09**	**1.66**	**1.45**	**1.34**	**1.20**	**1.13**	**1.07**	**1.04**	**1.01**	**0.99**	**0.98**	**0.97**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.90**
3	4.15	**2.31**	**1.80**	**1.57**	**1.44**	**1.29**	**1.21**	**1.15**	**1.11**	**1.08**	**1.06**	**1.04**	**1.03**	**1.01**	**1.00**	**0.99**	**0.98**	**0.98**	**0.97**	**0.96**
4	4.58	*2.47*	**1.91**	**1.66**	**1.51**	**1.35**	**1.26**	**1.20**	**1.15**	**1.12**	**1.10**	**1.09**	**1.07**	**1.05**	**1.04**	**1.03**	**1.02**	**1.02**	**1.01**	**1.00**
5	4.95	*2.60*	**2.00**	**1.72**	**1.57**	**1.40**	**1.31**	**1.24**	**1.19**	**1.16**	**1.14**	**1.12**	**1.11**	**1.09**	**1.07**	**1.06**	**1.05**	**1.05**	**1.04**	**1.03**
8	5.82	2.90	**2.18**	**1.87**	**1.69**	**1.50**	**1.39**	**1.32**	**1.27**	**1.24**	**1.21**	**1.19**	**1.18**	**1.15**	**1.14**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**
12	6.68	3.18	**2.35**	**2.00**	**1.80**	**1.59**	**1.47**	**1.39**	**1.33**	**1.30**	**1.27**	**1.25**	**1.23**	**1.21**	**1.19**	**1.18**	**1.17**	**1.16**	**1.15**	**1.14**
16	7.36	3.39	*2.48*	**2.09**	**1.88**	**1.65**	**1.53**	**1.44**	**1.38**	**1.34**	**1.31**	**1.29**	**1.28**	**1.25**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**
20	7.93	3.56	*2.58*	**2.16**	**1.94**	**1.70**	**1.57**	**1.48**	**1.42**	**1.38**	**1.35**	**1.32**	**1.31**	**1.28**	**1.26**	**1.25**	**1.24**	**1.23**	**1.21**	**1.21**
30	9.10	3.89	2.76	**2.30**	**2.05**	**1.78**	**1.65**	**1.54**	**1.48**	**1.44**	**1.41**	**1.38**	**1.36**	**1.33**	**1.32**	**1.30**	**1.29**	**1.28**	**1.26**	**1.25**
40	10.02	4.13	2.90	**2.40**	**2.13**	**1.85**	**1.70**	**1.59**	**1.53**	**1.48**	**1.45**	**1.42**	**1.40**	**1.37**	**1.35**	**1.34**	**1.32**	**1.32**	**1.30**	**1.29**
50	10.81	4.34	3.01	*2.48*	**2.19**	**1.90**	**1.74**	**1.63**	**1.56**	**1.51**	**1.48**	**1.45**	**1.43**	**1.40**	**1.38**	**1.36**	**1.35**	**1.34**	**1.33**	**1.31**
60	11.48	4.50	3.11	*2.54*	**2.24**	**1.94**	**1.78**	**1.66**	**1.59**	**1.54**	**1.51**	**1.48**	**1.46**	**1.42**	**1.40**	**1.39**	**1.37**	**1.36**	**1.35**	**1.33**
75	12.36	4.72	3.22	*2.63*	**2.31**	**1.98**	**1.82**	**1.70**	**1.62**	**1.57**	**1.54**	**1.51**	**1.49**	**1.45**	**1.43**	**1.41**	**1.40**	**1.39**	**1.37**	**1.36**
100	13.59	5.01	3.38	2.73	*2.40*	**2.05**	**1.88**	**1.75**	**1.67**	**1.61**	**1.58**	**1.55**	**1.52**	**1.49**	**1.47**	**1.45**	**1.44**	**1.42**	**1.40**	**1.39**
125	14.65	5.24	3.50	2.82	*2.46*	**2.10**	**1.92**	**1.78**	**1.70**	**1.65**	**1.61**	**1.58**	**1.55**	**1.52**	**1.49**	**1.48**	**1.46**	**1.45**	**1.43**	**1.42**
150	15.59	5.45	3.60	2.89	*2.52*	**2.14**	**1.95**	**1.82**	**1.73**	**1.67**	**1.63**	**1.60**	**1.58**	**1.54**	**1.52**	**1.50**	**1.48**	**1.47**	**1.45**	**1.44**
175	16.41	5.62	3.69	2.94	*2.56*	**2.18**	**1.98**	**1.84**	**1.75**	**1.70**	**1.66**	**1.62**	**1.60**	**1.56**	**1.53**	**1.52**	**1.50**	**1.49**	**1.47**	**1.45**
200	17.11	5.80	3.76	3.00	*2.61*	**2.20**	**2.01**	**1.86**	**1.78**	**1.71**	**1.67**	**1.64**	**1.61**	**1.57**	**1.55**	**1.53**	**1.52**	**1.51**	**1.48**	**1.47**

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Table 19-16. κ-Multipliers for 1-of-3 Intrawell Prediction Limits on Means of Order 2 (40 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.46	**2.06**	**1.65**	**1.45**	**1.33**	**1.20**	**1.13**	**1.07**	**1.04**	**1.01**	**0.99**	**0.98**	**0.97**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.90**
2	4.41	**2.44**	**1.90**	**1.65**	**1.51**	**1.35**	**1.26**	**1.20**	**1.15**	**1.12**	**1.10**	**1.09**	**1.07**	**1.05**	**1.04**	**1.03**	**1.02**	**1.02**	**1.01**	**1.00**
3	5.08	*2.68*	**2.06**	**1.77**	**1.61**	**1.44**	**1.34**	**1.27**	**1.22**	**1.19**	**1.17**	**1.15**	**1.13**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**	**1.06**	**1.05**
4	5.60	2.87	**2.17**	**1.86**	**1.69**	**1.50**	**1.39**	**1.32**	**1.27**	**1.23**	**1.21**	**1.19**	**1.18**	**1.15**	**1.14**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**
5	6.05	3.02	**2.27**	**1.93**	**1.75**	**1.54**	**1.44**	**1.36**	**1.30**	**1.27**	**1.24**	**1.22**	**1.21**	**1.19**	**1.17**	**1.16**	**1.15**	**1.14**	**1.13**	**1.12**
8	7.09	3.35	**2.47**	**2.08**	**1.87**	**1.65**	**1.53**	**1.44**	**1.38**	**1.34**	**1.31**	**1.29**	**1.28**	**1.25**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**
12	8.13	3.66	*2.65*	**2.22**	**1.98**	**1.73**	**1.60**	**1.51**	**1.45**	**1.40**	**1.37**	**1.35**	**1.33**	**1.30**	**1.29**	**1.27**	**1.26**	**1.25**	**1.24**	**1.23**
16	8.96	3.90	*2.78*	**2.32**	**2.06**	**1.80**	**1.66**	**1.56**	**1.49**	**1.45**	**1.41**	**1.39**	**1.37**	**1.34**	**1.32**	**1.31**	**1.30**	**1.29**	**1.27**	**1.26**
20	9.66	4.09	2.89	**2.39**	**2.13**	**1.85**	**1.70**	**1.59**	**1.53**	**1.48**	**1.45**	**1.42**	**1.40**	**1.37**	**1.35**	**1.34**	**1.32**	**1.32**	**1.30**	**1.29**
30	11.07	4.46	3.09	**2.54**	**2.24**	**1.93**	**1.78**	**1.66**	**1.59**	**1.54**	**1.50**	**1.48**	**1.46**	**1.43**	**1.40**	**1.39**	**1.37**	**1.36**	**1.35**	**1.34**
40	12.19	4.74	3.24	*2.64*	**2.33**	**2.00**	**1.83**	**1.71**	**1.63**	**1.58**	**1.55**	**1.52**	**1.49**	**1.46**	**1.44**	**1.42**	**1.41**	**1.40**	**1.38**	**1.37**
50	13.12	4.97	3.36	*2.73*	**2.39**	**2.05**	**1.87**	**1.75**	**1.67**	**1.61**	**1.58**	**1.55**	**1.52**	**1.49**	**1.47**	**1.45**	**1.44**	**1.42**	**1.41**	**1.39**
60	13.95	5.16	3.46	*2.80*	**2.45**	**2.09**	**1.91**	**1.78**	**1.70**	**1.64**	**1.60**	**1.57**	**1.55**	**1.51**	**1.49**	**1.47**	**1.46**	**1.44**	**1.42**	**1.41**
75	15.06	5.41	3.59	*2.88*	**2.52**	**2.14**	**1.95**	**1.81**	**1.73**	**1.67**	**1.63**	**1.60**	**1.58**	**1.54**	**1.52**	**1.50**	**1.48**	**1.47**	**1.45**	**1.43**
100	16.58	5.74	3.76	3.00	*2.60*	**2.21**	**2.01**	**1.86**	**1.78**	**1.72**	**1.67**	**1.64**	**1.61**	**1.58**	**1.55**	**1.53**	**1.52**	**1.50**	**1.48**	**1.47**
125	17.81	6.01	3.90	3.09	*2.67*	**2.26**	**2.05**	**1.90**	**1.81**	**1.75**	**1.70**	**1.67**	**1.64**	**1.60**	**1.58**	**1.56**	**1.54**	**1.53**	**1.51**	**1.49**
150	18.98	6.24	4.00	3.16	*2.73*	**2.30**	**2.08**	**1.93**	**1.84**	**1.77**	**1.73**	**1.69**	**1.67**	**1.63**	**1.60**	**1.58**	**1.56**	**1.55**	**1.53**	**1.51**
175	19.92	6.45	4.10	3.22	*2.78*	**2.34**	**2.12**	**1.96**	**1.86**	**1.79**	**1.75**	**1.71**	**1.68**	**1.64**	**1.62**	**1.60**	**1.58**	**1.57**	**1.55**	**1.53**
200	20.86	6.62	4.19	3.28	*2.83*	**2.37**	**2.14**	**1.98**	**1.88**	**1.82**	**1.77**	**1.73**	**1.70**	**1.66**	**1.63**	**1.61**	**1.60**	**1.58**	**1.56**	**1.55**

Table 19-16. κ-Multipliers for 1-of-3 Intrawell Prediction Limits on Means of Order 2 (40 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	4.17	**2.39**	**1.88**	**1.64**	**1.50**	**1.35**	**1.26**	**1.19**	**1.15**	**1.12**	**1.10**	**1.09**	**1.07**	**1.05**	**1.04**	**1.03**	**1.02**	**1.02**	**1.01**	**1.00**
2	5.29	**2.81**	**2.15**	**1.85**	**1.68**	**1.49**	**1.39**	**1.32**	**1.27**	**1.23**	**1.21**	**1.19**	**1.18**	**1.15**	**1.14**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**
3	6.08	3.08	**2.32**	**1.98**	**1.79**	**1.58**	**1.47**	**1.39**	**1.33**	**1.30**	**1.27**	**1.25**	**1.23**	**1.21**	**1.19**	**1.18**	**1.17**	**1.16**	**1.15**	**1.14**
4	6.71	3.29	**2.45**	**2.08**	**1.87**	**1.64**	**1.52**	**1.44**	**1.38**	**1.34**	**1.31**	**1.29**	**1.28**	**1.25**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**
5	7.23	3.46	**2.54**	**2.15**	**1.93**	**1.69**	**1.57**	**1.47**	**1.42**	**1.38**	**1.35**	**1.32**	**1.31**	**1.28**	**1.26**	**1.25**	**1.24**	**1.23**	**1.21**	**1.21**
8	8.48	3.83	**2.76**	**2.31**	**2.06**	**1.79**	**1.66**	**1.55**	**1.49**	**1.45**	**1.41**	**1.39**	**1.37**	**1.34**	**1.32**	**1.31**	**1.30**	**1.29**	**1.27**	**1.26**
12	9.72	4.18	*2.96*	**2.45**	**2.17**	**1.88**	**1.73**	**1.62**	**1.55**	**1.51**	**1.47**	**1.45**	**1.43**	**1.40**	**1.37**	**1.36**	**1.35**	**1.34**	**1.32**	**1.31**
16	10.71	4.44	3.10	**2.55**	**2.26**	**1.95**	**1.79**	**1.67**	**1.60**	**1.55**	**1.51**	**1.49**	**1.46**	**1.43**	**1.41**	**1.39**	**1.38**	**1.37**	**1.35**	**1.34**
20	11.54	4.66	3.22	**2.63**	**2.32**	**2.00**	**1.83**	**1.71**	**1.63**	**1.58**	**1.54**	**1.52**	**1.49**	**1.46**	**1.44**	**1.42**	**1.41**	**1.40**	**1.38**	**1.37**
30	13.21	5.07	3.44	**2.79**	**2.44**	**2.09**	**1.91**	**1.78**	**1.70**	**1.64**	**1.60**	**1.57**	**1.55**	**1.51**	**1.49**	**1.47**	**1.46**	**1.45**	**1.43**	**1.41**
40	14.56	5.38	3.60	*2.90*	**2.53**	**2.15**	**1.96**	**1.83**	**1.74**	**1.68**	**1.64**	**1.61**	**1.58**	**1.55**	**1.52**	**1.50**	**1.49**	**1.48**	**1.46**	**1.44**
50	15.70	5.64	3.73	*2.99*	**2.60**	**2.20**	**2.01**	**1.86**	**1.78**	**1.72**	**1.67**	**1.64**	**1.61**	**1.58**	**1.55**	**1.53**	**1.52**	**1.50**	**1.48**	**1.47**
60	16.67	5.86	3.84	*3.06*	**2.66**	**2.25**	**2.04**	**1.89**	**1.80**	**1.74**	**1.70**	**1.66**	**1.64**	**1.60**	**1.57**	**1.55**	**1.54**	**1.52**	**1.50**	**1.49**
75	17.99	6.14	3.98	3.15	**2.73**	**2.30**	**2.08**	**1.93**	**1.84**	**1.77**	**1.73**	**1.69**	**1.67**	**1.63**	**1.60**	**1.58**	**1.56**	**1.55**	**1.53**	**1.51**
100	19.80	6.50	4.16	3.27	**2.82**	**2.37**	**2.14**	**1.98**	**1.88**	**1.81**	**1.77**	**1.73**	**1.70**	**1.66**	**1.63**	**1.61**	**1.59**	**1.58**	**1.56**	**1.54**
125	21.33	6.83	4.31	3.37	*2.89*	**2.42**	**2.18**	**2.02**	**1.92**	**1.85**	**1.80**	**1.76**	**1.73**	**1.69**	**1.66**	**1.64**	**1.62**	**1.61**	**1.58**	**1.57**
150	22.62	7.09	4.42	3.45	*2.96*	**2.46**	**2.22**	**2.05**	**1.94**	**1.87**	**1.82**	**1.78**	**1.75**	**1.71**	**1.68**	**1.66**	**1.64**	**1.63**	**1.60**	**1.59**
175	23.91	7.29	4.54	3.52	*3.01*	**2.50**	**2.25**	**2.07**	**1.97**	**1.89**	**1.84**	**1.80**	**1.77**	**1.73**	**1.70**	**1.68**	**1.66**	**1.64**	**1.62**	**1.60**
200	24.84	7.50	4.63	3.57	*3.05*	**2.53**	**2.28**	**2.09**	**1.99**	**1.91**	**1.86**	**1.82**	**1.79**	**1.74**	**1.71**	**1.69**	**1.67**	**1.66**	**1.64**	**1.62**

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Table 19-17. κ-Multipliers for 1-of-1 Intrawell Prediction Limits on Means of Order 3 (1 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.25**	**1.04**	**0.96**	**0.91**	**0.88**	**0.84**	**0.82**	**0.81**	**0.79**	**0.79**	**0.78**	**0.78**	**0.77**	**0.77**	**0.76**	**0.76**	**0.76**	**0.76**	**0.75**	**0.75**
2	**1.78**	**1.41**	**1.27**	**1.20**	**1.15**	**1.09**	**1.06**	**1.04**	**1.02**	**1.01**	**1.00**	**0.99**	**0.99**	**0.98**	**0.98**	**0.97**	**0.97**	**0.97**	**0.96**	**0.96**
3	**2.12**	**1.63**	**1.45**	**1.36**	**1.30**	**1.23**	**1.19**	**1.16**	**1.14**	**1.13**	**1.12**	**1.11**	**1.11**	**1.10**	**1.09**	**1.08**	**1.08**	**1.08**	**1.07**	**1.07**
4	**2.39**	**1.79**	**1.58**	**1.47**	**1.41**	**1.33**	**1.28**	**1.25**	**1.23**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**	**1.17**	**1.16**	**1.16**	**1.15**	**1.15**	**1.14**
5	**2.62**	**1.92**	**1.68**	**1.56**	**1.49**	**1.40**	**1.35**	**1.31**	**1.29**	**1.27**	**1.26**	**1.25**	**1.24**	**1.23**	**1.22**	**1.22**	**1.21**	**1.21**	**1.20**	**1.20**
8	3.14	**2.21**	**1.90**	**1.75**	**1.66**	**1.55**	**1.49**	**1.45**	**1.42**	**1.40**	**1.38**	**1.37**	**1.36**	**1.35**	**1.34**	**1.33**	**1.33**	**1.32**	**1.31**	**1.31**
12	3.64	**2.47**	**2.09**	**1.91**	**1.80**	**1.68**	**1.61**	**1.56**	**1.53**	**1.50**	**1.49**	**1.47**	**1.46**	**1.45**	**1.44**	**1.43**	**1.42**	**1.42**	**1.41**	**1.40**
16	4.05	**2.66**	**2.23**	**2.03**	**1.91**	**1.77**	**1.69**	**1.64**	**1.60**	**1.57**	**1.56**	**1.54**	**1.53**	**1.51**	**1.50**	**1.49**	**1.49**	**1.48**	**1.47**	**1.46**
20	4.38	**2.82**	**2.34**	**2.12**	**1.99**	**1.84**	**1.76**	**1.70**	**1.66**	**1.63**	**1.61**	**1.59**	**1.58**	**1.56**	**1.55**	**1.54**	**1.53**	**1.53**	**1.52**	**1.51**
30	5.06	3.11	**2.55**	**2.29**	**2.13**	**1.96**	**1.87**	**1.80**	**1.76**	**1.73**	**1.70**	**1.69**	**1.67**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**	**1.59**
40	5.59	3.33	**2.70**	**2.41**	**2.24**	**2.05**	**1.95**	**1.88**	**1.83**	**1.79**	**1.77**	**1.75**	**1.74**	**1.71**	**1.70**	**1.69**	**1.68**	**1.67**	**1.66**	**1.65**
50	6.04	3.51	**2.82**	**2.50**	**2.32**	**2.12**	**2.01**	**1.93**	**1.88**	**1.85**	**1.82**	**1.80**	**1.78**	**1.76**	**1.75**	**1.73**	**1.72**	**1.72**	**1.70**	**1.69**
60	6.43	3.67	**2.92**	**2.58**	**2.39**	**2.18**	**2.06**	**1.98**	**1.92**	**1.89**	**1.86**	**1.84**	**1.82**	**1.80**	**1.78**	**1.77**	**1.76**	**1.75**	**1.74**	**1.73**
75	6.95	3.86	*3.04*	**2.68**	**2.47**	**2.24**	**2.12**	**2.03**	**1.98**	**1.94**	**1.91**	**1.89**	**1.87**	**1.85**	**1.83**	**1.81**	**1.80**	**1.80**	**1.78**	**1.77**
100	7.66	4.12	3.21	**2.81**	**2.58**	**2.33**	**2.20**	**2.11**	**2.04**	**2.00**	**1.97**	**1.95**	**1.93**	**1.90**	**1.88**	**1.87**	**1.86**	**1.85**	**1.84**	**1.82**
125	8.27	4.33	3.34	**2.91**	**2.66**	**2.40**	**2.26**	**2.16**	**2.10**	**2.05**	**2.02**	**2.00**	**1.98**	**1.95**	**1.93**	**1.91**	**1.90**	**1.89**	**1.88**	**1.87**
150	8.80	4.51	3.45	**2.99**	**2.73**	**2.46**	**2.31**	**2.21**	**2.14**	**2.09**	**2.06**	**2.03**	**2.01**	**1.98**	**1.96**	**1.95**	**1.94**	**1.93**	**1.91**	**1.90**
175	9.27	4.66	3.54	*3.06*	**2.79**	**2.50**	**2.35**	**2.24**	**2.17**	**2.13**	**2.09**	**2.06**	**2.04**	**2.01**	**1.99**	**1.98**	**1.96**	**1.95**	**1.94**	**1.93**
200	9.70	4.80	3.63	*3.12*	**2.84**	**2.55**	**2.39**	**2.28**	**2.20**	**2.15**	**2.12**	**2.09**	**2.07**	**2.04**	**2.02**	**2.00**	**1.99**	**1.98**	**1.96**	**1.95**

Table 19-17. κ-Multipliers for 1-of-1 Intrawell Prediction Limits on Means of Order 3 (1 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.65**	**1.35**	**1.24**	**1.17**	**1.13**	**1.08**	**1.05**	**1.03**	**1.01**	**1.00**	**1.00**	**0.99**	**0.99**	**0.98**	**0.97**	**0.97**	**0.97**	**0.96**	**0.96**	**0.96**
2	**2.24**	**1.74**	**1.55**	**1.45**	**1.39**	**1.32**	**1.28**	**1.24**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**	**1.16**	**1.16**	**1.15**	**1.15**	**1.15**	**1.14**
3	**2.64**	**1.98**	**1.74**	**1.62**	**1.54**	**1.45**	**1.40**	**1.36**	**1.34**	**1.32**	**1.31**	**1.30**	**1.29**	**1.28**	**1.27**	**1.26**	**1.26**	**1.25**	**1.25**	**1.24**
4	**2.96**	**2.15**	**1.87**	**1.73**	**1.64**	**1.54**	**1.49**	**1.44**	**1.42**	**1.40**	**1.38**	**1.37**	**1.36**	**1.35**	**1.34**	**1.33**	**1.33**	**1.32**	**1.31**	**1.31**
5	3.22	**2.29**	**1.98**	**1.82**	**1.73**	**1.62**	**1.55**	**1.51**	**1.48**	**1.45**	**1.44**	**1.43**	**1.42**	**1.40**	**1.39**	**1.38**	**1.38**	**1.37**	**1.37**	**1.36**
8	3.83	**2.60**	**2.21**	**2.01**	**1.90**	**1.76**	**1.69**	**1.63**	**1.60**	**1.57**	**1.55**	**1.54**	**1.53**	**1.51**	**1.50**	**1.49**	**1.48**	**1.48**	**1.47**	**1.46**
12	4.43	**2.89**	**2.41**	**2.18**	**2.04**	**1.89**	**1.81**	**1.74**	**1.70**	**1.67**	**1.65**	**1.64**	**1.62**	**1.60**	**1.59**	**1.58**	**1.57**	**1.57**	**1.56**	**1.55**
16	4.91	**3.10**	**2.56**	**2.30**	**2.15**	**1.98**	**1.89**	**1.82**	**1.77**	**1.74**	**1.72**	**1.70**	**1.69**	**1.67**	**1.65**	**1.64**	**1.63**	**1.63**	**1.61**	**1.61**
20	5.31	3.27	**2.67**	**2.39**	**2.23**	**2.05**	**1.95**	**1.87**	**1.83**	**1.79**	**1.77**	**1.75**	**1.74**	**1.71**	**1.70**	**1.69**	**1.68**	**1.67**	**1.66**	**1.65**
30	6.11	3.60	**2.89**	**2.57**	**2.38**	**2.17**	**2.06**	**1.98**	**1.92**	**1.89**	**1.86**	**1.84**	**1.82**	**1.80**	**1.78**	**1.77**	**1.76**	**1.75**	**1.74**	**1.73**
40	6.75	3.85	**3.05**	**2.69**	**2.49**	**2.26**	**2.14**	**2.05**	**1.99**	**1.95**	**1.92**	**1.90**	**1.88**	**1.86**	**1.84**	**1.83**	**1.82**	**1.81**	**1.79**	**1.78**
50	7.28	4.05	**3.18**	**2.79**	**2.57**	**2.33**	**2.20**	**2.10**	**2.04**	**2.00**	**1.97**	**1.95**	**1.93**	**1.90**	**1.88**	**1.87**	**1.86**	**1.85**	**1.84**	**1.82**
60	7.75	4.22	*3.29*	**2.87**	**2.64**	**2.39**	**2.25**	**2.15**	**2.09**	**2.04**	**2.01**	**1.99**	**1.97**	**1.94**	**1.92**	**1.90**	**1.89**	**1.88**	**1.87**	**1.86**
75	8.36	4.43	3.42	**2.98**	**2.73**	**2.45**	**2.31**	**2.20**	**2.14**	**2.09**	**2.06**	**2.03**	**2.01**	**1.98**	**1.96**	**1.95**	**1.94**	**1.93**	**1.91**	**1.90**
100	9.22	4.72	3.60	**3.11**	**2.84**	**2.54**	**2.39**	**2.27**	**2.20**	**2.15**	**2.12**	**2.09**	**2.07**	**2.04**	**2.02**	**2.00**	**1.99**	**1.98**	**1.96**	**1.95**
125	9.95	4.96	3.74	*3.22*	**2.92**	**2.61**	**2.45**	**2.33**	**2.25**	**2.20**	**2.17**	**2.14**	**2.11**	**2.08**	**2.06**	**2.04**	**2.03**	**2.02**	**2.00**	**1.99**
150	10.58	5.16	3.86	*3.30*	**3.00**	**2.67**	**2.50**	**2.37**	**2.30**	**2.24**	**2.20**	**2.17**	**2.15**	**2.12**	**2.09**	**2.07**	**2.06**	**2.05**	**2.03**	**2.02**
175	11.14	5.33	3.96	*3.38*	**3.06**	**2.72**	**2.54**	**2.41**	**2.33**	**2.27**	**2.23**	**2.20**	**2.18**	**2.14**	**2.12**	**2.10**	**2.09**	**2.08**	**2.06**	**2.04**
200	11.65	5.49	4.05	3.44	**3.11**	**2.76**	**2.58**	**2.44**	**2.36**	**2.30**	**2.26**	**2.23**	**2.21**	**2.17**	**2.14**	**2.13**	**2.11**	**2.10**	**2.08**	**2.07**

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Table 19-17. κ-Multipliers for 1-of-1 Intrawell Prediction Limits on Means of Order 3 (1 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.03**	**1.65**	**1.50**	**1.42**	**1.36**	**1.30**	**1.26**	**1.23**	**1.22**	**1.20**	**1.19**	**1.18**	**1.18**	**1.17**	**1.16**	**1.16**	**1.15**	**1.15**	**1.14**	**1.14**
2	**2.71**	**2.06**	**1.82**	**1.70**	**1.62**	**1.53**	**1.48**	**1.44**	**1.41**	**1.39**	**1.38**	**1.37**	**1.36**	**1.35**	**1.34**	**1.33**	**1.33**	**1.32**	**1.31**	**1.31**
3	**3.17**	**2.32**	**2.02**	**1.86**	**1.77**	**1.66**	**1.60**	**1.55**	**1.52**	**1.50**	**1.48**	**1.47**	**1.46**	**1.44**	**1.43**	**1.43**	**1.42**	**1.41**	**1.41**	**1.40**
4	3.53	**2.51**	**2.16**	**1.98**	**1.88**	**1.75**	**1.68**	**1.63**	**1.59**	**1.57**	**1.55**	**1.54**	**1.53**	**1.51**	**1.50**	**1.49**	**1.48**	**1.48**	**1.47**	**1.46**
5	3.83	**2.66**	**2.27**	**2.08**	**1.96**	**1.82**	**1.75**	**1.69**	**1.65**	**1.62**	**1.61**	**1.59**	**1.58**	**1.56**	**1.55**	**1.54**	**1.53**	**1.53**	**1.52**	**1.51**
8	4.54	**3.00**	**2.51**	**2.27**	**2.13**	**1.97**	**1.88**	**1.81**	**1.77**	**1.74**	**1.72**	**1.70**	**1.69**	**1.67**	**1.65**	**1.64**	**1.63**	**1.63**	**1.61**	**1.61**
12	5.24	**3.31**	**2.73**	**2.45**	**2.28**	**2.09**	**1.99**	**1.92**	**1.87**	**1.83**	**1.81**	**1.79**	**1.77**	**1.75**	**1.74**	**1.72**	**1.72**	**1.71**	**1.70**	**1.69**
16	5.80	3.55	**2.88**	**2.57**	**2.39**	**2.18**	**2.07**	**1.99**	**1.94**	**1.90**	**1.87**	**1.85**	**1.84**	**1.81**	**1.79**	**1.78**	**1.77**	**1.76**	**1.75**	**1.74**
20	6.26	3.74	**3.01**	**2.67**	**2.47**	**2.25**	**2.13**	**2.05**	**1.99**	**1.95**	**1.92**	**1.90**	**1.88**	**1.86**	**1.84**	**1.83**	**1.82**	**1.81**	**1.79**	**1.78**
30	7.20	4.10	**3.24**	**2.85**	**2.63**	**2.38**	**2.25**	**2.15**	**2.08**	**2.04**	**2.01**	**1.99**	**1.97**	**1.94**	**1.92**	**1.90**	**1.89**	**1.88**	**1.87**	**1.86**
40	7.95	4.38	**3.42**	**2.98**	**2.74**	**2.47**	**2.32**	**2.22**	**2.15**	**2.10**	**2.07**	**2.05**	**2.02**	**2.00**	**1.97**	**1.96**	**1.95**	**1.94**	**1.92**	**1.91**
50	8.58	4.60	3.56	**3.09**	**2.82**	**2.54**	**2.39**	**2.27**	**2.20**	**2.15**	**2.12**	**2.09**	**2.07**	**2.04**	**2.02**	**2.00**	**1.99**	**1.98**	**1.96**	**1.95**
60	9.12	4.79	3.67	**3.17**	**2.90**	**2.59**	**2.43**	**2.32**	**2.24**	**2.19**	**2.16**	**2.13**	**2.11**	**2.07**	**2.05**	**2.03**	**2.02**	**2.01**	**1.99**	**1.98**
75	9.84	5.03	3.81	**3.28**	**2.98**	**2.66**	**2.50**	**2.37**	**2.29**	**2.24**	**2.20**	**2.17**	**2.15**	**2.12**	**2.09**	**2.07**	**2.06**	**2.05**	**2.03**	**2.02**
100	10.84	5.35	4.01	**3.42**	**3.10**	**2.75**	**2.57**	**2.44**	**2.36**	**2.30**	**2.26**	**2.23**	**2.21**	**2.17**	**2.14**	**2.13**	**2.11**	**2.10**	**2.08**	**2.07**
125	11.69	5.62	4.16	*3.53*	**3.19**	**2.83**	**2.63**	**2.50**	**2.41**	**2.35**	**2.31**	**2.27**	**2.25**	**2.21**	**2.18**	**2.17**	**2.15**	**2.14**	**2.12**	**2.10**
150	12.43	5.84	4.29	3.63	**3.27**	**2.88**	**2.68**	**2.54**	**2.45**	**2.39**	**2.34**	**2.31**	**2.28**	**2.24**	**2.22**	**2.20**	**2.18**	**2.17**	**2.15**	**2.13**
175	13.09	6.03	4.40	3.71	**3.33**	**2.93**	**2.73**	**2.58**	**2.48**	**2.42**	**2.37**	**2.34**	**2.31**	**2.27**	**2.24**	**2.22**	**2.21**	**2.20**	**2.17**	**2.16**
200	13.68	6.21	4.50	3.78	**3.39**	**2.97**	**2.76**	**2.61**	**2.51**	**2.45**	**2.40**	**2.37**	**2.34**	**2.30**	**2.27**	**2.25**	**2.23**	**2.22**	**2.20**	**2.18**

Table 19-17. κ-Multipliers for 1-of-1 Intrawell Prediction Limits on Means of Order 3 (2 COC, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.78**	**1.41**	**1.27**	**1.20**	**1.15**	**1.09**	**1.06**	**1.04**	**1.02**	**1.01**	**1.00**	**0.99**	**0.99**	**0.98**	**0.98**	**0.97**	**0.97**	**0.97**	**0.96**	**0.96**
2	**2.39**	**1.79**	**1.58**	**1.47**	**1.41**	**1.33**	**1.28**	**1.25**	**1.23**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**	**1.17**	**1.16**	**1.16**	**1.15**	**1.15**	**1.14**
3	**2.81**	**2.03**	**1.77**	**1.63**	**1.55**	**1.46**	**1.41**	**1.37**	**1.34**	**1.32**	**1.31**	**1.30**	**1.29**	**1.28**	**1.27**	**1.26**	**1.26**	**1.25**	**1.25**	**1.24**
4	3.14	**2.21**	**1.90**	**1.75**	**1.66**	**1.55**	**1.49**	**1.45**	**1.42**	**1.40**	**1.38**	**1.37**	**1.36**	**1.35**	**1.34**	**1.33**	**1.33**	**1.32**	**1.31**	**1.31**
5	3.41	**2.35**	**2.01**	**1.84**	**1.74**	**1.62**	**1.56**	**1.51**	**1.48**	**1.46**	**1.44**	**1.43**	**1.42**	**1.40**	**1.39**	**1.39**	**1.38**	**1.37**	**1.37**	**1.36**
8	4.05	**2.66**	**2.23**	**2.03**	**1.91**	**1.77**	**1.69**	**1.64**	**1.60**	**1.57**	**1.56**	**1.54**	**1.53**	**1.51**	**1.50**	**1.49**	**1.49**	**1.48**	**1.47**	**1.46**
12	4.68	**2.95**	**2.44**	**2.19**	**2.05**	**1.89**	**1.81**	**1.74**	**1.70**	**1.67**	**1.65**	**1.64**	**1.62**	**1.60**	**1.59**	**1.58**	**1.57**	**1.57**	**1.56**	**1.55**
16	5.17	3.16	**2.58**	**2.31**	**2.16**	**1.98**	**1.89**	**1.82**	**1.77**	**1.74**	**1.72**	**1.70**	**1.69**	**1.67**	**1.65**	**1.64**	**1.63**	**1.63**	**1.62**	**1.61**
20	5.59	3.33	**2.70**	**2.41**	**2.24**	**2.05**	**1.95**	**1.88**	**1.83**	**1.79**	**1.77**	**1.75**	**1.74**	**1.71**	**1.70**	**1.69**	**1.68**	**1.67**	**1.66**	**1.65**
30	6.43	3.67	**2.92**	**2.58**	**2.39**	**2.18**	**2.06**	**1.98**	**1.92**	**1.89**	**1.86**	**1.84**	**1.82**	**1.80**	**1.78**	**1.77**	**1.76**	**1.75**	**1.74**	**1.73**
40	7.10	3.92	*3.08*	**2.71**	**2.49**	**2.26**	**2.14**	**2.05**	**1.99**	**1.95**	**1.92**	**1.90**	**1.88**	**1.86**	**1.84**	**1.83**	**1.82**	**1.81**	**1.79**	**1.78**
50	7.66	4.12	3.21	**2.81**	**2.58**	**2.33**	**2.20**	**2.11**	**2.04**	**2.00**	**1.97**	**1.95**	**1.93**	**1.90**	**1.88**	**1.87**	**1.86**	**1.85**	**1.84**	**1.82**
60	8.15	4.29	3.32	**2.89**	**2.65**	**2.39**	**2.25**	**2.15**	**2.09**	**2.04**	**2.01**	**1.99**	**1.97**	**1.94**	**1.92**	**1.90**	**1.89**	**1.88**	**1.87**	**1.86**
75	8.80	4.51	3.45	**2.99**	**2.73**	**2.46**	**2.31**	**2.21**	**2.14**	**2.09**	**2.06**	**2.03**	**2.01**	**1.98**	**1.96**	**1.95**	**1.94**	**1.93**	**1.91**	**1.90**
100	9.70	4.80	3.63	*3.12*	**2.84**	**2.55**	**2.39**	**2.28**	**2.20**	**2.15**	**2.12**	**2.09**	**2.07**	**2.04**	**2.02**	**2.00**	**1.99**	**1.98**	**1.96**	**1.95**
125	10.46	5.04	3.77	3.23	**2.93**	**2.62**	**2.45**	**2.33**	**2.25**	**2.20**	**2.17**	**2.14**	**2.11**	**2.08**	**2.06**	**2.04**	**2.03**	**2.02**	**2.00**	**1.99**
150	11.12	5.24	3.89	3.32	*3.00*	**2.67**	**2.50**	**2.37**	**2.30**	**2.24**	**2.20**	**2.17**	**2.15**	**2.12**	**2.09**	**2.07**	**2.06**	**2.05**	**2.03**	**2.02**
175	11.71	5.42	3.99	3.39	*3.06*	**2.72**	**2.54**	**2.41**	**2.33**	**2.28**	**2.23**	**2.20**	**2.18**	**2.15**	**2.12**	**2.10**	**2.09**	**2.08**	**2.06**	**2.04**
200	12.26	5.58	4.08	3.46	*3.12*	**2.76**	**2.58**	**2.44**	**2.36**	**2.30**	**2.26**	**2.23**	**2.21**	**2.17**	**2.14**	**2.13**	**2.11**	**2.10**	**2.08**	**2.07**

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Table 19-17. κ-Multipliers for 1-of-1 Intrawell Prediction Limits on Means of Order 3 (2 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.24**	**1.74**	**1.55**	**1.45**	**1.39**	**1.32**	**1.28**	**1.24**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**	**1.16**	**1.16**	**1.15**	**1.15**	**1.15**	**1.14**
2	**2.96**	**2.15**	**1.87**	**1.73**	**1.64**	**1.54**	**1.49**	**1.44**	**1.42**	**1.40**	**1.38**	**1.37**	**1.36**	**1.35**	**1.34**	**1.33**	**1.33**	**1.32**	**1.31**	**1.31**
3	3.44	**2.41**	**2.07**	**1.89**	**1.79**	**1.67**	**1.61**	**1.56**	**1.52**	**1.50**	**1.48**	**1.47**	**1.46**	**1.45**	**1.43**	**1.43**	**1.42**	**1.42**	**1.41**	**1.40**
4	3.83	**2.60**	**2.21**	**2.01**	**1.90**	**1.76**	**1.69**	**1.63**	**1.60**	**1.57**	**1.55**	**1.54**	**1.53**	**1.51**	**1.50**	**1.49**	**1.48**	**1.48**	**1.47**	**1.46**
5	4.15	**2.76**	**2.32**	**2.10**	**1.98**	**1.83**	**1.75**	**1.69**	**1.65**	**1.63**	**1.61**	**1.59**	**1.58**	**1.56**	**1.55**	**1.54**	**1.53**	**1.53**	**1.52**	**1.51**
8	4.91	**3.10**	**2.56**	**2.30**	**2.15**	**1.98**	**1.89**	**1.82**	**1.77**	**1.74**	**1.72**	**1.70**	**1.69**	**1.67**	**1.65**	**1.64**	**1.63**	**1.63**	**1.61**	**1.61**
12	5.65	3.42	**2.77**	**2.47**	**2.30**	**2.10**	**2.00**	**1.92**	**1.87**	**1.84**	**1.81**	**1.79**	**1.78**	**1.75**	**1.74**	**1.72**	**1.72**	**1.71**	**1.70**	**1.69**
16	6.25	3.65	**2.93**	**2.59**	**2.40**	**2.19**	**2.08**	**1.99**	**1.94**	**1.90**	**1.87**	**1.85**	**1.84**	**1.81**	**1.80**	**1.78**	**1.77**	**1.76**	**1.75**	**1.74**
20	6.75	3.85	**3.05**	**2.69**	**2.49**	**2.26**	**2.14**	**2.05**	**1.99**	**1.95**	**1.92**	**1.90**	**1.88**	**1.86**	**1.84**	**1.83**	**1.82**	**1.81**	**1.79**	**1.78**
30	7.75	4.22	*3.29*	**2.87**	**2.64**	**2.39**	**2.25**	**2.15**	**2.09**	**2.04**	**2.01**	**1.99**	**1.97**	**1.94**	**1.92**	**1.90**	**1.89**	**1.88**	**1.87**	**1.86**
40	8.55	4.50	3.46	**3.01**	**2.75**	**2.47**	**2.33**	**2.22**	**2.15**	**2.11**	**2.07**	**2.05**	**2.03**	**2.00**	**1.97**	**1.96**	**1.95**	**1.94**	**1.92**	**1.91**
50	9.22	4.72	3.60	**3.11**	**2.84**	**2.54**	**2.39**	**2.27**	**2.20**	**2.15**	**2.12**	**2.09**	**2.07**	**2.04**	**2.02**	**2.00**	**1.99**	**1.98**	**1.96**	**1.95**
60	9.81	4.92	3.72	**3.20**	**2.91**	**2.60**	**2.44**	**2.32**	**2.24**	**2.19**	**2.16**	**2.13**	**2.11**	**2.07**	**2.05**	**2.03**	**2.02**	**2.01**	**1.99**	**1.98**
75	10.58	5.16	3.86	*3.30*	**3.00**	**2.67**	**2.50**	**2.37**	**2.30**	**2.24**	**2.20**	**2.17**	**2.15**	**2.12**	**2.09**	**2.07**	**2.06**	**2.05**	**2.03**	**2.02**
100	11.65	5.49	4.05	3.44	**3.11**	**2.76**	**2.58**	**2.44**	**2.36**	**2.30**	**2.26**	**2.23**	**2.21**	**2.17**	**2.14**	**2.13**	**2.11**	**2.10**	**2.08**	**2.07**
125	12.55	5.76	4.21	3.56	**3.20**	**2.83**	**2.64**	**2.50**	**2.41**	**2.35**	**2.31**	**2.27**	**2.25**	**2.21**	**2.19**	**2.17**	**2.15**	**2.14**	**2.12**	**2.10**
150	13.33	5.98	4.34	3.65	*3.28*	**2.89**	**2.69**	**2.54**	**2.45**	**2.39**	**2.34**	**2.31**	**2.28**	**2.24**	**2.22**	**2.20**	**2.18**	**2.17**	**2.15**	**2.13**
175	14.04	6.18	4.45	3.73	*3.34*	**2.94**	**2.73**	**2.58**	**2.48**	**2.42**	**2.38**	**2.34**	**2.31**	**2.27**	**2.24**	**2.22**	**2.21**	**2.20**	**2.17**	**2.16**
200	14.69	6.36	4.54	3.80	*3.40*	**2.98**	**2.76**	**2.61**	**2.51**	**2.45**	**2.40**	**2.37**	**2.34**	**2.30**	**2.27**	**2.25**	**2.23**	**2.22**	**2.20**	**2.18**

Table 19-17. κ-Multipliers for 1-of-1 Intrawell Prediction Limits on Means of Order 3 (2 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.71**	**2.06**	**1.82**	**1.70**	**1.62**	**1.53**	**1.48**	**1.44**	**1.41**	**1.39**	**1.38**	**1.37**	**1.36**	**1.35**	**1.34**	**1.33**	**1.33**	**1.32**	**1.31**	**1.31**
2	3.53	**2.51**	**2.16**	**1.98**	**1.88**	**1.75**	**1.68**	**1.63**	**1.59**	**1.57**	**1.55**	**1.54**	**1.53**	**1.51**	**1.50**	**1.49**	**1.48**	**1.48**	**1.47**	**1.46**
3	4.10	**2.79**	**2.36**	**2.15**	**2.02**	**1.88**	**1.80**	**1.74**	**1.70**	**1.67**	**1.65**	**1.63**	**1.62**	**1.60**	**1.59**	**1.58**	**1.57**	**1.57**	**1.56**	**1.55**
4	4.54	**3.00**	**2.51**	**2.27**	**2.13**	**1.97**	**1.88**	**1.81**	**1.77**	**1.74**	**1.72**	**1.70**	**1.69**	**1.67**	**1.65**	**1.64**	**1.63**	**1.63**	**1.61**	**1.61**
5	4.92	**3.17**	**2.63**	**2.37**	**2.21**	**2.04**	**1.94**	**1.87**	**1.82**	**1.79**	**1.77**	**1.75**	**1.73**	**1.71**	**1.70**	**1.69**	**1.68**	**1.67**	**1.66**	**1.65**
8	5.80	3.55	**2.88**	**2.57**	**2.39**	**2.18**	**2.07**	**1.99**	**1.94**	**1.90**	**1.87**	**1.85**	**1.84**	**1.81**	**1.79**	**1.78**	**1.77**	**1.76**	**1.75**	**1.74**
12	6.67	3.90	**3.11**	**2.75**	**2.54**	**2.31**	**2.18**	**2.09**	**2.03**	**1.99**	**1.96**	**1.94**	**1.92**	**1.89**	**1.88**	**1.86**	**1.85**	**1.84**	**1.83**	**1.82**
16	7.36	4.16	**3.28**	**2.88**	**2.65**	**2.40**	**2.26**	**2.16**	**2.10**	**2.06**	**2.02**	**2.00**	**1.98**	**1.95**	**1.93**	**1.92**	**1.91**	**1.90**	**1.88**	**1.87**
20	7.95	4.38	**3.42**	**2.98**	**2.74**	**2.47**	**2.32**	**2.22**	**2.15**	**2.10**	**2.07**	**2.05**	**2.03**	**2.00**	**1.97**	**1.96**	**1.95**	**1.94**	**1.92**	**1.91**
30	9.12	4.79	3.67	**3.17**	**2.90**	**2.59**	**2.43**	**2.32**	**2.24**	**2.19**	**2.16**	**2.13**	**2.11**	**2.07**	**2.05**	**2.03**	**2.02**	**2.01**	**1.99**	**1.98**
40	10.06	5.10	3.86	**3.31**	**3.01**	**2.68**	**2.51**	**2.39**	**2.31**	**2.26**	**2.22**	**2.19**	**2.16**	**2.13**	**2.10**	**2.09**	**2.07**	**2.06**	**2.04**	**2.03**
50	10.84	5.35	4.01	**3.42**	**3.10**	**2.75**	**2.57**	**2.44**	**2.36**	**2.30**	**2.26**	**2.23**	**2.21**	**2.17**	**2.14**	**2.13**	**2.11**	**2.10**	**2.08**	**2.07**
60	11.53	5.57	4.13	*3.51*	**3.17**	**2.81**	**2.62**	**2.49**	**2.40**	**2.34**	**2.30**	**2.27**	**2.24**	**2.20**	**2.18**	**2.16**	**2.14**	**2.13**	**2.11**	**2.10**
75	12.43	5.84	4.29	3.63	**3.27**	**2.88**	**2.68**	**2.54**	**2.45**	**2.39**	**2.34**	**2.31**	**2.28**	**2.24**	**2.22**	**2.20**	**2.18**	**2.17**	**2.15**	**2.13**
100	13.68	6.21	4.50	3.78	**3.39**	**2.97**	**2.76**	**2.61**	**2.51**	**2.45**	**2.40**	**2.37**	**2.34**	**2.30**	**2.27**	**2.25**	**2.23**	**2.22**	**2.20**	**2.18**
125	14.75	6.51	4.66	3.89	*3.48*	**3.05**	**2.82**	**2.66**	**2.56**	**2.50**	**2.45**	**2.41**	**2.38**	**2.34**	**2.31**	**2.29**	**2.27**	**2.25**	**2.23**	**2.22**
150	15.66	6.76	4.80	3.99	*3.56*	**3.11**	**2.87**	**2.71**	**2.60**	**2.53**	**2.48**	**2.44**	**2.41**	**2.37**	**2.34**	**2.32**	**2.30**	**2.29**	**2.26**	**2.24**
175	16.49	6.98	4.92	4.08	*3.62*	**3.16**	**2.92**	**2.74**	**2.64**	**2.57**	**2.51**	**2.47**	**2.44**	**2.40**	**2.37**	**2.34**	**2.32**	**2.31**	**2.28**	**2.27**
200	17.24	7.18	5.03	4.15	3.68	**3.20**	**2.95**	**2.77**	**2.67**	**2.59**	**2.54**	**2.50**	**2.47**	**2.42**	**2.39**	**2.36**	**2.35**	**2.33**	**2.31**	**2.29**

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Table 19-17. κ-Multipliers for 1-of-1 Intrawell Prediction Limits on Means of Order 3 (5 COC, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.62**	**1.92**	**1.68**	**1.56**	**1.49**	**1.40**	**1.35**	**1.31**	**1.29**	**1.27**	**1.26**	**1.25**	**1.24**	**1.23**	**1.22**	**1.22**	**1.21**	**1.21**	**1.20**	**1.20**
2	3.41	**2.35**	**2.01**	**1.84**	**1.74**	**1.62**	**1.56**	**1.51**	**1.48**	**1.46**	**1.44**	**1.43**	**1.42**	**1.40**	**1.39**	**1.39**	**1.38**	**1.37**	**1.37**	**1.36**
3	3.95	**2.62**	**2.20**	**2.00**	**1.88**	**1.75**	**1.68**	**1.62**	**1.58**	**1.56**	**1.54**	**1.53**	**1.51**	**1.50**	**1.49**	**1.48**	**1.47**	**1.47**	**1.46**	**1.45**
4	4.38	**2.82**	**2.34**	**2.12**	**1.99**	**1.84**	**1.76**	**1.70**	**1.66**	**1.63**	**1.61**	**1.59**	**1.58**	**1.56**	**1.55**	**1.54**	**1.53**	**1.53**	**1.52**	**1.51**
5	4.74	**2.98**	**2.46**	**2.21**	**2.07**	**1.91**	**1.82**	**1.75**	**1.71**	**1.68**	**1.66**	**1.65**	**1.63**	**1.61**	**1.60**	**1.59**	**1.58**	**1.58**	**1.56**	**1.56**
8	5.59	3.33	**2.70**	**2.41**	**2.24**	**2.05**	**1.95**	**1.88**	**1.83**	**1.79**	**1.77**	**1.75**	**1.74**	**1.71**	**1.70**	**1.69**	**1.68**	**1.67**	**1.66**	**1.65**
12	6.43	3.67	**2.92**	**2.58**	**2.39**	**2.18**	**2.06**	**1.98**	**1.92**	**1.89**	**1.86**	**1.84**	**1.82**	**1.80**	**1.78**	**1.77**	**1.76**	**1.75**	**1.74**	**1.73**
16	7.10	3.92	*3.08*	**2.71**	**2.49**	**2.26**	**2.14**	**2.05**	**1.99**	**1.95**	**1.92**	**1.90**	**1.88**	**1.86**	**1.84**	**1.83**	**1.82**	**1.81**	**1.79**	**1.78**
20	7.66	4.12	3.21	**2.81**	**2.58**	**2.33**	**2.20**	**2.11**	**2.04**	**2.00**	**1.97**	**1.95**	**1.93**	**1.90**	**1.88**	**1.87**	**1.86**	**1.85**	**1.84**	**1.82**
30	8.80	4.51	3.45	**2.99**	**2.73**	**2.46**	**2.31**	**2.21**	**2.14**	**2.09**	**2.06**	**2.03**	**2.01**	**1.98**	**1.96**	**1.95**	**1.94**	**1.93**	**1.91**	**1.90**
40	9.70	4.80	3.63	*3.12*	**2.84**	**2.55**	**2.39**	**2.28**	**2.20**	**2.15**	**2.12**	**2.09**	**2.07**	**2.04**	**2.02**	**2.00**	**1.99**	**1.98**	**1.96**	**1.95**
50	10.46	5.04	3.77	3.23	**2.93**	**2.62**	**2.45**	**2.33**	**2.25**	**2.20**	**2.17**	**2.14**	**2.11**	**2.08**	**2.06**	**2.04**	**2.03**	**2.02**	**2.00**	**1.99**
60	11.12	5.24	3.89	3.32	*3.00*	**2.67**	**2.50**	**2.37**	**2.30**	**2.24**	**2.20**	**2.17**	**2.15**	**2.12**	**2.09**	**2.07**	**2.06**	**2.05**	**2.03**	**2.02**
75	11.99	5.50	4.04	3.43	*3.09*	**2.74**	**2.56**	**2.43**	**2.35**	**2.29**	**2.25**	**2.22**	**2.19**	**2.16**	**2.13**	**2.11**	**2.10**	**2.09**	**2.07**	**2.06**
100	13.21	5.85	4.23	3.57	*3.21*	**2.83**	**2.64**	**2.50**	**2.41**	**2.35**	**2.31**	**2.27**	**2.25**	**2.21**	**2.19**	**2.17**	**2.15**	**2.14**	**2.12**	**2.10**
125	14.23	6.13	4.39	3.68	3.30	**2.90**	**2.70**	**2.55**	**2.46**	**2.40**	**2.35**	**2.32**	**2.29**	**2.25**	**2.24**	**2.19**	**2.19**	**2.18**	**2.15**	**2.14**
150	15.14	6.36	4.52	3.77	3.37	**2.96**	**2.75**	**2.60**	**2.50**	**2.44**	**2.39**	**2.35**	**2.33**	**2.29**	**2.26**	**2.24**	**2.22**	**2.21**	**2.18**	**2.17**
175	15.92	6.57	4.63	3.85	3.44	*3.01*	**2.79**	**2.63**	**2.53**	**2.47**	**2.42**	**2.38**	**2.36**	**2.31**	**2.28**	**2.26**	**2.25**	**2.23**	**2.21**	**2.19**
200	16.65	6.75	4.73	3.92	3.49	*3.05*	**2.83**	**2.66**	**2.56**	**2.49**	**2.45**	**2.41**	**2.38**	**2.34**	**2.31**	**2.29**	**2.27**	**2.25**	**2.23**	**2.22**

Table 19-17. κ-Multipliers for 1-of-1 Intrawell Prediction Limits on Means of Order 3 (5 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.22	**2.29**	**1.98**	**1.82**	**1.73**	**1.62**	**1.55**	**1.51**	**1.48**	**1.45**	**1.44**	**1.43**	**1.42**	**1.40**	**1.39**	**1.38**	**1.38**	**1.37**	**1.37**	**1.36**
2	4.15	**2.76**	**2.32**	**2.10**	**1.98**	**1.83**	**1.75**	**1.69**	**1.65**	**1.63**	**1.61**	**1.59**	**1.58**	**1.56**	**1.55**	**1.54**	**1.53**	**1.53**	**1.52**	**1.51**
3	4.80	**3.05**	**2.52**	**2.27**	**2.12**	**1.96**	**1.87**	**1.80**	**1.76**	**1.73**	**1.70**	**1.69**	**1.67**	**1.65**	**1.64**	**1.63**	**1.62**	**1.61**	**1.60**	**1.59**
4	5.31	3.27	**2.67**	**2.39**	**2.23**	**2.05**	**1.95**	**1.87**	**1.83**	**1.79**	**1.77**	**1.75**	**1.74**	**1.71**	**1.70**	**1.69**	**1.68**	**1.67**	**1.66**	**1.65**
5	5.74	3.45	**2.79**	**2.49**	**2.31**	**2.12**	**2.01**	**1.93**	**1.88**	**1.84**	**1.82**	**1.80**	**1.78**	**1.76**	**1.75**	**1.73**	**1.72**	**1.72**	**1.70**	**1.69**
8	6.75	3.85	**3.05**	**2.69**	**2.49**	**2.26**	**2.14**	**2.05**	**1.99**	**1.95**	**1.92**	**1.90**	**1.88**	**1.86**	**1.84**	**1.83**	**1.82**	**1.81**	**1.79**	**1.78**
12	7.75	4.22	*3.29*	**2.87**	**2.64**	**2.39**	**2.25**	**2.15**	**2.09**	**2.04**	**2.01**	**1.99**	**1.97**	**1.94**	**1.92**	**1.90**	**1.89**	**1.88**	**1.87**	**1.86**
16	8.55	4.50	3.46	**3.01**	**2.75**	**2.47**	**2.33**	**2.22**	**2.15**	**2.11**	**2.07**	**2.05**	**2.03**	**2.00**	**1.97**	**1.96**	**1.95**	**1.94**	**1.92**	**1.91**
20	9.22	4.72	3.60	**3.11**	**2.84**	**2.54**	**2.39**	**2.27**	**2.20**	**2.15**	**2.12**	**2.09**	**2.07**	**2.04**	**2.02**	**2.00**	**1.99**	**1.98**	**1.96**	**1.95**
30	10.58	5.16	3.86	*3.30*	**3.00**	**2.67**	**2.50**	**2.37**	**2.30**	**2.24**	**2.20**	**2.17**	**2.15**	**2.12**	**2.09**	**2.07**	**2.06**	**2.05**	**2.03**	**2.02**
40	11.65	5.49	4.05	3.44	**3.11**	**2.76**	**2.58**	**2.44**	**2.36**	**2.30**	**2.26**	**2.23**	**2.21**	**2.17**	**2.14**	**2.13**	**2.11**	**2.10**	**2.08**	**2.07**
50	12.55	5.76	4.21	3.56	**3.20**	**2.83**	**2.64**	**2.50**	**2.41**	**2.35**	**2.31**	**2.27**	**2.25**	**2.21**	**2.19**	**2.17**	**2.15**	**2.14**	**2.12**	**2.10**
60	13.33	5.98	4.34	3.65	*3.28*	**2.89**	**2.69**	**2.54**	**2.45**	**2.39**	**2.34**	**2.31**	**2.28**	**2.24**	**2.22**	**2.20**	**2.18**	**2.17**	**2.15**	**2.13**
75	14.38	6.27	4.50	3.76	*3.37*	**2.96**	**2.75**	**2.59**	**2.50**	**2.44**	**2.39**	**2.35**	**2.33**	**2.29**	**2.26**	**2.24**	**2.22**	**2.21**	**2.18**	**2.17**
100	15.82	6.67	4.71	3.92	3.49	**3.05**	**2.83**	**2.66**	**2.56**	**2.50**	**2.45**	**2.41**	**2.38**	**2.34**	**2.31**	**2.29**	**2.27**	**2.25**	**2.23**	**2.22**
125	17.04	6.98	4.88	4.04	3.59	**3.12**	**2.89**	**2.72**	**2.61**	**2.54**	**2.49**	**2.45**	**2.42**	**2.38**	**2.35**	**2.31**	**2.31**	**2.29**	**2.27**	**2.25**
150	18.12	7.25	5.03	4.14	3.67	**3.18**	**2.94**	**2.76**	**2.65**	**2.58**	**2.53**	**2.49**	**2.46**	**2.41**	**2.37**	**2.35**	**2.34**	**2.32**	**2.30**	**2.28**
175	19.09	7.47	5.15	4.22	3.74	*3.23*	**2.98**	**2.80**	**2.69**	**2.61**	**2.56**	**2.51**	**2.48**	**2.44**	**2.40**	**2.38**	**2.36**	**2.35**	**2.32**	**2.30**
200	19.97	7.67	5.26	4.30	3.79	*3.28*	**3.02**	**2.83**	**2.72**	**2.64**	**2.59**	**2.54**	**2.51**	**2.46**	**2.43**	**2.40**	**2.38**	**2.37**	**2.34**	**2.32**

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Table 19-17. κ-Multipliers for 1-of-1 Intrawell Prediction Limits on Means of Order 3 (5 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.83	2.66	2.27	2.08	1.96	1.82	1.75	1.69	1.65	1.62	1.61	1.59	1.58	1.56	1.55	1.54	1.53	1.53	1.52	1.51
2	4.92	3.17	2.63	2.37	2.21	2.04	1.94	1.87	1.82	1.79	1.77	1.75	1.73	1.71	1.70	1.69	1.68	1.67	1.66	1.65
3	5.67	3.49	2.85	2.54	2.36	2.16	2.06	1.97	1.92	1.89	1.86	1.84	1.82	1.80	1.78	1.77	1.76	1.75	1.74	1.73
4	6.26	3.74	3.01	2.67	2.47	2.25	2.13	2.05	1.99	1.95	1.92	1.90	1.88	1.86	1.84	1.83	1.82	1.81	1.79	1.78
5	6.76	3.94	3.14	2.77	2.56	2.32	2.20	2.10	2.04	2.00	1.97	1.95	1.93	1.90	1.88	1.87	1.86	1.85	1.83	1.82
8	7.95	4.38	3.42	2.98	2.74	2.47	2.32	2.22	2.15	2.10	2.07	2.05	2.03	2.00	1.97	1.96	1.95	1.94	1.92	1.91
12	9.12	4.79	3.67	3.17	2.90	2.59	2.43	2.32	2.24	2.19	2.16	2.13	2.11	2.07	2.05	2.03	2.02	2.01	1.99	1.98
16	10.06	5.10	3.86	3.31	3.01	2.68	2.51	2.39	2.31	2.26	2.22	2.19	2.16	2.13	2.10	2.09	2.07	2.06	2.04	2.03
20	10.84	5.35	4.01	3.42	3.10	2.75	2.57	2.44	2.36	2.30	2.26	2.23	2.21	2.17	2.14	2.13	2.11	2.10	2.08	2.07
30	12.43	5.84	4.29	3.63	3.27	2.88	2.68	2.54	2.45	2.39	2.34	2.31	2.28	2.24	2.22	2.20	2.18	2.17	2.15	2.13
40	13.68	6.21	4.50	3.78	3.39	2.97	2.76	2.61	2.51	2.45	2.40	2.37	2.34	2.30	2.27	2.25	2.23	2.22	2.20	2.18
50	14.75	6.51	4.66	3.89	*3.48*	3.05	2.82	2.66	2.56	2.50	2.45	2.41	2.38	2.34	2.31	2.29	2.27	2.25	2.23	2.22
60	15.66	6.76	4.80	3.99	*3.56*	3.11	2.87	2.71	2.60	2.53	2.48	2.44	2.41	2.37	2.34	2.32	2.30	2.29	2.26	2.24
75	16.87	7.08	4.98	4.11	*3.65*	3.18	2.94	2.76	2.65	2.58	2.53	2.49	2.45	2.41	2.38	2.35	2.34	2.32	2.30	2.28
100	18.58	7.52	5.21	4.28	3.78	3.27	3.01	2.83	2.72	2.64	2.58	2.54	2.51	2.46	2.43	2.40	2.38	2.37	2.34	2.32
125	20.02	7.86	5.40	4.40	3.88	3.35	3.08	2.88	2.77	2.69	2.63	2.58	2.55	2.49	2.46	2.44	2.42	2.40	2.38	2.36
150	21.29	8.15	5.55	4.51	3.96	3.41	3.13	2.93	2.81	2.73	2.66	2.62	2.58	2.53	2.49	2.47	2.45	2.43	2.40	2.39
175	22.41	8.40	5.69	4.60	4.03	3.46	3.17	2.96	2.84	2.75	2.69	2.64	2.60	2.56	2.52	2.49	2.47	2.46	2.43	2.41
200	23.44	8.64	5.80	4.68	4.10	*3.50*	3.21	2.99	2.87	2.78	2.72	2.67	2.63	2.58	2.54	2.52	2.49	2.48	2.45	2.43

Table 19-17. κ-Multipliers for 1-of-1 Intrawell Prediction Limits on Means of Order 3 (10 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.41	2.35	2.01	1.84	1.74	1.62	1.56	1.51	1.48	1.46	1.44	1.43	1.42	1.40	1.39	1.39	1.38	1.37	1.37	1.36
2	4.38	2.82	2.34	2.12	1.99	1.84	1.76	1.70	1.66	1.63	1.61	1.59	1.58	1.56	1.55	1.54	1.53	1.53	1.52	1.51
3	5.06	3.11	2.55	2.29	2.13	1.96	1.87	1.80	1.76	1.73	1.70	1.69	1.67	1.65	1.64	1.63	1.62	1.61	1.60	1.59
4	5.59	3.33	2.70	2.41	2.24	2.05	1.95	1.88	1.83	1.79	1.77	1.75	1.74	1.71	1.70	1.69	1.68	1.67	1.66	1.65
5	6.04	3.51	2.82	2.50	2.32	2.12	2.01	1.93	1.88	1.85	1.82	1.80	1.78	1.76	1.75	1.73	1.72	1.72	1.70	1.69
8	7.10	3.92	*3.08*	2.71	2.49	2.26	2.14	2.05	1.99	1.95	1.92	1.90	1.88	1.86	1.84	1.83	1.82	1.81	1.79	1.78
12	8.16	4.29	3.32	2.89	2.65	2.39	2.25	2.15	2.09	2.04	2.01	1.99	1.97	1.94	1.92	1.90	1.89	1.88	1.87	1.86
16	8.99	4.57	3.49	*3.02*	2.76	2.48	2.33	2.22	2.15	2.11	2.07	2.05	2.03	2.00	1.97	1.96	1.95	1.94	1.92	1.91
20	9.70	4.80	3.63	*3.12*	2.84	2.55	2.39	2.28	2.20	2.15	2.12	2.09	2.07	2.04	2.02	2.00	1.99	1.98	1.96	1.95
30	11.12	5.24	3.89	3.32	*3.00*	2.67	2.50	2.37	2.30	2.24	2.20	2.17	2.15	2.12	2.09	2.07	2.06	2.05	2.03	2.02
40	12.25	5.57	4.08	3.46	*3.12*	2.76	2.58	2.44	2.36	2.30	2.26	2.23	2.21	2.17	2.15	2.13	2.11	2.10	2.08	2.07
50	13.20	5.84	4.23	3.57	*3.21*	2.83	2.64	2.50	2.41	2.35	2.31	2.27	2.25	2.21	2.19	2.17	2.15	2.14	2.12	2.10
60	14.03	6.07	4.36	3.66	3.28	2.89	2.69	2.54	2.45	2.39	2.34	2.31	2.28	2.24	2.22	2.19	2.18	2.17	2.15	2.13
75	15.12	6.36	4.53	3.78	3.37	2.96	2.75	2.59	2.50	2.44	2.39	2.35	2.33	2.29	2.26	2.24	2.22	2.21	2.18	2.17
100	16.66	6.77	4.74	3.93	3.50	*3.05*	2.83	2.66	2.56	2.49	2.45	2.41	2.38	2.34	2.31	2.29	2.27	2.25	2.23	2.22
125	17.96	7.09	4.91	4.05	3.59	*3.13*	2.89	2.70	2.61	2.54	2.49	2.45	2.42	2.38	2.35	2.32	2.31	2.29	2.27	2.25
150	19.09	7.37	5.06	4.15	3.67	*3.18*	2.94	2.76	2.65	2.58	2.53	2.49	2.46	2.41	2.38	2.35	2.34	2.32	2.30	2.28
175	20.10	7.61	5.18	4.24	3.74	*3.24*	*2.98*	2.80	2.69	2.61	2.56	2.52	2.48	2.44	2.40	2.38	2.36	2.35	2.32	2.30
200	21.01	7.82	5.29	4.31	3.80	*3.28*	*3.02*	2.83	2.72	2.64	2.58	2.54	2.51	2.46	2.43	2.40	2.38	2.37	2.34	2.32

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Table 19-17. κ-Multipliers for 1-of-1 Intrawell Prediction Limits on Means of Order 3 (10 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	4.15	**2.76**	**2.32**	**2.10**	**1.98**	**1.83**	**1.75**	**1.69**	**1.65**	**1.63**	**1.61**	**1.59**	**1.58**	**1.56**	**1.55**	**1.54**	**1.53**	**1.53**	**1.52**	**1.51**
2	5.31	3.27	**2.67**	**2.39**	**2.23**	**2.05**	**1.95**	**1.87**	**1.83**	**1.79**	**1.77**	**1.75**	**1.74**	**1.71**	**1.70**	**1.69**	**1.68**	**1.67**	**1.66**	**1.65**
3	6.11	3.60	**2.89**	**2.57**	**2.38**	**2.17**	**2.06**	**1.98**	**1.92**	**1.89**	**1.86**	**1.84**	**1.82**	**1.80**	**1.78**	**1.77**	**1.76**	**1.75**	**1.74**	**1.73**
4	6.75	3.85	**3.05**	**2.69**	**2.49**	**2.26**	**2.14**	**2.05**	**1.99**	**1.95**	**1.92**	**1.90**	**1.88**	**1.86**	**1.84**	**1.83**	**1.82**	**1.81**	**1.79**	**1.78**
5	7.28	4.05	**3.18**	**2.79**	**2.57**	**2.33**	**2.20**	**2.10**	**2.04**	**2.00**	**1.97**	**1.95**	**1.93**	**1.90**	**1.88**	**1.87**	**1.86**	**1.85**	**1.83**	**1.82**
8	8.55	4.50	3.46	**3.01**	**2.75**	**2.47**	**2.33**	**2.22**	**2.15**	**2.11**	**2.07**	**2.05**	**2.03**	**2.00**	**1.97**	**1.96**	**1.95**	**1.94**	**1.92**	**1.91**
12	9.81	4.92	3.72	**3.20**	**2.91**	**2.60**	**2.44**	**2.32**	**2.24**	**2.19**	**2.16**	**2.13**	**2.11**	**2.07**	**2.05**	**2.03**	**2.02**	**2.01**	**1.99**	**1.98**
16	10.81	5.23	3.90	*3.33*	**3.02**	**2.69**	**2.52**	**2.39**	**2.31**	**2.26**	**2.22**	**2.19**	**2.16**	**2.13**	**2.10**	**2.09**	**2.07**	**2.06**	**2.04**	**2.03**
20	11.65	5.49	4.05	3.44	**3.11**	**2.76**	**2.58**	**2.44**	**2.36**	**2.30**	**2.26**	**2.23**	**2.21**	**2.17**	**2.14**	**2.13**	**2.11**	**2.10**	**2.08**	**2.07**
30	13.33	5.98	4.34	3.65	*3.28*	**2.89**	**2.69**	**2.54**	**2.45**	**2.39**	**2.34**	**2.31**	**2.28**	**2.24**	**2.22**	**2.20**	**2.18**	**2.17**	**2.15**	**2.13**
40	14.68	6.36	4.54	3.80	*3.40*	**2.98**	**2.76**	**2.61**	**2.51**	**2.45**	**2.40**	**2.37**	**2.34**	**2.30**	**2.27**	**2.25**	**2.23**	**2.22**	**2.20**	**2.18**
50	15.82	6.67	4.71	3.91	3.49	**3.05**	**2.83**	**2.66**	**2.56**	**2.50**	**2.45**	**2.41**	**2.38**	**2.34**	**2.31**	**2.29**	**2.27**	**2.25**	**2.23**	**2.22**
60	16.82	6.92	4.85	4.01	3.57	**3.11**	**2.88**	**2.71**	**2.60**	**2.53**	**2.48**	**2.44**	**2.41**	**2.37**	**2.34**	**2.32**	**2.30**	**2.29**	**2.26**	**2.24**
75	18.13	7.25	5.03	4.14	3.67	**3.18**	**2.94**	**2.76**	**2.65**	**2.58**	**2.53**	**2.49**	**2.45**	**2.41**	**2.38**	**2.35**	**2.34**	**2.32**	**2.30**	**2.28**
100	19.98	7.66	5.27	4.30	3.79	*3.28*	**3.02**	**2.83**	**2.72**	**2.64**	**2.59**	**2.54**	**2.51**	**2.46**	**2.43**	**2.40**	**2.38**	**2.37**	**2.34**	**2.32**
125	21.50	8.03	5.45	4.42	3.89	*3.35*	**3.08**	**2.88**	**2.77**	**2.69**	**2.63**	**2.58**	**2.55**	**2.50**	**2.46**	**2.44**	**2.42**	**2.40**	**2.38**	**2.36**
150	22.85	8.33	5.61	4.53	3.98	*3.41*	**3.13**	**2.93**	**2.81**	**2.72**	**2.66**	**2.62**	**2.58**	**2.53**	**2.49**	**2.47**	**2.45**	**2.43**	**2.40**	**2.39**
175	24.02	8.61	5.74	4.63	4.04	*3.46*	**3.17**	**2.96**	**2.84**	**2.76**	**2.69**	**2.65**	**2.61**	**2.56**	**2.52**	**2.49**	**2.47**	**2.46**	**2.43**	**2.41**
200	25.20	8.85	5.80	4.70	4.11	*3.51*	*3.21*	**3.00**	**2.87**	**2.79**	**2.72**	**2.67**	**2.63**	**2.58**	**2.54**	**2.52**	**2.49**	**2.48**	**2.45**	**2.43**

Table 19-17. κ-Multipliers for 1-of-1 Intrawell Prediction Limits on Means of Order 3 (10 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	4.92	**3.17**	**2.63**	**2.37**	**2.21**	**2.04**	**1.94**	**1.87**	**1.82**	**1.79**	**1.77**	**1.75**	**1.73**	**1.71**	**1.70**	**1.69**	**1.68**	**1.67**	**1.66**	**1.65**
2	6.26	3.74	**3.01**	**2.67**	**2.47**	**2.25**	**2.13**	**2.05**	**1.99**	**1.95**	**1.92**	**1.90**	**1.88**	**1.86**	**1.84**	**1.83**	**1.82**	**1.81**	**1.79**	**1.78**
3	7.20	4.10	**3.24**	**2.85**	**2.63**	**2.38**	**2.25**	**2.15**	**2.08**	**2.04**	**2.01**	**1.99**	**1.97**	**1.94**	**1.92**	**1.90**	**1.89**	**1.88**	**1.87**	**1.86**
4	7.95	4.38	**3.42**	**2.98**	**2.74**	**2.47**	**2.32**	**2.22**	**2.15**	**2.10**	**2.07**	**2.05**	**2.03**	**2.00**	**1.97**	**1.96**	**1.95**	**1.94**	**1.92**	**1.91**
5	8.57	4.60	3.56	**3.09**	**2.82**	**2.54**	**2.39**	**2.27**	**2.20**	**2.15**	**2.12**	**2.09**	**2.07**	**2.04**	**2.02**	**2.00**	**1.99**	**1.98**	**1.96**	**1.95**
8	10.06	5.10	3.86	**3.31**	**3.01**	**2.68**	**2.51**	**2.39**	**2.31**	**2.26**	**2.22**	**2.19**	**2.16**	**2.13**	**2.10**	**2.09**	**2.07**	**2.06**	**2.04**	**2.03**
12	11.53	5.57	4.13	*3.51*	**3.17**	**2.81**	**2.62**	**2.49**	**2.40**	**2.34**	**2.30**	**2.27**	**2.24**	**2.20**	**2.18**	**2.16**	**2.14**	**2.13**	**2.11**	**2.10**
16	12.70	5.92	4.33	3.66	**3.29**	**2.90**	**2.70**	**2.56**	**2.46**	**2.40**	**2.36**	**2.32**	**2.30**	**2.26**	**2.23**	**2.21**	**2.19**	**2.18**	**2.16**	**2.14**
20	13.68	6.21	4.50	3.78	**3.39**	**2.98**	**2.76**	**2.61**	**2.51**	**2.45**	**2.40**	**2.37**	**2.34**	**2.30**	**2.27**	**2.25**	**2.23**	**2.22**	**2.20**	**2.18**
30	15.66	6.76	4.80	3.99	*3.56*	**3.11**	**2.87**	**2.71**	**2.60**	**2.53**	**2.48**	**2.44**	**2.41**	**2.37**	**2.34**	**2.32**	**2.30**	**2.29**	**2.26**	**2.24**
40	17.24	7.18	5.03	4.15	3.68	**3.20**	**2.95**	**2.77**	**2.67**	**2.59**	**2.54**	**2.50**	**2.47**	**2.42**	**2.39**	**2.36**	**2.35**	**2.33**	**2.31**	**2.29**
50	18.57	7.51	5.21	4.28	3.78	**3.27**	**3.01**	**2.83**	**2.72**	**2.64**	**2.58**	**2.54**	**2.51**	**2.46**	**2.43**	**2.40**	**2.38**	**2.37**	**2.34**	**2.32**
60	19.75	7.80	5.36	4.38	3.86	**3.33**	**3.07**	**2.87**	**2.76**	**2.68**	**2.62**	**2.57**	**2.54**	**2.49**	**2.46**	**2.43**	**2.41**	**2.40**	**2.37**	**2.35**
75	21.27	8.16	5.55	4.51	3.97	**3.41**	**3.13**	**2.92**	**2.81**	**2.72**	**2.66**	**2.62**	**2.58**	**2.53**	**2.49**	**2.47**	**2.45**	**2.43**	**2.40**	**2.39**
100	23.44	8.64	5.80	4.68	4.10	*3.50*	**3.21**	**2.99**	**2.87**	**2.78**	**2.72**	**2.67**	**2.63**	**2.58**	**2.54**	**2.52**	**2.49**	**2.48**	**2.45**	**2.43**
125	25.25	9.04	5.99	4.82	4.20	*3.58*	**3.27**	**3.05**	**2.92**	**2.83**	**2.76**	**2.71**	**2.67**	**2.62**	**2.58**	**2.55**	**2.53**	**2.51**	**2.48**	**2.46**
150	26.84	9.38	6.14	4.94	4.29	*3.64*	**3.32**	**3.11**	**2.96**	**2.86**	**2.80**	**2.75**	**2.71**	**2.65**	**2.61**	**2.58**	**2.56**	**2.54**	**2.51**	**2.49**
175	28.24	9.70	6.27	5.03	4.37	*3.70*	**3.36**	**3.14**	**3.00**	**2.89**	**2.83**	**2.77**	**2.73**	**2.67**	**2.63**	**2.60**	**2.58**	**2.56**	**2.53**	**2.51**
200	29.53	9.96	6.39	5.11	4.43	*3.74*	**3.40**	**3.18**	**3.02**	**2.92**	**2.85**	**2.80**	**2.76**	**2.70**	**2.66**	**2.63**	**2.60**	**2.58**	**2.55**	**2.53**

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Table 19-17. κ-Multipliers for 1-of-1 Intrawell Prediction Limits on Means of Order 3 (20 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	4.38	2.82	2.34	2.12	1.99	1.84	1.76	1.70	1.66	1.63	1.61	1.59	1.58	1.56	1.55	1.54	1.53	1.53	1.52	1.51
2	5.59	3.33	2.70	2.41	2.24	2.05	1.95	1.88	1.83	1.79	1.77	1.75	1.74	1.71	1.70	1.69	1.68	1.67	1.66	1.65
3	6.44	3.67	2.92	2.58	2.39	2.18	2.06	1.98	1.92	1.89	1.86	1.84	1.82	1.80	1.78	1.77	1.76	1.75	1.74	1.73
4	7.10	3.92	*3.08*	2.71	2.49	2.26	2.14	2.05	1.99	1.95	1.92	1.90	1.88	1.86	1.84	1.83	1.82	1.81	1.79	1.78
5	7.67	4.12	3.21	2.81	2.58	2.33	2.20	2.11	2.04	2.00	1.97	1.95	1.93	1.90	1.88	1.87	1.86	1.85	1.84	1.82
8	8.99	4.57	3.49	*3.02*	2.76	2.48	2.33	2.22	2.15	2.11	2.07	2.05	2.03	2.00	1.97	1.96	1.95	1.94	1.92	1.91
12	10.32	5.00	3.74	*3.21*	2.92	2.60	2.44	2.32	2.25	2.19	2.16	2.13	2.11	2.07	2.05	2.03	2.02	2.01	1.99	1.98
16	11.37	5.32	3.93	3.35	*3.03*	2.69	2.52	2.39	2.31	2.26	2.22	2.19	2.16	2.13	2.10	2.09	2.07	2.06	2.04	2.03
20	12.25	5.58	4.08	3.46	*3.12*	2.76	2.58	2.44	2.36	2.30	2.26	2.23	2.21	2.17	2.14	2.13	2.11	2.10	2.08	2.07
30	14.04	6.08	4.36	3.66	3.28	2.89	2.69	2.54	2.45	2.39	2.34	2.31	2.28	2.24	2.22	2.20	2.18	2.17	2.15	2.13
40	15.47	6.46	4.58	3.81	3.40	*2.98*	2.77	2.61	2.51	2.45	2.40	2.37	2.34	2.30	2.27	2.25	2.23	2.22	2.19	2.18
50	16.66	6.77	4.74	3.93	3.50	*3.05*	2.83	2.66	2.57	2.50	2.45	2.41	2.38	2.34	2.31	2.29	2.27	2.25	2.23	2.22
60	17.71	7.03	4.88	4.03	3.58	*3.11*	2.88	2.71	2.60	2.54	2.48	2.44	2.41	2.37	2.34	2.32	2.30	2.29	2.26	2.24
75	19.07	7.36	5.05	4.15	3.67	*3.19*	2.94	2.76	2.65	2.58	2.53	2.49	2.46	2.41	2.38	2.35	2.33	2.32	2.30	2.28
100	21.01	7.82	5.30	4.31	3.80	*3.28*	*3.02*	2.83	2.72	2.64	2.58	2.54	2.51	2.46	2.43	2.40	2.38	2.37	2.34	2.32
125	22.68	8.17	5.48	4.44	3.90	3.35	*3.08*	2.88	2.77	2.69	2.63	2.58	2.55	2.50	2.46	2.44	2.42	2.40	2.38	2.36
150	24.08	8.53	5.65	4.55	3.98	3.42	*3.13*	2.93	2.81	2.72	2.66	2.61	2.58	2.53	2.49	2.47	2.45	2.43	2.40	2.38
175	25.31	8.79	5.78	4.64	4.05	3.46	*3.18*	*2.97*	2.84	2.75	2.69	2.65	2.61	2.56	2.52	2.49	2.47	2.46	2.43	2.41
200	26.37	9.05	5.89	4.72	4.11	3.52	*3.21*	*3.00*	2.87	2.78	2.72	2.67	2.64	2.58	2.54	2.52	2.49	2.48	2.45	2.43

Table 19-17. κ-Multipliers for 1-of-1 Intrawell Prediction Limits on Means of Order 3 (20 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	5.31	3.27	2.67	2.39	2.23	2.05	1.95	1.87	1.83	1.79	1.77	1.75	1.74	1.71	1.70	1.69	1.68	1.67	1.66	1.65
2	6.75	3.85	3.05	2.69	2.49	2.26	2.14	2.05	1.99	1.95	1.92	1.90	1.88	1.86	1.84	1.83	1.82	1.81	1.79	1.78
3	7.75	4.22	*3.29*	2.87	2.64	2.39	2.25	2.15	2.09	2.04	2.01	1.99	1.97	1.94	1.92	1.90	1.89	1.88	1.87	1.86
4	8.55	4.50	3.46	3.01	2.75	2.47	2.33	2.22	2.15	2.11	2.07	2.05	2.03	2.00	1.97	1.96	1.95	1.94	1.92	1.91
5	9.22	4.72	3.60	3.11	2.84	2.54	2.39	2.27	2.20	2.15	2.12	2.09	2.07	2.04	2.02	2.00	1.99	1.98	1.96	1.95
8	10.81	5.23	3.90	*3.34*	3.02	2.69	2.52	2.39	2.31	2.26	2.22	2.19	2.16	2.13	2.10	2.09	2.07	2.06	2.04	2.03
12	12.39	5.71	4.18	3.54	3.19	2.82	2.63	2.49	2.40	2.34	2.30	2.27	2.24	2.20	2.18	2.16	2.14	2.13	2.11	2.10
16	13.66	6.07	4.38	3.68	*3.30*	2.91	2.70	2.56	2.47	2.40	2.36	2.32	2.30	2.26	2.23	2.21	2.19	2.18	2.16	2.14
20	14.72	6.36	4.55	3.80	*3.40*	2.98	2.77	2.61	2.51	2.45	2.40	2.37	2.34	2.30	2.27	2.25	2.23	2.22	2.20	2.18
30	16.85	6.93	4.85	4.02	3.57	3.11	2.88	2.71	2.60	2.53	2.48	2.44	2.41	2.37	2.34	2.32	2.30	2.29	2.26	2.24
40	18.54	7.35	5.08	4.17	3.69	3.20	2.96	2.78	2.67	2.59	2.54	2.50	2.47	2.42	2.39	2.36	2.35	2.33	2.31	2.29
50	20.00	7.70	5.26	4.30	3.79	*3.28*	3.02	2.83	2.72	2.64	2.58	2.54	2.51	2.46	2.43	2.40	2.38	2.37	2.34	2.32
60	21.27	8.00	5.42	4.41	3.87	*3.34*	3.07	2.88	2.76	2.68	2.62	2.58	2.54	2.49	2.46	2.43	2.41	2.40	2.37	2.35
75	22.85	8.37	5.60	4.54	3.98	*3.41*	3.13	2.93	2.80	2.72	2.66	2.62	2.58	2.53	2.49	2.47	2.45	2.43	2.40	2.39
100	25.22	8.88	5.87	4.70	4.11	*3.51*	*3.21*	3.00	2.87	2.78	2.72	2.67	2.63	2.58	2.54	2.52	2.49	2.48	2.45	2.43
125	27.07	9.32	6.06	4.84	4.22	3.58	*3.27*	3.05	2.92	2.83	2.76	2.71	2.68	2.62	2.58	2.55	2.53	2.51	2.48	2.46
150	28.83	9.67	6.24	4.95	4.31	3.65	*3.32*	3.10	2.96	2.86	2.80	2.75	2.71	2.65	2.61	2.58	2.56	2.54	2.51	2.49
175	30.23	9.98	6.39	5.05	4.37	3.70	*3.37*	3.13	2.99	2.89	2.82	2.77	2.74	2.68	2.64	2.60	2.58	2.56	2.53	2.51
200	31.64	10.28	6.53	5.14	4.44	3.75	*3.41*	3.16	3.02	2.92	2.85	2.80	2.76	2.70	2.66	2.63	2.60	2.58	2.55	2.53

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Table 19-17. κ-Multipliers for 1-of-1 Intrawell Prediction Limits on Means of Order 3 (20 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	6.26	3.74	**3.01**	**2.67**	**2.47**	**2.25**	**2.13**	**2.05**	**1.99**	**1.95**	**1.92**	**1.90**	**1.88**	**1.86**	**1.84**	**1.83**	**1.82**	**1.81**	**1.79**	**1.78**
2	7.95	4.38	**3.42**	**2.98**	**2.74**	**2.47**	**2.32**	**2.22**	**2.15**	**2.10**	**2.07**	**2.05**	**2.03**	**2.00**	**1.97**	**1.96**	**1.95**	**1.94**	**1.92**	**1.91**
3	9.12	4.79	3.67	**3.17**	**2.90**	**2.59**	**2.44**	**2.32**	**2.24**	**2.19**	**2.16**	**2.13**	**2.11**	**2.07**	**2.05**	**2.03**	**2.02**	**2.01**	**1.99**	**1.98**
4	10.06	5.10	3.86	**3.31**	**3.01**	**2.68**	**2.51**	**2.39**	**2.31**	**2.25**	**2.22**	**2.19**	**2.16**	**2.13**	**2.10**	**2.09**	**2.07**	**2.06**	**2.04**	**2.03**
5	10.85	5.35	4.01	**3.42**	**3.10**	**2.75**	**2.57**	**2.44**	**2.36**	**2.30**	**2.26**	**2.23**	**2.21**	**2.17**	**2.14**	**2.13**	**2.11**	**2.10**	**2.08**	**2.07**
8	12.71	5.92	4.33	3.66	**3.29**	**2.90**	**2.70**	**2.56**	**2.46**	**2.40**	**2.36**	**2.32**	**2.30**	**2.26**	**2.23**	**2.21**	**2.19**	**2.18**	**2.16**	**2.14**
12	14.57	6.45	4.63	3.87	**3.46**	**3.03**	**2.81**	**2.65**	**2.55**	**2.49**	**2.44**	**2.40**	**2.37**	**2.33**	**2.30**	**2.28**	**2.26**	**2.25**	**2.22**	**2.21**
16	16.04	6.86	4.85	4.03	*3.59*	**3.13**	**2.89**	**2.72**	**2.62**	**2.55**	**2.50**	**2.46**	**2.43**	**2.38**	**2.35**	**2.33**	**2.31**	**2.30**	**2.27**	**2.25**
20	17.29	7.18	5.03	4.15	3.68	**3.20**	**2.95**	**2.78**	**2.67**	**2.59**	**2.54**	**2.50**	**2.47**	**2.42**	**2.39**	**2.36**	**2.35**	**2.33**	**2.31**	**2.29**
30	19.80	7.81	5.36	4.38	3.86	**3.33**	**3.07**	**2.87**	**2.76**	**2.68**	**2.62**	**2.57**	**2.54**	**2.49**	**2.46**	**2.43**	**2.41**	**2.40**	**2.37**	**2.35**
40	21.80	8.29	5.61	4.55	3.99	**3.43**	**3.14**	**2.94**	**2.82**	**2.74**	**2.68**	**2.63**	**2.59**	**2.54**	**2.50**	**2.48**	**2.46**	**2.44**	**2.41**	**2.39**
50	23.47	8.68	5.81	4.68	4.10	*3.50*	**3.21**	**3.00**	**2.87**	**2.78**	**2.72**	**2.67**	**2.63**	**2.58**	**2.54**	**2.51**	**2.49**	**2.48**	**2.45**	**2.43**
60	24.96	9.01	5.98	4.80	4.19	*3.57*	**3.26**	**3.04**	**2.91**	**2.82**	**2.75**	**2.71**	**2.67**	**2.61**	**2.57**	**2.54**	**2.52**	**2.50**	**2.48**	**2.46**
75	26.89	9.45	6.19	4.93	4.29	*3.64*	**3.32**	**3.10**	**2.96**	**2.86**	**2.80**	**2.75**	**2.71**	**2.65**	**2.61**	**2.58**	**2.56**	**2.54**	**2.51**	**2.49**
100	29.53	10.02	6.46	5.12	4.43	*3.74*	**3.41**	**3.16**	**3.02**	**2.92**	**2.85**	**2.80**	**2.76**	**2.70**	**2.66**	**2.63**	**2.60**	**2.58**	**2.55**	**2.53**
125	31.99	10.46	6.68	5.26	4.54	3.82	*3.47*	**3.22**	**3.07**	**2.97**	**2.89**	**2.84**	**2.80**	**2.74**	**2.69**	**2.66**	**2.64**	**2.62**	**2.58**	**2.56**
150	33.75	10.90	6.88	5.38	4.64	3.89	*3.52*	**3.26**	**3.11**	**3.00**	**2.93**	**2.87**	**2.83**	**2.77**	**2.72**	**2.69**	**2.66**	**2.65**	**2.61**	**2.59**
175	35.86	11.25	7.03	5.49	4.70	3.94	*3.56*	**3.30**	**3.14**	**3.03**	**2.96**	**2.90**	**2.86**	**2.79**	**2.75**	**2.71**	**2.69**	**2.67**	**2.63**	**2.61**
200	37.27	11.51	7.16	5.58	4.77	3.99	*3.60*	**3.33**	**3.17**	**3.06**	**2.98**	**2.92**	**2.88**	**2.81**	**2.77**	**2.73**	**2.71**	**2.69**	**2.65**	**2.63**

Table 19-17. κ-Multipliers for 1-of-1 Intrawell Prediction Limits on Means of Order 3 (40 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	5.59	3.33	**2.70**	**2.41**	**2.24**	**2.05**	**1.95**	**1.88**	**1.83**	**1.79**	**1.77**	**1.75**	**1.74**	**1.71**	**1.70**	**1.69**	**1.68**	**1.67**	**1.66**	**1.65**
2	7.10	3.92	*3.08*	**2.71**	**2.49**	**2.26**	**2.14**	**2.05**	**1.99**	**1.95**	**1.92**	**1.90**	**1.88**	**1.86**	**1.84**	**1.83**	**1.82**	**1.81**	**1.79**	**1.78**
3	8.16	4.29	3.32	**2.89**	**2.65**	**2.39**	**2.25**	**2.15**	**2.09**	**2.04**	**2.01**	**1.99**	**1.97**	**1.94**	**1.92**	**1.90**	**1.89**	**1.88**	**1.87**	**1.86**
4	8.99	4.57	3.49	*3.02*	**2.76**	**2.48**	**2.33**	**2.22**	**2.15**	**2.11**	**2.07**	**2.05**	**2.03**	**2.00**	**1.97**	**1.96**	**1.95**	**1.94**	**1.92**	**1.91**
5	9.70	4.80	3.63	*3.12*	**2.84**	**2.55**	**2.39**	**2.28**	**2.20**	**2.15**	**2.12**	**2.09**	**2.07**	**2.04**	**2.02**	**2.00**	**1.99**	**1.98**	**1.96**	**1.95**
8	11.37	5.32	3.93	3.35	*3.03*	**2.69**	**2.52**	**2.39**	**2.31**	**2.26**	**2.22**	**2.19**	**2.16**	**2.13**	**2.10**	**2.09**	**2.07**	**2.06**	**2.04**	**2.03**
12	13.03	5.80	4.21	3.55	*3.19*	**2.82**	**2.63**	**2.49**	**2.40**	**2.34**	**2.30**	**2.27**	**2.24**	**2.20**	**2.18**	**2.16**	**2.14**	**2.13**	**2.11**	**2.10**
16	14.35	6.16	4.41	3.69	3.31	**2.91**	**2.71**	**2.56**	**2.47**	**2.40**	**2.36**	**2.32**	**2.30**	**2.26**	**2.23**	**2.21**	**2.19**	**2.18**	**2.16**	**2.14**
20	15.46	6.46	4.57	3.81	3.40	*2.98*	**2.77**	**2.61**	**2.51**	**2.45**	**2.40**	**2.37**	**2.34**	**2.30**	**2.27**	**2.25**	**2.23**	**2.22**	**2.19**	**2.18**
30	17.71	7.03	4.88	4.03	3.58	*3.11*	**2.88**	**2.71**	**2.60**	**2.53**	**2.48**	**2.44**	**2.41**	**2.37**	**2.34**	**2.32**	**2.30**	**2.28**	**2.26**	**2.24**
40	19.51	7.46	5.11	4.19	3.70	*3.21*	**2.96**	**2.78**	**2.67**	**2.59**	**2.54**	**2.50**	**2.47**	**2.42**	**2.39**	**2.36**	**2.35**	**2.33**	**2.31**	**2.29**
50	21.01	7.82	5.30	4.31	3.80	*3.28*	*3.02*	**2.83**	**2.72**	**2.64**	**2.58**	**2.54**	**2.51**	**2.46**	**2.43**	**2.40**	**2.38**	**2.37**	**2.34**	**2.32**
60	22.32	8.12	5.45	4.42	3.88	3.34	*3.07*	**2.87**	**2.76**	**2.68**	**2.62**	**2.58**	**2.54**	**2.49**	**2.46**	**2.43**	**2.41**	**2.40**	**2.37**	**2.35**
75	24.08	8.50	5.64	4.54	3.98	3.41	*3.13*	**2.93**	**2.81**	**2.72**	**2.66**	**2.62**	**2.58**	**2.53**	**2.49**	**2.47**	**2.45**	**2.43**	**2.40**	**2.39**
100	26.48	9.02	5.90	4.72	4.11	3.51	*3.21*	*3.00*	**2.87**	**2.78**	**2.72**	**2.67**	**2.63**	**2.58**	**2.54**	**2.51**	**2.49**	**2.48**	**2.45**	**2.43**
125	28.54	9.43	6.11	4.86	4.22	3.59	*3.27*	*3.05*	**2.92**	**2.83**	**2.76**	**2.71**	**2.67**	**2.62**	**2.58**	**2.55**	**2.53**	**2.51**	**2.48**	**2.46**
150	30.35	9.80	6.28	4.97	4.31	3.65	*3.33*	*3.09*	*2.96*	**2.86**	**2.80**	**2.75**	**2.71**	**2.65**	**2.61**	**2.58**	**2.56**	**2.54**	**2.51**	**2.49**
175	31.88	10.11	6.43	5.07	4.38	3.70	3.37	*3.13*	*2.99*	**2.89**	**2.83**	**2.77**	**2.73**	**2.68**	**2.63**	**2.60**	**2.58**	**2.56**	**2.53**	**2.51**
200	33.40	10.40	6.56	5.16	4.45	3.75	3.41	*3.16*	*3.02*	**2.92**	**2.85**	**2.80**	**2.76**	**2.70**	**2.66**	**2.63**	**2.60**	**2.58**	**2.55**	**2.53**

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Table 19-17. κ-Multipliers for 1-of-1 Intrawell Prediction Limits on Means of Order 3 (40 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	6.75	3.85	**3.05**	**2.69**	**2.49**	**2.26**	**2.14**	**2.05**	**1.99**	**1.95**	**1.92**	**1.90**	**1.88**	**1.86**	**1.84**	**1.83**	**1.82**	**1.81**	**1.79**	**1.78**
2	8.55	4.50	3.46	**3.01**	**2.75**	**2.47**	**2.33**	**2.22**	**2.15**	**2.11**	**2.07**	**2.05**	**2.03**	**2.00**	**1.97**	**1.96**	**1.95**	**1.94**	**1.92**	**1.91**
3	9.81	4.92	3.72	**3.20**	**2.91**	**2.60**	**2.44**	**2.32**	**2.24**	**2.19**	**2.16**	**2.13**	**2.11**	**2.07**	**2.05**	**2.03**	**2.02**	**2.01**	**1.99**	**1.98**
4	10.81	5.23	3.90	*3.33*	**3.02**	**2.69**	**2.52**	**2.39**	**2.31**	**2.26**	**2.22**	**2.19**	**2.16**	**2.13**	**2.10**	**2.09**	**2.07**	**2.06**	**2.04**	**2.03**
5	11.66	5.49	4.05	3.44	**3.11**	**2.76**	**2.58**	**2.44**	**2.36**	**2.30**	**2.26**	**2.23**	**2.21**	**2.17**	**2.14**	**2.13**	**2.11**	**2.10**	**2.08**	**2.07**
8	13.65	6.07	4.38	3.68	*3.30*	**2.91**	**2.70**	**2.56**	**2.47**	**2.40**	**2.36**	**2.32**	**2.30**	**2.26**	**2.23**	**2.21**	**2.19**	**2.18**	**2.16**	**2.14**
12	15.64	6.61	4.68	3.89	3.47	**3.04**	**2.82**	**2.65**	**2.56**	**2.49**	**2.44**	**2.40**	**2.37**	**2.33**	**2.30**	**2.28**	**2.26**	**2.25**	**2.22**	**2.21**
16	17.23	7.02	4.90	4.05	3.60	**3.13**	**2.89**	**2.72**	**2.62**	**2.55**	**2.50**	**2.46**	**2.43**	**2.38**	**2.35**	**2.33**	**2.31**	**2.30**	**2.27**	**2.25**
20	18.56	7.35	5.08	4.17	3.69	**3.20**	**2.96**	**2.78**	**2.67**	**2.59**	**2.54**	**2.50**	**2.47**	**2.42**	**2.39**	**2.36**	**2.35**	**2.33**	**2.31**	**2.29**
30	21.25	8.00	5.42	4.40	3.87	*3.34*	**3.07**	**2.87**	**2.76**	**2.68**	**2.62**	**2.58**	**2.54**	**2.49**	**2.46**	**2.43**	**2.41**	**2.40**	**2.37**	**2.35**
40	23.41	8.49	5.67	4.57	4.00	*3.43*	**3.15**	**2.94**	**2.82**	**2.74**	**2.68**	**2.63**	**2.59**	**2.54**	**2.51**	**2.48**	**2.46**	**2.44**	**2.41**	**2.39**
50	25.22	8.89	5.86	4.71	4.11	*3.51*	*3.21*	**3.00**	**2.87**	**2.78**	**2.72**	**2.67**	**2.63**	**2.58**	**2.54**	**2.51**	**2.49**	**2.48**	**2.45**	**2.43**
60	26.81	9.23	6.03	4.82	4.19	3.57	*3.26*	**3.04**	**2.91**	**2.82**	**2.75**	**2.70**	**2.67**	**2.61**	**2.57**	**2.54**	**2.52**	**2.51**	**2.48**	**2.46**
75	28.89	9.66	6.24	4.95	4.30	3.65	*3.32*	**3.10**	**2.96**	**2.86**	**2.80**	**2.75**	**2.71**	**2.65**	**2.61**	**2.58**	**2.56**	**2.54**	**2.51**	**2.49**
100	31.76	10.24	6.53	5.14	4.44	3.75	*3.40*	**3.16**	**3.02**	**2.92**	**2.85**	**2.80**	**2.76**	**2.70**	**2.66**	**2.63**	**2.60**	**2.58**	**2.55**	**2.53**
125	34.22	10.72	6.75	5.29	4.55	3.82	*3.47*	*3.22*	**3.07**	**2.97**	**2.89**	**2.84**	**2.80**	**2.74**	**2.69**	**2.66**	**2.64**	**2.62**	**2.58**	**2.56**
150	36.33	11.13	6.94	5.41	4.64	3.89	*3.52*	*3.26*	**3.11**	**3.00**	**2.93**	**2.87**	**2.83**	**2.76**	**2.72**	**2.69**	**2.66**	**2.65**	**2.61**	**2.59**
175	38.32	11.48	7.10	5.51	4.72	3.94	*3.56*	*3.30*	**3.14**	**3.03**	**2.96**	**2.90**	**2.86**	**2.79**	**2.75**	**2.71**	**2.69**	**2.67**	**2.63**	**2.61**
200	40.08	11.81	7.25	5.60	4.79	3.99	3.60	*3.33*	**3.17**	**3.06**	**2.98**	**2.93**	**2.88**	**2.81**	**2.77**	**2.73**	**2.71**	**2.69**	**2.65**	**2.63**

Table 19-17. κ-Multipliers for 1-of-1 Intrawell Prediction Limits on Means of Order 3 (40 COC, Quarterly)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	7.95	4.38	**3.42**	**2.98**	**2.74**	**2.47**	**2.32**	**2.22**	**2.15**	**2.10**	**2.07**	**2.05**	**2.03**	**2.00**	**1.97**	**1.96**	**1.95**	**1.94**	**1.92**	**1.91**
2	10.06	5.10	3.86	**3.31**	**3.01**	**2.68**	**2.51**	**2.39**	**2.31**	**2.26**	**2.22**	**2.19**	**2.16**	**2.13**	**2.10**	**2.09**	**2.07**	**2.06**	**2.04**	**2.03**
3	11.53	5.57	4.13	*3.51*	**3.17**	**2.81**	**2.62**	**2.49**	**2.40**	**2.34**	**2.30**	**2.27**	**2.24**	**2.20**	**2.18**	**2.16**	**2.14**	**2.13**	**2.11**	**2.10**
4	12.71	5.92	4.33	3.66	**3.29**	**2.90**	**2.70**	**2.56**	**2.46**	**2.40**	**2.36**	**2.32**	**2.30**	**2.26**	**2.23**	**2.21**	**2.19**	**2.18**	**2.16**	**2.14**
5	13.70	6.21	4.50	3.78	**3.39**	**2.98**	**2.76**	**2.61**	**2.51**	**2.45**	**2.40**	**2.37**	**2.34**	**2.30**	**2.27**	**2.25**	**2.23**	**2.22**	**2.19**	**2.18**
8	16.04	6.85	4.85	4.03	*3.59*	**3.13**	**2.89**	**2.72**	**2.62**	**2.55**	**2.50**	**2.46**	**2.43**	**2.38**	**2.35**	**2.33**	**2.31**	**2.30**	**2.27**	**2.25**
12	18.37	7.46	5.18	4.25	3.76	**3.26**	**3.00**	**2.82**	**2.71**	**2.63**	**2.58**	**2.53**	**2.50**	**2.45**	**2.42**	**2.39**	**2.38**	**2.36**	**2.33**	**2.32**
16	20.23	7.92	5.42	4.42	3.89	**3.35**	**3.08**	**2.89**	**2.77**	**2.69**	**2.63**	**2.59**	**2.55**	**2.50**	**2.47**	**2.44**	**2.42**	**2.41**	**2.38**	**2.36**
20	21.80	8.29	5.61	4.55	3.99	**3.43**	**3.15**	**2.94**	**2.82**	**2.74**	**2.67**	**2.63**	**2.59**	**2.54**	**2.51**	**2.48**	**2.46**	**2.44**	**2.41**	**2.39**
30	24.96	9.02	5.97	4.79	4.18	*3.57*	**3.26**	**3.04**	**2.91**	**2.82**	**2.75**	**2.70**	**2.67**	**2.61**	**2.57**	**2.54**	**2.52**	**2.51**	**2.48**	**2.46**
40	27.48	9.57	6.24	4.97	4.32	*3.66*	**3.34**	**3.11**	**2.97**	**2.88**	**2.81**	**2.76**	**2.72**	**2.66**	**2.62**	**2.59**	**2.57**	**2.55**	**2.52**	**2.50**
50	29.59	10.01	6.46	5.12	4.43	*3.74*	**3.40**	**3.16**	**3.02**	**2.92**	**2.85**	**2.80**	**2.76**	**2.70**	**2.66**	**2.63**	**2.60**	**2.58**	**2.55**	**2.53**
60	31.46	10.39	6.64	5.24	4.52	3.81	**3.46**	**3.21**	**3.06**	**2.96**	**2.89**	**2.83**	**2.79**	**2.73**	**2.69**	**2.65**	**2.63**	**2.61**	**2.58**	**2.56**
75	33.87	10.88	6.87	5.38	4.63	3.88	*3.52*	**3.26**	**3.11**	**3.00**	**2.93**	**2.87**	**2.83**	**2.77**	**2.72**	**2.69**	**2.66**	**2.65**	**2.61**	**2.59**
100	37.32	11.53	7.18	5.58	4.78	3.99	*3.60*	**3.33**	**3.17**	**3.06**	**2.98**	**2.93**	**2.88**	**2.81**	**2.77**	**2.73**	**2.71**	**2.69**	**2.65**	**2.63**
125	40.20	12.07	7.43	5.73	4.89	4.07	*3.67*	**3.39**	**3.22**	**3.11**	**3.02**	**2.96**	**2.92**	**2.85**	**2.80**	**2.77**	**2.74**	**2.72**	**2.68**	**2.66**
150	42.66	12.51	7.63	5.87	4.99	4.13	*3.72*	**3.43**	**3.26**	**3.14**	**3.06**	**3.00**	**2.95**	**2.88**	**2.83**	**2.80**	**2.77**	**2.75**	**2.71**	**2.68**
175	45.00	12.92	7.81	5.98	5.07	4.19	*3.76*	*3.47*	**3.29**	**3.18**	**3.09**	**3.02**	**2.98**	**2.91**	**2.86**	**2.82**	**2.79**	**2.77**	**2.73**	**2.71**
200	47.11	13.27	7.97	6.08	5.14	4.24	*3.80*	*3.50*	**3.32**	**3.20**	**3.11**	**3.05**	**3.00**	**2.93**	**2.89**	**2.84**	**2.81**	**2.79**	**2.75**	**2.73**

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Table 19-18. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Means of Order 3 (1 COC, Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	0.67	0.53	0.46	0.42	0.40	0.37	0.35	0.34	0.33	0.32	0.31	0.31	0.31	0.30	0.30	0.29	0.29	0.29	0.29	0.29
2	1.04	0.80	0.70	0.64	0.61	0.56	0.54	0.52	0.50	0.49	0.49	0.48	0.47	0.47	0.46	0.46	0.46	0.45	0.45	0.45
3	1.28	0.96	0.84	0.77	0.72	0.67	0.64	0.61	0.60	0.59	0.58	0.57	0.56	0.56	0.55	0.55	0.54	0.54	0.54	0.53
4	1.47	1.08	0.93	0.85	0.80	0.74	0.71	0.68	0.66	0.65	0.64	0.63	0.62	0.62	0.61	0.60	0.60	0.60	0.59	0.59
5	1.62	1.17	1.01	0.92	0.86	0.80	0.76	0.73	0.71	0.70	0.68	0.68	0.67	0.66	0.65	0.65	0.64	0.64	0.64	0.63
8	1.97	1.38	1.17	1.06	0.99	0.91	0.87	0.83	0.81	0.79	0.78	0.77	0.76	0.75	0.74	0.74	0.73	0.73	0.72	0.72
12	2.31	1.56	1.31	1.18	1.10	1.01	0.95	0.91	0.89	0.87	0.86	0.84	0.84	0.82	0.81	0.81	0.80	0.80	0.79	0.79
16	2.58	1.69	1.41	1.26	1.17	1.07	1.02	0.97	0.94	0.92	0.91	0.90	0.89	0.87	0.86	0.86	0.85	0.85	0.84	0.83
20	2.80	1.80	1.48	1.33	1.23	1.12	1.06	1.02	0.99	0.96	0.95	0.94	0.93	0.91	0.90	0.89	0.89	0.88	0.88	0.87
30	3.24	2.01	1.63	1.45	1.34	1.22	1.15	1.09	1.06	1.04	1.02	1.01	1.00	0.98	0.97	0.96	0.95	0.95	0.94	0.93
40	3.60	2.16	1.74	1.53	1.42	1.28	1.21	1.15	1.11	1.09	1.07	1.05	1.04	1.03	1.01	1.00	1.00	0.99	0.98	0.98
50	3.89	2.28	1.82	1.60	1.47	1.33	1.25	1.19	1.15	1.13	1.11	1.09	1.08	1.06	1.05	1.04	1.03	1.03	1.01	1.01
60	4.15	2.39	1.89	1.66	1.52	1.37	1.29	1.23	1.18	1.16	1.14	1.12	1.11	1.09	1.08	1.07	1.06	1.05	1.04	1.03
75	4.48	2.52	1.98	1.73	1.58	1.42	1.33	1.27	1.22	1.19	1.17	1.16	1.14	1.12	1.11	1.10	1.09	1.08	1.07	1.07
100	4.95	2.70	2.09	1.82	1.66	1.48	1.39	1.32	1.27	1.24	1.22	1.20	1.19	1.17	1.15	1.14	1.13	1.12	1.11	1.11
125	5.35	*2.84*	2.19	1.89	1.72	1.53	1.43	1.36	1.31	1.28	1.25	1.24	1.22	1.20	1.18	1.17	1.16	1.16	1.14	1.14
150	5.69	2.96	2.26	1.95	1.77	1.58	1.47	1.39	1.34	1.31	1.28	1.26	1.25	1.23	1.21	1.20	1.19	1.18	1.17	1.16
175	6.00	3.07	2.33	2.00	1.81	1.61	1.50	1.42	1.37	1.33	1.31	1.29	1.27	1.25	1.23	1.22	1.21	1.20	1.19	1.18
200	6.28	3.16	2.39	2.04	1.85	1.64	1.53	1.44	1.39	1.35	1.33	1.31	1.29	1.27	1.25	1.24	1.23	1.22	1.21	1.20

Table 19-18. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Means of Order 3 (1 COC, Semi-Annual)

w/n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	0.95	0.75	0.67	0.62	0.59	0.55	0.53	0.51	0.50	0.49	0.48	0.48	0.47	0.47	0.46	0.46	0.45	0.45	0.45	0.45
2	1.36	1.04	0.91	0.84	0.79	0.73	0.70	0.67	0.66	0.64	0.64	0.63	0.62	0.61	0.61	0.60	0.60	0.60	0.59	0.59
3	1.64	1.21	1.05	0.96	0.90	0.83	0.80	0.76	0.74	0.73	0.72	0.71	0.70	0.69	0.69	0.68	0.68	0.67	0.67	0.66
4	1.85	1.33	1.14	1.04	0.98	0.90	0.86	0.83	0.80	0.79	0.78	0.77	0.76	0.75	0.74	0.74	0.73	0.73	0.72	0.72
5	2.02	1.43	1.22	1.11	1.04	0.96	0.91	0.87	0.85	0.83	0.82	0.81	0.80	0.79	0.78	0.78	0.77	0.77	0.76	0.76
8	2.43	1.65	1.38	1.25	1.17	1.07	1.01	0.97	0.94	0.92	0.91	0.90	0.89	0.87	0.86	0.86	0.85	0.85	0.84	0.83
12	2.83	1.85	1.53	1.37	1.27	1.16	1.10	1.05	1.02	1.00	0.98	0.97	0.96	0.94	0.93	0.92	0.92	0.91	0.90	0.90
16	3.14	2.00	1.63	1.46	1.35	1.23	1.16	1.11	1.07	1.05	1.03	1.02	1.01	0.99	0.98	0.97	0.96	0.96	0.95	0.94
20	3.41	2.12	1.72	1.52	1.41	1.28	1.20	1.15	1.11	1.09	1.07	1.05	1.04	1.02	1.01	1.00	1.00	0.99	0.98	0.97
30	3.94	2.34	1.87	1.65	1.52	1.37	1.29	1.22	1.18	1.16	1.14	1.12	1.11	1.09	1.08	1.07	1.06	1.05	1.04	1.03
40	4.35	2.51	1.98	1.74	1.59	1.43	1.34	1.28	1.23	1.20	1.18	1.17	1.15	1.13	1.12	1.11	1.10	1.09	1.08	1.07
50	4.70	2.65	2.07	1.81	1.65	1.48	1.39	1.32	1.27	1.24	1.22	1.20	1.19	1.17	1.15	1.14	1.13	1.12	1.11	1.10
60	5.01	2.76	2.15	1.87	1.70	1.52	1.42	1.35	1.30	1.27	1.25	1.23	1.21	1.19	1.18	1.17	1.16	1.15	1.14	1.13
75	5.41	*2.91*	2.24	1.94	1.76	1.57	1.47	1.39	1.34	1.31	1.28	1.26	1.25	1.23	1.21	1.20	1.19	1.18	1.17	1.16
100	5.97	3.11	2.37	2.03	1.84	1.64	1.53	1.44	1.39	1.35	1.33	1.31	1.29	1.27	1.25	1.24	1.23	1.22	1.21	1.20
125	6.45	3.27	2.46	2.11	1.91	1.69	1.57	1.48	1.43	1.39	1.36	1.34	1.32	1.30	1.28	1.27	1.26	1.25	1.24	1.23
150	6.86	3.40	2.55	2.17	1.96	1.73	1.61	1.52	1.46	1.42	1.39	1.37	1.35	1.32	1.31	1.29	1.28	1.27	1.26	1.25
175	7.22	3.52	2.62	2.22	2.00	1.76	1.64	1.54	1.48	1.44	1.41	1.39	1.37	1.34	1.33	1.31	1.30	1.29	1.28	1.27
200	7.56	3.63	2.68	2.27	2.04	1.79	1.66	1.57	1.51	1.46	1.43	1.41	1.39	1.36	1.34	1.33	1.32	1.31	1.30	1.28

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Table 19-18. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Means of Order 3 (1 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.22**	**0.97**	**0.86**	**0.80**	**0.77**	**0.72**	**0.69**	**0.67**	**0.65**	**0.64**	**0.63**	**0.62**	**0.62**	**0.61**	**0.61**	**0.60**	**0.60**	**0.60**	**0.59**	**0.59**
2	**1.68**	**1.27**	**1.11**	**1.02**	**0.96**	**0.89**	**0.85**	**0.82**	**0.80**	**0.78**	**0.77**	**0.76**	**0.76**	**0.75**	**0.74**	**0.73**	**0.73**	**0.73**	**0.72**	**0.72**
3	**1.99**	**1.45**	**1.25**	**1.14**	**1.07**	**0.99**	**0.94**	**0.91**	**0.88**	**0.86**	**0.85**	**0.84**	**0.83**	**0.82**	**0.81**	**0.81**	**0.80**	**0.80**	**0.79**	**0.79**
4	**2.23**	**1.58**	**1.35**	**1.23**	**1.15**	**1.06**	**1.01**	**0.96**	**0.94**	**0.92**	**0.90**	**0.89**	**0.89**	**0.87**	**0.86**	**0.86**	**0.85**	**0.85**	**0.84**	**0.83**
5	**2.43**	**1.69**	**1.43**	**1.29**	**1.21**	**1.11**	**1.05**	**1.01**	**0.98**	**0.96**	**0.95**	**0.93**	**0.92**	**0.91**	**0.90**	**0.89**	**0.89**	**0.88**	**0.87**	**0.87**
8	**2.91**	**1.93**	**1.60**	**1.44**	**1.34**	**1.22**	**1.15**	**1.10**	**1.07**	**1.05**	**1.03**	**1.01**	**1.00**	**0.99**	**0.98**	**0.97**	**0.96**	**0.96**	**0.95**	**0.94**
12	3.37	**2.14**	**1.75**	**1.56**	**1.44**	**1.31**	**1.24**	**1.18**	**1.14**	**1.12**	**1.10**	**1.08**	**1.07**	**1.05**	**1.04**	**1.03**	**1.02**	**1.02**	**1.01**	**1.00**
16	3.73	**2.31**	**1.86**	**1.65**	**1.52**	**1.38**	**1.30**	**1.23**	**1.19**	**1.17**	**1.14**	**1.13**	**1.12**	**1.10**	**1.08**	**1.07**	**1.07**	**1.06**	**1.05**	**1.04**
20	4.04	**2.44**	**1.95**	**1.72**	**1.58**	**1.43**	**1.34**	**1.27**	**1.23**	**1.20**	**1.18**	**1.16**	**1.15**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**
30	4.66	**2.69**	**2.12**	**1.85**	**1.69**	**1.52**	**1.42**	**1.35**	**1.30**	**1.27**	**1.25**	**1.23**	**1.21**	**1.19**	**1.18**	**1.17**	**1.16**	**1.15**	**1.14**	**1.13**
40	5.14	**2.87**	**2.24**	**1.94**	**1.77**	**1.58**	**1.48**	**1.40**	**1.35**	**1.32**	**1.29**	**1.27**	**1.26**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**
50	5.55	**3.02**	**2.33**	**2.02**	**1.83**	**1.63**	**1.52**	**1.44**	**1.39**	**1.35**	**1.33**	**1.31**	**1.29**	**1.27**	**1.25**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**
60	5.91	3.15	**2.41**	**2.08**	**1.89**	**1.67**	**1.56**	**1.47**	**1.42**	**1.38**	**1.35**	**1.33**	**1.32**	**1.29**	**1.27**	**1.26**	**1.25**	**1.24**	**1.23**	**1.22**
75	6.38	3.32	**2.51**	**2.15**	**1.95**	**1.72**	**1.60**	**1.51**	**1.46**	**1.42**	**1.39**	**1.37**	**1.35**	**1.32**	**1.31**	**1.29**	**1.28**	**1.27**	**1.26**	**1.25**
100	7.04	3.53	**2.65**	**2.25**	**2.03**	**1.79**	**1.66**	**1.56**	**1.50**	**1.46**	**1.43**	**1.41**	**1.39**	**1.36**	**1.34**	**1.33**	**1.32**	**1.31**	**1.30**	**1.28**
125	7.59	3.71	**2.75**	**2.33**	**2.09**	**1.84**	**1.70**	**1.60**	**1.54**	**1.50**	**1.47**	**1.44**	**1.42**	**1.39**	**1.37**	**1.36**	**1.35**	**1.34**	**1.32**	**1.31**
150	8.07	3.86	**2.84**	**2.40**	**2.15**	**1.88**	**1.74**	**1.64**	**1.57**	**1.53**	**1.49**	**1.47**	**1.45**	**1.42**	**1.40**	**1.38**	**1.37**	**1.36**	**1.35**	**1.33**
175	8.51	4.00	**2.92**	**2.45**	**2.19**	**1.92**	**1.77**	**1.66**	**1.60**	**1.55**	**1.52**	**1.49**	**1.47**	**1.44**	**1.42**	**1.40**	**1.39**	**1.38**	**1.36**	**1.35**
200	8.90	4.11	**2.98**	**2.50**	**2.23**	**1.95**	**1.80**	**1.69**	**1.62**	**1.57**	**1.53**	**1.51**	**1.49**	**1.46**	**1.44**	**1.42**	**1.41**	**1.40**	**1.38**	**1.37**

Table 19-18. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Means of Order 3 (2 COC, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.04**	**0.80**	**0.70**	**0.64**	**0.61**	**0.56**	**0.54**	**0.52**	**0.50**	**0.49**	**0.49**	**0.48**	**0.47**	**0.47**	**0.46**	**0.46**	**0.46**	**0.45**	**0.45**	**0.45**
2	**1.47**	**1.08**	**0.93**	**0.85**	**0.80**	**0.74**	**0.71**	**0.68**	**0.66**	**0.65**	**0.64**	**0.63**	**0.62**	**0.62**	**0.61**	**0.60**	**0.60**	**0.60**	**0.59**	**0.59**
3	**1.75**	**1.25**	**1.07**	**0.97**	**0.91**	**0.84**	**0.80**	**0.77**	**0.75**	**0.73**	**0.72**	**0.71**	**0.71**	**0.70**	**0.69**	**0.68**	**0.68**	**0.68**	**0.67**	**0.67**
4	**1.97**	**1.38**	**1.17**	**1.06**	**0.99**	**0.91**	**0.87**	**0.83**	**0.81**	**0.79**	**0.78**	**0.77**	**0.76**	**0.75**	**0.74**	**0.74**	**0.73**	**0.73**	**0.72**	**0.72**
5	**2.15**	**1.48**	**1.24**	**1.12**	**1.05**	**0.96**	**0.91**	**0.88**	**0.85**	**0.83**	**0.82**	**0.81**	**0.80**	**0.79**	**0.78**	**0.78**	**0.77**	**0.77**	**0.76**	**0.76**
8	**2.58**	**1.69**	**1.41**	**1.26**	**1.17**	**1.07**	**1.02**	**0.97**	**0.94**	**0.92**	**0.91**	**0.90**	**0.89**	**0.87**	**0.86**	**0.86**	**0.85**	**0.85**	**0.84**	**0.83**
12	2.99	**1.89**	**1.55**	**1.38**	**1.28**	**1.17**	**1.10**	**1.05**	**1.02**	**1.00**	**0.98**	**0.97**	**0.96**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.90**	**0.90**
16	3.32	**2.04**	**1.65**	**1.47**	**1.36**	**1.23**	**1.16**	**1.11**	**1.07**	**1.05**	**1.03**	**1.02**	**1.01**	**0.99**	**0.98**	**0.97**	**0.96**	**0.96**	**0.95**	**0.94**
20	3.60	**2.16**	**1.74**	**1.53**	**1.42**	**1.28**	**1.21**	**1.15**	**1.11**	**1.09**	**1.07**	**1.05**	**1.04**	**1.03**	**1.01**	**1.00**	**1.00**	**0.99**	**0.98**	**0.98**
30	4.15	**2.39**	**1.89**	**1.66**	**1.52**	**1.37**	**1.29**	**1.23**	**1.18**	**1.16**	**1.14**	**1.12**	**1.11**	**1.09**	**1.08**	**1.07**	**1.06**	**1.05**	**1.04**	**1.03**
40	4.58	**2.56**	**2.00**	**1.75**	**1.60**	**1.44**	**1.35**	**1.28**	**1.24**	**1.20**	**1.18**	**1.17**	**1.15**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**
50	4.95	**2.70**	**2.09**	**1.82**	**1.66**	**1.48**	**1.39**	**1.32**	**1.27**	**1.24**	**1.22**	**1.20**	**1.19**	**1.17**	**1.15**	**1.14**	**1.13**	**1.12**	**1.11**	**1.11**
60	5.27	*2.81*	**2.17**	**1.88**	**1.71**	**1.53**	**1.43**	**1.35**	**1.30**	**1.27**	**1.25**	**1.23**	**1.21**	**1.19**	**1.18**	**1.17**	**1.16**	**1.15**	**1.14**	**1.13**
75	5.69	2.96	**2.26**	**1.95**	**1.77**	**1.58**	**1.47**	**1.39**	**1.34**	**1.31**	**1.28**	**1.26**	**1.25**	**1.23**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**	**1.16**
100	6.28	3.16	**2.39**	**2.04**	**1.85**	**1.64**	**1.53**	**1.44**	**1.39**	**1.35**	**1.33**	**1.31**	**1.29**	**1.27**	**1.25**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**
125	6.77	3.33	**2.48**	**2.12**	**1.91**	**1.69**	**1.57**	**1.48**	**1.43**	**1.39**	**1.36**	**1.34**	**1.32**	**1.30**	**1.28**	**1.27**	**1.26**	**1.25**	**1.24**	**1.23**
150	7.21	3.46	**2.57**	**2.18**	**1.96**	**1.73**	**1.61**	**1.52**	**1.46**	**1.42**	**1.39**	**1.37**	**1.35**	**1.32**	**1.31**	**1.29**	**1.28**	**1.27**	**1.26**	**1.25**
175	7.59	3.58	**2.64**	**2.23**	**2.01**	**1.77**	**1.64**	**1.54**	**1.48**	**1.44**	**1.41**	**1.39**	**1.37**	**1.34**	**1.33**	**1.31**	**1.30**	**1.29**	**1.28**	**1.27**
200	7.94	3.69	*2.70*	**2.28**	**2.04**	**1.79**	**1.66**	**1.57**	**1.51**	**1.46**	**1.43**	**1.41**	**1.39**	**1.36**	**1.34**	**1.33**	**1.32**	**1.31**	**1.30**	**1.28**

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Table 19-18. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Means of Order 3 (2 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.36**	**1.04**	**0.91**	**0.84**	**0.79**	**0.73**	**0.70**	**0.67**	**0.66**	**0.64**	**0.64**	**0.63**	**0.62**	**0.61**	**0.61**	**0.60**	**0.60**	**0.60**	**0.59**	**0.59**
2	**1.85**	**1.33**	**1.14**	**1.04**	**0.98**	**0.90**	**0.86**	**0.83**	**0.80**	**0.79**	**0.78**	**0.77**	**0.76**	**0.75**	**0.74**	**0.74**	**0.73**	**0.73**	**0.72**	**0.72**
3	**2.18**	**1.52**	**1.28**	**1.16**	**1.09**	**1.00**	**0.95**	**0.91**	**0.89**	**0.87**	**0.85**	**0.84**	**0.84**	**0.82**	**0.81**	**0.81**	**0.80**	**0.80**	**0.79**	**0.79**
4	**2.43**	**1.65**	**1.38**	**1.25**	**1.17**	**1.07**	**1.01**	**0.97**	**0.94**	**0.92**	**0.91**	**0.90**	**0.89**	**0.87**	**0.86**	**0.86**	**0.85**	**0.85**	**0.84**	**0.83**
5	**2.64**	**1.76**	**1.46**	**1.31**	**1.22**	**1.12**	**1.06**	**1.01**	**0.98**	**0.96**	**0.95**	**0.94**	**0.93**	**0.91**	**0.90**	**0.89**	**0.89**	**0.88**	**0.87**	**0.87**
8	3.14	**2.00**	**1.63**	**1.46**	**1.35**	**1.23**	**1.16**	**1.11**	**1.07**	**1.05**	**1.03**	**1.02**	**1.01**	**0.99**	**0.98**	**0.97**	**0.96**	**0.96**	**0.95**	**0.94**
12	3.64	**2.22**	**1.79**	**1.58**	**1.46**	**1.32**	**1.24**	**1.18**	**1.14**	**1.12**	**1.10**	**1.08**	**1.07**	**1.05**	**1.04**	**1.03**	**1.02**	**1.02**	**1.01**	**1.00**
16	4.03	**2.38**	**1.90**	**1.67**	**1.53**	**1.38**	**1.30**	**1.24**	**1.20**	**1.17**	**1.15**	**1.13**	**1.12**	**1.10**	**1.08**	**1.07**	**1.07**	**1.06**	**1.05**	**1.04**
20	4.35	**2.51**	**1.98**	**1.74**	**1.59**	**1.43**	**1.34**	**1.28**	**1.23**	**1.20**	**1.18**	**1.17**	**1.15**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**
30	5.01	**2.76**	**2.15**	**1.87**	**1.70**	**1.52**	**1.42**	**1.35**	**1.30**	**1.27**	**1.25**	**1.23**	**1.21**	**1.19**	**1.18**	**1.17**	**1.16**	**1.15**	**1.14**	**1.13**
40	5.53	*2.95*	**2.27**	**1.96**	**1.78**	**1.59**	**1.48**	**1.40**	**1.35**	**1.32**	**1.29**	**1.27**	**1.26**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**
50	5.97	3.11	**2.37**	**2.03**	**1.84**	**1.64**	**1.53**	**1.44**	**1.39**	**1.35**	**1.33**	**1.31**	**1.29**	**1.27**	**1.25**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**
60	6.36	3.24	**2.45**	**2.09**	**1.89**	**1.68**	**1.56**	**1.48**	**1.42**	**1.38**	**1.35**	**1.33**	**1.32**	**1.29**	**1.27**	**1.26**	**1.25**	**1.24**	**1.23**	**1.22**
75	6.86	3.40	**2.55**	**2.17**	**1.96**	**1.73**	**1.61**	**1.52**	**1.46**	**1.42**	**1.39**	**1.37**	**1.35**	**1.32**	**1.31**	**1.29**	**1.28**	**1.27**	**1.26**	**1.25**
100	7.56	3.63	**2.68**	**2.27**	**2.04**	**1.79**	**1.66**	**1.57**	**1.51**	**1.46**	**1.43**	**1.41**	**1.39**	**1.36**	**1.34**	**1.33**	**1.32**	**1.31**	**1.30**	**1.28**
125	8.15	3.81	**2.79**	**2.35**	**2.10**	**1.84**	**1.71**	**1.60**	**1.54**	**1.50**	**1.47**	**1.44**	**1.42**	**1.39**	**1.37**	**1.36**	**1.35**	**1.34**	**1.32**	**1.31**
150	8.67	3.96	*2.87*	**2.41**	**2.16**	**1.88**	**1.74**	**1.64**	**1.57**	**1.53**	**1.49**	**1.47**	**1.45**	**1.42**	**1.40**	**1.38**	**1.37**	**1.36**	**1.35**	**1.33**
175	9.14	4.10	*2.95*	**2.47**	**2.20**	**1.92**	**1.77**	**1.66**	**1.60**	**1.55**	**1.52**	**1.49**	**1.47**	**1.44**	**1.42**	**1.40**	**1.39**	**1.38**	**1.36**	**1.35**
200	9.55	4.22	*3.02*	**2.52**	**2.24**	**1.95**	**1.80**	**1.69**	**1.62**	**1.57**	**1.54**	**1.51**	**1.49**	**1.46**	**1.44**	**1.42**	**1.41**	**1.40**	**1.38**	**1.37**

Table 19-18. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Means of Order 3 (2 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.68**	**1.27**	**1.11**	**1.02**	**0.96**	**0.89**	**0.85**	**0.82**	**0.80**	**0.78**	**0.77**	**0.76**	**0.76**	**0.75**	**0.74**	**0.73**	**0.73**	**0.73**	**0.72**	**0.72**
2	**2.23**	**1.58**	**1.35**	**1.23**	**1.15**	**1.06**	**1.01**	**0.96**	**0.94**	**0.92**	**0.90**	**0.89**	**0.89**	**0.87**	**0.86**	**0.86**	**0.85**	**0.85**	**0.84**	**0.83**
3	**2.61**	**1.78**	**1.49**	**1.35**	**1.26**	**1.15**	**1.09**	**1.05**	**1.02**	**0.99**	**0.98**	**0.97**	**0.96**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.90**	**0.90**
4	**2.91**	**1.93**	**1.60**	**1.44**	**1.34**	**1.22**	**1.15**	**1.10**	**1.07**	**1.05**	**1.03**	**1.01**	**1.00**	**0.99**	**0.98**	**0.97**	**0.96**	**0.96**	**0.95**	**0.94**
5	3.15	**2.04**	**1.68**	**1.50**	**1.40**	**1.27**	**1.20**	**1.14**	**1.11**	**1.08**	**1.07**	**1.05**	**1.04**	**1.02**	**1.01**	**1.00**	**1.00**	**0.99**	**0.98**	**0.97**
8	3.73	**2.31**	**1.86**	**1.65**	**1.52**	**1.38**	**1.30**	**1.23**	**1.19**	**1.17**	**1.14**	**1.13**	**1.12**	**1.10**	**1.08**	**1.07**	**1.07**	**1.06**	**1.05**	**1.04**
12	4.31	**2.55**	**2.03**	**1.78**	**1.63**	**1.47**	**1.38**	**1.31**	**1.26**	**1.23**	**1.21**	**1.19**	**1.18**	**1.16**	**1.14**	**1.13**	**1.13**	**1.12**	**1.11**	**1.10**
16	4.76	**2.73**	**2.14**	**1.87**	**1.71**	**1.53**	**1.43**	**1.36**	**1.31**	**1.28**	**1.26**	**1.24**	**1.22**	**1.20**	**1.19**	**1.17**	**1.17**	**1.16**	**1.15**	**1.14**
20	5.14	**2.87**	**2.24**	**1.94**	**1.77**	**1.58**	**1.48**	**1.40**	**1.35**	**1.32**	**1.29**	**1.27**	**1.26**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**
30	5.91	3.15	**2.41**	**2.08**	**1.89**	**1.67**	**1.56**	**1.47**	**1.42**	**1.38**	**1.35**	**1.33**	**1.32**	**1.29**	**1.27**	**1.26**	**1.25**	**1.24**	**1.23**	**1.22**
40	6.52	3.36	**2.54**	**2.17**	**1.97**	**1.74**	**1.62**	**1.53**	**1.47**	**1.43**	**1.40**	**1.38**	**1.36**	**1.33**	**1.31**	**1.30**	**1.29**	**1.28**	**1.27**	**1.26**
50	7.04	3.53	**2.65**	**2.25**	**2.03**	**1.79**	**1.66**	**1.56**	**1.50**	**1.46**	**1.43**	**1.41**	**1.39**	**1.36**	**1.34**	**1.33**	**1.32**	**1.31**	**1.30**	**1.28**
60	7.49	3.68	**2.73**	**2.32**	**2.08**	**1.83**	**1.70**	**1.60**	**1.53**	**1.49**	**1.46**	**1.44**	**1.42**	**1.39**	**1.37**	**1.35**	**1.34**	**1.33**	**1.32**	**1.31**
75	8.07	3.86	**2.84**	**2.40**	**2.15**	**1.88**	**1.74**	**1.64**	**1.57**	**1.53**	**1.49**	**1.47**	**1.45**	**1.42**	**1.40**	**1.38**	**1.37**	**1.36**	**1.35**	**1.33**
100	8.90	4.11	**2.98**	**2.50**	**2.23**	**1.95**	**1.80**	**1.69**	**1.62**	**1.57**	**1.53**	**1.51**	**1.49**	**1.46**	**1.44**	**1.42**	**1.41**	**1.40**	**1.38**	**1.37**
125	9.59	4.31	*3.10*	**2.58**	**2.30**	**2.00**	**1.84**	**1.72**	**1.65**	**1.60**	**1.57**	**1.54**	**1.52**	**1.49**	**1.46**	**1.45**	**1.44**	**1.43**	**1.41**	**1.40**
150	10.20	4.49	*3.19*	**2.65**	**2.35**	**2.04**	**1.88**	**1.76**	**1.68**	**1.63**	**1.59**	**1.57**	**1.54**	**1.51**	**1.49**	**1.47**	**1.46**	**1.45**	**1.43**	**1.42**
175	10.75	4.64	3.28	**2.71**	**2.40**	**2.08**	**1.91**	**1.78**	**1.71**	**1.65**	**1.62**	**1.59**	**1.56**	**1.53**	**1.51**	**1.49**	**1.48**	**1.47**	**1.45**	**1.43**
200	11.25	4.77	3.35	**2.76**	**2.44**	**2.11**	**1.93**	**1.81**	**1.73**	**1.67**	**1.64**	**1.61**	**1.58**	**1.55**	**1.52**	**1.51**	**1.49**	**1.48**	**1.46**	**1.45**

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Table 19-18. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Means of Order 3 (5 COC, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**1.62**	**1.17**	**1.01**	**0.92**	**0.86**	**0.80**	**0.76**	**0.73**	**0.71**	**0.70**	**0.68**	**0.68**	**0.67**	**0.66**	**0.65**	**0.65**	**0.64**	**0.64**	**0.64**	**0.63**
2	**2.15**	**1.48**	**1.24**	**1.12**	**1.05**	**0.96**	**0.91**	**0.88**	**0.85**	**0.83**	**0.82**	**0.81**	**0.80**	**0.79**	**0.78**	**0.78**	**0.77**	**0.77**	**0.76**	**0.76**
3	**2.51**	**1.66**	**1.38**	**1.24**	**1.16**	**1.06**	**1.00**	**0.96**	**0.93**	**0.91**	**0.90**	**0.89**	**0.88**	**0.86**	**0.85**	**0.85**	**0.84**	**0.84**	**0.83**	**0.82**
4	2.80	**1.80**	**1.48**	**1.33**	**1.23**	**1.12**	**1.06**	**1.02**	**0.99**	**0.96**	**0.95**	**0.94**	**0.93**	**0.91**	**0.90**	**0.89**	**0.89**	**0.88**	**0.88**	**0.87**
5	3.04	**1.91**	**1.56**	**1.39**	**1.29**	**1.17**	**1.11**	**1.06**	**1.03**	**1.00**	**0.99**	**0.97**	**0.96**	**0.95**	**0.94**	**0.93**	**0.92**	**0.92**	**0.91**	**0.90**
8	3.60	**2.16**	**1.74**	**1.53**	**1.42**	**1.28**	**1.21**	**1.15**	**1.11**	**1.09**	**1.07**	**1.05**	**1.04**	**1.03**	**1.01**	**1.00**	**1.00**	**0.99**	**0.98**	**0.98**
12	4.15	**2.39**	**1.89**	**1.66**	**1.52**	**1.37**	**1.29**	**1.23**	**1.18**	**1.16**	**1.14**	**1.12**	**1.11**	**1.09**	**1.08**	**1.07**	**1.06**	**1.05**	**1.04**	**1.03**
16	4.58	**2.56**	**2.00**	**1.75**	**1.60**	**1.44**	**1.35**	**1.28**	**1.24**	**1.20**	**1.18**	**1.17**	**1.15**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**
20	4.95	**2.70**	**2.09**	**1.82**	**1.66**	**1.48**	**1.39**	**1.32**	**1.27**	**1.24**	**1.22**	**1.20**	**1.19**	**1.17**	**1.15**	**1.14**	**1.13**	**1.12**	**1.11**	**1.11**
30	5.69	2.96	**2.26**	**1.95**	**1.77**	**1.58**	**1.47**	**1.39**	**1.34**	**1.31**	**1.28**	**1.26**	**1.25**	**1.23**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**	**1.16**
40	6.28	3.16	**2.39**	**2.04**	**1.85**	**1.64**	**1.53**	**1.44**	**1.39**	**1.35**	**1.33**	**1.31**	**1.29**	**1.27**	**1.25**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**
50	6.78	3.33	**2.48**	**2.12**	**1.91**	**1.69**	**1.57**	**1.48**	**1.43**	**1.39**	**1.36**	**1.34**	**1.32**	**1.30**	**1.28**	**1.27**	**1.26**	**1.25**	**1.24**	**1.23**
60	7.21	3.46	**2.57**	**2.18**	**1.96**	**1.73**	**1.61**	**1.52**	**1.46**	**1.42**	**1.39**	**1.37**	**1.35**	**1.32**	**1.31**	**1.29**	**1.28**	**1.27**	**1.26**	**1.25**
75	7.77	3.64	**2.67**	**2.26**	**2.03**	**1.78**	**1.65**	**1.56**	**1.49**	**1.45**	**1.42**	**1.40**	**1.38**	**1.35**	**1.34**	**1.32**	**1.31**	**1.30**	**1.29**	**1.28**
100	8.55	3.87	*2.81*	**2.35**	**2.11**	**1.85**	**1.71**	**1.61**	**1.54**	**1.50**	**1.47**	**1.44**	**1.42**	**1.39**	**1.37**	**1.36**	**1.35**	**1.34**	**1.32**	**1.31**
125	9.22	4.06	*2.92*	**2.44**	**2.17**	**1.89**	**1.75**	**1.65**	**1.58**	**1.53**	**1.50**	**1.47**	**1.45**	**1.42**	**1.40**	**1.39**	**1.38**	**1.37**	**1.35**	**1.34**
150	9.84	4.22	3.01	**2.50**	**2.23**	**1.94**	**1.79**	**1.68**	**1.61**	**1.56**	**1.53**	**1.50**	**1.48**	**1.45**	**1.43**	**1.41**	**1.40**	**1.39**	**1.37**	**1.36**
175	10.35	4.37	3.09	**2.56**	**2.27**	**1.97**	**1.82**	**1.70**	**1.63**	**1.58**	**1.55**	**1.52**	**1.50**	**1.47**	**1.45**	**1.43**	**1.42**	**1.41**	**1.39**	**1.38**
200	10.82	4.49	3.15	**2.61**	**2.31**	**2.00**	**1.84**	**1.73**	**1.65**	**1.60**	**1.57**	**1.54**	**1.52**	**1.49**	**1.46**	**1.45**	**1.44**	**1.43**	**1.41**	**1.40**

Table 19-18. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Means of Order 3 (5 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.02**	**1.43**	**1.22**	**1.11**	**1.04**	**0.96**	**0.91**	**0.87**	**0.85**	**0.83**	**0.82**	**0.81**	**0.80**	**0.79**	**0.78**	**0.78**	**0.77**	**0.77**	**0.76**	**0.76**
2	**2.64**	**1.76**	**1.46**	**1.31**	**1.22**	**1.12**	**1.06**	**1.01**	**0.98**	**0.96**	**0.95**	**0.94**	**0.93**	**0.91**	**0.90**	**0.89**	**0.89**	**0.88**	**0.87**	**0.87**
3	3.07	**1.96**	**1.61**	**1.44**	**1.33**	**1.21**	**1.14**	**1.09**	**1.06**	**1.04**	**1.02**	**1.01**	**0.99**	**0.98**	**0.97**	**0.96**	**0.95**	**0.95**	**0.94**	**0.93**
4	3.41	**2.12**	**1.72**	**1.52**	**1.41**	**1.28**	**1.20**	**1.15**	**1.11**	**1.09**	**1.07**	**1.05**	**1.04**	**1.02**	**1.01**	**1.00**	**1.00**	**0.99**	**0.98**	**0.97**
5	3.69	**2.24**	**1.80**	**1.59**	**1.47**	**1.33**	**1.25**	**1.19**	**1.15**	**1.12**	**1.11**	**1.09**	**1.08**	**1.06**	**1.05**	**1.04**	**1.03**	**1.02**	**1.01**	**1.01**
8	4.35	**2.51**	**1.98**	**1.74**	**1.59**	**1.43**	**1.34**	**1.28**	**1.23**	**1.20**	**1.18**	**1.17**	**1.15**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**
12	5.01	**2.76**	**2.15**	**1.87**	**1.70**	**1.52**	**1.42**	**1.35**	**1.30**	**1.27**	**1.25**	**1.23**	**1.21**	**1.19**	**1.18**	**1.17**	**1.16**	**1.15**	**1.14**	**1.13**
16	5.53	*2.95*	**2.27**	**1.96**	**1.78**	**1.59**	**1.48**	**1.40**	**1.35**	**1.32**	**1.29**	**1.27**	**1.26**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**
20	5.97	3.11	**2.37**	**2.03**	**1.84**	**1.64**	**1.53**	**1.44**	**1.39**	**1.35**	**1.33**	**1.31**	**1.29**	**1.27**	**1.25**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**
30	6.86	3.40	**2.55**	**2.17**	**1.96**	**1.73**	**1.61**	**1.51**	**1.46**	**1.42**	**1.39**	**1.37**	**1.35**	**1.32**	**1.31**	**1.29**	**1.28**	**1.27**	**1.26**	**1.25**
40	7.56	3.63	**2.68**	**2.27**	**2.04**	**1.79**	**1.66**	**1.57**	**1.51**	**1.46**	**1.43**	**1.41**	**1.39**	**1.36**	**1.34**	**1.33**	**1.32**	**1.31**	**1.30**	**1.28**
50	8.15	3.81	**2.79**	**2.35**	**2.10**	**1.84**	**1.71**	**1.61**	**1.54**	**1.50**	**1.47**	**1.44**	**1.42**	**1.39**	**1.37**	**1.36**	**1.35**	**1.34**	**1.32**	**1.31**
60	8.67	3.96	*2.88*	**2.41**	**2.16**	**1.88**	**1.74**	**1.64**	**1.57**	**1.53**	**1.49**	**1.47**	**1.45**	**1.42**	**1.40**	**1.38**	**1.37**	**1.36**	**1.35**	**1.33**
75	9.34	4.16	*2.99*	**2.49**	**2.22**	**1.94**	**1.79**	**1.68**	**1.61**	**1.56**	**1.53**	**1.50**	**1.48**	**1.45**	**1.43**	**1.41**	**1.40**	**1.39**	**1.37**	**1.36**
100	10.31	4.42	3.13	**2.60**	**2.31**	**2.00**	**1.84**	**1.73**	**1.65**	**1.60**	**1.57**	**1.54**	**1.52**	**1.49**	**1.46**	**1.45**	**1.44**	**1.42**	**1.41**	**1.40**
125	11.09	4.64	3.25	**2.68**	**2.37**	**2.05**	**1.89**	**1.77**	**1.69**	**1.64**	**1.60**	**1.57**	**1.55**	**1.52**	**1.49**	**1.48**	**1.46**	**1.45**	**1.43**	**1.42**
150	11.80	4.82	3.35	**2.75**	**2.43**	**2.09**	**1.92**	**1.80**	**1.72**	**1.67**	**1.63**	**1.60**	**1.57**	**1.54**	**1.52**	**1.50**	**1.48**	**1.47**	**1.46**	**1.44**
175	12.42	4.98	3.44	**2.81**	**2.48**	**2.13**	**1.95**	**1.82**	**1.74**	**1.69**	**1.65**	**1.62**	**1.59**	**1.56**	**1.54**	**1.52**	**1.50**	**1.49**	**1.47**	**1.46**
200	12.97	5.12	3.52	*2.86*	**2.52**	**2.16**	**1.98**	**1.85**	**1.76**	**1.71**	**1.67**	**1.64**	**1.61**	**1.58**	**1.55**	**1.53**	**1.52**	**1.51**	**1.49**	**1.47**

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Table 19-18. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Means of Order 3 (5 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.43**	**1.69**	**1.43**	**1.29**	**1.21**	**1.11**	**1.05**	**1.01**	**0.98**	**0.96**	**0.95**	**0.93**	**0.92**	**0.91**	**0.90**	**0.89**	**0.89**	**0.88**	**0.87**	**0.87**
2	3.15	**2.04**	**1.68**	**1.50**	**1.40**	**1.27**	**1.20**	**1.14**	**1.11**	**1.08**	**1.07**	**1.05**	**1.04**	**1.02**	**1.01**	**1.00**	**1.00**	**0.99**	**0.98**	**0.97**
3	3.65	**2.27**	**1.84**	**1.63**	**1.50**	**1.36**	**1.28**	**1.22**	**1.18**	**1.15**	**1.13**	**1.12**	**1.11**	**1.09**	**1.07**	**1.06**	**1.06**	**1.05**	**1.04**	**1.03**
4	4.04	**2.44**	**1.95**	**1.72**	**1.58**	**1.43**	**1.34**	**1.27**	**1.23**	**1.20**	**1.18**	**1.16**	**1.15**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**
5	4.37	**2.57**	**2.04**	**1.79**	**1.64**	**1.48**	**1.39**	**1.32**	**1.27**	**1.24**	**1.22**	**1.20**	**1.19**	**1.17**	**1.15**	**1.14**	**1.13**	**1.12**	**1.11**	**1.10**
8	5.14	**2.87**	**2.24**	**1.94**	**1.77**	**1.58**	**1.48**	**1.40**	**1.35**	**1.32**	**1.29**	**1.27**	**1.26**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**
12	5.91	3.15	**2.41**	**2.08**	**1.89**	**1.67**	**1.56**	**1.47**	**1.42**	**1.38**	**1.35**	**1.33**	**1.32**	**1.29**	**1.27**	**1.26**	**1.25**	**1.24**	**1.23**	**1.22**
16	6.52	3.36	**2.54**	**2.17**	**1.97**	**1.74**	**1.62**	**1.53**	**1.47**	**1.43**	**1.40**	**1.38**	**1.36**	**1.33**	**1.31**	**1.30**	**1.29**	**1.28**	**1.27**	**1.26**
20	7.04	3.54	**2.65**	**2.25**	**2.03**	**1.79**	**1.66**	**1.56**	**1.50**	**1.46**	**1.43**	**1.41**	**1.39**	**1.36**	**1.34**	**1.33**	**1.32**	**1.31**	**1.30**	**1.28**
30	8.08	3.86	**2.84**	**2.40**	**2.15**	**1.88**	**1.74**	**1.64**	**1.57**	**1.53**	**1.49**	**1.47**	**1.45**	**1.42**	**1.40**	**1.38**	**1.37**	**1.36**	**1.35**	**1.33**
40	8.90	4.11	**2.98**	**2.50**	**2.23**	**1.95**	**1.80**	**1.69**	**1.62**	**1.57**	**1.53**	**1.51**	**1.49**	**1.46**	**1.44**	**1.42**	**1.41**	**1.40**	**1.38**	**1.37**
50	9.59	4.32	*3.10*	**2.58**	**2.30**	**2.00**	**1.84**	**1.72**	**1.65**	**1.60**	**1.57**	**1.54**	**1.52**	**1.49**	**1.46**	**1.45**	**1.43**	**1.43**	**1.41**	**1.40**
60	10.20	4.49	*3.19*	**2.65**	**2.35**	**2.04**	**1.88**	**1.76**	**1.68**	**1.63**	**1.59**	**1.57**	**1.54**	**1.51**	**1.49**	**1.47**	**1.46**	**1.45**	**1.43**	**1.42**
75	11.00	4.71	3.32	**2.74**	**2.42**	**2.09**	**1.92**	**1.80**	**1.72**	**1.67**	**1.63**	**1.60**	**1.57**	**1.54**	**1.52**	**1.50**	**1.48**	**1.47**	**1.46**	**1.44**
100	12.11	5.00	3.48	**2.85**	**2.51**	**2.16**	**1.98**	**1.85**	**1.76**	**1.71**	**1.67**	**1.64**	**1.61**	**1.58**	**1.55**	**1.53**	**1.52**	**1.51**	**1.49**	**1.47**
125	13.05	5.24	3.60	**2.94**	**2.58**	**2.21**	**2.02**	**1.88**	**1.80**	**1.74**	**1.70**	**1.67**	**1.64**	**1.61**	**1.58**	**1.56**	**1.54**	**1.53**	**1.51**	**1.50**
150	13.91	5.45	3.71	**3.01**	**2.64**	**2.26**	**2.06**	**1.92**	**1.83**	**1.77**	**1.72**	**1.69**	**1.67**	**1.63**	**1.60**	**1.58**	**1.57**	**1.56**	**1.53**	**1.52**
175	14.61	5.62	3.80	*3.08*	**2.69**	**2.29**	**2.09**	**1.94**	**1.85**	**1.79**	**1.75**	**1.71**	**1.69**	**1.65**	**1.62**	**1.60**	**1.58**	**1.57**	**1.55**	**1.54**
200	15.31	5.78	3.89	*3.13*	**2.73**	**2.32**	**2.12**	**1.97**	**1.88**	**1.81**	**1.77**	**1.73**	**1.71**	**1.67**	**1.64**	**1.62**	**1.60**	**1.59**	**1.57**	**1.55**

Table 19-18. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Means of Order 3 (10 COC, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.15**	**1.48**	**1.24**	**1.12**	**1.05**	**0.96**	**0.91**	**0.88**	**0.85**	**0.83**	**0.82**	**0.81**	**0.80**	**0.79**	**0.78**	**0.78**	**0.77**	**0.77**	**0.76**	**0.76**
2	2.80	**1.80**	**1.48**	**1.33**	**1.23**	**1.12**	**1.06**	**1.02**	**0.99**	**0.96**	**0.95**	**0.94**	**0.93**	**0.91**	**0.90**	**0.89**	**0.89**	**0.88**	**0.87**	**0.87**
3	3.24	**2.01**	**1.63**	**1.45**	**1.34**	**1.22**	**1.15**	**1.09**	**1.06**	**1.04**	**1.02**	**1.01**	**0.99**	**0.98**	**0.97**	**0.96**	**0.95**	**0.95**	**0.94**	**0.93**
4	3.60	**2.16**	**1.74**	**1.53**	**1.42**	**1.28**	**1.21**	**1.15**	**1.11**	**1.09**	**1.07**	**1.05**	**1.04**	**1.03**	**1.01**	**1.00**	**1.00**	**0.99**	**0.98**	**0.98**
5	3.89	**2.28**	**1.82**	**1.60**	**1.47**	**1.33**	**1.25**	**1.19**	**1.15**	**1.13**	**1.11**	**1.09**	**1.08**	**1.06**	**1.05**	**1.04**	**1.03**	**1.03**	**1.01**	**1.01**
8	4.59	**2.56**	**2.00**	**1.75**	**1.60**	**1.44**	**1.35**	**1.28**	**1.23**	**1.20**	**1.18**	**1.17**	**1.15**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**
12	5.27	*2.81*	**2.17**	**1.88**	**1.71**	**1.53**	**1.43**	**1.35**	**1.30**	**1.27**	**1.25**	**1.23**	**1.21**	**1.19**	**1.18**	**1.17**	**1.16**	**1.15**	**1.14**	**1.13**
16	5.82	3.01	**2.29**	**1.97**	**1.79**	**1.59**	**1.48**	**1.40**	**1.35**	**1.32**	**1.29**	**1.27**	**1.26**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**
20	6.28	3.16	**2.39**	**2.04**	**1.85**	**1.64**	**1.53**	**1.44**	**1.39**	**1.35**	**1.33**	**1.31**	**1.29**	**1.27**	**1.25**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**
30	7.21	3.46	**2.57**	**2.18**	**1.96**	**1.73**	**1.61**	**1.52**	**1.46**	**1.42**	**1.39**	**1.37**	**1.35**	**1.32**	**1.31**	**1.29**	**1.28**	**1.27**	**1.26**	**1.25**
40	7.95	3.69	*2.70*	**2.28**	**2.04**	**1.79**	**1.66**	**1.57**	**1.51**	**1.46**	**1.43**	**1.41**	**1.39**	**1.36**	**1.34**	**1.33**	**1.32**	**1.31**	**1.30**	**1.28**
50	8.57	3.87	*2.81*	**2.36**	**2.11**	**1.84**	**1.71**	**1.61**	**1.54**	**1.50**	**1.47**	**1.44**	**1.42**	**1.39**	**1.37**	**1.36**	**1.35**	**1.34**	**1.32**	**1.31**
60	9.11	4.03	*2.90*	**2.42**	**2.16**	**1.89**	**1.74**	**1.64**	**1.57**	**1.53**	**1.49**	**1.47**	**1.45**	**1.42**	**1.40**	**1.38**	**1.37**	**1.36**	**1.35**	**1.33**
75	9.81	4.22	3.01	**2.50**	**2.23**	**1.94**	**1.79**	**1.68**	**1.61**	**1.56**	**1.53**	**1.50**	**1.48**	**1.45**	**1.43**	**1.41**	**1.40**	**1.39**	**1.37**	**1.36**
100	10.82	4.49	3.16	**2.61**	**2.31**	**2.00**	**1.84**	**1.73**	**1.65**	**1.60**	**1.57**	**1.54**	**1.52**	**1.49**	**1.46**	**1.45**	**1.44**	**1.43**	**1.41**	**1.40**
125	11.67	4.71	3.27	*2.69*	**2.38**	**2.05**	**1.89**	**1.77**	**1.69**	**1.64**	**1.60**	**1.57**	**1.55**	**1.52**	**1.49**	**1.48**	**1.46**	**1.45**	**1.43**	**1.42**
150	12.40	4.90	3.37	*2.76*	**2.44**	**2.10**	**1.92**	**1.80**	**1.72**	**1.67**	**1.63**	**1.60**	**1.57**	**1.54**	**1.52**	**1.50**	**1.48**	**1.47**	**1.46**	**1.44**
175	13.09	5.05	3.45	*2.82*	**2.48**	**2.13**	**1.95**	**1.82**	**1.74**	**1.69**	**1.65**	**1.62**	**1.59**	**1.56**	**1.54**	**1.52**	**1.50**	**1.49**	**1.47**	**1.46**
200	13.67	5.20	3.53	*2.87*	**2.52**	**2.16**	**1.98**	**1.85**	**1.76**	**1.71**	**1.67**	**1.64**	**1.61**	**1.58**	**1.55**	**1.53**	**1.52**	**1.51**	**1.49**	**1.47**

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Table 19-18. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Means of Order 3 (10 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	**2.64**	**1.76**	**1.46**	**1.31**	**1.22**	**1.12**	**1.06**	**1.01**	**0.98**	**0.96**	**0.95**	**0.94**	**0.93**	**0.91**	**0.90**	**0.89**	**0.89**	**0.88**	**0.87**	**0.87**
2	3.41	**2.12**	**1.72**	**1.52**	**1.41**	**1.28**	**1.20**	**1.15**	**1.11**	**1.09**	**1.07**	**1.05**	**1.04**	**1.02**	**1.01**	**1.00**	**1.00**	**0.99**	**0.98**	**0.97**
3	3.94	**2.34**	**1.87**	**1.65**	**1.52**	**1.37**	**1.29**	**1.22**	**1.18**	**1.16**	**1.14**	**1.12**	**1.11**	**1.09**	**1.08**	**1.07**	**1.06**	**1.05**	**1.04**	**1.03**
4	4.35	**2.51**	**1.98**	**1.74**	**1.59**	**1.43**	**1.34**	**1.28**	**1.23**	**1.20**	**1.18**	**1.17**	**1.15**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**
5	4.71	**2.65**	**2.07**	**1.81**	**1.65**	**1.48**	**1.39**	**1.32**	**1.27**	**1.24**	**1.22**	**1.20**	**1.19**	**1.17**	**1.15**	**1.14**	**1.13**	**1.12**	**1.11**	**1.10**
8	5.53	*2.95*	**2.27**	**1.96**	**1.78**	**1.59**	**1.48**	**1.40**	**1.35**	**1.32**	**1.29**	**1.27**	**1.26**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**
12	6.36	3.24	**2.45**	**2.09**	**1.89**	**1.68**	**1.56**	**1.48**	**1.42**	**1.38**	**1.35**	**1.33**	**1.32**	**1.29**	**1.27**	**1.26**	**1.25**	**1.24**	**1.23**	**1.22**
16	7.01	3.45	**2.58**	**2.19**	**1.98**	**1.74**	**1.62**	**1.53**	**1.47**	**1.43**	**1.40**	**1.38**	**1.36**	**1.33**	**1.31**	**1.30**	**1.29**	**1.28**	**1.27**	**1.26**
20	7.56	3.63	**2.68**	**2.27**	**2.04**	**1.79**	**1.66**	**1.57**	**1.50**	**1.46**	**1.43**	**1.41**	**1.39**	**1.36**	**1.34**	**1.33**	**1.32**	**1.31**	**1.30**	**1.28**
30	8.67	3.96	*2.87*	**2.41**	**2.16**	**1.88**	**1.74**	**1.64**	**1.57**	**1.53**	**1.49**	**1.47**	**1.45**	**1.42**	**1.40**	**1.38**	**1.37**	**1.36**	**1.35**	**1.33**
40	9.55	4.22	*3.02*	**2.51**	**2.24**	**1.95**	**1.80**	**1.69**	**1.62**	**1.57**	**1.54**	**1.51**	**1.49**	**1.46**	**1.44**	**1.42**	**1.41**	**1.40**	**1.38**	**1.37**
50	10.30	4.43	3.13	**2.60**	**2.31**	**2.00**	**1.84**	**1.73**	**1.65**	**1.60**	**1.57**	**1.54**	**1.52**	**1.49**	**1.46**	**1.45**	**1.44**	**1.43**	**1.41**	**1.40**
60	10.94	4.60	3.23	**2.67**	**2.36**	**2.04**	**1.88**	**1.76**	**1.68**	**1.63**	**1.59**	**1.57**	**1.54**	**1.51**	**1.49**	**1.47**	**1.46**	**1.45**	**1.43**	**1.42**
75	11.79	4.82	3.35	**2.75**	**2.43**	**2.10**	**1.92**	**1.80**	**1.72**	**1.66**	**1.63**	**1.60**	**1.57**	**1.54**	**1.52**	**1.50**	**1.48**	**1.47**	**1.45**	**1.44**
100	12.99	5.12	3.51	*2.86*	**2.52**	**2.16**	**1.98**	**1.85**	**1.76**	**1.71**	**1.67**	**1.64**	**1.61**	**1.58**	**1.55**	**1.53**	**1.52**	**1.51**	**1.49**	**1.46**
125	14.01	5.37	3.64	*2.95*	**2.59**	**2.22**	**2.02**	**1.89**	**1.80**	**1.74**	**1.70**	**1.67**	**1.64**	**1.61**	**1.58**	**1.56**	**1.54**	**1.53**	**1.51**	**1.49**
150	14.89	5.58	3.75	*3.03*	**2.65**	**2.26**	**2.06**	**1.92**	**1.83**	**1.77**	**1.73**	**1.69**	**1.67**	**1.63**	**1.60**	**1.58**	**1.57**	**1.55**	**1.54**	**1.52**
175	15.67	5.76	3.85	*3.09*	**2.70**	**2.29**	**2.09**	**1.94**	**1.85**	**1.79**	**1.75**	**1.72**	**1.69**	**1.65**	**1.62**	**1.60**	**1.59**	**1.57**	**1.55**	**1.54**
200	16.41	5.91	3.92	3.15	**2.74**	**2.33**	**2.12**	**1.97**	**1.87**	**1.81**	**1.77**	**1.73**	**1.71**	**1.67**	**1.64**	**1.62**	**1.60**	**1.59**	**1.57**	**1.55**

Table 19-18. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Means of Order 3 (10 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.15	**2.04**	**1.68**	**1.50**	**1.40**	**1.27**	**1.20**	**1.14**	**1.11**	**1.08**	**1.07**	**1.05**	**1.04**	**1.02**	**1.01**	**1.00**	**1.00**	**0.99**	**0.98**	**0.97**
2	4.04	**2.44**	**1.95**	**1.72**	**1.58**	**1.43**	**1.34**	**1.27**	**1.23**	**1.20**	**1.18**	**1.16**	**1.15**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**
3	4.66	**2.68**	**2.12**	**1.85**	**1.69**	**1.52**	**1.42**	**1.35**	**1.30**	**1.27**	**1.25**	**1.23**	**1.21**	**1.19**	**1.18**	**1.17**	**1.16**	**1.15**	**1.14**	**1.13**
4	5.14	**2.87**	**2.24**	**1.94**	**1.77**	**1.58**	**1.48**	**1.40**	**1.35**	**1.32**	**1.29**	**1.27**	**1.26**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**
5	5.55	**3.02**	**2.33**	**2.02**	**1.83**	**1.63**	**1.52**	**1.44**	**1.39**	**1.35**	**1.33**	**1.31**	**1.29**	**1.27**	**1.25**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**
8	6.52	3.36	**2.54**	**2.17**	**1.97**	**1.74**	**1.62**	**1.53**	**1.47**	**1.43**	**1.40**	**1.38**	**1.36**	**1.33**	**1.31**	**1.30**	**1.29**	**1.28**	**1.27**	**1.26**
12	7.49	3.68	**2.73**	**2.32**	**2.08**	**1.83**	**1.70**	**1.60**	**1.53**	**1.49**	**1.46**	**1.44**	**1.42**	**1.39**	**1.37**	**1.35**	**1.34**	**1.33**	**1.32**	**1.31**
16	8.25	3.92	**2.87**	**2.42**	**2.17**	**1.90**	**1.75**	**1.65**	**1.58**	**1.54**	**1.50**	**1.48**	**1.46**	**1.43**	**1.41**	**1.39**	**1.38**	**1.37**	**1.35**	**1.34**
20	8.90	4.11	**2.98**	**2.50**	**2.23**	**1.95**	**1.80**	**1.69**	**1.62**	**1.57**	**1.53**	**1.51**	**1.49**	**1.46**	**1.44**	**1.42**	**1.41**	**1.40**	**1.38**	**1.37**
30	10.21	4.49	*3.20*	**2.65**	**2.35**	**2.04**	**1.88**	**1.76**	**1.68**	**1.63**	**1.59**	**1.57**	**1.54**	**1.51**	**1.49**	**1.47**	**1.46**	**1.45**	**1.43**	**1.42**
40	11.23	4.77	3.35	**2.76**	**2.44**	**2.11**	**1.93**	**1.81**	**1.73**	**1.67**	**1.63**	**1.61**	**1.58**	**1.55**	**1.52**	**1.51**	**1.49**	**1.48**	**1.46**	**1.45**
50	12.11	5.00	3.48	**2.85**	**2.51**	**2.16**	**1.98**	**1.85**	**1.76**	**1.71**	**1.67**	**1.64**	**1.61**	**1.58**	**1.55**	**1.53**	**1.52**	**1.51**	**1.49**	**1.47**
60	12.87	5.19	3.58	**2.92**	**2.57**	**2.20**	**2.01**	**1.88**	**1.79**	**1.73**	**1.69**	**1.66**	**1.64**	**1.60**	**1.57**	**1.56**	**1.54**	**1.53**	**1.50**	**1.50**
75	13.87	5.44	3.71	**3.01**	**2.64**	**2.26**	**2.06**	**1.92**	**1.83**	**1.77**	**1.72**	**1.69**	**1.67**	**1.63**	**1.60**	**1.58**	**1.57**	**1.56**	**1.53**	**1.52**
100	15.28	5.79	3.88	*3.13*	**2.73**	**2.32**	**2.12**	**1.97**	**1.88**	**1.81**	**1.77**	**1.73**	**1.71**	**1.67**	**1.64**	**1.62**	**1.60**	**1.59**	**1.57**	**1.55**
125	16.46	6.05	4.03	*3.22*	**2.81**	**2.38**	**2.16**	**2.01**	**1.91**	**1.85**	**1.80**	**1.76**	**1.74**	**1.70**	**1.66**	**1.64**	**1.63**	**1.61**	**1.59**	**1.58**
150	17.48	6.30	4.14	3.30	**2.87**	**2.42**	**2.20**	**2.04**	**1.94**	**1.87**	**1.82**	**1.79**	**1.76**	**1.72**	**1.69**	**1.66**	**1.65**	**1.63**	**1.61**	**1.60**
175	18.46	6.49	4.25	3.37	**2.92**	**2.46**	**2.23**	**2.06**	**1.96**	**1.90**	**1.85**	**1.81**	**1.78**	**1.73**	**1.70**	**1.68**	**1.66**	**1.65**	**1.63**	**1.61**
200	19.24	6.67	4.33	3.43	**2.97**	**2.49**	**2.26**	**2.09**	**1.98**	**1.92**	**1.86**	**1.83**	**1.80**	**1.75**	**1.72**	**1.70**	**1.68**	**1.67**	**1.64**	**1.63**

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Table 19-18. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Means of Order 3 (20 COC, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	2.80	**1.80**	**1.48**	**1.33**	**1.23**	**1.12**	**1.06**	**1.02**	**0.99**	**0.96**	**0.95**	**0.94**	**0.93**	**0.91**	**0.90**	**0.89**	**0.89**	**0.88**	**0.87**	**0.87**
2	3.60	**2.16**	**1.74**	**1.53**	**1.42**	**1.28**	**1.21**	**1.15**	**1.11**	**1.09**	**1.07**	**1.05**	**1.04**	**1.03**	**1.01**	**1.00**	**1.00**	**0.99**	**0.98**	**0.98**
3	4.15	**2.39**	**1.89**	**1.66**	**1.52**	**1.37**	**1.29**	**1.23**	**1.18**	**1.16**	**1.14**	**1.12**	**1.11**	**1.09**	**1.08**	**1.07**	**1.06**	**1.05**	**1.04**	**1.03**
4	4.58	**2.56**	**2.00**	**1.75**	**1.60**	**1.44**	**1.35**	**1.28**	**1.23**	**1.20**	**1.18**	**1.17**	**1.15**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**
5	4.95	**2.70**	**2.09**	**1.82**	**1.66**	**1.48**	**1.39**	**1.32**	**1.27**	**1.24**	**1.22**	**1.20**	**1.19**	**1.17**	**1.15**	**1.14**	**1.13**	**1.12**	**1.11**	**1.11**
8	5.82	3.01	**2.29**	**1.97**	**1.79**	**1.59**	**1.48**	**1.40**	**1.35**	**1.32**	**1.29**	**1.27**	**1.26**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**
12	6.68	3.29	**2.47**	**2.10**	**1.90**	**1.68**	**1.56**	**1.48**	**1.42**	**1.38**	**1.36**	**1.33**	**1.32**	**1.29**	**1.27**	**1.26**	**1.25**	**1.24**	**1.23**	**1.22**
16	7.37	3.51	**2.60**	**2.20**	**1.98**	**1.74**	**1.62**	**1.53**	**1.47**	**1.43**	**1.40**	**1.38**	**1.36**	**1.33**	**1.31**	**1.30**	**1.29**	**1.28**	**1.27**	**1.26**
20	7.95	3.69	*2.70*	**2.28**	**2.04**	**1.79**	**1.66**	**1.57**	**1.51**	**1.46**	**1.43**	**1.41**	**1.39**	**1.36**	**1.34**	**1.33**	**1.32**	**1.31**	**1.30**	**1.28**
30	9.11	4.03	*2.89*	**2.42**	**2.16**	**1.89**	**1.74**	**1.64**	**1.57**	**1.53**	**1.49**	**1.47**	**1.45**	**1.42**	**1.40**	**1.38**	**1.37**	**1.36**	**1.35**	**1.33**
40	10.05	4.28	3.04	**2.52**	**2.24**	**1.95**	**1.80**	**1.69**	**1.62**	**1.57**	**1.54**	**1.51**	**1.49**	**1.46**	**1.44**	**1.42**	**1.41**	**1.40**	**1.38**	**1.37**
50	10.81	4.49	3.16	**2.61**	**2.31**	**2.00**	**1.84**	**1.73**	**1.65**	**1.60**	**1.57**	**1.54**	**1.52**	**1.49**	**1.46**	**1.45**	**1.44**	**1.42**	**1.41**	**1.40**
60	11.48	4.67	3.25	**2.67**	**2.37**	**2.05**	**1.88**	**1.76**	**1.68**	**1.63**	**1.59**	**1.57**	**1.54**	**1.51**	**1.49**	**1.47**	**1.46**	**1.45**	**1.43**	**1.42**
75	12.42	4.89	3.37	*2.76*	**2.44**	**2.10**	**1.92**	**1.80**	**1.72**	**1.67**	**1.63**	**1.60**	**1.57**	**1.54**	**1.52**	**1.50**	**1.48**	**1.47**	**1.46**	**1.44**
100	13.65	5.20	3.53	*2.87*	**2.52**	**2.16**	**1.98**	**1.85**	**1.77**	**1.71**	**1.67**	**1.64**	**1.61**	**1.58**	**1.55**	**1.53**	**1.52**	**1.51**	**1.49**	**1.47**
125	14.77	5.45	3.66	*2.96*	**2.59**	**2.22**	**2.03**	**1.89**	**1.80**	**1.74**	**1.70**	**1.67**	**1.64**	**1.60**	**1.58**	**1.56**	**1.54**	**1.53**	**1.51**	**1.50**
150	15.70	5.65	3.78	3.03	**2.65**	**2.26**	**2.06**	**1.92**	**1.83**	**1.77**	**1.72**	**1.69**	**1.67**	**1.63**	**1.60**	**1.58**	**1.57**	**1.55**	**1.53**	**1.52**
175	16.41	5.86	3.87	3.11	*2.70*	**2.29**	**2.09**	**1.94**	**1.85**	**1.79**	**1.75**	**1.71**	**1.69**	**1.65**	**1.62**	**1.60**	**1.59**	**1.57**	**1.55**	**1.54**
200	17.11	6.01	3.96	3.15	*2.74*	**2.33**	**2.12**	**1.97**	**1.88**	**1.81**	**1.77**	**1.73**	**1.71**	**1.67**	**1.64**	**1.62**	**1.60**	**1.59**	**1.57**	**1.55**

Table 19-18. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Means of Order 3 (20 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.41	**2.12**	**1.72**	**1.52**	**1.41**	**1.28**	**1.20**	**1.15**	**1.11**	**1.09**	**1.07**	**1.05**	**1.04**	**1.02**	**1.01**	**1.00**	**1.00**	**0.99**	**0.98**	**0.97**
2	4.35	**2.51**	**1.98**	**1.74**	**1.59**	**1.43**	**1.34**	**1.28**	**1.23**	**1.20**	**1.18**	**1.17**	**1.15**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**
3	5.01	**2.76**	**2.15**	**1.87**	**1.70**	**1.52**	**1.42**	**1.35**	**1.30**	**1.27**	**1.25**	**1.23**	**1.21**	**1.19**	**1.18**	**1.17**	**1.16**	**1.15**	**1.14**	**1.13**
4	5.53	*2.95*	**2.27**	**1.96**	**1.78**	**1.59**	**1.48**	**1.40**	**1.35**	**1.32**	**1.29**	**1.27**	**1.26**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**
5	5.97	3.11	**2.37**	**2.03**	**1.84**	**1.64**	**1.53**	**1.44**	**1.39**	**1.35**	**1.33**	**1.31**	**1.29**	**1.27**	**1.25**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**
8	7.01	3.45	**2.58**	**2.19**	**1.98**	**1.74**	**1.62**	**1.53**	**1.47**	**1.43**	**1.40**	**1.38**	**1.36**	**1.33**	**1.31**	**1.30**	**1.29**	**1.28**	**1.27**	**1.26**
12	8.04	3.78	**2.77**	**2.33**	**2.09**	**1.83**	**1.70**	**1.60**	**1.53**	**1.49**	**1.46**	**1.44**	**1.42**	**1.39**	**1.37**	**1.35**	**1.34**	**1.33**	**1.32**	**1.31**
16	8.86	4.02	*2.91*	**2.43**	**2.18**	**1.90**	**1.75**	**1.65**	**1.58**	**1.54**	**1.50**	**1.48**	**1.46**	**1.43**	**1.41**	**1.39**	**1.38**	**1.37**	**1.35**	**1.34**
20	9.55	4.22	*3.02*	**2.52**	**2.24**	**1.95**	**1.80**	**1.69**	**1.62**	**1.57**	**1.53**	**1.51**	**1.49**	**1.46**	**1.44**	**1.42**	**1.41**	**1.40**	**1.38**	**1.37**
30	10.96	4.60	3.23	**2.67**	**2.36**	**2.04**	**1.88**	**1.76**	**1.68**	**1.63**	**1.59**	**1.57**	**1.54**	**1.51**	**1.49**	**1.47**	**1.46**	**1.45**	**1.43**	**1.42**
40	12.07	4.89	3.39	**2.78**	**2.45**	**2.11**	**1.94**	**1.81**	**1.73**	**1.67**	**1.64**	**1.61**	**1.58**	**1.55**	**1.52**	**1.51**	**1.49**	**1.48**	**1.46**	**1.45**
50	13.01	5.12	3.51	*2.86*	**2.52**	**2.16**	**1.98**	**1.85**	**1.76**	**1.71**	**1.67**	**1.64**	**1.61**	**1.58**	**1.55**	**1.53**	**1.52**	**1.51**	**1.49**	**1.46**
60	13.83	5.32	3.62	*2.94*	**2.58**	**2.20**	**2.02**	**1.88**	**1.79**	**1.74**	**1.69**	**1.66**	**1.64**	**1.60**	**1.57**	**1.55**	**1.54**	**1.53**	**1.50**	**1.50**
75	14.88	5.58	3.75	*3.02*	**2.65**	**2.26**	**2.06**	**1.92**	**1.83**	**1.77**	**1.73**	**1.69**	**1.67**	**1.63**	**1.60**	**1.58**	**1.57**	**1.55**	**1.53**	**1.52**
100	16.41	5.92	3.93	3.15	**2.74**	**2.33**	**2.12**	**1.97**	**1.88**	**1.81**	**1.77**	**1.73**	**1.71**	**1.67**	**1.64**	**1.62**	**1.60**	**1.59**	**1.57**	**1.55**
125	17.70	6.21	4.06	3.24	**2.81**	**2.38**	**2.16**	**2.01**	**1.91**	**1.85**	**1.80**	**1.77**	**1.74**	**1.70**	**1.67**	**1.64**	**1.63**	**1.61**	**1.59**	**1.58**
150	18.75	6.45	4.19	3.33	*2.87*	**2.42**	**2.20**	**2.04**	**1.94**	**1.88**	**1.82**	**1.79**	**1.76**	**1.72**	**1.69**	**1.66**	**1.65**	**1.63**	**1.61**	**1.60**
175	19.69	6.65	4.28	3.38	*2.93*	**2.46**	**2.23**	**2.07**	**1.96**	**1.90**	**1.85**	**1.81**	**1.78**	**1.74**	**1.70**	**1.68**	**1.66**	**1.65**	**1.63**	**1.61**
200	20.62	6.86	4.37	3.44	*2.97*	**2.49**	**2.26**	**2.09**	**1.98**	**1.92**	**1.87**	**1.83**	**1.80**	**1.76**	**1.72**	**1.70**	**1.68**	**1.67**	**1.64**	**1.63**

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Table 19-18. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Means of Order 3 (20 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	4.04	**2.44**	**1.95**	**1.72**	**1.58**	**1.43**	**1.34**	**1.27**	**1.23**	**1.20**	**1.18**	**1.16**	**1.15**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**
2	5.14	**2.87**	**2.24**	**1.94**	**1.77**	**1.58**	**1.48**	**1.40**	**1.35**	**1.32**	**1.29**	**1.27**	**1.26**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**
3	5.91	3.15	**2.41**	**2.08**	**1.89**	**1.67**	**1.56**	**1.47**	**1.42**	**1.38**	**1.35**	**1.33**	**1.32**	**1.29**	**1.27**	**1.26**	**1.25**	**1.24**	**1.23**	**1.22**
4	6.52	3.36	**2.54**	**2.17**	**1.97**	**1.74**	**1.62**	**1.53**	**1.47**	**1.43**	**1.40**	**1.38**	**1.36**	**1.33**	**1.31**	**1.30**	**1.29**	**1.28**	**1.27**	**1.26**
5	7.04	3.53	**2.65**	**2.25**	**2.03**	**1.79**	**1.66**	**1.56**	**1.50**	**1.46**	**1.43**	**1.41**	**1.39**	**1.36**	**1.34**	**1.33**	**1.32**	**1.31**	**1.30**	**1.28**
8	8.25	3.92	**2.87**	**2.42**	**2.17**	**1.90**	**1.75**	**1.65**	**1.58**	**1.54**	**1.50**	**1.48**	**1.46**	**1.43**	**1.41**	**1.39**	**1.38**	**1.37**	**1.35**	**1.34**
12	9.46	4.28	*3.08*	**2.57**	**2.29**	**1.99**	**1.83**	**1.72**	**1.65**	**1.60**	**1.56**	**1.53**	**1.51**	**1.48**	**1.46**	**1.44**	**1.43**	**1.42**	**1.40**	**1.39**
16	10.43	4.55	3.23	**2.68**	**2.37**	**2.05**	**1.89**	**1.77**	**1.69**	**1.64**	**1.60**	**1.57**	**1.55**	**1.52**	**1.50**	**1.48**	**1.47**	**1.45**	**1.44**	**1.42**
20	11.24	4.77	3.35	**2.76**	**2.44**	**2.11**	**1.93**	**1.81**	**1.73**	**1.67**	**1.64**	**1.61**	**1.58**	**1.55**	**1.52**	**1.51**	**1.49**	**1.48**	**1.46**	**1.45**
30	12.88	5.20	3.58	**2.92**	**2.57**	**2.20**	**2.01**	**1.88**	**1.79**	**1.73**	**1.69**	**1.66**	**1.64**	**1.60**	**1.57**	**1.56**	**1.54**	**1.53**	**1.50**	**1.50**
40	14.18	5.52	3.75	**3.04**	**2.66**	**2.27**	**2.07**	**1.93**	**1.84**	**1.78**	**1.73**	**1.70**	**1.68**	**1.64**	**1.61**	**1.59**	**1.57**	**1.56**	**1.54**	**1.53**
50	15.29	5.79	3.89	*3.13*	**2.73**	**2.32**	**2.12**	**1.97**	**1.88**	**1.81**	**1.77**	**1.73**	**1.71**	**1.67**	**1.64**	**1.62**	**1.60**	**1.59**	**1.57**	**1.55**
60	16.23	6.01	4.00	*3.21*	**2.79**	**2.37**	**2.15**	**2.00**	**1.90**	**1.84**	**1.79**	**1.76**	**1.73**	**1.69**	**1.66**	**1.64**	**1.62**	**1.61**	**1.59**	**1.57**
75	17.46	6.30	4.15	3.30	**2.87**	**2.42**	**2.20**	**2.04**	**1.94**	**1.87**	**1.83**	**1.79**	**1.76**	**1.72**	**1.69**	**1.66**	**1.65**	**1.64**	**1.61**	**1.60**
100	19.22	6.68	4.34	3.43	**2.97**	**2.49**	**2.26**	**2.09**	**1.98**	**1.92**	**1.87**	**1.83**	**1.80**	**1.75**	**1.72**	**1.70**	**1.68**	**1.67**	**1.64**	**1.63**
125	20.74	6.97	4.48	3.53	**3.04**	**2.55**	**2.30**	**2.13**	**2.02**	**1.95**	**1.90**	**1.86**	**1.83**	**1.78**	**1.75**	**1.72**	**1.71**	**1.69**	**1.67**	**1.65**
150	22.03	7.27	4.61	3.62	*3.11*	**2.59**	**2.34**	**2.16**	**2.05**	**1.98**	**1.92**	**1.88**	**1.85**	**1.80**	**1.77**	**1.74**	**1.73**	**1.71**	**1.68**	**1.67**
175	23.20	7.50	4.72	3.69	*3.16*	**2.63**	**2.37**	**2.19**	**2.07**	**2.00**	**1.94**	**1.90**	**1.88**	**1.82**	**1.79**	**1.77**	**1.74**	**1.73**	**1.70**	**1.68**
200	24.38	7.68	4.83	3.75	*3.21*	**2.67**	**2.40**	**2.21**	**2.09**	**2.02**	**1.96**	**1.92**	**1.89**	**1.84**	**1.80**	**1.78**	**1.76**	**1.74**	**1.72**	**1.70**

Table 19-18. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Means of Order 3 (40 COC, Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	3.60	**2.16**	**1.74**	**1.53**	**1.42**	**1.28**	**1.21**	**1.15**	**1.11**	**1.09**	**1.07**	**1.05**	**1.04**	**1.03**	**1.01**	**1.00**	**1.00**	**0.99**	**0.98**	**0.98**
2	4.59	**2.56**	**2.00**	**1.75**	**1.60**	**1.44**	**1.35**	**1.28**	**1.23**	**1.20**	**1.18**	**1.17**	**1.15**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**
3	5.27	*2.81*	**2.17**	**1.88**	**1.71**	**1.53**	**1.43**	**1.35**	**1.30**	**1.27**	**1.25**	**1.23**	**1.21**	**1.19**	**1.18**	**1.17**	**1.16**	**1.15**	**1.14**	**1.13**
4	5.82	3.01	**2.29**	**1.97**	**1.79**	**1.59**	**1.48**	**1.40**	**1.35**	**1.32**	**1.29**	**1.27**	**1.26**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**
5	6.28	3.16	**2.39**	**2.04**	**1.85**	**1.64**	**1.53**	**1.44**	**1.39**	**1.35**	**1.33**	**1.31**	**1.29**	**1.27**	**1.25**	**1.24**	**1.23**	**1.22**	**1.21**	**1.20**
8	7.37	3.51	**2.60**	**2.20**	**1.98**	**1.74**	**1.62**	**1.53**	**1.47**	**1.43**	**1.40**	**1.38**	**1.36**	**1.33**	**1.31**	**1.30**	**1.29**	**1.28**	**1.27**	**1.26**
12	8.45	3.84	*2.79*	**2.34**	**2.10**	**1.84**	**1.70**	**1.60**	**1.54**	**1.49**	**1.46**	**1.44**	**1.42**	**1.39**	**1.37**	**1.35**	**1.34**	**1.33**	**1.32**	**1.31**
16	9.31	4.08	*2.93*	**2.44**	**2.18**	**1.90**	**1.76**	**1.65**	**1.58**	**1.54**	**1.50**	**1.48**	**1.46**	**1.43**	**1.41**	**1.39**	**1.38**	**1.37**	**1.35**	**1.34**
20	10.03	4.28	3.04	**2.52**	**2.25**	**1.95**	**1.80**	**1.69**	**1.62**	**1.57**	**1.54**	**1.51**	**1.49**	**1.46**	**1.44**	**1.42**	**1.41**	**1.40**	**1.38**	**1.37**
30	11.50	4.67	3.25	**2.67**	**2.37**	**2.05**	**1.88**	**1.76**	**1.68**	**1.63**	**1.59**	**1.57**	**1.54**	**1.51**	**1.49**	**1.47**	**1.46**	**1.45**	**1.43**	**1.42**
40	12.66	4.96	3.41	*2.79*	**2.45**	**2.11**	**1.94**	**1.81**	**1.73**	**1.67**	**1.64**	**1.61**	**1.58**	**1.55**	**1.52**	**1.51**	**1.49**	**1.48**	**1.46**	**1.45**
50	13.64	5.20	3.53	*2.87*	**2.52**	**2.16**	**1.98**	**1.85**	**1.76**	**1.71**	**1.67**	**1.64**	**1.61**	**1.58**	**1.55**	**1.53**	**1.52**	**1.50**	**1.48**	**1.46**
60	14.49	5.40	3.64	*2.94*	**2.58**	**2.21**	**2.02**	**1.88**	**1.79**	**1.74**	**1.69**	**1.66**	**1.64**	**1.60**	**1.57**	**1.55**	**1.54**	**1.53**	**1.50**	**1.48**
75	15.65	5.66	3.77	3.03	**2.65**	**2.26**	**2.06**	**1.92**	**1.83**	**1.77**	**1.73**	**1.69**	**1.67**	**1.63**	**1.60**	**1.58**	**1.57**	**1.55**	**1.53**	**1.52**
100	17.23	6.02	3.95	3.15	*2.74*	**2.33**	**2.12**	**1.97**	**1.88**	**1.81**	**1.77**	**1.73**	**1.71**	**1.67**	**1.64**	**1.62**	**1.60**	**1.59**	**1.57**	**1.55**
125	18.59	6.29	4.08	3.25	*2.82*	**2.38**	**2.16**	**2.01**	**1.91**	**1.85**	**1.80**	**1.76**	**1.74**	**1.70**	**1.67**	**1.65**	**1.63**	**1.62**	**1.59**	**1.58**
150	19.69	6.53	4.20	3.33	*2.88*	**2.43**	**2.20**	**2.04**	**1.94**	**1.87**	**1.82**	**1.79**	**1.76**	**1.72**	**1.69**	**1.67**	**1.66**	**1.64**	**1.61**	**1.60**
175	20.78	6.73	4.31	3.40	*2.93*	**2.46**	**2.23**	**2.06**	**1.97**	**1.90**	**1.85**	**1.81**	**1.78**	**1.74**	**1.71**	**1.69**	**1.67**	**1.66**	**1.63**	**1.61**
200	21.60	6.94	4.41	3.45	*2.97*	**2.50**	**2.26**	**2.09**	**1.99**	**1.91**	**1.87**	**1.83**	**1.80**	**1.76**	**1.73**	**1.71**	**1.69**	**1.68**	**1.64**	**1.62**

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Table 19-18. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Means of Order 3 (40 COC, Semi-Annual)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	4.35	**2.51**	**1.98**	**1.74**	**1.59**	**1.43**	**1.34**	**1.28**	**1.23**	**1.20**	**1.18**	**1.17**	**1.15**	**1.13**	**1.12**	**1.11**	**1.10**	**1.09**	**1.08**	**1.07**
2	5.53	*2.95*	**2.27**	**1.96**	**1.78**	**1.59**	**1.48**	**1.40**	**1.35**	**1.32**	**1.29**	**1.27**	**1.26**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**
3	6.36	3.24	**2.45**	**2.09**	**1.89**	**1.68**	**1.56**	**1.48**	**1.42**	**1.38**	**1.36**	**1.33**	**1.32**	**1.29**	**1.27**	**1.26**	**1.25**	**1.24**	**1.23**	**1.22**
4	7.01	3.45	**2.58**	**2.19**	**1.98**	**1.74**	**1.62**	**1.53**	**1.47**	**1.43**	**1.40**	**1.38**	**1.36**	**1.33**	**1.31**	**1.30**	**1.29**	**1.28**	**1.27**	**1.26**
5	7.56	3.63	**2.68**	**2.27**	**2.04**	**1.79**	**1.66**	**1.57**	**1.50**	**1.46**	**1.43**	**1.41**	**1.39**	**1.36**	**1.34**	**1.33**	**1.32**	**1.31**	**1.30**	**1.28**
8	8.86	4.02	*2.91*	**2.43**	**2.18**	**1.90**	**1.75**	**1.65**	**1.58**	**1.54**	**1.50**	**1.48**	**1.46**	**1.43**	**1.41**	**1.39**	**1.38**	**1.37**	**1.35**	**1.34**
12	10.16	4.38	3.11	**2.58**	**2.29**	**1.99**	**1.83**	**1.72**	**1.65**	**1.60**	**1.56**	**1.53**	**1.51**	**1.48**	**1.46**	**1.44**	**1.43**	**1.42**	**1.40**	**1.39**
16	11.19	4.66	3.27	**2.69**	**2.38**	**2.06**	**1.89**	**1.77**	**1.69**	**1.64**	**1.60**	**1.57**	**1.55**	**1.52**	**1.50**	**1.48**	**1.47**	**1.46**	**1.44**	**1.42**
20	12.06	4.89	3.39	**2.78**	**2.45**	**2.11**	**1.94**	**1.81**	**1.73**	**1.67**	**1.64**	**1.61**	**1.58**	**1.55**	**1.52**	**1.51**	**1.49**	**1.48**	**1.46**	**1.45**
30	13.81	5.32	3.62	*2.94*	**2.58**	**2.20**	**2.02**	**1.88**	**1.79**	**1.74**	**1.69**	**1.66**	**1.64**	**1.60**	**1.57**	**1.55**	**1.54**	**1.53**	**1.50**	**1.48**
40	15.21	5.65	3.79	*3.05*	**2.67**	**2.27**	**2.07**	**1.93**	**1.84**	**1.78**	**1.74**	**1.70**	**1.68**	**1.64**	**1.61**	**1.59**	**1.57**	**1.56**	**1.54**	**1.53**
50	16.41	5.92	3.92	3.14	**2.74**	**2.33**	**2.12**	**1.97**	**1.88**	**1.81**	**1.77**	**1.73**	**1.71**	**1.67**	**1.64**	**1.62**	**1.60**	**1.59**	**1.57**	**1.55**
60	17.43	6.15	4.04	3.22	**2.80**	**2.37**	**2.15**	**2.00**	**1.90**	**1.84**	**1.79**	**1.76**	**1.73**	**1.69**	**1.66**	**1.64**	**1.62**	**1.61**	**1.59**	**1.57**
75	18.80	6.44	4.18	3.32	*2.88*	**2.42**	**2.20**	**2.04**	**1.94**	**1.87**	**1.82**	**1.79**	**1.76**	**1.72**	**1.69**	**1.66**	**1.65**	**1.63**	**1.61**	**1.60**
100	20.64	6.84	4.38	3.44	*2.97*	**2.50**	**2.26**	**2.09**	**1.98**	**1.92**	**1.86**	**1.83**	**1.80**	**1.76**	**1.72**	**1.70**	**1.68**	**1.67**	**1.64**	**1.62**
125	22.29	7.14	4.53	3.55	*3.05*	**2.55**	**2.30**	**2.13**	**2.02**	**1.95**	**1.90**	**1.86**	**1.83**	**1.79**	**1.75**	**1.72**	**1.70**	**1.69**	**1.67**	**1.65**
150	23.65	7.42	4.66	3.63	*3.11*	**2.59**	**2.34**	**2.16**	**2.05**	**1.98**	**1.92**	**1.88**	**1.85**	**1.81**	**1.78**	**1.75**	**1.73**	**1.71**	**1.69**	**1.67**
175	24.88	7.66	4.77	3.71	3.16	**2.63**	**2.37**	**2.19**	**2.07**	**2.00**	**1.94**	**1.91**	**1.87**	**1.83**	**1.80**	**1.76**	**1.74**	**1.73**	**1.70**	**1.69**
200	25.98	7.86	4.87	3.76	3.21	**2.67**	**2.40**	**2.21**	**2.09**	**2.02**	**1.97**	**1.92**	**1.89**	**1.85**	**1.82**	**1.78**	**1.76**	**1.75**	**1.72**	**1.70**

Table 19-18. κ-Multipliers for 1-of-2 Intrawell Prediction Limits on Means of Order 3 (40 COC, Quarterly)

w / n	4	6	8	10	12	16	20	25	30	35	40	45	50	60	70	80	90	100	125	150
1	5.14	**2.87**	**2.24**	**1.94**	**1.77**	**1.58**	**1.48**	**1.40**	**1.35**	**1.32**	**1.29**	**1.27**	**1.26**	**1.23**	**1.22**	**1.21**	**1.20**	**1.19**	**1.18**	**1.17**
2	6.52	3.36	**2.54**	**2.17**	**1.97**	**1.74**	**1.62**	**1.53**	**1.47**	**1.43**	**1.40**	**1.38**	**1.36**	**1.33**	**1.31**	**1.30**	**1.29**	**1.28**	**1.27**	**1.26**
3	7.49	3.68	**2.73**	**2.32**	**2.08**	**1.83**	**1.70**	**1.60**	**1.53**	**1.49**	**1.46**	**1.44**	**1.42**	**1.39**	**1.37**	**1.35**	**1.34**	**1.33**	**1.32**	**1.31**
4	8.25	3.92	**2.87**	**2.42**	**2.17**	**1.90**	**1.75**	**1.65**	**1.58**	**1.54**	**1.50**	**1.48**	**1.46**	**1.43**	**1.41**	**1.39**	**1.38**	**1.37**	**1.35**	**1.34**
5	8.90	4.11	**2.98**	**2.50**	**2.23**	**1.95**	**1.80**	**1.69**	**1.62**	**1.57**	**1.53**	**1.51**	**1.49**	**1.46**	**1.44**	**1.42**	**1.41**	**1.40**	**1.38**	**1.37**
8	10.42	4.55	3.23	**2.68**	**2.37**	**2.06**	**1.89**	**1.77**	**1.69**	**1.64**	**1.60**	**1.57**	**1.55**	**1.52**	**1.50**	**1.48**	**1.47**	**1.45**	**1.44**	**1.42**
12	11.95	4.96	3.45	**2.83**	**2.50**	**2.15**	**1.97**	**1.84**	**1.76**	**1.70**	**1.66**	**1.63**	**1.61**	**1.57**	**1.55**	**1.53**	**1.51**	**1.50**	**1.48**	**1.47**
16	13.16	5.27	3.62	**2.95**	**2.59**	**2.22**	**2.03**	**1.89**	**1.80**	**1.74**	**1.70**	**1.67**	**1.64**	**1.61**	**1.58**	**1.56**	**1.55**	**1.53**	**1.52**	**1.50**
20	14.18	5.52	3.75	**3.04**	**2.66**	**2.27**	**2.07**	**1.93**	**1.84**	**1.78**	**1.73**	**1.70**	**1.68**	**1.64**	**1.61**	**1.59**	**1.57**	**1.56**	**1.54**	**1.53**
30	16.24	6.01	4.00	*3.21*	**2.79**	**2.37**	**2.15**	**2.00**	**1.90**	**1.84**	**1.79**	**1.76**	**1.73**	**1.69**	**1.66**	**1.64**	**1.62**	**1.61**	**1.59**	**1.57**
40	17.88	6.37	4.18	3.33	**2.89**	**2.44**	**2.21**	**2.05**	**1.95**	**1.88**	**1.83**	**1.80**	**1.77**	**1.72**	**1.69**	**1.67**	**1.66**	**1.64**	**1.62**	**1.60**
50	19.28	6.67	4.33	3.43	**2.96**	**2.49**	**2.26**	**2.09**	**1.98**	**1.92**	**1.87**	**1.83**	**1.80**	**1.75**	**1.72**	**1.70**	**1.68**	**1.67**	**1.64**	**1.62**
60	20.47	6.93	4.46	3.51	**3.02**	**2.54**	**2.29**	**2.12**	**2.01**	**1.94**	**1.89**	**1.85**	**1.82**	**1.77**	**1.74**	**1.72**	**1.70**	**1.69**	**1.66**	**1.64**
75	22.08	7.26	4.61	3.61	*3.10*	**2.59**	**2.34**	**2.16**	**2.05**	**1.98**	**1.92**	**1.88**	**1.85**	**1.80**	**1.77**	**1.75**	**1.73**	**1.71**	**1.68**	**1.67**
100	24.34	7.69	4.82	3.75	*3.20*	**2.67**	**2.40**	**2.21**	**2.09**	**2.02**	**1.96**	**1.92**	**1.89**	**1.84**	**1.80**	**1.78**	**1.76**	**1.75**	**1.72**	**1.70**
125	26.11	8.07	4.99	3.86	*3.29*	**2.72**	**2.44**	**2.25**	**2.13**	**2.05**	**2.00**	**1.95**	**1.92**	**1.86**	**1.83**	**1.81**	**1.79**	**1.77**	**1.74**	**1.72**
150	27.89	8.37	5.13	3.95	3.35	**2.77**	**2.48**	**2.28**	**2.16**	**2.08**	**2.02**	**1.98**	**1.94**	**1.89**	**1.85**	**1.83**	**1.81**	**1.79**	**1.76**	**1.74**
175	29.26	8.61	5.25	4.02	3.41	**2.81**	**2.51**	**2.31**	**2.18**	**2.10**	**2.04**	**2.00**	**1.96**	**1.91**	**1.87**	**1.85**	**1.83**	**1.81**	**1.77**	**1.76**
200	30.62	8.89	5.37	4.09	3.46	**2.85**	**2.54**	**2.33**	**2.20**	**2.12**	**2.06**	**2.01**	**1.98**	**1.93**	**1.90**	**1.86**	**1.84**	**1.83**	**1.79**	**1.77**

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Table 19-19. Per-Constituent Significance Levels (α) for Non-Parametric 1-of-2 Plan (PL=X_n)

w\n	4	6	8	10	12	16	20	25	30	35	40
1	0.6667-1	0.3571-1	0.2222-1	0.1515-1	0.1099-1	0.6536-2	0.4329-2	0.2849-2	0.2016-2	0.1502-2	0.1161-2
2	0.1190	0.6667-1	0.4242-1	0.2930-1	0.2143-1	0.1287-1	0.8564-2	0.5656-2	0.4011-2	0.2991-2	0.2316-2
3	0.1619	0.9394-1	0.6094-1	0.4258-1	0.3137-1	0.1900-1	0.1271-1	0.8422-2	0.5984-2	0.4468-2	0.3462-2
4	0.1980	0.1183	0.7802-1	0.5509-1	0.4087-1	0.2496-1	0.1677-1	0.1115-1	0.7937-2	0.5934-2	0.4602-2
5	0.2290	0.1402	0.9387-1	0.6691-1	0.4995-1	0.3074-1	0.2075-1	0.1384-1	0.9870-2	0.7388-2	0.5735-2
8	0.3016	0.1954	0.1355	0.9890-1	0.7507-1	0.4717-1	0.3222-1	0.2168-1	0.1555-1	0.1168-1	0.9091-2
10	0.3386	0.2255	0.1594	0.1178	0.9028-1	0.5744-1	0.3952-1	0.2674-1	0.1925-1	0.1449-1	0.1130-1
12	0.3696	0.2519	0.1808	0.1352	0.1045	0.6721-1	0.4656-1	0.3168-1	0.2287-1	0.1726-1	0.1347-1
15	0.4080	0.2859	0.2094	0.1589	0.1241	0.8105-1	0.5667-1	0.3885-1	0.2819-1	0.2134-1	0.1669-1
20	0.4576	0.3320	0.2496	0.1932	0.1532	0.1022	0.7248-1	0.5025-1	0.3673-1	0.2794-1	0.2194-1
25	0.4955	0.3690	0.2830	0.2225	0.1787	0.1214	0.8714-1	0.6102-1	0.4491-1	0.3433-1	0.2704-1
30	0.5259	0.3997	0.3116	0.2482	0.2014	0.1390	0.1008	0.7125-1	0.5276-1	0.4051-1	0.3201-1
35	0.5509	0.4257	0.3363	0.2708	0.2218	0.1551	0.1136	0.8097-1	0.6030-1	0.4649-1	0.3685-1
40	0.5721	0.4483	0.3582	0.2911	0.2403	0.1701	0.1257	0.9024-1	0.6757-1	0.5230-1	0.4157-1
45	0.5904	0.4680	0.3776	0.3095	0.2572	0.1840	0.1370	0.9910-1	0.7458-1	0.5793-1	0.4618-1
50	0.6063	0.4856	0.3951	0.3262	0.2727	0.1970	0.1478	0.1076	0.8134-1	0.6341-1	0.5068-1
60	0.6330	0.5155	0.4256	0.3556	0.3005	0.2208	0.1677	0.1235	0.9422-1	0.7393-1	0.5938-1
70	0.6546	0.5403	0.4512	0.3809	0.3246	0.2420	0.1858	0.1383	0.1063	0.8391-1	0.6770-1
80	0.6726	0.5613	0.4733	0.4029	0.3460	0.2611	0.2024	0.1521	0.1177	0.9340-1	0.7568-1
90	0.6880	0.5795	0.4927	0.4224	0.3651	0.2785	0.2178	0.1650	0.1285	0.1025	0.8334-1
100	0.7012	0.5954	0.5098	0.4399	0.3823	0.2944	0.2320	0.1771	0.1387	0.1111	0.9072-1
120	0.7231	0.6221	0.5389	0.4699	0.4122	0.3226	0.2576	0.1992	0.1577	0.1274	0.1047
140	0.7407	0.6438	0.5629	0.4950	0.4376	0.3471	0.2802	0.2191	0.1751	0.1424	0.1177
160	0.7552	0.6619	0.5832	0.5165	0.4595	0.3686	0.3004	0.2372	0.1910	0.1564	0.1300
180	0.7674	0.6773	0.6007	0.5351	0.4787	0.3877	0.3185	0.2537	0.2057	0.1694	0.1415
200	0.7778	0.6907	0.6160	0.5516	0.4958	0.4049	0.3351	0.2689	0.2194	0.1817	0.1524

Footnote. PL = Prediction Limit; X_n = Maximum order statistic

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Table 19-19. Per-Constituent Significance Levels (α) for Non-Parametric 1-of-2 Plan (PL=X_n)

w\n	50	60	70	80	90	100	120	140	160	180	200
1	**0.7541-3**	**0.5288-3**	*0.3912-3*	*0.3011-3*	*0.2389-3*	*0.1941-3*	*0.1355-3*	0.9989-4	0.7668-4	0.6071-4	0.4926-4
2	**0.1505-2**	**0.1056-2**	*0.7816-3*	*0.6017-3*	*0.4775-3*	*0.3881-3*	*0.2709-3*	0.1997-3	0.1533-3	0.1214-3	0.9850-4
3	**0.2253-2**	**0.1582-2**	*0.1171-2*	*0.9018-3*	*0.7157-3*	*0.5818-3*	*0.4061-3*	0.2995-3	0.2299-3	0.1821-3	0.1477-3
4	**0.2998-2**	**0.2106-2**	*0.1560-2*	*0.1201-2*	*0.9536-3*	*0.7752-3*	*0.5413-3*	0.3992-3	0.3065-3	0.2427-3	0.1969-3
5	**0.3739-2**	**0.2628-2**	*0.1948-2*	*0.1500-2*	*0.1191-2*	*0.9685-3*	*0.6764-3*	0.4989-3	0.3831-3	0.3033-3	0.2462-3
8	**0.5946-2**	**0.4187-2**	*0.3106-2*	*0.2395-2*	*0.1902-2*	*0.1547-2*	*0.1081-2*	0.7975-3	0.6125-3	0.4851-3	0.3937-3
10	**0.7403-2**	**0.5219-2**	*0.3874-2*	*0.2988-2*	*0.2374-2*	*0.1932-2*	*0.1350-2*	0.9963-3	0.7653-3	0.6062-3	0.4919-3
12	**0.8848-2**	**0.6244-2**	*0.4638-2*	*0.3580-2*	*0.2845-2*	*0.2315-2*	*0.1619-2*	0.1195-2	0.9179-3	0.7271-3	0.5902-3
15	**0.1099-1**	**0.7772-2**	*0.5779-2*	*0.4463-2*	*0.3549-2*	*0.2889-2*	*0.2021-2*	0.1492-2	0.1147-2	0.9084-3	0.7374-3
20	**0.1451-1**	**0.1029-1**	*0.7665-2*	*0.5926-2*	*0.4717-2*	*0.3842-2*	*0.2690-2*	0.1987-2	0.1527-2	0.1210-2	0.9825-3
25	**0.1797-1**	**0.1277-1**	*0.9530-2*	*0.7377-2*	*0.5876-2*	*0.4789-2*	*0.3356-2*	0.2480-2	0.1907-2	0.1511-2	0.1227-2
30	**0.2136-1**	**0.1522-1**	*0.1138-1*	*0.8816-2*	*0.7028-2*	*0.5732-2*	*0.4019-2*	0.2972-2	0.2286-2	0.1812-2	0.1472-2
35	**0.2469-1**	**0.1764-1**	*0.1320-1*	*0.1024-1*	*0.8173-2*	*0.6669-2*	*0.4680-2*	0.3462-2	0.2664-2	0.2112-2	0.1716-2
40	**0.2796-1**	**0.2002-1**	*0.1501-1*	*0.1166-1*	*0.9310-2*	*0.7601-2*	*0.5338-2*	0.3951-2	0.3041-2	0.2412-2	0.1959-2
45	**0.3118-1**	**0.2238-1**	*0.1680-1*	*0.1307-1*	*0.1044-1*	*0.8529-2*	*0.5994-2*	0.4439-2	0.3417-2	0.2711-2	0.2203-2
50	**0.3434-1**	**0.2470-1**	*0.1858-1*	*0.1446-1*	*0.1156-1*	*0.9451-2*	*0.6647-2*	0.4925-2	0.3793-2	0.3009-2	0.2446-2
60	**0.4051-1**	**0.2927-1**	*0.2207-1*	*0.1722-1*	*0.1379-1*	*0.1128-1*	*0.7947-2*	0.5893-2	0.4541-2	0.3605-2	0.2931-2
70	**0.4648-1**	**0.3372-1**	*0.2551-1*	*0.1993-1*	*0.1598-1*	*0.1309-1*	*0.9237-2*	0.6856-2	0.5287-2	0.4199-2	0.3414-2
80	**0.5227-1**	**0.3807-1**	*0.2887-1*	*0.2261-1*	*0.1815-1*	*0.1489-1*	*0.1052-1*	0.7814-2	0.6029-2	0.4790-2	0.3896-2
90	**0.5789-1**	**0.4232-1**	*0.3218-1*	*0.2524-1*	*0.2030-1*	*0.1666-1*	*0.1179-1*	0.8766-2	0.6768-2	0.5380-2	0.4377-2
100	**0.6335-1**	**0.4648-1**	*0.3543-1*	*0.2784-1*	*0.2242-1*	*0.1842-1*	*0.1305-1*	0.9713-2	0.7504-2	0.5967-2	0.4857-2
120	**0.7382-1**	**0.5453-1**	*0.4176-1*	*0.3293-1*	*0.2659-1*	*0.2189-1*	*0.1555-1*	0.1159-1	0.8966-2	0.7136-2	0.5812-2
140	**0.8376-1**	**0.6225-1**	*0.4789-1*	*0.3788-1*	*0.3066-1*	*0.2529-1*	*0.1801-1*	0.1345-1	0.1042-1	0.8297-2	0.6762-2
160	**0.9322-1**	**0.6967-1**	*0.5382-1*	*0.4270-1*	*0.3464-1*	*0.2863-1*	*0.2044-1*	0.1529-1	0.1185-1	0.9451-2	0.7706-2
180	**0.1022**	**0.7682-1**	*0.5957-1*	*0.4741-1*	*0.3854-1*	*0.3191-1*	*0.2284-1*	0.1711-1	0.1328-1	0.1060-1	0.8646-2
200	**0.1109**	**0.8371-1**	*0.6515-1*	*0.5199-1*	*0.4236-1*	*0.3513-1*	*0.2520-1*	0.1892-1	0.1470-1	0.1173-1	0.9580-2

Footnote. PL = Prediction Limit; X_n = Maximum order statistic

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Table 19-19. Per-Constituent Significance Levels (α) for Non-Parametric 1-of-2 Plan (PL=X_{n-1})

w\n	4	6	8	10	12	16	20	25	30	35	40
1	0.2000	0.1071	0.6667-1	0.4545-1	0.3297-1	0.1961-1	0.1299-1	0.8547-2	0.6048-2	0.4505-2	0.3484-2
2	0.3286	0.1905	0.1232	0.8591-1	0.6319-1	0.3818-1	0.2550-1	0.1688-1	0.1199-1	0.8948-2	0.6932-2
3	0.4190	0.2576	0.1720	0.1223	0.9104-1	0.5582-1	0.3758-1	0.2502-1	0.1783-1	0.1333-1	0.1034-1
4	0.4866	0.3130	0.2147	0.1551	0.1168	0.7260-1	0.4924-1	0.3296-1	0.2356-1	0.1766-1	0.1372-1
5	0.5391	0.3598	0.2524	0.1851	0.1408	0.8860-1	0.6052-1	0.4072-1	0.2920-1	0.2193-1	0.1706-1
8	0.6450	0.4651	0.3436	0.2612	0.2038	0.1325	0.9224-1	0.6297-1	0.4556-1	0.3442-1	0.2688-1
10	0.6911	0.5163	0.3914	0.3030	0.2397	0.1588	0.1118	0.7702-1	0.5603-1	0.4248-1	0.3327-1
12	0.7261	0.5577	0.4317	0.3396	0.2719	0.1831	0.1303	0.9048-1	0.6617-1	0.5036-1	0.3953-1
15	0.7653	0.6071	0.4820	0.3867	0.3144	0.2163	0.1561	0.1097	0.8082-1	0.6182-1	0.4871-1
20	0.8099	0.6672	0.5466	0.4499	0.3733	0.2648	0.1950	0.1394	0.1039	0.8006-1	0.6344-1
25	0.8398	0.7103	0.5955	0.4997	0.4214	0.3063	0.2295	0.1665	0.1253	0.9732-1	0.7752-1
30	0.8613	0.7429	0.6340	0.5402	0.4616	0.3424	0.2605	0.1914	0.1454	0.1137	0.9101-1
35	0.8776	0.7686	0.6652	0.5739	0.4957	0.3743	0.2884	0.2145	0.1643	0.1293	0.1039
40	0.8903	0.7893	0.6910	0.6024	0.5252	0.4026	0.3138	0.2358	0.1821	0.1441	0.1164
45	0.9006	0.8064	0.7129	0.6270	0.5510	0.4280	0.3370	0.2558	0.1989	0.1582	0.1283
50	0.9091	0.8208	0.7316	0.6484	0.5738	0.4509	0.3584	0.2744	0.2149	0.1717	0.1398
60	0.9222	0.8438	0.7621	0.6840	0.6123	0.4909	0.3965	0.3084	0.2443	0.1971	0.1616
70	0.9320	0.8613	0.7860	0.7125	0.6438	0.5246	0.4295	0.3385	0.2711	0.2205	0.1820
80	0.9395	0.8751	0.8053	0.7359	0.6700	0.5535	0.4584	0.3656	0.2955	0.2421	0.2010
90	0.9455	0.8864	0.8212	0.7555	0.6923	0.5787	0.4841	0.3901	0.3179	0.2622	0.2189
100	0.9505	0.8957	0.8345	0.7722	0.7115	0.6008	0.5070	0.4124	0.3386	0.2810	0.2358
120	0.9580	0.9102	0.8558	0.7991	0.7430	0.6380	0.5464	0.4515	0.3756	0.3151	0.2668
140	0.9635	0.9211	0.8720	0.8200	0.7678	0.6681	0.5792	0.4849	0.4079	0.3454	0.2947
160	0.9677	0.9296	0.8847	0.8367	0.7879	0.6931	0.6069	0.5138	0.4363	0.3725	0.3201
180	0.9710	0.9364	0.8951	0.8505	0.8046	0.7143	0.6308	0.5391	0.4616	0.3970	0.3432
200	0.9737	0.9419	0.9037	0.8619	0.8186	0.7325	0.6516	0.5615	0.4844	0.4192	0.3644

Footnote. PL = Prediction Limit; X_{n-1} = 2nd largest order statistic

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Table 19-19. Per-Constituent Significance Levels (α) for Non-Parametric 1-of-2 Plan (PL=X_{n-1})

w\n	50	60	70	80	90	100	120	140	160	180	200
1	0.2262-2	0.1586-2	0.1174-2	0.9033-3	0.7167-3	0.5824-3	0.4064-3	0.2997-3	0.2300-3	*0.1821-3*	*0.1478-3*
2	0.4509-2	0.3165-2	0.2343-2	0.1804-2	0.1432-2	0.1164-2	0.8124-3	0.5990-3	0.4599-3	*0.3642-3*	*0.2955-3*
3	0.6740-2	0.4736-2	0.3508-2	0.2702-2	0.2145-2	0.1744-2	0.1218-2	0.8981-3	0.6896-3	*0.5461-3*	*0.4431-3*
4	0.8956-2	0.6299-2	0.4669-2	0.3598-2	0.2857-2	0.2323-2	0.1623-2	0.1197-2	0.9191-3	*0.7279-3*	*0.5907-3*
5	0.1116-1	0.7854-2	0.5825-2	0.4491-2	0.3567-2	0.2901-2	0.2027-2	0.1495-2	0.1149-2	*0.9096-3*	*0.7382-3*
8	0.1767-1	0.1248-1	0.9270-2	0.7155-2	0.5688-2	0.4629-2	0.3237-2	0.2389-2	0.1836-2	*0.1454-2*	*0.1180-2*
10	0.2194-1	0.1552-1	0.1155-1	0.8919-2	0.7094-2	0.5776-2	0.4041-2	0.2984-2	0.2293-2	*0.1817-2*	*0.1475-2*
12	0.2615-1	0.1853-1	0.1380-1	0.1067-1	0.8494-2	0.6918-2	0.4843-2	0.3577-2	0.2749-2	*0.2179-2*	*0.1769-2*
15	0.3237-1	0.2300-1	0.1716-1	0.1328-1	0.1058-1	0.8624-2	0.6041-2	0.4465-2	0.3433-2	*0.2721-2*	*0.2209-2*
20	0.4247-1	0.3032-1	0.2268-1	0.1759-1	0.1403-1	0.1145-1	0.8029-2	0.5939-2	0.4568-2	*0.3622-2*	*0.2942-2*
25	0.5226-1	0.3746-1	0.2811-1	0.2184-1	0.1744-1	0.1424-1	0.1000-1	0.7406-2	0.5700-2	*0.4521-2*	*0.3673-2*
30	0.6176-1	0.4445-1	0.3344-1	0.2603-1	0.2082-1	0.1702-1	0.1197-1	0.8866-2	0.6827-2	*0.5418-2*	*0.4403-2*
35	0.7098-1	0.5129-1	0.3869-1	0.3017-1	0.2415-1	0.1976-1	0.1392-1	0.1032-1	0.7951-2	*0.6311-2*	*0.5130-2*
40	0.7994-1	0.5799-1	0.4384-1	0.3425-1	0.2746-1	0.2249-1	0.1586-1	0.1177-1	0.9070-2	*0.7202-2*	*0.5856-2*
45	0.8866-1	0.6454-1	0.4892-1	0.3828-1	0.3073-1	0.2519-1	0.1778-1	0.1320-1	0.1019-1	*0.8091-2*	*0.6580-2*
50	0.9714-1	0.7096-1	0.5391-1	0.4226-1	0.3396-1	0.2786-1	0.1970-1	0.1464-1	0.1130-1	*0.8977-2*	*0.7303-2*
60	0.1134	0.8342-1	0.6367-1	0.5006-1	0.4033-1	0.3315-1	0.2349-1	0.1748-1	0.1351-1	*0.1074-1*	*0.8743-2*
70	0.1289	0.9540-1	0.7313-1	0.5768-1	0.4658-1	0.3835-1	0.2724-1	0.2030-1	0.1570-1	*0.1250-1*	*0.1018-1*
80	0.1437	0.1069	0.8231-1	0.6512-1	0.5270-1	0.4346-1	0.3094-1	0.2310-1	0.1788-1	*0.1424-1*	*0.1160-1*
90	0.1577	0.1181	0.9123-1	0.7238-1	0.5870-1	0.4849-1	0.3460-1	0.2587-1	0.2004-1	*0.1597-1*	*0.1302-1*
100	0.1712	0.1288	0.9990-1	0.7948-1	0.6459-1	0.5344-1	0.3821-1	0.2861-1	0.2219-1	*0.1770-1*	*0.1444-1*
120	0.1963	0.1492	0.1165	0.9320-1	0.7604-1	0.6310-1	0.4532-1	0.3403-1	0.2645-1	*0.2112-1*	*0.1724-1*
140	0.2196	0.1683	0.1323	0.1063	0.8708-1	0.7248-1	0.5227-1	0.3935-1	0.3064-1	*0.2450-1*	*0.2002-1*
160	0.2410	0.1863	0.1473	0.1189	0.9774-1	0.8158-1	0.5907-1	0.4459-1	0.3478-1	*0.2785-1*	*0.2278-1*
180	0.2610	0.2032	0.1616	0.1310	0.1080	0.9041-1	0.6572-1	0.4973-1	0.3886-1	*0.3116-1*	*0.2551-1*
200	0.2797	0.2192	0.1753	0.1427	0.1180	0.9900-1	0.7222-1	0.5480-1	0.4289-1	*0.3443-1*	*0.2822-1*

Footnote. PL = Prediction Limit; X_{n-1} = 2nd largest order statistic

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Table 19-20. Per-Constituent Significance Levels (α) for Non-Parametric 1-of-3 Plan (PL=X_n)

w\n	4	6	8	10	12	16	20	25	30	35	40
1	0.2857-1	0.1190-1	0.6061-2	0.3497-2	0.2198-2	0.1032-2	0.5647-3	0.3053-3	0.1833-3	*0.1185-3*	*0.8103-4*
2	0.5238-1	0.2273-1	0.1179-1	0.6868-2	0.4342-2	0.2051-2	0.1125-2	0.6091-3	0.3661-3	*0.2369-3*	*0.1620-3*
3	0.7283-1	0.3267-1	0.1722-1	0.1013-1	0.6435-2	0.3056-2	0.1681-2	0.9117-3	0.5483-3	*0.3550-3*	*0.2428-3*
4	0.9076-1	0.4187-1	0.2240-1	0.1328-1	0.8481-2	0.4049-2	0.2233-2	0.1213-2	0.7301-3	*0.4728-3*	*0.3235-3*
5	0.1067	0.5045-1	0.2735-1	0.1633-1	0.1048-1	0.5031-2	0.2781-2	0.1513-2	0.9113-3	*0.5905-3*	*0.4041-3*
8	0.1463	0.7320-1	0.4101-1	0.2499-1	0.1624-1	0.7906-2	0.4401-2	0.2405-2	0.1452-2	*0.9422-3*	*0.6453-3*
10	0.1678	0.8643-1	0.4929-1	0.3038-1	0.1990-1	0.9769-2	0.5462-2	0.2994-2	0.1810-2	*0.1176-2*	*0.8056-3*
12	0.1865	0.9846-1	0.5704-1	0.3552-1	0.2342-1	0.1159-1	0.6509-2	0.3577-2	0.2167-2	*0.1408-2*	*0.9654-3*
15	0.2107	0.1147	0.6780-1	0.4279-1	0.2848-1	0.1426-1	0.8054-2	0.4444-2	0.2697-2	*0.1755-2*	*0.1204-2*
20	0.2437	0.1380	0.8386-1	0.5396-1	0.3640-1	0.1853-1	0.1056-1	0.5866-2	0.3573-2	*0.2330-2*	*0.1601-2*
25	0.2704	0.1580	0.9810-1	0.6412-1	0.4376-1	0.2261-1	0.1300-1	0.7262-2	0.4438-2	*0.2900-2*	*0.1995-2*
30	0.2928	0.1754	0.1109	0.7348-1	0.5065-1	0.2652-1	0.1537-1	0.8632-2	0.5292-2	*0.3465-2*	*0.2386-2*
35	0.3121	0.1908	0.1225	0.8215-1	0.5713-1	0.3028-1	0.1767-1	0.9978-2	0.6136-2	*0.4025-2*	*0.2776-2*
40	0.3289	0.2046	0.1332	0.9024-1	0.6326-1	0.3389-1	0.1991-1	0.1130-1	0.6971-2	*0.4581-2*	*0.3162-2*
45	0.3438	0.2172	0.1431	0.9783-1	0.6907-1	0.3738-1	0.2210-1	0.1260-1	0.7796-2	*0.5132-2*	*0.3547-2*
50	0.3573	0.2287	0.1523	0.1050	0.7461-1	0.4075-1	0.2423-1	0.1388-1	0.8612-2	*0.5679-2*	*0.3929-2*
60	0.3805	0.2492	0.1689	0.1181	0.8494-1	0.4717-1	0.2836-1	0.1639-1	0.1022-1	*0.6760-2*	*0.4688-2*
70	0.4001	0.2669	0.1837	0.1301	0.9445-1	0.5323-1	0.3231-1	0.1882-1	0.1179-1	*0.7824-2*	*0.5437-2*
80	0.4171	0.2826	0.1970	0.1410	0.1033	0.5895-1	0.3610-1	0.2118-1	0.1333-1	*0.8874-2*	*0.6179-2*
90	0.4319	0.2966	0.2091	0.1510	0.1115	0.6439-1	0.3975-1	0.2347-1	0.1484-1	*0.9908-2*	*0.6913-2*
100	0.4451	0.3093	0.2202	0.1603	0.1192	0.6957-1	0.4327-1	0.2571-1	0.1632-1	*0.1093-1*	*0.7639-2*
120	0.4677	0.3314	0.2399	0.1771	0.1333	0.7926-1	0.4996-1	0.3003-1	0.1921-1	*0.1293-1*	*0.9069-2*
140	0.4865	0.3502	0.2570	0.1920	0.1459	0.8819-1	0.5624-1	0.3415-1	0.2200-1	*0.1488-1*	*0.1047-1*
160	0.5026	0.3666	0.2722	0.2054	0.1574	0.9648-1	0.6216-1	0.3810-1	0.2470-1	*0.1678-1*	*0.1185-1*
180	0.5166	0.3811	0.2858	0.2175	0.1680	0.1042	0.6777-1	0.4189-1	0.2732-1	*0.1864-1*	*0.1320-1*
200	0.5289	0.3941	0.2980	0.2286	0.1777	0.1115	0.7311-1	0.4554-1	0.2987-1	*0.2045-1*	*0.1453-1*

Footnote. PL = Prediction Limit; X_n = Maximum order statistic

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Table 19-20. Per-Constituent Significance Levels (α) for Non-Parametric 1-of-3 Plan (PL=X_n)

w\n	50	60	70	80	90	100	120	140	160	180	200
1	*0.4269-4*	*0.2518-4*	*0.1608-4*	0.1088-4	0.7706-5	0.5654-5	0.3304-5	0.2096-5	0.1411-5	0.9953-6	0.7280-6
2	*0.8534-4*	*0.5035-4*	*0.3215-4*	0.2177-4	0.1541-4	0.1131-4	0.6609-5	0.4191-5	0.2823-5	0.1991-5	0.1456-5
3	*0.1280-3*	*0.7551-4*	*0.4822-4*	0.3264-4	0.2312-4	0.1696-4	0.9913-5	0.6287-5	0.4234-5	0.2986-5	0.2184-5
4	*0.1706-3*	*0.1007-3*	*0.6429-4*	0.4352-4	0.3082-4	0.2261-4	0.1322-4	0.8382-5	0.5645-5	0.3981-5	0.2912-5
5	*0.2131-3*	*0.1258-3*	*0.8035-4*	0.5440-4	0.3852-4	0.2827-4	0.1652-4	0.1048-4	0.7056-5	0.4976-5	0.3640-5
8	*0.3406-3*	*0.2011-3*	*0.1285-3*	0.8701-4	0.6162-4	0.4522-4	0.2643-4	0.1676-4	0.1129-4	0.7962-5	0.5823-5
10	*0.4255-3*	*0.2513-3*	*0.1606-3*	0.1087-3	0.7701-4	0.5652-4	0.3304-4	0.2095-4	0.1411-4	0.9952-5	0.7279-5
12	*0.5102-3*	*0.3015-3*	*0.1926-3*	0.1305-3	0.9240-4	0.6782-4	0.3964-4	0.2514-4	0.1693-4	0.1194-4	0.8735-5
15	*0.6371-3*	*0.3766-3*	*0.2407-3*	0.1630-3	0.1155-3	0.8476-4	0.4955-4	0.3143-4	0.2117-4	0.1493-4	0.1092-4
20	*0.8480-3*	*0.5016-3*	*0.3207-3*	0.2173-3	0.1539-3	0.1130-3	0.6605-4	0.4190-4	0.2822-4	0.1990-4	0.1456-4
25	*0.1058-2*	*0.6263-3*	*0.4006-3*	0.2715-3	0.1923-3	0.1412-3	0.8255-4	0.5237-4	0.3527-4	0.2488-4	0.1820-4
30	*0.1268-2*	*0.7507-3*	*0.4804-3*	0.3256-3	0.2307-3	0.1694-3	0.9905-4	0.6283-4	0.4232-4	0.2985-4	0.2183-4
35	*0.1476-2*	*0.8749-3*	*0.5600-3*	0.3797-3	0.2691-3	0.1976-3	0.1155-3	0.7330-4	0.4937-4	0.3482-4	0.2547-4
40	*0.1684-2*	*0.9989-3*	*0.6396-3*	0.4337-3	0.3074-3	0.2257-3	0.1320-3	0.8376-4	0.5642-4	0.3980-4	0.2911-4
45	*0.1892-2*	*0.1123-2*	*0.7191-3*	0.4877-3	0.3457-3	0.2539-3	0.1485-3	0.9422-4	0.6347-4	0.4477-4	0.3275-4
50	*0.2098-2*	*0.1246-2*	*0.7984-3*	0.5416-3	0.3840-3	0.2820-3	0.1650-3	0.1047-3	0.7052-4	0.4974-4	0.3639-4
60	*0.2509-2*	*0.1492-2*	*0.9568-3*	0.6493-3	0.4605-3	0.3382-3	0.1979-3	0.1256-3	0.8461-4	0.5968-4	0.4366-4
70	*0.2918-2*	*0.1737-2*	*0.1115-2*	0.7568-3	0.5369-3	0.3944-3	0.2308-3	0.1465-3	0.9870-4	0.6962-4	0.5093-4
80	*0.3324-2*	*0.1981-2*	*0.1272-2*	0.8641-3	0.6131-3	0.4505-3	0.2637-3	0.1674-3	0.1128-3	0.7956-4	0.5820-4
90	*0.3727-2*	*0.2224-2*	*0.1429-2*	0.9712-3	0.6893-3	0.5066-3	0.2966-3	0.1883-3	0.1269-3	0.8950-4	0.6548-4
100	*0.4128-2*	*0.2466-2*	*0.1586-2*	0.1078-2	0.7654-3	0.5626-3	0.3294-3	0.2092-3	0.1409-3	0.9944-4	0.7275-4
120	*0.4922-2*	*0.2948-2*	*0.1898-2*	0.1291-2	0.9172-3	0.6744-3	0.3951-3	0.2509-3	0.1691-3	0.1193-3	0.8728-4
140	*0.5707-2*	*0.3425-2*	*0.2208-2*	0.1504-2	0.1069-2	0.7860-3	0.4607-3	0.2926-3	0.1972-3	0.1392-3	0.1018-3
160	*0.6482-2*	*0.3900-2*	*0.2517-2*	0.1715-2	0.1220-2	0.8974-3	0.5262-3	0.3343-3	0.2253-3	0.1590-3	0.1163-3
180	*0.7249-2*	*0.4370-2*	*0.2825-2*	0.1926-2	0.1370-2	0.1009-2	0.5916-3	0.3759-3	0.2534-3	0.1788-3	0.1309-3
200	*0.8007-2*	*0.4837-2*	*0.3130-2*	0.2136-2	0.1520-2	0.1120-2	0.6569-3	0.4175-3	0.2815-3	0.1987-3	0.1454-3

Footnote. PL = Prediction Limit; X_n = Maximum order statistic

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Table 19-20. Per-Constituent Significance Levels (α) for Non-parametric 1-of-3 Plan (PL=X_{n-1})

w\n	4	6	8	10	12	16	20	25	30	35	40
1	0.1143	0.4762-1	0.2424-1	0.1399-1	0.8791-2	0.4128-2	0.2259-2	0.1221-2	0.7331-3	0.4742-3	0.3241-3
2	0.1952	0.8766-1	0.4615-1	0.2710-1	0.1721-1	0.8162-2	0.4487-2	0.2432-2	0.1463-2	0.9468-3	0.6475-3
3	0.2568	0.1221	0.6615-1	0.3944-1	0.2528-1	0.1211-1	0.6686-2	0.3635-2	0.2189-2	0.1418-2	0.9701-3
4	0.3059	0.1523	0.8453-1	0.5111-1	0.3303-1	0.1597-1	0.8856-2	0.4828-2	0.2911-2	0.1887-2	0.1292-2
5	0.3464	0.1791	0.1015	0.6218-1	0.4050-1	0.1975-1	0.1100-1	0.6012-2	0.3630-2	0.2355-2	0.1613-2
8	0.4353	0.2448	0.1460	0.9230-1	0.6139-1	0.3064-1	0.1727-1	0.9512-2	0.5767-2	0.3750-2	0.2572-2
10	0.4780	0.2799	0.1714	0.1103	0.7421-1	0.3757-1	0.2133-1	0.1180-1	0.7175-2	0.4673-2	0.3208-2
12	0.5124	0.3101	0.1942	0.1269	0.8628-1	0.4424-1	0.2529-1	0.1406-1	0.8570-2	0.5590-2	0.3841-2
15	0.5536	0.3485	0.2244	0.1496	0.1032	0.5384-1	0.3107-1	0.1739-1	0.1064-1	0.6955-2	0.4786-2
20	0.6046	0.3997	0.2670	0.1827	0.1286	0.6883-1	0.4031-1	0.2280-1	0.1403-1	0.9202-2	0.6346-2
25	0.6419	0.4399	0.3023	0.2114	0.1512	0.8274-1	0.4910-1	0.2804-1	0.1735-1	0.1142-1	0.7889-2
30	0.6708	0.4728	0.3323	0.2366	0.1716	0.9573-1	0.5749-1	0.3312-1	0.2060-1	0.1360-1	0.9417-2
35	0.6940	0.5004	0.3584	0.2591	0.1901	0.1079	0.6550-1	0.3805-1	0.2378-1	0.1575-1	0.1093-1
40	0.7132	0.5240	0.3814	0.2793	0.2072	0.1194	0.7319-1	0.4285-1	0.2690-1	0.1787-1	0.1243-1
45	0.7294	0.5445	0.4018	0.2977	0.2229	0.1302	0.8058-1	0.4751-1	0.2997-1	0.1997-1	0.1391-1
50	0.7433	0.5626	0.4202	0.3145	0.2375	0.1405	0.8768-1	0.5206-1	0.3298-1	0.2203-1	0.1537-1
60	0.7661	0.5932	0.4521	0.3443	0.2638	0.1596	0.1011	0.6082-1	0.3884-1	0.2608-1	0.1827-1
70	0.7842	0.6182	0.4790	0.3701	0.2871	0.1771	0.1137	0.6917-1	0.4450-1	0.3004-1	0.2110-1
80	0.7989	0.6392	0.5021	0.3927	0.3079	0.1931	0.1255	0.7715-1	0.4998-1	0.3389-1	0.2389-1
90	0.8112	0.6571	0.5223	0.4128	0.3266	0.2080	0.1367	0.8480-1	0.5529-1	0.3766-1	0.2663-1
100	0.8216	0.6727	0.5402	0.4309	0.3437	0.2218	0.1472	0.9214-1	0.6045-1	0.4135-1	0.2932-1
120	0.8385	0.6987	0.5705	0.4621	0.3738	0.2468	0.1667	0.1060	0.7032-1	0.4848-1	0.3457-1
140	0.8518	0.7195	0.5955	0.4885	0.3996	0.2690	0.1844	0.1189	0.7968-1	0.5532-1	0.3966-1
160	0.8625	0.7367	0.6165	0.5111	0.4221	0.2889	0.2006	0.1310	0.8857-1	0.6190-1	0.4459-1
180	0.8713	0.7512	0.6346	0.5308	0.4421	0.3069	0.2156	0.1424	0.9705-1	0.6824-1	0.4937-1
200	0.8788	0.7637	0.6504	0.5482	0.4599	0.3233	0.2295	0.1531	0.1052	0.7436-1	0.5403-1

Footnote. PL = Prediction Limit; X_{n-1} = 2nd largest order statistic

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Table 19-20. Per-Constituent Significance Levels (α) for Non-parametric 1-of-3 Plan (PL=X_{n-1})

w\n	50	60	70	80	90	100	120	140	160	180	200
1	0.1708-3	0.1007-3	0.6431-4	0.4353-4	*0.3082-4*	*0.2262-4*	*0.1322-4*	*0.8382-5*	*0.5645-5*	*0.3981-5*	*0.2912-5*
2	0.3413-3	0.2014-3	0.1286-3	0.8705-4	*0.6164-4*	*0.4523-4*	*0.2643-4*	*0.1676-4*	*0.1129-4*	*0.7962-5*	*0.5824-5*
3	0.5116-3	0.3020-3	0.1928-3	0.1306-3	*0.9245-4*	*0.6784-4*	*0.3965-4*	*0.2515-4*	*0.1693-4*	*0.1194-4*	*0.8735-5*
4	0.6817-3	0.4024-3	0.2571-3	0.1740-3	*0.1233-3*	*0.9045-4*	*0.5286-4*	*0.3353-4*	*0.2258-4*	*0.1592-4*	*0.1165-4*
5	0.8516-3	0.5029-3	0.3212-3	0.2175-3	*0.1540-3*	*0.1130-3*	*0.6608-4*	*0.4191-4*	*0.2822-4*	*0.1990-4*	*0.1456-4*
8	0.1360-2	0.8037-3	0.5136-3	0.3479-3	*0.2464-3*	*0.1808-3*	*0.1057-3*	*0.6704-4*	*0.4515-4*	*0.3185-4*	*0.2329-4*
10	0.1698-2	0.1004-2	0.6417-3	0.4347-3	*0.3079-3*	*0.2260-3*	*0.1321-3*	*0.8380-4*	*0.5644-4*	*0.3981-4*	*0.2912-4*
12	0.2035-2	0.1204-2	0.7697-3	0.5214-3	*0.3694-3*	*0.2711-3*	*0.1585-3*	*0.1006-3*	*0.6773-4*	*0.4777-4*	*0.3494-4*
15	0.2539-2	0.1503-2	0.9614-3	0.6515-3	*0.4616-3*	*0.3388-3*	*0.1981-3*	*0.1257-3*	*0.8465-4*	*0.5970-4*	*0.4367-4*
20	0.3375-2	0.2000-2	0.1280-2	0.8679-3	*0.6151-3*	*0.4516-3*	*0.2641-3*	*0.1675-3*	*0.1129-3*	*0.7960-4*	*0.5822-4*
25	0.4206-2	0.2495-2	0.1598-2	0.1084-2	*0.7684-3*	*0.5642-3*	*0.3300-3*	*0.2094-3*	*0.1411-3*	*0.9949-4*	*0.7277-4*
30	0.5032-2	0.2989-2	0.1916-2	0.1300-2	*0.9215-3*	*0.6768-3*	*0.3959-3*	*0.2512-3*	*0.1692-3*	*0.1194-3*	*0.8732-4*
35	0.5853-2	0.3481-2	0.2232-2	0.1515-2	*0.1074-2*	*0.7892-3*	*0.4618-3*	*0.2930-3*	*0.1974-3*	*0.1393-3*	*0.1019-3*
40	0.6669-2	0.3971-2	0.2548-2	0.1730-2	*0.1227-2*	*0.9015-3*	*0.5276-3*	*0.3348-3*	*0.2256-3*	*0.1591-3*	*0.1164-3*
45	0.7481-2	0.4459-2	0.2863-2	0.1945-2	*0.1380-2*	*0.1014-2*	*0.5934-3*	*0.3766-3*	*0.2538-3*	*0.1790-3*	*0.1310-3*
50	0.8288-2	0.4945-2	0.3177-2	0.2159-2	*0.1532-2*	*0.1126-2*	*0.6592-3*	*0.4184-3*	*0.2819-3*	*0.1989-3*	*0.1455-3*
60	0.9888-2	0.5913-2	0.3804-2	0.2586-2	*0.1836-2*	*0.1350-2*	*0.7906-3*	*0.5019-3*	*0.3382-3*	*0.2386-3*	*0.1746-3*
70	0.1147-1	0.6874-2	0.4427-2	0.3012-2	*0.2140-2*	*0.1573-2*	*0.9218-3*	*0.5854-3*	*0.3945-3*	*0.2784-3*	*0.2037-3*
80	0.1304-1	0.7828-2	0.5048-2	0.3437-2	*0.2443-2*	*0.1797-2*	*0.1053-2*	*0.6688-3*	*0.4508-3*	*0.3181-3*	*0.2327-3*
90	0.1458-1	0.8776-2	0.5665-2	0.3860-2	*0.2745-2*	*0.2019-2*	*0.1184-2*	*0.7521-3*	*0.5070-3*	*0.3578-3*	*0.2618-3*
100	0.1612-1	0.9717-2	0.6280-2	0.4282-2	*0.3046-2*	*0.2242-2*	*0.1315-2*	*0.8354-3*	*0.5632-3*	*0.3975-3*	*0.2908-3*
120	0.1914-1	0.1158-1	0.7501-2	0.5122-2	*0.3647-2*	*0.2685-2*	*0.1576-2*	*0.1002-2*	*0.6756-3*	*0.4768-3*	*0.3489-3*
140	0.2209-1	0.1342-1	0.8712-2	0.5957-2	*0.4244-2*	*0.3128-2*	*0.1837-2*	*0.1168-2*	*0.7878-3*	*0.5561-3*	*0.4070-3*
160	0.2500-1	0.1524-1	0.9912-2	0.6786-2	*0.4840-2*	*0.3568-2*	*0.2097-2*	*0.1334-2*	*0.8999-3*	*0.6353-3*	*0.4650-3*
180	0.2784-1	0.1703-1	0.1110-1	0.7610-2	*0.5432-2*	*0.4007-2*	*0.2357-2*	*0.1500-2*	*0.1012-2*	*0.7145-3*	*0.5230-3*
200	0.3064-1	0.1880-1	0.1228-1	0.8429-2	*0.6022-2*	*0.4445-2*	*0.2616-2*	*0.1665-2*	*0.1124-2*	*0.7936-3*	*0.5810-3*

Footnote. PL = Prediction Limit; X_{n-1} = 2nd largest order statistic

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Table 19-21. Per-Constituent Significance Levels (α) for Non-Parametric 1-of-4 Plan (PL=X_n)

w\n	4	6	8	10	12	16	20	25	30	35	40
1	0.1429-1	0.4762-2	0.2020-2	0.9990-3	0.5495-3	0.2064-3	0.9411-4	*0.4210-4*	*0.2156-4*	*0.1216-4*	*0.7366-5*
2	0.2655-1	0.9191-2	0.3963-2	0.1975-2	0.1091-2	0.4114-3	0.1879-3	*0.8413-4*	*0.4311-4*	*0.2431-4*	*0.1473-4*
3	0.3735-1	0.1334-1	0.5835-2	0.2930-2	0.1625-2	0.6151-3	0.2814-3	*0.1261-3*	*0.6463-4*	*0.3645-4*	*0.2209-4*
4	0.4701-1	0.1725-1	0.7645-2	0.3865-2	0.2152-2	0.8176-3	0.3745-3	*0.1680-3*	*0.8613-4*	*0.4859-4*	*0.2945-4*
5	0.5578-1	0.2096-1	0.9397-2	0.4781-2	0.2671-2	0.1019-2	0.4674-3	*0.2098-3*	*0.1076-3*	*0.6072-4*	*0.3681-4*
8	0.7815-1	0.3105-1	0.1435-1	0.7427-2	0.4192-2	0.1615-2	0.7441-3	*0.3348-3*	*0.1719-3*	*0.9707-4*	*0.5886-4*
10	0.9067-1	0.3710-1	0.1744-1	0.9115-2	0.5176-2	0.2006-2	0.9271-3	*0.4179-3*	*0.2147-3*	*0.1213-3*	*0.7355-4*
12	0.1018	0.4271-1	0.2038-1	0.1075-1	0.6137-2	0.2394-2	0.1109-2	*0.5006-3*	*0.2574-3*	*0.1454-3*	*0.8822-4*
15	0.1165	0.5045-1	0.2454-1	0.1310-1	0.7542-2	0.2966-2	0.1380-2	*0.6242-3*	*0.3213-3*	*0.1817-3*	*0.1102-3*
20	0.1372	0.6193-1	0.3095-1	0.1682-1	0.9790-2	0.3901-2	0.1826-2	*0.8290-3*	*0.4275-3*	*0.2419-3*	*0.1468-3*
25	0.1545	0.7203-1	0.3680-1	0.2030-1	0.1194-1	0.4812-2	0.2265-2	*0.1032-2*	*0.5331-3*	*0.3019-3*	*0.1834-3*
30	0.1693	0.8109-1	0.4221-1	0.2358-1	0.1399-1	0.5702-2	0.2698-2	*0.1234-2*	*0.6383-3*	*0.3618-3*	*0.2199-3*
35	0.1823	0.8931-1	0.4724-1	0.2670-1	0.1597-1	0.6571-2	0.3126-2	*0.1434-2*	*0.7431-3*	*0.4215-3*	*0.2563-3*
40	0.1939	0.9684-1	0.5195-1	0.2966-1	0.1787-1	0.7423-2	0.3548-2	*0.1633-2*	*0.8474-3*	*0.4811-3*	*0.2926-3*
45	0.2043	0.1038	0.5639-1	0.3249-1	0.1971-1	0.8256-2	0.3965-2	*0.1830-2*	*0.9512-3*	*0.5405-3*	*0.3289-3*
50	0.2138	0.1103	0.6059-1	0.3521-1	0.2149-1	0.9074-2	0.4376-2	*0.2026-2*	*0.1055-2*	*0.5998-3*	*0.3652-3*
60	0.2306	0.1220	0.6837-1	0.4032-1	0.2489-1	0.1066-1	0.5186-2	*0.2414-2*	*0.1260-2*	*0.7179-3*	*0.4375-3*
70	0.2451	0.1325	0.7547-1	0.4508-1	0.2810-1	0.1220-1	0.5977-2	*0.2796-2*	*0.1464-2*	*0.8353-3*	*0.5095-3*
80	0.2578	0.1419	0.8201-1	0.4954-1	0.3115-1	0.1368-1	0.6751-2	*0.3174-2*	*0.1667-2*	*0.9522-3*	*0.5813-3*
90	0.2692	0.1505	0.8807-1	0.5373-1	0.3405-1	0.1512-1	0.7509-2	*0.3548-2*	*0.1867-2*	*0.1069-2*	*0.6529-3*
100	0.2794	0.1584	0.9374-1	0.5770-1	0.3683-1	0.1651-1	0.8253-2	*0.3917-2*	*0.2067-2*	*0.1184-2*	*0.7242-3*
120	0.2973	0.1725	0.1041	0.6506-1	0.4204-1	0.1919-1	0.9700-2	*0.4642-2*	*0.2461-2*	*0.1414-2*	*0.8662-3*
140	0.3125	0.1849	0.1133	0.7177-1	0.4688-1	0.2174-1	0.1110-1	*0.5352-2*	*0.2850-2*	*0.1642-2*	*0.1007-2*
160	0.3258	0.1959	0.1217	0.7796-1	0.5140-1	0.2416-1	0.1245-1	*0.6047-2*	*0.3234-2*	*0.1868-2*	*0.1148-2*
180	0.3375	0.2058	0.1294	0.8370-1	0.5564-1	0.2649-1	0.1376-1	*0.6728-2*	*0.3612-2*	*0.2092-2*	*0.1287-2*
200	0.3480	0.2148	0.1365	0.8907-1	0.5965-1	0.2872-1	0.1503-1	*0.7396-2*	*0.3986-2*	*0.2313-2*	*0.1426-2*

Footnote. PL = Prediction Limit; X_n = Maximum order statistic

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Table 19-21. Per-Constituent Significance Levels (α) for Non-Parametric 1-of-4 Plan (PL=X_n)

w\n	50	60	70	80	90	100	120	140	160	180	200
1	0.3162-5	0.1574-5	0.8691-6	0.5183-6	0.3279-6	0.2175-6	0.1066-6	0.5821-7	0.3442-7	0.2164-7	0.1427-7
2	0.6324-5	0.3148-5	0.1738-5	0.1037-5	0.6558-6	0.4350-6	0.2132-6	0.1164-6	0.6884-7	0.4327-7	0.2855-7
3	0.9485-5	0.4721-5	0.2607-5	0.1555-5	0.9837-6	0.6524-6	0.3198-6	0.1746-6	0.1033-6	0.6491-7	0.4282-7
4	0.1265-4	0.6295-5	0.3476-5	0.2073-5	0.1312-5	0.8699-6	0.4264-6	0.2328-6	0.1377-6	0.8655-7	0.5709-7
5	0.1581-4	0.7868-5	0.4345-5	0.2591-5	0.1640-5	0.1087-5	0.5330-6	0.2911-6	0.1721-6	0.1082-6	0.7137-7
8	0.2528-4	0.1259-4	0.6952-5	0.4146-5	0.2623-5	0.1740-5	0.8527-6	0.4657-6	0.2754-6	0.1731-6	0.1142-6
10	0.3160-4	0.1573-4	0.8689-5	0.5182-5	0.3279-5	0.2175-5	0.1066-5	0.5821-6	0.3442-6	0.2164-6	0.1427-6
12	0.3791-4	0.1888-4	0.1043-4	0.6218-5	0.3935-5	0.2610-5	0.1279-5	0.6985-6	0.4131-6	0.2596-6	0.1713-6
15	0.4738-4	0.2359-4	0.1303-4	0.7772-5	0.4918-5	0.3262-5	0.1599-5	0.8731-6	0.5163-6	0.3245-6	0.2141-6
20	0.6314-4	0.3145-4	0.1737-4	0.1036-4	0.6557-5	0.4349-5	0.2132-5	0.1164-5	0.6884-6	0.4327-6	0.2855-6
25	0.7890-4	0.3931-4	0.2171-4	0.1295-4	0.8196-5	0.5436-5	0.2665-5	0.1455-5	0.8605-6	0.5409-6	0.3568-6
30	0.9464-4	0.4716-4	0.2605-4	0.1554-4	0.9835-5	0.6523-5	0.3198-5	0.1746-5	0.1033-5	0.6491-6	0.4282-6
35	0.1104-3	0.5501-4	0.3039-4	0.1813-4	0.1147-4	0.7610-5	0.3730-5	0.2037-5	0.1205-5	0.7573-6	0.4996-6
40	0.1261-3	0.6285-4	0.3473-4	0.2072-4	0.1311-4	0.8697-5	0.4263-5	0.2328-5	0.1377-5	0.8654-6	0.5709-6
45	0.1418-3	0.7069-4	0.3907-4	0.2331-4	0.1475-4	0.9784-5	0.4796-5	0.2619-5	0.1549-5	0.9736-6	0.6423-6
50	0.1575-3	0.7853-4	0.4340-4	0.2589-4	0.1639-4	0.1087-4	0.5329-5	0.2910-5	0.1721-5	0.1082-5	0.7137-6
60	0.1888-3	0.9420-4	0.5207-4	0.3107-4	0.1966-4	0.1304-4	0.6394-5	0.3492-5	0.2065-5	0.1298-5	0.8564-6
70	0.2201-3	0.1098-3	0.6073-4	0.3624-4	0.2294-4	0.1522-4	0.7460-5	0.4074-5	0.2409-5	0.1515-5	0.9991-6
80	0.2514-3	0.1255-3	0.6939-4	0.4141-4	0.2621-4	0.1739-4	0.8525-5	0.4656-5	0.2754-5	0.1731-5	0.1142-5
90	0.2825-3	0.1411-3	0.7805-4	0.4658-4	0.2949-4	0.1956-4	0.9591-5	0.5238-5	0.3098-5	0.1947-5	0.1285-5
100	0.3137-3	0.1567-3	0.8670-4	0.5175-4	0.3276-4	0.2173-4	0.1066-4	0.5820-5	0.3442-5	0.2164-5	0.1427-5
120	0.3758-3	0.1879-3	0.1040-3	0.6208-4	0.3931-4	0.2608-4	0.1279-4	0.6984-5	0.4130-5	0.2596-5	0.1713-5
140	0.4378-3	0.2191-3	0.1213-3	0.7241-4	0.4585-4	0.3042-4	0.1492-4	0.8147-5	0.4818-5	0.3029-5	0.1998-5
160	0.4996-3	0.2501-3	0.1385-3	0.8273-4	0.5239-4	0.3476-4	0.1705-4	0.9311-5	0.5507-5	0.3462-5	0.2284-5
180	0.5612-3	0.2812-3	0.1558-3	0.9304-4	0.5892-4	0.3910-4	0.1918-4	0.1047-4	0.6195-5	0.3894-5	0.2569-5
200	0.6226-3	0.3122-3	0.1730-3	0.1033-3	0.6546-4	0.4344-4	0.2131-4	0.1164-4	0.6883-5	0.4327-5	0.2854-5

Footnote. PL = Prediction Limit; X_n = Maximum order statistic

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Table 19-21. Per-Constituent Significance Levels (α) for Non-Parametric 1-of-4 Plan (PL=X_{n-1})

w\n	4	6	8	10	12	16	20	25	30	35	40
1	0.7143-1	0.2381-1	0.1010-1	0.4995-2	0.2747-2	0.1032-2	0.4705-3	0.2105-3	0.1078-3	0.6079-4	0.3683-4
2	0.1247	0.4462-1	0.1950-1	0.9784-2	0.5423-2	0.2052-2	0.9382-3	0.4204-3	0.2154-3	0.1215-3	0.7364-4
3	0.1669	0.6314-1	0.2831-1	0.1439-1	0.8032-2	0.3060-2	0.1403-2	0.6296-3	0.3229-3	0.1822-3	0.1104-3
4	0.2017	0.7983-1	0.3660-1	0.1882-1	0.1058-1	0.4056-2	0.1865-2	0.8382-3	0.4302-3	0.2428-3	0.1472-3
5	0.2312	0.9503-1	0.4444-1	0.2310-1	0.1307-1	0.5042-2	0.2324-2	0.1046-2	0.5372-3	0.3033-3	0.1839-3
8	0.2991	0.1339	0.6571-1	0.3514-1	0.2021-1	0.7935-2	0.3686-2	0.1666-2	0.8574-3	0.4846-3	0.2940-3
10	0.3333	0.1557	0.7837-1	0.4258-1	0.2474-1	0.9815-2	0.4582-2	0.2077-2	0.1070-2	0.6051-3	0.3673-3
12	0.3619	0.1750	0.9006-1	0.4962-1	0.2909-1	0.1166-1	0.5467-2	0.2485-2	0.1282-2	0.7254-3	0.4404-3
15	0.3972	0.2004	0.1061	0.5954-1	0.3534-1	0.1436-1	0.6778-2	0.3093-2	0.1598-2	0.9054-3	0.5500-3
20	0.4427	0.2357	0.1296	0.7463-1	0.4508-1	0.1870-1	0.8917-2	0.4094-2	0.2123-2	0.1204-2	0.7322-3
25	0.4776	0.2649	0.1500	0.8825-1	0.5411-1	0.2286-1	0.1100-1	0.5083-2	0.2643-2	0.1502-2	0.9138-3
30	0.5057	0.2897	0.1681	0.1007	0.6255-1	0.2686-1	0.1304-1	0.6058-2	0.3159-2	0.1798-2	0.1095-2
35	0.5289	0.3112	0.1843	0.1121	0.7048-1	0.3071-1	0.1504-1	0.7021-2	0.3671-2	0.2092-2	0.1275-2
40	0.5487	0.3301	0.1991	0.1228	0.7795-1	0.3443-1	0.1699-1	0.7973-2	0.4179-2	0.2385-2	0.1455-2
45	0.5658	0.3470	0.2125	0.1327	0.8504-1	0.3803-1	0.1889-1	0.8912-2	0.4684-2	0.2677-2	0.1635-2
50	0.5807	0.3623	0.2250	0.1420	0.9177-1	0.4152-1	0.2077-1	0.9841-2	0.5185-2	0.2968-2	0.1814-2
60	0.6060	0.3888	0.2472	0.1590	0.1043	0.4818-1	0.2440-1	0.1167-1	0.6177-2	0.3545-2	0.2170-2
70	0.6266	0.4114	0.2667	0.1743	0.1158	0.5449-1	0.2791-1	0.1345-1	0.7155-2	0.4117-2	0.2524-2
80	0.6439	0.4309	0.2840	0.1882	0.1265	0.6048-1	0.3130-1	0.1520-1	0.8120-2	0.4684-2	0.2876-2
90	0.6587	0.4480	0.2996	0.2009	0.1364	0.6618-1	0.3457-1	0.1692-1	0.9073-2	0.5247-2	0.3226-2
100	0.6715	0.4633	0.3137	0.2127	0.1457	0.7163-1	0.3775-1	0.1860-1	0.1001-1	0.5805-2	0.3574-2
120	0.6930	0.4895	0.3386	0.2338	0.1626	0.8187-1	0.4384-1	0.2187-1	0.1186-1	0.6907-2	0.4265-2
140	0.7103	0.5113	0.3599	0.2523	0.1778	0.9135-1	0.4960-1	0.2502-1	0.1367-1	0.7993-2	0.4948-2
160	0.7247	0.5300	0.3785	0.2688	0.1916	0.1002	0.5508-1	0.2807-1	0.1543-1	0.9062-2	0.5624-2
180	0.7370	0.5462	0.3950	0.2837	0.2042	0.1085	0.6031-1	0.3103-1	0.1716-1	0.1012-1	0.6293-2
200	0.7476	0.5605	0.4097	0.2972	0.2158	0.1163	0.6531-1	0.3390-1	0.1886-1	0.1115-1	0.6956-2

Footnote. PL = Prediction Limit; X_{n-1} = 2nd largest order statistic

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Table 19-21. Per-Constituent Significance Levels (α) for Non-Parametric 1-of-4 Plan (PL=X_{n-1})

w\n	50	60	70	80	90	100	120	140	160	180	200
1	**0.1581-4**	*0.7869-5*	*0.4345-5*	*0.2591-5*	*0.1640-5*	*0.1087-5*	*0.5330-6*	*0.2911-6*	0.1721-6	0.1082-6	0.7137-7
2	**0.3162-4**	*0.1574-4*	*0.8691-5*	*0.5183-5*	*0.3279-5*	*0.2175-5*	*0.1066-5*	*0.5821-6*	0.3442-6	0.2164-6	0.1427-6
3	**0.4742-4**	*0.2360-4*	*0.1304-4*	*0.7774-5*	*0.4919-5*	*0.3262-5*	*0.1599-5*	*0.8732-6*	0.5163-6	0.3246-6	0.2141-6
4	**0.6321-4**	*0.3147-4*	*0.1738-4*	*0.1036-4*	*0.6558-5*	*0.4349-5*	*0.2132-5*	*0.1164-5*	0.6884-6	0.4327-6	0.2855-6
5	**0.7900-4**	*0.3933-4*	*0.2172-4*	*0.1296-4*	*0.8197-5*	*0.5437-5*	*0.2665-5*	*0.1455-5*	0.8605-6	0.5409-6	0.3568-6
8	**0.1264-3**	*0.6292-4*	*0.3475-4*	*0.2073-4*	*0.1312-4*	*0.8698-5*	*0.4264-5*	*0.2328-5*	0.1377-5	0.8655-6	0.5709-6
10	**0.1579-3**	*0.7864-4*	*0.4344-4*	*0.2591-4*	*0.1639-4*	*0.1087-4*	*0.5329-5*	*0.2910-5*	0.1721-5	0.1082-5	0.7137-6
12	**0.1894-3**	*0.9435-4*	*0.5212-4*	*0.3109-4*	*0.1967-4*	*0.1305-4*	*0.6395-5*	*0.3493-5*	0.2065-5	0.1298-5	0.8564-6
15	**0.2367-3**	*0.1179-3*	*0.6514-4*	*0.3886-4*	*0.2459-4*	*0.1631-4*	*0.7994-5*	*0.4366-5*	0.2582-5	0.1623-5	0.1071-5
20	**0.3153-3**	*0.1572-3*	*0.8684-4*	*0.5180-4*	*0.3278-4*	*0.2174-4*	*0.1066-4*	*0.5821-5*	0.3442-5	0.2164-5	0.1427-5
25	**0.3939-3**	*0.1964-3*	*0.1085-3*	*0.6474-4*	*0.4097-4*	*0.2718-4*	*0.1332-4*	*0.7276-5*	0.4303-5	0.2705-5	0.1784-5
30	**0.4723-3**	*0.2356-3*	*0.1302-3*	*0.7768-4*	*0.4916-4*	*0.3261-4*	*0.1599-4*	*0.8731-5*	0.5163-5	0.3245-5	0.2141-5
35	**0.5506-3**	*0.2747-3*	*0.1519-3*	*0.9061-4*	*0.5735-4*	*0.3804-4*	*0.1865-4*	*0.1019-4*	0.6023-5	0.3786-5	0.2498-5
40	**0.6288-3**	*0.3138-3*	*0.1735-3*	*0.1035-3*	*0.6554-4*	*0.4348-4*	*0.2131-4*	*0.1164-4*	0.6884-5	0.4327-5	0.2855-5
45	**0.7069-3**	*0.3529-3*	*0.1952-3*	*0.1165-3*	*0.7373-4*	*0.4891-4*	*0.2398-4*	*0.1310-4*	0.7744-5	0.4868-5	0.3211-5
50	**0.7849-3**	*0.3920-3*	*0.2168-3*	*0.1294-3*	*0.8191-4*	*0.5434-4*	*0.2664-4*	*0.1455-4*	0.8605-5	0.5409-5	0.3568-5
60	**0.9405-3**	*0.4700-3*	*0.2601-3*	*0.1552-3*	*0.9828-4*	*0.6520-4*	*0.3197-4*	*0.1746-4*	0.1033-4	0.6491-5	0.4282-5
70	**0.1096-2**	*0.5480-3*	*0.3033-3*	*0.1811-3*	*0.1146-3*	*0.7606-4*	*0.3729-4*	*0.2037-4*	0.1205-4	0.7572-5	0.4996-5
80	**0.1250-2**	*0.6258-3*	*0.3464-3*	*0.2069-3*	*0.1310-3*	*0.8691-4*	*0.4262-4*	*0.2328-4*	0.1377-4	0.8654-5	0.5709-5
90	**0.1405-2**	*0.7035-3*	*0.3896-3*	*0.2327-3*	*0.1473-3*	*0.9776-4*	*0.4794-4*	*0.2619-4*	0.1549-4	0.9735-5	0.6423-5
100	**0.1559-2**	*0.7810-3*	*0.4327-3*	*0.2584-3*	*0.1637-3*	*0.1086-3*	*0.5327-4*	*0.2910-4*	0.1721-4	0.1082-4	0.7136-5
120	**0.1865-2**	*0.9359-3*	*0.5188-3*	*0.3100-3*	*0.1963-3*	*0.1303-3*	*0.6391-4*	*0.3491-4*	0.2065-4	0.1298-4	0.8563-5
140	**0.2170-2**	*0.1090-2*	*0.6047-3*	*0.3614-3*	*0.2290-3*	*0.1520-3*	*0.7456-4*	*0.4073-4*	0.2409-4	0.1514-4	0.9990-5
160	**0.2474-2**	*0.1244-2*	*0.6905-3*	*0.4129-3*	*0.2616-3*	*0.1737-3*	*0.8520-4*	*0.4654-4*	0.2753-4	0.1731-4	0.1142-4
180	**0.2775-2**	*0.1398-2*	*0.7761-3*	*0.4642-3*	*0.2942-3*	*0.1953-3*	*0.9583-4*	*0.5236-4*	0.3097-4	0.1947-4	0.1284-4
200	**0.3075-2**	*0.1551-2*	*0.8616-3*	*0.5155-3*	*0.3268-3*	*0.2170-3*	*0.1065-3*	*0.5817-4*	0.3441-4	0.2163-4	0.1427-4

Footnote. PL = Prediction Limit; X_{n-1} = 2nd largest order statistic

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Table 19-22. Per-Constituent Significance Levels (α) for Non-Parametric Modified California Plan (PL=X_n)

w\n	4	6	8	10	12	16	20	25	30	35	40
1	0.5714-1	0.2619-1	0.1414-1	0.8492-2	0.5495-2	0.2683-2	0.1506-2	0.8315-3	0.5067-3	0.3313-3	0.2284-3
2	0.9971-1	0.4830-1	0.2684-1	0.1638-1	0.1071-1	0.5289-2	0.2985-2	0.1654-2	0.1010-2	0.6610-3	0.4559-3
3	0.1335	0.6746-1	0.3838-1	0.2377-1	0.1568-1	0.7824-2	0.4438-2	0.2468-2	0.1510-2	0.9892-3	0.6827-3
4	0.1614	0.8438-1	0.4898-1	0.3072-1	0.2043-1	0.1029-1	0.5867-2	0.3274-2	0.2006-2	0.1316-2	0.9088-3
5	0.1852	0.9954-1	0.5879-1	0.3728-1	0.2498-1	0.1270-1	0.7272-2	0.4071-2	0.2499-2	0.1641-2	0.1134-2
8	0.2402	0.1374	0.8449-1	0.5507-1	0.3762-1	0.1958-1	0.1136-1	0.6416-2	0.3959-2	0.2607-2	0.1805-2
10	0.2682	0.1580	0.9925-1	0.6565-1	0.4532-1	0.2391-1	0.1398-1	0.7943-2	0.4916-2	0.3244-2	0.2249-2
12	0.2917	0.1761	0.1126	0.7541-1	0.5255-1	0.2807-1	0.1653-1	0.9442-2	0.5862-2	0.3876-2	0.2691-2
15	0.3211	0.1996	0.1304	0.8878-1	0.6263-1	0.3401-1	0.2023-1	0.1164-1	0.7260-2	0.4813-2	0.3347-2
20	0.3593	0.2319	0.1558	0.1084	0.7777-1	0.4323-1	0.2610-1	0.1519-1	0.9535-2	0.6349-2	0.4428-2
25	0.3891	0.2581	0.1772	0.1255	0.9125-1	0.5173-1	0.3163-1	0.1859-1	0.1175-1	0.7854-2	0.5492-2
30	0.4133	0.2802	0.1958	0.1406	0.1034	0.5962-1	0.3687-1	0.2187-1	0.1390-1	0.9330-2	0.6542-2
35	0.4336	0.2992	0.2121	0.1541	0.1145	0.6701-1	0.4186-1	0.2504-1	0.1600-1	0.1078-1	0.7576-2
40	0.4510	0.3158	0.2267	0.1665	0.1247	0.7395-1	0.4662-1	0.2811-1	0.1805-1	0.1220-1	0.8596-2
45	0.4662	0.3307	0.2399	0.1778	0.1342	0.8051-1	0.5118-1	0.3107-1	0.2006-1	0.1360-1	0.9603-2
50	0.4796	0.3440	0.2520	0.1882	0.1431	0.8672-1	0.5555-1	0.3395-1	0.2201-1	0.1497-1	0.1060-1
60	0.5025	0.3671	0.2732	0.2069	0.1591	0.9825-1	0.6380-1	0.3947-1	0.2580-1	0.1766-1	0.1255-1
70	0.5214	0.3867	0.2916	0.2233	0.1734	0.1088	0.7148-1	0.4470-1	0.2944-1	0.2025-1	0.1445-1
80	0.5374	0.4036	0.3077	0.2379	0.1863	0.1185	0.7868-1	0.4968-1	0.3295-1	0.2278-1	0.1631-1
90	0.5514	0.4185	0.3221	0.2510	0.1981	0.1275	0.8545-1	0.5442-1	0.3633-1	0.2523-1	0.1812-1
100	0.5636	0.4318	0.3350	0.2630	0.2089	0.1359	0.9185-1	0.5897-1	0.3959-1	0.2762-1	0.1990-1
120	0.5842	0.4545	0.3575	0.2841	0.2281	0.1512	0.1037	0.6752-1	0.4581-1	0.3221-1	0.2335-1
140	0.6011	0.4734	0.3765	0.3023	0.2449	0.1649	0.1145	0.7545-1	0.5167-1	0.3658-1	0.2667-1
160	0.6154	0.4896	0.3931	0.3183	0.2598	0.1772	0.1244	0.8286-1	0.5721-1	0.4077-1	0.2986-1
180	0.6277	0.5038	0.4076	0.3324	0.2732	0.1885	0.1335	0.8981-1	0.6248-1	0.4478-1	0.3295-1
200	0.6384	0.5162	0.4206	0.3452	0.2853	0.1988	0.1421	0.9637-1	0.6749-1	0.4863-1	0.3594-1

Footnote. PL = Prediction Limit; X_n = Maximum order statistic

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Table 19-22. Per-Constituent Significance Levels (α) for Non-Parametric Modified California Plan (PL=X_n)

w\n	50	60	70	80	90	100	120	140	160	180	200
1	0.1217-3	0.7240-4	0.4650-4	0.3161-4	0.2246-4	*0.1653-4*	*0.9700-5*	*0.6170-5*	*0.4165-5*	*0.2943-5*	*0.2155-5*
2	0.2432-3	0.1447-3	0.9296-4	0.6321-4	0.4492-4	*0.3305-4*	*0.1940-4*	*0.1234-4*	*0.8330-5*	*0.5885-5*	*0.4311-5*
3	0.3645-3	0.2169-3	0.1394-3	0.9479-4	0.6736-4	*0.4957-4*	*0.2910-4*	*0.1851-4*	*0.1249-4*	*0.8827-5*	*0.6466-5*
4	0.4856-3	0.2891-3	0.1858-3	0.1264-3	0.8980-4	*0.6608-4*	*0.3879-4*	*0.2468-4*	*0.1666-4*	*0.1177-4*	*0.8621-5*
5	0.6064-3	0.3611-3	0.2321-3	0.1579-3	0.1122-3	*0.8259-4*	*0.4848-4*	*0.3084-4*	*0.2082-4*	*0.1471-4*	*0.1078-4*
8	0.9674-3	0.5768-3	0.3710-3	0.2524-3	0.1795-3	*0.1321-3*	*0.7755-4*	*0.4934-4*	*0.3331-4*	*0.2354-4*	*0.1724-4*
10	0.1207-2	0.7202-3	0.4633-3	0.3154-3	0.2242-3	*0.1651-3*	*0.9693-4*	*0.6167-4*	*0.4164-4*	*0.2942-4*	*0.2155-4*
12	0.1446-2	0.8632-3	0.5556-3	0.3782-3	0.2690-3	*0.1980-3*	*0.1163-3*	*0.7400-4*	*0.4996-4*	*0.3530-4*	*0.2586-4*
15	0.1802-2	0.1077-2	0.6937-3	0.4724-3	0.3360-3	*0.2474-3*	*0.1453-3*	*0.9248-4*	*0.6244-4*	*0.4412-4*	*0.3232-4*
20	0.2392-2	0.1432-2	0.9231-3	0.6291-3	0.4476-3	*0.3297-3*	*0.1937-3*	*0.1233-3*	*0.8324-4*	*0.5882-4*	*0.4309-4*
25	0.2977-2	0.1785-2	0.1152-2	0.7853-3	0.5590-3	*0.4118-3*	*0.2420-3*	*0.1541-3*	*0.1040-3*	*0.7352-4*	*0.5386-4*
30	0.3556-2	0.2136-2	0.1379-2	0.9411-3	0.6701-3	*0.4938-3*	*0.2903-3*	*0.1848-3*	*0.1248-3*	*0.8821-4*	*0.6462-4*
35	0.4131-2	0.2485-2	0.1606-2	0.1097-2	0.7810-3	*0.5757-3*	*0.3385-3*	*0.2156-3*	*0.1456-3*	*0.1029-3*	*0.7538-4*
40	0.4700-2	0.2832-2	0.1832-2	0.1252-2	0.8918-3	*0.6574-3*	*0.3867-3*	*0.2463-3*	*0.1664-3*	*0.1176-3*	*0.8615-4*
45	0.5266-2	0.3178-2	0.2058-2	0.1406-2	0.1002-2	*0.7391-3*	*0.4348-3*	*0.2770-3*	*0.1871-3*	*0.1323-3*	*0.9690-4*
50	0.5826-2	0.3521-2	0.2282-2	0.1560-2	0.1113-2	*0.8206-3*	*0.4830-3*	*0.3077-3*	*0.2079-3*	*0.1469-3*	*0.1077-3*
60	0.6934-2	0.4203-2	0.2729-2	0.1868-2	0.1333-2	*0.9833-3*	*0.5790-3*	*0.3690-3*	*0.2493-3*	*0.1763-3*	*0.1292-3*
70	0.8025-2	0.4878-2	0.3172-2	0.2173-2	0.1552-2	*0.1146-2*	*0.6750-3*	*0.4303-3*	*0.2908-3*	*0.2056-3*	*0.1507-3*
80	0.9100-2	0.5546-2	0.3612-2	0.2478-2	0.1770-2	*0.1307-2*	*0.7707-3*	*0.4915-3*	*0.3322-3*	*0.2349-3*	*0.1722-3*
90	0.1016-1	0.6207-2	0.4050-2	0.2780-2	0.1988-2	*0.1469-2*	*0.8664-3*	*0.5526-3*	*0.3736-3*	*0.2642-3*	*0.1936-3*
100	0.1120-1	0.6863-2	0.4484-2	0.3081-2	0.2205-2	*0.1630-2*	*0.9618-3*	*0.6136-3*	*0.4149-3*	*0.2935-3*	*0.2151-3*
120	0.1325-1	0.8155-2	0.5344-2	0.3680-2	0.2636-2	*0.1950-2*	*0.1152-2*	*0.7356-3*	*0.4975-3*	*0.3520-3*	*0.2580-3*
140	0.1524-1	0.9424-2	0.6194-2	0.4272-2	0.3064-2	*0.2269-2*	*0.1342-2*	*0.8572-3*	*0.5800-3*	*0.4104-3*	*0.3009-3*
160	0.1719-1	0.1067-1	0.7032-2	0.4860-2	0.3490-2	*0.2586-2*	*0.1531-2*	*0.9786-3*	*0.6624-3*	*0.4688-3*	*0.3438-3*
180	0.1909-1	0.1190-1	0.7861-2	0.5442-2	0.3912-2	*0.2902-2*	*0.1720-2*	*0.1100-2*	*0.7446-3*	*0.5271-3*	*0.3866-3*
200	0.2094-1	0.1310-1	0.8680-2	0.6018-2	0.4332-2	*0.3216-2*	*0.1908-2*	*0.1221-2*	*0.8268-3*	*0.5854-3*	*0.4293-3*

Footnote. PL = Prediction Limit; X_n = Maximum order statistic

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Table 19-22. Per-Constituent Significance Levels (α) for Non-Parametric Modified California Plan (PL=X_{n-1})

w\n	4	6	8	10	12	16	20	25	30	35	40
1	0.2000	0.9524-1	0.5253-1	0.3197-1	0.2088-1	0.1032-1	0.5835-2	0.3242-2	0.1984-2	0.1301-2	0.8987-3
2	0.3182	0.1663	0.9619-1	0.6018-1	0.3998-1	0.2014-1	0.1149-1	0.6424-2	0.3944-2	0.2591-2	0.1792-2
3	0.3981	0.2221	0.1334	0.8541-1	0.5760-1	0.2950-1	0.1698-1	0.9550-2	0.5881-2	0.3871-2	0.2680-2
4	0.4567	0.2677	0.1658	0.1082	0.7393-1	0.3846-1	0.2232-1	0.1262-1	0.7795-2	0.5140-2	0.3563-2
5	0.5019	0.3059	0.1943	0.1290	0.8916-1	0.4705-1	0.2751-1	0.1564-1	0.9688-2	0.6400-2	0.4441-2
8	0.5932	0.3920	0.2635	0.1821	0.1295	0.7085-1	0.4230-1	0.2440-1	0.1524-1	0.1012-1	0.7046-2
10	0.6335	0.4343	0.3000	0.2116	0.1528	0.8534-1	0.5157-1	0.3001-1	0.1885-1	0.1255-1	0.8758-2
12	0.6647	0.4689	0.3313	0.2377	0.1739	0.9889-1	0.6042-1	0.3545-1	0.2238-1	0.1495-1	0.1045-1
15	0.7004	0.5107	0.3707	0.2717	0.2022	0.1177	0.7300-1	0.4333-1	0.2754-1	0.1848-1	0.1296-1
20	0.7422	0.5632	0.4228	0.3185	0.2424	0.1458	0.9234-1	0.5576-1	0.3582-1	0.2421-1	0.1705-1
25	0.7715	0.6022	0.4635	0.3566	0.2761	0.1705	0.1100	0.6742-1	0.4373-1	0.2974-1	0.2104-1
30	0.7934	0.6327	0.4964	0.3884	0.3051	0.1926	0.1262	0.7840-1	0.5131-1	0.3510-1	0.2494-1
35	0.8105	0.6574	0.5239	0.4157	0.3304	0.2126	0.1412	0.8880-1	0.5858-1	0.4030-1	0.2874-1
40	0.8244	0.6780	0.5474	0.4393	0.3528	0.2308	0.1552	0.9866-1	0.6558-1	0.4535-1	0.3246-1
45	0.8358	0.6954	0.5677	0.4602	0.3729	0.2475	0.1683	0.1080	0.7232-1	0.5026-1	0.3610-1
50	0.8455	0.7104	0.5855	0.4789	0.3910	0.2630	0.1806	0.1170	0.7882-1	0.5504-1	0.3967-1
60	0.8611	0.7352	0.6155	0.5108	0.4227	0.2907	0.2032	0.1338	0.9119-1	0.6422-1	0.4658-1
70	0.8732	0.7549	0.6400	0.5374	0.4496	0.3150	0.2234	0.1492	0.1028	0.7296-1	0.5322-1
80	0.8829	0.7710	0.6604	0.5600	0.4728	0.3366	0.2419	0.1636	0.1138	0.8130-1	0.5962-1
90	0.8909	0.7845	0.6778	0.5796	0.4931	0.3559	0.2587	0.1770	0.1241	0.8928-1	0.6580-1
100	0.8976	0.7961	0.6929	0.5968	0.5112	0.3735	0.2742	0.1895	0.1339	0.9693-1	0.7177-1
120	0.9083	0.8149	0.7179	0.6257	0.5421	0.4042	0.3020	0.2124	0.1522	0.1114	0.8315-1
140	0.9165	0.8297	0.7379	0.6492	0.5676	0.4304	0.3262	0.2329	0.1689	0.1248	0.9386-1
160	0.9231	0.8417	0.7543	0.6689	0.5893	0.4531	0.3477	0.2514	0.1843	0.1373	0.1040
180	0.9285	0.8516	0.7682	0.6857	0.6079	0.4731	0.3669	0.2684	0.1985	0.1490	0.1136
200	0.9330	0.8601	0.7801	0.7002	0.6243	0.4909	0.3843	0.2839	0.2118	0.1601	0.1227

Footnote. PL = Prediction Limit; X_{n-1} = 2nd largest order statistic

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Table 19-22. Per-Constituent Significance Levels (α) for Non-Parametric Modified California Plan (PL=X_{n-1})

w\n	50	60	70	80	90	100	120	140	160	180	200
1	0.4806-3	0.2864-3	0.1842-3	0.1254-3	0.8919-4	0.6568-4	0.3859-4	0.2457-4	0.1659-4	0.1173-4	0.8593-5
2	0.9597-3	0.5723-3	0.3682-3	0.2507-3	0.1783-3	0.1313-3	0.7716-4	0.4913-4	0.3318-4	0.2345-4	0.1718-4
3	0.1437-2	0.8576-3	0.5520-3	0.3759-3	0.2674-3	0.1969-3	0.1157-3	0.7368-4	0.4977-4	0.3518-4	0.2578-4
4	0.1913-2	0.1142-2	0.7355-3	0.5010-3	0.3564-3	0.2625-3	0.1543-3	0.9823-4	0.6635-4	0.4690-4	0.3437-4
5	0.2387-2	0.1426-2	0.9187-3	0.6259-3	0.4454-3	0.3281-3	0.1928-3	0.1228-3	0.8294-4	0.5862-4	0.4296-4
8	0.3801-2	0.2275-2	0.1467-2	0.1000-2	0.7119-3	0.5245-3	0.3084-3	0.1964-3	0.1327-3	0.9379-4	0.6873-4
10	0.4736-2	0.2838-2	0.1831-2	0.1249-2	0.8892-3	0.6553-3	0.3853-3	0.2454-3	0.1658-3	0.1172-3	0.8590-4
12	0.5665-2	0.3399-2	0.2195-2	0.1497-2	0.1066-2	0.7860-3	0.4623-3	0.2945-3	0.1990-3	0.1407-3	0.1031-3
15	0.7048-2	0.4236-2	0.2738-2	0.1869-2	0.1332-2	0.9817-3	0.5776-3	0.3680-3	0.2486-3	0.1758-3	0.1288-3
20	0.9325-2	0.5621-2	0.3639-2	0.2486-2	0.1773-2	0.1307-2	0.7695-3	0.4904-3	0.3314-3	0.2343-3	0.1717-3
25	0.1157-1	0.6992-2	0.4533-2	0.3101-2	0.2212-2	0.1632-2	0.9612-3	0.6127-3	0.4141-3	0.2928-3	0.2146-3
30	0.1378-1	0.8351-2	0.5423-2	0.3713-2	0.2650-2	0.1956-2	0.1153-2	0.7349-3	0.4968-3	0.3513-3	0.2575-3
35	0.1596-1	0.9696-2	0.6306-2	0.4322-2	0.3086-2	0.2279-2	0.1344-2	0.8569-3	0.5794-3	0.4098-3	0.3004-3
40	0.1810-1	0.1103-1	0.7184-2	0.4928-2	0.3522-2	0.2602-2	0.1534-2	0.9789-3	0.6619-3	0.4682-3	0.3432-3
45	0.2022-1	0.1235-1	0.8057-2	0.5531-2	0.3955-2	0.2923-2	0.1725-2	0.1101-2	0.7444-3	0.5266-3	0.3861-3
50	0.2231-1	0.1366-1	0.8924-2	0.6132-2	0.4388-2	0.3244-2	0.1915-2	0.1222-2	0.8269-3	0.5850-3	0.4289-3
60	0.2642-1	0.1625-1	0.1064-1	0.7327-2	0.5248-2	0.3883-2	0.2295-2	0.1465-2	0.9916-3	0.7017-3	0.5145-3
70	0.3041-1	0.1879-1	0.1234-1	0.8511-2	0.6103-2	0.4520-2	0.2673-2	0.1708-2	0.1156-2	0.8182-3	0.6000-3
80	0.3432-1	0.2129-1	0.1402-1	0.9685-2	0.6953-2	0.5153-2	0.3051-2	0.1950-2	0.1320-2	0.9347-3	0.6855-3
90	0.3813-1	0.2375-1	0.1568-1	0.1085-1	0.7798-2	0.5783-2	0.3427-2	0.2192-2	0.1484-2	0.1051-2	0.7709-3
100	0.4185-1	0.2617-1	0.1732-1	0.1200-1	0.8637-2	0.6411-2	0.3802-2	0.2433-2	0.1648-2	0.1167-2	0.8563-3
120	0.4906-1	0.3091-1	0.2055-1	0.1429-1	0.1030-1	0.7657-2	0.4550-2	0.2914-2	0.1975-2	0.1399-2	0.1027-2
140	0.5598-1	0.3551-1	0.2372-1	0.1653-1	0.1195-1	0.8891-2	0.5293-2	0.3393-2	0.2302-2	0.1631-2	0.1197-2
160	0.6262-1	0.3998-1	0.2681-1	0.1875-1	0.1357-1	0.1012-1	0.6032-2	0.3871-2	0.2627-2	0.1862-2	0.1367-2
180	0.6902-1	0.4433-1	0.2985-1	0.2093-1	0.1518-1	0.1133-1	0.6766-2	0.4347-2	0.2951-2	0.2093-2	0.1537-2
200	0.7520-1	0.4856-1	0.3283-1	0.2308-1	0.1677-1	0.1253-1	0.7497-2	0.4821-2	0.3275-2	0.2324-2	0.1707-2

Footnote. PL = Prediction Limit; X_{n-1} = 2nd largest order statistic

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Table 19-23. Per-Constituent Significance Levels (α) for Non-Parametric 1-of-1 Plan for Median ($PL=X_n$)

w/n	4	6	8	10	12	16	20	25	30	35	40
1	0.1429	0.8333-1	0.5455-1	0.3846-1	0.2857-1	0.1754-1	0.1186-1	0.7937-2	0.5682-2	0.4267-2	0.3322-2
2	0.2333	0.1455	0.9890-1	0.7143-1	0.5392-1	0.3377-1	0.2308-1	0.1557-1	0.1120-1	0.8443-2	0.6588-2
3	0.2979	0.1945	0.1361	0.1002	0.7669-1	0.4885-1	0.3372-1	0.2293-1	0.1658-1	0.1253-1	0.9798-2
4	0.3473	0.2347	0.1681	0.1258	0.9735-1	0.6295-1	0.4386-1	0.3003-1	0.2181-1	0.1653-1	0.1296-1
5	0.3867	0.2686	0.1961	0.1487	0.1162	0.7619-1	0.5353-1	0.3690-1	0.2691-1	0.2046-1	0.1606-1
8	0.4704	0.3458	0.2630	0.2057	0.1647	0.1116	0.8012-1	0.5621-1	0.4147-1	0.3178-1	0.2509-1
10	0.5094	0.3841	0.2980	0.2367	0.1918	0.1323	0.9614-1	0.6815-1	0.5062-1	0.3898-1	0.3089-1
12	0.5404	0.4157	0.3277	0.2636	0.2158	0.1512	0.1110	0.7943-1	0.5937-1	0.4593-1	0.3652-1
15	0.5770	0.4544	0.3650	0.2982	0.2473	0.1767	0.1315	0.9527-1	0.7184-1	0.5592-1	0.4467-1
20	0.6218	0.5035	0.4139	0.3448	0.2907	0.2132	0.1618	0.1192	0.9105-1	0.7154-1	0.5756-1
25	0.6543	0.5405	0.4520	0.3821	0.3262	0.2441	0.1882	0.1407	0.1086	0.8604-1	0.6965-1
30	0.6794	0.5698	0.4828	0.4128	0.3560	0.2708	0.2115	0.1601	0.1248	0.9956-1	0.8106-1
35	0.6996	0.5938	0.5084	0.4388	0.3816	0.2943	0.2324	0.1779	0.1397	0.1122	0.9185-1
40	0.7162	0.6139	0.5303	0.4613	0.4039	0.3153	0.2513	0.1942	0.1537	0.1242	0.1021
45	0.7303	0.6312	0.5492	0.4809	0.4236	0.3341	0.2685	0.2092	0.1667	0.1354	0.1118
50	0.7424	0.6462	0.5658	0.4984	0.4413	0.3511	0.2844	0.2232	0.1790	0.1461	0.1211
60	0.7623	0.6711	0.5939	0.5280	0.4716	0.3810	0.3125	0.2486	0.2014	0.1658	0.1385
70	0.7781	0.6912	0.6167	0.5526	0.4970	0.4065	0.3369	0.2710	0.2216	0.1838	0.1545
80	0.7911	0.7079	0.6359	0.5733	0.5187	0.4286	0.3585	0.2910	0.2398	0.2003	0.1693
90	0.8019	0.7220	0.6523	0.5912	0.5375	0.4481	0.3777	0.3091	0.2566	0.2155	0.1831
100	0.8112	0.7342	0.6665	0.6068	0.5540	0.4655	0.3949	0.3256	0.2719	0.2296	0.1959
120	0.8264	0.7542	0.6902	0.6330	0.5820	0.4952	0.4249	0.3547	0.2993	0.2551	0.2194
140	0.8383	0.7702	0.7092	0.6543	0.6049	0.5200	0.4503	0.3797	0.3232	0.2776	0.2404
160	0.8481	0.7833	0.7249	0.6721	0.6242	0.5411	0.4721	0.4015	0.3443	0.2977	0.2593
180	0.8562	0.7944	0.7382	0.6872	0.6407	0.5594	0.4912	0.4207	0.3632	0.3158	0.2764
200	0.8632	0.8039	0.7497	0.7003	0.6550	0.5754	0.5081	0.4380	0.3802	0.3323	0.2922

Footnote. PL = Prediction Limit; X_n = Maximum order statistic

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Table 19-23. Per-Constituent Significance Levels (α) for Non-Parametric 1-of-1 Plan for Median ($PL=X_n$)

w\n	50	60	70	80	90	100	120	140	160	180	200
1	0.2177-2	0.1536-2	0.1142-2	0.8816-3	0.7013-3	0.5711-3	0.3998-3	0.2955-3	0.2272-3	0.1801-3	0.1463-3
2	0.4329-2	0.3059-2	0.2276-2	0.1759-2	0.1400-2	0.1140-2	0.7988-3	0.5905-3	0.4541-3	0.3601-3	0.2925-3
3	0.6456-2	0.4570-2	0.3403-2	0.2632-2	0.2096-2	0.1708-2	0.1197-2	0.8849-3	0.6808-3	0.5399-3	0.4386-3
4	0.8560-2	0.6069-2	0.4524-2	0.3501-2	0.2789-2	0.2273-2	0.1594-2	0.1179-2	0.9071-3	0.7195-3	0.5845-3
5	0.1064-1	0.7555-2	0.5637-2	0.4365-2	0.3479-2	0.2837-2	0.1990-2	0.1472-2	0.1133-2	0.8989-3	0.7304-3
8	0.1675-1	0.1194-1	0.8938-2	0.6935-2	0.5535-2	0.4518-2	0.3174-2	0.2350-2	0.1809-2	0.1436-2	0.1167-2
10	0.2071-1	0.1481-1	0.1111-1	0.8628-2	0.6892-2	0.5630-2	0.3958-2	0.2933-2	0.2259-2	0.1793-2	0.1458-2
12	0.2460-1	0.1764-1	0.1325-1	0.1030-1	0.8239-2	0.6735-2	0.4739-2	0.3513-2	0.2707-2	0.2149-2	0.1748-2
15	0.3028-1	0.2180-1	0.1642-1	0.1279-1	0.1024-1	0.8380-2	0.5904-2	0.4381-2	0.3378-2	0.2683-2	0.2182-2
20	0.3939-1	0.2854-1	0.2158-1	0.1686-1	0.1353-1	0.1109-1	0.7829-2	0.5817-2	0.4489-2	0.3568-2	0.2903-2
25	0.4809-1	0.3505-1	0.2660-1	0.2085-1	0.1676-1	0.1376-1	0.9734-2	0.7241-2	0.5593-2	0.4448-2	0.3621-2
30	0.5642-1	0.4134-1	0.3150-1	0.2475-1	0.1993-1	0.1639-1	0.1162-1	0.8655-2	0.6691-2	0.5325-2	0.4337-2
35	0.6441-1	0.4743-1	0.3627-1	0.2857-1	0.2306-1	0.1898-1	0.1348-1	0.1006-1	0.7782-2	0.6196-2	0.5049-2
40	0.7209-1	0.5334-1	0.4092-1	0.3231-1	0.2612-1	0.2153-1	0.1533-1	0.1145-1	0.8866-2	0.7064-2	0.5758-2
45	0.7948-1	0.5907-1	0.4546-1	0.3598-1	0.2914-1	0.2406-1	0.1716-1	0.1283-1	0.9943-2	0.7927-2	0.6465-2
50	0.8661-1	0.6464-1	0.4990-1	0.3958-1	0.3211-1	0.2654-1	0.1897-1	0.1420-1	0.1101-1	0.8786-2	0.7169-2
60	0.1001	0.7531-1	0.5847-1	0.4659-1	0.3792-1	0.3142-1	0.2253-1	0.1691-1	0.1314-1	0.1049-1	0.8567-2
70	0.1128	0.8544-1	0.6668-1	0.5334-1	0.4355-1	0.3617-1	0.2603-1	0.1957-1	0.1523-1	0.1218-1	0.9955-2
80	0.1247	0.9507-1	0.7456-1	0.5986-1	0.4901-1	0.4080-1	0.2946-1	0.2220-1	0.1731-1	0.1385-1	0.1133-1
90	0.1359	0.1043	0.8213-1	0.6617-1	0.5433-1	0.4532-1	0.3282-1	0.2480-1	0.1936-1	0.1551-1	0.1270-1
100	0.1466	0.1130	0.8942-1	0.7228-1	0.5949-1	0.4974-1	0.3613-1	0.2735-1	0.2138-1	0.1715-1	0.1405-1
120	0.1662	0.1295	0.1032	0.8395-1	0.6943-1	0.5827-1	0.4258-1	0.3236-1	0.2537-1	0.2039-1	0.1674-1
140	0.1841	0.1447	0.1161	0.9496-1	0.7888-1	0.6644-1	0.4881-1	0.3723-1	0.2927-1	0.2358-1	0.1938-1
160	0.2006	0.1588	0.1282	0.1054	0.8789-1	0.7428-1	0.5484-1	0.4198-1	0.3309-1	0.2670-1	0.2198-1
180	0.2157	0.1719	0.1397	0.1153	0.9651-1	0.8181-1	0.6068-1	0.4661-1	0.3683-1	0.2978-1	0.2455-1
200	0.2297	0.1843	0.1504	0.1247	0.1048	0.8905-1	0.6635-1	0.5113-1	0.4050-1	0.3280-1	0.2708-1

Footnote. PL = Prediction Limit; X_n = Maximum order statistic

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Table 19-23. Per-Constituent Significance Levels (α) for Non-Parametric 1-of-1 Plan for Median ($PL=X_{n-1}$)

w\n	4	6	8	10	12	16	20	25	30	35	40
1	0.3714	0.2262	0.1515	0.1084	0.8132-1	0.5057-1	0.3444-1	0.2320-1	0.1668-1	0.1257-1	0.9805-2
2	0.5381	0.3636	0.2587	0.1923	0.1480	0.9501-1	0.6589-1	0.4497-1	0.3259-1	0.2469-1	0.1933-1
3	0.6336	0.4570	0.3394	0.2597	0.2041	0.1345	0.9476-1	0.6546-1	0.4781-1	0.3639-1	0.2860-1
4	0.6957	0.5251	0.4026	0.3152	0.2520	0.1699	0.1214	0.8481-1	0.6238-1	0.4771-1	0.3762-1
5	0.7395	0.5771	0.4537	0.3620	0.2935	0.2019	0.1461	0.1031	0.7634-1	0.5866-1	0.4640-1
8	0.8173	0.6796	0.5622	0.4672	0.3913	0.2821	0.2107	0.1527	0.1151	0.8950-1	0.7144-1
10	0.8474	0.7232	0.6120	0.5183	0.4410	0.3257	0.2474	0.1820	0.1385	0.1086	0.8714-1
12	0.8689	0.7559	0.6509	0.5595	0.4822	0.3634	0.2801	0.2088	0.1604	0.1266	0.1021
15	0.8916	0.7922	0.6957	0.6087	0.5327	0.4115	0.3232	0.2450	0.1907	0.1519	0.1234
20	0.9158	0.8329	0.7483	0.6685	0.5962	0.4754	0.3827	0.2971	0.2353	0.1899	0.1559
25	0.9311	0.8600	0.7847	0.7115	0.6432	0.5251	0.4310	0.3410	0.2741	0.2238	0.1854
30	0.9416	0.8792	0.8115	0.7439	0.6796	0.5653	0.4713	0.3788	0.3083	0.2542	0.2122
35	0.9493	0.8937	0.8321	0.7694	0.7087	0.5984	0.5054	0.4117	0.3387	0.2817	0.2369
40	0.9552	0.9051	0.8484	0.7900	0.7326	0.6264	0.5348	0.4407	0.3660	0.3068	0.2596
45	0.9599	0.9141	0.8618	0.8071	0.7527	0.6503	0.5604	0.4665	0.3907	0.3298	0.2807
50	0.9637	0.9216	0.8729	0.8214	0.7697	0.6711	0.5831	0.4896	0.4131	0.3509	0.3003
60	0.9694	0.9332	0.8903	0.8443	0.7972	0.7054	0.6213	0.5295	0.4526	0.3887	0.3357
70	0.9736	0.9417	0.9034	0.8617	0.8185	0.7328	0.6523	0.5628	0.4862	0.4215	0.3670
80	0.9767	0.9482	0.9137	0.8755	0.8356	0.7551	0.6782	0.5912	0.5153	0.4503	0.3948
90	0.9792	0.9535	0.9219	0.8867	0.8495	0.7737	0.7002	0.6156	0.5409	0.4759	0.4198
100	0.9812	0.9577	0.9286	0.8960	0.8612	0.7895	0.7191	0.6370	0.5635	0.4988	0.4425
120	0.9843	0.9642	0.9391	0.9105	0.8797	0.8149	0.7500	0.6726	0.6018	0.5382	0.4819
140	0.9864	0.9689	0.9468	0.9213	0.8936	0.8346	0.7743	0.7012	0.6331	0.5711	0.5153
160	0.9881	0.9726	0.9527	0.9297	0.9045	0.8502	0.7940	0.7248	0.6594	0.5990	0.5440
180	0.9894	0.9754	0.9575	0.9365	0.9134	0.8630	0.8103	0.7447	0.6818	0.6230	0.5690
200	0.9904	0.9777	0.9613	0.9420	0.9206	0.8737	0.8241	0.7616	0.7011	0.6440	0.5910

Footnote. PL = Prediction Limit; X_{n-1} = 2nd largest order statistic

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Table 19-23. Per-Constituent Significance Levels (α) for Non-Parametric 1-of-1 Plan for Median ($PL=X_{n-1}$)

w/n	50	60	70	80	90	100	120	140	160	180	200
1	0.6446-2	0.4558-2	0.3393-2	0.2623-2	0.2088-2	0.1702-2	0.1193-2	0.8822-3	0.6788-3	0.5385-3	0.4375-3
2	0.1277-1	0.9053-2	0.6750-2	0.5225-2	0.4163-2	0.3395-2	0.2381-2	0.1762-2	0.1356-2	0.1076-2	0.8744-3
3	0.1897-1	0.1349-1	0.1007-1	0.7806-2	0.6225-2	0.5079-2	0.3565-2	0.2639-2	0.2032-2	0.1613-2	0.1311-2
4	0.2507-1	0.1786-1	0.1336-1	0.1037-1	0.8273-2	0.6754-2	0.4745-2	0.3514-2	0.2707-2	0.2148-2	0.1746-2
5	0.3105-1	0.2218-1	0.1662-1	0.1291-1	0.1031-1	0.8420-2	0.5920-2	0.4387-2	0.3380-2	0.2683-2	0.2181-2
8	0.4837-1	0.3480-1	0.2620-1	0.2041-1	0.1634-1	0.1337-1	0.9419-2	0.6989-2	0.5390-2	0.4282-2	0.3483-2
10	0.5942-1	0.4295-1	0.3243-1	0.2531-1	0.2029-1	0.1662-1	0.1173-1	0.8713-2	0.6723-2	0.5343-2	0.4347-2
12	0.7012-1	0.5090-1	0.3854-1	0.3015-1	0.2420-1	0.1985-1	0.1403-1	0.1043-1	0.8050-2	0.6401-2	0.5210-2
15	0.8553-1	0.6247-1	0.4750-1	0.3726-1	0.2998-1	0.2462-1	0.1744-1	0.1298-1	0.1003-1	0.7980-2	0.6499-2
20	0.1097	0.8088-1	0.6189-1	0.4878-1	0.3937-1	0.3242-1	0.2304-1	0.1719-1	0.1330-1	0.1060-1	0.8635-2
25	0.1321	0.9829-1	0.7566-1	0.5989-1	0.4850-1	0.4003-1	0.2855-1	0.2134-1	0.1654-1	0.1319-1	0.1076-1
30	0.1531	0.1148	0.8887-1	0.7063-1	0.5738-1	0.4747-1	0.3396-1	0.2544-1	0.1975-1	0.1576-1	0.1286-1
35	0.1727	0.1305	0.1015	0.8102-1	0.6601-1	0.5473-1	0.3928-1	0.2949-1	0.2292-1	0.1831-1	0.1496-1
40	0.1911	0.1454	0.1137	0.9107-1	0.7441-1	0.6183-1	0.4451-1	0.3348-1	0.2606-1	0.2084-1	0.1704-1
45	0.2085	0.1596	0.1254	0.1008	0.8259-1	0.6877-1	0.4966-1	0.3743-1	0.2917-1	0.2335-1	0.1910-1
50	0.2249	0.1732	0.1367	0.1103	0.9056-1	0.7556-1	0.5472-1	0.4132-1	0.3225-1	0.2584-1	0.2115-1
60	0.2552	0.1987	0.1582	0.1283	0.1059	0.8872-1	0.6460-1	0.4897-1	0.3832-1	0.3076-1	0.2521-1
70	0.2826	0.2222	0.1782	0.1454	0.1206	0.1013	0.7419-1	0.5644-1	0.4427-1	0.3560-1	0.2922-1
80	0.3075	0.2439	0.1969	0.1616	0.1345	0.1135	0.8348-1	0.6373-1	0.5011-1	0.4037-1	0.3318-1
90	0.3304	0.2641	0.2146	0.1769	0.1479	0.1252	0.9251-1	0.7085-1	0.5585-1	0.4507-1	0.3709-1
100	0.3514	0.2830	0.2312	0.1915	0.1607	0.1364	0.1013	0.7782-1	0.6148-1	0.4970-1	0.4095-1
120	0.3889	0.3172	0.2619	0.2187	0.1848	0.1577	0.1181	0.9129-1	0.7244-1	0.5875-1	0.4853-1
140	0.4214	0.3475	0.2895	0.2436	0.2070	0.1776	0.1341	0.1042	0.8302-1	0.6754-1	0.5593-1
160	0.4500	0.3747	0.3146	0.2665	0.2277	0.1963	0.1492	0.1166	0.9326-1	0.7609-1	0.6315-1
180	0.4754	0.3992	0.3375	0.2876	0.2470	0.2138	0.1636	0.1285	0.1032	0.8441-1	0.7021-1
200	0.4981	0.4214	0.3586	0.3072	0.2651	0.2304	0.1774	0.1400	0.1128	0.9251-1	0.7711-1

Footnote. PL = Prediction Limit; X_{n-1} = 2nd largest order statistic

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Table 19-24. Per-Constituent Significance Levels (α) for Non-Parametric 1-of-2 Plan for Median ($PL=X_n$)

w\n	4	6	8	10	12	16	20	25	30	35	40
1	0.5238-1	0.2121-1	0.1019-1	0.5495-2	0.3221-2	0.1321-2	0.6385-3	0.3002-3	0.1592-3	0.9207-4	0.5690-4
2	0.8898-1	0.3853-1	0.1918-1	0.1055-1	0.6265-2	0.2605-2	0.1266-2	0.5976-3	0.3174-3	0.1838-3	0.1137-3
3	0.1171	0.5324-1	0.2725-1	0.1526-1	0.9157-2	0.3853-2	0.1884-2	0.8923-3	0.4749-3	0.2753-3	0.1703-3
4	0.1400	0.6608-1	0.3461-1	0.1966-1	0.1191-1	0.5069-2	0.2492-2	0.1185-2	0.6315-3	0.3664-3	0.2268-3
5	0.1593	0.7747-1	0.4138-1	0.2381-1	0.1455-1	0.6255-2	0.3092-2	0.1474-2	0.7873-3	0.4573-3	0.2832-3
8	0.2035	0.1057	0.5901-1	0.3502-1	0.2187-1	0.9651-2	0.4839-2	0.2329-2	0.1250-2	0.7280-3	0.4517-3
10	0.2259	0.1210	0.6910-1	0.4167-1	0.2633-1	0.1180-1	0.5965-2	0.2888-2	0.1555-2	0.9071-3	0.5634-3
12	0.2448	0.1344	0.7820-1	0.4781-1	0.3052-1	0.1386-1	0.7062-2	0.3438-2	0.1856-2	0.1085-2	0.6746-3
15	0.2683	0.1518	0.9038-1	0.5623-1	0.3638-1	0.1682-1	0.8661-2	0.4248-2	0.2304-2	0.1350-2	0.8406-3
20	0.2991	0.1758	0.1078	0.6863-1	0.4521-1	0.2143-1	0.1121-1	0.5562-2	0.3036-2	0.1786-2	0.1115-2
25	0.3232	0.1954	0.1226	0.7947-1	0.5312-1	0.2571-1	0.1363-1	0.6834-2	0.3753-2	0.2216-2	0.1387-2
30	0.3430	0.2120	0.1354	0.8913-1	0.6030-1	0.2972-1	0.1594-1	0.8067-2	0.4456-2	0.2640-2	0.1656-2
35	0.3597	0.2264	0.1468	0.9786-1	0.6690-1	0.3349-1	0.1815-1	0.9265-2	0.5145-2	0.3059-2	0.1922-2
40	0.3741	0.2391	0.1571	0.1058	0.7301-1	0.3706-1	0.2028-1	0.1043-1	0.5821-2	0.3472-2	0.2186-2
45	0.3867	0.2505	0.1664	0.1132	0.7871-1	0.4044-1	0.2233-1	0.1157-1	0.6486-2	0.3879-2	0.2448-2
50	0.3980	0.2608	0.1749	0.1200	0.8404-1	0.4367-1	0.2430-1	0.1268-1	0.7139-2	0.4282-2	0.2707-2
60	0.4173	0.2787	0.1901	0.1323	0.9382-1	0.4972-1	0.2806-1	0.1482-1	0.8413-2	0.5074-2	0.3219-2
70	0.4334	0.2941	0.2034	0.1432	0.1026	0.5530-1	0.3160-1	0.1687-1	0.9649-2	0.5849-2	0.3723-2
80	0.4473	0.3075	0.2151	0.1530	0.1106	0.6049-1	0.3494-1	0.1884-1	0.1085-1	0.6607-2	0.4220-2
90	0.4593	0.3194	0.2257	0.1620	0.1180	0.6535-1	0.3812-1	0.2074-1	0.1202-1	0.7349-2	0.4708-2
100	0.4700	0.3300	0.2352	0.1702	0.1248	0.6993-1	0.4115-1	0.2257-1	0.1315-1	0.8078-2	0.5190-2
120	0.4882	0.3484	0.2520	0.1847	0.1371	0.7835-1	0.4683-1	0.2606-1	0.1535-1	0.9495-2	0.6133-2
140	0.5034	0.3640	0.2665	0.1975	0.1480	0.8598-1	0.5207-1	0.2934-1	0.1744-1	0.1086-1	0.7051-2
160	0.5163	0.3775	0.2792	0.2087	0.1578	0.9296-1	0.5695-1	0.3245-1	0.1945-1	0.1219-1	0.7947-2
180	0.5274	0.3893	0.2904	0.2189	0.1666	0.9941-1	0.6151-1	0.3540-1	0.2138-1	0.1347-1	0.8822-2
200	0.5373	0.3999	0.3006	0.2281	0.1748	0.1054	0.6582-1	0.3822-1	0.2324-1	0.1472-1	0.9677-2

Footnote. PL = Prediction Limit; X_n = Maximum order statistic

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Table 19-24. Per-Constituent Significance Levels (α) for Non-Parametric 1-of-2 Plan for Median ($PL=X_n$)

w\n	50	60	70	80	90	100	120	140	160	180	200
1	0.2513-4	0.1276-4	0.7145-5	0.4307-5	0.2749-5	0.1835-5	0.9090-6	*0.5001-6*	*0.2974-6*	*0.1878-6*	*0.1243-6*
2	0.5024-4	0.2550-4	0.1429-4	0.8613-5	0.5497-5	0.3671-5	0.1818-5	*0.1000-5*	*0.5949-6*	*0.3756-6*	*0.2487-6*
3	0.7531-4	0.3825-4	0.2143-4	0.1292-4	0.8244-5	0.5506-5	0.2727-5	*0.1500-5*	*0.8923-6*	*0.5634-6*	*0.3730-6*
4	0.1004-3	0.5098-4	0.2856-4	0.1722-4	0.1099-4	0.7340-5	0.3636-5	*0.2000-5*	*0.1190-5*	*0.7511-6*	*0.4973-6*
5	0.1254-3	0.6370-4	0.3570-4	0.2153-4	0.1374-4	0.9175-5	0.4545-5	*0.2501-5*	*0.1487-5*	*0.9389-6*	*0.6216-6*
8	0.2003-3	0.1018-3	0.5709-4	0.3443-4	0.2198-4	0.1468-4	0.7271-5	*0.4001-5*	*0.2379-5*	*0.1502-5*	*0.9946-6*
10	0.2501-3	0.1272-3	0.7134-4	0.4303-4	0.2747-4	0.1835-4	0.9088-5	*0.5001-5*	*0.2974-5*	*0.1878-5*	*0.1243-5*
12	0.2998-3	0.1526-3	0.8557-4	0.5162-4	0.3296-4	0.2201-4	0.1090-4	*0.6001-5*	*0.3569-5*	*0.2253-5*	*0.1492-5*
15	0.3741-3	0.1905-3	0.1069-3	0.6451-4	0.4119-4	0.2751-4	0.1363-4	*0.7501-5*	*0.4461-5*	*0.2817-5*	*0.1865-5*
20	0.4975-3	0.2537-3	0.1424-3	0.8596-4	0.5489-4	0.3667-4	0.1817-4	*0.1000-4*	*0.5948-5*	*0.3755-5*	*0.2486-5*
25	0.6203-3	0.3167-3	0.1779-3	0.1074-3	0.6859-4	0.4583-4	0.2271-4	*0.1250-4*	*0.7434-5*	*0.4694-5*	*0.3108-5*
30	0.7424-3	0.3794-3	0.2133-3	0.1288-3	0.8228-4	0.5498-4	0.2725-4	*0.1500-4*	*0.8921-5*	*0.5633-5*	*0.3729-5*
35	0.8640-3	0.4420-3	0.2486-3	0.1502-3	0.9596-4	0.6413-4	0.3179-4	*0.1750-4*	*0.1041-4*	*0.6571-5*	*0.4351-5*
40	0.9849-3	0.5045-3	0.2839-3	0.1715-3	0.1096-3	0.7327-4	0.3632-4	*0.1999-4*	*0.1189-4*	*0.7510-5*	*0.4972-5*
45	0.1105-2	0.5667-3	0.3191-3	0.1929-3	0.1233-3	0.8241-4	0.4086-4	*0.2249-4*	*0.1338-4*	*0.8448-5*	*0.5594-5*
50	0.1225-2	0.6288-3	0.3542-3	0.2142-3	0.1369-3	0.9155-4	0.4539-4	*0.2499-4*	*0.1487-4*	*0.9387-5*	*0.6215-5*
60	0.1463-2	0.7525-3	0.4244-3	0.2568-3	0.1642-3	0.1098-3	0.5446-4	*0.2998-4*	*0.1784-4*	*0.1126-4*	*0.7458-5*
70	0.1699-2	0.8755-3	0.4943-3	0.2992-3	0.1914-3	0.1280-3	0.6352-4	*0.3497-4*	*0.2081-4*	*0.1314-4*	*0.8701-5*
80	0.1933-2	0.9979-3	0.5639-3	0.3416-3	0.2186-3	0.1463-3	0.7257-4	*0.3997-4*	*0.2378-4*	*0.1502-4*	*0.9943-5*
90	0.2164-2	0.1120-2	0.6334-3	0.3839-3	0.2458-3	0.1645-3	0.8162-4	*0.4495-4*	*0.2675-4*	*0.1689-4*	*0.1119-4*
100	0.2394-2	0.1241-2	0.7026-3	0.4261-3	0.2729-3	0.1826-3	0.9067-4	*0.4994-4*	*0.2972-4*	*0.1877-4*	*0.1243-4*
120	0.2848-2	0.1481-2	0.8405-3	0.5103-3	0.3270-3	0.2190-3	0.1087-3	*0.5991-4*	*0.3565-4*	*0.2252-4*	*0.1491-4*
140	0.3295-2	0.1720-2	0.9775-3	0.5941-3	0.3810-3	0.2552-3	0.1268-3	*0.6988-4*	*0.4159-4*	*0.2627-4*	*0.1740-4*
160	0.3735-2	0.1956-2	0.1114-2	0.6776-3	0.4348-3	0.2914-3	0.1449-3	*0.7984-4*	*0.4752-4*	*0.3002-4*	*0.1988-4*
180	0.4169-2	0.2189-2	0.1249-2	0.7608-3	0.4885-3	0.3275-3	0.1629-3	*0.8979-4*	*0.5345-4*	*0.3377-4*	*0.2236-4*
200	0.4596-2	0.2421-2	0.1384-2	0.8437-3	0.5421-3	0.3635-3	0.1809-3	*0.9974-4*	*0.5938-4*	*0.3752-4*	*0.2485-4*

Footnote. PL = Prediction Limit; X_n = Maximum order statistic

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Table 19-24. Per-Constituent Significance Levels (α) for Non-Parametric 1-of-2 Plan for Median ($PL=X_{n-1}$)

w\n	4	6	8	10	12	16	20	25	30	35	40
1	0.2048	0.8874-1	0.4429-1	0.2448-1	0.1460-1	0.6125-2	0.3001-2	0.1427-2	0.7629-3	0.4439-3	0.2755-3
2	0.3138	0.1515	0.8008-1	0.4576-1	0.2786-1	0.1195-1	0.5917-2	0.2832-2	0.1519-2	0.8852-3	0.5500-3
3	0.3849	0.1996	0.1101	0.6462-1	0.4003-1	0.1751-1	0.8754-2	0.4216-2	0.2267-2	0.1324-2	0.8234-3
4	0.4363	0.2383	0.1360	0.8158-1	0.5129-1	0.2283-1	0.1152-1	0.5579-2	0.3009-2	0.1760-2	0.1096-2
5	0.4758	0.2705	0.1586	0.9698-1	0.6178-1	0.2794-1	0.1421-1	0.6922-2	0.3745-2	0.2194-2	0.1367-2
8	0.5558	0.3429	0.2135	0.1363	0.8957-1	0.4215-1	0.2193-1	0.1084-1	0.5913-2	0.3480-2	0.2175-2
10	0.5914	0.3785	0.2425	0.1582	0.1057	0.5085-1	0.2679-1	0.1337-1	0.7329-2	0.4326-2	0.2708-2
12	0.6192	0.4079	0.2674	0.1776	0.1204	0.5902-1	0.3146-1	0.1583-1	0.8722-2	0.5163-2	0.3238-2
15	0.6515	0.4437	0.2990	0.2031	0.1401	0.7045-1	0.3814-1	0.1942-1	0.1077-1	0.6402-2	0.4025-2
20	0.6902	0.4892	0.3413	0.2386	0.1684	0.8764-1	0.4852-1	0.2514-1	0.1409-1	0.8427-2	0.5319-2
25	0.7178	0.5237	0.3748	0.2678	0.1925	0.1030	0.5810-1	0.3057-1	0.1729-1	0.1040-1	0.6592-2
30	0.7389	0.5511	0.4024	0.2925	0.2135	0.1169	0.6702-1	0.3574-1	0.2039-1	0.1233-1	0.7844-2
35	0.7557	0.5736	0.4257	0.3140	0.2321	0.1296	0.7538-1	0.4068-1	0.2339-1	0.1422-1	0.9076-2
40	0.7694	0.5926	0.4459	0.3329	0.2487	0.1413	0.8324-1	0.4542-1	0.2631-1	0.1607-1	0.1029-1
45	0.7810	0.6090	0.4635	0.3498	0.2638	0.1522	0.9067-1	0.4997-1	0.2914-1	0.1789-1	0.1149-1
50	0.7910	0.6232	0.4792	0.3650	0.2775	0.1623	0.9771-1	0.5436-1	0.3190-1	0.1967-1	0.1266-1
60	0.8072	0.6471	0.5061	0.3915	0.3019	0.1808	0.1108	0.6268-1	0.3721-1	0.2312-1	0.1497-1
70	0.8201	0.6665	0.5283	0.4139	0.3229	0.1973	0.1228	0.7047-1	0.4227-1	0.2646-1	0.1722-1
80	0.8306	0.6827	0.5473	0.4334	0.3414	0.2121	0.1339	0.7781-1	0.4711-1	0.2969-1	0.1942-1
90	0.8394	0.6965	0.5637	0.4504	0.3579	0.2257	0.1441	0.8475-1	0.5175-1	0.3281-1	0.2156-1
100	0.8469	0.7085	0.5781	0.4656	0.3727	0.2381	0.1537	0.9134-1	0.5621-1	0.3584-1	0.2365-1
120	0.8592	0.7283	0.6025	0.4917	0.3985	0.2604	0.1712	0.1036	0.6464-1	0.4166-1	0.2770-1
140	0.8688	0.7443	0.6224	0.5135	0.4204	0.2797	0.1868	0.1148	0.7252-1	0.4717-1	0.3158-1
160	0.8767	0.7575	0.6392	0.5320	0.4393	0.2969	0.2009	0.1252	0.7993-1	0.5242-1	0.3532-1
180	0.8832	0.7687	0.6536	0.5481	0.4560	0.3123	0.2138	0.1349	0.8692-1	0.5743-1	0.3892-1
200	0.8888	0.7783	0.6662	0.5623	0.4708	0.3263	0.2257	0.1439	0.9354-1	0.6223-1	0.4240-1

Footnote. PL = Prediction Limit; X_{n-1} = 2nd largest order statistic

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Table 19-24. Per-Constituent Significance Levels (α) for Non-Parametric 1-of-2 Plan for Median ($PL=X_{n-1}$)

w\n	50	60	70	80	90	100	120	140	160	180	200
1	0.1225-3	0.6242-4	0.3507-4	0.2119-4	0.1354-4	0.9057-5	0.4495-5	0.2477-5	0.1475-5	0.9321-6	0.6175-6
2	0.2447-3	0.1248-3	0.7011-4	0.4236-4	0.2708-4	0.1811-4	0.8991-5	0.4954-5	0.2950-5	0.1864-5	0.1235-5
3	0.3667-3	0.1870-3	0.1051-3	0.6353-4	0.4062-4	0.2717-4	0.1349-4	0.7431-5	0.4425-5	0.2796-5	0.1853-5
4	0.4884-3	0.2493-3	0.1401-3	0.8470-4	0.5416-4	0.3622-4	0.1798-4	0.9908-5	0.5900-5	0.3728-5	0.2470-5
5	0.6099-3	0.3114-3	0.1751-3	0.1058-3	0.6769-4	0.4527-4	0.2247-4	0.1239-4	0.7374-5	0.4660-5	0.3088-5
8	0.9731-3	0.4975-3	0.2799-3	0.1693-3	0.1083-3	0.7241-4	0.3595-4	0.1981-4	0.1180-4	0.7456-5	0.4940-5
10	0.1214-2	0.6212-3	0.3497-3	0.2115-3	0.1353-3	0.9050-4	0.4494-4	0.2477-4	0.1475-4	0.9320-5	0.6175-5
12	0.1454-2	0.7447-3	0.4194-3	0.2537-3	0.1623-3	0.1086-3	0.5392-4	0.2972-4	0.1770-4	0.1118-4	0.7410-5
15	0.1813-2	0.9294-3	0.5237-3	0.3169-3	0.2028-3	0.1357-3	0.6739-4	0.3715-4	0.2212-4	0.1398-4	0.9262-5
20	0.2406-2	0.1236-2	0.6972-3	0.4222-3	0.2702-3	0.1808-3	0.8983-4	0.4952-4	0.2949-4	0.1864-4	0.1235-4
25	0.2994-2	0.1541-2	0.8702-3	0.5272-3	0.3376-3	0.2260-3	0.1123-3	0.6189-4	0.3686-4	0.2330-4	0.1544-4
30	0.3577-2	0.1845-2	0.1043-2	0.6320-3	0.4048-3	0.2710-3	0.1347-3	0.7426-4	0.4423-4	0.2795-4	0.1852-4
35	0.4155-2	0.2147-2	0.1215-2	0.7367-3	0.4720-3	0.3161-3	0.1571-3	0.8663-4	0.5160-4	0.3261-4	0.2161-4
40	0.4728-2	0.2448-2	0.1386-2	0.8411-3	0.5391-3	0.3610-3	0.1795-3	0.9899-4	0.5896-4	0.3727-4	0.2469-4
45	0.5297-2	0.2747-2	0.1557-2	0.9453-3	0.6061-3	0.4060-3	0.2019-3	0.1114-3	0.6633-4	0.4192-4	0.2778-4
50	0.5861-2	0.3045-2	0.1727-2	0.1049-2	0.6730-3	0.4509-3	0.2243-3	0.1237-3	0.7369-4	0.4658-4	0.3087-4
60	0.6976-2	0.3636-2	0.2067-2	0.1257-2	0.8066-3	0.5406-3	0.2690-3	0.1484-3	0.8841-4	0.5589-4	0.3704-4
70	0.8074-2	0.4223-2	0.2404-2	0.1464-2	0.9398-3	0.6302-3	0.3137-3	0.1731-3	0.1031-3	0.6520-4	0.4321-4
80	0.9156-2	0.4804-2	0.2740-2	0.1670-2	0.1073-2	0.7196-3	0.3583-3	0.1978-3	0.1178-3	0.7451-4	0.4938-4
90	0.1022-1	0.5380-2	0.3074-2	0.1875-2	0.1205-2	0.8088-3	0.4030-3	0.2224-3	0.1326-3	0.8381-4	0.5554-4
100	0.1128-1	0.5951-2	0.3406-2	0.2079-2	0.1338-2	0.8980-3	0.4475-3	0.2471-3	0.1473-3	0.9311-4	0.6171-4
120	0.1334-1	0.7080-2	0.4065-2	0.2486-2	0.1601-2	0.1076-2	0.5366-3	0.2964-3	0.1767-3	0.1117-3	0.7404-4
140	0.1535-1	0.8190-2	0.4717-2	0.2891-2	0.1864-2	0.1253-2	0.6254-3	0.3456-3	0.2060-3	0.1303-3	0.8637-4
160	0.1731-1	0.9284-2	0.5362-2	0.3292-2	0.2125-2	0.1429-2	0.7141-3	0.3947-3	0.2354-3	0.1489-3	0.9870-4
180	0.1923-1	0.1036-1	0.6001-2	0.3691-2	0.2385-2	0.1605-2	0.8027-3	0.4439-3	0.2647-3	0.1675-3	0.1110-3
200	0.2111-1	0.1142-1	0.6634-2	0.4087-2	0.2643-2	0.1781-2	0.8911-3	0.4929-3	0.2941-3	0.1860-3	0.1233-3

Footnote. PL = Prediction Limit; X_{n-1} = 2nd largest order statistic

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D STATISTICAL TABLES

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Table 21-1. Land's Factors ($H_{.01}$) for Confidence Bounds on Lognormal Arithmetic Mean for *n* = 3(1)19(2)25(3)31(5)36

s_y\n	3	4	5	6	7	8	9	10	11	12	13	14
0.10	-4.435	-3.437	-3.047	-2.849	-2.730	-2.653	-2.598	-2.558	-2.527	-2.503	-2.484	-2.467
0.20	-3.720	-3.089	-2.819	-2.677	-2.590	-2.534	-2.494	-2.465	-2.442	-2.425	-2.411	-2.400
0.30	-3.260	-2.836	-2.646	-2.544	-2.482	-2.441	-2.413	-2.393	-2.378	-2.366	2.357	-2.350
0.40	-2.943	-2.649	-2.514	-2.442	-2.399	-2.371	-2.353	-2.340	-2.330	-2.324	-2.319	-2.315
0.50	-2.714	-2.508	-2.414	-2.364	-2.337	-2.320	-2.309	-2.302	-2.298	-2.295	-2.294	-2.293
0.60	-2.544	-2.402	-2.338	-2.307	-2.292	-2.283	-2.279	-2.278	-2.278	-2.279	-2.281	-2.283
0.70	-2.415	-2.321	-2.282	-2.266	-2.261	-2.260	-2.262	-2.265	-2.269	-2.274	-2.278	-2.283
0.80	-2.317	-2.260	-2.242	-2.238	-2.241	-2.247	-2.255	-2.262	-2.270	-2.277	-2.284	-2.291
0.90	-2.242	-2.216	-2.214	-2.221	-2.232	-2.244	-2.256	-2.268	-2.279	-2.289	-2.298	-2.308
1.00	-2.185	-2.184	-2.196	-2.214	-2.232	-2.249	-2.265	-2.280	-2.295	-2.308	-2.320	-2.331
1.25	-2.099	-2.147	-2.189	-2.227	-2.260	-2.290	-2.316	-2.339	-2.361	-2.380	-2.398	-2.414
1.50	-2.069	-2.153	-2.220	-2.275	-2.322	-2.362	-2.397	-2.428	-2.456	-2.481	-2.504	-2.525
1.75	-2.075	-2.190	-2.277	-2.348	-2.407	-2.457	-2.501	-2.540	-2.574	-2.605	-2.633	-2.659
2.00	-2.106	-2.247	-2.355	-2.440	-2.511	-2.571	-2.623	-2.668	-2.709	-2.746	-2.778	-2.809
2.50	-2.217	-2.408	-2.552	-2.665	-2.758	-2.836	-2.904	-2.964	-3.017	-3.064	-3.107	-3.147
3.00	-2.371	-2.610	-2.788	-2.927	-3.042	-3.140	-3.223	-3.296	-3.361	-3.419	-3.472	-3.521
3.50	-2.553	-2.839	-3.050	-3.216	-3.352	-3.467	-3.566	-3.652	-3.729	-3.799	-3.861	-3.918
4.00	-2.756	-3.087	-3.331	-3.523	-3.680	-3.812	-3.926	-4.026	-4.115	-4.195	-4.267	-4.333
4.50	-2.973	-3.349	-3.626	-3.842	-4.020	-4.170	-4.299	-4.412	-4.513	-4.603	-4.685	-4.760
5.00	-3.202	-3.622	-3.930	-4.171	-4.370	-4.537	-4.681	-4.808	-4.920	-5.021	-5.112	-5.195
6.00	-3.683	-4.189	-4.559	-4.850	-5.089	-5.291	-5.465	-5.618	-5.754	-5.875	-5.986	-6.087
7.00	-4.185	-4.775	-5.208	-5.548	-5.827	-6.064	-6.267	-6.446	-6.605	-6.748	-6.877	-6.995
8.00	-4.700	-5.374	-5.868	-6.258	-6.577	-6.847	-7.081	-7.286	-7.468	-7.632	-7.780	-7.916
9.00	-5.223	-5.980	-6.536	-6.975	-7.334	-7.639	-7.902	-8.133	-8.339	-8.523	-8.690	-8.843
10.00	-5.753	-6.593	-7.211	-7.698	-8.098	-8.437	-8.730	-8.987	-9.215	-9.420	-9.607	-9.776

Source: Land (1975)
Footnote. Notation n = 3(1)19(2)25(3)31(5)36 is shorthand for n from 3 to 19 by unit steps, from 19 to 25 by 2's, from 25 to 31 by 3's, and from 31 to 36 by 5's

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Table 21-1. Land's Factors ($H_{.01}$) for Confidence Bounds on Lognormal Arithmetic Mean for n = 3(1)19(2)25(3)31(5)36

s_y\n	15	16	17	18	19	21	23	25	28	31	36
0.10	-2.454	-2.442	-2.432	-2.424	-2.416	-2.404	-2.395	-2.386	-2.377	-2.369	-2.361
0.20	-2.390	-2.383	-2.376	-2.370	-2.365	-2.357	-2.351	-2.346	-2.340	-2.336	-2.331
0.30	-2.344	-2.339	-2.335	-2.332	-2.329	-2.325	-2.322	2.320	-2.317	-2.316	-2.315
0.40	-2.312	-2.310	-2.308	-2.307	-2.306	-2.306	-2.305	-2.305	-2.306	-2.308	-2.310
0.50	-2.293	-2.293	-2.294	-2.294	-2.295	-2.298	-2.300	-2.302	-2.306	-2.310	-2.316
0.60	-2.285	-2.288	-2.290	-2.292	-2.295	-2.300	-2.305	-2.309	-2.316	-2.322	-2.330
0.70	-2.287	-2.292	-2.296	-2.300	-2.304	-2.312	-2.319	-2.325	-2.334	-2.342	-2.354
0.80	-2.298	-2.304	-2.310	-2.315	-2.321	-2.331	-2.341	-2.349	-2.361	-2.373	-2.386
0.90	-2.316	-2.324	-2.332	-2.339	-2.346	-2.358	-2.370	-2.380	-2.394	-2.406	-2.425
1.00	-2.341	-2.351	-2.360	-2.369	-2.377	-2.392	-2.406	-2.418	-2.434	-2.449	-2.470
1.25	-2.429	-2.443	-2.456	-2.468	-2.479	-2.500	-2.519	-2.535	-2.558	-2.578	-2.606
1.50	2.545	-2.563	-2.579	-2.595	-2.609	-2.635	-2.659	-2.680	-2.709	-2.734	-2.769
1.75	-2.682	-2.704	-2.724	-2.743	-2.760	-2.792	-2.821	-2.847	-2.881	-2.911	-2.954
2.00	-2.836	-2.862	-2.886	-2.908	-2.929	-2.966	-3.000	-3.030	-3.070	-3.105	-3.155
2.50	-3.183	-3.216	-3.247	-3.275	-3.302	-3.351	-3.394	-3.434	-3.486	-3.531	-3.569
3.00	-3.564	-3.605	-3.643	-3.679	-3.711	-3.771	-3.825	-3.873	-3.936	-3.992	-4.071
3.50	-3.970	-4.019	-4.063	-4.105	-4.144	-4.215	-4.279	-4.335	-4.410	-4.476	-4.570
4.00	-4.393	-4.449	-4.500	-4.549	-4.593	-4.676	-4.749	-4.814	-4.901	-4.977	-5.086
4.50	-4.828	-4.891	-4.950	-5.005	-5.055	-5.148	-5.231	-5.305	-5.404	-5.491	-5.614
5.00	-5.272	-5.343	-5.408	-5.469	-5.526	-5.630	-5.723	-5.805	-5.916	-6.012	-6.150
6.00	-6.179	-6.264	-6.343	-6.418	-6.486	-6.612	-6.724	-6.824	-6.958	-7.075	-7.241
7.00	-7.104	-7.204	-7.297	-7.383	-7.465	-7.611	-7.742	-7.860	-8.017	-8.154	-8.348
8.00	-8.040	-8.154	-8.261	-8.360	-8.453	-8.621	-8.772	-8.906	-9.086	-9.244	-9.467
9.00	-8.983	-9.113	-9.232	-9.344	-9.449	-9.640	-9.809	-9.961	-10.160	-10.340	-10.590
10.00	-9.932	-10.080	-10.210	-10.330	-10.450	-10.660	-10.850	-11.020	-11.250	-11.440	-11.720

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Table 21-2. Land's Factors ($H_{.025}$) for Confidence Bounds on Lognormal Arithmetic Mean for *n* = 3(1)19(2)25(3)31(5)36

s_y\n	3	4	5	6	7	8	9	10	11	12	13	14
0.10	-2.988	-2.504	-2.314	-2.215	-2.157	-2.117	-2.090	-2.070	-2.055	-2.042	-2.032	-2.025
0.20	-2.639	-2.316	-2.183	-2.113	-2.071	-2.044	-2.025	-2.012	-2.001	-1.994	-1.987	-1.982
0.30	-2.396	-2.176	-2.083	-2.034	-2.006	-1.988	-1.976	-1.968	-1.962	-1.958	-1.954	-1.952
0.40	-2.220	-2.070	-2.007	-1.975	-1.958	-1.948	-1.941	-1.938	-1.935	-1.934	-1.933	-1.933
0.50	-2.090	-1.989	-1.950	-1.932	-1.923	-1.919	-1.918	-1.918	-1.919	-1.920	-1.922	-1.924
0.60	-1.992	-1.929	-1.908	-1.901	-1.900	-1.902	-1.905	-1.908	-1.913	-1.917	-1.920	-1.924
0.70	-1.919	-1.885	-1.879	-1.882	-1.887	-1.894	-1.901	-1.908	-1.914	-1.921	-1.926	-1.932
0.80	-1.864	-1.854	-1.860	-1.871	-1.830	-1.894	-1.904	-1.914	-1.923	-1.932	-1.939	-1.946
0.90	-1.823	-1.833	-1.850	-1.869	-1.885	-1.901	-1.915	-1.927	-1.939	-1.949	-1.958	-1.967
1.00	-1.794	-1.820	-1.848	-1.873	-1.894	-1.913	-1.931	-1.946	-1.959	-1.972	-1.983	-1.993
1.25	-1.759	-1.819	-1.867	-1.907	-1.939	-1.967	-1.992	-2.013	-2.032	-2.049	-2.064	-2.079
1.50	-1.761	-1.849	-1.914	-1.966	-2.009	-2.045	-2.076	-2.104	-2.128	-2.150	-2.169	-2.187
1.75	-1.789	-1.899	-1.981	-2.045	-2.097	-2.141	-2.179	-2.212	-2.242	-2.268	-2.291	-2.313
2.00	-1.834	-1.965	-2.062	-2.138	-2.200	-2.252	-2.296	-2.335	-2.369	-2.400	-2.428	-2.452
2.50	-1.960	-2.132	-2.259	-2.357	-2.438	-2.505	-2.562	-2.612	-2.656	-2.696	-2.731	-2.764
3.00	-2.118	-2.331	-2.487	-2.607	-2.706	-2.788	-2.858	-2.919	-2.973	-3.022	-3.065	-3.105
3.50	-2.299	-2.552	-2.736	-2.879	-2.994	-3.091	-3.174	-3.246	-3.310	-3.367	-3.418	-3.465
4.00	-2.496	-2.789	-3.001	-3.164	-3.298	-3.409	-3.505	-3.588	-3.661	-3.727	-3.786	-3.840
4.50	-2.706	-3.037	-3.276	-3.461	-3.612	-3.738	-3.846	-3.940	-4.023	-4.097	-4.164	-4.226
5.00	-2.925	-3.294	-3.560	-3.766	-3.934	-4.074	-4.194	-4.300	-4.392	-4.475	-4.550	-4.618
6.00	-3.382	-3.826	-4.145	-4.393	-4.594	-4.763	-4.908	-5.035	-5.147	-5.247	-5.337	-5.419
7.00	-3.856	-4.372	-4.744	-5.033	-5.269	-5.467	-5.637	-5.785	-5.916	-6.033	-6.139	-6.235
8.00	-4.341	-4.929	-5.354	-5.685	-5.955	-6.181	-6.375	-6.545	-6.695	-6.829	-6.950	-7.060
9.00	-4.832	-5.492	-5.971	-6.343	-6.646	-6.901	-7.120	-7.311	-7.480	-7.631	-7.768	-7.892
10.00	-5.328	-6.061	-6.592	-7.006	-7.343	-7.626	-7.869	-8.082	-8.270	-8.438	-8.590	-8.728

Source: Land (1975)
Footnote. Notation n = 3(1)19(2)25(3)31(5)36 is shorthand for n from 3 to 19 by unit steps, from 19 to 25 by 2's, from 25 to 31 by 3's, and from 31 to 36 by 5's

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Table 21-2. Land's Factors ($H_{.025}$) for Confidence Bounds on Lognormal Arithmetic Mean for n = 3(1)19(2)25(3)31(5)36

s_y\n	15	16	17	18	19	21	23	25	28	31	36
0.10	-2.018	-2.012	-2.008	-2.003	-2.000	-1.993	-1.989	-1.985	-1.980	-1.977	-1.972
0.20	-1.978	-1.974	-1.972	-1.969	-1.967	-1.964	-1.961	-1.959	-1.957	-1.956	-1.954
0.30	-1.950	-1.949	-1.947	-1.946	-1.946	-1.945	-1.945	-1.945	-1.945	-1.945	-1.946
0.40	-1.933	-1.934	-1.934	-1.935	-1.935	-1.936	-1.938	-1.940	-1.942	-1.944	-1.948
0.50	-1.926	-1.928	-1.930	-1.932	-1.933	-1.937	-1.941	-1.944	-1.948	-1.952	-1.958
0.60	-1.928	-1.931	-1.934	-1.938	-1.940	-1.946	-1.951	-1.956	-1.962	-1.968	-1.976
0.70	-1.937	-1.942	-1.946	-1.951	-1.955	-1.906	-1.969	-1.975	-1.983	-1.991	-2.001
0.80	-1.953	-1.959	-1.965	-1.971	-1.976	-1.985	-1.993	-2.001	-2.011	-2.020	-2.032
0.90	-1.975	-1.983	-1.990	-1.996	-2.003	-2.014	-2.023	-2.003	-2.044	-2.055	-2.069
1.00	-2.003	-2.012	-2.109	-2.027	-2.024	-2.047	-2.059	-2.069	-2.083	-2.095	-2.112
1.25	-2.091	-2.104	-2.114	-2.125	-2.134	-2.151	-2.167	-2.181	-2.199	-2.215	-2.237
1.50	-2.203	-2.218	-2.232	-2.245	-2.257	-2.278	-2.298	-2.315	-2.338	-2.358	-2.386
1.75	2.332	-2.351	-2.367	-2.383	-2.396	-2.423	-2.446	-2.467	-2.495	-2.518	-2.552
2.00	-2.476	-2.496	-2.516	-2.534	-2.551	-2.581	-2.608	-2.633	-2.665	-2.693	-2.733
2.50	-2.793	-2.821	-2.845	-2.869	-2.890	-2.930	-2.956	-2.997	-3.038	-3.074	-3.125
3.00	-3.141	-3.174	-3.205	-3.233	-3.260	-3.308	-3.351	-3.389	-3.440	-3.484	-3.547
3.50	-3.508	-3.547	-3.583	-3.617	-3.649	-3.706	-3.757	-3.802	-3.862	-3.914	-3.988
4.00	-3.889	-3.935	-3.976	-4.015	-4.052	-4.118	-4.176	-4.229	-4.298	-4.358	-4.444
4.50	-4.281	-4.332	-4.380	-4.424	-4.465	-4.539	-4.606	-4.665	-4.744	-4.812	-4.910
5.00	-4.680	-4.738	-4.790	-4.840	-4.886	-4.969	-5.043	-5.110	-5.197	-5.273	-5.382
6.00	-5.494	-5.564	-5.628	-5.687	-5.743	-5.844	-5.933	-6.013	-6.119	-6.212	-6.343
7.00	-6.324	-6.404	-6.480	-6.549	-6.614	-6.732	-6.837	-6.931	-7.056	-7.164	-7.318
8.00	-7.161	-7.254	-7.340	-7.420	-7.495	-7.630	-7.750	-7.858	-8.001	-8.125	-8.301
9.00	-8.006	-8.111	-8.208	-8.298	-8.382	-8.535	-8.670	-8.791	-8.952	-9.092	-9.292
10.00	-8.855	-8.972	-9.079	-9.179	-9.273	-9.443	-9.594	-9.729	-9.908	-10.060	-10.290

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Table 21-3. Land's Factors ($H_{.05}$) for Confidence Bounds on Lognormal Arithmetic Mean for *n* = 3(1)19(2)25(3)31(5)36

s_y\n	3	4	5	6	7	8	9	10	11	12	13	14
0.10	-2.130	-1.898	-1.806	-1.759	-1.731	-1.712	-1.699	-1.690	-1.683	-1.677	-1.673	-1.669
0.20	-1.969	-1.791	-1.729	-1.697	-1.678	-1.667	-1.658	-1.653	-1.649	-1.646	-1.644	-1.642
0.30	-1.816	-1.710	-1.669	-1.650	-1.639	-1.633	-1.629	-1.627	-1.626	-1.625	-1.625	-1.624
0.40	-1.717	-1.650	-1.625	-1.615	-1.611	-1.610	-1.610	-1.611	-1.612	-1.613	-1.614	-1.615
0.50	-1.644	-1.605	-1.594	-1.592	-1.594	-1.596	-1.599	-1.603	-1.606	-1.609	-1.612	-1.615
0.60	-1.589	-1.572	-1.573	-1.578	-1.584	-1.591	-1.597	-1.602	-1.608	-1.612	-1.617	-1.621
0.70	-1.549	-1.550	-1.560	-1.572	-1.582	-1.592	-1.600	-1.608	-1.615	-1.622	-1.628	-1.633
0.80	-1.521	-1.537	-1.555	-1.572	-1.586	-1.599	-1.610	-1.620	-1.629	-1.636	-1.644	-1.651
0.90	-1.502	-1.530	-1.556	-1.577	-1.595	-1.611	-1.625	-1.637	-1.647	-1.656	-1.665	-1.673
1.00	-1.490	-1.530	-1.562	-1.588	-1.610	-1.628	-1.644	-1.658	-1.670	-1.681	-1.690	-1.699
1.25	-1.486	-1.549	-1.596	-1.632	-1.662	-1.687	-1.708	-1.727	-1.743	-1.758	-1.770	-1.782
1.50	-1.508	-1.590	-1.650	-1.696	-1.733	-1.764	-1.791	-1.814	-1.834	-1.853	-1.869	-1.883
1.75	-1.547	-1.647	-1.719	-1.774	-1.819	-1.857	-1.889	-1.916	-1.940	-1.962	-1.981	-1.998
2.00	-1.598	-1.714	-1.799	-1.864	-1.917	-1.960	-1.998	-2.029	-2.058	-2.083	-2.106	-2.126
2.50	-1.727	-1.877	-1.986	-2.070	-2.138	-2.193	-2.241	-2.283	-2.319	-2.351	-2.380	-2.406
3.00	-1.880	-2.065	-2.199	-2.301	-2.384	-2.452	-2.510	-2.560	-2.604	-2.644	-2.679	-2.711
3.50	-2.051	-2.272	-2.429	-2.550	-2.647	-2.727	-2.795	-2.855	-2.907	-2.953	-2.995	-3.033
4.00	-2.237	-2.491	-2.672	-2.810	-2.922	-3.015	-3.093	-3.161	-3.221	-3.275	-3.323	-3.366
4.50	-2.434	-2.720	-2.924	-3.080	-3.206	-3.310	-3.399	-3.476	-3.544	-3.605	-3.659	-3.708
5.00	-2.638	-2.957	-3.183	-3.356	-3.497	-3.613	-3.712	-3.798	-3.873	-3.941	-4.001	-4.056
6.00	-3.062	-3.444	-3.715	-3.923	-4.092	-4.231	-4.351	-4.455	-4.546	-4.627	-4.700	-4.766
7.00	-3.499	-3.943	-4.260	-4.502	-4.699	-4.862	-5.002	-5.123	-5.230	-5.325	-5.411	-5.488
8.00	-3.945	-4.451	-4.812	-5.090	-5.315	-5.502	-5.661	-5.800	-5.922	-6.031	-6.129	-6.218
9.00	-4.397	-4.965	-5.371	-5.684	-5.936	-6.146	-6.326	-6.482	-6.620	-6.742	-6.853	-6.954
10.00	-4.852	-5.483	-5.933	-6.280	-6.560	-6.795	-6.994	-7.168	-7.321	-7.458	-7.581	-7.592

Source: Land (1975)
Footnote. Notation n = 3(1)19(2)25(3)31(5)36 is shorthand for n from 3 to 19 by unit steps, from 19 to 25 by 2's, from 25 to 31 by 3's, and from 31 to 36 by 5's

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Table 21-3. Land's Factors ($H_{.05}$) for Confidence Bounds on Lognormal Arithmetic Mean for n = 3(1)19(2)25(3)31(5)36

s_y\n	15	16	17	18	19	21	23	25	28	31	36
0.10	-1.666	-1.663	-1.661	-1.659	-1.658	-1.655	-1.653	-1.651	-1.649	-1.648	-1.647
0.20	-1.640	-1.639	-1.638	-1.638	-1.637	-1.636	-1.636	-1.635	-1.636	-1.636	-1.636
0.30	-1.625	-1.625	-1.625	-1.626	-1.626	-1.627	-1.628	-1.629	-1.630	-1.632	-1.633
0.40	-1.617	-1.618	-1.620	-1.622	-1.622	-1.625	-1.627	-1.629	-1.632	-1.635	-1.639
0.50	-1.618	-1.620	-1.622	-1.625	-1.627	-1.631	-1.634	-1.638	-1.642	-1.646	-1.651
0.60	-1.625	-1.629	-1.632	-1.635	-1.638	-1.643	-1.648	-1.652	-1.658	-1.662	-1.659
0.70	-1.638	-1.643	-1.647	-1.651	-1.654	-1.661	-1.667	-1.672	-1.679	-1.686	-2.694
0.80	-1.656	-1.662	-1.667	-1.672	-1.677	-1.685	-1.691	-1.698	-1.706	-1.714	-1.724
0.90	-1.680	-1.686	-1.692	-1.698	-1.703	-1.713	-1.721	-1.728	-1.738	-1.747	-1.759
1.00	-1.707	-1.715	-1.722	-1.728	-1.734	-1.745	-1.755	-1.763	-1.774	-1.784	-1.798
1.25	-1.793	-1.803	-1.812	-1.820	-1.828	-1.842	-1.854	-1.866	-1.880	-1.893	-1.911
1.50	-1.896	-1.909	-1.920	-1.930	-1.940	-1.958	-1.973	-1.987	-2.005	-2.020	-2.043
1.75	-2.015	-2.029	-2.043	-2.055	-2.067	-2.088	-2.107	-2.123	-2.145	-2.164	-2.190
2.00	-2.144	-2.162	-2.177	-2.192	-2.205	-2.230	-2.251	-2.271	-2.269	-2.318	-2.349
2.50	-2.430	-2.452	-2.472	-2.491	-2.508	-2.540	-2.568	-2.593	-2.625	-2.654	-2.694
3.00	-2.740	-2.767	2.792	-2.815	-2.836	-2.874	-2.908	-2.939	-2.979	-3.014	-3.063
3.50	-3.067	-3.099	3.128	-3.155	-3.180	-3.226	-3.266	-3.302	-3.349	-3.391	-3.448
4.00	-3.406	-3.443	3.476	-3.507	-3.536	-3.589	-3.635	-3.677	-3.731	-3.779	-3.846
4.50	-3.753	-3.794	3.833	-3.868	-3.901	-3.960	-4.013	-4.060	-4.122	-4.176	-4.252
5.00	-4.107	-4.153	4.195	-4.235	-4.272	-4.338	-4.397	-4.449	-4.518	-4.579	-4.664
6.00	-4.827	-4.882	4.934	-4.981	-5.026	-5.106	-5.177	-5.241	-5.325	-5.397	-5.500
7.00	-5.559	-5.624	5.685	-5.741	-5.793	-5.886	-5.970	-6.045	-6.142	-6.227	-6.348
8.00	-6.300	-6.374	6.443	-6.507	-6.566	-6.674	-6.770	-6.855	-6.968	-7.066	-7.204
9.00	-7.045	-7.129	7.207	-7.278	-7.346	-7.468	-7.575	-7.672	-7.798	-7.909	-8.064
10.00	-7.794	-7.888	7.974	-8.054	-8.129	-8.264	-8.385	-8.491	-8.632	-10.060	-8.928

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Table 21-4. Land's Factors ($H_{.10}$) for Confidence Bounds on Lognormal Arithmetic Mean for *n* = 3(1)19(2)25(3)31(5)36

s_y\n	3	4	5	6	7	8	9	10	11	12	13	14
0.10	-1.431	-1.351	-1.320	-1.305	-1.296	-1.291	-1.287	-1.285	-1.283	-1.281	-1.281	-1.280
0.20	-1.350	-1.299	-1.281	-1.273	-1.268	-1.267	-1.266	-1.266	-1.266	-1.266	-1.266	-1.266
0.30	-1.289	-1.260	-1.252	-1.251	-1.250	-1.251	-1.253	-1.254	-1.255	-1.257	-1.258	-1.259
0.40	-1.245	-1.233	-1.233	-1.236	-1.239	-1.243	-1.246	-1.249	-1.252	-1.254	-1.257	-1.258
0.50	-1.213	-1.214	-1.221	-1.228	-1.234	-1.240	-1.245	-1.250	-1.254	-1.257	-1.261	-1.264
0.60	-1.190	-1.202	-1.215	-1.226	-1.235	-1.243	-1.250	-1.256	-1.261	-1.266	-1.270	-1.274
0.70	-1.176	-1.197	-1.215	-1.229	-1.241	-1.251	-1.259	-1.266	-1.273	-1.278	-1.283	-1.288
0.80	-1.168	-1.197	-1.219	-1.237	-1.251	-1.262	-1.272	-1.280	-1.288	-1.294	-1.301	-1.306
0.90	-1.165	-1.201	-1.227	-1.248	-1.264	-1.277	-1.289	-1.298	-1.307	-1.314	-1.321	-1.327
1.00	-1.166	-1.208	-1.239	-1.262	-1.281	-1.296	-1.309	-1.320	-1.329	-1.337	-1.345	-1.353
1.25	-1.184	-1.240	-1.280	-1.310	-1.334	-1.353	-1.370	-1.384	-1.396	-1.407	-1.471	-1.426
1.50	-1.217	-1.285	-1.334	-1.371	-1.400	-1.424	-1.444	-1.462	-1.477	-1.491	-1.503	-1.514
1.75	-1.260	-1.341	-1.398	-1.442	-1.477	-1.505	-1.530	-1.551	-1.569	-1.585	-1.599	-1.612
2.00	-1.310	-1.403	-1.470	-1.521	-1.562	-1.595	-1.623	-1.647	1.669	-1.688	-1.704	-1.719
2.50	-1.426	-1.547	-1.634	-1.700	-1.751	-1.794	-1.830	-1.862	-1.889	-1.913	-1.934	-1.953
3.00	-1.560	-1.712	-1.817	-1.897	-1.960	-2.013	-2.057	-2.095	-2.128	-2.157	-2.183	-2.207
3.50	-1.710	-1.889	-2.014	-2.108	-2.183	-2.244	-2.296	-2.341	-2.380	-2.415	-2.446	-2.473
4.00	-1.871	-2.078	-2.221	-2.329	-2.415	-2.485	-2.545	-2.596	-2.641	-2.681	-2.717	-2.749
4.50	-2.041	-2.274	-2.435	-2.557	-2.653	-2.733	-2.801	-2.858	-2.910	-2.955	-2.995	-3.031
5.00	-2.217	-2.475	-2.654	-2.789	-2.897	-2.986	-3.061	-3.126	-3.183	-3.233	-3.278	-3.319
6.00	-2.581	-2.889	-3.104	-3.267	-3.396	-3.503	-3.593	-3.671	-3.740	-3.800	-3.855	-3.904
7.00	-2.955	-3.314	-3.564	-3.753	-3.904	-4.029	-4.135	-4.226	-4.306	-4.377	-4.441	-4.498
8.00	-3.336	-3.744	-4.030	-4.246	-4.418	-4.561	-4.683	-4.787	-4.879	-4.960	-5.033	-5.099
9.00	-3.721	-4.180	-4.500	-4.742	-4.937	-5.098	-5.234	-5.352	-5.455	-5.547	-5.629	-5.703
10.00	-4.109	-4.618	-4.973	-5.243	-5.459	-5.638	-5.789	-5.920	-6.035	-6.137	-6.228	-6.311

Source: Land (1975)
Footnote. Notation n = 3(1)19(2)25(3)31(5)36 is shorthand for n from 3 to 19 by unit steps, from 19 to 25 by 2's, from 25 to 31 by 3's, and from 31 to 36 by 5's

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Table 21-4. Land's Factors ($H_{.10}$) for Confidence Bounds on Lognormal Arithmetic Mean for *n* = 3(1)19(2)25(3)31(5)36

s_y\n	15	16	17	18	19	21	23	25	28	31	36
0.10	-1.279	-1.278	-1.278	-1.278	-1.278	-1.277	-1.277	-1.277	-1.277	-1.277	-1.277
0.20	-1.266	-1.267	-1.267	-1.267	-1.268	-1.268	-1.270	-1.270	-1.271	-1.272	-1.272
0.30	-1.260	-1.261	-1.262	-1.263	-1.265	-1.266	-1.268	-1.269	-1.271	-1.272	-1.275
0.40	-1.261	-1.262	-1.264	-1.266	-1.267	-1.270	-1.272	-1.274	-1.277	-1.279	-1.282
0.50	-1.266	-1.269	-1.271	-1.273	-1.275	-1.279	-1.281	-1.284	-1.288	-1.291	-1.295
0.60	-1.277	-1.280	-1.283	-1.286	-1.288	-1.292	-1.296	-1.299	-1.304	-1.307	-1.313
0.70	-1.292	-1.296	-1.299	-1.302	-1.305	-1.310	-1.315	-1.319	-1.324	-1.329	-1.336
0.80	-1.311	-1.315	-1.319	-1.323	-1.326	-1.332	-1.338	-1.342	-1.349	-1.354	-1.361
0.90	-1.333	-1.338	-1.342	-1.346	-1.351	-1.358	-1.364	-1.369	-1.377	-1.383	-1.391
1.00	-1.358	-1.364	-1.369	-1.374	-1.378	-1.387	-1.393	-1.399	-1.408	-1.414	-1.424
1.25	-1.434	-1.441	-1.448	-1.455	-1.460	-1.470	-1.479	-1.487	-1.498	-1.507	-1.519
1.50	-1.523	-1.533	-1.541	-1.548	-1.555	-1.568	-1.579	-1.589	-1.602	-1.613	-1.629
1.75	-1.624	-1.634	-1.645	-1.654	-1.662	-1.677	-1.690	-1.703	-1.718	-1.732	-1.750
2.00	-1.733	-1.746	-1.757	-1.767	-1.777	-1.795	-1.810	-1.825	-1.843	-1.859	-1.881
2.50	-1.971	-1.987	-2.002	-2.016	-2.029	-2.051	-2.072	-2.090	-2.113	-2.133	-2.161
3.00	-2.229	-2.248	2.266	-2.283	-2.298	-2.326	-2.351	-2.373	-2.402	-2.427	-2.461
3.50	-2.499	-2.522	2.544	-2.563	-2.581	-2.615	-2.644	-2.670	-2.704	-2.733	-2.775
4.00	-2.778	-2.805	2.830	-2.853	-2.874	-2.913	-2.946	-2.976	-3.015	-3.050	-3.097
4.50	-3.064	-3.095	3.123	-3.149	-3.173	-3.217	-3.255	-3.288	-3.333	-3.372	-3.426
5.00	-3.356	-3.390	3.421	-3.450	-3.477	-3.525	-3.567	-3.605	-3.655	-3.698	-3.759
6.00	-3.949	-3.989	4.027	-4.062	-4.094	-4.153	-4.204	-4.250	-4.311	-4.363	-4.436
7.00	-4.549	-4.599	4.642	-4.683	-4.721	-4.790	-4.850	-4.604	-4.975	-5.037	-5.122
8.00	-5.159	-5.213	5.264	-5.311	-5.354	-5.433	-5.002	-5.564	-5.645	-5.715	-5.815
9.00	-5.771	-5.833	5.890	-5.942	-5.992	-6.080	-6.158	-6.228	-6.319	-6.399	-6.510
10.00	-6.386	-6.455	6.518	-6.578	-6.632	-6.730	-6.817	-6.894	-6.996	-8.755	-7.208

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Table 21-5. Land's Factors ($H_{.90}$) for Confidence Bounds on Lognormal Arithmetic Mean for *n* = 3(1)19(2)25(3)31(5)36

s_y \ n	3	4	5	6	7	8	9	10	11	12	13	14
0.10	1.686	1.506	1.438	1.403	1.381	1.367	1.356	1.349	1.343	1.338	1.334	1.330
0.20	1.885	1.620	1.522	1.472	1.442	1.422	1.407	1.396	1.387	1.380	1.374	1.369
0.30	2.156	1.763	1.627	1.558	1.517	1.489	1.469	1.453	1.441	1.432	1.424	1.417
0.40	2.521	1.942	1.755	1.662	1.607	1.569	1.543	1.523	1.507	1.494	1.483	1.474
0.50	2.990	2.160	1.907	1.785	1.712	1.664	1.630	1.604	1.583	1.567	1.553	1.542
0.60	3.542	2.417	2.084	1.926	1.834	1.773	1.729	1.696	1.671	1.650	1.633	1.619
0.70	4.136	2.708	2.284	2.085	1.970	1.894	1.849	1.800	1.768	1.743	1.722	1.705
0.80	4.742	3.023	2.503	2.260	2.119	2.027	1.962	1.914	1.876	1.845	1.820	1.799
0.90	5.349	3.353	2.736	2.447	2.280	2.171	2.094	2.036	1.992	1.955	1.926	1.901
1.00	5.955	3.691	2.980	2.644	2.450	2.324	2.234	2.167	2.115	2.073	2.038	2.010
1.25	7.466	4.558	3.617	3.167	2.904	2.732	2.610	2.518	2.448	2.391	2.344	2.305
1.50	8.973	5.436	4.276	3.713	3.383	3.166	3.012	2.896	2.806	2.733	2.674	2.623
1.75	10.480	6.319	4.944	4.273	3.877	3.615	3.429	3.289	3.180	3.092	3.109	2.959
2.00	11.980	7.206	5.619	4.842	4.380	4.075	3.857	3.693	3.564	3.461	3.376	3.305
2.50	14.990	8.986	6.979	5.990	5.401	5.010	4.730	4.518	4.353	4.220	4.110	4.017
3.00	18.000	10.770	8.346	7.147	6.434	5.958	5.617	5.359	5.157	4.994	4.860	4.746
3.50	21.000	12.560	9.717	8.312	7.473	6.913	6.511	6.208	5.970	5.778	5.619	5.486
4.00	24.000	14.340	11.090	9.480	8.516	7.873	7.411	7.062	6.788	6.566	6.384	6.299
4.50	27.010	16.130	12.470	10.650	9.562	8.836	8.314	7.919	7.610	7.360	7.154	6.978
5.00	30.010	17.920	13.840	11.820	10.610	9.800	9.219	8.779	8.434	8.155	7.924	7.729
6.00	36.020	21.490	16.600	14.170	12.710	11.740	11.030	10.500	10.090	9.751	9.473	9.238
7.00	42.020	25.070	19.350	16.510	14.810	13.670	12.850	12.230	11.750	11.350	11.030	10.750
8.00	48.030	28.650	22.110	18.860	16.910	15.610	14.670	13.960	13.410	12.960	12.580	12.270
9.00	54.030	32.230	24.870	21.210	19.020	17.550	16.500	15.700	15.070	14.560	14.140	13.790
10.00	60.040	35.810	27.630	23.560	21.120	19.490	18.320	17.430	16.730	16.170	15.700	15.310

Source: Land (1975)
Footnote. Notation n = 3(1)19(2)25(3)31(5)36 is shorthand for n from 3 to 19 by unit steps, from 19 to 25 by 2's, from 25 to 31 by 3's, and from 31 to 36 by 5's

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Table 21-5. Land's Factors ($H_{.90}$) for Confidence Bounds on Lognormal Arithmetic Mean for n = 3(1)19(2)25(3)31(5)36

s_y\n	15	16	17	18	19	21	23	25	28	31	36
0.10	1.328	1.325	1.323	1.322	1.320	1.317	1.315	1.313	1.310	1.308	1.306
0.20	1.365	1.361	1.358	1.355	1.353	1.348	1.345	1.342	1.338	1.335	1.332
0.30	1.411	1.406	1.402	1.398	1.394	1.388	1.383	1.379	1.374	1.370	1.364
0.40	1.467	1.460	1.455	1.449	1.444	1.437	1.430	1.425	1.417	1.412	1.404
0.50	1.532	1.524	1.516	1.509	1.503	1.494	1.485	1.478	1.469	1.462	1.452
0.60	1.606	1.596	1.586	1.578	1.570	1.558	1.548	1.539	1.528	1.519	1.507
0.70	1.690	1.766	1.666	1.655	1.646	1.631	1.618	1.607	1.594	1.583	1.568
0.80	1.781	1.765	1.752	1.739	1.728	1.710	1.695	1.682	1.667	1.654	1.636
0.90	1.880	1.861	1.845	1.831	1.819	1.797	1.779	1.764	1.745	1.731	1.710
1.00	1.985	1.963	1.945	1.929	1.914	1.889	1.868	1.851	1.830	1.812	1.789
1.25	2.271	2.242	2.217	2.195	2.174	2.141	2.113	2.089	2.060	2.036	2.005
1.50	2.581	2.544	2.512	2.483	2.458	2.415	2.379	2.349	2.312	2.282	2.242
1.75	2.907	2.862	2.823	2.788	2.757	2.705	2.662	2.625	2.579	2.543	2.494
2.00	3.244	3.191	3.145	3.104	3.069	3.005	2.954	2.911	2.858	2.814	2.758
2.50	3.938	3.870	3.810	3.757	3.710	3.629	3.562	3.506	3.463	3.380	3.305
3.00	4.650	4.565	4.492	4.427	4.369	4.270	4.188	4.119	4.033	3.964	3.872
3.50	5.370	5.271	5.184	5.107	5.039	4.921	4.825	4.743	4.641	4.559	4.450
4.00	6.097	5.983	5.883	5.794	5.715	5.580	5.468	5.374	5.257	5.161	5.036
4.50	6.829	6.699	6.586	6.485	6.396	6.243	6.116	6.009	5.876	5.769	5.626
5.00	7.563	7.418	7.292	7.179	7.080	6.909	6.767	6.648	6.500	6.379	6.219
6.00	9.037	8.862	8.710	8.575	8.454	8.248	8.076	-7.933	7.753	7.607	7.415
7.00	10.520	10.310	10.130	9.975	9.833	9.592	9.391	9.222	9.013	8.842	8.616
8.00	12.000	11.770	11.560	11.380	11.220	10.940	10.710	10.520	10.280	10.080	9.821
9.00	13.480	13.220	12.990	12.780	12.600	12.290	12.030	11.810	11.540	11.320	11.030
10.00	14.970	14.680	14.420	14.190	13.990	13.640	13.350	13.110	12.810	12.560	12.240

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Table 21-6. Land's Factors ($H_{.95}$) for Confidence Bounds on Lognormal Arithmetic Mean for *n* = 3(1)19(2)25(3)31(5)36

s_y \ n	3	4	5	6	7	8	9	10	11	12	13	14
0.10	2.750	2.222	2.035	1.942	1.886	1.849	1.822	1.802	1.787	1.775	1.763	1.756
0.20	3.295	2.463	2.198	2.069	1.992	1.943	1.908	1.881	1.860	1.843	1.830	1.818
0.30	4.109	2.777	2.402	2.226	2.125	2.058	2.011	1.977	1.949	1.927	1.909	1.894
0.40	5.220	3.175	2.651	2.415	2.282	2.195	2.134	2.089	2.054	2.026	2.003	1.984
0.50	6.495	3.658	2.947	2.638	2.465	2.354	2.277	2.220	2.176	2.141	2.112	2.088
0.60	7.807	4.209	3.287	2.892	2.673	2.534	2.439	2.368	2.314	2.271	2.235	2.206
0.70	9.120	4.801	3.662	3.173	2.904	2.735	2.618	2.532	2.466	2.414	2.371	2.336
0.80	10.430	5.414	4.062	3.477	3.155	2.952	2.813	2.710	2.632	2.570	2.520	2.479
0.90	11.740	6.038	4.478	3.796	3.420	3.184	3.021	2.902	2.810	2.738	2.679	2.631
1.00	13.050	6.669	4.905	4.127	3.698	3.426	3.239	3.103	2.998	2.915	2.848	2.792
1.25	16.330	8.265	6.001	4.990	4.426	4.069	3.820	3.639	3.500	3.389	3.300	3.226
1.50	19.600	9.874	7.120	5.880	5.184	4.741	4.433	4.207	4.033	3.896	3.784	3.691
1.75	22.870	11.490	8.250	6.786	5.960	5.432	5.065	4.795	4.587	4.422	4.288	4.176
2.00	26.140	13.110	9.387	7.701	6.747	6.135	5.710	5.396	5.154	4.962	4.805	4.675
2.50	32.690	16.350	11.670	9.546	8.339	7.563	7.021	6.621	6.312	6.067	5.866	5.698
3.00	39.230	19.600	13.970	11.400	9.945	9.006	8.350	7.864	7.489	7.191	6.947	6.743
3.50	45.770	22.850	16.270	13.270	11.560	10.460	9.688	9.118	8.677	8.326	8.039	7.799
4.00	52.310	26.110	18.580	15.140	13.180	11.920	11.030	10.380	9.872	9.469	9.140	8.864
4.50	58.850	29.360	20.880	17.010	14.800	13.380	12.380	11.640	11.070	10.620	10.240	9.933
5.00	65.390	32.620	23.190	18.880	16.430	14.840	13.730	12.910	12.270	11.770	11.350	11.010
6.00	78.470	39.130	27.810	22.630	19.680	17.780	16.440	15.450	14.690	14.080	13.580	13.160
7.00	91.550	45.650	32.430	26.390	22.940	20.720	19.160	18.000	17.100	16.390	15.810	15.320
8.00	104.600	52.160	37.060	30.140	26.200	23.660	21.870	20.550	19.530	18.710	18.040	17.480
9.00	117.700	58.680	41.680	33.900	29.460	26.600	24.590	23.100	21.950	21.030	20.280	19.650
10.00	130.800	65.200	46.310	37.660	32.730	29.540	27.310	25.660	24.380	23.350	22.510	21.820

Source: Land (1975)
Footnote. Notation n = 3(1)19(2)25(3)31(5)36 is shorthand for n from 3 to 19 by unit steps, from 19 to 25 by 2's, from 25 to 31 by 3's, and from 31 to 36 by 5's

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Table 21-6. Land's Factors ($H_{.95}$) for Confidence Bounds on Lognormal Arithmetic Mean for n = 3(1)19(2)25(3)31(5)36

$s_y \backslash n$	15	16	17	18	19	21	23	25	28	31	36
0.10	1.749	1.743	1.738	1.733	1.729	1.722	1.716	1.711	1.706	1.701	1.695
0.20	1.809	1.800	1.793	1.787	1.781	1.771	1.763	1.756	1.749	1.742	1.734
0.30	1.882	1.871	1.861	1.853	1.845	1.833	1.822	1.813	1.802	1.793	1.783
0.40	1.968	1.954	1.942	1.931	1.921	1.905	1.892	1.881	1.867	1.856	1.841
0.50	2.068	2.050	2.035	2.021	2.009	1.989	1.973	1.959	1.942	1.928	1.910
0.60	2.181	2.160	2.141	2.124	2.110	2.085	2.065	2.048	2.027	2.010	1.988
0.70	2.306	2.280	2.258	2.238	2.221	2.191	2.167	2.147	2.122	2.102	2.075
0.80	2.443	2.412	2.386	2.362	2.342	2.307	2.279	2.255	2.225	2.202	2.171
0.90	2.589	2.554	2.523	2.496	2.472	2.432	2.399	2.371	2.337	2.310	2.273
1.00	2.744	2.704	2.669	2.638	2.611	2.564	2.526	2.495	2.456	2.423	2.383
1.25	3.163	3.109	3.062	3.021	2.984	2.923	2.873	2.830	2.779	2.737	2.682
1.50	3.612	3.544	3.485	3.434	3.388	3.311	3.248	3.195	3.130	3.077	3.008
1.75	4.081	4.000	3.929	3.867	3.812	3.719	3.643	3.579	3.501	3.437	3.355
2.00	4.564	4.470	4.387	4.314	4.251	4.141	4.052	3.977	3.886	3.812	3.715
2.50	5.557	5.435	5.328	5.236	5.153	5.013	4.898	4.802	4.683	4.588	4.463
3.00	6.570	6.422	6.293	6.179	6.078	5.907	5.766	5.649	5.504	5.388	5.234
3.50	7.596	7.422	7.269	7.136	7.016	6.815	6.649	6.510	6.340	6.201	6.020
4.00	8.630	8.429	8.254	8.100	7.963	7.731	7.540	7.380	7.184	7.024	6.816
4.50	9.669	9.442	9.244	9.070	8.916	8.652	8.437	8.257	8.034	7.854	7.618
5.00	10.710	10.460	10.240	10.040	9.872	9.579	9.338	9.137	8.889	8.688	8.424
6.00	12.810	12.500	12.230	12.000	11.790	11.440	11.150	10.910	10.610	10.360	10.050
7.00	14.900	14.550	14.240	13.960	13.720	13.310	12.970	12.680	12.330	12.050	11.680
8.00	17.010	16.600	16.240	15.930	15.650	15.180	14.790	14.470	14.060	13.740	13.310
9.00	19.110	18.650	18.250	17.900	17.590	17.050	16.620	16.250	15.800	15.430	14.950
10.00	21.220	20.710	20.260	19.870	19.520	18.930	18.440	18.040	17.530	12.560	16.590

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Table 21-7. Land's Factors ($H_{.975}$) for Confidence Bounds on Lognormal Arithmetic Mean for *n* = 3(1)19(2)25(3)31(5)36

s_y \ n	3	4	5	6	7	8	9	10	11	12	13	14
0.10	4.367	3.100	2.703	2.513	2.403	2.330	2.879	2.242	2.212	2.190	2.169	2.155
0.20	5.849	3.571	2.987	2.723	2.573	2.476	2.409	2.359	2.321	2.291	2.265	2.245
0.30	8.166	4.210	3.348	2.982	2.781	2.653	2.565	2.501	2.451	2.411	2.380	2.353
0.40	10.860	5.031	3.794	3.296	3.030	2.864	2.750	2.667	2.604	2.554	2.514	2.480
0.50	13.590	5.989	4.322	3.664	3.319	3.107	2.963	2.859	2.780	2.718	2.668	2.626
0.60	16.310	7.019	4.914	4.081	3.647	3.382	3.204	3.076	2.979	2.903	2.842	2.791
0.70	19.040	8.083	5.548	4.534	4.005	3.684	3.469	3.314	3.198	3.106	3.033	2.973
0.80	21.760	9.164	6.208	5.014	4.389	4.009	3.754	3.572	3.434	3.327	3.240	3.169
0.90	24.490	10.250	6.885	5.512	4.791	4.351	4.056	3.844	3.685	3.561	3.461	3.379
1.00	27.210	11.350	7.572	6.024	5.206	4.707	4.371	4.130	3.949	3.807	3.693	3.599
1.25	34.020	14.110	9.320	7.339	6.285	5.636	5.199	4.884	4.647	4.461	4.312	4.189
1.50	40.830	16.880	11.090	8.684	7.397	6.602	6.064	5.676	5.383	5.153	4.968	4.815
1.75	47.630	19.650	12.880	10.050	8.528	7.588	6.951	6.490	6.142	5.869	5.648	5.466
2.00	54.440	22.430	14.670	11.420	9.671	8.588	7.853	7.320	6.916	6.599	6.344	6.133
2.50	68.050	28.000	18.270	14.180	11.980	10.610	9.681	9.006	8.493	8.091	7.765	7.497
3.00	81.660	33.580	21.870	16.960	14.300	12.650	11.530	10.710	10.090	9.605	9.210	8.884
3.50	95.270	39.160	25.490	19.740	16.640	14.710	13.390	12.430	11.700	11.130	10.670	10.290
4.00	108.900	44.740	29.110	22.530	18.980	16.770	15.260	14.160	13.320	12.670	12.140	11.700
4.50	122.500	50.320	32.730	25.320	21.320	18.830	17.130	15.890	14.950	14.210	13.610	13.110
5.00	136.100	55.900	36.350	28.120	23.670	20.890	19.000	17.630	16.580	15.750	15.090	14.540
6.00	163.300	67.070	43.590	33.710	28.370	25.030	22.760	21.100	19.850	18.850	18.050	17.390
7.00	190.600	78.240	50.840	39.310	33.070	29.180	26.520	24.590	23.120	21.960	21.020	20.250
8.00	217.800	89.410	58.100	44.910	37.770	33.330	30.280	28.080	26.390	25.070	23.990	23.110
9.00	245.000	100.600	65.350	50.510	42.480	37.470	34.050	31.570	29.670	28.180	26.970	25.970
10.00	272.200	111.800	72.600	56.110	47.190	41.620	37.820	35.060	32.950	31.290	29.950	28.840

Source: Land (1975)
Footnote. Notation n = 3(1)19(2)25(3)31(5)36 is shorthand for n from 3 to 19 by unit steps, from 19 to 25 by 2's, from 25 to 31 by 3's, and from 31 to 36 by 5's

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Table 21-7. Land's Factors ($H_{.975}$) for Confidence Bounds on Lognormal Arithmetic Mean for n = 3(1)19(2)25(3)31(5)36

s_y\n	15	16	17	18	19	21	23	25	28	31	36
0.10	2.141	2.130	2.120	2.112	2.104	2.091	2.081	2.072	2.062	2.053	2.043
0.20	2.227	2.212	2.199	2.188	2.178	2.161	2.147	2.135	2.121	2.110	2.096
0.30	2.331	2.311	2.295	2.280	2.267	2.246	2.228	2.213	2.194	2.180	2.161
0.40	2.452	2.428	2.407	2.388	2.372	2.345	2.323	2.305	2.281	2.263	2.239
0.50	2.592	2.562	2.536	2.513	2.493	2.460	2.432	2.409	2.381	2.359	2.329
0.60	2.749	2.712	2.681	2.653	2.630	2.588	2.555	2.528	2.494	2.467	2.432
0.70	2.922	2.879	2.841	2.808	2.780	2.731	2.692	2.659	2.619	2.587	2.545
0.80	3.109	3.059	3.015	2.976	2.943	2.886	2.840	2.802	2.755	2.717	2.668
0.90	3.310	3.251	3.200	3.157	3.117	3.052	2.999	2.955	2.901	2.858	2.801
1.00	3.521	3.454	3.397	3.347	3.302	3.227	3.167	3.116	3.056	3.007	2.943
1.25	4.086	3.998	3.922	3.856	3.798	3.700	3.621	3.555	3.474	3.410	3.327
1.50	4.688	4.579	4.485	4.402	4.330	4.209	4.109	4.027	3.927	3.847	3.743
1.75	5.314	5.183	5.070	4.972	4.887	4.740	4.622	4.524	4.404	4.307	4.183
2.00	5.956	5.804	5.674	5.559	5.461	5.289	5.151	5.037	4.897	4.784	4.639
2.50	7.271	7.078	6.911	6.765	6.636	6.419	6.243	6.096	5.916	5.772	5.585
3.00	8.610	8.376	8.174	7.996	7.840	7.576	7.361	7.182	6.963	6.787	6.559
3.50	9.964	9.689	9.451	9.242	9.058	8.748	8.495	8.284	8.027	7.820	7.551
4.00	11.330	11.010	10.740	10.500	10.290	9.930	9.639	9.397	9.101	8.863	8.554
4.50	12.700	12.340	12.030	11.760	11.520	11.120	10.790	10.520	10.180	9.913	9.564
5.00	14.070	13.670	13.330	13.030	12.760	12.310	11.950	11.640	11.270	10.970	10.580
6.00	16.830	16.350	15.930	15.570	15.250	14.710	14.270	13.900	13.450	13.090	12.620
7.00	19.590	19.030	18.550	18.130	17.750	17.120	16.600	16.170	15.650	15.220	14.670
8.00	22.360	21.720	21.170	20.680	20.250	19.530	18.940	18.450	17.840	17.360	16.730
9.00	25.130	24.410	23.790	23.240	22.760	21.940	21.280	20.720	20.050	19.500	18.790
10.00	27.900	27.100	26.410	25.800	25.270	24.360	23.620	23.000	22.250	17.130	20.850

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Table 21-8. Land's Factors ($H_{.99}$) for Confidence Bounds on Lognormal Arithmetic Mean for *n* = 3(1)19(2)25(3)31(5)36

s_y\n	3	4	5	6	7	8	9	10	11	12	13	14
0.10	8.328	4.665	3.760	3.360	3.137	2.994	2.897	2.825	2.770	2.727	2.691	2.663
0.20	13.940	5.768	4.310	3.731	3.422	3.231	3.101	3.006	2.935	2.878	2.833	2.796
0.30	20.880	7.336	5.035	4.199	3.775	3.519	3.348	3.225	3.132	3.060	3.002	2.955
0.40	27.850	9.244	5.934	4.771	4.199	3.862	3.640	3.482	3.364	3.273	3.200	3.140
0.50	34.820	11.290	6.966	5.434	4.691	4.258	3.976	3.778	3.631	3.517	3.426	3.353
0.60	41.780	13.390	8.077	6.167	5.240	4.702	4.353	4.109	3.929	3.790	3.680	3.590
0.70	48.750	15.520	9.231	6.947	5.831	5.183	4.764	4.471	4.255	4.089	3.958	3.851
0.80	55.710	17.650	10.410	7.757	6.452	5.693	5.201	4.858	4.604	4.110	4.256	4.131
0.90	62.580	19.800	11.600	8.856	7.095	6.225	5.659	5.264	4.973	4.750	4.572	4.428
1.00	69.650	21.950	12.810	9.430	7.753	6.772	6.133	5.686	5.357	5.103	4.903	4.740
1.25	87.060	27.350	15.850	11.580	9.442	8.186	7.365	6.789	6.363	6.036	5.775	5.564
1.50	104.500	32.770	18.920	13.760	11.170	9.641	8.640	7.936	7.414	7.102	6.693	6.432
1.75	121.900	38.190	22.010	15.950	12.920	11.120	9.940	9.109	8.492	8.016	7.638	7.330
2.00	139.300	43.610	25.100	18.160	14.680	12.610	11.260	10.300	9.587	9.039	8.602	8.245
2.50	174.100	54.470	31.290	22.600	18.220	15.630	13.920	12.710	11.810	11.120	10.560	10.110
3.00	208.900	65.340	37.500	27.050	21.790	18.660	16.600	15.140	14.060	13.220	12.540	12.010
3.50	243.800	76.210	43.720	31.520	25.360	21.710	19.300	17.590	16.320	15.340	14.560	13.910
4.00	278.600	87.080	49.940	35.980	28.940	24.760	22.000	20.050	18.590	17.470	16.570	15.840
4.50	313.400	97.960	56.160	40.450	32.530	27.820	24.710	22.510	20.870	19.600	18.590	17.760
5.00	348.200	108.800	62.380	44.930	36.120	30.880	27.420	24.980	23.150	21.740	20.620	19.700
6.00	417.900	130.600	74.840	53.880	43.300	37.010	32.860	29.920	27.730	26.030	24.680	23.570
7.00	487.500	152.300	87.290	62.840	50.490	43.140	38.300	34.870	32.310	30.330	28.750	27.450
8.00	557.200	174.100	99.750	71.790	57.680	49.280	43.740	39.820	36.890	34.630	32.820	31.340
9.00	626.900	195.900	112.200	80.750	64.870	55.430	49.190	44.770	41.480	38.930	36.900	35.230
10.00	696.500	217.600	124.700	89.720	72.070	61.570	54.640	49.730	46.070	43.240	40.980	39.130

Source: Land (1975)
Footnote. Notation n = 3(1)19(2)25(3)31(5)36 is shorthand for n from 3 to 19 by unit steps, from 19 to 25 by 2's, from 25 to 31 by 3's, and from 31 to 36 by 5's

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Table 21-8. Land's Factors ($H_{.99}$) for Confidence Bounds on Lognormal Arithmetic Mean for n = 3(1)19(2)25(3)31(5)36

s_y\n	15	16	17	18	19	21	23	25	28	31	36
0.10	2.638	2.618	2.600	2.584	2.571	2.548	2.529	2.514	2.495	2.480	2.462
0.20	2.764	2.737	2.714	2.694	2.676	2.647	2.623	2.602	2.579	2.559	2.534
0.30	2.914	2.880	2.851	2.826	2.803	2.767	2.735	2.710	2.679	2.655	2.623
0.40	3.090	3.047	3.011	2.979	2.951	2.904	2.867	2.836	2.798	2.767	2.729
0.50	3.291	3.239	3.194	3.155	3.121	3.064	3.017	2.979	2.933	2.896	2.849
0.60	3.515	3.453	3.398	3.351	3.311	3.242	3.186	3.141	3.085	3.041	2.984
0.70	3.762	3.687	3.623	3.567	3.519	3.438	3.372	3.318	3.253	3.200	3.134
0.80	4.027	3.940	3.865	3.800	3.744	3.649	3.573	3.510	3.434	3.373	3.296
0.90	4.309	4.209	4.123	4.049	3.983	3.875	3.787	3.716	3.628	3.559	3.471
1.00	4.605	4.491	4.394	4.309	4.235	4.112	4.013	3.931	3.833	3.755	3.655
1.25	5.388	5.240	5.114	5.004	4.908	4.749	4.620	4.513	4.385	4.283	4.143
1.50	6.217	6.034	5.878	5.743	5.625	5.426	5.267	5.136	4.978	4.852	4.691
1.75	7.074	6.857	6.671	6.510	6.369	6.134	5.944	5.788	5.599	5.449	5.256
2.00	7.949	7.699	7.483	7.297	7.134	6.861	6.641	6.460	6.241	6.066	5.842
2.50	9.735	9.415	9.145	8.907	8.700	8.353	8.073	7.842	7.562	7.339	7.052
3.00	11.550	11.170	10.840	10.550	10.300	9.875	9.536	9.256	8.916	8.645	8.269
3.50	13.380	12.930	12.540	12.210	11.910	11.420	11.020	10.690	10.290	9.970	9.560
4.00	15.230	14.710	14.260	13.880	13.540	12.970	12.510	12.130	11.670	11.310	10.840
4.50	17.070	16.490	15.990	15.550	15.170	14.350	14.010	13.590	13.070	12.660	12.120
5.00	18.930	18.280	17.720	17.240	16.810	16.100	15.520	15.050	14.470	14.010	13.420
6.00	22.650	21.870	21.190	20.610	20.100	19.240	18.550	17.980	17.280	16.730	16.010
7.00	26.380	25.460	24.680	24.000	23.400	22.390	21.580	20.920	20.100	19.450	18.620
8.00	30.110	29.060	28.170	27.390	26.700	25.550	24.630	23.860	22.930	22.190	21.230
9.00	33.840	32.670	31.660	30.780	30.010	28.720	27.670	26.810	25.760	24.930	23.800
10.00	37.580	36.280	35.150	34.180	33.320	31.880	30.720	29.770	28.600	21.640	26.470

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Table 21-9. Factors (τ) for Parametric Upper Conf. Bounds on Percentiles (P)

	P = 0.80					P = 0.90				
n \ (1−α)	**0.80**	**0.90**	**0.95**	**0.975**	**0.99**	**0.80**	**0.90**	**0.95**	**0.975**	**0.99**
2	3.417	6.987	14.051	28.140	70.376	5.049	10.253	20.581	41.201	103.029
3	2.016	3.039	4.424	6.343	10.111	2.871	4.258	6.155	8.797	13.995
4	1.675	2.295	3.026	3.915	5.417	2.372	3.188	4.162	5.354	7.380
5	1.514	1.976	2.483	3.058	3.958	2.145	2.742	3.407	4.166	5.362
6	1.417	1.795	2.191	2.621	3.262	2.012	2.494	3.006	3.568	4.411
7	1.352	1.676	2.005	2.353	2.854	1.923	2.333	2.755	3.206	3.859
8	1.304	1.590	1.875	2.170	2.584	1.859	2.219	2.582	2.960	3.497
9	1.266	1.525	1.779	2.036	2.391	1.809	2.133	2.454	2.783	3.240
10	1.237	1.474	1.703	1.933	2.246	1.770	2.066	2.355	2.647	3.048
11	1.212	1.433	1.643	1.851	2.131	1.738	2.011	2.275	2.540	2.898
12	1.192	1.398	1.593	1.784	2.039	1.711	1.966	2.210	2.452	2.777
13	1.174	1.368	1.551	1.728	1.963	1.689	1.928	2.155	2.379	2.677
14	1.159	1.343	1.514	1.681	1.898	1.669	1.895	2.109	2.317	2.593
15	1.145	1.321	1.483	1.639	1.843	1.652	1.867	2.068	2.264	2.521
16	1.133	1.301	1.455	1.603	1.795	1.637	1.842	2.033	2.218	2.459
17	1.123	1.284	1.431	1.572	1.753	1.623	1.819	2.002	2.177	2.405
18	1.113	1.268	1.409	1.543	1.716	1.611	1.800	1.974	2.141	2.357
19	1.104	1.254	1.389	1.518	1.682	1.600	1.782	1.949	2.108	2.314
20	1.096	1.241	1.371	1.495	1.652	1.590	1.765	1.926	2.079	2.276
21	1.089	1.229	1.355	1.474	1.625	1.581	1.750	1.905	2.053	2.241
22	1.082	1.218	1.340	1.455	1.600	1.572	1.737	1.886	2.028	2.209
23	1.076	1.208	1.326	1.437	1.577	1.564	1.724	1.869	2.006	2.180
24	1.070	1.199	1.313	1.421	1.556	1.557	1.712	1.853	1.985	2.154
25	1.065	1.190	1.302	1.406	1.537	1.550	1.702	1.838	1.966	2.129
26	1.060	1.182	1.291	1.392	1.519	1.544	1.691	1.824	1.949	2.106
27	1.055	1.174	1.280	1.379	1.502	1.538	1.682	1.811	1.932	2.085
28	1.051	1.167	1.271	1.367	1.486	1.533	1.673	1.799	1.917	2.065
29	1.047	1.160	1.262	1.355	1.472	1.528	1.665	1.788	1.903	2.047
30	1.043	1.154	1.253	1.344	1.458	1.523	1.657	1.777	1.889	2.030
31	1.039	1.148	1.245	1.334	1.445	1.518	1.650	1.767	1.877	2.014
32	1.035	1.143	1.237	1.325	1.433	1.514	1.643	1.758	1.865	1.998
33	1.032	1.137	1.230	1.316	1.422	1.510	1.636	1.749	1.853	1.984
34	1.029	1.132	1.223	1.307	1.411	1.506	1.630	1.740	1.843	1.970
35	1.026	1.127	1.217	1.299	1.400	1.502	1.624	1.732	1.833	1.957
36	1.023	1.123	1.211	1.291	1.391	1.498	1.618	1.725	1.823	1.945
37	1.020	1.118	1.205	1.284	1.381	1.495	1.613	1.717	1.814	1.934
38	1.017	1.114	1.199	1.277	1.372	1.492	1.608	1.710	1.805	1.922
39	1.015	1.110	1.194	1.270	1.364	1.489	1.603	1.704	1.797	1.912
40	1.013	1.106	1.188	1.263	1.356	1.486	1.598	1.697	1.789	1.902
41	1.010	1.103	1.183	1.257	1.348	1.483	1.593	1.691	1.781	1.892
42	1.008	1.099	1.179	1.251	1.341	1.480	1.589	1.685	1.774	1.883
43	1.006	1.096	1.174	1.246	1.333	1.477	1.585	1.680	1.767	1.874
44	1.004	1.092	1.170	1.240	1.327	1.475	1.581	1.674	1.760	1.865
45	1.002	1.089	1.165	1.235	1.320	1.472	1.577	1.669	1.753	1.857
46	1.000	1.086	1.161	1.230	1.314	1.470	1.573	1.664	1.747	1.849
47	0.998	1.083	1.157	1.225	1.308	1.468	1.570	1.659	1.741	1.842
48	0.996	1.080	1.154	1.220	1.302	1.465	1.566	1.654	1.735	1.835
49	0.994	1.078	1.150	1.216	1.296	1.463	1.563	1.650	1.730	1.828
50	0.993	1.075	1.146	1.211	1.291	1.461	1.559	1.646	1.724	1.821
55	0.985	1.063	1.130	1.191	1.266	1.452	1.545	1.626	1.700	1.790
60	0.978	1.052	1.116	1.174	1.245	1.444	1.532	1.609	1.679	1.764
65	0.972	1.043	1.104	1.159	1.226	1.437	1.521	1.594	1.661	1.741
70	0.967	1.035	1.094	1.146	1.210	1.430	1.511	1.581	1.645	1.722
75	0.963	1.028	1.084	1.135	1.196	1.425	1.503	1.570	1.630	1.704
80	0.959	1.022	1.076	1.124	1.183	1.420	1.495	1.559	1.618	1.688
85	0.955	1.016	1.068	1.115	1.171	1.415	1.488	1.550	1.606	1.674
90	0.951	1.011	1.061	1.106	1.161	1.411	1.481	1.542	1.596	1.661
95	0.948	1.006	1.055	1.098	1.151	1.408	1.475	1.534	1.586	1.650
100	0.945	1.001	1.049	1.091	1.142	1.404	1.470	1.527	1.578	1.639

Source: Hahn & Meeker (1991)

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Table 21-9. Factors (τ) for Parametric Upper Conf. Bounds on Percentiles (P)

	P = 0.95					P = 0.99				
n \ (1−α)	**0.80**	**0.90**	**0.95**	**0.975**	**0.99**	**0.80**	**0.90**	**0.95**	**0.975**	**0.99**
2	6.464	13.090	26.260	52.559	131.426	9.156	18.500	37.094	74.234	185.617
3	3.604	5.311	7.656	10.927	17.370	5.010	7.340	10.553	15.043	23.896
4	2.968	3.957	5.144	6.602	9.083	4.110	5.438	7.042	9.018	12.387
5	2.683	3.400	4.203	5.124	6.578	3.711	4.666	5.741	6.980	8.939
6	2.517	3.092	3.708	4.385	5.406	3.482	4.243	5.062	5.967	7.335
7	2.407	2.894	3.399	3.940	4.728	3.331	3.972	4.642	5.361	6.412
8	2.328	2.754	3.187	3.640	4.285	3.224	3.783	4.354	4.954	5.812
9	2.268	2.650	3.031	3.424	3.972	3.142	3.641	4.143	4.662	5.389
10	2.220	2.568	2.911	3.259	3.738	3.078	3.532	3.981	4.440	5.074
11	2.182	2.503	2.815	3.129	3.556	3.026	3.443	3.852	4.265	4.829
12	2.149	2.448	2.736	3.023	3.410	2.982	3.371	3.747	4.124	4.633
13	2.122	2.402	2.671	2.936	3.290	2.946	3.309	3.659	4.006	4.472
14	2.098	2.363	2.614	2.861	3.189	2.914	3.257	3.585	3.907	4.337
15	2.078	2.329	2.566	2.797	3.102	2.887	3.212	3.520	3.822	4.222
16	2.059	2.299	2.524	2.742	3.028	2.863	3.172	3.464	3.749	4.123
17	2.043	2.272	2.486	2.693	2.963	2.841	3.137	3.414	3.684	4.037
18	2.029	2.249	2.453	2.650	2.905	2.822	3.105	3.370	3.627	3.960
19	2.016	2.227	2.423	2.611	2.854	2.804	3.077	3.331	3.575	3.892
20	2.004	2.208	2.396	2.576	2.808	2.789	3.052	3.295	3.529	3.832
21	1.993	2.190	2.371	2.544	2.766	2.774	3.028	3.263	3.487	3.777
22	1.983	2.174	2.349	2.515	2.729	2.761	3.007	3.233	3.449	3.727
23	1.973	2.159	2.328	2.489	2.694	2.749	2.987	3.206	3.414	3.681
24	1.965	2.145	2.309	2.465	2.662	2.738	2.969	3.181	3.382	3.640
25	1.957	2.132	2.292	2.442	2.633	2.727	2.952	3.158	3.353	3.601
26	1.949	2.120	2.275	2.421	2.606	2.718	2.937	3.136	3.325	3.566
27	1.943	2.109	2.260	2.402	2.581	2.708	2.922	3.116	3.300	3.533
28	1.936	2.099	2.246	2.384	2.558	2.700	2.909	3.098	3.276	3.502
29	1.930	2.089	2.232	2.367	2.536	2.692	2.896	3.080	3.254	3.473
30	1.924	2.080	2.220	2.351	2.515	2.684	2.884	3.064	3.233	3.447
31	1.919	2.071	2.208	2.336	2.496	2.677	2.872	3.048	3.213	3.421
32	1.914	2.063	2.197	2.322	2.478	2.671	2.862	3.034	3.195	3.398
33	1.909	2.055	2.186	2.308	2.461	2.664	2.852	3.020	3.178	3.375
34	1.904	2.048	2.176	2.296	2.445	2.658	2.842	3.007	3.161	3.354
35	1.900	2.041	2.167	2.284	2.430	2.652	2.833	2.995	3.145	3.334
36	1.895	2.034	2.158	2.272	2.415	2.647	2.824	2.983	3.131	3.315
37	1.891	2.028	2.149	2.262	2.402	2.642	2.816	2.972	3.116	3.297
38	1.888	2.022	2.141	2.251	2.389	2.637	2.808	2.961	3.103	3.280
39	1.884	2.016	2.133	2.241	2.376	2.632	2.800	2.951	3.090	3.264
40	1.880	2.010	2.125	2.232	2.364	2.627	2.793	2.941	3.078	3.249
41	1.877	2.005	2.118	2.223	2.353	2.623	2.786	2.932	3.066	3.234
42	1.874	2.000	2.111	2.214	2.342	2.619	2.780	2.923	3.055	3.220
43	1.871	1.995	2.105	2.206	2.331	2.615	2.773	2.914	3.044	3.206
44	1.868	1.990	2.098	2.198	2.321	2.611	2.767	2.906	3.034	3.193
45	1.865	1.986	2.092	2.190	2.312	2.607	2.761	2.898	3.024	3.180
46	1.862	1.981	2.086	2.183	2.303	2.604	2.756	2.890	3.014	3.168
47	1.859	1.977	2.081	2.176	2.294	2.600	2.750	2.883	3.005	3.157
48	1.857	1.973	2.075	2.169	2.285	2.597	2.745	2.876	2.996	3.146
49	1.854	1.969	2.070	2.163	2.277	2.594	2.740	2.869	2.988	3.135
50	1.852	1.965	2.065	2.156	2.269	2.590	2.735	2.862	2.980	3.125
55	1.841	1.948	2.042	2.128	2.233	2.576	2.713	2.833	2.943	3.078
60	1.832	1.933	2.022	2.103	2.202	2.564	2.694	2.807	2.911	3.038
65	1.823	1.920	2.005	2.082	2.176	2.554	2.677	2.785	2.883	3.004
70	1.816	1.909	1.990	2.063	2.153	2.544	2.662	2.765	2.859	2.974
75	1.810	1.899	1.976	2.047	2.132	2.536	2.649	2.748	2.838	2.947
80	1.804	1.890	1.964	2.032	2.114	2.528	2.638	2.733	2.819	2.924
85	1.799	1.882	1.954	2.019	2.097	2.522	2.627	2.719	2.802	2.902
90	1.794	1.874	1.944	2.006	2.082	2.516	2.618	2.706	2.786	2.883
95	1.790	1.867	1.935	1.995	2.069	2.510	2.609	2.695	2.772	2.866
100	1.786	1.861	1.927	1.985	2.056	2.505	2.601	2.684	2.759	2.850

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Table 21-10. Factors (τ) for Parametric Lower Conf. Bounds on Percentiles (P)

	P = 0.80					P = 0.90				
n\(1−α)	**0.80**	**0.90**	**0.95**	**0.975**	**0.99**	**0.80**	**0.90**	**0.95**	**0.975**	**0.99**
2	0.288	-0.084	-0.521	-1.229	-3.204	0.737	0.403	0.138	-0.143	-0.707
3	0.377	0.111	-0.127	-0.380	-0.792	0.799	0.535	0.334	0.159	-0.072
4	0.432	0.209	0.021	-0.158	-0.405	0.847	0.617	0.444	0.298	0.123
5	0.470	0.272	0.110	-0.038	-0.227	0.883	0.675	0.519	0.389	0.238
6	0.499	0.319	0.173	0.043	-0.117	0.911	0.719	0.575	0.455	0.319
7	0.522	0.355	0.220	0.103	-0.040	0.933	0.755	0.619	0.507	0.381
8	0.540	0.384	0.258	0.150	0.020	0.952	0.783	0.655	0.550	0.431
9	0.556	0.408	0.290	0.188	0.067	0.968	0.808	0.686	0.585	0.472
10	0.569	0.428	0.316	0.220	0.107	0.981	0.828	0.712	0.615	0.508
11	0.580	0.446	0.339	0.247	0.140	0.993	0.847	0.734	0.642	0.538
12	0.591	0.461	0.359	0.271	0.169	1.004	0.863	0.754	0.665	0.565
13	0.599	0.475	0.376	0.292	0.194	1.013	0.877	0.772	0.685	0.589
14	0.608	0.487	0.392	0.310	0.216	1.022	0.890	0.788	0.704	0.610
15	0.615	0.498	0.406	0.327	0.236	1.029	0.901	0.802	0.721	0.629
16	0.621	0.508	0.419	0.342	0.254	1.036	0.912	0.815	0.736	0.647
17	0.627	0.518	0.430	0.356	0.271	1.043	0.921	0.827	0.750	0.663
18	0.633	0.526	0.441	0.369	0.286	1.049	0.930	0.839	0.763	0.678
19	0.638	0.534	0.451	0.380	0.299	1.054	0.939	0.849	0.775	0.692
20	0.643	0.541	0.460	0.391	0.312	1.059	0.946	0.858	0.786	0.705
21	0.647	0.548	0.468	0.401	0.324	1.064	0.953	0.867	0.796	0.716
22	0.651	0.554	0.476	0.410	0.335	1.068	0.960	0.876	0.806	0.728
23	0.655	0.560	0.484	0.419	0.345	1.073	0.966	0.884	0.815	0.738
24	0.659	0.565	0.491	0.427	0.355	1.076	0.972	0.891	0.823	0.748
25	0.662	0.570	0.497	0.435	0.364	1.080	0.978	0.898	0.831	0.757
26	0.665	0.575	0.503	0.442	0.373	1.084	0.983	0.904	0.839	0.766
27	0.669	0.580	0.509	0.449	0.381	1.087	0.988	0.911	0.846	0.774
28	0.671	0.584	0.515	0.456	0.388	1.090	0.993	0.917	0.853	0.782
29	0.674	0.588	0.520	0.462	0.396	1.093	0.997	0.922	0.860	0.790
30	0.677	0.592	0.525	0.468	0.403	1.096	1.002	0.928	0.866	0.797
31	0.679	0.596	0.530	0.473	0.409	1.099	1.006	0.933	0.872	0.804
32	0.682	0.600	0.534	0.479	0.416	1.101	1.010	0.938	0.878	0.810
33	0.684	0.603	0.539	0.484	0.422	1.104	1.013	0.942	0.883	0.817
34	0.686	0.606	0.543	0.489	0.427	1.106	1.017	0.947	0.888	0.823
35	0.688	0.610	0.547	0.494	0.433	1.108	1.020	0.951	0.893	0.828
36	0.690	0.613	0.551	0.498	0.438	1.111	1.024	0.955	0.898	0.834
37	0.692	0.616	0.554	0.502	0.443	1.113	1.027	0.959	0.903	0.839
38	0.694	0.618	0.558	0.507	0.448	1.115	1.030	0.963	0.907	0.844
39	0.696	0.621	0.561	0.511	0.453	1.117	1.033	0.967	0.911	0.849
40	0.698	0.624	0.565	0.514	0.457	1.119	1.036	0.970	0.916	0.854
41	0.699	0.626	0.568	0.518	0.462	1.120	1.038	0.974	0.920	0.859
42	0.701	0.629	0.571	0.522	0.466	1.122	1.041	0.977	0.923	0.863
43	0.702	0.631	0.574	0.525	0.470	1.124	1.044	0.980	0.927	0.867
44	0.704	0.633	0.577	0.529	0.474	1.126	1.046	0.983	0.931	0.872
45	0.705	0.635	0.579	0.532	0.478	1.127	1.048	0.986	0.934	0.876
46	0.707	0.637	0.582	0.535	0.481	1.129	1.051	0.989	0.938	0.880
47	0.708	0.640	0.585	0.538	0.485	1.130	1.053	0.992	0.941	0.883
48	0.709	0.642	0.587	0.541	0.488	1.132	1.055	0.995	0.944	0.887
49	0.711	0.643	0.590	0.544	0.492	1.133	1.057	0.997	0.947	0.891
50	0.712	0.645	0.592	0.547	0.495	1.134	1.059	1.000	0.950	0.894
55	0.718	0.654	0.603	0.559	0.510	1.141	1.069	1.012	0.964	0.910
60	0.723	0.661	0.612	0.571	0.523	1.146	1.077	1.022	0.976	0.924
65	0.727	0.668	0.621	0.581	0.535	1.151	1.085	1.032	0.987	0.937
70	0.731	0.674	0.628	0.589	0.545	1.156	1.091	1.040	0.997	0.948
75	0.735	0.679	0.635	0.597	0.554	1.160	1.097	1.048	1.006	0.958
80	0.738	0.684	0.641	0.605	0.563	1.163	1.103	1.054	1.014	0.968
85	0.741	0.689	0.647	0.611	0.571	1.167	1.108	1.061	1.021	0.976
90	0.743	0.693	0.652	0.618	0.578	1.170	1.112	1.066	1.028	0.984
95	0.746	0.697	0.657	0.623	0.584	1.172	1.116	1.072	1.034	0.991
100	0.748	0.700	0.661	0.628	0.591	1.175	1.120	1.077	1.040	0.998

Source: Adapted from Hahn & Meeker (1991)

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Table 21-10. Factors (τ) for Parametric Lower Conf. Bounds on Percentiles (P)

	P = 0.95					P = 0.99				
n \ (1−α)	**0.80**	**0.90**	**0.95**	**0.975**	**0.99**	**0.80**	**0.90**	**0.95**	**0.975**	**0.99**
2	1.077	0.717	0.475	0.273	0.000	1.672	1.225	0.954	0.761	0.564
3	1.126	0.840	0.639	0.478	0.295	1.710	1.361	1.130	0.958	0.782
4	1.172	0.922	0.743	0.601	0.443	1.760	1.455	1.246	1.088	0.924
5	1.209	0.982	0.818	0.687	0.543	1.801	1.525	1.331	1.182	1.027
6	1.238	1.028	0.875	0.752	0.618	1.834	1.578	1.396	1.256	1.108
7	1.261	1.065	0.920	0.804	0.678	1.862	1.622	1.449	1.315	1.173
8	1.281	1.096	0.958	0.847	0.727	1.885	1.658	1.493	1.364	1.227
9	1.298	1.122	0.990	0.884	0.768	1.904	1.688	1.530	1.406	1.273
10	1.313	1.144	1.017	0.915	0.804	1.922	1.715	1.563	1.442	1.314
11	1.325	1.163	1.041	0.943	0.835	1.937	1.738	1.591	1.474	1.349
12	1.337	1.180	1.062	0.967	0.862	1.950	1.758	1.616	1.502	1.381
13	1.347	1.196	1.081	0.989	0.887	1.962	1.776	1.638	1.528	1.409
14	1.356	1.210	1.098	1.008	0.909	1.973	1.793	1.658	1.551	1.434
15	1.364	1.222	1.114	1.026	0.929	1.983	1.808	1.677	1.572	1.458
16	1.372	1.234	1.128	1.042	0.948	1.992	1.822	1.694	1.591	1.479
17	1.379	1.244	1.141	1.057	0.965	2.000	1.834	1.709	1.608	1.499
18	1.385	1.254	1.153	1.071	0.980	2.008	1.846	1.724	1.625	1.517
19	1.391	1.263	1.164	1.084	0.995	2.015	1.857	1.737	1.640	1.534
20	1.397	1.271	1.175	1.095	1.008	2.022	1.867	1.749	1.654	1.550
21	1.402	1.279	1.184	1.107	1.021	2.028	1.876	1.761	1.667	1.565
22	1.407	1.286	1.193	1.117	1.033	2.034	1.885	1.772	1.680	1.579
23	1.412	1.293	1.202	1.127	1.044	2.039	1.893	1.782	1.691	1.592
24	1.416	1.300	1.210	1.136	1.054	2.045	1.901	1.791	1.702	1.605
25	1.420	1.306	1.217	1.145	1.064	2.049	1.908	1.801	1.713	1.616
26	1.424	1.311	1.225	1.153	1.074	2.054	1.915	1.809	1.723	1.627
27	1.427	1.317	1.231	1.161	1.083	2.058	1.922	1.817	1.732	1.638
28	1.431	1.322	1.238	1.168	1.091	2.063	1.928	1.825	1.741	1.648
29	1.434	1.327	1.244	1.175	1.099	2.067	1.934	1.833	1.749	1.658
30	1.437	1.332	1.250	1.182	1.107	2.070	1.940	1.840	1.757	1.667
31	1.440	1.336	1.255	1.189	1.114	2.074	1.945	1.846	1.765	1.676
32	1.443	1.341	1.261	1.195	1.121	2.078	1.951	1.853	1.773	1.684
33	1.446	1.345	1.266	1.201	1.128	2.081	1.956	1.859	1.780	1.692
34	1.449	1.349	1.271	1.206	1.135	2.084	1.960	1.865	1.787	1.700
35	1.451	1.352	1.276	1.212	1.141	2.087	1.965	1.871	1.793	1.708
36	1.453	1.356	1.280	1.217	1.147	2.090	1.970	1.876	1.799	1.715
37	1.456	1.360	1.284	1.222	1.153	2.093	1.974	1.882	1.806	1.722
38	1.458	1.363	1.289	1.227	1.158	2.096	1.978	1.887	1.811	1.728
39	1.460	1.366	1.293	1.232	1.164	2.098	1.982	1.892	1.817	1.735
40	1.462	1.369	1.297	1.236	1.169	2.101	1.986	1.896	1.823	1.741
41	1.464	1.372	1.300	1.241	1.174	2.103	1.989	1.901	1.828	1.747
42	1.466	1.375	1.304	1.245	1.179	2.106	1.993	1.905	1.833	1.753
43	1.468	1.378	1.308	1.249	1.183	2.108	1.996	1.910	1.838	1.758
44	1.470	1.381	1.311	1.253	1.188	2.110	2.000	1.914	1.843	1.764
45	1.472	1.383	1.314	1.257	1.192	2.112	2.003	1.918	1.847	1.769
46	1.473	1.386	1.317	1.260	1.197	2.114	2.006	1.922	1.852	1.774
47	1.475	1.389	1.321	1.264	1.201	2.116	2.009	1.925	1.856	1.779
48	1.477	1.391	1.324	1.267	1.205	2.118	2.012	1.929	1.860	1.784
49	1.478	1.393	1.327	1.271	1.209	2.120	2.015	1.933	1.865	1.789
50	1.480	1.396	1.329	1.274	1.212	2.122	2.018	1.936	1.869	1.793
55	1.487	1.406	1.343	1.289	1.230	2.131	2.031	1.952	1.887	1.815
60	1.493	1.415	1.354	1.303	1.245	2.138	2.042	1.966	1.903	1.833
65	1.498	1.424	1.364	1.315	1.259	2.145	2.052	1.979	1.918	1.850
70	1.503	1.431	1.374	1.326	1.272	2.151	2.061	1.990	1.931	1.865
75	1.508	1.438	1.382	1.335	1.283	2.156	2.069	2.000	1.943	1.879
80	1.512	1.444	1.390	1.344	1.293	2.161	2.077	2.010	1.954	1.891
85	1.515	1.449	1.397	1.352	1.302	2.166	2.083	2.018	1.964	1.903
90	1.519	1.454	1.403	1.360	1.311	2.170	2.090	2.026	1.973	1.913
95	1.522	1.459	1.409	1.367	1.319	2.174	2.095	2.033	1.981	1.923
100	1.525	1.463	1.414	1.373	1.326	2.177	2.101	2.040	1.989	1.932

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Table 21-11. Achievable Conf. Levels for One-Sided Non-Parametric Conf. Bounds Around Median, Upper 95th Percentile, and Upper 99th Percentile (n ≤ 20)

	Rank of	Confidence Level					
n	Bound	UCL 50th	LCL 50th	UCL 95th	LCL 95th	UCL 99th	LCL 99th
4	4	0.9375	0.0625	0.1855	0.8145	0.0394	0.9606
4	3	0.6875	0.3125	0.0140	0.9860	0.0006	0.9994
4	2	0.3125	0.6875	0.0005	0.9995	0.0000	1.0000
4	1	0.0625	0.9375	0.0000	1.0000	0.0000	1.0000
5	5	0.9688	0.0312	0.2262	0.7738	0.0490	0.9510
5	4	0.8125	0.1875	0.0226	0.9774	0.0010	0.9990
5	3	0.5000	0.5000	0.0012	0.9988	0.0000	1.0000
5	2	0.1875	0.8125	0.0000	1.0000	0.0000	1.0000
5	1	0.0312	0.9688	0.0000	1.0000	0.0000	1.0000
6	6	0.9844	0.0156	0.2649	0.7351	0.0585	0.9415
6	5	0.8906	0.1094	0.0328	0.9672	0.0015	0.9985
6	4	0.6562	0.3438	0.0022	0.9978	0.0000	1.0000
6	3	0.3438	0.6562	0.0001	0.9999	0.0000	1.0000
6	2	0.1094	0.8906	0.0000	1.0000	0.0000	1.0000
6	1	0.0156	0.9844	0.0000	1.0000	0.0000	1.0000
7	7	0.9922	0.0078	0.3017	0.6983	0.0679	0.9321
7	6	0.9375	0.0625	0.0444	0.9556	0.0020	0.9980
7	5	0.7734	0.2266	0.0038	0.9962	0.0000	1.0000
7	4	0.5000	0.5000	0.0002	0.9998	0.0000	1.0000
7	3	0.2266	0.7734	0.0000	1.0000	0.0000	1.0000
7	2	0.0625	0.9375	0.0000	1.0000	0.0000	1.0000
7	1	0.0078	0.9922	0.0000	1.0000	0.0000	1.0000
8	8	0.9961	0.0039	0.3366	0.6634	0.0773	0.9227
8	7	0.9648	0.0352	0.0572	0.9428	0.0027	0.9973
8	6	0.8555	0.1445	0.0058	0.9942	0.0001	0.9999
8	5	0.6367	0.3633	0.0004	0.9996	0.0000	1.0000
8	4	0.3633	0.6367	0.0000	1.0000	0.0000	1.0000
8	3	0.1445	0.8555	0.0000	1.0000	0.0000	1.0000
8	2	0.0352	0.9648	0.0000	1.0000	0.0000	1.0000
8	1	0.0039	0.9961	0.0000	1.0000	0.0000	1.0000
9	9	0.9980	0.0020	0.3698	0.6302	0.0865	0.9135
9	8	0.9805	0.0195	0.0712	0.9288	0.0034	0.9966
9	7	0.9102	0.0898	0.0084	0.9916	0.0001	0.9999
9	6	0.7461	0.2539	0.0006	0.9994	0.0000	1.0000
9	5	0.5000	0.5000	0.0000	1.0000	0.0000	1.0000
9	4	0.2539	0.7461	0.0000	1.0000	0.0000	1.0000
9	3	0.0898	0.9102	0.0000	1.0000	0.0000	1.0000
9	2	0.0195	0.9805	0.0000	1.0000	0.0000	1.0000
9	1	0.0020	0.9980	0.0000	1.0000	0.0000	1.0000
10	10	0.9990	0.0010	0.4013	0.5987	0.0956	0.9044
10	9	0.9893	0.0107	0.0861	0.9139	0.0043	0.9957
10	8	0.9453	0.0547	0.0115	0.9885	0.0001	0.9999
10	7	0.8281	0.1719	0.0010	0.9990	0.0000	1.0000
10	6	0.6230	0.3770	0.0001	0.9999	0.0000	1.0000
10	5	0.3770	0.6230	0.0000	1.0000	0.0000	1.0000
10	4	0.1719	0.8281	0.0000	1.0000	0.0000	1.0000
10	3	0.0547	0.9453	0.0000	1.0000	0.0000	1.0000
10	2	0.0107	0.9893	0.0000	1.0000	0.0000	1.0000
10	1	0.0010	0.9990	0.0000	1.0000	0.0000	1.0000

Footnote. LCL = lower confidence limit; UCL = upper confidence limit; 50th = median

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Table 21-11. Achievable Conf. Levels for One-Sided Non-Parametric Conf. Bounds Around Median, Upper 95th Percentile, and Upper 99th Percentile (n ≤ 20)

	Rank of	Confidence Level					
n	Bound	UCL 50th	LCL 50th	UCL 95th	LCL 95th	UCL 99th	LCL 99th
11	11	0.9995	0.0005	0.4312	0.5688	0.1047	0.8953
11	10	0.9941	0.0059	0.1019	0.8981	0.0052	0.9948
11	9	0.9673	0.0327	0.0152	0.9848	0.0002	0.9998
11	8	0.8867	0.1133	0.0016	0.9984	0.0000	1.0000
11	7	0.7256	0.2744	0.0001	0.9999	0.0000	1.0000
11	6	0.5000	0.5000	0.0000	1.0000	0.0000	1.0000
11	5	0.2744	0.7256	0.0000	1.0000	0.0000	1.0000
11	4	0.1133	0.8867	0.0000	1.0000	0.0000	1.0000
11	3	0.0327	0.9673	0.0000	1.0000	0.0000	1.0000
11	2	0.0059	0.9941	0.0000	1.0000	0.0000	1.0000
11	1	0.0005	0.9995	0.0000	1.0000	0.0000	1.0000
12	12	0.9998	0.0002	0.4596	0.5404	0.1136	0.8864
12	11	0.9968	0.0032	0.1184	0.8816	0.0062	0.9938
12	10	0.9807	0.0193	0.0196	0.9804	0.0002	0.9998
12	9	0.9270	0.0730	0.0022	0.9978	0.0000	1.0000
12	8	0.8062	0.1938	0.0002	0.9998	0.0000	1.0000
12	7	0.6128	0.3872	0.0000	1.0000	0.0000	1.0000
12	6	0.3872	0.6128	0.0000	1.0000	0.0000	1.0000
12	5	0.1938	0.8062	0.0000	1.0000	0.0000	1.0000
12	4	0.0730	0.9270	0.0000	1.0000	0.0000	1.0000
12	3	0.0193	0.9807	0.0000	1.0000	0.0000	1.0000
12	2	0.0032	0.9968	0.0000	1.0000	0.0000	1.0000
12	1	0.0002	0.9998	0.0000	1.0000	0.0000	1.0000
13	13	0.9999	0.0001	0.4867	0.5133	0.1225	0.8775
13	12	0.9983	0.0017	0.1354	0.8646	0.0072	0.9928
13	11	0.9888	0.0112	0.0245	0.9755	0.0003	0.9997
13	10	0.9539	0.0461	0.0031	0.9969	0.0000	1.0000
13	9	0.8666	0.1334	0.0003	0.9997	0.0000	1.0000
13	8	0.7095	0.2905	0.0000	1.0000	0.0000	1.0000
13	7	0.5000	0.5000	0.0000	1.0000	0.0000	1.0000
13	6	0.2905	0.7095	0.0000	1.0000	0.0000	1.0000
13	5	0.1334	0.8666	0.0000	1.0000	0.0000	1.0000
13	4	0.0461	0.9539	0.0000	1.0000	0.0000	1.0000
13	3	0.0112	0.9888	0.0000	1.0000	0.0000	1.0000
13	2	0.0017	0.9983	0.0000	1.0000	0.0000	1.0000
13	1	0.0001	0.9999	0.0000	1.0000	0.0000	1.0000
14	14	0.9999	0.0001	0.5123	0.4877	0.1313	0.8687
14	13	0.9991	0.0009	0.1530	0.8470	0.0084	0.9916
14	12	0.9935	0.0065	0.0301	0.9699	0.0003	0.9997
14	11	0.9713	0.0287	0.0042	0.9958	0.0000	1.0000
14	10	0.9102	0.0898	0.0004	0.9996	0.0000	1.0000
14	9	0.7880	0.2120	0.0000	1.0000	0.0000	1.0000
14	8	0.6047	0.3953	0.0000	1.0000	0.0000	1.0000
14	7	0.3953	0.6047	0.0000	1.0000	0.0000	1.0000
14	6	0.2120	0.7880	0.0000	1.0000	0.0000	1.0000
14	5	0.0898	0.9102	0.0000	1.0000	0.0000	1.0000
14	4	0.0287	0.9713	0.0000	1.0000	0.0000	1.0000
14	3	0.0065	0.9935	0.0000	1.0000	0.0000	1.0000
14	2	0.0009	0.9991	0.0000	1.0000	0.0000	1.0000
14	1	0.0001	0.9999	0.0000	1.0000	0.0000	1.0000

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Table 21-11. Achievable Conf. Levels for One-Sided Non-Parametric Conf. Bounds Around Median, Upper 95th Percentile, and Upper 99th Percentile (n ≤ 20)

	Rank of	Confidence Level					
n	Bound	UCL 50th	LCL 50th	UCL 95th	LCL 95th	UCL 99th	LCL 99th
15	**15**	1.0000	0.0000	0.5367	0.4633	0.1399	0.8601
15	**14**	0.9995	0.0005	0.1710	0.8290	0.0096	0.9904
15	**13**	0.9963	0.0037	0.0362	0.9638	0.0004	0.9996
15	**12**	0.9824	0.0176	0.0055	0.9945	0.0000	1.0000
15	**11**	0.9408	0.0592	0.0006	0.9994	0.0000	1.0000
15	**10**	0.8491	0.1509	0.0001	0.9999	0.0000	1.0000
15	**9**	0.6964	0.3036	0.0000	1.0000	0.0000	1.0000
15	**8**	0.5000	0.5000	0.0000	1.0000	0.0000	1.0000
15	**7**	0.3036	0.6964	0.0000	1.0000	0.0000	1.0000
15	**6**	0.1509	0.8491	0.0000	1.0000	0.0000	1.0000
15	**5**	0.0592	0.9408	0.0000	1.0000	0.0000	1.0000
15	**4**	0.0176	0.9824	0.0000	1.0000	0.0000	1.0000
15	**3**	0.0037	0.9963	0.0000	1.0000	0.0000	1.0000
15	**2**	0.0005	0.9995	0.0000	1.0000	0.0000	1.0000
15	**1**	0.0000	1.0000	0.0000	1.0000	0.0000	1.0000
16	**16**	1.0000	0.0000	0.5599	0.4401	0.1485	0.8515
16	**15**	0.9997	0.0003	0.1892	0.8108	0.0109	0.9891
16	**14**	0.9979	0.0021	0.0429	0.9571	0.0005	0.9995
16	**13**	0.9894	0.0106	0.0070	0.9930	0.0000	1.0000
16	**12**	0.9616	0.0384	0.0009	0.9991	0.0000	1.0000
16	**11**	0.8949	0.1051	0.0001	0.9999	0.0000	1.0000
16	**10**	0.7728	0.2272	0.0000	1.0000	0.0000	1.0000
16	**9**	0.5982	0.4018	0.0000	1.0000	0.0000	1.0000
16	**8**	0.4018	0.5982	0.0000	1.0000	0.0000	1.0000
16	**7**	0.2272	0.7728	0.0000	1.0000	0.0000	1.0000
16	**6**	0.1051	0.8949	0.0000	1.0000	0.0000	1.0000
16	**5**	0.0384	0.9616	0.0000	1.0000	0.0000	1.0000
16	**4**	0.0106	0.9894	0.0000	1.0000	0.0000	1.0000
16	**3**	0.0021	0.9979	0.0000	1.0000	0.0000	1.0000
16	**2**	0.0003	0.9997	0.0000	1.0000	0.0000	1.0000
16	**1**	0.0000	1.0000	0.0000	1.0000	0.0000	1.0000
17	**17**	1.0000	0.0000	0.5819	0.4181	0.1571	0.8429
17	**16**	0.9999	0.0001	0.2078	0.7922	0.0123	0.9877
17	**15**	0.9988	0.0012	0.0503	0.9497	0.0006	0.9994
17	**14**	0.9936	0.0064	0.0088	0.9912	0.0000	1.0000
17	**13**	0.9755	0.0245	0.0012	0.9988	0.0000	1.0000
17	**12**	0.9283	0.0717	0.0001	0.9999	0.0000	1.0000
17	**11**	0.8338	0.1662	0.0000	1.0000	0.0000	1.0000
17	**10**	0.6855	0.3145	0.0000	1.0000	0.0000	1.0000
17	**9**	0.5000	0.5000	0.0000	1.0000	0.0000	1.0000
17	**8**	0.3145	0.6855	0.0000	1.0000	0.0000	1.0000
17	**7**	0.1662	0.8338	0.0000	1.0000	0.0000	1.0000
17	**6**	0.0717	0.9283	0.0000	1.0000	0.0000	1.0000
17	**5**	0.0245	0.9755	0.0000	1.0000	0.0000	1.0000
17	**4**	0.0064	0.9936	0.0000	1.0000	0.0000	1.0000
17	**3**	0.0012	0.9988	0.0000	1.0000	0.0000	1.0000
17	**2**	0.0001	0.9999	0.0000	1.0000	0.0000	1.0000
17	**1**	0.0000	1.0000	0.0000	1.0000	0.0000	1.0000

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Table 21-11. Achievable Conf. Levels for One-Sided Non-Parametric Conf. Bounds Around Median, Upper 95th Percentile, and Upper 99th Percentile (n ≤ 20)

	Rank of	Confidence Level					
n	Bound	UCL 50th	LCL 50th	UCL 95th	LCL 95th	UCL 99th	LCL 99th
18	**18**	1.0000	0.0000	0.6028	0.3972	0.1655	0.8345
18	**17**	0.9999	0.0001	0.2265	0.7735	0.0138	0.9862
18	**16**	0.9993	0.0007	0.0581	0.9419	0.0007	0.9993
18	**15**	0.9962	0.0038	0.0109	0.9891	0.0000	1.0000
18	**14**	0.9846	0.0154	0.0015	0.9985	0.0000	1.0000
18	**13**	0.9519	0.0481	0.0002	0.9998	0.0000	1.0000
18	**12**	0.8811	0.1189	0.0000	1.0000	0.0000	1.0000
18	**11**	0.7597	0.2403	0.0000	1.0000	0.0000	1.0000
18	**10**	0.5927	0.4073	0.0000	1.0000	0.0000	1.0000
18	**9**	0.4073	0.5927	0.0000	1.0000	0.0000	1.0000
18	**8**	0.2403	0.7597	0.0000	1.0000	0.0000	1.0000
18	**7**	0.1189	0.8811	0.0000	1.0000	0.0000	1.0000
18	**6**	0.0481	0.9519	0.0000	1.0000	0.0000	1.0000
18	**5**	0.0154	0.9846	0.0000	1.0000	0.0000	1.0000
18	**4**	0.0038	0.9962	0.0000	1.0000	0.0000	1.0000
18	**3**	0.0007	0.9993	0.0000	1.0000	0.0000	1.0000
18	**2**	0.0001	0.9999	0.0000	1.0000	0.0000	1.0000
18	**1**	0.0000	1.0000	0.0000	1.0000	0.0000	1.0000
19	**19**	1.0000	0.0000	0.6226	0.3774	0.1738	0.8262
19	**18**	1.0000	0.0000	0.2453	0.7547	0.0153	0.9847
19	**17**	0.9996	0.0004	0.0665	0.9335	0.0009	0.9991
19	**16**	0.9978	0.0022	0.0132	0.9868	0.0000	1.0000
19	**15**	0.9904	0.0096	0.0020	0.9980	0.0000	1.0000
19	**14**	0.9682	0.0318	0.0002	0.9998	0.0000	1.0000
19	**13**	0.9165	0.0835	0.0000	1.0000	0.0000	1.0000
19	**12**	0.8204	0.1796	0.0000	1.0000	0.0000	1.0000
19	**11**	0.6762	0.3238	0.0000	1.0000	0.0000	1.0000
19	**10**	0.5000	0.5000	0.0000	1.0000	0.0000	1.0000
19	**9**	0.3238	0.6762	0.0000	1.0000	0.0000	1.0000
19	**8**	0.1796	0.8204	0.0000	1.0000	0.0000	1.0000
19	**7**	0.0835	0.9165	0.0000	1.0000	0.0000	1.0000
19	**6**	0.0318	0.9682	0.0000	1.0000	0.0000	1.0000
19	**5**	0.0096	0.9904	0.0000	1.0000	0.0000	1.0000
19	**4**	0.0022	0.9978	0.0000	1.0000	0.0000	1.0000
19	**3**	0.0004	0.9996	0.0000	1.0000	0.0000	1.0000
19	**2**	0.0000	1.0000	0.0000	1.0000	0.0000	1.0000
19	**1**	0.0000	1.0000	0.0000	1.0000	0.0000	1.0000

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Table 21-11. Achievable Conf. Levels for One-Sided Non-Parametric Conf. Bounds Around Median, Upper 95th Percentile, and Upper 99th Percentile (n ≤ 20)

	Rank of	Confidence Level					
n	Bound	UCL 50th	LCL 50th	UCL 95th	LCL 95th	UCL 99th	LCL 99th
20	**20**	1.0000	0.0000	0.6415	0.3585	0.1821	0.8179
20	**19**	1.0000	0.0000	0.2642	0.7358	0.0169	0.9831
20	**18**	0.9998	0.0002	0.0755	0.9245	0.0010	0.9990
20	**17**	0.9987	0.0013	0.0159	0.9841	0.0000	1.0000
20	**16**	0.9941	0.0059	0.0026	0.9974	0.0000	1.0000
20	**15**	0.9793	0.0207	0.0003	0.9997	0.0000	1.0000
20	**14**	0.9423	0.0577	0.0000	1.0000	0.0000	1.0000
20	**13**	0.8684	0.1316	0.0000	1.0000	0.0000	1.0000
20	**12**	0.7483	0.2517	0.0000	1.0000	0.0000	1.0000
20	**11**	0.5881	0.4119	0.0000	1.0000	0.0000	1.0000
20	**10**	0.4119	0.5881	0.0000	1.0000	0.0000	1.0000
20	**9**	0.2517	0.7483	0.0000	1.0000	0.0000	1.0000
20	**8**	0.1316	0.8684	0.0000	1.0000	0.0000	1.0000
20	**7**	0.0577	0.9423	0.0000	1.0000	0.0000	1.0000
20	**6**	0.0207	0.9793	0.0000	1.0000	0.0000	1.0000
20	**5**	0.0059	0.9941	0.0000	1.0000	0.0000	1.0000
20	**4**	0.0013	0.9987	0.0000	1.0000	0.0000	1.0000
20	**3**	0.0002	0.9998	0.0000	1.0000	0.0000	1.0000
20	**2**	0.0000	1.0000	0.0000	1.0000	0.0000	1.0000
20	**1**	0.0000	1.0000	0.0000	1.0000	0.0000	1.0000

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D STATISTICAL TABLES

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Table 22-1. Combinations of n (≤ 40) and α (≤ .20) Achieving (1–β) Power to Detect Increases of 1.5 × GWPS

1–β = 0.50		1–β = 0.60		1–β = 0.70		1–β = 0.80		1–β = 0.90		1–β = 0.95		1–β = 0.99	
n	α	n	α	n	α	n	α	n	α	n	α	n	α
4	0.177	6	0.179	8	0.197	12	0.195	19	0.191	26	0.188		
5	0.149	7	0.156	9	0.175	13	0.177	20	0.177	27	0.176		
6	0.127	8	0.136	10	0.156	14	0.160	21	0.163	28	0.164		
7	0.108	9	0.119	11	0.139	15	0.146	22	0.151	29	0.153		
8	0.093	10	0.104	12	0.124	16	0.132	23	0.139	30	0.143		
9	0.080	11	0.092	13	0.111	17	0.120	24	0.129	31	0.133		
10	0.069	12	0.081	14	0.099	18	0.109	25	0.119	32	0.124		
11	0.060	13	0.071	15	0.089	19	0.099	26	0.110	33	0.116		
12	0.052	14	0.063	16	0.079	20	0.090	27	0.101	34	0.108		
13	0.045	15	0.056	17	0.071	21	0.082	28	0.093	35	0.101		
14	0.039	16	0.049	18	0.064	22	0.074	29	0.086	36	0.094		
15	0.034	17	0.043	19	0.057	23	0.068	30	0.079	37	0.087		
16	0.030	18	0.038	20	0.051	24	0.061	31	0.073	38	0.081		
17	0.026	19	0.034	21	0.046	25	0.056	32	0.067	39	0.076		
18	0.023	20	0.030	22	0.041	26	0.051	33	0.062	40	0.070		
19	0.020	21	0.027	23	0.037	27	0.046	34	0.057				
20	0.018	22	0.024	24	0.033	28	0.042	35	0.053				
21	0.015	23	0.021	25	0.030	29	0.038	36	0.049				
22	0.014	24	0.019	26	0.027	30	0.034	37	0.045				
23	0.012	25	0.017	27	0.024	31	0.031	38	0.041				
24	0.010	26	0.015	28	0.022	32	0.029	39	0.038				
25	0.009	27	0.013	29	0.020	33	0.026	40	0.035				
26	0.008	28	0.012	30	0.018	34	0.023						
27	0.007	29	0.010	31	0.016	35	0.021						
28	0.006	30	0.009	32	0.014	36	0.019						
29	0.006	31	0.008	33	0.013	37	0.018						
30	0.005	32	0.007	34	0.011	38	0.016						
31	0.004	33	0.007	35	0.010	39	0.015						
32	0.004	34	0.006	36	0.009	40	0.013						
33	0.003	35	0.005	37	0.008								
34	0.003	36	0.005	38	0.007								
35	0.003	37	0.004	39	0.007								
36	0.002	38	0.004	40	0.006								
37	0.002	39	0.003										
38	0.002	40	0.003										
39	0.002												
40	0.002												

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Table 22-2. Combinations of n (≤ 40) and α (≤ .20) Achieving (1–β) Power to Detect Increases of 2 × GWPS

1–β = 0.50		1–β = 0.60		1–β = 0.70		1–β = 0.80		1–β = 0.90		1–β = 0.95		1–β = 0.99	
n	α	n	α	n	α	n	α	n	α	n	α	n	α
3	0.091	3	0.123	3	0.164	4	0.163	5	0.199	7	0.183	11	0.180
4	0.057	4	0.080	4	0.113	5	0.119	6	0.152	8	0.144	12	0.148
5	0.037	5	0.054	5	0.079	6	0.086	7	0.116	9	0.113	13	0.121
6	0.024	6	0.036	6	0.055	7	0.063	8	0.088	10	0.089	14	0.099
7	0.016	7	0.025	7	0.039	8	0.046	9	0.067	11	0.069	15	0.080
8	0.011	8	0.017	8	0.027	9	0.034	10	0.051	12	0.054	16	0.065
9	0.007	9	0.012	9	0.019	10	0.024	11	0.039	13	0.042	17	0.053
10	0.005	10	0.008	10	0.014	11	0.018	12	0.029	14	0.033	18	0.043
11	0.003	11	0.006	11	0.010	12	0.013	13	0.022	15	0.025	19	0.034
12	0.002	12	0.004	12	0.007	13	0.010	14	0.017	16	0.020	20	0.027
13	0.002	13	0.003	13	0.005	14	0.007	15	0.013	17	0.015	21	0.022
14	0.001	14	0.002	14	0.004	15	0.005	16	0.010	18	0.012	22	0.018
≥15	<0.001	15	0.001	15	0.003	16	0.004	17	0.007	19	0.009	23	0.014
		≥16	<0.001	16	0.002	17	0.003	18	0.005	20	0.007	24	0.011
				17	0.001	18	0.002	19	0.004	21	0.005	25	0.009
				≥18	<0.001	19	0.002	20	0.003	22	0.004	26	0.007
						20	0.001	21	0.002	23	0.003	27	0.006
						≥21	<0.001	22	0.002	24	0.002	28	0.004
								23	0.001	25	0.002	29	0.004
								≥24	<0.001	26	0.002	30	0.003
										27	0.001	31	0.002
										≥28	<0.001	32	0.002
												33	0.002
												34	0.001
												≥35	<0.001

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Table 22-3. Minimum Individual Test α Meeting Power Criteria Given *n* and *CV*

	50% Power at *R* = 1.5					80% Power at *R* = 2				
CV	**n=4**	**n=6**	**n=8**	**n=10**	**n=12**	**n=4**	**n=6**	**n=8**	**n=10**	**n=12**
0.1	*0.003*	*0.000*	*0.000*	*0.000*	*0.000*	*0.001*	*0.000*	*0.000*	*0.000*	*0.000*
0.2	0.022	*0.005*	*0.001*	*0.000*	*0.000*	0.014	*0.002*	*0.000*	*0.000*	*0.000*
0.3	0.056	0.021	*0.008*	*0.003*	*0.001*	0.050	0.013	*0.003*	*0.001*	*0.000*
0.4	0.097	0.048	0.025	0.014	*0.007*	0.113	0.043	0.017	*0.007*	*0.003*
0.5	0.137	0.082	0.051	0.032	0.021	0.191	0.093	0.047	0.024	0.013
0.6	0.174	0.116	0.080	0.056	0.040	0.270	0.156	0.094	0.057	0.035
0.7	0.206	0.148	0.110	0.083	0.064	0.342	0.222	0.149	0.101	0.069
0.8	0.233	0.177	0.139	0.110	0.088	0.402	0.284	0.206	0.151	0.112
0.9	0.256	0.203	0.165	0.136	0.113	0.451	0.339	0.261	0.203	0.158
1.0	0.276	0.226	0.189	0.160	0.136	0.492	0.386	0.310	0.251	0.205
1.2	0.309	0.263	0.229	0.201	0.178	**0.553**	0.462	0.393	0.337	0.291
1.4	0.333	0.293	0.261	0.235	0.214	**0.596**	**0.517**	0.456	0.406	0.362
1.6	0.352	0.316	0.287	0.263	0.243	**0.626**	**0.558**	**0.505**	0.459	0.420
1.8	0.368	0.335	0.308	0.286	0.267	**0.650**	**0.590**	**0.542**	**0.502**	0.466
2.0	0.380	0.350	0.326	0.305	0.288	**0.667**	**0.614**	**0.572**	**0.536**	**0.504**
2.2	0.391	0.363	0.341	0.322	0.305	**0.682**	**0.634**	**0.596**	**0.564**	**0.534**
2.4	0.400	0.374	0.353	0.335	0.320	**0.693**	**0.650**	**0.616**	**0.586**	**0.560**
2.6	0.407	0.383	0.364	0.347	0.333	**0.703**	**0.664**	**0.632**	**0.605**	**0.581**
2.8	0.414	0.391	0.373	0.358	0.344	**0.711**	**0.675**	**0.646**	**0.621**	**0.599**
3.0	0.419	0.398	0.381	0.367	0.354	**0.718**	**0.685**	**0.658**	**0.635**	**0.614**

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Table 22-4. Minimum *n* (≥ 4) to Detect Decreases of .75 x GWPS for Given *CV*, Power (1–β), & Error Rate (α)

CV = 0.2						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	4	4	4	4	4	4
0.15	4	4	4	4	4	5
0.10	4	4	4	4	4	5
0.05	4	4	4	4	5	6
0.01	6	6	6	7	8	9

CV = 0.4						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	4	4	4	6	8	11
0.15	4	4	5	7	10	12
0.10	4	5	6	8	11	15
0.05	6	8	9	11	15	18
0.01	11	13	15	18	22	26

CV = 0.6						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	4	5	7	11	16	22
0.15	5	7	9	13	19	25
0.10	7	9	12	16	23	30
0.05	11	14	17	22	30	37
0.01	21	25	30	36	45	54

CV = 0.8						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	6	8	12	18	28	38
0.15	8	11	15	22	33	43
0.10	11	15	20	28	40	51
0.05	18	23	29	38	51	65
0.01	35	42	50	61	78	94

CV = 1.0						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	8	12	18	27	42	58
0.15	11	16	23	33	50	67
0.10	17	23	31	42	61	79
0.05	27	35	44	58	79	100
0.01	52	63	76	93	120	145

CV = 1.2						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	11	17	25	38	60	82
0.15	16	23	33	47	71	95
0.10	23	32	44	60	87	113
0.05	37	49	63	82	113	143
0.01	74	90	109	133	172	208

CV = 1.4						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	14	22	34	51	81	111
0.15	21	31	44	64	96	129
0.10	31	43	59	81	118	153
0.05	50	66	85	111	153	193
0.01	99	121	147	180	233	281

CV = 1.6						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	18	29	44	67	106	144
0.15	26	40	58	83	125	168
0.10	40	56	77	106	153	199
0.05	65	85	110	144	199	252
0.01	128	157	190	234	303	366

Table 22-4. Minimum *n* (≥ 4) to Detect Decreases of .75 x GWPS for Given *CV*, Power (1–β), & Error Rate (α)

CV = 1.8						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	22	36	56	84	133	182
0.15	33	50	72	104	158	212
0.10	50	70	97	133	193	252
0.05	81	107	139	182	252	318
0.01	162	198	240	296	383	463

CV = 2.0						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	27	44	68	103	164	225
0.15	40	61	89	128	195	261
0.10	61	87	119	164	238	310
0.05	100	132	171	225	310	392
0.01	199	243	296	364	472	571

CV = 2.2						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	32	54	83	125	198	271
0.15	48	74	108	155	236	315
0.10	73	104	144	198	288	375
0.05	120	159	207	271	375	474
0.01	239	293	357	440	570	690

CV = 2.4						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	38	63	98	148	235	323
0.15	57	88	128	184	280	375
0.10	87	124	171	235	342	446
0.05	143	189	246	323	446	563
0.01	284	348	425	523	678	821

CV = 2.6						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	44	74	115	174	276	378
0.15	67	103	150	216	329	439
0.10	102	145	200	276	402	523
0.05	167	221	288	378	523	661
0.01	333	408	498	614	795	963

CV = 2.8						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	51	86	133	201	320	438
0.15	77	119	173	250	381	509
0.10	118	168	232	320	465	606
0.05	193	256	334	438	606	766
0.01	386	473	577	711	922	1116

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Table 22-5. Minimum *n* (≥ 4) to Detect Decreases of .5 x GWPS for Given *CV*, Power (1–β), & Error Rate (α)

CV = 0.2						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	4	4	4	4	4	4
0.15	4	4	4	4	4	4
0.10	4	4	4	4	4	4
0.05	4	4	4	4	4	4
0.01	4	4	4	4	4	4

CV = 0.4						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	4	4	4	4	4	4
0.15	4	4	4	4	4	4
0.10	4	4	4	4	4	4
0.05	4	4	4	4	4	4
0.01	4	4	5	5	5	6

CV = 0.6						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	4	4	4	4	4	4
0.15	4	4	4	4	4	5
0.10	4	4	4	4	4	5
0.05	4	4	4	4	5	6
0.01	6	6	6	7	8	9

CV = 0.8						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	4	4	4	4	5	6
0.15	4	4	4	4	5	7
0.10	4	4	4	5	6	8
0.05	4	5	5	6	8	9
0.01	7	8	9	10	11	13

CV = 1.0						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	4	4	4	4	6	8
0.15	4	4	4	5	7	9
0.10	4	4	5	6	9	11
0.05	5	6	7	8	11	13
0.01	9	10	11	13	16	19

CV = 1.2						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	4	4	4	6	8	11
0.15	4	4	5	7	10	12
0.10	4	5	6	8	11	15
0.05	6	8	9	11	15	18
0.01	11	13	15	18	22	26

CV = 1.4						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	4	4	5	7	11	14
0.15	4	5	6	8	12	16
0.10	5	6	8	11	15	19
0.05	8	9	11	14	19	24
0.01	14	17	19	23	29	34

CV = 1.6						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	4	5	6	9	13	18
0.15	4	6	8	11	16	20
0.10	6	8	10	13	19	24
0.05	9	11	14	18	24	30
0.01	18	21	24	29	36	44

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Table 22-5. Minimum *n* (≥ 4) to Detect Decreases of .5 x GWPS for Given *CV*, Power (1–β), & Error Rate (α)

CV = 1.8						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	4	5	7	11	16	22
0.15	5	7	9	13	19	25
0.10	7	9	12	16	23	30
0.05	11	14	17	22	30	37
0.01	21	25	30	36	45	54

CV = 2.0						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	4	6	9	13	20	27
0.15	6	8	11	16	23	31
0.10	9	11	15	20	28	36
0.05	13	17	21	27	36	46
0.01	25	30	36	43	55	66

CV = 2.2						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	5	7	10	15	23	32
0.15	7	10	13	19	28	37
0.10	10	13	17	23	34	44
0.05	16	20	25	32	44	55
0.01	30	36	43	52	66	79

CV = 2.4						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	6	8	12	18	28	38
0.15	8	11	15	22	33	43
0.10	11	15	20	28	40	51
0.05	18	23	29	38	51	65
0.01	35	42	50	61	78	94

CV = 2.6						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	6	9	14	21	32	44
0.15	9	13	18	25	38	51
0.10	13	18	24	32	46	60
0.05	21	27	34	44	60	76
0.01	40	48	58	71	91	110

CV = 2.8						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	7	11	16	24	37	51
0.15	10	15	21	29	44	58
0.10	15	20	27	37	53	69
0.05	24	30	39	51	69	87
0.01	46	56	67	82	105	127

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Table 22-6. Minimum *n* (≥ 4) to Detect Decreases of .25 x GWPS for Given *CV*, Power (1–β), & Error Rate (α)

CV = 0.2						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	4	4	4	4	4	4
0.15	4	4	4	4	4	4
0.10	4	4	4	4	4	4
0.05	4	4	4	4	4	4
0.01	4	4	4	4	4	4

CV = 0.4						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	4	4	4	4	4	4
0.15	4	4	4	4	4	4
0.10	4	4	4	4	4	4
0.05	4	4	4	4	4	4
0.01	4	4	4	4	4	4

CV = 0.6						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	4	4	4	4	4	4
0.15	4	4	4	4	4	4
0.10	4	4	4	4	4	4
0.05	4	4	4	4	4	4
0.01	4	4	4	4	4	4

CV = 0.8						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	4	4	4	4	4	4
0.15	4	4	4	4	4	4
0.10	4	4	4	4	4	4
0.05	4	4	4	4	4	4
0.01	4	4	4	4	4	4

CV = 1.0						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	4	4	4	4	4	4
0.15	4	4	4	4	4	4
0.10	4	4	4	4	4	4
0.05	4	4	4	4	4	4
0.01	4	4	4	4	5	5

CV = 1.2						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	4	4	4	4	4	4
0.15	4	4	4	4	4	4
0.10	4	4	4	4	4	4
0.05	4	4	4	4	4	4
0.01	4	4	5	5	5	6

CV = 1.4						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	4	4	4	4	4	4
0.15	4	4	4	4	4	4
0.10	4	4	4	4	4	4
0.05	4	4	4	4	4	5
0.01	5	5	5	5	6	7

CV = 1.6						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	4	4	4	4	4	4
0.15	4	4	4	4	4	4
0.10	4	4	4	4	4	5
0.05	4	4	4	4	5	6
0.01	5	5	6	6	7	8

Table 22-6. Minimum *n* (≥ 4) to Detect Decreases of .25 x GWPS for Given *CV*, Power (1–β), & Error Rate (α)

CV = 1.8						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	4	4	4	4	4	4
0.15	4	4	4	4	4	5
0.10	4	4	4	4	4	5
0.05	4	4	4	4	5	6
0.01	6	6	6	7	8	9

CV = 2.0						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	4	4	4	4	4	5
0.15	4	4	4	4	4	5
0.10	4	4	4	4	5	6
0.05	4	4	4	5	6	7
0.01	6	6	7	8	9	10

CV = 2.2						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	4	4	4	4	4	6
0.15	4	4	4	4	5	6
0.10	4	4	4	4	6	7
0.05	4	4	5	6	7	8
0.01	7	7	8	9	10	12

CV = 2.4						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	4	4	4	4	5	6
0.15	4	4	4	4	5	7
0.10	4	4	4	5	6	8
0.05	4	5	5	6	8	9
0.01	7	8	9	10	11	13

CV = 2.6						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	4	4	4	4	5	7
0.15	4	4	4	4	6	8
0.10	4	4	4	5	7	9
0.05	5	5	6	7	9	11
0.01	8	8	9	11	13	15

CV = 2.8						
α\1-β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**
0.20	4	4	4	4	6	8
0.15	4	4	4	5	7	8
0.10	4	4	5	6	8	10
0.05	5	6	6	8	10	12
0.01	8	9	10	12	14	17

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Table 22-7. Minimum n to Detect kp_0 Exceedances Over Percentile ($1–p_0$) with Power ($1–\beta$) and Error Rate (α)

Percentile = 90th							
				k = 2			
α\1–β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**	**0.99**
0.20	7	13	22	35	59	83	140
0.10	15	24	36	53	81	109	173
0.05	25	26	50	69	102	133	203
0.02	38	52	69	91	128	163	240
0.01	49	64	83	108	147	184	266
				k = 2.5			
α\1–β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**	**0.99**
0.20	3	6	11	17	29	42	71
0.10	7	11	17	25	40	54	87
0.05	11	17	24	33	49	65	101
0.02	17	24	32	43	61	79	118
0.01	22	29	39	51	70	89	130
				k = 3			
α\1–β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**	**0.99**
0.20	2	4	7	11	18	26	44
0.10	4	7	10	15	24	33	53
0.05	7	10	14	20	30	39	61
0.02	10	14	19	26	37	47	71
0.01	13	17	23	30	42	53	78

Percentile = 95th							
				k = 2			
α\1–β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**	**0.99**
0.20	14	27	47	77	130	184	311
0.10	32	51	77	114	177	239	382
0.05	52	76	107	150	221	291	447
0.02	81	110	147	197	277	355	525
0.01	103	136	177	231	318	401	581
				k = 2.5			
α\1–β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**	**0.99**
0.20	6	13	23	38	66	95	162
0.10	14	24	37	56	88	121	196
0.05	23	35	51	73	109	145	227
0.02	36	51	69	94	136	175	264
0.01	46	63	83	110	155	197	290
				k = 3			
α\1–β	**0.50**	**0.60**	**0.70**	**0.80**	**0.90**	**0.95**	**0.99**
0.20	4	8	14	24	42	60	103
0.10	8	14	22	34	55	76	124
0.05	13	21	30	44	67	90	142
0.02	21	29	41	56	82	108	164
0.01	26	36	49	66	94	120	179

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Table 22-7. Minimum n to Detect kp_0 Exceedences Over Percentile ($1-p_0$) with Power ($1-\beta$) and Error Rate (α)

Percentile = 98th							
				k = 2			
α\1−β	0.50	0.60	0.70	0.80	0.90	0.95	0.99
0.20	35	71	122	200	341	485	823
0.10	81	132	200	297	464	630	1009
0.05	133	196	278	391	580	764	1178
0.02	207	285	381	512	726	930	1382
0.01	266	353	459	602	832	1050	1528
				k = 3			
α\1−β	0.50	0.60	0.70	0.80	0.90	0.95	0.99
0.20	9	20	37	64	112	162	281
0.10	21	36	58	90	147	204	335
0.05	34	53	79	116	179	241	383
0.02	52	76	107	149	219	288	442
0.01	67	94	127	173	249	321	482
				k = 4			
α\1−β	0.50	0.60	0.70	0.80	0.90	0.95	0.99
0.20	4	10	19	34	61	89	156
0.10	9	18	29	47	78	109	183
0.05	15	25	39	59	93	128	207
0.02	23	36	52	74	113	150	235
0.01	30	44	61	86	126	166	255
				k = 5			
α\1−β	0.50	0.60	0.70	0.80	0.90	0.95	0.99
0.20	3	6	12	22	40	59	104
0.10	6	11	18	30	50	71	121
0.05	9	15	24	37	60	82	135
0.02	13	21	31	46	71	96	152
0.01	17	26	37	53	79	105	164

Percentile = 99th							
				k = 2			
α\1−β	0.50	0.60	0.70	0.80	0.90	0.95	0.99
0.20	71	143	247	407	693	987	1677
0.10	163	266	404	602	943	1281	2054
0.05	268	397	563	793	1178	1552	2395
0.02	418	576	772	1038	1473	1889	2810
0.01	536	713	930	1221	1689	2133	3105
				k = 3			
α\1−β	0.50	0.60	0.70	0.80	0.90	0.95	0.99
0.20	18	41	75	130	229	332	578
0.10	41	73	118	184	300	417	688
0.05	67	107	161	236	366	494	786
0.02	105	154	216	303	448	588	904
0.01	134	189	258	352	507	656	987
				k = 4			
α\1−β	0.50	0.60	0.70	0.80	0.90	0.95	0.99
0.20	8	20	39	69	125	184	324
0.10	19	35	59	96	160	225	379
0.05	30	51	79	120	192	263	427
0.02	47	72	105	152	231	309	485
0.01	60	88	125	175	259	341	525
				k = 5			
α\1−β	0.50	0.60	0.70	0.80	0.90	0.95	0.99
0.20	5	13	25	45	83	123	219
0.10	11	21	37	61	104	148	252
0.05	17	30	49	76	123	171	282
0.02	27	43	64	94	147	198	317
0.01	34	52	75	108	164	218	341

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Table 22-8. Minimum n to Detect kp_0 Exceedences Over Percentile ($1-p_0$) with Power ($1-\beta$) and Error Rate (α)

Percentile = 90th

k = .50

α\1–β	0.50	0.60	0.70	0.80	0.90	0.95	0.99
0.20	26	38	54	77	114	150	231
0.10	60	78	100	130	177	221	318
0.05	98	121	148	184	239	291	401
0.02	152	181	214	256	321	380	505
0.01	195	227	264	311	382	447	581

k = .25

α\1–β	0.50	0.60	0.70	0.80	0.90	0.95	0.99
0.20	12	16	20	27	37	47	68
0.10	27	32	39	48	61	74	100
0.05	44	51	59	70	86	101	131
0.02	68	77	87	100	119	136	171
0.01	87	97	109	123	144	163	201

Percentile = 95th

k = .50

α\1–β	0.50	0.60	0.70	0.80	0.90	0.95	0.99
0.20	54	80	113	159	236	311	479
0.10	125	163	209	270	368	460	661
0.05	206	254	311	384	500	606	834
0.02	321	380	449	537	672	794	1052
0.01	412	478	555	653	800	934	1212

k = .25

α\1–β	0.50	0.60	0.70	0.80	0.90	0.95	0.99
0.20	24	32	42	55	76	96	139
0.10	56	68	82	99	127	152	206
0.05	92	107	124	146	179	209	271
0.02	143	161	182	209	248	283	355
0.01	183	204	228	257	300	339	417

Percentile = 98th

k = .50

α\1–β	0.50	0.60	0.70	0.80	0.90	0.95	0.99
0.20	139	205	290	407	602	793	1221
0.10	322	419	537	693	943	1178	1689
0.05	531	653	798	987	1281	1552	2133
0.02	827	979	1154	1379	1723	2036	2694
0.01	1061	1232	1428	1677	2054	2395	3105

k = .25

α\1–β	0.50	0.60	0.70	0.80	0.90	0.95	0.99
0.20	62	82	107	140	193	244	354
0.10	144	173	209	254	324	388	525
0.05	236	274	318	373	458	533	692
0.02	368	415	469	535	635	724	907
0.01	472	525	585	659	770	868	1067

Percentile = 99th

k = .50

α\1–β	0.50	0.60	0.70	0.80	0.90	0.95	0.99
0.20	281	413	584	820	1213	1597	2457
0.10	651	846	1083	1397	1900	2373	3402
0.05	1072	1319	1611	1990	2582	3129	4297
0.02	1671	1976	2330	2782	3475	4106	5430
0.01	2144	2487	2883	3384	4144	4830	6259

k = .25

α\1–β	0.50	0.60	0.70	0.80	0.90	0.95	0.99
0.20	125	166	215	282	389	490	711
0.10	290	350	420	512	653	782	1056
0.05	477	553	641	753	922	1075	1393
0.02	743	838	945	1080	1281	1460	1827
0.01	953	1060	1181	1330	1553	1749	2149

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Techniques of Water-Resources Investigations
of the United States Geological Survey

CHAPTER D2

GUIDELINES FOR COLLECTION AND FIELD ANALYSIS OF GROUND-WATER SAMPLES FOR SELECTED UNSTABLE CONSTITUENTS

By Warren W. Wood

Book 1
COLLECTION OF WATER-DATA BY DIRECT MEASUREMENT

UNITED STATES DEPARTMENT OF THE INTERIOR

CECIL D. ANDRUS, Secretary

GEOLOGICAL SURVEY

Dallas L. Peck, Director

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PREFACE

The Department of the Interior has a basic responsibility for the appraisal, conservation, and efficient utilization of the Nation's natural resources, including water as a resource, as well as water involved in the use and development of other resources. As one of the several Interior agencies, the U.S. Geological Survey's primary function in relation to water is to assess its availability and utility as a national resource for all uses. The U.S. Geological Survey's responsibility for water appraisal includes not only assessments of the location, quantity, and availability of water but also determinations of water quality. Inherent in this responsibility is the need for extensive water-quality studies related to the physical, chemical, and biological adequacy of natural and developed surface- and ground-water supplies. Included, also, is the need for supporting research to increase the effectiveness of these studies.

As part of its mission the Geological Survey is responsible for a large part of water-quality data for rivers, lakes, and ground water that is used by planners, developers, water-quality managers, and pollution-control agencies. A high degree of reliability and standardization of these data is paramount.

The series of manuals on techniques describes procedures for planning and executing specialized work in water-resources investigations. The material is grouped under major subject headings called books and is further subdivided into sections and chapters. Book 1 is on the collection of water data by direct measurement. Section D is on water quality.

The unit of publication, the chapter, is limited to a narrow field of subject matter. This format permits flexibility in revision and publication as the need arises. "Guidelines for Collection and Field Analysis of Ground-water Samples for Selected Unstable Constituents" is the second chapter to be published under Section D of Book 1. The chapter number includes the letter of the section.

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GUIDELINES FOR COLLECTION AND FIELD ANALYSIS OF GROUND-WATER SAMPLES FOR SELECTED UNSTABLE CONSTITUENTS

By Warren W. Wood

Abstract

The unstable nature of many chemical and physical constituents in ground water requires special collection procedures and field analysis immediately after collection. This report describes the techniques and equipment commonly used in the collection and field analysis of samples for pH, temperature, carbonate, bicarbonate, specific conductance, Eh, and dissolved oxygen.

Introduction

Samples of ground water are obtained and analyzed to evaluate the chemical and physical quality of the water and to aid in understanding the geochemical and hydrologic relationships in an aquifer. These objectives require that the water sample represent the geochemical environment as accurately as possible.

Some properties or constituents in ground water may change dramatically within a few minutes or hours after sample collection. Immediate analysis in the field is required if dependable results for these parameters are to be obtained. Samples for other constituents may be stabilized by preservative treatment. Some examples of preservative treatment are refrigeration or the addition of toxic metals such as mercury to minimize chemical changes due to biologic activity and the addition of acid to prevent the precipitation of metal ions.

This manual is designed to provide guidelines for the collection and field analysis of common unstable constituents or properties of relatively shallow ground water and is intended to be a supplement to the manual on "Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases" (Brown and others, 1970). Techniques for sampling and analyses for unusual or uncommon constituents as well as deep ground waters have been omitted from this report. The reader is referred to Presser and Barnes (1974) for techniques on collection and field analysis of ammonia and hydrogen sulfide gas.

The techniques and equipment described in this manual are derived from many workers including William Back, Ivan Barnes, H. C. Claasen, Bruce B. Hanshaw, Gerth E. Hendrickson, John D. Hem, Blair Jones, Donald Langmuir, F. J. Pearson, Jr., Jack Rawson, and Isaac Winograd. My sincere thanks goes to these and other workers from whom I have acquired information included in this manual.

The recent development of sophisticated portable field equipment has permitted a very accurate and precise analysis of water for some unstable constituents or properties at the collection site; however, all methods described in this manual are subject to revision as improved techniques and equipment are developed or become available.

The English units used in this report may be converted to metric units by the following factors:

From	*Multiply by*	*To obtain*
feet	0.3048	metres
gallons	3.785	litres
gallons per minute	.06309	litres per second
inches	25.4	millimetres
	2.54	centimetres
ounces	28.349	grams

General criteria for sampling of ground water for geochemical studies

A working hypothesis on geochemical controls affecting the water in an aquifer is essential before collection of water samples is begun. All water analyses for the area of study, including those that are available from city, county, state, and Federal agencies, should be evaluated prior to the development of a sampling program, even though the accuracy of these analyses may be inadequate for the purposes of a particular study. Surface-water analyses, particularly of samples collected under base-flow conditions, should not be overlooked in evaluating existing chemical and physical data. Additional information on geochemical conditions can often be obtained by the extrapolation of data from known areas or regions of similar hydrologic, geologic, and climatic environments.

The working hypothesis on the chemical controls affecting the water quality of an aquifer, as developed from existing data, will aid in selecting the sites for the collection of samples; identifying the number and types of field or laboratory analyses required; and determining the methods for sample collection, treatment, and preservation. This information is required so that the applicable equipment, instruments, containers, and preservatives can be obtained and the sampling and analytical schedules can be organized.

Method of sample collection

Springs

Excellent samples for the determination of some water-quality constituents can be obtained from springs if suitable sampling precautions are taken. Small springs in unconsolidated deposits can be sampled by driving a well point or slotted pipe to a depth of 1 metre or less into the ground adjacent to the spring. The water will often flow from this type of installation. If it does not flow, a small "pitcher pump" can be used to collect the sample. Attempts to collect samples from small springs and seeps, without the use of pipes, result in almost certain contamination of the sample by soil bacteria, particulate matter, and atmospheric oxygen. It is often difficult, even when using a driven pipe, to collect a sample that does not contain dissolved oxygen. If the water contains easily oxidized metals such as iron and manganese, the dissolved-oxygen contamination may preclude the use of a small spring or seep as a satisfactory site for the collection of samples for the determination of these metals and other properties or constituents such as pH and oxidation-reduction potential. If the sample is to be used for the determination of trace metals, it is necessary to use plastic pipe and well screen that has been thoroughly cleaned, rather than iron pipe.

Large springs in consolidated rock usually are better sampling points than other types of springs. However, obtaining a representative sample of vigorously upswelling water at the orifice of a large spring may be difficult and may require a boat manned by several people. Even if the spring depression is narrow and can be waded, collection of a representative sample by forcing a bottle held by hand or attached to a rod down into the upswelling water is difficult. In either case, where the sample is collected directly in the bottle, the sample is always contaminated with oxygen.

Although thief-type samplers (fig. 1) can be used to collect unoxygenated samples, they are usually difficult to emplace in a "boiling spring." An additional problem with the use of thief samplers is that the closing messenger may not function properly in upswelling waters. Both nonmetallic and brass thief samplers are available. The nonmetallic type should be used for the collection of samples to be analyzed for trace metals.

A heavy metal pipe pushed into the mouth of a spring can be used to provide a steady flow from which the sample can be collected. Although this sampling system minimizes the potential for atmospheric contamination, experience has shown that dissolved oxygen is inevitably present in samples collected in this manner. The samples collected by use of the metal pipe may not be suitable for the analysis of trace metals or other properties affected by dissolved oxygen.

An inexpensive ($20–$30) submersible-elec-

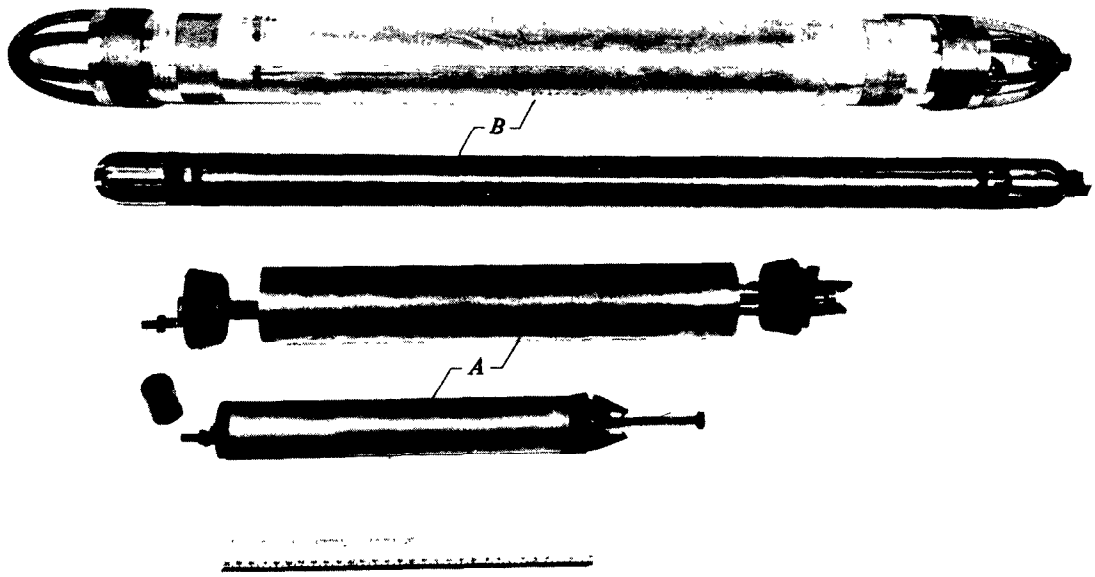


Figure 1 —Thief-type samplers. A, Foerst. B, Ball-valve

tric pump of the type sold at garden-supply stores and used for home water fountains can be a very effective sampler. These pumps, which have plastic housing, impellers, and tubing, can be used to collect samples for trace metals as well as major constituents. A suggested procedure is to secure the pump to a pole or pipe and push it into the mouth of a spring. With the delivery tube running to the shore, the pump is started and the sample collected. These pumps will deliver 10–20 litres per minute and greatly simplify the process of sampling from springs.

The main disadvantage of this pump system is that it requires an independent power supply. However, these pumps have a low power requirement, usually less than 2 amps, and can be used with a 12-volt automobile battery fitted with an inexpensive ($10–$20) inverter. The inverter, which converts 12-volt direct current to 110-volt alternating current, is connected to the battery, and the pump is plugged into the inverter. Because the cord supplied with these pumps usually is too short for most sampling, a waterproof connector and extension cord must be added. A portable gasoline-powered generator will also provide a satisfactory power supply, but it is usually more awkward to use than the automobile battery and inverter arrangement.

In spite of the limitations and sampling difficulties, sample collection from springs can be useful for many constituents if the limitations are recognized and considered prior to sampling.

Wells

The depth of the pump in a well and the water level during pumping should be known before samples are obtained. If the water level is at or near the pump intake, atmospheric oxygen may be entrained in the discharge and easily oxidized metals such as iron may precipitate prior to sampling. If water-level and pump depth information is not available, the discharge should be checked for dissolved oxygen before samples are collected. If ground water in the region being studied normally contains no oxygen, the presence of oxygen indicates contamination by the pumping process. However, in ground-water systems that contain little oxidizable material, dissolved oxygen may exist naturally. The presence of naturally dissolved oxygen may be verified by sampling other wells in the aquifer.

Multiple-screen or open-hole wells that receive water from several aquifers should be avoided in sampling for geochemical studies. Pumping from between well packers can sometimes be used to obtain samples from a particu-

lar aquifer in multiple-aquifer wells if the sample information justifies the cost involved. A driller's log that gives the construction details of the well as well as a lithologic description of the units penetrated is essential.

If any uncertainty exists as to depth of the producing aquifer or depth of the well, the total depth of the well should be measured and a flowmeter survey conducted to determine the source of the water prior to sampling. Difference in temperature of water compared to other wells in the area may represent different production depths. A flowmeter survey can also be useful in determining if multiple-aquifer flow exists in the system and can offer an explanation for chemical quality anomalies that are often observed within an apparent single-aquifer system.

To obtain a representative sample from an aquifer at a given location, a well must be pumped until the temperature, pH, and specific conductance are constant. This is the minimum required precaution for insuring that a sample adequately represents the water in the aquifer. pH is usually the last parameter to obtain a reproducible reading and, consequently, is the most sensitive test for many wells. There is no specific volume of water that constitutes a minimum pumping time. Municipal, irrigation, and industrial wells that are in nearly constant use require only a few minutes of pumping before stable conditions are observed and samples can be collected with confidence.

Standby, observation, new, and little-used wells may require a day or more of pumping before the water is of constant quality. A log of specific conductance, pH, and temperature for water pumped from these seldom used wells should be kept until these parameters stabilize. Measurement of drawdown during this stabilization period is often helpful because changes in the proportions of discharge coming from different producing zones may be reflected by new pumping levels.

The most representative water samples usually can be obtained from municipal, industrial, or irrigation wells. Because of their constant pumping and high yield, these wells draw water from a large area of the aquifer and usually insure a representative sample. In addition, other hydrologic data are usually available at these sites. Available data on approximate discharge and duration of pumping prior to sampling should be recorded for any of these wells.

Potential contamination, precipitation of solutes, and loss of dissolved gases can be minimized by collecting the sample as close to the wellhead as possible. Many domestic and other types of wells are poorly designed for sampling. The plumbing is often inaccessible, and samples can be obtained only after water has gone through a pressure tank, water softener, or iron filter. Analysis of water from these wells are of little value in geochemical studies.

Wells that do not have a suitable sampling point often can be modified so that a representative sample can be collected. However, before any modifications are performed, permission of the well owner should be obtained. Any field kit used for such modifications should include a battery-powered electric drill and bits and taps for ⅛-inch and ¼-inch pipe thread. In addition, plugs, petcocks, plastic tubing, and wrenches for these pipe sizes should be included in a field kit. (See table 1 for a suggested list.) Adaptors, reducers, couplings, and nipples of all standard sizes and material are essential for utilizing existing sampling taps. Many sampling taps on industrial and municipal wells have either a garden-hose fitting or a smooth-surface faucet that requires a special adaptor.

Often the only wells for which complete hydrologic data are available are small-diameter observation wells that are not equipped with a pump. If the diameter of the well is sufficiently large, a submersible pump can be used to obtain samples. If the water level is less than 7 metres below the surface, a pitcher pump may be used for sample collecting. In using this method, however, it is difficult to prevent oxygenation.

For small-diameter wells, a hand-operated thief sampler can be used to collect samples from any depth in the wells. The quality of the water standing in an unused well generally does not reflect the quality of the water in the aquifer. Before sampling with a thief sampler, the well should be bailed until the specific con-

Table 1 —Supplies and equipment included in a field kit suitable for water sampling from a well

Two each square-head male pipe-thread plugs, ⅛, ¼, ½, and ¾ inch.
Two each reducer bushings, ¾ to ½, ½ to ¼, and ¼ to ⅛ inch, male pipe thread to female pipe thread
Two each reducer couplings, 1 to ¾, ¾ to ½, ½ to ¼, and ¼ to ⅛-inch pipe thread
Two each long nipples, male pipe thread, 1, ¾, ½, ¼, and ⅛ inch.
One each tees, ¾ and ½ inch.
One each elbows, ¾ and ½ inch.
15–50 feet of ⅜-inch plastic tubing.
15–50 feet of ¼-inch plastic tubing.
15–50 feet of ½-inch plastic garden hose with fittings.
Two each male connectors garden hose to pipe filtering.
1–6 feet of soft rubber hose, ¼-inch ID, and ⅜-inch ID.
Three each male connectors, ¼-inch tube to ⅛-inch pipe thread
⅜-inch tube to ⅛-inch pipe thread
⅜-inch tube to ¼-inch pipe thread
¼-inch tube to ¼-inch pipe thread
Two each tubing union tees, ¼ and ½-inch tubing.
Two each tubing unions, ¼ and ⅜ inch.
Two each male branch tees, ¼ and ⅜ inch.
Two each low pressure needle valves, ¼ and ⅜-inch tubing.
A tool box containing two pipe wrenches and two crescent wrenches as well as screwdriver, pliers, hacksaw, and so forth.
Several shutoff and control valves of the common tube and pipe sizes are desirable.

ductance, pH, and temperature of the water are constant. Collection of a sample by bailing and filtering a sample from a thief sampler without introducing dissolved oxygen is nearly impossible.

For some wells, it may be advantageous to use a motor-operated small-diameter unit controlled by an uphole power source and switch. Motorized units are of course more expensive than hand operated ones, and the operation is more involved because a truck with a power winch must be used to raise and lower the unit. Again, the well should be bailed until the values of pH, temperature, and specific conductance are constant.

A small-diameter hand-operated bailer may also be used to collect samples from wells. Figure 2 shows such a homemade bailer that can be made in about an hour at a cost of a few dollars. Copper tubing, stainless steel, or PVC

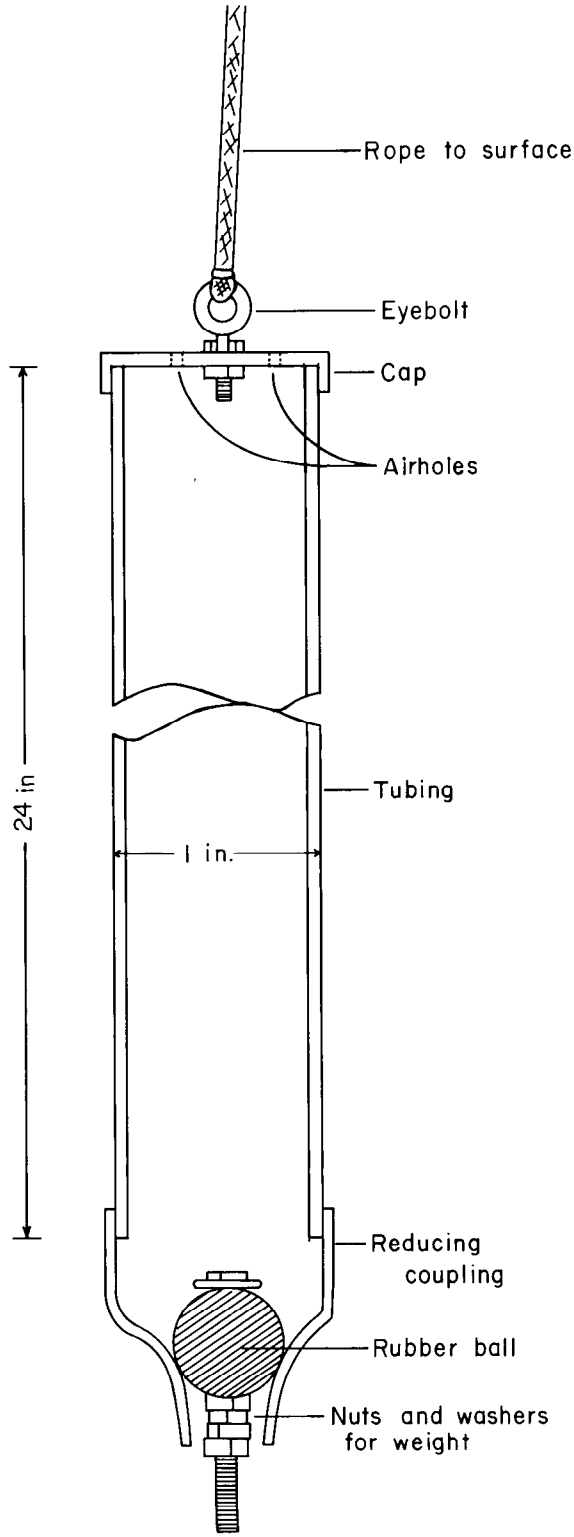


Figure 2 --"Homemade" bailer for collecting water samples from small-diameter wells

Figure 2 - "Homemade" bailer for collecting water samples from small-diameter wells

(polyvinyl chloride) plastic can be used; if plastic is used, a weight must be attached to the unit so that it will submerge. Plastic and stainless-steel construction is preferable if analyses are to be made for trace metals. The sample is contaminated with oxygen in this system, and particulate matter is often collected if the bailer strikes the bottom of the well. With any bailer or thief-type sampler, there is always the danger that the sample is a mixture of stagnant water in the well bore and water from the aquifer. Even the precaution of checking the sample for constancy of pH, temperature, and specific conductance may not give complete assurance of a representative sample.

A problem of fluid quantity exists with any of the bailer or thief-type methods of collection because an inordinate amount of time may be required to make 50 or 100 trips with a sampler to insure that the stagnant water in a well has been removed. Airlift pumping is an effective method of developing small-diameter wells but is generally a poor method of collecting a sample for chemical analysis. The air used for pumping obviously contaminates the sample, but perhaps more importantly, the turbulance with which the water is brought to the surface may have significant effects on pH, carbonate, bicarbonate, and temperature.

A useful combination of sampling techniques in small-diameter wells is to use the air pump to remove water until chemical conditions are stable and then to make several trips with a thief sampler or bailer to collect the sample. With all bailer or thief methods, it is extremely difficult to avoid oxidizing iron or manganese when filtering. For this reason, analyses for these elements should not be made if the bailer sample contains particulate matter that requires filtering.

Unfortunately, there are no well-defined criteria that apply to all methods of sampling for trace metals. The only general rule is to avoid contact with any metals in the collection system. Because this rule is often in conflict with the practical problems of collecting the sample, some compromise is usually necessary, and each sampling situation must be evaluated individually.

Unsaturated zone

Water sampling beneath a waste-disposal pond, feedlot, sanitary landfill, recharge pond, or any other system in which there is unsaturated flow requires special techniques. One method that has been used consists of a buried porous-ceramic cup (suction-lysimeter) with two lines to the surface, by which vacuum and pressure are applied, and from which the sample is collected. The construction details of this device are shown in figure 3. Additional details are given by Wood (1973).

In general, the system is operated by applying a vacuum greater than soil-moisture tension to a buried porous cup and thereby inducing the water to flow into the cup. To withdraw the sample, an increased vacuum is applied which causes water to flow past the check valve into the vacuum line. Gas pressure (inert gas) is then applied to one tube of the two-tube sys-

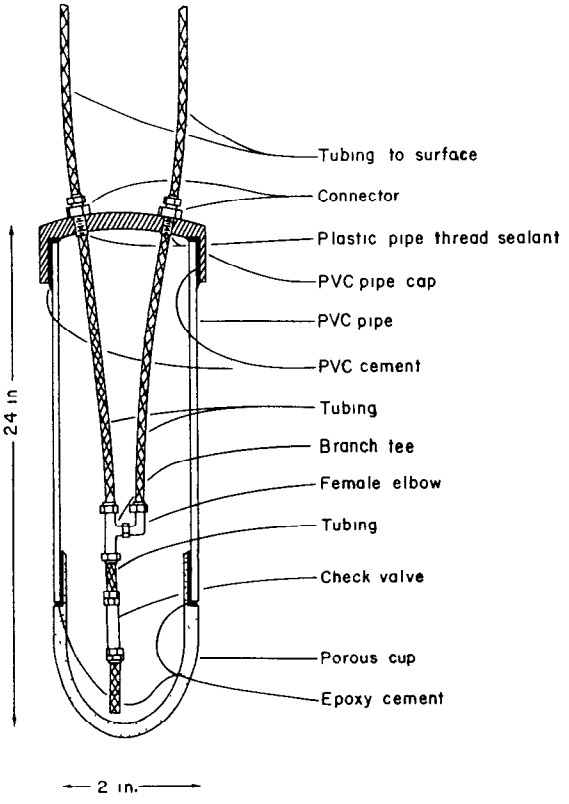


Figure 3.—Porous-cup assembly used for sampling in the unsaturated zone.

tem to force the sample to the surface. A check valve in the cup assembly prevents pressurization of the porous cup and backflow of the sample. This system has been used successfully in fine sand where there has been significant amount of flow; whether it will give satisfactory results in all unsaturated flow requirements has not yet been ascertained.

Sample filtration and acidification

Water that appears to be clear may contain considerable amounts of particulate matter in suspension. This is particularly true of water from new or little-used wells, such as those used for water-level observations or standby municipal and industrial supplies. The quantity of sediment discharged from a well is affected by the type of pump, construction of the well, screen size, type of screen, the pumping rate, and drawdown as well as the chemical stability of the system. The particulate matter in a water sample must be removed prior to most analyses, particularly if the sample is to be acidified, because the addition of acid will cause much of the particulate matter to dissolve. For example, the acid used for bicarbonate titration will dissolve particulate calcium carbonate, resulting in an analysis that shows an anomalously high bicarbonate content. The addition of acid prior to filtering may also result in exchange of hydrogen ions from the acid with cations from the particulate matter, thereby increasing the cation concentration of the water.

The wrong filtering technique will do as much damage to the accuracy of some analyses as will no filtering at all. Samples used for temperature measurements, dissolved oxygen, Eh, and pH should not be filtered. Vacuum filtering exposes the sample to the atmosphere and may also remove dissolved carbon dioxide from the water. The removal of carbon dioxide may significantly change the concentration of bicarbonate, carbonate, and influence the pH. Ground-water samples for the determination of these and other properties or constituents affected by the loss of carbon dioxide or contamination by oxygen should not be vacuum filtered.

A simple modification of the Skougstad-type plastic filter (Brown and others, 1970), commonly used by the U.S. Geological Survey, permits exclusion of the atmosphere during filtering. The top of the unit may be modified to include an inlet-delivery tube that extends to within a fraction of an inch of the bottom of the inside of the filter. The old pressure inlet is used as the new outlet, and control valves are placed on the inlet and the outlet tubes (fig. 4). This modification permits incoming water from a sampling line connected to the well discharge to fill the filter from the bottom, expelling air and overflow sample through the exit line. Discharge to the filter unit is controlled by the valve on the intake.

Before beginning filtration, the filter unit should be completely disassembled and thoroughly washed with the water to be sampled. Take special care to install a new styrofoam filter-support pad or insure that there are no stains or particulate matter on the old pad. A new membrane filter of the proper diameter (102 mm) and pore size (0.45 μm) is fitted to the filter unit, and the top and bottom are securely fastened.

Water introduced into the filter will immediately begin to drip from the discharge tube, and this water can be used to rinse pipets, sample bottles, and other equipment. Once the filter unit is full and all air is expelled, water is permitted to continue flowing through the

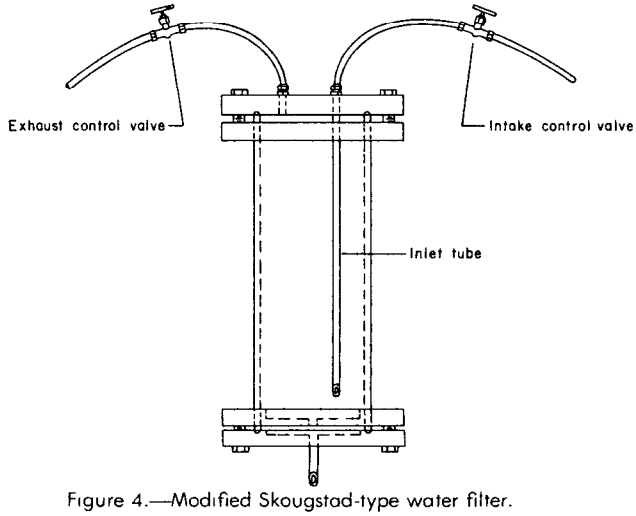


Figure 4.—Modified Skougstad-type water filter.

filter and out the exit tube until three or four filter volumes have flushed through the unit. This procedure makes certain that water that has been in contact with the atmosphere and any soluble impurities in the unit are removed.

The valve on the exit tube is closed, and the pressure from the well is used to filter the water. Pressure is controlled by the valve on the inlet tube and should be adjusted so that it is only sufficient to create a gentle flow from the discharge tube. A large pressure drop across the filter should be avoided to minimize the loss of dissolved gases from the sample. A sample bottle that has been thoroughly rinsed several times with the sample filtrate is placed under the filter for collection of the sample.

If water pressure is insufficient for filtering, an inert gas such as nitrogen or argon can be used to force the sample through the filter. To utilize gas pressure for filtration, the filter unit is filled with water as above, and the gas source is attached to the exit tube, the inlet tube is closed, the pressure is applied,and the sample collected from the discharge tube. Compressed air or carbon dioxide should not be used because these gases will influence the composition of the sample.

The 0.45-micrometre porosity filter has been widely adopted for separation of suspended matter from water samples. It represents a compromise between complete removal of the particulate material and speed with which filtration may be completed. Colloidal material with particles less than 0.45 micrometre in diameter is generally present in surface water and may occur in some ground water. Such material can pass through the filter and may strongly influence analytical values for iron and manganese (Kennedy and others, 1974). The problem may be partly alleviated by using 0.10-micrometre porosity filters (Kennedy and others, 1974).

The filtering process produces a "filter cake" of particulate material that decreases the particle size that can pass through the filter. Building of a filter cake may destroy the comparative uniformity of trace metals in successive aliquots. There is no apparent solution to this dilemma, but careful notation of the volume of water filtered and the amount of suspended material in the sample may be useful in evaluating analytical results.

The use of 0.1-micrometre filter membrane may reduce variance of trace metals between aliquots. The use of this filter membrane, however, requires considerably more filtration time because of rapid plugging from suspended solids in the sample. The 0.1-micrometre membrane filter should be used only in special situations that have been discussed with the district water-quality specialist or with personnel of the Central Laboratory System.

Porosity of the filter used should be recorded with the analytical data. Chemical analysis of particulate material retained by the filter may be important for some studies. To use this information the total volume of water filtered must be known.

If the filtered samples are to be acidified, double-distilled reagent-grade nitric acid should be added to the sample bottles after a few millilitres of the sample have been collected, to minimize oxidation, precipitation, and adsorption. Acid is more effective in preventing precipitation than in removing the precipitated minerals from the walls of the sample bottles. Sufficient acid must be added so that the resultant pH is 3.0 or less; usually 1 millilitre of acid to 1 litre of sample is sufficient. Convenient containers for transporting ultra high purity acid in the field are 2-ounce polyethylene or Teflon dropping bottles (fig. 5). Disposable glass ampoules of acid obtained from the Central Laboratory are even more convenient to use than the dropping bottles, and the chance of contamination is less with the ampoules. The ampoules can be carried in the field in their styrofoam shipping case with little danger of breakage.

Sampling for trace metals analysis

Some of the preceding sections have shown that the collection of water samples for trace metals analysis without contamination by atmosphereic oxygen is difficult. Contamination of samples with the trace metals themselves also may present a serious problem because of the widespread use of metallic casing, screen,

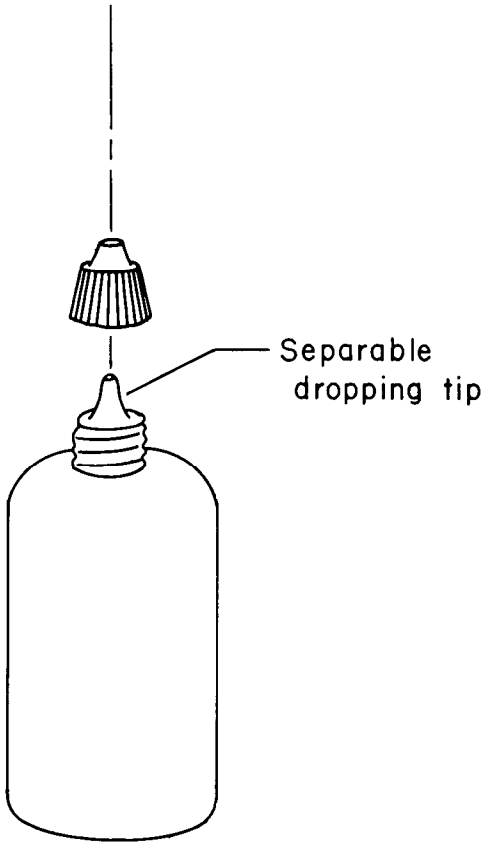


Figure 5 —Acid bottle used for field sampling

and pump columns for well construction. One solution to this potential contamination problem is the installation of a nonmetallic well and screen equipped with a nonmetallic pump or sampling device. This procedure is extremely expensive for an areal survey and is seldom practiced. Another solution to this problem is to confine the sampling to springs which are not in contact with metallic objects.

Because of the lack of definable springs in many aquifers and the near nonexistence of nonmetallic well construction, some compromise on the collection of samples for trace metals analysis is necessary. The usual compromise is to sample from a high capacity well which has been installed and operating for several years. The rationale of this choice is based upon the short time of contact of the water with the well structure (often less than 30 seconds). Except under unusual circumstances, the short contact should preclude contamination of the sample with trace metals. If samples from wells with metal construction are collected for trace metals analysis, this should be clearly stated with the published data.

Field-analysis procedures

Specific conductance

The specific conductance of a water sample is a measure of its ability to carry an electrical current under specific conditions. Specific conductance, which is a measure of the ionized salts, gives an indication of the concentration of dissolved solids in the water.

There are several reasons for determining the specific conductance of a sample in the field at the time of collection rather than waiting for a laboratory measurement. The field determination can be used as an aid in evaluating whether a sample is representative of water in the aquifer. For example, in new or little used wells, or in wells that have been recently drilled, grouted, or cemented, chemical changes in the pumped water may be rather large, and the well may require prolonged pumping to insure that the sample is representative of water in the aquifer. Specific-conductance determinations can be used to indicate that sufficient water has been pumped and that the quality of the water is stabilized.

A specific-conductance value that is markedly different from values obtained in nearby wells may indicate a different source of water, such as induced recharge, contamination from the surface, or leakage from a formation that contains water of different quality. Detection of an anomaly may indicate that more detailed sampling or reevaluation of the well is required. If so, the work can usually be done more economically at the time the original sample is collected rather than several weeks or months later.

The specific conductance of a sample can change with time owing to the precipitation of minerals from the water once the sample is in the environment of the container. A sample that has been acidified or otherwise treated will not yield an accurate representation of the specific conductance of the water in the

aquifer; therefore, it is essential to obtain an accurate field determination.

Summary of the method

The ability of a solution to conduct an electrical current is a function of the concentration and charge of the ions in solution and of the rate at which the ions can move under the influence of an electrical potential. As the number of ions per unit volume of solution increases, the rate at which individual ions can move decreases because of interionic attraction and other effects. A graph of total ion concentration versus specific conductance, even for solutions of a single salt, is a straight line only for values below 1,000 micromhos/cm. As specific conductance increases to above 5,000 micromhos/cm, the regression line curves significantly; beyond 50,000 micromhos/cm, the specific conductance may be an unsatisfactory index of ion concentration.

The temperature of the electrolyte affects the ionic velocities and, consequently, the specific conductance. For example, the specific conductance of potassium chloride (KCl) solutions changes about 2 percent per degree Celsius near 25°C.

Specific-conductance meters used in the field should be battery operated, should be equipped with temperature compensator, and should read directly in micromhos/cm at 25°C. The direct reading meter is recommended to save time in converting resistance values to specific conductance and to insure that the value is read in the field.

The cell should be checked before initial use and should be checked daily during regular use. A 0.00702 *N* potassium chloride (KCl) solution (dissolve 0.5234 g KCl dried at 180°C for 1 hour in distilled water and dilute to exactly 1 litre) has a specific conductance of 1,000 micromhos/cm at 25°C. Routine checks are made by using the 0.00702 *N* standard solution at the ambient temperature. The temperature control on the instrument is set at 25°C, and the ambient temperature of the standard KCl solution is recorded. A value of specific conductance is obtained and compared with the values given in figure 6 for the ambient temperature. The value obtained should be within 5 percent of that in figure 6.

Next, the temperature-adjustment knob is moved to the ambient temperature, and the meter is read. The value obtained should be 1,000 micromhos/cm, regardless of the ambient temperature. This procedure checks the temperature compensator, the conductance cell, and the electrical circuit of the instrument.

If the value obtained for the standard solution is not within the specified precision, the cell must be reconditioned and replatinized according to the instructions given in Brown, Skougstad, and Fishman (1970) or in the literature supplied by the manufacturer of the instrument. The carbon-type electrode supplied with some conductance meters needs no platinizing and should be replaced if it fails to perform to the specified accuracy.

Application and interferences

Apparatus

1. Mark V Electronic Switchgear (Chemicon Co.)[1] with cell constants of 0.1 and 1.0 or equivalent direct-reading meter.
2. Thermometer, 0–50°C graduated in 0.1°C.

Procedure

The following general procedure is supplemental to the instructions supplied by the manufacturer:

1. Rinse measuring cell with several volumes of sample water.
2. Bring temperature of cell to that of water being measured by immersing measuring cell in well discharge for at least 5 minutes. Some plastic cells have a high heat capacity and will cause drifting of the reading if not in thermal equilibrium with the sample.
3. Record reading, temperature, time, date, cell constant, and any meter constants.
4. Remeasure, with fresh sample, until reproducible readings are obtained.

Temperature

The temperature of ground water is important for numerous applications. For example, temperature measurements are critical in

[1]The use of brand names in this report is for identification purposes only and does not imply endorsement by the U S Geological Survey

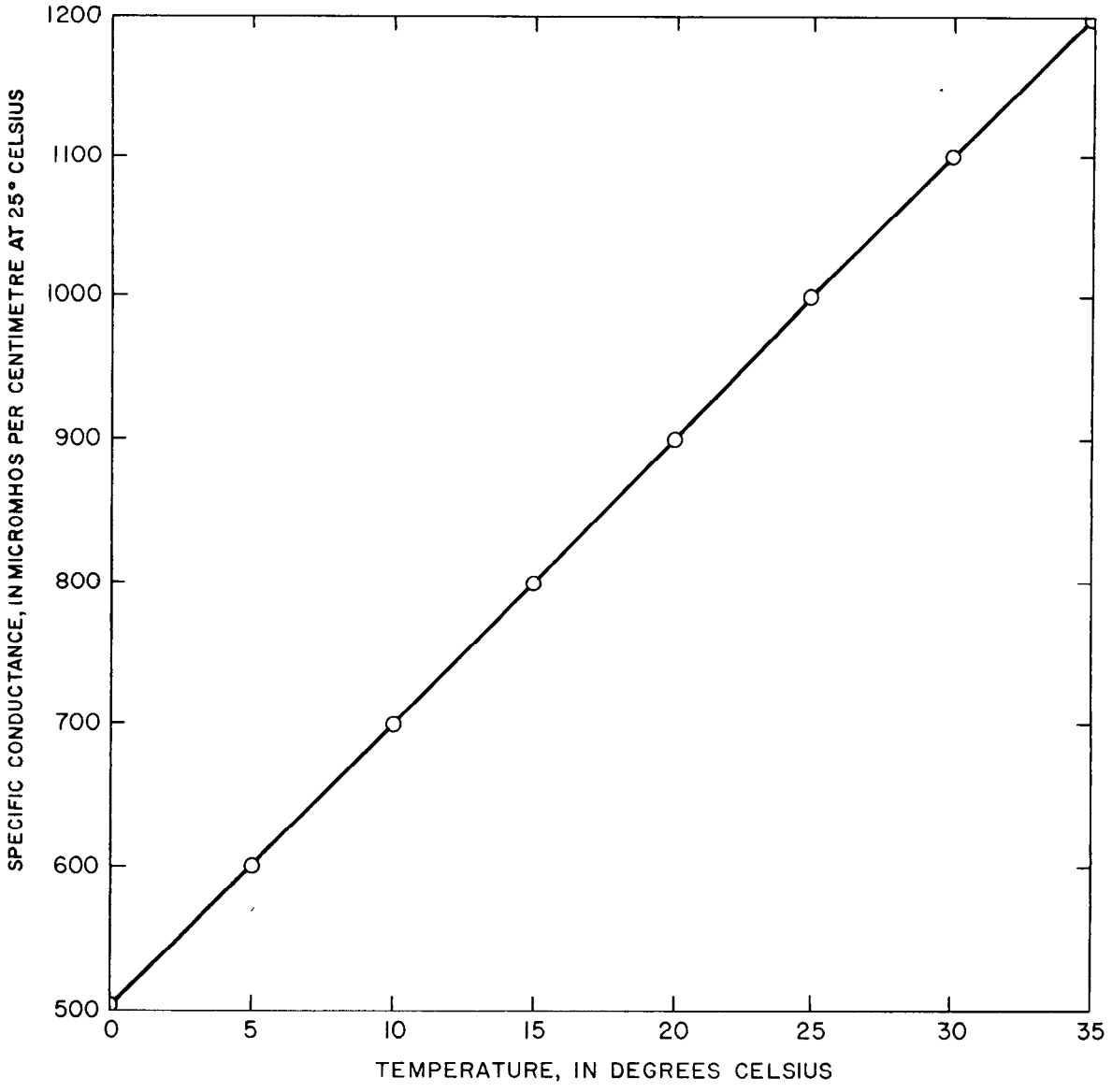


Figure 6 —Specific conductance of a 0 00702 N potassium chloride solution at various temperatures

identifying recharge from nearby surface-water sources. For accurate geochemical evaluation of equilibrium thermodynamics, it is desirable to know the temperature of the water in the aquifer within ±0.1°C.

Summary of the method

The temperature is recorded by a mercury-filled thermometer that is permitted to equilibrate in a sample that is continuously pumped into a dewar flask. The well should be pumped continuously until three identical consecutive readings of temperature are obtained.

Application and interference

The foregoing method may be used to measure the temperature of any ground-water sample but is most accurate when the ambient temperature is within 20°C of the ground-water temperature. New or little-used wells may develop new producing zones during pumping, thereby varying the proportion of

water entering the well from different depths and causing either an instantaneous change or continual drift in the temperature measurements. Drawdown may cause dewatering of certain beds and may cause a change in the temperature. Insufficient pumping time to allow equilibration of water temperature in the casing and pump column will also cause drifting of the temperature.

Apparatus

1. Dewar flask (a "thermos" bottle with a narrow mouth is adequate).
2. Partial immersion thermometer calibrated in 0.1°C or 0.2°F with the usual range of 5–25°C, or any range expected in the ground water in the study area. To minimize breaking the thermometer, steel or brass armor is suggested. The thermometer should be accurate to ±0.1°C as checked against the Bureau of Standards calibrated thermometer.

Procedure

Samples should be collected as close to the wellhead as possible. A continuous stream of water should be conducted through a short plastic tube into the bottom of the flask, allowing a continuous flow of water out of the flask. Readings should be taken after 5 minutes of flow at 1-minute intervals and recorded until no change is observed. If collection by continuous flow is impossible, the sample should be collected in the dewar flask and stoppered, with the thermometer inserted through the access hole. The first sample should be allowed to equilibrate 1 or 2 minutes and should then be discarded. The flask should be quickly refilled, and the temperature should be recorded immediately. This process should be continued until three identical consecutive readings are obtained. A box similar to that shown in figure 7 is useful for carrying equipment and preventing breakage.

pH of solutions

The pH of a solution is a measure of effective hydrogen-ion concentration or, more accurately, it is the negative logarithm of the hydrogen-ion activity in moles per litre:

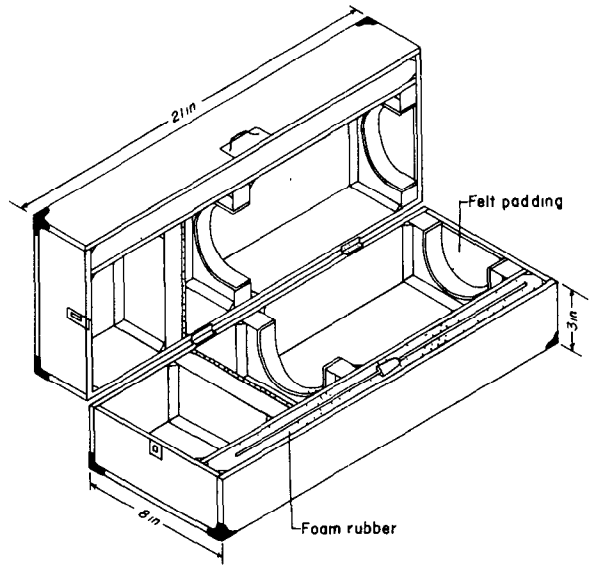


Figure 7.—Carrying box for thermometer, reading lens, and dewar flask

$$pH = -\log [H+].$$

In aqueous solutions, pH is controlled by reactions that produce or consume H+ including practically all dissociations of acids, bases, and hydrolysis. The primary control over pH in most potable ground water is the carbonate system including gaseous and dissolved carbon dioxide, bicarbonate, and carbonate ions. Other dissolved gases, such as hydrogen sulfide and ammonia, can also affect the pH of the solution.

Summary

The pH is determined with a glass hydrogen ion electrode compared against a reference electrode of known potential by means of a pH meter or other potential measuring device with a very high input impedance. A detailed description of pH and reference electrodes and their operations are given in Langmuir (1971), Durst (1969), and Garrels and Christ (1965). Because pH is exponentially related to concentration, great care must be exercised in making a measurement. Details of measurement are given by Barnes (1964).

Interference

A high sodium concentration will give an anomalous pH reading, which must be cor-

rected according to the recommendation of the manufacturer of the pH electrode. This correction is usually necessary only if pH is greater than 11, and sodium concentration is more than 10 moles per litre. Measurement of pH is temperature sensitive, so the standard buffers should be within ±1°C of the sample solution for precise determinations.

Apparatus, reagents, and checklist

1. Orion 401 pH meter or equivalent (a meter with a scale, at least 15 cm long, is necessary for detailed work of ±0.02 pH units).
2. pH buffer solutions 4.00, 7.00, and 10.00; 500 ml each.
3. Corning triple-purpose pH electrode 476021, or equivalent.
4. Orion single-junction reference electrode 90–01, or equivalent.
5. Filling solution for reference electrode.
6. Holder for electrodes, Multiflex or equivalent.
7. Plastic pail.
8. Thermometer.
9. Distilled water.
10. 500-ml plastic squeeze wash bottle for distilled water (color coded so as not to be confused with other reagents in wash bottles).
11. Box of small Kimwipes or equivalent.
12. Mixed bed deionizer in a delivery tube, 16-ounce size Deeminac or equivalent (useful for final treatment if commercial distilled water must be purchased).
13. Three 100-ml plastic beakers.
14. One 250-ml plastic beakers.
15. Card table or other portable table on which to work.

Procedure

The following procedure has been found useful in supplementing the pH meter manufacturer's instructions:

1. Check and fill reference electrode with internal filling solution recommended by the manufacturer. On Orion reference electrode, press cap and permit some of the filling solution to drain from the electrode to insure complete electrolite contact before inserting electrode in sample.
2. Adjust buffer solution and electrodes to ±1°C of the sample temperature by letting sample water run over submerged bottles and electrodes. (Be careful not to let sample water enter the filling hole of the reference electrode.) To prevent floating of partially filled buffer bottles, epoxy heavy steel washers to the bottom of the bottles. Alternatively, a small water bath can be constructed that holds two buffer bottles and sample beaker firmly in place during determination (fig. 8).
3. Record temperature of water.
4. Level meter and check to insure that the needle is properly adjusted.
5. Place 7.00 buffer in color-coded insulated beaker and place electrodes in the buffer. The pH of the buffer is equal to 7.00 only at 25°C; therefore, it is necessary to use the temperature-correction curve supplied by the manufacturer. Figure 9 is an example of a typical curve of temperature versus pH for a commercial buffer of pH 7.00. Turn on meter and adjust to correct pH value. If the electrodes have not been used recently, or have been allowed to dry for several days, it may take 10–20 minutes for them to stabilize. If electrodes will not stabilize, try either a new reference or pH electrode. To keep electrode from drying out and ready for use, the electrode tip should be immersed in a rubber or plastic sack (such as the finger cut from a plastic glove) in which has been placed a few millilitres of buffer solution.
6. Turn meter off or to standby position and remove electrodes from 7.00 buffer. Rinse thoroughly with distilled water and blot dry. Place electrodes in either pH 4.00 or pH 10.00 buffer, bracketing the expected pH of the sample. Switch on meter and allow several minutes for stabilization to occur before making final adjustment. Turn meter to off or standby position.
7. Check adherence of the response of the electrodes to the theoretical Nernst slope. According to manufacturer's instructions, and before adjusting meter with pH 7.00 buffer, the slope indicator is set to 100 percent, and the temperature compensator is set to the correct temperature (of water and buffer). After the electrode is placed in the second buffer, the temperature compensator is adjusted until the correct value of the second buffer is obtained.

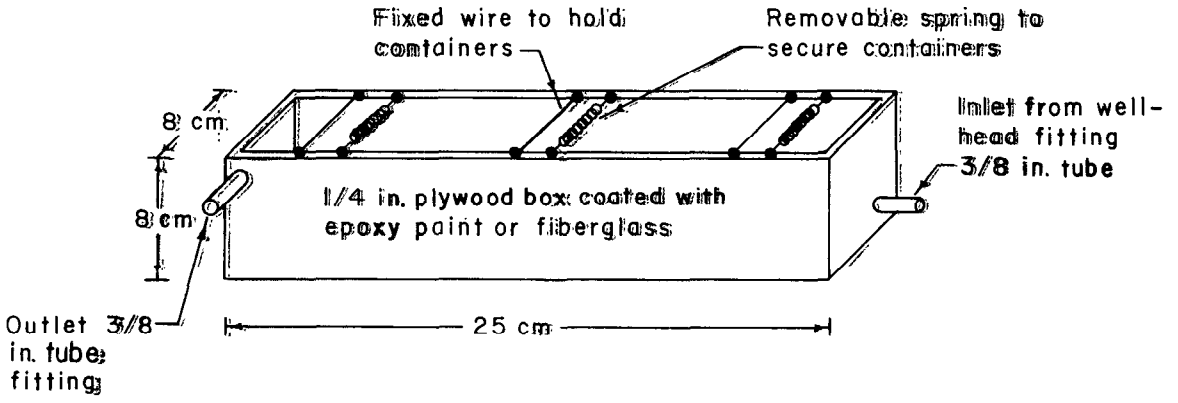


Figure 8.—Portable water bath for maintaining buffers and sample at wellhead temperature.

Then the slope indicator is adjusted until the temperature compensator points to the temperature of the solution. The percentage of theoretical slope can now be read on the slope scale.

Experience has shown that if the observed percentage differs from the theoretical value by ±10 percent, the reference electrode should be replaced and the slope rechecked by repeating steps 5–8. The theoretical Nernst slope for temperatures commonly encountered in ground water is shown in figure 10. Comparison of electrode response to the theoretical response (Nernst equation) is a check on the efficiency of the electrode system. The lack of agreement between the observed electrode system and the Nernst equation does not indicate that the observed pH values are inaccurate. All that is indicated is a potential source of trouble and some part of the system is not operating as efficiently as it should. Generally, combination pH-reference electrodes do not conform to the theoretical curve as closely as do the individual electrodes.

8. Rinse electrode with distilled water and blot dry. Recheck value of pH 7.00 buffer. If value is within ±0.02 pH of the correct value, proceed with next step. If drift from original setting has occurred, repeat steps 5–8.

9. Thoroughly rinse electrode with sample water and then place electrodes in a sample collected in a 250-ml plastic beaker. Turn on meter. Do not swirl or stir sample. Allow at least 2 minutes for equilibration. Record value. Turn meter to off or standby position. Repeat

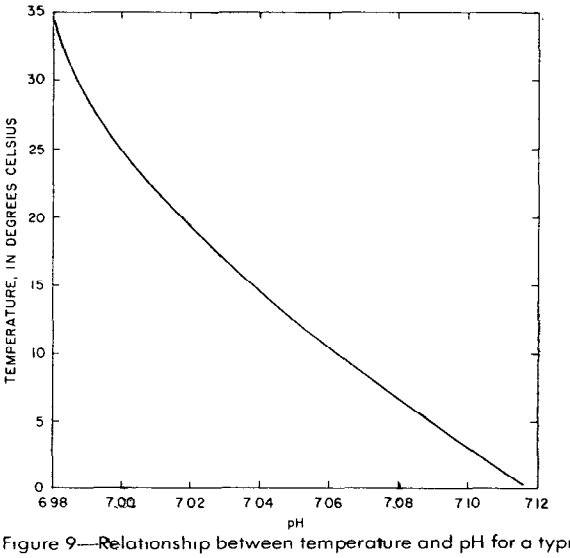


Figure 9—Relationship between temperature and pH for a typical commercial buffer solution

step 9, using newly collected samples until three consecutive readings differ by no more than ±0.02 pH unit. If equilibrium is not attained in several minutes, out gassing of CO_2 may be occurring. In such cases the initial reading may be the best. Out gassing may be reduced if the electrode system is placed through a tightly fitting stopper into the water-filled beaker.

10. Place electrodes in temperature equilibrated buffer 7.00. Turn on meter. If reading is within ±0.02 of original buffer reading, then analysis is complete. Turn meter off or to standby position. If reading has changed from original value, repeat steps 5–10. NOTE: In

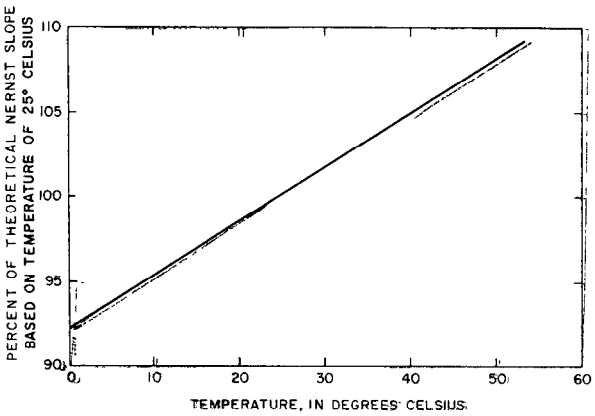


Figure 10.—Relationship between temperature and the Nernst slope.

dry windy climates, such as in the southwestern United States, a static charge tends to build on the plastic face of a pH meter, which causes erratic movement of the indicator needle. Antistatic spray, of the type used for phonograph records, sprayed on the meter face will minimize this interference. It is also desirable to keep the meter protected from extreme temperature changes during measurement, as this will affect the stability of the electronic system and consequently the precision of the measurement. In cold waters, slow electrode response may occur from the precipitation of the saturated filling solution in the reference electrode, thereby reducing the fluid contact. This can be remedied by allowing the filling solution to reach ambient temperature before filling the reference electrode.

Carbonate and bicarbonate

For chemical equilibrium calculations related to carbonate minerals, it is essential to have an accurate value for pH, carbonate, and bicarbonate concentrations. Carbonate and bicarbonate determinations for ground water must be made in the field at the time of sampling if the concentrations are to accurately represent those originally present in the water. These parameters are particularly subject to change if the sample is collected and stored in certain types of plastic bottles that are permeable to carbon dioxide.

Summary of the method

Detailed descriptions of the theory and practice of potentiometric titration of carbonate and bicarbonate is given in Barnes (1964), Weber and Stumm (1963), and Brown, Skougstad, and Fishman (1970). In general, the carbonate (CO_3^{-2}) and bicarbonate (HCO_3^-) concentrations are determined by titration of the water sample with a standard solution of strong acid. The following equations govern the reactions involved:

(1) $CO_3^{=} + H^+ \Longleftrightarrow HCO_3^-$

(This reaction is complete near pH 8.3)

and

(2) $HCO_3^- + H^+ \Longleftrightarrow H_2O + CO_2$,

(This reaction is complete near pH 4.5)

The end point of the carbonate or bicarbonate titration process is determined from (A) a plot of pH versus titrant volume, where the end point corresponds to an inflection point of the curve (fig. 11) or (B) a plot of

$$\frac{\Delta \text{ pH}}{\Delta \text{ ml of titrant}}$$

the rate of change in pH per unit volume of titrant versus the average titrant volume between two successive values. The end point is the value at which occurs the maximum rate of change of pH per volume of titrant added (fig. 11).

The approach in (B) is less subjective and permits consistent choice of the end point, but requires exacting analytical procedures and the assurance of complete equilibration of pH after each increment of acid added.

Salts of weak organic and inorganic acids, such as silica, which cannot be corrected for, may yield erroneous results when present in large amounts. In addition, oils, greases, and colloidal material, if present, may tend to foul the pH electrode and prevent its proper operation.

Apparatus and reagents

1. All equipment and reagents used for pH determinations. (See section on pH determination.)

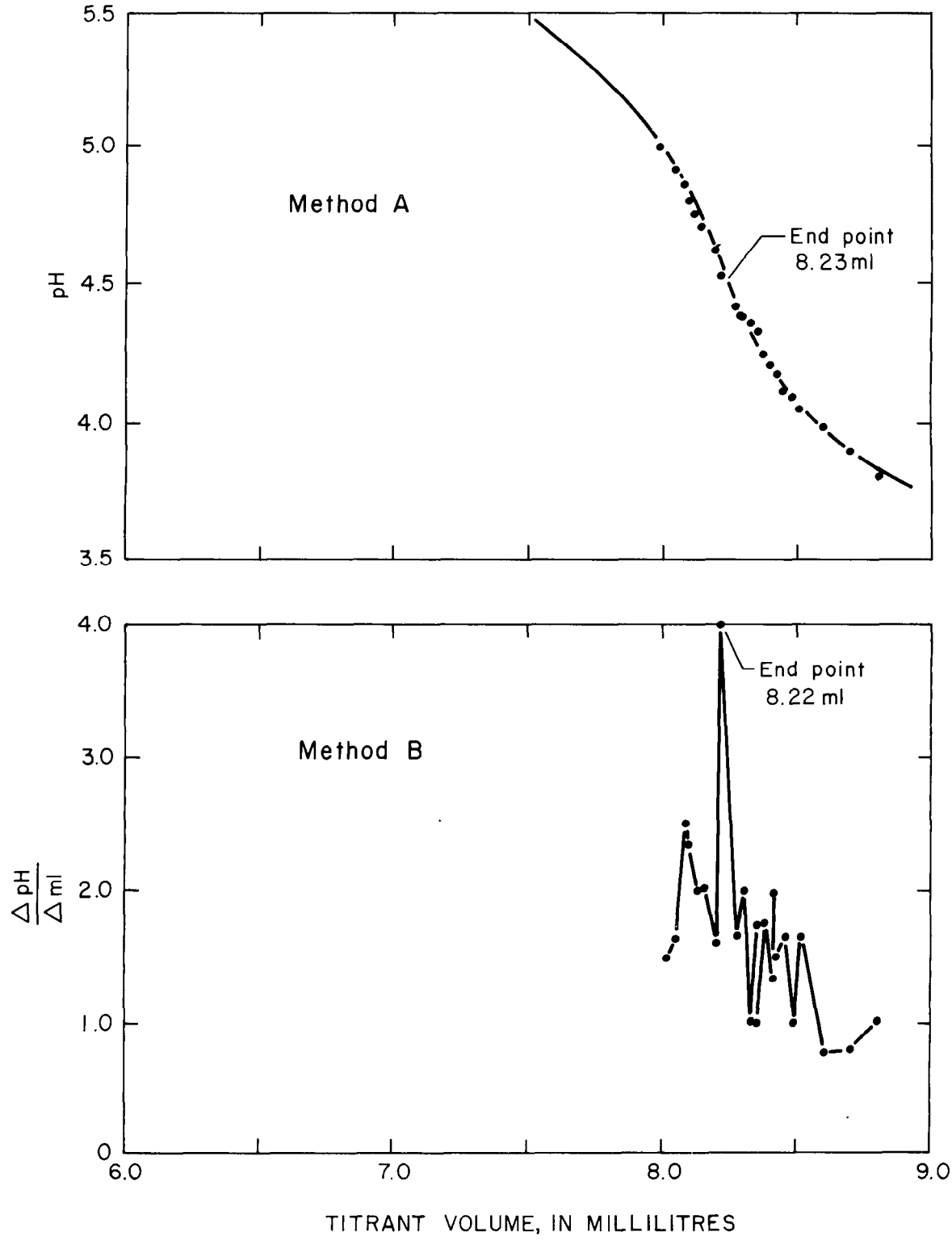


Figure 11.—Two methods of determining the end point for bicarbonate determinations.

2. Buret, 25-ml capacity with 0.1-ml graduation and Teflon stopcock.

3. Portable battery-powered magnetic stirrer, Lapine or equivalent with extra batteries.

4. Teflon coated stirring bar, small size.

5. Ring stand, clamp holder, and universal V-jawed clamp.

6. 25- and 50-ml class A volumetric pipets.

7. 250-ml plastic-squeeze acid bottle with nozzle for filling buret (color-coded bottle to prevent confusion with distilled water bottle).

8. 1 litre of 0.01639 *N* sulfuric acid packaged in two 500-ml plastic bottles to prevent breakage. (Prepared according to Brown and others, 1970).

9. Wire pen cleaner for dislodging foreign debris in buret tip.

10. Cap to prevent dust from entering buret.

11. Buret meniscus reader (useful for poor light conditions often encountered in the field).

A padded wooden box (fig. 12) is useful for carrying volumetric glassware and small accessories such as meniscus reader, stirring bar, wire pen cleaner, and so forth.

Procedure

1. Adjust temperature of titrant to ±2°C of the sample by immersion of securely stoppered acid-storage bottles in a water bath of the sample fluid; set up and fill buret to 0.00 ml; cap buret with dust cover.

2. From a pressure-filtered sample (see section on filtration) pipet 50 ml into a clean dry 100-ml beaker. Under no circumstances should the sample be diluted or concentrated in any way. The pipet is rinsed three times with the sample water before final sample is placed in the beaker. If titration cannot be completed with one filling of the buret, discard sample and use a smaller sample size. There is a great chance for error in refilling a buret during a titration.

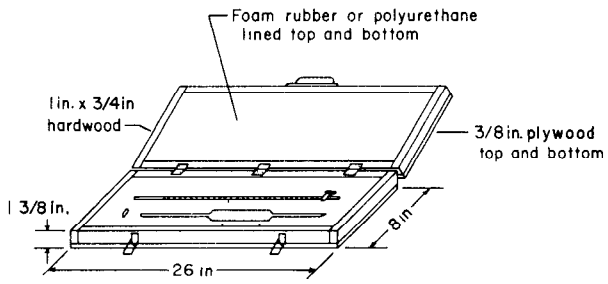


Figure 12 —Carrying box for volumetric glassware electrodes and other small fragile items.

3. Insert pH and reference electrodes into the sample. The electrodes should be calibrated in 7.00 and 4.00 buffer solutions at the temperature of the sample, then washed in sample or distilled water and blotted, not wiped, dry. (See section on pH determinations.) Insert the clean dry stirring bar and adjust stirrer to slow speed.

4. If pH is greater than 8.3, add sulfuric acid by drops, recording volume accurately with 0.05-ml increments and pH values to 0.02 pH units until pH is below 8.00 (See table 2 for useful recording format.)

When the pH of sample during titration declines below 8.00, or the initial value is less than 8.3, add acid in increments of 1 ml and record pH value at each increment. Continue this procedure until pH declines to approximately 5.5. From pH 5.5 to pH 4.0, add acid by

Table 2 —Results of a typical bicarbonate titration showing method of recording the data

pH	millilitres of acid	$\frac{\Delta \text{ pH}}{\Delta \text{ vol}}$
7.94	0.00	----
7.57	1.20	0.31
7.11	2.00	.57
6.79	3 00	.32
6 67	4.00	12
6 40	5 00	.27
6.14	6.00	.26
5.78	7.00	.36
4.98	8.00	80
4.95	8.02	1.50
4.90	8.05	1.67
4.85	8 07	2.50
4.78	8.10	2.33
4.74	8.12	2 00
4.68	8.15	2.00
4.60	8.20	1.60
4.52	8.22	4.00
4.42	8 28	1.67
4.38	8.30	2.00
4.35	8.33	1.00
4.30	8.35	1 67
4.25	8.39	1 67
4.21	8.41	2 00
4 18	8.43	1.50
4.13	8.46	1.67
4.10	8.48	1.50
4.05	8 51	1.67
3 98	8.60	78
3 90	8.70	.80
3 80	8.80	1.00

drops, recording pH at each volume increment. The most sensitive part of the titration is usually between 4.8 and 4.3. Adding acid in fractions of a drop is desirable in this range. (Carefully touch ¼ or ½ drop to sample surface and pull away from buret tip.) Allow 15–20 seconds for equilibration.

Calculations

Calculations for the carbonate content are made by using the equation

$$CO_3^{=} \text{ in mg/l} = \frac{1{,}000}{ml_{(s)}} \times (ml_{(a)} \text{ to end point near pH 8.3}) \times (0.9835).$$

Calculations for bicarbonate are made by using the equation

$$HCO_3^{-} \text{ in mg/l} = \frac{1{,}000}{ml_{(s)}} \times (ml_{(a)} \text{ between end points near 8.3 and 4.5} - (ml_{(a)} \text{ to end point near 8.3}),$$

where $ml_{(a)}$ and $ml_{(s)}$ = volumes of standard 0.01639 N sulfuric acid and samples, respectively, and end points are determined as in figure 11. Because of the relatively small amount of time required for this analysis, it is best to repeat titration to insure precision.

Eh (Oxidation-reduction potential)

A chemical reaction in which an element undergoes a loss or gain of orbital electrons is referred to as oxidation or reduction and may be represented by the following general expression:

$$\text{reduced species} \rightarrow \text{oxidized species} + ne^{-},$$

where ne- is the number of electrons involved per atom. The standard oxidation potential, $E°$, for a half-cell reaction of this type is the potential that would occur if the two species are both present at unit activity at 25°C and one atmosphere pressure. When the activities of participating species differ from unity, the potential observed at equilibrium is termed the redox potential (oxidation-reduction potential). The redox potential, represented by the symbol Eh, is related to the standard potential and the activities of participating substances by the Nernst equation:

$$Eh = E° + \frac{RT}{nF} \ln \frac{\text{oxidized state}}{\text{reduced state}},$$

where $E°$ is the standard potential of the reaction, R is the universal gas constant, T is the absolute temperature in degrees Kelvin, F is the Faraday constant, n is the number of electrons involved in a half-cell reaction, and $\ln \frac{\text{oxidized state}}{\text{reduced state}}$ is the natural logarithm of the ratio of the products of the activities of oxidized species to that of the reduced species. The potential is reported as volts or millivolts, relative to the potential of the hydrogen electrode, taken as zero, and may be positive or negative (the greater the negative value, the more the reducing tendency of the system). An excellent review article on Eh-pH determination has been presented by Langmuir (1971).

Some writers have preferred the notation "pE," defined as the negative logarithm of the molar activity of the electrons, which avoids some of the unit conversion calculations required by the Nernst equation (Stumm, 1966).

Eh is generally a qualitative tool for the ground-water geochemist. However, it has been used very effectively in explaining the concentration of many minerals that exhibit more than one oxidation state under natural conditions. See, for example, the relation of iron in natural water to Eh as shown by Back and Barnes (1965).

Summary of the method

Eh is measured with a noble metal (usually platinum) and a reference electrode system using a pH meter that can be read in millivolts. Reference solutions with known Eh are used to obtain the potential and to check the accuracy of the electrode system. Unlike pH buffer solutions, the Eh reference solutions are not used to adjust the system to the correct range of values. The potassium ferric-ferro cyanide solution described by ZoBell (1946), which has been proved satisfactory as a standard reference solution by many geochemists, is the standard recommended in this manual.

At 25°C, the potential of the ZoBell solution relative to the standard hydrogen electrode is +0.428 volts. The potential varies with temperature according to the following equation:

$$Eh = 0.428 - 0.0022\ (t-25)\ \text{volt}$$

(Ivan Barnes, oral commun., 1972).

At 25°C, the saturated calomel (mercury-mercurous chloride) reference electrode, which is commonly used, has a reference voltage of +0.244 volts relative to the potential of the standard hydrogen electrode. The voltage varies with temperature according to the following equation:

$$Eh = 0.244 - 0.00066\ (t-25)\ \text{volt}$$

(Garrels and Christ, 1965, p. 127),

where t is the temperature in degrees Celsius.

By combining the half-cell potentials for the platinum-calomel electrode system and ZoBell solution and utilizing the equations for potential variation with temperature (emf = $Eh_{ZoBell} - Eh_{Calomel}$), the theoretical potentials for the system at different temperatures can be calculated. The relationship of theoretical potentials of this system to temperature is shown in figure 13. The relationship for a silver–silver chloride reference electrode and platinum electrode system to temperature is also plotted in figure 13.

The measurement of Eh of a system requires that the observed potential be adjusted to a potential relative to the standard hydrogen electrode.

In equation form,

$$Eh_{Sys} = E_{obs} + Eh_{ZoBell+ref} - E_{ZoBell\ (obs)},$$

where

Eh_{Sys} = The true Eh of the environment, relative to the standard hydrogen electrode,

E_{obs} = the observed potential of the environment, relative to the reference electrode,

$Eh_{ZoBell+ref}$ = the theoretical Eh of the reference electrode and ZoBell solution, relative to the standard hydrogen electrode, and

$E_{ZoBell(obs)}$ = the observed potential of ZoBell solution, relative to the reference electrode.

Application and interferences

Redox potential measurements in laboratory solutions where activities of oxidized and reduced species may approach unity can be expected to match theoretical calculated potentials reasonably well. Experience has shown that many natural water systems do not give measured Eh values that can be quantitatively interpreted. Measurements made in water containing dissolved oxygen, for example, give values lower than might theoretically be expected. Garrels and Christ (1965) attribute this to a slow, rate-determining step in the reaction of aqueous oxygen with other ions. If dissolved oxygen (DO) is above 0.01 mg/l, the DO determination may be more useful than attempting to determine Eh. It is also generally useless to try to measure Eh in systems containing hydrogen sulfide.

Back and Barnes (1965) were able to correlate measured redox potentials with dissolved ferrous iron contents of ground water in moderately reducing systems. Most other experiences with Eh measurements that are described in the literature lead one to conclude that the measurement is primarily a qualitative tool. It may give useful information about systems whose solid and solute components are reasonably well known from other kinds of

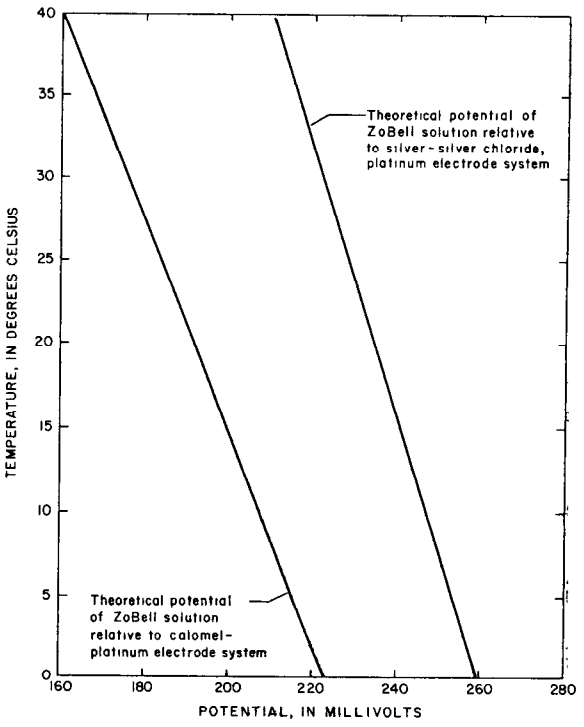


Figure 13.—The potential of ZoBell solution, relative to reference-electrode systems, at various temperatures

measurements. Limitations and uncertainties inherent in Eh measurements were discussed by Stumm (1966) and Doyle (1968). Charged colloidal material and differences in composition and concentration of the unknown and reference solutions may create errors. Oil and grease may coat the noble-metal electrode, preventing contact with the sample.

Apparatus and reagents

1. Orion 401 specific-ion meter or equivalent.
2. Orion combination electrode 96–78–00 or equivalent and Orion electrode filling solution 90–00–01 or equivalent. (Thimble platinum and separate reference electrodes are also suitable.)
3. ZoBell reference solution:

Dissolve

1.4080 g of potassium ferrocyanide $K_4Fe(CN)_6 3H_2O$ (0.00333*M*)

1.0975 g of potassium ferricyanide $K_3Fe(CN)_6$ (0.00333*M*)

7.4555 g of potassium chloride KCl (0.10*M*)

in distilled water to make 1 litre. This solution is stable for several months but should be kept in a black plastic bottle and out of sunlight as much as possible. It has a standard potential of +428 millivolts at 25°C. This solution is poisonous and should be handled with care.

4. Ring stand, clamp holder, and universal V-jawed clamp.
5. Eh cell (fig. 14).
6. Plastic 100-ml beaker.
7. Water bath for ZoBell solution (plastic pail or bottom half of a 1-gallon plastic bottle).
8. Thermometer.
9. Equipment for measuring dissolved oxygen.
10. Small strips of crocus cloth for polishing platinum electrode.

Procedure

1. Fill combination electrode with proper filling solution (Orion 90–00–01 or equivalent). Depress body and let some of the fluid drain to waste. Bring ZoBell solution to the temperature of sample by allowing sample to flow over closed bottle. Record temperature. While the ZoBell solution is equilibrating to the sample temperature, determine the presence of dissolved oxygen in the water sample. If dissolved oxygen is greater than 0.05 mg/l, do not proceed with the Eh measurement. If dissolved oxygen is absent, proceed with step 2.

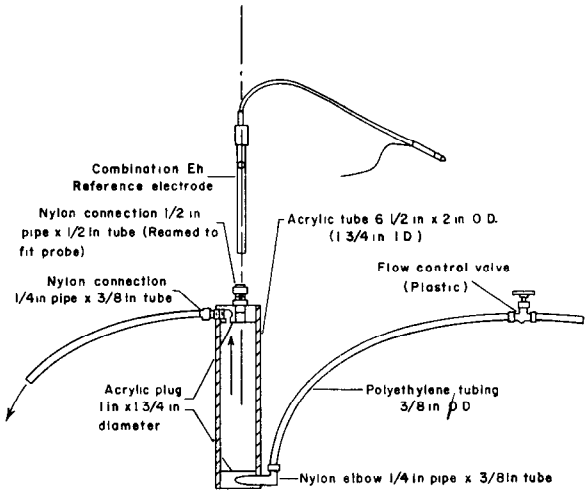


Figure 14 —Eh measuring cell

2. Place combination electrode in the ZoBell solution that has been equilibrated to the sample temperature. Plug electrode leads into meter and turn function switch on meter to millivolt mode. Allow several minutes for electrode to equilibrate while maintaining the bottle of ZoBell solution in the water bath. Record reading. If reading differs by more than 10 millivolts from the theoretical value at that temperature (fig. 13), replace reference electrode fluid and repeat measurement. If that procedure will not bring the reading within 10 millivolts of the theoretical value, polish the platinum end of the electrode with a piece of crocus cloth and recheck reading. If this procedure fails, the electrode should be replaced. If reading is within ±10 millivolts of the theoretical value, rinse electrode with sample water and proceed with step 3.

3. Place electrode in the plastic Eh cell pointing up (fig. 13) and let the water flow through the cell. Filler hole in side of electrode should be above the top of Eh cell. Make sure all air bubbles are removed from the system. Use control valve on inlet to insure that the head of sample is below level of reference solution of the electrode or some of the sample will be forced into the reference electrode and

change the potential of the system. Clamp Eh cell onto the ring stand.

4. Turn function switch on meter to millivolt mode and allow the water to flow through the cell until the readings stabilize. Stabilization usually occurs within 20 minutes but may require as much as an hour or more. Turn off sample flow to prevent any streaming potential and immediately record meter reading. This is the observed Eh of the sample, or more specifically, the observed full-cell emf relative to the reference electrode.

5. Record the data and calculate the Eh relative to the standard hydrogen electrode as follows:

Data record

A. Temperature of sample _____
B. Observed potential, in millivolts, of ZoBell solution, relative to reference electrode, at sample temperature _____
C. Theoretical potential, in millivolts, of ZoBell solution, relative to reference electrode, of sample temperature (fig. 13) _____
D. Theoretical potential, in millivolts, of reference electrode system and ZoBell solution, relative to the standard hydrogen electrode, at sample temperature (fig. 15) _____
E. Observed potential of sample, in millivolts _____

Calculations

I Checking the electrode

Calculate difference between observed potential and theoretical potential of ZoBell solution, relative to reference electrode,

$$B - C = \text{difference}.$$

If this difference is less than ±10 millivolts, proceed with next step. If difference is greater than ±10 millivolts, see step 2 of procedure for remedial measures.

II Calculate the Eh of the system

E−B+D=Eh value of the system. Report Eh value [either positive (+) or negative (−)] to nearest 10 millivolts.

A field example may help to clarify the procedure:

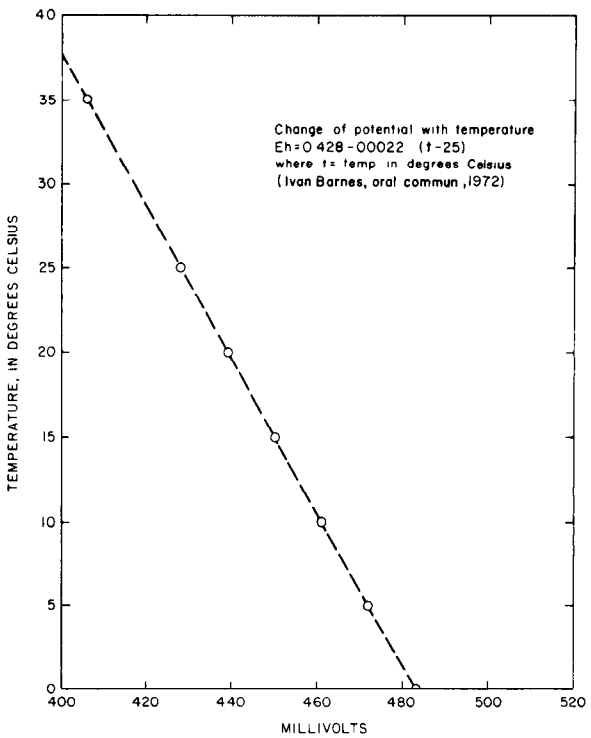


Figure 15.—The potential of ZoBell solution, relative to the standard hydrogen electrode, at various temperatures.

October 6, 1971 @ 0930, St. Paul, Minnesota; G. Ehrlich, H. Reeder, W. Wood
Well 2–N, artificial-recharge site 539 feet deep, 6-inch diameter, finished in the Prairie duChein
Pumping 10 gal/min for 22 hours
Temperature of water from well is 10.0°C

The observed potential of ZoBell solution, relative to the combination reference–platinum electrode, at 10°C was +215 millivolts. (Theoretical potential for ZoBell solution, relative to this electrode system, at 10.0°C is +207 millivolts (fig. 13). The 8-millivolt difference was considered small, and the decision was made to proceed with the measurements.) The observed potential of the water sample after system stabilized in 30 minutes was −120 millivolts.

Data record:

A. Temperature of sample _____ 10°C
B. Observed potential, in millivolts, of ZoBell solution, relative to reference

electrode, at sample temperature ---- +215

(C. Theoretical potential, in millivolts, of ZoBell solution relative to reference electrode, at sample temperature (from fig. 13) ---------- +207

(D. Theoretical potential, in millivolts, of reference electrode system and ZoBell solution, relative to standard hydrogen electrode, at sample temperature (fig. 15) ---------- +461

(E. Observed potential of sample, in millivolts ---------- −120

(Calculations:

(I. B−C=(+215)−(207)=+8 millivolts

(II. Eh_{sys}=E−B+D=(−120)−(215)+(461)=+126 millivolts

(Report at +130 millivolts.

Dissolved oxygen

Oxygen dissolved in ground water usually is derived from contact with the atmosphere before recharge to the aquifer. The solubility of oxygen in water is dependent upon the partial pressure of oxygen in the atmosphere, the dissolved solids, and the temperature. The experience of the author has indicated that the presence of dissolved oxygen in ground water is a more common occurrence than is generally believed. This is particularly true in hydrologically stressed systems. Dissolved oxygen can exist at great depths in aquifers which have little or no oxidizable material in the water flow path and can also be present in any aquifer where the water's residence time is short compared to the rate of oxygen consumption.

Summary of the method

Methods commonly used for the determination of dissolved oxygen are described in "Standard Methods for the Examination of Water and Wastewater" (American Public Health Association and others, 1971). Some of these methods are subject to rather serious interferences. Regardless of the method used, great care must be taken to prevent atmospheric aeration of the sample during collection and analysis. Use of a flow chamber to prevent contact of the sample with the atmosphere and use of a portable dissolved-oxygen meter for analysis eliminates or minimizes the effects of most interferences and yields a continuous record of dissolved oxygen during the pumping of a well.

The sensing element of the dissolved-oxygen meter is basically a polarographic system in which two solid metal electrodes in contact with an electrolyte are separated from the test solution by an oxygen-permeable membrane. The membrane serves as a diffusion barrier against impurities. The rate that oxygen diffuses through the membrane is proportional to the pressure differential across the membrane. When oxygen diffuses through the membrane, it is rapidly consumed at the cathode. Thus, the rate of diffusion is proportional to the absolute pressure of oxygen outside the membrane. When a suitable polarizing voltage is applied across the cell, the consumption of oxygen at the cathode causes a current to flow through the cell. This current is directly proportional to the quantity of oxygen consumed.

For precise dissolved-oxygen determinations, the meter should be calibrated before each use. Preferably, the calibration should be accomplished on the water under test. One sample of the water should be deoxygenated by adding an excess of sodium sulfite; a second sample should be aerated to saturation. The dissolved-oxygen concentration of the air-saturated sample can be determined from figures 16 and 17, provided the water temperature, barometric pressure, and altitude of the sampling site are known. In the absence of interferences, a more precise dissolved-oxygen value for the aerated sample can be determined by use of the Alsterberg azide modification of the Winkler method (Brown and others, 1970, p. 126) or any approved modification of this technique. Where interfering substances are suspected, calibration should be accomplished on distilled water aerated to saturation.

The meter must be precisely calibrated according to the manufacturer's instructions before each use. In general, satisfactory calibration can be accomplished by using air-saturated water. In this procedure, the water sample is aerated by being shaken in the presence of air for 15–20 minutes (a 1-litre uncapped narrow-mouthed bottle half full works well) or by using a battery-powered aerator for

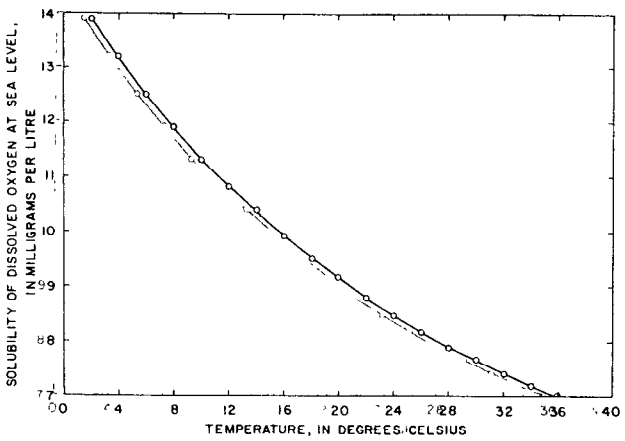


Figure 16.—Solubility of oxygen in water at sea level as a function of temperature.

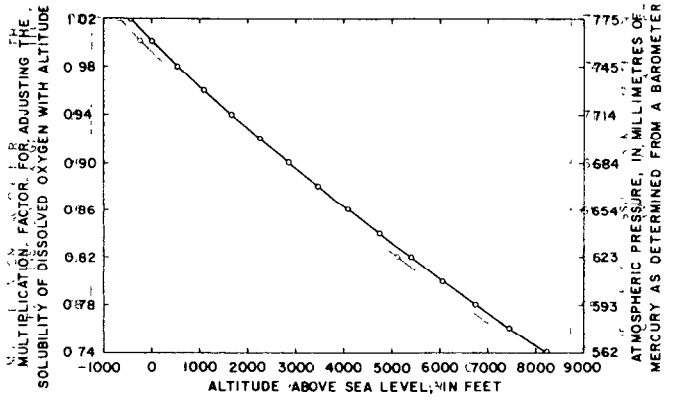


Figure 17.—Correction factor for the solubility of oxygen at different atmospheric pressures and altitudes.

5–10 minutes. Temperature of the water is then measured. Figure 16 shows the dissolved-oxygen concentration of air-saturated water at sea level as a function of temperature. Figure 17 shows correction factors that must be applied to the apparent oxygen concentration when the atmospheric pressure varies from 760 mm of mercury. By use of these figures, the correct value of oxygen dissolved in the air-saturated sample can be obtained and the meter calibrated.

Application and interferences

The membrane-electrode method is applicable for the measurement of dissolved oxygen in any well or spring from which a sample can be collected without aeration.

Oxygen-permeable membranes used for the electrode system are permeable to a variety of other gases, none of which is easily depolarized at the indicator electrode. In addition, the concentrations of most of these gases in ground water probably are too small to cause significant interference with dissolved-oxygen determinations. However, use of the membrane electrode in water containing such gases as hydrogen sulfide without loss of sensitivity requires frequent changing of the membrane, replacement of the electrolyte, and recalibration of the electrode.

Apparatus and reagents

11. Yellow Springs model 54 ARC oxygen meter with sensor, or equivalent.
2. Flow chamber with flow control valve (fig. 18).
3. Ring stand, clampholder and universal V-jawed clamp.
4. Bottle of electrolyte for the sensor.
5. Extra membranes for the sensor.
6. Thermometer.
7. Two 8-ounce plastic bottles.
8. 1-litre plastic bottle for aeration of the reference sample.
9. Battery-operated aerator.

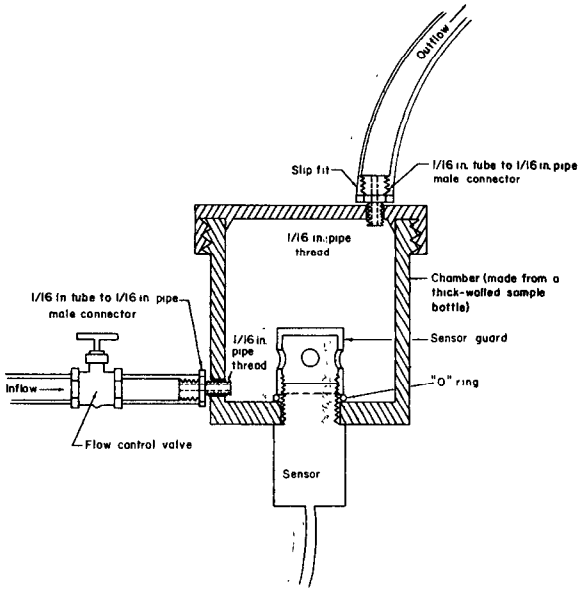


Figure 18.—Flow chamber for determination of dissolved oxygen from a pumped well.

10. Battery-operated magnetic stirrer and stirring bars.
11. Saturated solution of sodium sulfite.
12. Cobaltous chloride solution.
13. Reagents and plasticware for Alsterberg azide modification of Winkler method for dissolved-oxygen determination (Brown and others, 1970, p. 126).

Procedure

1. Pour sample into an 8-ounce plastic bottle to which has been added several millilitres of saturated solution of sodium sulfite and a trace of cobaltous chloride. Replace cap and stir on magnetic stirrer for several minutes.
2. Prepare oxygen meter for calibration according to manufacturer's instructions.
3. Switch meter to the 0–10 position. Remove sensor guard and insert the sensor in deaerated sample. If dissolved oxygen in sample is greater than 0.0 mg/l, add saturated sodium sulfite in small increments until a reading of 0.0 mg/l is obtained. Add an excess of several millilitres after a reading of 0.0 mg/l is obtained.
4. Pour a second sample into a 1-litre plastic bottle and aerate for 5–10 minutes with battery-operated aerator.
5. Determine the dissolved-oxygen concentration on an aliquot of the aerated sample by the Alsterberg azide method (Brown and others, 1970, p. 126). If the barometric pressure is known, the dissolved-oxygen concentration of the air-saturated sample can be determined from figures 16 and 17.
6. Pour an aliquot of the aerated sample into a clean 8-ounce plastic bottle. Switch meter to the 0–10 position and insert the sensor in aerated sample. Adjust speed of magnetic stirrer until maximum reading is obtained.
7. With the calibration control, adjust the dissolved-oxygen reading to the value obtained by step 5.
8. Place sensor in the flow chamber (fig. 18). Place the "O" ring over the sensor, being careful not to disturb the membrane. Replace sensor guard and tighten until the "O" ring is depressed very slightly. Place the top on the flow chamber and gently open the flow control valve. Measure the dissolved-oxygen concentration at about 5–10 minute intervals until a stable reading is obtained. Record the value to the nearest 0.1mg/l.

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APPENDIX D-II

Continuous Recording Instrumentation Specification Sheets

Downhole Pressure and Temperature Gauge

NAO Region Technical Specification Sheet

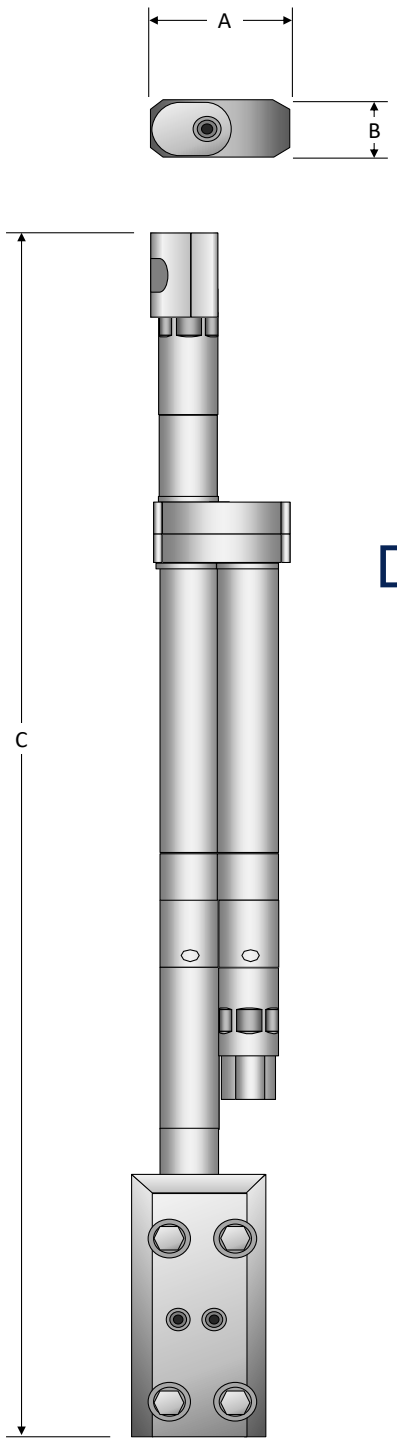
Baker Hughes

Product: SureSENS QPT Elite Dual Gauge

Material Number: H307570135

Drawn By: Brenton Smith
Tyrone Dominique
Date: 10/11/2024
Drawing Number: NAO H307570135 REV0

Drawing



Technical Information

DESCRIPTION:

SURESENS QPT ELITE DUAL
(ANNULUS/TUBING) 10K PSI 150 DEGC CLBD
TEMP .750 IN DIA X 1.790 IN 26.328 IN
LG BMS-N201 NI ALLOY 718 120 KSI MYS 1
CBLHD MANIFOLD TOOL ADDRESS 1 TOOL
ADDRESS 2 NO ADDRESS 3 ANNULUS PRESSURE
SOURCE 1 TUBING PRESSURE SOURCE 2 NO
PRESSURE SOURCE 3

DIMENSIONAL DATA (INCHES):

A	1.790 IN WIDTH
B	0.750 IN DEPTH
C	26.328 IN LENGTH

Downhole Pressure and Temperature Gauge

PERFORMANCE PARAMETERS:
(EXCLUSIVE OF THREADS)

TRANSDUCER	SHEAR MODE QUARTZ
TRANSDUCER RATING	10,000 PSI
PRESSURE RANGE	15-11,000 PSI
TEMPERATURE RATING (OPERATING)	-99.4 TO 302°F (-73 TO 302°C)
TEMPERATURE SHOCK	5.4°F (3°C) PER MINUTE
VIBRATION	>10 G, 10 HZ - 2 KHZ
SHOCK	500 G
PRESSURE MEASURE RANGE (CALIBRATED)	200 -10,000 PSI
PRESSURE ACCURACY	±0.015% 1.5 PSI (AT FULL SCALE)
PRESSURE RESOLUTION	0.0001
PRESSURE STABILITY	±0.02% FULL SCALE, 2.0 PSI/YEAR
TEMP MEASUREMENT RANGE (CALIBRATED)	77 TO 302°F (25 TO 302°C)
TEMPERATURE ACCURACY	0.27°F (0.15°C)
TEMPERATURE RESOLUTION	0.0001°F
TEMPERATURE STABILITY	0.018°F (<0.01°C) PER YEAR
MAX SAMPLE RATE/SECOND	>16
TOOL ADDRESS	T1/T2

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SureSENS QPT ELITE Downhole Pressure Temperature Gauge

Product Family H30757

Last Four Revisions					
Rev.	RDR	Amendment Detail	Reviewer	Approver	Effective Date
H	5226/RM	Added NOTE to product selection chart; additional changes throughout document; revision level is being aligned to reflect master document/document family for SU 100950.	Rendall, Lorn	Lake, Ben	28 Apr 2023
G	—/RM	The content of this document has not been effected; revision level is being aligned to reflect master document/document family for SU 100950.	Rendall, Lorn	Lake, Ben	10 Dec 2022
F	4996/RM	Updates throughout document; revision level is being aligned to reflect master document/document family for SU 100950.	Rendall, Lorn	Lake, Ben	18 May 2022
E	3236/RM	Updates throughout document	Freeman, Joe	Scott, Thomas M	27 Sep 2018

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1 Introduction

The SureSENS™ QPT ELITE tools are pressure/temperature gauges suitable for single or multipoint reservoir monitoring in either single or multiple-gauge configurations. The gauge is highly robust, ensuring mechanical integrity by deep-penetration and high-vacuum, electron-beam fusion welds, without the need for filler material.

2 Description

The Baker Hughes Company SureSENS QPT ELITE gauge for permanent downhole installations measures static and dynamic pressures and temperatures with introducing a step change in reliability and accuracy. The gauge is qualified for operation at pressures less than 35,000 psi (2,413.1 bar) and temperatures up to 437°F (225°C).

The static pressure information obtained can be used to determine production performance, calculate reserves, and provide input to reservoir simulations. The dynamic pressure data can help determine reservoir characteristics and optimize production rates.

The SureSENS QPT ELITE gauge includes the new ELITE electronics package, built upon our industry leading STAR hybrid electronic package design. The ELITE electronics package incorporates an application specific integrated circuit (ASIC), providing a new level of reliability to the industry.

3 Application

The cost-effectiveness and flexibility of the SureSENS system enables deployment in single- or multiple-gauge applications and is especially suited to downhole applications, which have bottomhole pressures of less than 35,000 psi (2,413.1 bar) and bottomhole temperatures of less than 437°F (225°C). The applications can be tied back to a surface or floating facility, or interfaced with a subsea infrastructure. The flexibility of the system enables the selection of a number of parameter measurements, including single-point zonal pressure measurements to multiple-point pressure measurements (multiple zones or intelligent applications), as well as applications where differential pressure measurements are required (e.g., fluid characterization or flowmeter applications).

4 Features and Benefits

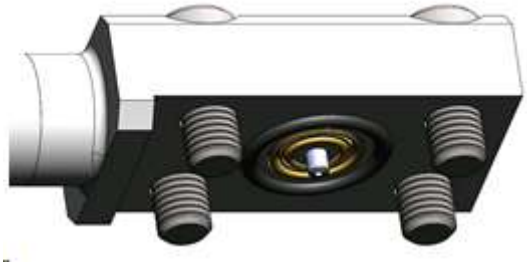
- ELITE electronics package
  - Provides superior reliability in demanding high-pressure/high-temperature (HP/HT) conditions.
- Flexible, compact design
  - Easily change gauge and pressure porting configurations without modifying the carrier.
  - Multiple gauge combinations can be deployed on single standardized carrier.
- Unique construction configurations with less connections
  - Eliminates the need for additional splices.
  - Increases reliability.
  - Reduces installation time.

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- Supports multiple monitoring devices on single tubing encapsulated conductor (TEC) cable
  - Deploys multiple gauges, flowmeters, and valve positions to provide redundant readings.
  - Serves as platform for future developments.
- Proprietary counting method and broad sample gate duration
  - Derives finest P/T measurement resolution attainable.

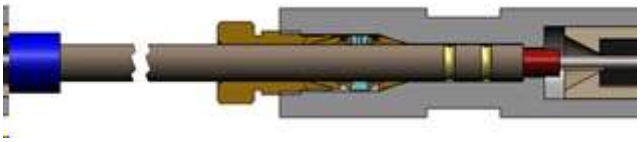
Pressure Interface Manifold

The gauge pressure interface connection to the carrier are dual metal C-rings that can be externally tested in the direction which it will experience pressure, eliminating the need for an internal pressure test tool.



Cable Head

The TEC's primary seal is a dual metal-to-metal pressure-testable interface, and the mechanical package is completely integrated into the gauge assembly, which eliminates the requirement for external Y-block components.



Gauge Addressing

The SureSENS QPT ELITE gauge supports multiple node addresses that range from 1–32 with a maximum of 32 gauges in multidrop applications. For these applications, the bottom gauge will not require a feed through. All other gauges above the bottom gauge deployment will require a TEC feedthrough which connects each gauge in the well without the use of a Y-splice assembly.

Each gauge has its own unique address expressed in the nomenclature T1, T2, T3, etc. Default tool addressing will be Single – T1, Dual – T1/T2, Triple – T1/T2/T3.

Example: If three dual gauges were to be deployed in the same well, all six tools must have an individual tool address, this would require three different material numbers to be ordered* as shown in address designation for multidrop application (Table 1).

Table 1: Address Designation for Multidrop Application

Example Configuration	Tool Address
Dual gauge 3 with feedthrough	T5/T6
Dual gauge 2 with feedthrough	T3/T4
Dual gauge 1	T1/T2

Note: Tools with the same addresses cannot be run on a single TEC system.

*Refer to product selection chart (Table 6) for information on tool addresses.

5 Engineering Tables and Information

Table 2: Specification Guide

Description	Value				
Length (in.)	25.5 to 26.5 (60.96 cm to 67.31 cm)				
Diameter (in.)	0.75 to 2.50 (19.05 mm to 57.15 mm)				
Seals	Metallic seals and EB welds				
Transducer	Shear mode quartz				
Transducer options (psi)	10,000 (689.5 bar)	16,000 (1,103.2 bar)	20,000 (1,379.0 bar)	25,000 (1,723.6 bar)	30,000 (2,068.4 bar)
Material	*Inconel*® 718		MP35N		
Pressure range (psi) (operating at 150°C)	15–11,000 (1–758.4 bar)	15–18,000 (1–1,241.1 bar)	15–23,500 (1–1,620.3 bar)	15–28,000 (1–1,930.5 bar)	15–33,000 (1–2,275.3 bar)
Temperature rating (operating)	-99 to 302°F (-73 to 150°C)	-99.4 to 437°F (-73 to 225°C)			
Storage temperature (°F)	-40 to 302 (-40 to 150°C)				
Temperature shock (°F)	5.4 (3°C) per minute				
Vibration	>10 G, 10 Hz-2 kHz				
Shock	500 G				
Pressure measure range (calibrated)	200–10,000 psi (13.8–689.5 bar)	200–16,000 psi (13.8–1,103.2 bar)	200–20,000 psi (13.8–1,379.0 bar)	200–25,000 psi (13.8–1,723.6 bar)	200–30,000 psi (13.8–2,068.4 bar)
Pressure accuracy	±0.015% 1.5 psi (at full scale)	±0.02% 3.2 psi (at full scale)	±0.02% 4.0 psi (at full scale)	±0.02% 5.0 psi (at full scale)	±0.025% 7.0 psi (at full scale)
Pressure resolution (psi)	0.0001				
Pressure stability	±0.02% full scale, 2.0 psi/year	±0.02% full scale, 3.2 psi/year	±0.02% full scale, 4.0 psi/year	±0.02% full scale, 5.0 psi/year	±0.02% full scale 7.0 psi/year
Temperature measurement range (calibrated)	77 to 302°F (25 to 150°C)	77 to 437°F (25 to 225°C)			
Temperature accuracy (°F)	0.27 (0.15°C)				
Temperature resolution (°F)	0.0001				
Temperature stability	0.018°F (<0.1°C) per year				
Maximum sample rate/second	>16				
Number of gauges support/TEC	32				
Cable distance transmission (ft)	50,000 (15,240 m)				

Inconel is a registered trademark of Special Metals Corporation.

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Ordering Guide

Deliverables

All orders for SureSENS QPT ELITE gauges will have the following items delivered:

- SureSENS QPT ELITE gauge
- Certificate of conformance (COC)

Note: All installation kits and redress kits are ordered separately.

Note: Coefficient files and calibration information are available at go/gauge.

Table 3: Accessory Equipment

Material	Description
10456966	Opposing ferrule seal (OFS) install kit
10456879	Manifold install kit
H0J0324100*	OFS blanking plug assembly
H0J1236900**	External pressure testing fixture

*To be used in applications where the lowest gauge in the completion has been ordered with electrical feedthrough and requires to be blanked off.

**For applications where OFS seals require to be tested in the direction of pressure

Table 4: Opposing Ferrule Seal Install Kit Bill of Material

Description	Qty. Req'd	Material
1/4-in. Front Ferrule	2	10369916
1/4-in. Rear Ferrule	2	10369914
Activator	1	H0J0145801
Expansion Ring	1	H0J0145100
Gland Nut	1	H0J0145201
Spring Insert	1	10372093
Test Port Plug	1	H0J0385400
Tungrease CF-33E	1	H0J0626700

Table 5: Manifold Install Kit Bill of Materials

Description	Qty. Req'd	Material
0.375-in. OD Crush Ring	1	10452446
0.436-in. OD Crush Ring	1	10452447
Port Block Seal	1	P630-0035-ZZ
2-017 *Kalrez*® O-ring	1	10599692

Description	Qty. Req'd	Material
Blanking Plugs	2	H0J0385400

Kalrez is a registered trademark of DuPont Performance Elastomers L.L.C.

Figure 1: Configuration examples.

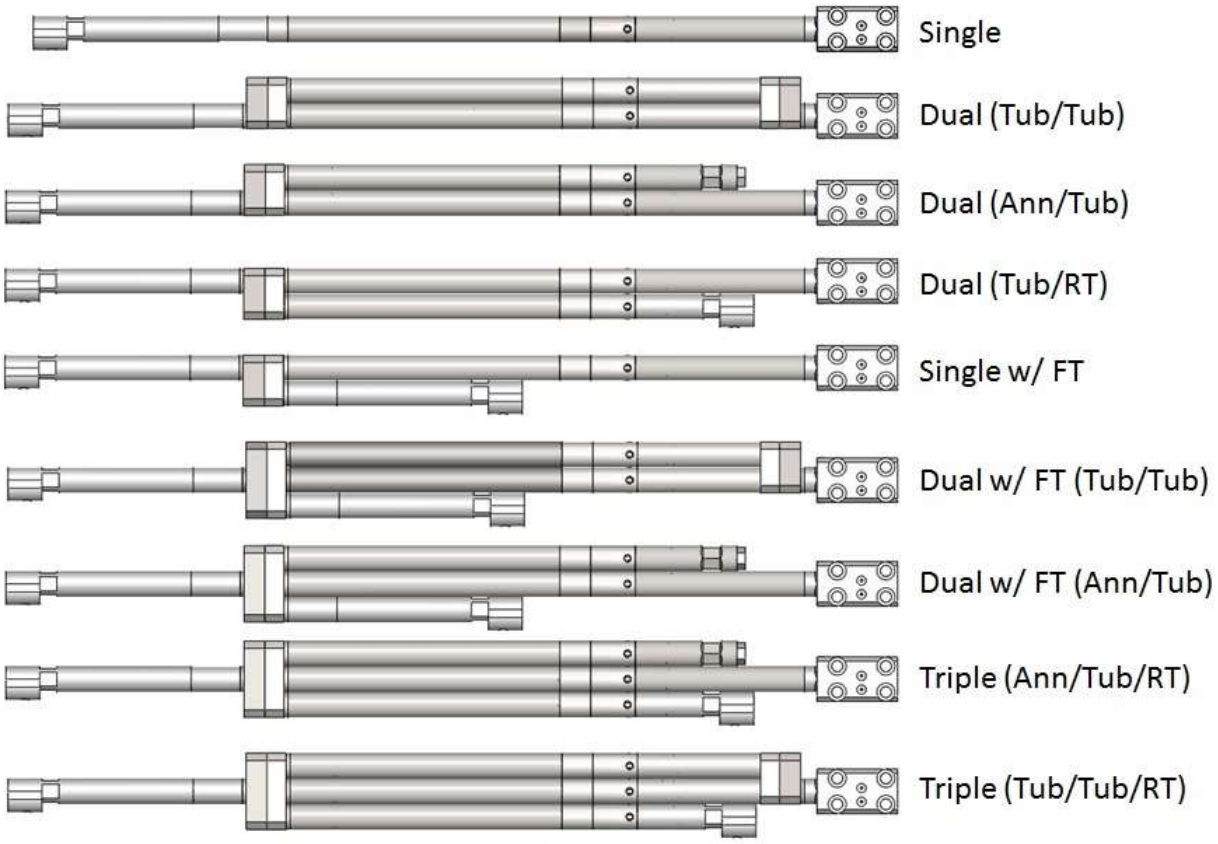


Figure 2: Sensor placement in multisensor assembly.



Table 6: Product Selection Chart

Tool Address	Pressure Rating (psi)						OFS Install Kit	Manifold Install Kit
	10,000	16,000	20,000	25,000	30,000	35,000	Qty Required	Qty Required
Single (Tubing)								
T1	H307570100	H307570150	H307570200	H307570250	H307570300	—	1	1
Single with Feedthrough (Tubing)								
T1	H307570101	H307570151	H307570201	H307570251	H307570301	—	2	1
T2	H307570102	H307570152	H307570202	H307570252	H307570302	—	2	1
T3	H307570103	H307570153	H307570203	H307570253	H307570303	—	2	1
T4	H307570104	H307570154	H307570204	H307570254	H307570304	—	2	1
T5	H307570105	H307570155	H307570205	H307570255	H307570305	—	2	1
T6	H307570106	H307570156	H307570206	H307570256	H307570306	—	2	1
T7	H307570107	H307570157	H307570207	H307570257	H307570307	—	2	1
T8	H307570108	H307570158	H307570208	H307570258	H307570308	—	2	1
T9	H307570109	H307570159	H307570209	H307570259	H307570309	—	2	1
T10	H307570110	H307570160	H307570210	H307570260	H307570310	—	2	1
T11	H307570111	H307570161	H307570211	H307570261	H307570311	—	2	1
T12	H307570112	H307570162	H307570212	H307570262	H307570312	—	2	1
T13	H307570113	H307570163	H307570213	H307570263	H307570313	—	2	1
T14	H307570114	H307570164	H307570214	H307570264	H307570314	—	2	1
T15	H307570115	H307570165	H307570215	H307570265	H307570315	—	2	1
T16	H307570116	H307570166	H307570216	H307570266	H307570316	—	2	1
T17	H307570117	H307570167	H307570217	H307570267	H307570317	—	2	1
T18	H307570118	H307570168	H307570218	H307570268	H307570318	—	2	1
T19	H307570119	H307570169	H307570219	H307570269	H307570319	—	2	1
T20	H307570120	H307570170	H307570220	H307570270	H307570320	—	2	1
T21	H307570121	H307570171	H307570221	H307570271	H307570321	—	2	1
T22	H307570122	H307570172	H307570222	H307570272	H307570322	—	2	1
T23	—	—	—	—	—	—	2	1
T24	—	—	—	—	—	—	2	1
T25	—	—	—	—	—	—	2	1
T26	—	—	—	—	—	—	2	1
T27	—	—	—	—	—	—	2	1
T28	—	—	—	—	—	—	2	1
T29	—	—	—	—	—	—	2	1
T30	—	—	—	—	—	—	2	1
T31	—	—	—	—	—	—	2	1
T32	—	—	—	—	—	—	2	1
Dual (Tubing/Tubing)								
T1/T2	H307570123	H307570173	H307570223	H307570273	H307570323	—	1	1
Dual with Feedthrough (Tubing/Tubing)								
T1/T2	H307570124	H307570174	H307570224	H307570274	H307570324	—	2	1
T3/T4	H307570125	H307570175	H307570225	H307570275	H307570325	—	2	1
T5/T6	H307570126	H307570176	H307570226	H307570276	H307570326	—	2	1
T7/T8	H307570127	H307570177	H307570227	H307570277	H307570327	—	2	1
T9/T10	H307570128	H307570178	H307570228	H307570278	H307570328	—	2	1
T11/T12	H307570129	H307570179	H307570229	H307570279	H307570329	—	2	1
T13/T14	H307570130	H307570180	H307570230	H307570280	H307570330	—	2	1
T15/T16	H307570131	H307570181	H307570231	H307570281	H307570331	—	2	1
T17/T18	H307570132	H307570182	H307570232	H307570282	H307570332	—	2	1
T19/T20	H307570133	H307570183	H307570233	H307570283	H307570333	—	2	1

Tool Address	Pressure Rating (psi)						OFS Install Kit	Manifold Install Kit
	10,000	16,000	20,000	25,000	30,000	35,000	Qty Required	Qty Required
T21/T22	H307570134	H307570184	H307570234	H307570284	H307570334	—	2	1
T23/T24	—	—	—	—	—	—	2	1
T25/T26	—	—	—	—	—	—	2	1
T27/T28	—	—	—	—	—	—	2	1
T29/T30	—	—	—	—	—	—	2	1
T31/T32	—	—	—	—	—	—	2	1
Dual (Annulus/Tubing)								
T1/T2	H307570135	H307570185	H307570235	H307570285	H307570335	—	1	1
Dual with Feedthrough (Annulus/Tubing)								
T1/T2	H307570136	H307570186	H307570236	H307570286	H307570336	—	2	1
T3/T4	H307570137	H307570187	H307570237	H307570287	H307570337	—	2	1
T5/T6	H307570138	H307570188	H307570238	H307570288	H307570338	—	2	1
T7/T8	H307570139	H307570189	H307570239	H307570289	H307570339	—	2	1
T9/T10	H307570140	H307570190	H307570240	H307570290	H307570340	—	2	1
T11/T12	H307570141	H307570191	H307570241	H307570291	H307570341	—	2	1
T13/T14	H307570142	H307570192	H307570242	H307570292	H307570342	—	2	1
T15/T16	H307570143	H307570193	H307570243	H307570293	H307570343	—	2	1
T17/T18	H307570144	H307570194	H307570244	H307570294	H307570344	—	2	1
T19/T20	H307570145	H307570195	H307570245	H307570295	H307570345	—	2	1
T21/T22	H307570146	H307570196	H307570246	H307570296	H307570346	—	2	1
T23/T24	—	—	—	—	—	—	2	1
T25/T26	—	—	—	—	—	—	2	1
T27/T28	—	—	—	—	—	—	2	1
T29/T30	—	—	—	—	—	—	2	1
T31/T32	—	—	—	—	—	—	2	1
Dual (Tubing/Remote Tap)								
T1/T2	H307570147	H307570197	H307570247	H307570297	H307570347	—	2	1
Triple (Annulus/Tubing/Remote Tap)								
T1/T2/T3	H307570148	H307570198	H307570248	H307570298	H307570348	—	2	1
Triple (Tubing/Tubing/Remote Tap)								
T1/T2/T3	H307570149	H307570199	H307570249	H307570299	H307570349	—	2	1

Only the single and dual configurations can be deployed with a feedthrough, for configurations not listed contact product line.

Search SAP for configurations not specified in the document.

6 HSE&S



Read, understand and follow all Baker Hughes Company instructions and specifications in this unit while assembling, disassembling, maintaining or repairing this equipment. Failure to do so may result in property damage, serious injury or fatality.

7 Preservation of Product

For preservation of product requirements refer to the global procedure *for OFS Preservation of Product (QA-GLB-En-100042)* and *CWI Storage and Preservation Guidelines (AMO-GLB-En-101887)* located on Baker Hughes Operating System (BHOS).

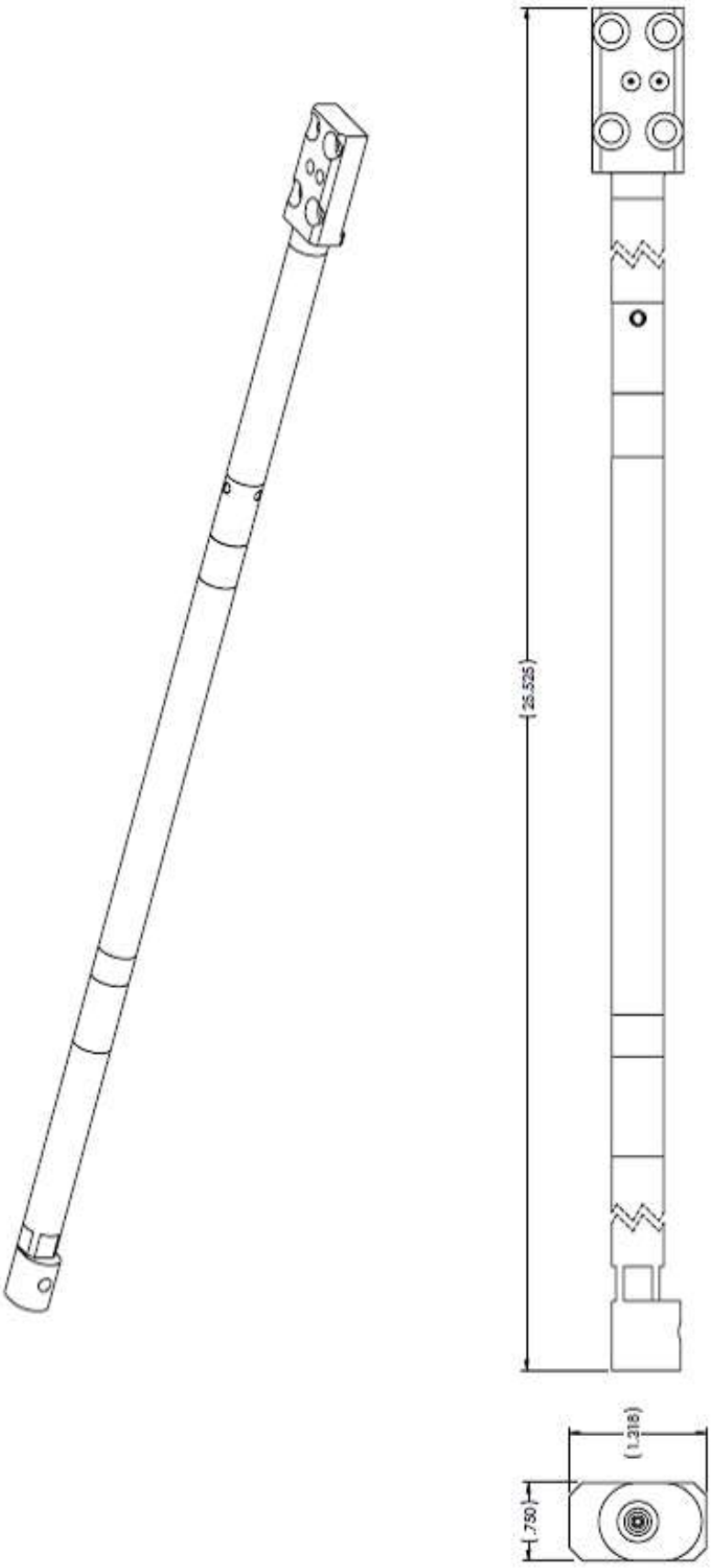
Storage Recommendations

Adequate storage facilities must be established for equipment to prevent inadvertent damage due to moisture, humidity, vibration, shock and handling. Equipment will be appropriately protected during transport and handling.

8 Assembly and Dimensional Information

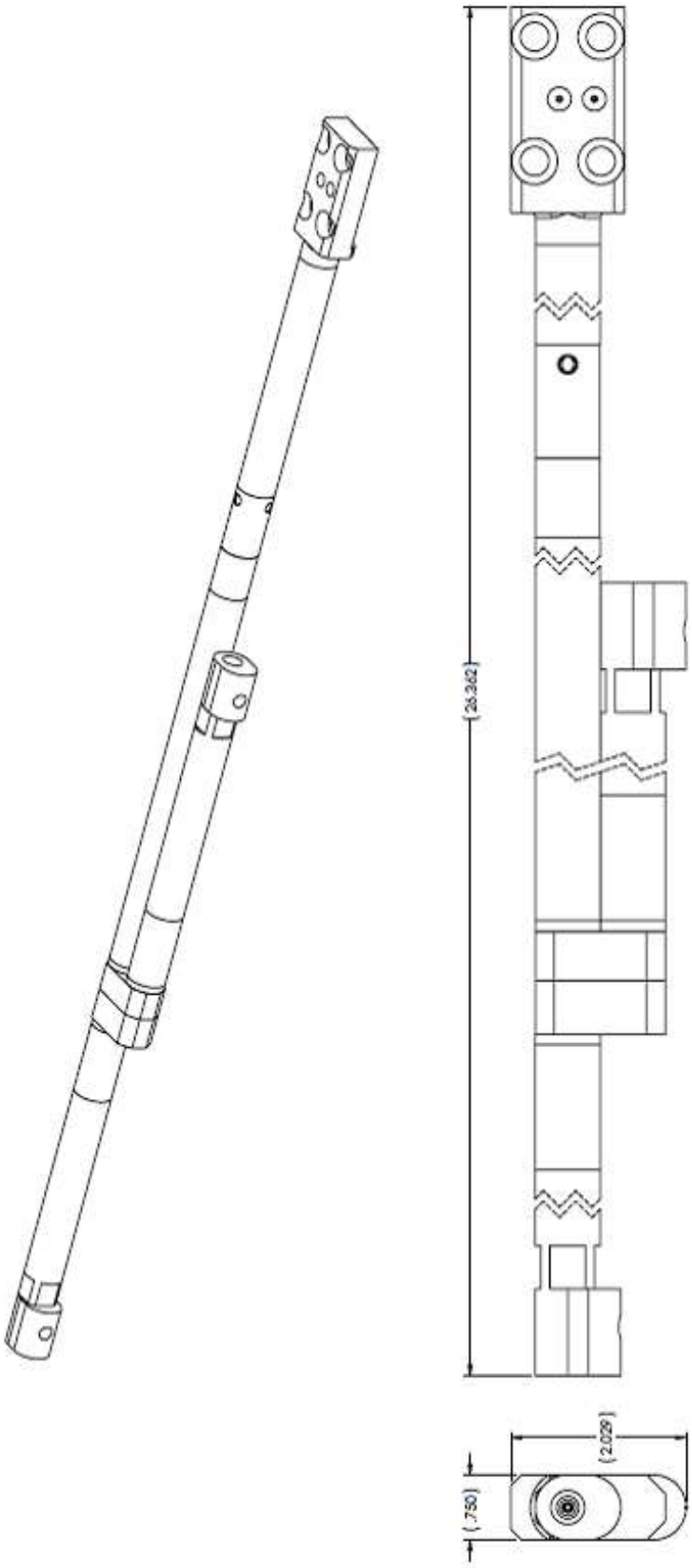
SureSENS QPT ELITE Downhole Pressure Temperature Gauge

Figure 3: Assembly Drawing J06-522-00 (single tubing)



SureSENS QPT ELITE Downhole Pressure Temperature Gauge

Figure 4: Assembly Drawing J06-526-00 (tubing with feedthrough)



9 Appendix

Hand Tools Required

- Encapsulation stripping tool
- 12-in. steel rule or dial calipers
- Tubing cutter
- Triangular file
- Large vise grips
- 3/16-in. through 5/16-in. coaxial cable stripper (IDEAL 45-165)
- 1/8-in. coaxial cable stripper (IDEAL 45-162)
- 12-20 AWG wire stripper
- DMC AF8 crimp tool
- Swaging tool (Material PGA-80-09000)
- 12-in. adjustable wrench
- Torque wrench ft.lb scale with interchangeable head (Snap-on QC2I75 or CDI 75MFIMHSS)
- Jam nut torque wrench head (BH Material H0J0531502 or Snap-on QJRXS16A)
- 5/8-in. wrench
- Torque wrench (in.lb scale)
- 3/16-in. hex socket bit

If deploying the external pressure testing fixture the following will be required:

- Clamp assembly (Material H0J1237000)
- Modified drive adapter (Material H0J1166900 or CDI TCQJRXS12A)
- 3/8-in. crows foot wench (Material 10601424 or Snap-on FRH120S) not required if using CDI TCQJRXS12A

Consumables Required

- P600 emery paper
- Silicone grease DC111
- TUNAP Tungrease CF-33 grease paste

Pressure Test Equipment Required

- Hand pump or HPU with transformer oil (Shell *DIALA* or equivalent)
- Chart recorder or pressure recording digital gauge
- High pressure lines with 1/4-in. autoclave high-pressure connections
- High-pressure T-piece
- High-pressure needle valve
- Pressure test adaptor (Material H0J0419300)

Volumetric Flow Meter



Sentinel LCT

Panametrics ultrasonic flowmeter for liquid custody transfer measurement

Benefits

- Extremely reliable and highly accurate flowmeter, designed specifically for custody transfer measurements.
- Viscosity independent. Measurement accuracy will not be affected by a change in viscosity or density.
- Fully welded construction with no moving parts. No filters or strainers required.
- Full bore design, zero pressure drop.
- Robust Path Configuration™ through extensive use of CFD (Computational Fluid Dynamics).
- Optionally built-in flow computer for API MPMS 11.1 corrections for temperature and pressure.

Applications

- Liquid custody transfer measurement
- Allocation measurement
- Pipeline leak detection
- Crude oil and refined products
- High temperature flow
- Cryogenic flow
- Any liquid flow needing high accuracy and precision

Panametrics
a Baker Hughes business

Custody transfer flow measurement from panametrics

Panametrics introduces Sentinel LCT, a new addition to our series of advanced ultrasonic flowmeters. Sentinel LCT demonstrates new levels of performance and accuracy, reacts to changes in flow rate with incredible speed and is based on proven technology. Sentinel LCT is designed specifically for the custody transfer measurement of crude oil and other liquid refined products and requirements. Please contact Panametrics for details.

It's all about reliability

The design philosophy behind Sentinel LCT was simple; build a flowmeter that combined absolute reliability with the highest accuracy. Using ultrasonic technology was the first choice; with no moving parts the meter will not suffer from any mechanical wear or tear. Using a fully welded construction without any gaskets or threaded connections was another choice; there is simply nothing in the meter's geometry that can change to allow th meter to drift.

Robust Path Configuration™

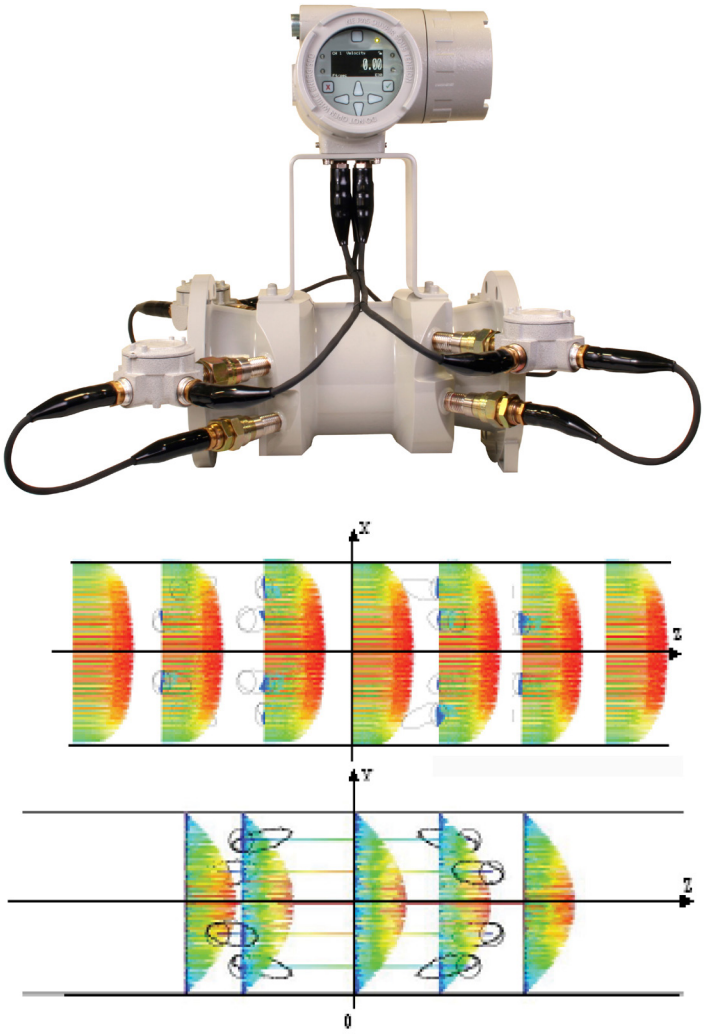
Before Sentinel LCT was ever tested on a calibration loop, the meter was already extensively tested in the virtual world. Computational Fluid Dynamics (CFD) was used to simulate different path configurations under different flow scenarios.

CFD allowed us to test different ultrasonic path configurations under a number of different flow scenarios, from laminar flows that are typically seen in very heavy crudes to highly turbulent flows that are seen in gasoline and LPG applications. Only after CFD simulation provided the optimal path configuration, was the Sentinel LCT tested in a calibration loop to prove the CFD results.

Testing on different viscosity oil products proved the CFD analysis to be right. Sentinel LCT easily met the targeted 0.15% accuracy.

A true multi-viscosity flowmeter

Starting with a meter that already has minimal sensitivity to viscosity changes, Sentinel LCT uses a number of proprietary algorithms to even further reduce the viscosity effects. As a result, Sentinel LCT is a true multi-viscosity meter, meaning no prover run or change of settings is required when the viscosity changes. The meter stays within 0.15% accuracy over the whole range between minimum and maximum viscosity, using only one calibration curve.



CFD analysis of the ultrasonic port effects. The top graph shows the effect under turbulent flow, the bottom graph under laminar flow conditions. Also not the different flow profiles under these conditions.

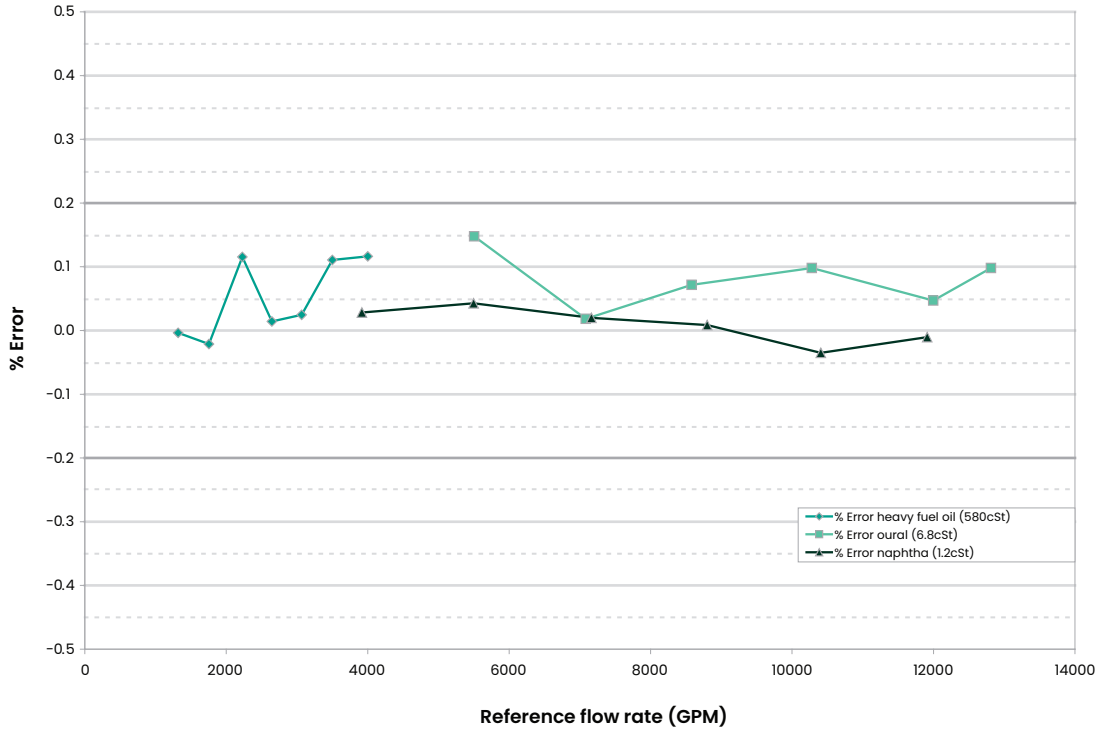
Maintenance free

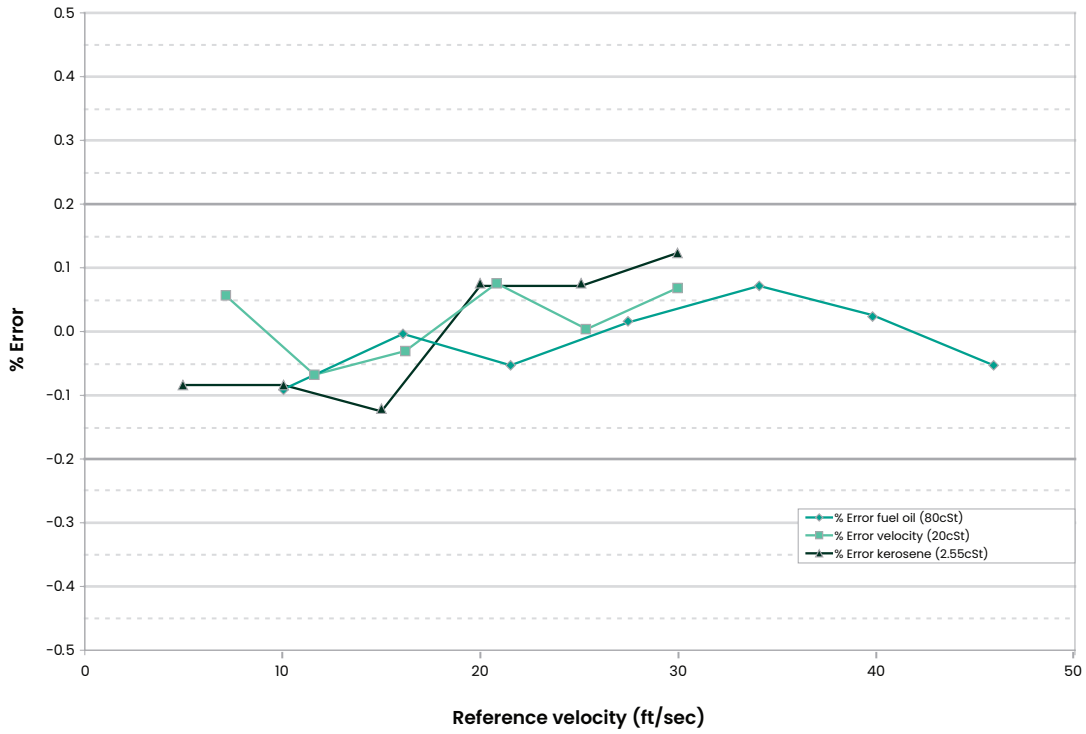
Not only does the meter lack any mechanical parts that require maintenance, the meter also does not require any filter or strainers. Inspecting and replacing clogged filters is not required, simply because they are not there. Theoretically the meter does not even require any recalibrations; however, local legal requirements might require differently.

No pressure drop

Due to the unique ultrasonic path configuration, the flowmeter design does not have any diameter reductions. This means the design is completely full bore in the same diameter as your pipeline. As a result the pressure drop over the meter is simply equal to a section of pipe with the same length.

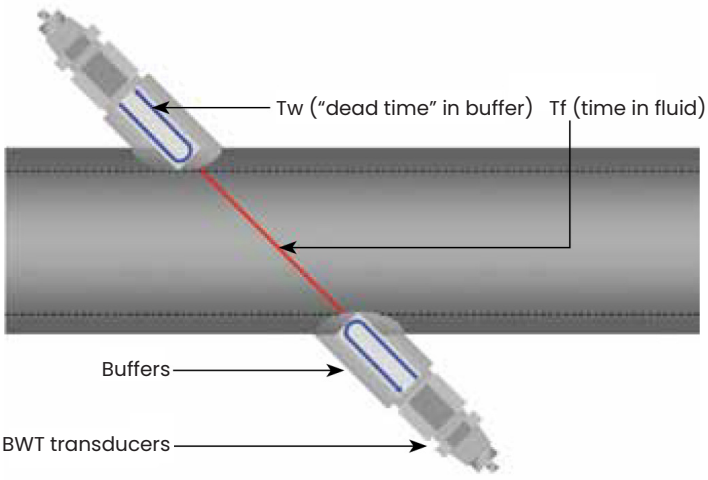
24” Sentinel LCT combined performance results: NMi witnessed results for OIML R117-1 certification at SPSE





Active Temperature Compensation™

Ultrasonic flowmeters use transit time to determine the liquid or gas flow in a pipeline. Measured transit time consists not only of the time the ultrasonic signal spends in a fluid, but also of a portion of "dead time," being the time that the electrical signal is converted into an acoustical signal and the time the acoustic signal travels inside the transducer. To allow for the utmost accuracy, Sentinel LCT uses pulse echo to actively measure the dead time. By sending a pulse and measuring its reflection, the dead time is measured in real time rather than using a preset value. As a result of this Panametrics invention, Sentinel LCT maintains custody transfer accuracy as process temperature conditions dynamically change.



Built-in flow computer

Optionally the Sentinel SEN898 electronics have a built-in flow computer that allows for temperature, pressure and density corrections according to API MPMS 11.1. By connecting an external pressure, temperature and, if required, density measurement, all API corrections are done inside the SEN898 electronics, reducing the need for an external flow computer.

One-time calibration

The Sentinel LCT requires a single calibration event (multi-viscosity or water, depending on the application) to work over the entire user flow range without the need for frequent calibration checks or prover runs.

There is no need for recalibration when replacing sensors or electronics. NMI tested and certified that the Sentinel LCT maintains custody transfer accuracy and calibration integrity after component exchanges!

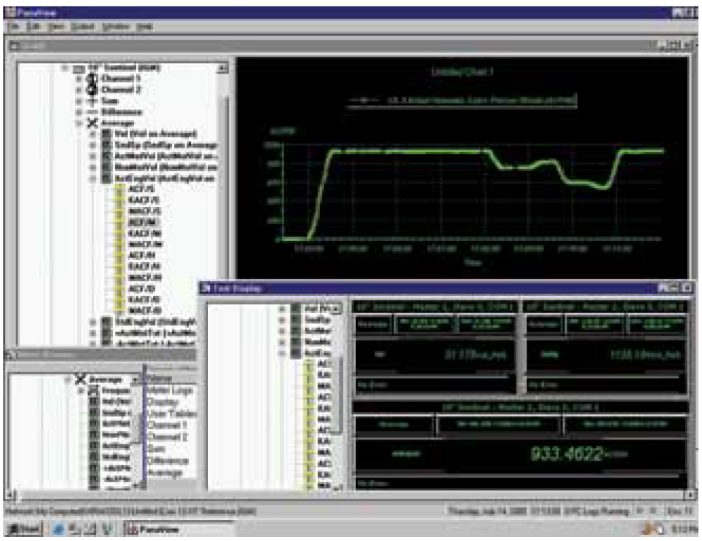


Advanced electronics

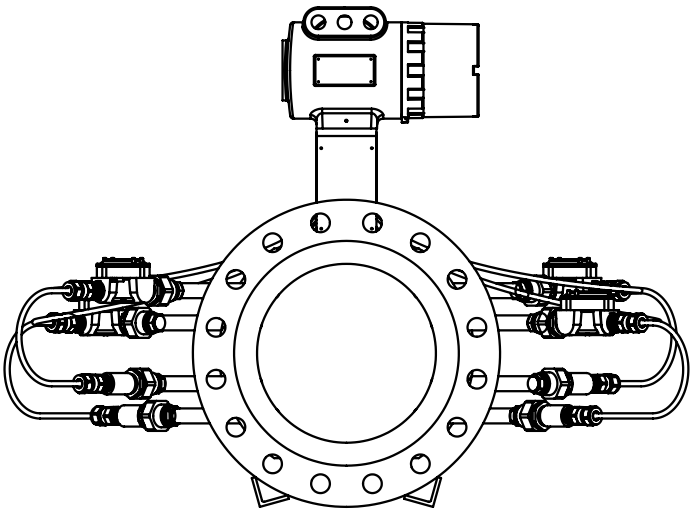
Sentinel LCT has advanced digital signal processors that pack significant power in a simple package. Several output options are standard. The electonics can be mounted on the flowcell section or up to 300 feet away. Cable connections can easily be accessed, even when the meter has been mounted to a wall. HART is standard on all meters. Local diagnostics can be done via magnetic contacts through the glass, or by using the USB connection and our PanaView™ software.

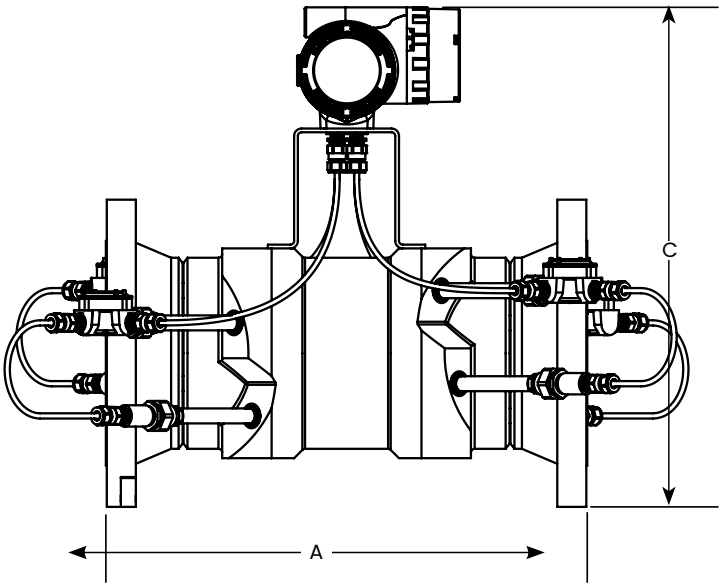
PanaView™ for diagnostics

PanaView software facilitates communication between a PC and the Sentinel LCT flowmeter. This software monitors the Sentinel flowmeter to provide a secure and comprehensive check on the meter configuration with a full audit trail. It also allows live flow readings and tracking of flow diagnostics.



Dimensions and weights

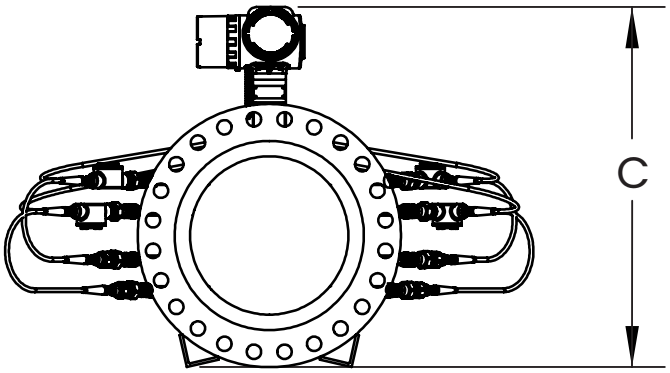


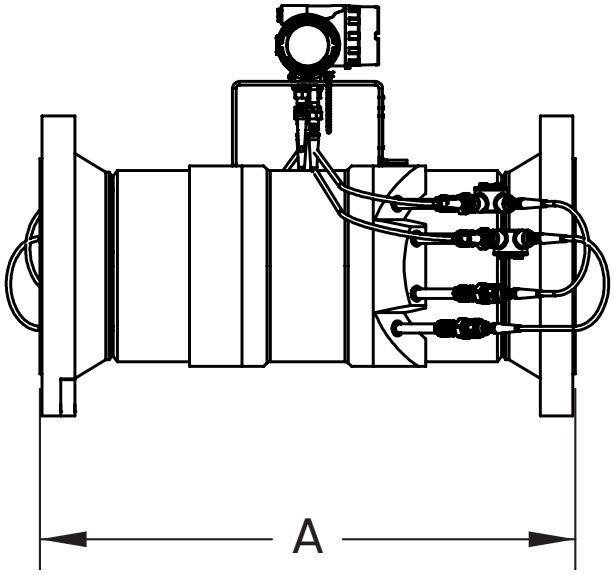


Dimensions and weights in English units				
Diameter	Flange	A (in)	C (in)	Weight (lb)
4	150#	20	23.49	149
	300#	20	23.99	176
	600$	20	24.36	200
6	150#	22	25.76	209
	300#	24	26.51	265
	600$	26	27.26	338
8	150#	26	27.59	268
	300#	28	28.34	343
	600$	30	29.09	452
10	150#	28	29.84	367
	300#	30	30.59	487
	600$	32	31.84	739
12	150#	30	32.59	478
	300#	32	33.34	681
	600$	36	34.09	957
14	150#	36	34.09	790
	300#	38	35.09	1079
	600$	40	35.46	1339
16	150#	38	36.84	989
	300#	40	37.84	1348
	600$	42	38.59	1770
18	150#	38	37.84	1056
	300#	40	39.34	1527
	600$	44	39.96	2076
20	150#	46	41.25	1424
	300#	48	42.75	2120
	600$	50	43.50	2819
24	150#	48	44.59	1990
	300#	50	49.59	2947
	600#	52	47.09	3946

Dimensions and weights in metric units				
Diameter	Flange	A (mm)	C (mm)	Weight (kg)
4	150#	508	597	68
	300#	508	609	80
	600$	508	619	91
6	150#	559	654	95
	300#	610	673	120
	600$	660	692	153
8	150#	660	701	122
	300#	711	720	156
	600$	762	739	205
10	150#	711	758	166
	300#	762	777	221
	600$	813	809	335
12	150#	762	828	217
	300#	813	847	309
	600$	914	866	434
14	150#	914	866	358
	300#	965	891	489
	600$	1016	901	607
16	150#	965	936	449
	300#	1016	961	611
	600$	1067	980	803
18	150#	965	961	479
	300#	1016	999	693
	600$	1118	1015	942
20	150#	1168	1048	646
	300#	1219	1086	962
	600$	1270	1105	1280
24	150#	1219	1133	903
	300#	1270	1183	1337
	600#	1321	1196	1790

Dimensions and weights: single plane





Weights are based on carbon steel spool and stainless steel enclosure.

Diameter, Inches	Flange	A		B		Weight	
		in	mm	in	mm	lb	mm
12	150#	30	762	33.59	853	476	216
	300#	32	813	34.34	872	685	310
	600$	36	914	35.09	891	1010	458
14	150#	36	914	34.84	885	740	336
	300#	38	965	35.84	910	1080	490
	600$	40	1016	36.21	920	1217	552
16	150#	38	965	37.64	948	843	382
	300#	40	1016	38.34	974	1257	570
	600$	42	1067	39.09	993	1680	762
18	150#	38	965	38.84	986	843	382
	300#	40	1016	40.34	1025	1572	713
	600$	44	1118	40.96	1040	2116	960
20	150#	46	1168	41.34	1050	1292	586
	300#	48	1219	42.84	1088	1588	720
	600$	50	1270	43.59	1107	1899	861
24	150#	48	1219	35.59	1158	1908	866
	300#	50	1270	47.59	1207	2932	1330
	600$	52	1321	48.09	1221	3476	1577
28	150#	56	1422	49.29	1252	876	398
	300#	56	1422	51.41	1306	1858	843
30	150#	60	1524	51.41	1306	1858	843
	300#	60	1524	53.54	1360	2130	970
32	150#	64	1626	53.92	1369	1300	590
	300#	64	1626	55.67	1414	2400	1090
36	150#	70	1778	58.05	1474	2180	990
	300#	70	1778	60.05	1525	3750	1700

APPENDIX D-III

MS USDW 1 & MS USDW 2 Drilling and Logging Procedures and Schematics

MS USDW 1
Drilling and Logging Procedure and Schematic

Minerva South USDW Well No. 001

MONITORING WELL DRILLING & LOGGING PROCEDURE

The following paragraphs discuss the drilling procedures to be implemented to construct the monitoring well to an approximate depth of 1,970 ft. The monitoring wells will be constructed in accordance with LAC Title 56 Chapter 3. Drilled is responsible for maintaining hole stability during all operations. Final acceptance is contingent on casing and screen being installed to correct depth as approved by owner.

Location Preparation

1. Survey and stake location as required to fit rig chosen to drill the well. Obtain ground level elevation.
2. Level and grade location as required. Prepare containment pit for solids returns when drilling the well.
3. Prior to mobilization, confirm that the office of conservation has received and responded to well installation notification as required in LAC43:VI.701.B.
4. Assure sufficient fresh water supply on site for drilling operations.
5. Mobilize at least one approved portable toilet to site.
6. Assure that rig inspection has been performed prior to rig moving to site.

Mobilization and Rig Up of Drilling Equipment

1. Move in drilling rig and associated equipment and rig up. Assure that drilling rig is leveled.
2. Check drill stem, stabilizers and drill bit inspection papers. Do not accept rig if there is any doubt about the condition of the rig or associated equipment. Confirm the number of tubulars on location.
3. Arrange for delivery of 4 1/2-inch, 3.3 lb/ft, fiberglass casing to location. Offload casing to pipe racks.

Surface Borehole and Surface Casing Installation

1. Pick up 12 1/2-inch drill bit with appropriate stabilized drilling assembly.
2. Rotary drill down to 40 ft.
3. Pull the drilling assembly out of the hole and install diverter. Rig up diverter flowline to containment pit for solids returns.
4. Run back in hole with 12 1/2-inch drilling assembly and rotary drill 12 1/2-inch borehole to approximately 1,970 ft at penetration rates of between 50 to 80 feet per hour to avoid loading the fluid returns with excessive cuttings. The hole should be

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tested for plumbness and alignment should be exercised following the American Water Works Association Standards for Water Wells (AWWA A-100). Record depth and thickness of formations penetrated. Collect drill cuttings from each potential aquifer. Record any unusual occurrences such as loss circulation, cave ins, etc.

Note: In the event the unusual occurrence is observable evidence of naturally occurring methane gas, natural gas or similar sub-surface gas, such as bubbling drilling mud or gas venting at the well bore or other nearby surface location or feature, the contractor shall report such event verbally to the Environmental Division of the Office of Conservation within 24 hours per LAC56:III.323.C.4.

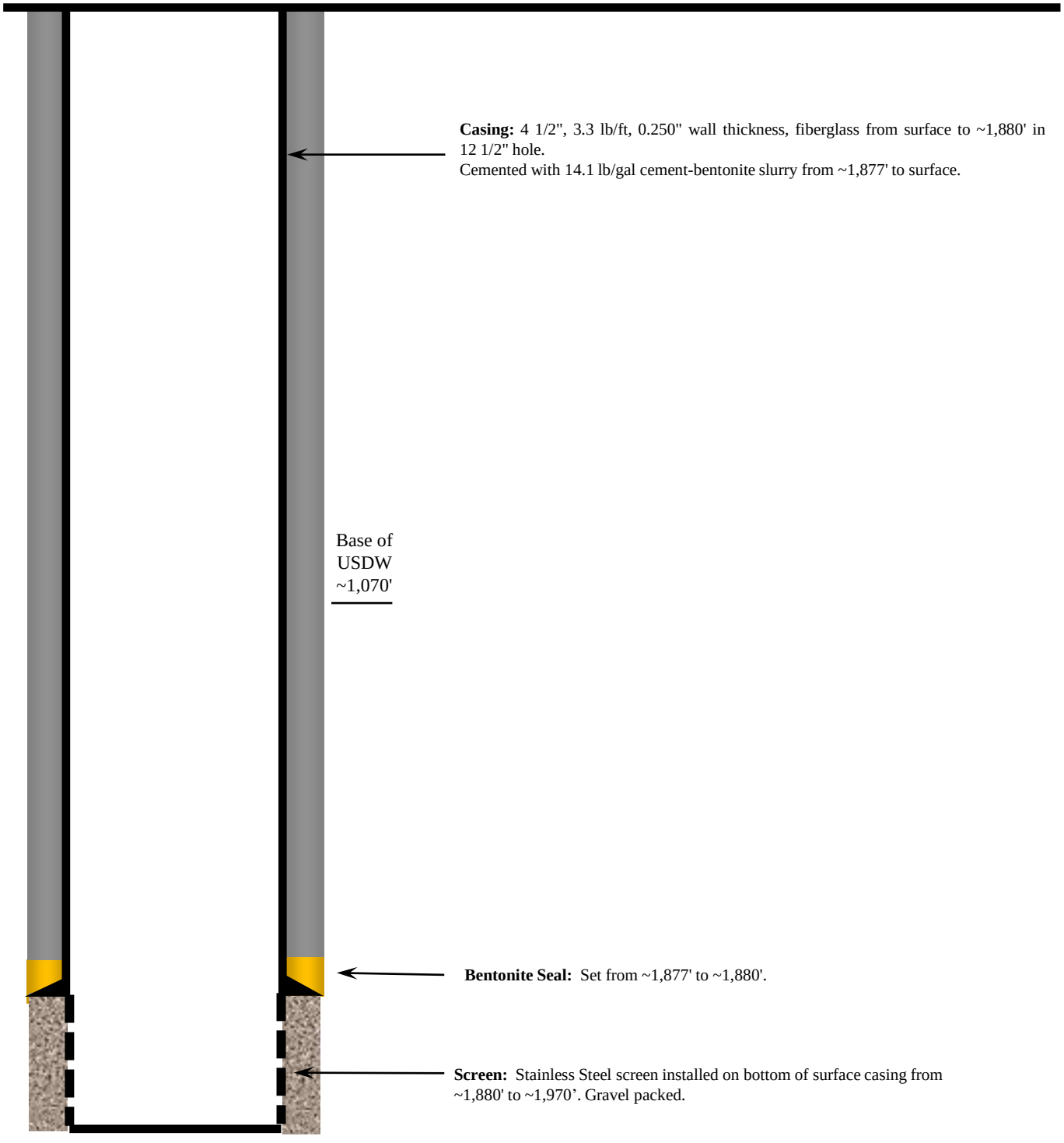
5. Pull drilling assembly out of the hole.
6. Run spontaneous potential, resistivity and natural gamma ray logs. Identify lowermost underground source of drinking water (USDW) and sand package below USDW.
7. Plug back borehole as needed to provide base for screen.
8. Pick up first joint of 4 1/2-inch, 3.3 lb/ft, fiberglass casing and install stainless steel screen.
9. Make up and run the remaining 4 1/2-inch, 3.3 lb/ft, fiberglass casing to approximately 1,970 ft (to place screened section across sand package) while making up joints to appropriate torque. Fill the casing every 5 joints with fresh water as needed while running into the well. Run centralizers and tremie pipe while making up and running the fiberglass casing.
10. Mobilize cementers to location. Rig up to water supply. Gravel pack screened section while pulling tremie pipe to top of screen. Mix bentonite plug and pump it down the hole through the tremie pipe to fill three feet in the annular space above the screen. Pull up above the bentonite plug. Mix 14.1 ppg cement-bentonite slurry and pump it down the hole through the tremie pipe. Slowly work the tremie pipe uphole until cement reaches the surface.
11. Wait on cement for at least 12 hours.
12. If cement fell back, top off annulus space as needed.
13. Construct a concrete slab at least four inches thick and extending at least 2.5 ft from the well in all directions at surface. The surface of the slab shall be sloped to drain away from the well.
14. Cut casing if needed to be at least one ft above ground and install protective cover or cap.

Rig Down and Demobilization

1. Clean up as needed and rig down drilling rig and associated equipment.
2. Release drilling rig and demobilize from location.

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MINERVA SOUTH USDW WELL NO. 001
PROPOSED CONSTRUCTION SCHEMATIC
CAMERON PARISH, LOUISIANA



Total Depth = ~1,970'
All Depths Referenced to Ground Level
Not to Scale

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TERRA DYNAMICS INC

DRAWN BY: SAGP	CHECKED BY: RRM	FILE: 24-149	DATE: 09/26/24	REV.: -

MS USDW 2
Drilling and Logging Procedure and Schematic

Minerva South USDW Well No. 002

MONITORING WELL DRILLING & LOGGING PROCEDURE

The following paragraphs discuss the drilling procedures to be implemented to construct the monitoring well to an approximate depth of 1,970 ft. The monitoring wells will be constructed in accordance with LAC Title 56 Chapter 3. Drilled is responsible for maintaining hole stability during all operations. Final acceptance is contingent on casing and screen being installed to correct depth as approved by owner.

Location Preparation

1. Survey and stake location as required to fit rig chosen to drill the well. Obtain ground level elevation.
2. Level and grade location as required. Prepare containment pit for solids returns when drilling the well.
3. Prior to mobilization, confirm that the office of conservation has received and responded to well installation notification as required in LAC43:VI.701.B.
4. Assure sufficient fresh water supply on site for drilling operations.
5. Mobilize at least one approved portable toilet to site.
6. Assure that rig inspection has been performed prior to rig moving to site.

Mobilization and Rig Up of Drilling Equipment

1. Move in drilling rig and associated equipment and rig up. Assure that drilling rig is leveled.
2. Check drill stem, stabilizers and drill bit inspection papers. Do not accept rig if there is any doubt about the condition of the rig or associated equipment. Confirm the number of tubulars on location.
3. Arrange for delivery of 4 1/2-inch, 3.3 lb/ft, fiberglass casing to location. Offload casing to pipe racks.

Surface Borehole and Surface Casing Installation

1. Pick up 12 1/2-inch drill bit with appropriate stabilized drilling assembly.
2. Rotary drill down to 40 ft.
3. Pull the drilling assembly out of the hole and install diverter. Rig up diverter flowline to containment pit for solids returns.
4. Run back in hole with 12 1/2-inch drilling assembly and rotary drill 12 1/2-inch borehole to approximately 1,970 ft at penetration rates of between 50 to 80 feet per hour to avoid loading the fluid returns with excessive cuttings. The hole should be

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tested for plumbness and alignment should be exercised following the American Water Works Association Standards for Water Wells (AWWA A-100). Record depth and thickness of formations penetrated. Collect drill cuttings from each potential aquifer. Record any unusual occurrences such as loss circulation, cave ins, etc.

Note: In the event the unusual occurrence is observable evidence of naturally occurring methane gas, natural gas or similar sub-surface gas, such as bubbling drilling mud or gas venting at the well bore or other nearby surface location or feature, the contractor shall report such event verbally to the Environmental Division of the Office of Conservation within 24 hours per LAC56:III.323.C.4.

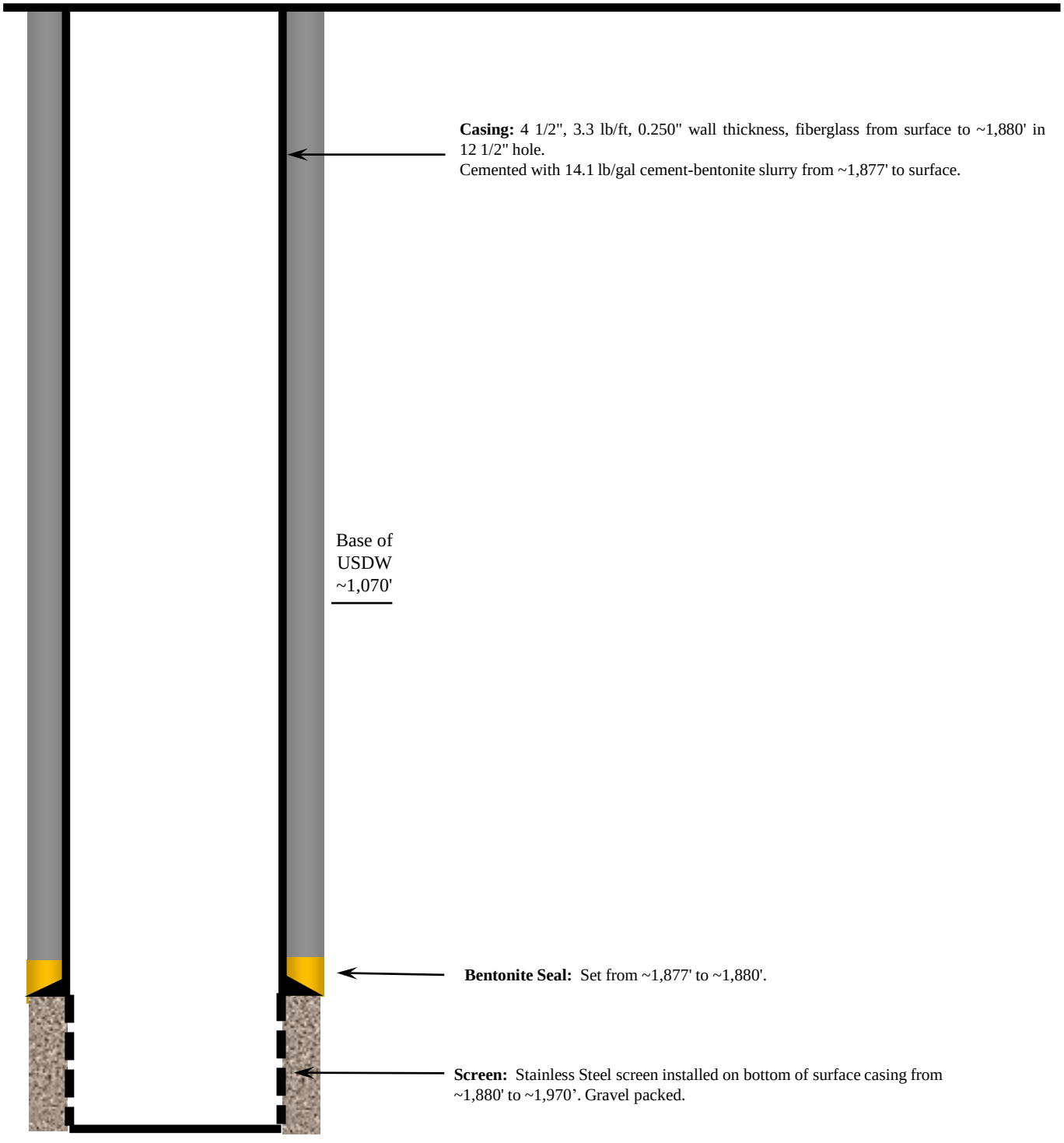
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6. Run spontaneous potential, resistivity and natural gamma ray logs. Identify lowermost underground source of drinking water (USDW) and sand package below USDW.
7. Plug back borehole as needed to provide base for screen.
8. Pick up first joint of 4 1/2-inch, 3.3 lb/ft, fiberglass casing and install stainless steel screen.
9. Make up and run the remaining 4 1/2-inch, 3.3 lb/ft, fiberglass casing to approximately 1,970 ft (to place screened section across sand package) while making up joints to appropriate torque. Fill the casing every 5 joints with fresh water as needed while running into the well. Run centralizers and tremie pipe while making up and running the fiberglass casing.
10. Mobilize cementers to location. Rig up to water supply. Gravel pack screened section while pulling tremie pipe to top of screen. Mix bentonite plug and pump it down the hole through the tremie pipe to fill three feet in the annular space above the screen. Pull up above the bentonite plug. Mix 14.1 ppg cement-bentonite slurry and pump it down the hole through the tremie pipe. Slowly work the tremie pipe uphole until cement reaches the surface.
11. Wait on cement for at least 12 hours.
12. If cement fell back, top off annulus space as needed.
13. Construct a concrete slab at least four inches thick and extending at least 2.5 ft from the well in all directions at surface. The surface of the slab shall be sloped to drain away from the well.
14. Cut casing if needed to be at least one ft above ground and install protective cover or cap.

Rig Down and Demobilization

1. Clean up as needed and rig down drilling rig and associated equipment.
2. Release drilling rig and demobilize from location.

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MINERVA SOUTH USDW WELL NO. 002
PROPOSED CONSTRUCTION SCHEMATIC
CALCASIEU PARISH, LOUISIANA



Total Depth = ~1,970'
All Depths Referenced to Ground Level
Not to Scale

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APPENDIX D-IV

Mechanical Integrity Testing Tool

Specification Sheets

Distributed Temperature Sensing (DTS)

Baker Hughes

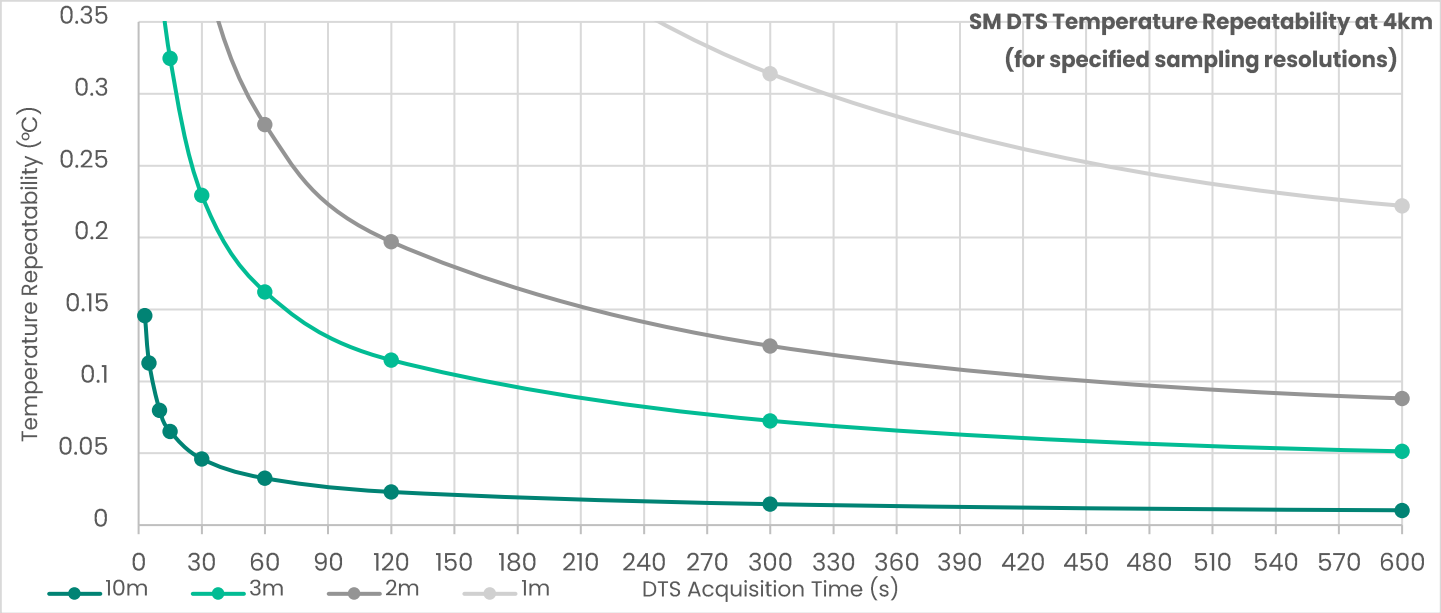
SureVIEW™ DTS Interrogator

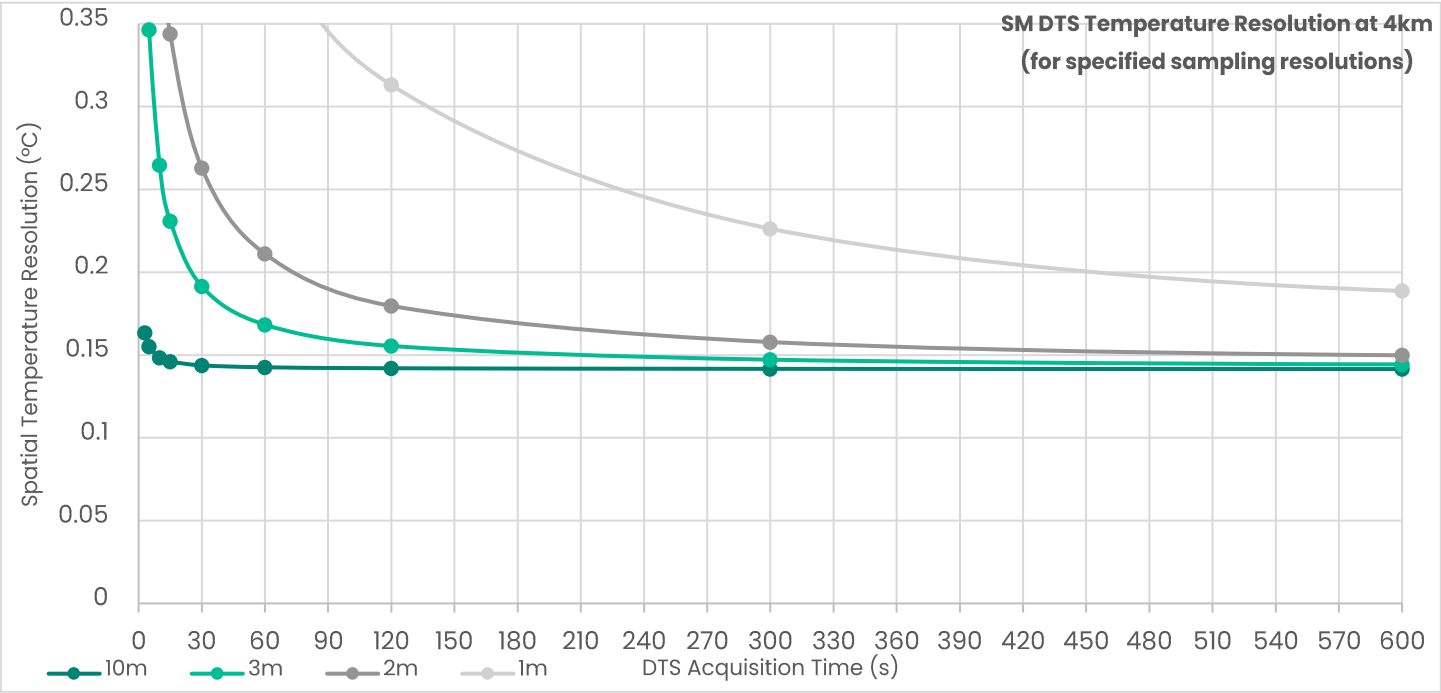


The SureVIEW™ DTS fiber optic interrogator provides convenient multi-well performance monitoring with continuous, rapidly updating temperature profiles along the length of the completion. The interrogator is designed to provide highly accurate temperature data from a single SM fiber, which reduces cost by eliminating the need for dual-ended fibre configurations.

SureVIEW™ DTS Surface Interrogator Specifications	
Description	**Value**
Form Factor	19 in. Rack
Height	2U
Depth (in.)	19.8
Certifications	TUV (US, Can), CE
Public Software Interfaces	OPC/UA, Modbus
Maximum Distance Range (km)	20+
Minimum Spatial Resolution (m)	1.0
Minimum Sampling Interval (m)	0.33
Fastest Acquisition Rate (sec)	3.3
Number of Channels	8 or 16
Internal Data Storage Capability	250 GB
Fiber Types	9/125 µm SMF CoreBright™
Optical Connectors	Fiber Pigtails
Computer Interfaces	Ethernet, DPI, USB
Power Consumption (W)	100 W maximum

SureVIEW™ DTS Surface Interrogator Specifications	
Description	**Value**
Voltage Input	22-27 VDC
Differential Attenuation Compensation	Yes
Fiber Configuration	Single-Ended or J-Type
Absolute Temperature Accuracy (°C)	±2 (worst-case, rapid cycling over full operating range)
Operating temperature (°C)	0 to 40
Storage temperature (°C)	-40 to 80
Operating relative humidity (%)	5 to 95
Sensing temperature Range (°C)	0 to 300





Call your local Baker Hughes representative today to learn more about how SureVIEW monitoring systems can reliably enhance your production operations.

bakerhughes.com

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Noise Log

Sondex™
a Baker Hughes business

Noise Tool (NTO)

Detects liquid or gas movement sounds in leaks, channels, or perforations

Application

- Evaluate flow profiles
- Locate channels behind a well case
- Locate gas-liquid interfaces
- Locate leaks in a well case
- Locate gas entries

Features

- Several NTO can be combined in one string
- Real time fast Fourier Transform (FFT) spectrum monitor
- Color variable-density log (VDL) style spectral log
- Road noise filter
- Configurable sampling modes (average, minimum, and maximum)
- Combinable with all Ultrawire tools
- No cable attenuation
- Configurable frequency cuts
- SRO or memory operation quantitative measurement

A leaking well can damage the environment and result in lost production. The **Noise Tool (NTO)** houses a sensitive hydrophone that is highly effective in the detection of flow inside and outside the cased well. The electronics digitize the noise downhole and sends a frequency spectrum to the surface to be recorded. Both the frequency spectrum and six high-pass frequency cuts are displayed on a log, providing a quantitative measurement of the downhole noise.

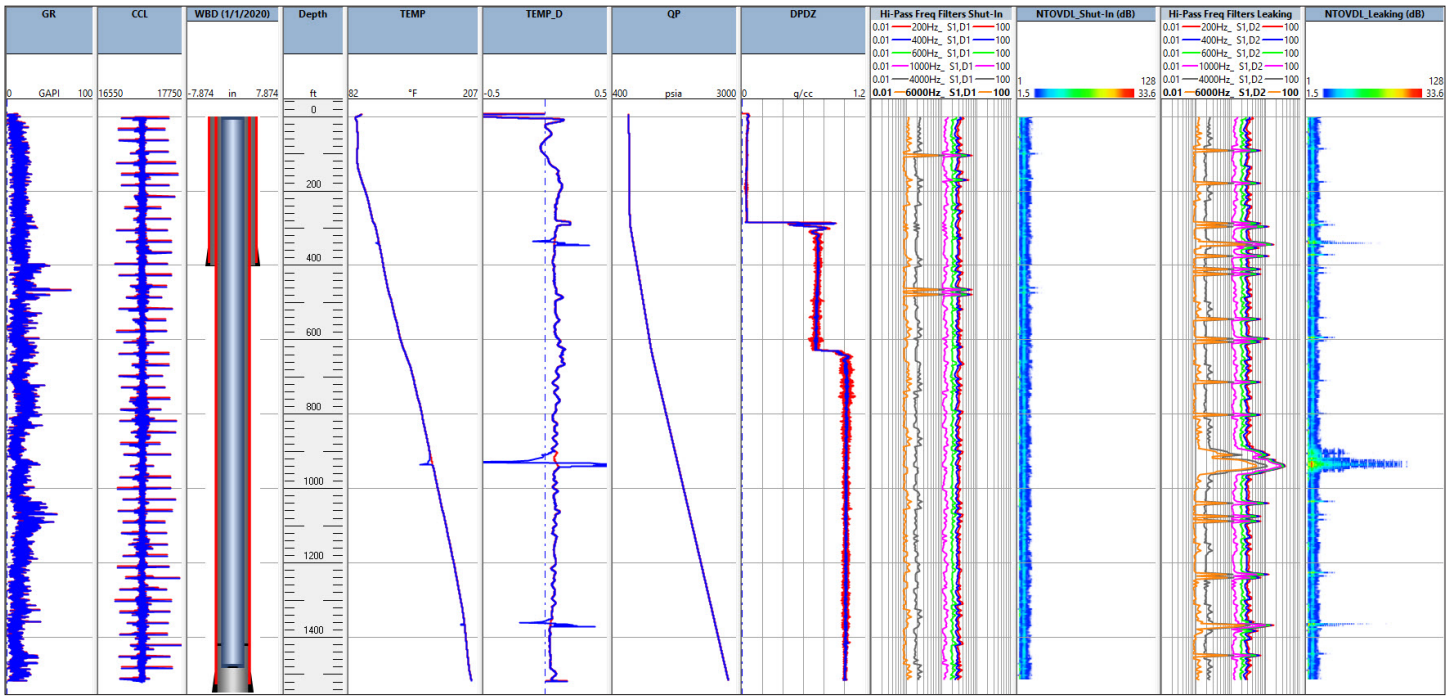
The NTO can be combined with other **Sondex Wireline tools** and logs data in both memory or surface readout tool strings. Consequently, any cased-hole logging intervention, such as production logging, cement evaluation, or pipe inspection, becomes an opportunity to verify the integrity of downhole components at minimal additional cost.

Multiple NTO can be combined within a single toolstring, thereby making it possible to pinpoint the depth of any particular noise source effectively and efficiently. The NTO is typically run in combination with a casing collar locator and temperature tool as well as any other **Sondex Ultrawire tool** such as Gamma ray, pressure, cement bond, calliper, metal thickness, or production log.



Specifications

	FlexSand LS
Temperazture rating	350°F (177°C)
Pressure rating	20,000 psi (138 MPa)
Tool diameter	$1^{11}/_{16}$ in. OD (43 mm)
Tool length	24 in. (609.6 mm)
Tool weight	10 lb (4.53 kg)
Frequency range	100 Hz to 12,700 Hz
Amplifier gain	22.4 to 67.8 dB (or x13 to x2455)
Resolution	16 bit
Dynamic range	72 dB
Data reading rate	0.5 sec
Sample length	10 ms
Sample rate	25.6 kHz
Number of spectral channels	128



Combined plot of NTO data with other measurements like pressure and temperature. Comparison of shut-in and leaking surveys allow identification of leak location

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Oxygen Activation Log

DCN: W17R008.A2

RESERVOIR PERFORMANCE MONITOR (RPM)

Advancing Reservoir Performance
Formation evaluation and reservoir monitoring

TIER 1

COMPREHENSIVE RESERVOIR EVALUATION AND MANAGEMENT

The Reservoir Performance Monitor (RPM™) platform is an advanced, slimhole, multifunction, pulsed neutron reservoir monitoring instrument. Its instrumentation combines multiple nuclear measurements in one system with industry-leading accuracy and precision. Carbon/oxygen (C/O) and pulsed neutron capture (PNC) measurements acquired with the RPM tool provide water saturation and three-phase holdup determination, while oxygen activation measurements allow detection of water flow and channels.

RPM services address a broad scope of reservoir evaluation and management applications, including reservoir saturation and produced fluids monitoring, formation evaluation, production profiling, workover and well abandonment evaluation, borehole diagnostics, location of bypassed oil, gas detection and quantification, and identification of water production.

The RPM instrument employs three high-resolution gammaray detectors arrayed above an efficient and reliable neutron generator. State-of-the-art detector electronics measure both the arrival time and energy of detected gamma rays. The generator is pulsed at distinct frequencies, and the data acquisition system operates in various timing modes to obtain the different logging measurements. The system hardware is combinable with other production logging instruments; and it is constructed in short, modular sections to facilitate shipping and handling.

ACCURACY IS PARAMOUNT

The accuracy of the RPM service has been ensured by extensive physical characterization in Baker Hughes' Houston Technology Center. The tool's measurements have also been enhanced by 3-D and Monte Carlo modeling to provide accurate response in a wide range of borehole, casing, formation, and fluid conditions; and Baker Hughes' unique Dynamic Response Generator™ feature delivers accuracy and confidence in any borehole geometry.

Unique downhole conditions can be modeled to ensure that analysis of the reservoir is the most accurate available. And extensive pre-job planning tools are available for design of a data acquisition program that optimizes the final answers delivered by the service.

EFFICIENCY IS DESIGNED IN

Flexibility and operating efficiency make the RPM tool a complete multimode, multisensor, solution-based system. All operating modes are selectable by surface commands.

The RPM instrument can be run in combination with conventional production logging sensors to provide a complete picture of a well's production and reserves in a single trip. It can also be combined with Baker Hughes' unique Multi-Capacitance Flow Meter (MCFM™) instrument in the POLARIS™ system for evaluation of highly deviated wells.

WHY THE RPM TOOL WORKS SO WELL

The RPM instrument uses high-energy neutrons to measure both the inelastic and capture gamma rays.

The inelastic gamma rays, produced by fast neutron collisions during the accelerator pulse, are used for carbon/oxygen measurement to determine the formation water saturation in formations with fresh or unknown connate water salinity.

The capture gamma rays, generated by the absorption of slow or "thermal" neutrons after the pulse, are used to measure formation water saturation in formations with saline connate water. The sensitivity of the capture process to salinity produces a log response similar to a conductivity measurement, where the measured thermal neutron absorption cross section (∑) is used to determine water saturation.

Baker Hughes

RESERVOIR PERFORMANCE MONITOR (RPM)

TIER 1



APPLICATIONS AND SOLUTIONS

FORMATION EVALUATION

- Cased hole water and gas saturation measurements
  - Through casing (with through-tubing deployment capability)
  - When openhole logs are unavailable or uneconomical
- Quantification of total hydrocarbons in medium- to high-salinity conditions
- Quantification of liquid hydrocarbons in low- and mixed-salinity conditions
- Identification and quantification of gas, independent of salinity
- Evaluation of porosity
- Identification of mineralogy

RESERVOIR MONITORING AND MANAGEMENT

- Monitoring fluid contacts
  - Time-lapse fluid monitoring
  - Gas/oil/water contact levels
  - Production and reservoir depletion
  - Identification of bypassed hydrocarbons
- Reservoir management base logs

BOREHOLE DIAGNOSTICS

- Identification of water channeling and casing leaks
- Production/injection profiling in multiple-string completions
- Multiphase borehole fluid holdup determination

WORKOVER APPLICATIONS

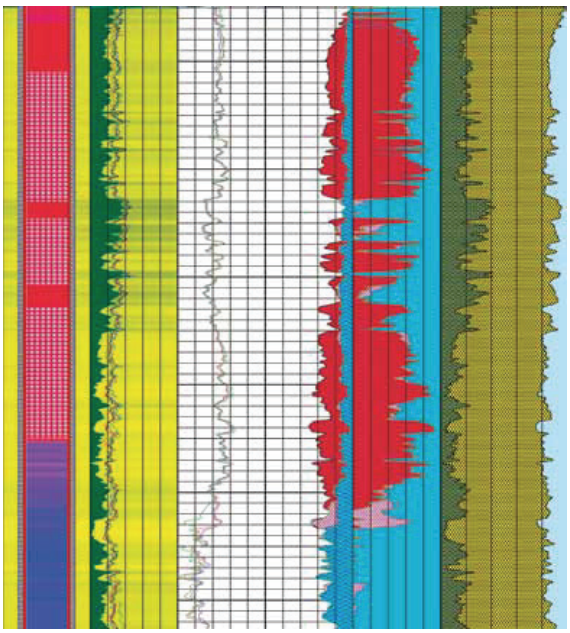
- Location of bypassed hydrocarbons, independent of water salinities
- Evaluation of stimulation operations
- Log-inject-log surveys for determining irreducible hydrocarbons
- Production/injection profiling

The RPM instrument employs three high-resolution gamma-ray detectors arrayed above an efficient and reliable neutron generator.

PULSED NEUTRON CAPTURE

In the Pulsed Neutron Capture (PNC) logging mode, the detectors record the arrival time of the gamma rays, from which the formation ∑ is determined. Time spectra from short-spaced and long-spaced detectors can be processed individually to provide traditional ∑ information. The multiple spectra are processed simultaneously to correct for borehole and diffusion effects, producing a real-time corrected formation ∑ measurement. Multiple additional measurements are provided to measure formation porosity, shale volume, and borehole fluid changes, as well as to identify formation gas.

Advanced interpretation of PNC data is available through Baker Hughes' GEOScience centers using the SEARCH™ analysis program. The identification of gas zones and the measurement of formation gas saturation is performed using the PNC mode. In this application, Baker Hughes combines special instrumentation, response characterization, and an interpretation algorithm to produce a state-of-the-art gas measurement.



Apparent measurements from near and far detectors are combined to produce a real-time corrected formation ∑.

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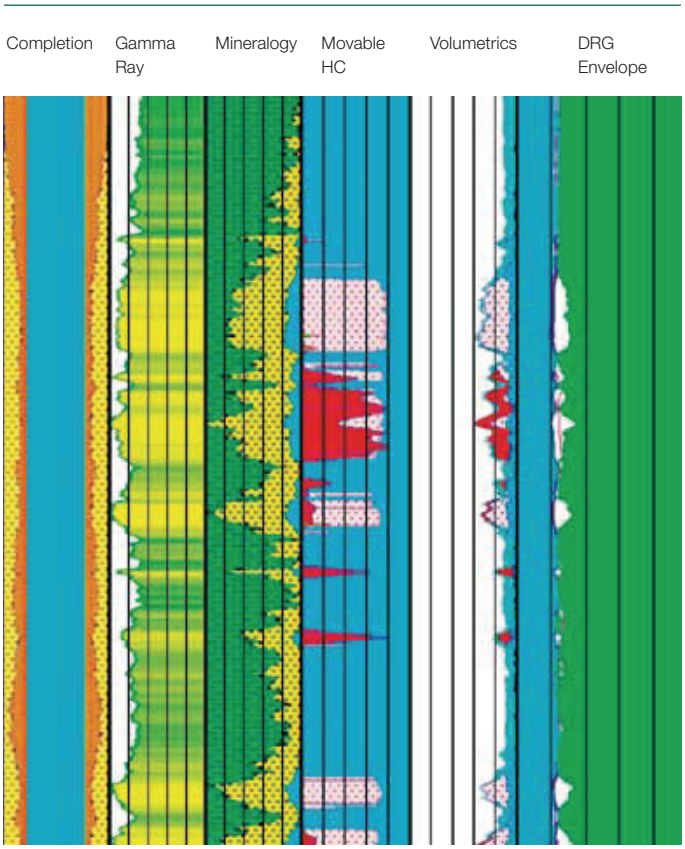
RESERVOIR PERFORMANCE MONITOR (RPM)

TIER 1

CARBON/OXYGEN LOGGING

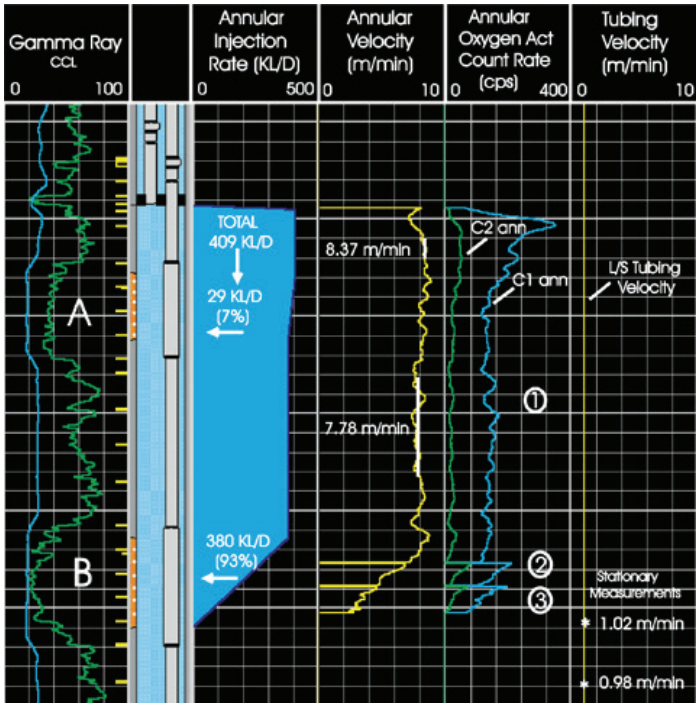
When formation waters are fresh, brackish, or of mixed or unknown salinity, the RPM-C/O acquisition mode is used to detect hydrocarbons. In this mode, direct measurements of the oxygen and carbon content of the reservoir are made, allowing differentiation of hydrocarbon zones from water-bearing zones.

Since chlorine has virtually no inelastic reaction cross section, the C/O measurement can be used to determine formation water saturation independent of salinity.



Interpretation of basic C/O data for monitoring hydrocarbon depletion of a sandstone reservoir.

FOUR MODES FOR OPERATING VERSATILITY



AFL volumetric analysis in a dual-string injection well determined that 7% of the injected fluids were entering zone A and 93% were going into zone B.

WATER FLOW LOGGING

The RPM Annular Flow Log (AFL™) and Hydrolog™ measurements use the principle of oxygen activation to measure water flow. In this application, oxygen is made artificially and temporarily radioactive through the neutronexchange reaction, allowing it to be used as a short-lived tracer. Detection of the movement of the activated oxygen can determine water velocity. These measurements provide a powerful diagnostic tool to identify movement inside the casing, outside the casing, or in the tubing-casing annulus. The measurement techniques allow detection of water movement from 2 to 500 feet per minute in simple and complex completions.

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RESERVOIR PERFORMANCE MONITOR (RPM)

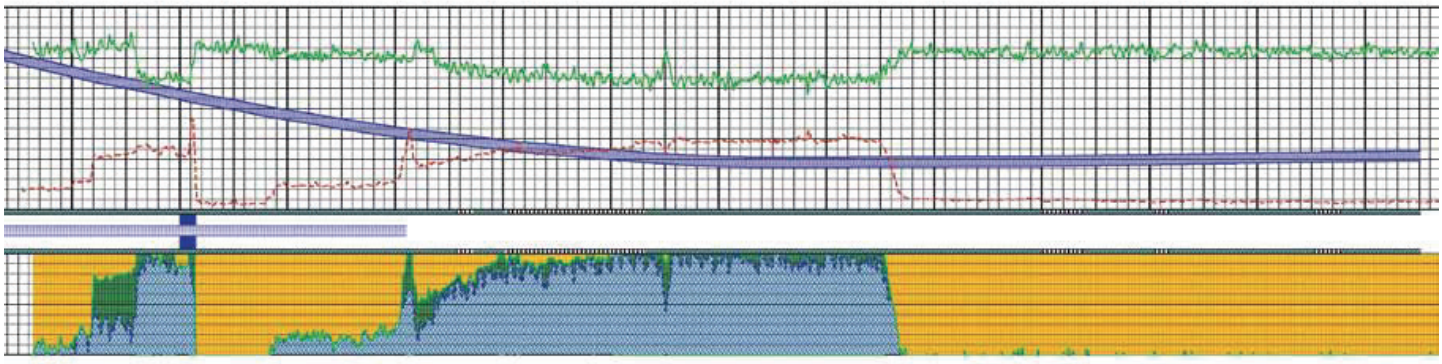
TIER 1

LOG YOUR MOST HOSTILE WELLS

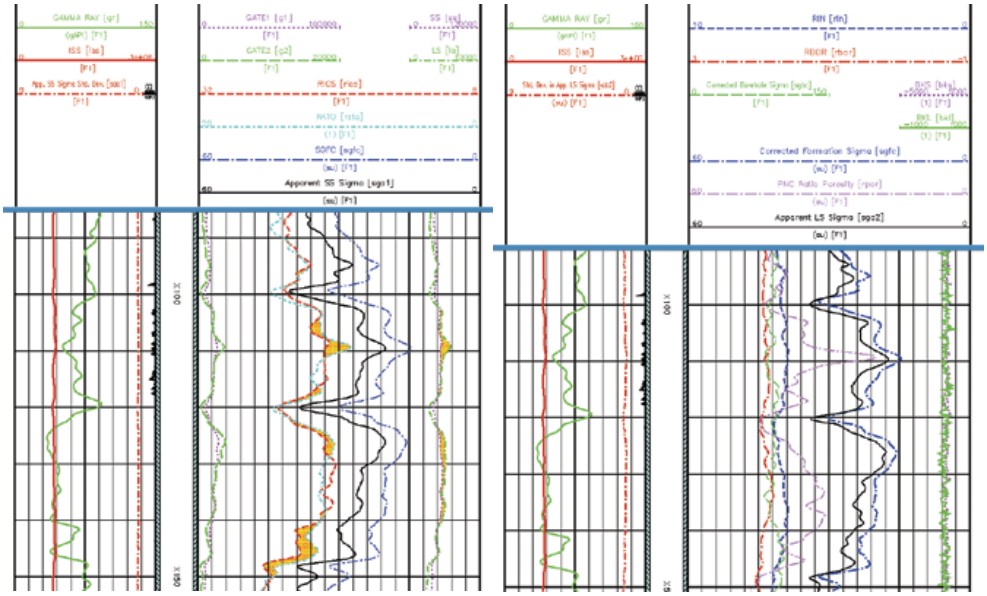
The RPM-C instrument can provide accurate data in wells in which other pulsed neutron tools cannot even survive. It has industry-best standard environmental specifications of 350°F (177°C) and 20,000 psi (138 MPa). Specially modified hardware enables reliable service at temperatures to 500°F (260°C) and pressures to 30,000 psi (207 MPa).

HOLDUP IMAGING

The RPM Pulsed Neutron Holdup Imager (PNHI™) logging mode was designed for measurement of holdups of gas, oil, and water in horizontal boreholes. The PNHI measurement produces a continuous image of the borehole contents, independent of flow regime and unaffected by gravity segregation of the produced fluids.



The PNHI log can determine gas, oil, and water holdups in horizontal boreholes.



Although RPM-PNC data acquisition and processing provide analysis results and statistics that are superior to conventional PDK-100 measurements, the RPM-PNC log display and PDK-100 presentation are similar. In time-lapse studies, an emulation of the PDK-100 curve can be provided with RPM-PNC processing for easy comparison of their measurements.

BUILD ON THE DATA YOU ALREADY HAVE

RPM data can be matched with previous-generation PDK-100™ measurements for easy comparison in mature fields. The RPM service provides real-time emulation of PDK-100 measurements for comparison with historical logs. For remedial work and timelapse monitoring, RPM data can be overlaid with existing log measurements in real time, allowing rapid workover planning.

An advanced feature of the RPM service allows real-time computation of “intrinsic” ∑. Innovative data analysis techniques provide a ∑ measurement that is corrected for borehole and diffusion effects, without prior knowledge of borehole salinity.

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RESERVOIR PERFORMANCE MONITOR (RPM)

TIER 1

INDUSTRY-BEST STANDARD ENVIRONMENT SPECIFICATIONS

RPM TOOL SPECIFICATIONS		
Temperature (standard)	350°F	177°C
Temperature (NautilusSM service)	Up to 500°F	260°C
Pressure (standard)	20,000 psi	138 MPa
Pressure (Nautilus service)	25,000 psi	172 MPa
Tool OD	1.69 in	42.9 mm
Length (without telemetry)	18.6 ft	5.7 m
Weight	75 lb	34 kg
Minimum restriction	1.80 in	45.7 mm
Maximum hole size	12.25 in	311.2 mm
Tool compressive strength	570 lb	259 kg
Tool tensile strength	22,000 lb	9,979 kg
Depth of investigation	12 in	305 mm
Maximum bend rate	30°/100 ft	30°/30.5 m

OUR EXPERIENCE AT YOUR SERVICE

Expert support at the wellsite and from the Baker Hughes GEOScience Center provide the foundation for superior reservoir surveillance solutions.

Since inception, Tier 1 has provided cased-hole logging services. When required, we work with technology leaders that provide specific logging solutions. The RPM from Baker Hughes is an example of how Tier 1 will provide the best in service quality while deploying logging equipment supported by the experts of the technology.

Baker Hughes

Casing Inspection Log

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WELL INTEGRITY: PIPE EVALUATION

High-Resolution Vertilog (HRVRT) service

Evaluate pipe integrity with the fastest and most precise tool in the market

Applications

- Identify internal versus external corrosion problems
- Locate holes, corrosion, depth of penetration, and other defects
- Determine the effectiveness of cathodic protection and corrosion inhibitors
- Discriminate between actual corrosion and well completion equipment

Features and benefits

- Multiaxial sensors with next-generation multiaxis data technology
  - Offer improved defect descriptions with greater accuracy and reliability
  - Allow increased circumferential and axial resolution
- Dynamic range of applications in a variety of downhole conditions
  - Offers greater flexibility in logging below casing
  - Enables negotiation around casing patches and other hardware
  - Eliminates unnecessary remediation work and reduces unplanned production outages
- Deployable on wireline or **TeleCoil™ intelligent coiled tubing**
  - Provides flexibility for reaching optimal performance

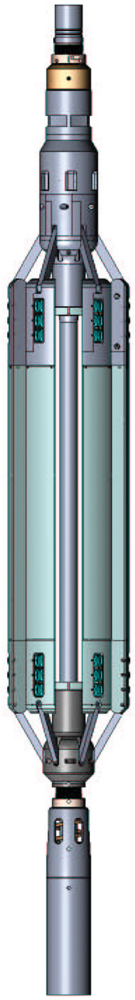
The **High-Resolution Vertilog™ (HRVRT™) service** provides the industry's most precise pipe integrity and corrosion evaluation, accurately characterizing casing and tubing strength. The service eliminates unnecessary remediation work and reduces unplanned production outages.

This service also provides flexible and efficient data acquisition, reducing operating time while improving data accuracy and operational safety. In conventional magnetic flux-leakage (MFL) tools, the flux leakage sensors are coils; however, in the Sondex high-resolution tool, the coil is replaced by multiple "hall effect" sensors. The HRVRT service uses MFL measurements to identify and quantify internal and external corrosion defects.

The overlapping arrays of the multiaxial sensors, flux-leakage sensors, and discriminator sensors offer full circumferential inspection of the tubing or casing string. This process differentiates between metal-loss (corrosion) and metal-gain (hardware) features, and distinguishes between general corrosion and isolated pitting. The service provides tubular burst-and-collapse strengths based on customer-defined criteria, facilitating consistent and rapid evaluation of the well's integrity.

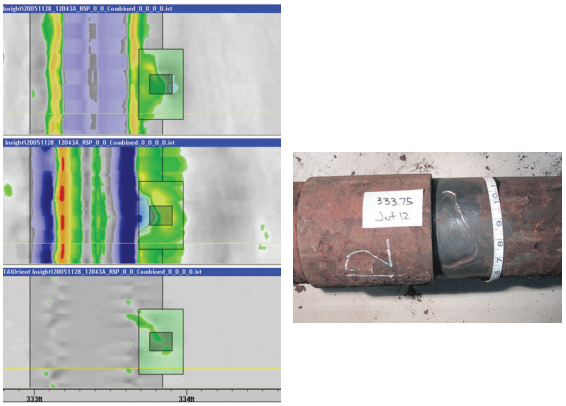
The HRVRT service provides a quantifiable defect description with an increased accuracy for length, width, and depth determination. This data is accurate for input into burst pressure calculations.

The HRVRT data acquisition is independent of logging speed. This allows it to better characterize defects in the well (especially near the wellhead), eliminate unnecessary remediation work, and reduce unplanned production outages.

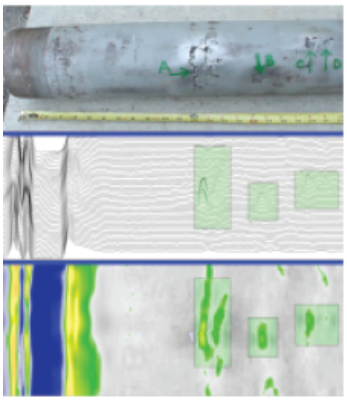


High-Resolution Vertilog (HRVRT) service specifications

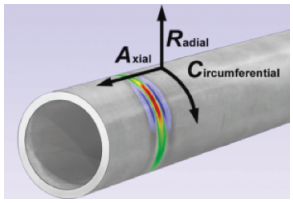
Tool series		4993	4994	4995	4997
Casing applications (in.)		3 1/2	4 1/2	5, 5 1/2	7, 7 5/8, 8 5/8, 9 5/8
Dynamic range	Maximum	3.3 in. (8.38 cm)	5.3 in. (13.46 cm)	5.3 in. (13.46 cm)	9.425 in. (23.99 cm)
	Minimum	2.7 in. (6.86 cm)	3.63 in. (9.22 cm)	4.0 in. (10.16 cm)	5.5 in. (13.97 cm)
Casing weight	Maximum	9.3 lb/ft (1.28 kg/m)	17 lb/ft (2.52 kg/m)	32 lb/ft (4.4 kg/m)	54 lb/ft (7.46 kg/m)
	Minimum	9.2 lb/ft (1.27 kg/m)	6.75 lb/ft (0.93 kg/m)	11.5 lb/ft (1.58 kg/m)	13 lb/ft (1.8 kg/m)
Tool length		15.5 ft (4.72 m)	15.5 ft (4.72 m)	15.5 ft (4 .72 m)	19.75 ft (6.01 m)
Tool weight		300 lb (136.08 kg)	310 lb (140.9 kg)	340 lb (154.54 kg)	726 lb (329.54 kg)
Sensors	Axial	24 hall effect	48 hall effect	48 hall effect	96 hall effect
	Radial	24 hall effect	48 hall effect	48 hall effect	96 hall effect
	Circumferential	24 hall effect	48 hall effect	48 hall effect	96 hall effect
	Discriminator	N/A (MIT)	48 hall effect	48 hall effect	96 hall effect
Logging speed		200 ft/min (61 m/min)	180 ft/min (54.8 m/min)	180 ft/min (54.8 m/min)	160 ft/min (48.8 m/min)
Maximum pressure		15,000 psi/103.4 Mpa			
Maximum temperature		350°F/175°C			



The pipe and cross-sectional measurements of the defect and its analysis



Excellent agreement in the comparison of the HRVRT instrument measurements, analysis, and pipe



Multidirectional measurements for accuracy

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6.12.13 High Resolution Vertilog (HVRT)

TECHNICAL DATA SHEET ELECTRIC WIRELINE/ LOGGING	DOWNHOLE EQUIPMENT AND INSTRUMENTS
Contractor:	Baker Hughes
Equipment/instrument name:	High-Resolution Vertilog
Type/series no.	4994/4995/4996
Standard abbreviation - service/tool	HRVRT
Application - open/cased hole	CH
Parameters measured	Magnetic flux leakage
Detection	axial, radial and circumferential fields
Coverage	100%
Sensors	1/4" x 1/4" Tri-Axial Hall
Calibration - none/shop/rig/downhole	Shop
Maximum operating pressure	15,000 psi
Maximum operating temperature	175° C
Maximum borehole/casing/tubing size	9.5/8"
Minimum borehole/casing/tubing size	4 1/2"
Min./max. opening size (if applicable)	NA
Mud type or weight limitations	N/A
Outside diameter (max. , closed)	See below
Length	See below
Weight (in air)	See below
Fishing neck OD.	3 3/8" Cablehead / 1 3/8" head
Radioactive source type and size	N/A
Logging speed min./max.	61 m/min
Surface acquisition system requirements	ECLIPS or CASE
Cable requirements (no. conductors, etc.)	1 or 7 conductor cable
Special capabilities: 4994: Tubing/Casing range: 41/2". Inst. Length: 4.72mt. Inst. Weight: 141kg. O.D. closed: 3.63" 4995: Tubing/Casing range: 5-5.5". Inst. Length: 4.72mt. Inst. Weight: 154kg. O.D. closed: 4" 4996: Casing range: 7-9 5/8"". Inst. Length: 6mt. Inst. Weight: 330kg. O.D. closed: 5.5"	

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6.12.35 Ultrasonic Cement Evaluation (ULTeX)

Table 6.3 No Title

TECHNICAL DATA SHEET ELECTRIC WIRELINE LOGGING	DOWNHOLE EQUIPMENT AND INSTRUMENTS
Contractor:	Baker Hughes
Equipment/instrument name:	Ultrasonic Isolation eXplorer
Type/series no.	1674 EA, MA
Standard abbreviation - service/tool	ULTeX
Application - open/cased hole	CH
Parameters measured	Cement Integrity, Casing ID, Casing Thickness
Range of measurement	0 - 10 Mrayl
Sensitivity	N/A
Accuracy	Cement Impedance: 0 - 3.3 Mrayl +/- 0.50 Mrayl > 3.3 Mrayl +/- 15% Casing Thickness: +/- 6%
Calibration - none/shop/rig/downhole	Shop & Downhole
Maximum operating pressure	20,000 psi
Maximum operating temperature	175° C for 4 Hrs.
Maximum borehole/casing/tubing size	13-3/8"
Minimum borehole/casing/tubing size	5.0”
Min./max. opening size (if applicable)	N/A
Mud type or weight limitations	OBM, 1.6 g/cc (12 db/cm per MHz)
Outside diameter	3-5/8”
Length	3.92 m (EA + MA sections)
Weight (in air)	98 kg (EA + MA sections)
Fishing neck OD.	3 3/8” cablehead
Radioactive source type and size	N/A
Logging speed min./max.	3 m/min (10ft/min)
Surface acquisition system requirements	ECLIPS
Cable requirements (no. conductors, etc.)	Multiconductor cable
Special capabilities:	High circumferrential resolution cemet bond,

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TECHNICAL DATA SHEET ELECTRIC WIRELINE LOGGING	DOWNHOLE EQUIPMENT AND INSTRUMENTS
	casing ID and casing thickness measurement. Simultaneous Cement and casing evalution.
Combination possibilities/limitations:	GR/CCL/ORIT. Combinable with INTeX.

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Cement Bond Log

DCN: W17R007.A1

SEGMENTED BOND TOOL (SBT)

WELL INTEGRITY EVALUATION SERVICE

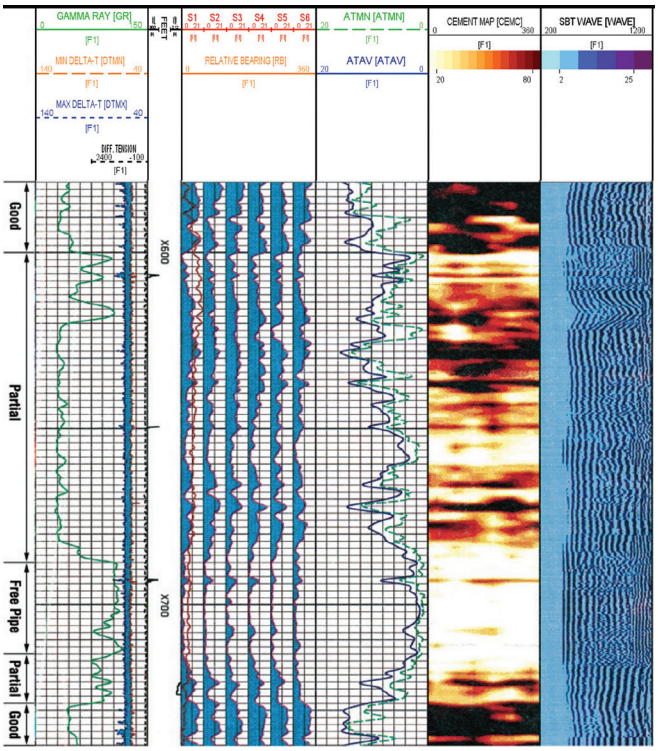
Confirm hydraulic isolation and avoid remedial work by evaluating cement bond integrity.

The Baker Hughes Segmented Bond Tool (SBT™) well integrity evaluation service quantitatively measures the cement bond integrity in six angular segments around the casing, delivering the information needed to confirm hydraulic isolation and determining whether remedial work is required before any completions are attempted. The SBT service operates at the ultrasonic frequency range, and quantitatively measures the cement bond integrity in six angular segments around the casing to ensure a strong hydraulic seal in these locations, thus improving productivity and well life span. The service can find and define channels in the cement annulus, enabling the operator to determine next steps. Conversely, the SBT service can reliably find zones of uniform bonding within a few feet of casing. Under conditions where a short-bonded interval produces an adequate hydraulic seal, squeeze jobs can be avoided.

The SBT service offers significant operating advantages over conventional and pulse-echo tools due to its insensitivity to heavy or gas-cut borehole fluids, dense muds, emulsions, fast formations, temperature and pressure variations, and moderate tool eccentering. The service can evaluate cement in heavyweight casings up to 1-in. thick.

For ease of interpretation, SBT measurements are displayed in two log presentations. Both presentations are available in the logging mode, as the SBT data are acquired, processed, and plotted in real time. The secondary presentation consists of six continuous segmented arrays, a variable-attenuation cement map, and a tool-orientation trace overlay—a field deliverable that does not require engineer interaction. It also provides a 5-ft-spaced variable-density log measurement, used to qualitatively understand the bonding between cement and the formation.

The SBT™ Beyond service enables the SBT service to extend the maximum casing size from 16 in. to 24 in., thus offering a tool covering the widest casing size range in the cement evaluation segment. The SBT Beyond service is capable of evaluating cement behind casing sizes larger than 133/8 in., which is unique in the industry. Combined with the benefit of this wide casing thickness range of the SBT service (up to 1-in. thickness), the SBT Beyond service addresses challenges in segments where pulse-echo devices cannot perform.



The field deliverable is a real-time, non-processed log that is not dependent on the logging engineer's input.

For more information on how the SBT service can help you determine if remedial work is required before completions are attempted, contact your Baker Hughes representative today or visit **bakerhughes.com/SBT**.

SEGMENTED BOND TOOL (SBT)

WELL INTEGRITY EVALUATION SERVICE

TIER 1 ENERGY SOLUTIONS | BAKER HUGHES a GE company

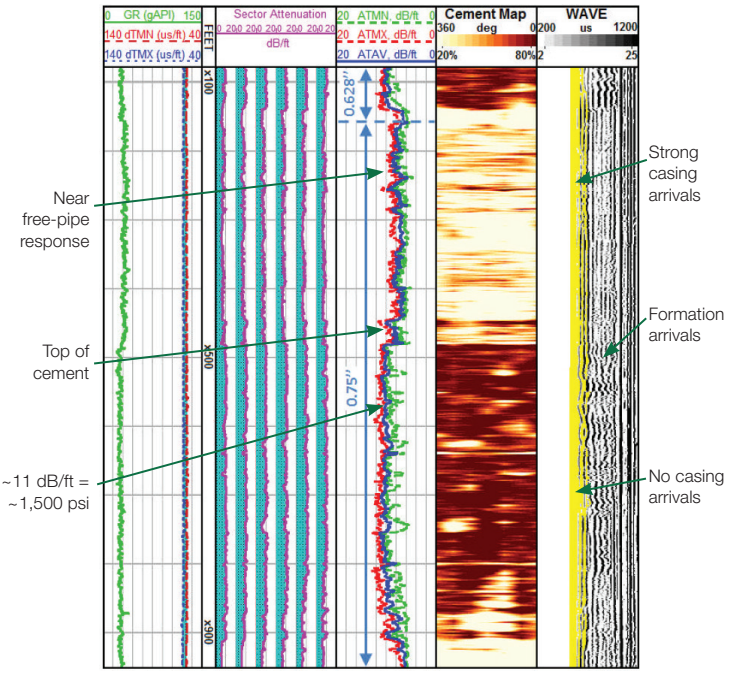
FEATURES & BENEFITS

- Pad-mounted
  - Identifies intervals of uniform bonding and detects cement channels or voids
  - Identifies channeling and poor cement bond sections to reduce risk
  - Reduces analysis time, using a 360° easy-to-interpret cement map
  - Provides accurate measurement in any type of formation condition, up to 1-in.-thick casing
  - Provides accurate measurement, even in fast formations, heavy mud, and thick wall casing
  - Evaluates multiple-size casing strings in one logging pass
- Insensitive to moderate eccentering
  - Enables deployment in the most challenging scenarios
- Fully compensated measurement
  - Unaffected by varying wellbore fluid conditions, pressure, and temperature
- Casing range from 4.5 to 24 in.
  - Provides the widest casing range coverage in the industry

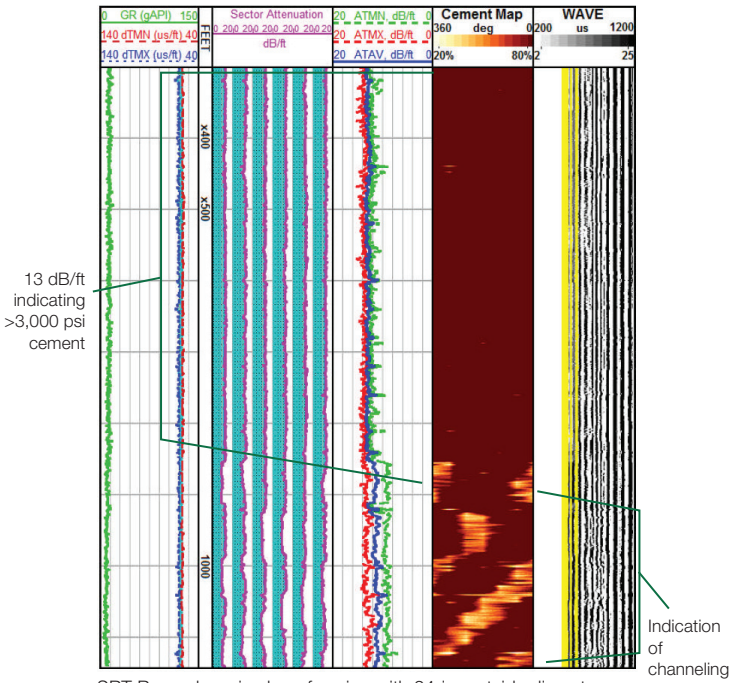
APPLICATIONS

- Provides quantitative analysis of cement bond to the casing around the borehole
- Provides qualitative analysis of cement bond with the formation

Length	32.1 ft.	
Diameter	3.38 in.	
Pressure rating	20,000 psi	
Temperature	350°F	177°C
Weight	481 lb.	
Min. casing size	4.5 in.	
Max. casing size	24 in.	
Measurement range	0–25 dB/ft	
Radial resolution	360° coverage	
Vertical resolution	3 in.	76.2 mm



SBT Beyond service log of casing with 20-in. outside diameter (OD) and 0.984-in. wall thickness



SBT Beyond service log of casing with 24-in. outside diameter (OD) and 0.75-in. wall thickness

6.12.8 Segmented Bond Tool (SBT)

TECHNICAL DATA SHEET ELECTRIC WIRELINE/ LOGGING	DOWNHOLE EQUIPMENT AND INSTRUMENTS
Contractor:	Baker Hughes
Equipment/instrument name:	Segmented Bond Tool
Type/series no.	1424 EA, MB
Standard abbreviation - service/tool	**SBT**
Application - open/cased hole	CH
Parameters measured	Cement integrity, segmented inspection, borehole deviation
Range of measurement	0 - 22 dB/ft compensated attenuation
Sensitivity	N/A
Accuracy	+/- 0.50 dB/ft
Calibration - none/shop/rig/downhole	rig
Maximum operating pressure	20,000 psi
Maximum operating temperature	177° C for 30 minutes
Maximum borehole/casing/tubing size	16"
Minimum borehole/casing/tubing size	4.2"
Min./max. opening size (if applicable)	3 3/8" - 16" (16" – 24")
Mud type or weight limitations	N/A
Outside diameter (max. , closed)	3 3/8"
Length	7.62 m
Weight (in air)	157.8 kg
Fishing neck OD.	3 3/8" cablehead
Radioactive source type and size	N/A
Logging speed min./max.	up to 9 m/min
Surface acquisition system requirements	ECLIPS or CASE
Cable requirements (no. conductors, etc.)	Single conductor cable
Special capabilities: Direct attenuation measurement, 6 sectors, unaffected by mud type or mild decentralisation, cement map imaging, separate VDL measurement. SBT Beyond service extends range from 16 – 24".	

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TECHNICAL DATA SHEET ELECTRIC WIRELINE/ LOGGING	DOWNHOLE EQUIPMENT AND INSTRUMENTS
Combination possibilities/limitations: GR/CCL/CN. Combinable with XMAC-F1, Multi-Finger Caliper (MFC), RPM and HRVRT.	

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Casing Collar Locator Log

6.12.2 Casing Collar Locator (CCL)

TECHNICAL DATA SHEET ELECTRIC WIRELINE/LOGGING	DOWNHOLE EQUIPMENT AND INSTRUMENTS
Contractor:	Baker Hughes
Equipment/instrument name:	Casing Collar Locator
Type/series no.	2321NA
Standard abbreviation - service/tool	**CCL**
Application - open/cased hole	Casing Collar
Parameters measured	N/A
Range of measurement	N/A
Sensitivity	N/A
Accuracy	N/A
Calibration - none/shop/rig/downhole	none
Maximum operating pressure	20,000 psi
Maximum operating temperature	204° C for 30 minutes
Maximum borehole/casing/tubing size	N/A
Minimum borehole/casing/tubing size	1.9″
Min./max. opening size (if applicable)	N/A
Mud type or weight limitations	N/A
Outside diameter (max. , closed)	1.7″
Length	0.58 m
Weight (in air)	6.1 kg
Fishing neck OD.	1 3/8″ cablehead
Radioactive source type and size	N/A
Logging speed min./max.	Up to 45 m/min
Surface acquisition system requirements	ECLIPS or CASE
Cable requirements (no. conductors, etc.)	Single conductor cable
Special capabilities: N/A	
Combination possibilities/limitations:	

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APPENDIX D-V

Determination of Mechanical Integrity of Injection Wells

DETERMINATION OF THE MECHANICAL INTEGRITY OF INJECTION WELLS

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 5 -- UNDERGROUND INJECTION CONTROL (UIC) BRANCH
REGIONAL GUIDANCE #5

Revised February, 2008

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 5 -- UNDERGROUND INJECTION CONTROL (UIC) SECTION
REGIONAL GUIDANCE #5

DETERMINATION OF THE MECHANICAL INTEGRITY
OF INJECTION WELLS

Revised February, 2008

1 ISSUE

Demonstrations of mechanical integrity (MI) are the most common means of demonstrating that there is no movement of fluids into or between underground sources of drinking water (USDWs) associated with injection wells. Although relatively simple in theory, MI tests (MITs) must be conducted so that their validity as well as their outcome is evident. The Underground Injection Control (UIC) Branch of the Water Division in Region 5, United States Environmental Protection Agency (USEPA), as the authority in matters of MI in Region 5, should establish guidelines which will assist operators and regulators of injection wells in Region 5 subject to demonstrations of MI to conduct those demonstrations such that the results will be useful.

2 PURPOSE OF GUIDANCE

The guidelines were developed by the UIC Branch of Region 5 USEPA, to assist owner/operators of injection wells in Region 5 to demonstrate MI. Procedures varying from these guidelines may be accepted if first approved by the Director of the USEPA.

Pursuant to 40 C.F.R. &sect 146.8(a) "an injection well has mechanical integrity if: (1) there is no significant leak in the casing, tubing, or packer; and (2) there is no significant fluid movement into an USDW through vertical channels adjacent to the injection well bore". The absence of significant leaks is demonstrated through the use of tests which have been approved for that purpose by the Administrator (MI tests). The methods presently accepted for establishing MI pursuant to 40 C.F.R. &sect 146.8(a)(1) [part 1] of MI for wells operating in states in which the UIC Branch implements the UIC regulations, include: 1) the standard annulus pressure test (SAPT), 2) the standard annulus monitoring test (SAMT), 3) the radioactive tracer survey (RTS), and for certain Class III wells: the water-brine interface test (W-BIT. Other methods, including the Ada pressure test(AT) and the cementing pressure/single point resistivity test, are approved for national use under certain circumstances, but are not used in Region 5. In addition, the dual completion monitoring test (DCMT) is used by a few wells in Michigan and Indiana although interim approval has expired. The procedures for this test are under review. Accepted methods for demonstrating MI pursuant to 40 C.F.R. &sect 146.8(a)(2) [part 2] include: 1) the results of a temperature log, 2) noise log, 3) oxygen activation log, 4) the re.sults of a radioactive tracer survey (RTS) (when the injection zone is separated from the lowermost USDW by a single confining layer), or 5) for all Class II wells and for Class III wells in which the casing precludes the use of logging techniques, cementing records demonstrating the presence of adequate cementto prevent fluid migration into USDWs pursuant to 40 C.F.R. &sect 146.8(c)(2) and (c)(3) respectively. Demonstrations of both part 1 and part 2 of MI must be made before injection can be authorized.

The procedures which are recommended in the attachments to this document will, in most cases, result in development of valid data which Region 5 will be able to interpret with confidence. Deviations from these procedures may result in anomalies which will complicate or even invalidate test results. If the recommended test results do not result in definitive information, any anomalies noted should be investigated immediately, including re-doing the tests. Results which provide demonstrations of MI are the purpose of this guidance, but adherence to guidance may not ensure development of acceptable results in all cases. In such cases, mere adherence to guidance does not absolve the operator from the requirement to demonstrate MI. In cases in which there is doubt about the certainty of outcomes,

reference to and comparison with previous tests can often be used to clarify the test results. In this vein, comparison of tests through time, especially the comparison of temperature and radioactive tracer logs can make interpretation easier and make progressive change apparent. In all cases, operators should submit proposed testing procedures to the UIC Branch's Direct Implementation (DI) Section for approval before the testing is done. This can prevent misunderstandings and possible retesting.

3 DISCUSSION

3.1 Mechanical Integrity Pursuant to 40 C.F.R. &sect 146.8(a)(1)

There are a limited number of means by which part 1 of MI (the absence of significant leaks in tubing, casing, and packer) may be demonstrated. Therefore, little discussion of the relative merits of the various tests is necessary.

3.1.1 The Standard Annulus Pressure Test (SAPT)
The SAPT is the most common means used to demonstrate part 1 of MI. This test is based on the principle that a pressure applied to fluids filling a sealed vessel will persist. A well's annulus system, though closed to transfer of matter, is not closed to energy transfer because it is not isolated from transfer of heat from its surroundings, therefore an allowance for small pressure changes is necessary. The test provides an immediate demonstration of whether or not leaks, detectable by these means, exist. A discussion of and procedures for the SAPT are outlined in Attachment 1.

3.1.2 The Standard Annulus Monitoring Test (SAMT)
Pursuant to 40 C.F.R. &sect 146.8(b), monitoring of the annulus pressure is an approved method for establishing part 1 of MI for all wells. Annulus pressure monitoring for Class I wells required at &sect 146.13(b)(2) to verify the maintenance of a minimum pressure differential is not the SAMT, because changes in pressure due to loss of annulus liquid are attenuated by the presence of a gas blanket which is replenished as pressure decreases. If annulus monitoring is used to demonstrate MI, an initial SAPT is required. Annulus monitoring may continue throughout the life of the well or the operator may choose, at any time, to conduct a SAPT every five years and after well reworks (on rule authorized Class II wells and on permitted wells if the particular UIC permit allows it), thereby discontinuing the SAMT. A discussion of the merits and procedures for the SAMT is provided in Attachment 2.

3.1.3 The Radioactive Tracer Survey (RTS)
On September 18, 1987, the USEPA published a Federal Register (FR) notice at 35324 et seq. FR 52, No. 181, giving interim approval for the use of the RTS as an alternative MIT. In a FR Notice at 46837 et seq. FR 52, No. 237 on December 10, 1987, the USEPA announced final approval of the RTS as a demonstration of part 1 and 2 (as limited), and provided clarifications and additional information based on comments received and the use of the test during the interim approval period. A discussion of and procedures for conducting the RTS as a demonstration of part 1 of MI in Region 5 are outlined in Attachment 3.

3.1.4 Water-Brine Interface Test (W-BIT)
On January 10, 1992, approval of the W-BIT was announced in the Federal Register at 1109 et seq FR 57, No. 7. The test is valid only for Class III wells and only when construction and operating conditions make testing with the SAPT impractical. Although there are no special recommendations applicable in Region 5, additional explanation of the basis for the test is provided in Attachment 4, and a full description of the procedures for conducting the W-BIT is available in the above referenced FR Notice.

3.1.5 Ada Pressure Test
The Ada test is a variant of the SAPT. It is used to test wells which have perforations above the injection zone. It can be used to test the integrity of the casing above the perforations. To conduct the test gas pressure is used to depress the liquid level to a point just above the perforations. The

pressure is measured over a period of time. If the pressure change is less than the established limit, the well has mechanical integrity.

3.1.6 Water-in-Annulus Test (WIAT)
The WIAT was announced at 14678 et seq 54 FR No. 19 on April 12, 1989, for existing Class II wells for enhanced oil recovery in the counties in which the Bradford oil field is located in New York and Pennsylvania. Approval of the test was extended to similar wells in the Redhaw oil field in Ashland County, Ohio. The test is used for wells which are constructed without long string casing. The level of water near the top of the annulus between the surface casing, which protects all USDWs, and the injection tubing which is set on a formation packer and may have some cement on the top of the packer, is observed under specified conditions. The presence and nature of relatively small leaks can be determined.

3.2 Mechanical Integrity Pursuant to 40 C.F.R. &sect 146.8(a)(2)

Owner/operators have a choice of a number of methods for demonstrating that wells have part 2 of MI (no significant fluid movement into a USDW through vertical channels adjacent to the injection well bore). The conditions under which these tests can be used to best effect differ significantly; therefore, a listing of relative advantages and disadvantages of the various options is provided in the attachments concerning each of the approved methods for demonstrating part 2 of MI.

3.2.1 Temperature Logs (TL)
Temperature logs are a very versatile and sensitive means of identifying fluids which have moved along channels adjacent to the well bore. In addition to demonstrations of part 2 of MI, temperature logs can be used to monitor fluid movement through the confining zone adjacent to the well bore and can often locate small casing leaks. To be effective for demonstrations of MI, there must be adequate time available for short-term temperature effects along the well bore to dissipate. Background information and general procedures for running t emperature logs are provided in Attachment 5.

3.2.2 Noise Logs (NL)
The use of noise logs is based on the observation that flow behind the casing in the well bore will, at some points, be turbulent. Turbulent flow causes noise which may travel for significant distances along the well bore. Noise logs are appropriate where it is impractical for injection operations to be suspended for the length of time needed to allow temperature stabilization to proceed to the point at which a temperature log can be run with good results. They can also be used to locate some tubing or casing leaks. Background information and procedures for using noise logs to demonstrate part 2 of MI are found in Attachment 6.

3.2.3 Oxygen Activation Method (OAL)
On February 1, 1991, the USEPA published a FR Notice (FRN)granting final approval, effective March 4, 1991, for use of the oxygen activation method or log (OAL) as a means of demonstrating part 2 of MI. Details of the operation and conditions under which the OAL can be used can be found at 4063 et seq. FR 56, No. 22 which is included in this guidance as Attachment 7.

3.2.4 Radioactive Tracer Survey
The same FRNs which describe how the RTS can be used for demonstrating part 1 of MI also describe its use for demonstrating part 2 of MI. This method may be used only where there is only a single confining formation separating the lowermost USDW from the injection zone with no aquifers within it. Additional requirements and limitations of the RTS are described in the previously mentioned FR Notices (See III.C.). The use of the RTS as a means of demonstrating part 2 of MI is described in Attachment 8.

3.2.5 Cement Records
The most common demonstration of part 2 of MI for Class II wells is based on cementing records. Demonstrations of MI for Class III wells can also be based on cementing records if the configuration of

wells prevents the use of logging methods. If records show that casings are cemented in a way which will prevent the movement of liquids into or between USDWs, the well has part 2 of MI. A discussion of the use of cementing records is provided in Attachment 9.

3.3 Additional Mechanical Integrity Tests

Other alternative MITs will be added to this guidance if approved by the Administrator of the EPA for use in Region 5. In order for a test to be approved, it must be submitted to the Water Division Director in Region 5 with all supporting evidence. If the proposal is approved by the Director, then it will be submitted to the Administrator, and will be evaluated by the national UIC Technical Workgroup which will evaluate its effectiveness. If approved by the Administrator, the approval and any limitations placed on the test will be promulgated in the Federal Register. In addition, specific procedures outlined in this guidance may be modified after additional data are obtained or to accommodate a particular type of well construction. National UIC Guidances #15 and #34 include information relating to approval of alternate methods of testing mechanical integrity.

3.4 Tests which are not MI Tests but are Specifically Required by Regulation

3.4.1 Radioactive Tracer Survey
The regulations at 40 C.F.R. 146.68(d)(2) require annual demonstrations of the integrity of cement at the top of the injection interval in Class I hazardous-waste injection wells. The RTS is more often used for that purpose than to demonstrate either part 1 or 2 of MI. The procedures for demonstrating cement integrity using the RTS are presented in Attachment 10*.

3.4.2 Casing Inspection Logs (CIL)
The regulations at 40 C.F.R. 146.68(d)(4)require periodic monitoring of change in casing thickness for Class I wells injecting hazardous wastes. The procedures for running the logs and presentation of the results are set by the logging company. Because the standards adopted by the logging companies are appropriate, no additional information is provided for running casing inspection logs.

4 CONDUCTING TESTS WITHOUT A REPRESENTATIVE OF THE USEPA

It is, and has been, the policy of Region 5 to witness mechanical integrity testing to the extent practicable. Tests for which a mechanical or third-party record is produced may be conducted without an Agency witness when it proves impossible to resolve scheduling conflicts with both the USEPA contract inspectors and the Regional technical staff.

In order to conduct testing without an USEPA representative the following procedures should be followed:

1. The owner/operator must submit proposed procedures including the information that no USEPA representative is available, and receive permission from the DI Section of the UIC Branch to proceed;
2. The test must be documented using either a mechanical device which records the value of the parameter of interest, or by a service company job record;
3. A report of the testing including all data available at the conclusion of the test and a certification of accuracy which is signed by an authorized representative of the company must be submitted to the DI Section within 10 c alendar days of the completion of testing; and
4. A final report, including any additional interpretation necessary for evaluation of the testing, must be submitted prior to or with the next regularly scheduled monitoring report or as required under the appropriate permit for the injection well.

NOTE: Pursuant to &sect 146.8(f) of the UIC regulations, Region 5 may, at any time, require a test witnessed by a USEPA representative to verify the results of an unwitnessed test. This is possible if results are ambiguous or if documentation is lacking.

5 ACTIONS TO BE TAKEN IN THE EVENT OF A FAILURE TO DEMONSTRATE MI OR LOSS OF MI DURING OPERATIONS

If upon investigation, the well appears to be lacking MI, the operator should cease injection immediately and attempt to mitigate any environmental effects of the loss of MI. The Director may allow up to 48 hours of injection if necessary to allow for a smooth shut down of operations. Pursuant to 144.28(b) or 144.51(l)(6), owners/operators are required to report any known loss of MI which might endanger health or the environment to Region 5 within 24 hours. To report a failure, operators may call Region 5 at (312) 353-4148; during nonbusiness hours a message can be left on the voice mail system. Also, pursuant to 144.28(b) or 144.51(l)(6) a written submission shall be prepared and sent to Region 5 within five days of the time the operator becomes aware of a loss of MI.

Injection into wells which have lost MI can be resumed only after a letter authorizing injection is received from the Director. The Director will prepare such a letter only if: 1) the well is repaired, a report detailing the means used to effect the repair is submitted, and MI is demonstrated or 2) the owner/operator demonstrates, by means acceptable to the Director, an absence of flow into or between USDWs pursuant to 40 C.F.R. &sect 144.28(f)(4) or 40 C.F.R. 144.51(q)(3). As an alternative, the well can be plugged in accordance with 40 C.F.R. &sect 146.10. The plugging procedures must remove any threat posed by the absence of MI. If the failure is of part 1 of MI, this is usually accomplished through cementing the leaking portion. If the failure is of part 2 the means required to eliminate the fluid movement might be more demanding.

Falsification of MI testing is a violation of 18 USC &sect 1001 and violators may be subject to criminal penalties.

ATTACHMENT 1
STANDARD ANNULUS PRESSURE TEST (SAPT)

1 Basis

Pascal's Law states that any pressure applied to a fluid filling a closed vessel will be transmitted, undiminished, throughout the vessel. This fact is the basis for the selection of the SAPT as the primary means to determine if a well's casing, tubing, packer, and wellhead (the annulus system) are liquid tight. To fully test the well bore, the pressure applied to the annulus system must be transmitted through the entire well bore. Therefore, no mechanical plug may be placed above the packer in any well subject to testing by means of the SAPT.

Because the annulus system is not an isolated system (e.g. it transmits energy, but not matter), the measured pressure applied may not be constant through time. The temperatures along the well bore must change as injection rates and temperatures change because of heat exchange between injectate and the surrounding rock. When the well is shut in part of the well bore may cool and part may become warmer. As this happens, the liquid in the annulus contracts or expands. Because liquids are only very slightly compressible, it is very unlikely that the pressure will appear to remain absolutely stable either while the well is shut in or being used for injection.

2 Advantages and Disadvantages of the SAPT

Advantages of the SAPT

1. Easy to interpret
2. Inexpensive to perform

Disadvantage of the SAPT

Provides a demonstration at a single point in time

3 Equipment and Forms

Pressure measurements must be made using a gauge which can be read with sufficient accuracy to identify pressure change which would result in failure of the test and to record accurate intervening values required per the procedures in Part D below. If the test pressure is 300 pounds per square inch, gauge (psig), then the gauge face should be marked in increments of 5 pounds per square inch (psi) or less. A gauge measuring injection pressure should be available.

The "Annulus Pressure Test" form (Attachment 11) is used to record SAPTs. Pressure measurements at intervals through the test period and the signature of an authorized witness are essential for acceptance. The most recent record of calibration for the gauge used for the MI test must be submitted along with the Annulus Pressure Test form. If authorization has been granted to conduct the test without a USEPA witness, the mechanical record of the test must be submitted as well.

4 Procedure for the SAPT:

To properly conduct the SAPT:

1. The tubing/casing annulus (annulus) must be completely filled with liquid (variations must be approved by Region 5). Temperature stabilization of the well and annulus liquid is necessary prior to conducting the test. This may be achieved by filling the annulus with liquid and either ceasing injection or maintaining stabilized injection (i.e., continuous injection at a constant rate and constant injection fluid temperature) before and through the test;

   No unapproved substances may be added to the annulus liquid. Use of any substance which might affect the outcome of testing may constitute falsification of the test procedure, invalidate the test, and may subject the owner/operator to civil or criminal prosecution;
2. After stabilization, the annuluses of Class II wells should be pressurized to a surface pressure of no less than 300 psig. The annuluses of Class I wells should be pressurized to the greater of 300 psig or a pressure which exceeds the maximum allowable injection pressure by 100 psi, unless an alternate pressure is approved by Region 5. A positive pressure differential between the pressure in the annular space and the injection tubing pressure of at least 100 psi should be maintained throughout the entire annulus (from the top of the packer to the surface) of all Class I and II wells. Specific gravity differences between liquids in the annulus and the tubing should be accounted for when determining the appropriate test pressure. Following pressurization, the annular system must be isolated from the source of pressure and the sealpot (if present) by a closed valve. If not inconvenient, the connection to the pressure source should be disconnected entirely;
3. The annulus system must remain isolated for a period of no less than 30 minutes for Class II, III, and V wells. The isolation must be maintained for one hour for Class I wells. During the period of isolation measurements of pressure should be made at ten-minute intervals; and
4. After the SAPT test period has been completed, the valve to the annulus should be opened and liquid returns from the annulus observed and measured. This may be done by allowing liquid to flow into a sealpot assembly and measuring the volume of the returns or by opening a valve and catching the liquid flowback in a container. The volume of annulus liquid returns recovered is proportional to the volume of the annulus and the amount of pressurization. The liquid return test can serve as an indication as to whether the full length of the annulus has been tested. As an alternative, the amount of liquid needed to increase the pressure can be measured. If the entire length of the annulus, from the wellhead to the packer, set at the approved depth, is not tested, then the test is void.

5 Interpretation

The interpretation and confirmation of the SAPT include:

1. Comparison of the pressure change through the test period to 3% of the test pressure (0.03 X test pressure). If the annulus test pressure changes by this amount or more (gain or loss), the well has failed to demonstrate MI (for all wells), and operation may constitute a violation

of the UIC regulations. If the annulus test pressure changes by less than 3 percent (gain or loss) over the test period, the well has demonstrated MI, pursuant to 40 C.F.R. &sect 146.8(a)(1); and

2. Evaluation of the amount of liquid returned. If less than a cup of liquid is returned, the annulus may be blocked at a shallow depth. In the past criminal charges have been brought as a result of investigations inspired by the observation that very little liquid was returned. The owing formula can be used to find how much liquid should be returned:

$dV = (P_t - P_f) \times V_f \times h \times 0.0000032$

where:
dV = the amount returned, gals;
P_t = the pressure used to test the annulus, psi;
P_f = annulus pressure after depressurization, psi;
V_f = the volume of one foot of the annulus from Halliburton table 221-B, gals;
h = length of the annulus, ft; and
0.0000032 gal/gal/psi = the compressibility of water.

The result is the number of gallons of liquid which should be returned. It is also the amount of liquid needed to pressurize the annulus to the test pressure once the annulus is filled with liquid. For a small annulus which might be typical of a Class II well (4-1/2 inch, 11.6 lb/ft. casing and 2-3/8 inch tubing, pressurized to 300 psi), just under one half gallon of liquid should be returned for each 1,000 feet of depth to the packer. If several gallons of liquid are returned, it is fairly certain that the entire length of the casing and tubing have been tested.

ATTACHMENT 2
STANDARD ANNULUS MONITORING TEST (SAMT)

1 Basis

The SAMT is essentially a continuing SAPT; however, interpretation is complicated by operational effects, principally: 1) injection tubing expansion or contraction as a result of injection pressure changes and 2) well bore temperature changes associated with a) starting or stopping injection or b) daily and seasonal changes of injectate temperature. To eliminate additional complexities, the regulations now require that the pressure be greater than atmospheric pressure.

This means that the annulus pressure should be raised to some pressure and the annulus should then be sealed. The pressure will change in response to temperature changes or even pressure changes in the injection tubing. Allowing for some seasonal variation, the range of temperature change should be consistent. In the event of a casing leak opposite a permeable zone, the pressure will normally fall, probably to zero and, if not, the range of pressure change will be much diminished because the aquifer with which the leak communicates will buffer volumetric changes in the annulus. In the event of a tubing or packer leak, the annulus pressure will track injection pressure. These two pressures will probably not be equal because of pressure loss due to friction in the injection tubing and density differences.

Region 5 Class I UIC permits require that a positive pressure differential be maintained between the annulus and injection tubing in Class I wells. The purpose of this requirement is to ensure that any leak in the injection tubing will result in an inward leak so that the injectate will not leak into the annulus. This is an important safeguard when the injectate is corrosive or very dangerous. Compliance with this requirement is not equivalent to use of SAMT if the pressure is artificially maintained through the addition of gas to a seal pot.

Unless any leak will result in an unimpeded pressure change, leaks might not be evident. To enhance the value of maintaining a positive pressure differential, Region 5 permits require volume measurement of all liquid additions and subtractions from the annulus systems of Class I wells. The results of these measurements are accumulated and a continuing need to add or remove fluid to maintain a set pressure is evidence of a leak in the well, although not necessarily an absence of MI. When a loss becomes evident, the Director may require a SAPT to confirm MI. If the well demonstrates MI, the Director may allow continued use if the leak does not cause violation of any UIC regulation.

2 Advantages and Disadvantages of the SAMT

Advantages

1. Provides a continuous demonstration of MI
2. Inexpensive for simple annulus systems
3. Easy to interpret for simple annulus systems

Disadvantages

Is difficult or impossible to interpret for wells with annulus pressure maintenance systems

3 Equipment and Forms

In order to make determinations quickly and simply, measurements of both the annulus and injection pressures should be made. Operators of Class I wells must use either an analog chart recorder or electronic equipment recording in a digital format at short intervals. Class II operators must record these pressure measurements at a frequency set by permit conditions. Other arrangements are possible, but must be established as permit conditions.

There is no set form for reporting the results of the SAMT. Each operator using the SAMT proposes a monthly reporting form to the DI Section. To effectively use the SAMT, the form must list not only the annulus pressure as measured at least once in any 24 hour period, but also the injection pressure measured at the same time. In addition, information about the injection rate, the temperature of the injection fluid, and the injection pressure may be useful. Changes in any of these parameters can affect the annulus pressure.

4 Procedure for the SAMT:

For Class I wells and other wells having a sealpot assembly and pressure maintenance the operator must:

1. Establish a positive pressure differential between the annulus and injection tubing sufficient to avoid changes which impinge on the required pressure differential (most Class I permits require at least a 100 psi pressure differential);
2. Isolate the annulus from any source of pressure maintenance;
3. Perform an SAPT, recording pressure at ten-minute intervals. If the pressure change is less than 3% in 30 minutes for Class II and III wells or 3% in 60 minutes for Class I wells, the test is passed and the SAMT begins;
4. Report the results of near-continuous measurements of annulus pressure and injection pressure in tabular and graphical formats along with tabulations of injection rate and pressure and injectate temperature as required by permit; and
5. Report the volume (in gallons) of any liquid added to or removed from the well's annulus system.

For wells not using a sealpot assembly the operator must:

1. Establish a pressure greater than atmospheric on the casing/tubing annulus;
2. Isolate the annulus from any source of pressure maintenance;

3. Perform an SAPT, recording pressure at ten-minute intervals. If the pressure change is less than 3% in 30 minutes for Class II or III wells or 60 minutes for Class I wells, the test is passed and the SAMT begins;
4. Report the results of periodic measurements of annulus and injection pressures and conditions under which pressure measurements are made, e.g. injecting or not injecting, and approximate injectate temperature; and
5. Report the volume (in gallons) of liquid added to or removed from the well's annulus system.

After any well failure, MI must be confirmed using the SAPT before resuming the SAMT.

5 Interpretation

The standard used for evaluating SAMT demonstrations is the same as that used for the SAPT, i.e., 3% pressure loss in either 30 or 60 minutes. However, it is only possible to apply this standard when external factors which might affect the annulus pressure are stable and a change in annulus pressure is established. Otherwise, liquid property changes occurring in response to change in ambient conditions make determination of a leak-induced pressure change impossible.

To provide an effective, real-time demonstration of MI, frequent inspection of pressure records is needed. This review should focus on the pressure in the annulus relative to: 1) atmospheric pressure, 2) the injection pressure measured at the surface, and 3) pressure in aquifers along the well bore. The following occurrences may indicate a loss of MI:

5.1 For wells with injection pressure greater than the annulus pressure

1. Annulus pressure increases and tracks injection pressure - probable tubing or packer leak;
2. Annulus pressure decreases:
    a. and goes to near zero - probable casing leak;
    b. stabilizes and returns to normal behavior - possible packer slip;
3. Annulus pressure is very stable regardless of injection - probable deep casing leak in well with light annulus liquid;
4. Annulus pressure fluctuates - probable temperature effects due to operational effects of injectate temperature changes;

5.2 For wells with injection pressure greater than zero but less than annulus pressure

1. Annulus pressure increases - if the well is deep, penetrates high pressure zones, and the annulus liquid is light it may indicate a deep casing leak, possibly due to an increase in injectate temperature;
2. Annulus pressure decreases:
    a. to near zero and/or becomes very stable - probable deep casing leak in well with lighter annulus liquid;
    b. and tracks injection pressure - probable tubing leak;
    c. stabilizes, and resumes normal behavior - could be a decrease in average injectate temperature or packer slip;
3. Annulus pressure fluctuates - probable temperature effects due to operational effects of injectate temperature changes;

5.3 <u>For wells which inject on a vacuum</u>

1. Annulus pressure decreases - could be either a casing, tubing, or packer leak;
2. Annulus pressure increases: and
    a. stabilizes - if the well is deep, penetrates high pressure zones, and the annulus liquid is light it may indicate a deep casing leak;
    b. begins to behave normally at a higher pressure - possibly due to an increase in injectate temperature.

In the event that a loss of MI is suspected an SAPT should be performed to ensure that the well has MI. If the SAPT confirms MI, then the operator may resume the use of the SAMT.

ATTACHMENT 3
RADIOACTIVE TRACER SURVEY (RTS)
FOR DEMONSTRATION OF 146.8(a)(1)

1 Basis

During injection, radioactive (RA) tracers can be added to injected liquids at a point above the interval to be checked for leaks. The RA material will mix with a portion of the injectate so that a slug of RA injectate passes through the section of the well to be tested. Any leak of the mixed injectate will be marked with some RA tracer. The leaked tracer material may be traced using a detector device on a wire line. The movement of the leaked tracer material is unlikely to keep pace with the movement of the slug of marked injectate which continues down the well and will be identifiable.

When tracer material is observed to split, the movement of the portion which appears to have separated should be carefully traced. The most accurate way to do this is by positioning the detector ahead of the moving tracer and observing its passage. When the tracer fails to arrive at the detector, the upper limit of movement is fixed. This method is superior to chasing the slug because it appears to be more sensitive and the record does not distort the shape of the slug as a result of tool movement. However, great care is needed to identify small increases in gamma ray activity.

2 Advantages and Disadvantages of the Radioactive Tracer Survey

Advantage
Locates the depth of the leak within the well bore

Disadvantages
1. Expensive relative to SAPT
2. Approved testing methods always require injection. Velocity shots used for the location of very small leaks may be used without injection, but require long periods of investigation

3 Equipment and Reporting Forms

The equipment required is readily available. In the past, almost any company engaged in geophysical logging was able to conduct RA tracer surveys. Some companies have discontinued the service due to restrictions imposed on the handling of RA material. The equipment consists of a sonde (tool) which is lowered into the well on a cable which allows transmission of data from the tool to receivers in a winch/instrument truck on the surface. The tool consists of an injector stage, one or more gamma radiation detector devices, and a collar locator.

The relative positions of the injector and detectors are variable. If only one detector is used, it must be located below the ejector. If more than one is used, it is common and advantageous for one detector to be located above the ejector. Three detectors are sometimes used with two being below the detector. This allows very accurate measurement of the speed of the injectate to be made. It also simplifies the location of the upward limit of leaking by eliminating some repositioning of the tool.

The purpose of the collar locator is to pinpoint the location of leaks in reference to permanent markers. This may also be done by means of correlation to a gamma ray trace which is scaled to show lithologic effects. Using a collar locator immediately lets the analyst know whether an identified leak is at a collar, while using a gamma ray correlation log clarifies the stratigraphic location of the leak.

The RA tracer is usually Iodine 131, because of its short (eight day) half life. Other tracers may be used for special applications. In any case, the tracer material used must be anionic to minimize its molecular attraction to well and rock materials.

In addition to the log of the test as presented bythe service company which performed the test, the digital data from which the log was produced must also be submitted. Information which is helpful to interpretation should be reocrded on the log form, including: 1) a schematic drawing or description of the configuration of the tool, 2) the injection rate, 3) the time at the beginning and end of each logging run, and 4) the time at which any peak is recorded. It is also helpful to use time markers on the logs to accurately fix the times at which changes in radioactivity are recorded.

We request that logging engineers review the information sheet which will be returned to permittees along with approval of procedures so that they will provide the informatiion needed to fully interpret the logs. The information sheets need not be filled out and returned.

Further testing may be necessary if possible migration out of an authorized injection interval is noted. This may include a series of time drives and slug chases to determine the extent of the leak or channel.

4 Procedures for Running the Radioactive Tracer Survey (RTS) as a Demonstration of Part 1 of MI

The demonstration can be effective for locating leaks in both the tubing and the casing. However, the RTS is useful for demonstrating an absence of leaks only in tubing strings through which the tracer material may flow. A demonstration that there are no leaks in the tubing requires that steps 1 through 8 listed below be followed. To test the casing, the tubing may be removed and the same steps followed, or the packer may be unseated and the method used to check cement integrity, described in Attachment 10, may be followed.

Testing is always conducted while injecting, and the operator should ensure that adequate water can be supplied for the test. The injection rate may be governed by the ability of the winch operator to track the RA slug as it moves downward. However, the injection rate should be as close to the maximum injection rate as practical. The following practices usually result in interpretable results:

1. Ensure that there is a significant pressure differential across the tubing wall to be tested. If the tubing is to be tested, special permission may be needed to perform the test with excess pressure in the tubing, because permits may require a positive pressure differential within the annulus. Although introduction of tracer material into the annulus can allow testing while maintaining a positive pressure differential, testing within the range of USDWs defeats the purpose of the positive pressure differential, because a casing leak would allow a release of radioactive material into an USDW. Further, practical difficulties make testing with the tracer in the annulus a complex operation;
2. Set the gamma ray (GR) detector sensitivity so that lithologic effects are just identifiable, usually 25 to 50 counts per second per inch. This ensures maximum sensitivity to leaked RA material. Noisy logs are much more difficult to interpret;
3. Make a background GR log over the interval to be tested before any RA material is introduced into the well;
4. Record measurements over a period of three to five minutes with the tool stationary at two points which are representative of the extremes of natural radiation within the interval to be tested. This will allow the interpreter to observe the effects of natural variations of GR emission on the record;
5. Release a slug of RA material above the interval to be tested. The greater the intensity of radioactivity of the slug the more resolution the method will have. Deflections caused by the slug should be 50 times greater than those caused by lithologic effects;
6. Follow the slug with the logging tool or make repeated passes upward through the slug as it moves down the well. Any increase in radioactivity which remains behind the slug should be investigated by supplementary passes through the interval as needed to determine whether

it is a result of material adhering to the tubing or of a leak. All logging should be done at a single logging speed which is appropriate for the injection rate to allow quantitative measurements of deflections to be evaluated

7. If repeated passes are used, the logs resulting from the slug-tracking exercise should overlap so that the return of radioactivity to the level which existed before the slug's passing is demonstrated for the entire length of the section of the well being tested. The logs of all passes should be presented as a composite log on a common depth track. If means to differentiate the log traces are available no other presentation is required. If the traces cannot be differentiated on the composite log, they should also be presented individually;
8. After any ejection, the slug should be followed until it has moved below the interval being tested. If the slug splits, both slug portions must be accounted for. This can be accomplished by concentrating first on the upward moving portion, and resuming tracking of the downward moving slug after the upward moving slug is tracked to its final destination; and
9. After completion of the passes, a final log should be made through the entire tested interval to check for residual radioactivity which might be associated with exit of tracer material from the well bore.

If the tubing has been removed from the well and the casing is being tested, leaked RA material will exit the well bore into a porous, permeable zone or fracture or move along the well bore to a porous, permeable zone or fracture. The movement of the tracer should be followed and the depth at which it exits the well bore recorded.

Leaks in the casing can be located with the tubing in the well by monitoring for upward movement at the base of the tubing with the packer released, as described in Attachment 8. Except in the unlikely case that the pressure in the aquifer with which a leak allows communication is higher than the injection pressure at the same depth less the friction loss from the leak to the end of the tubing, an absence of upward movement when the top of the annulus is sealed, means that there is no leak in the casing. However extreme care must be taken to ensure that upward movement will be identified. A release of a longer- period slug may increase the strength of the upward moving slug. Any upward movement of RA tracer will continue until the tracer reaches the leak and exits the well bore.

If the operator wishes, the portions of the injection interval which accept waste may be determined by making more frequent passes while the slug is within the injection interval. The sensitivity may be reset so that the log trace remains on scale.

5 Interpretation

1. Where a measurable amount of RA tracer material leaks from the tubing, it will be observed as a small area of increased radioactivity after the slug has passed;
2. If an area of elevated radioactivity is observed, additional runs should clarify what becomes of the RA material responsible. This will demonstrate whether only the tubing is leaking, or both the tubing and casing lack integrity. In most cases, if a well's casing has integrity but a tubing leak exists, pressure equalization and cessation of leaking will occur until a change in injection pressure allows the leak to resume. This is why it is important to ensure a pressure differential between the injection tubing and annulus.

   If annulus pressure is lower than injection pressure and both the tubing and casing are leaking, any tracer material that leaks out of the tubing will generally move toward and out through the casing leak. This is because the annulus pressure normally will be higher than the hydrostatic pressures within adjacent formations at all depths.

   If only the tubing is leaking, the tracer material will remain near the leak, spreading slowly both up and down from the leak location.

   Adherence of tracer material to the tubing can be differentiated from a tubing leak because any material adhering to the tubing will eventually be washed away with no movement evident.

If no evidence of leaking is observed, the well has demonstrated part 1 of MI. Be aware that demonstrations of MI using the RTS will be examined very closely, and any conditions which threaten the ability to interpret them accurately must be removed.

ATTACHMENT 4
WATER-BRINE INTERFACE TEST (W-BIT)

1 Basis

The water-brine interface test is based on:

1. The differences in liquid pressure gradients of the brine filling salt solution mining caverns and fresh water;
2. Pressurization of the cavern resulting from salt-solution mining; and
3. Pascal's Law, the transmission of pressure throughout a closed vessel.

The strategy governing the test is that a decrease in wellhead pressure will be observed in the event of loss of a fluid of lower density filling a standpipe open to a reservoir filled with a fluid of higher density. In practice, this situation is produced by:

1. Flushing the well to be tested with sufficient fresh water to dissolve any salt precipitated on the interior of the casing;
2. Withdrawing water until cavern brine is brought to the surface; and
3. Depressing the cavern brine to the base of the well casing by the injection of a volume of fresh water sufficient to fill the casing to within 25 feet of the casing shoe.

Because the cavern is pressurized sufficiently to cause the heavy brine to flow to the surface, the pressure within the well filled with fresh water is greater than the hydrostatic pressures in any aquifer through which the well passes. Therefore, any leak will allow fresh water to flow outward, to be replaced by dense brine flowing into the well from the cavern. Because the liquid pressure gradient of the brine from the cavern which replaces the leaked fresh water is greater than that of the freshwater, less pressure is transmitted from the cavern upward through the well to the well head.

It has been found that pressure within the cavern is not constant. To avoid the possibility that this variation might mask any change due to leakage, a reference well is used. This well, which is often the tubing within the well being tested, is filled with a static fluid column. If there is a leak in either the tubing or the casing, fresh water will be lost from the annulus. While the rate of leakage into the tubing is likely to be less than would be leakage from the casing, due to a lower pressure differential, particularly if the leak is near the base of the casing, the resultant emplacement of fresh water into the tubing will increase the wellhead pressure so that the effect is doubled.

The loss of one foot of annulus liquid during the W-BIT will cause a wellhead pressure reduction of approximately 0.11 psi:

$dP = dL \times (0.433 \text{ psi/ft.} - SG_c \times 0.433)$

$-0.11 \text{ psi} = 1 \text{ ft.} \times (0.433 \text{ psi/ft.} - 1.25 \times 0.433 \text{ psi/ft.})$,

where:
dP = pressure change resulting from fluid loss,
0.433 psi/ft. = pressure gradient of fresh water (SG = 1.0),
and
SG_c = specific gravity of cavern fluid = 1.25,

while the loss of one foot of pressurized annulus liquid from an annulus 1,000 feet in length will cause a loss of 312.5 psi:

dP = dV/V/0.0000032 ft./ft./psi

-312.5 psi = -1 ft./1000 ft./0.0000032 ft./ft/psi.

where:
dP = pressure change,
dV = volume leaked = -1 ft.,
V = annulus volume = 1000 ft., and
0.0000032 ft./ft./psi = the compressibility of water.

The test must be run for a longer period than the SAPT and measurements must be much more accurate to compensate for the lesser pressure change associated with leaked volume.

2 Advantages and Disadvantages

Advantages

1. Does not require removal of tubing and installation of a packer for wells used for injection and withdrawal of liquids;
2. Inexpensive for simple annulus systems.

Disadvantages

1. The W-BIT is approved only for Class III wells which cannot be tested by means of the SAPT
2. Requires use of a deadweight pressure gauge, which may be expensive to acquire;
3. Requires a 36-hour interval between initial and final pressure measurements.

3 Equipment and Forms

A dead weight pressure gauges and an operator trained in its use are needed. A convenient worksheet has been developed by members of the Salt Institute.

4 Procedures

The UIC Branch has not identified any common errors in conducting the W-BIT, and we believe that no additional guidance is needed beyond that provided in the Federal Register notices announcing its approval. A schematic drawing of the well construction must be submitted with a description of the proposed test procedures.

5 Interpretation

The calculations which are part of the test result in the calculation of a rate of pressure change. If this pressure change is less than 0.05 psi/hr., then the test demonstrates the MI of the tested well. If the rate of change is more than the standard, the well lacks MI.

ATTACHMENT 5
TEMPERATURE LOG (TL)

1 Basis

In almost every case, an aquifer into which water has flowed in the recent past is heated or cooled because the earth's temperature increases steadily with depth. This makes it unlikely that the water moving into a reservoir is the same temperature as that which is displaced. Given sensors of sufficient sensitivity, the change in temperature is identifiable. In addition, the zone from which the water came is likely to be identifiable if flow is continuing. Temperature logs can also confirm that there is no flow of injectate through the rock surrounding the well bore and often will identify small casing leaks.

During injection the ability of the injectate flowing through the well to maintain its own temperature dominates all other effects so that, for the purpose of establishing MI, the well must be shut in during temperature logging. The principal requirement for running temperature logs is that the well be shut in long enough so that temperature effects related to well construction can dissipate, leaving a relatively simple temperature profile. Experience has shown that 36 hours is usually sufficient in Region 5.

In new wells, baseline temperature logs should be made as long as possible after drilling the well, but before injection begins, because temperature effects due to circulation of drilling fluid will persist for several weeks after drilling is completed and infiltration of drilling fluids causes temperature anomalies which may persist for several months. A;though these anomalies can makr permeable zones, the existence of a temperature log which reflects the natural geothermal gradient can be of great value in assisting later analyses and for understanding other geophysical effects.

2 Advantages and Disadvantages of Temperature Logging

Advantages:

1. Continuous log with high vertical resolution
2. The most sensitive indicator of part 2 of MI
3. In addition to fluid movement within the well bore, fluid migration through the confining layers may be identified
4. Water-filled porosity can be determined if sufficient information is available
5. Injection pressure need not be maintained to ensure identification of well bore flow near the injection interval
6. Flow need not be occurring at the time of logging for its effects to be identifiable
7. Low cost per single survey covering entire well bore

Disadvantages:

1. Gas entry may be marked by cooling, but movement and exit may be obscure
2. Interpretation for complete understanding requires a greater degree of expertise than other logging methods
3. Fluid-filled well bore through interval to be tested may be required
4. Well must be shut in long enough to remove most construction and near-well bore effects

3 Equipment and Reporting Forms

The temperature logging tool is a wireline sonde operated from a winch truck. Temperature logging tools contain circuitry which responds to temperature change by changing resistance to current flow. The response is linear and temperature logs can distinguish very small changes in temperatures. Calibration of logging tools is often poor because the effects they are normally expected to measure have importance as relative rather than absolute values, although correct absolute temperatures also have value for other purposes. To be effective, temperature logging tools must have good thermal coupling to the borehole environment, which means that they are not generally useful in air-filled

holes. Sampling is done at short intervals as the sonde is lowered into the well, so that a record of the entire well bore is produced. Because the tool does not react to temperature change instantaneously and the tool is continuously moving, the measured temperature changes lag actual wellbore temperature changes by a consistent amount. The more slowly the tool moves, the closer are the measured temperatures to actual temperatures. If the tool speed is erratic, the recorded temperature profile will also be irregular. Despite the possible inaccuracies due to poor calibration and tool response time, the absolute values recorded can generally be compared with some confidence.

A reporting form has been developed to accompany the log to assure that other information useful for interpretation is submitted. Alternatively, all the information requested on the reporting form can be placed on the log. This includes: average and amximum logging speed, time since the last injection, temperature of the liquid most recently injected (average temperatures for the most recent year, month, and day) and calibration information. If there are frequent changes in the temperature of the injectate or if process changes have caused a significant change in the temperature of the injectate, it is very important to record the average temperatures of the injectate before existing logs were made and the date of the change in injectate temperature and the volume of liquid injected before and since that time. In the case of Class III wells, it is important to note whether the well was last used for injection or production.

The scaling of logs is a matter of importance. Features of significance are emphasized by compressing the depth scale and expanding the temperature scale. A depth scale of one or two inches per 100 feet, and a temperature scale of one inch to two degrees Fahrenheit are appropriate in almost every case.

If multiple logs are run while shut in, they should be displayed on the same axes (depth scale) for comparison. To avoid confusion, it may be necessary to reduce the temperature scale, but reducing it to less than four degrees per inch should be done only when necessary to avoid superimposing logging traces which cannot then be followed.

Gamma ray logs must be run simultaneously with the temperature log. Gamma ray logs provide depth control and important information about the rock types along the well bore. The digital logging data must also be submitted. We request submission of data collected at intervals of one foot. More frequent readings increase the volume of data, but increased resolution serves no purpose.

4 Procedures for Running the Temperature Log

The following steps should be followed for effective temperature logging:

1. Shut well in for sufficient time for temperature effects resulting from well construction features to dissipate. This typically requires at least 36 hours in Region 5. If 36 hours prior to logging are not available, proof that sufficient time has elapsed can be demonstrated by comparison with another log of a well at the same site. The second log may have been made previously or a second log may be made six hours after the first;
2. Calibrate the log if at all possible. This can be done by comparing measurements made using the tool in any two liquids to the known temperatures of those liquids. For instance, both a thermometer and the thermistor to be used for the logging may be used to measure the temperature of water at ambient conditions and a bucket of ice water. Even a single measurement made in a well-mixed bucket of ice water may be very helpful;
3. Log the well from the surface downward, lowering the tool at a rate of no more than 30 feet per minute. The 30 feet per minute limitation is a practical balance between the tool response time and normal time constraints, slower speeds provide increasing detail. Time coding of the log, either a tick or gap in the log grid at one minute intervals or a logging-speed trace, should be used to confirm the tool speed;
4. If the well has not been shut in for at least 36 hours before the log is run, comparison with either a second log run six hours before the time the log of record is started or a log from another well at the same site showing no anomalies should be available to demonstrate normal patterns of temperature change.

5. The log data on a disc in either LAS or ASCII format is needed for ease of interpretation. A gamma ray log, made at the time of logging, or from a previous logging, and correlated to the temperature data is needed for accurate interpretation.

5 Interpretation

Confirm the validity of the log at the well site by comparing two logs made at the same site. When lithology and injectate characteristics are similar, then thermal effects along the well bore should also be very similar. After the temperature effects caused by casing joints, packers, well diameter, casing string differences, and cement have dissipated, the temperature profiles should be similar, although not identical. If construction features are evident, a longer shut-in period is probably needed.

Identification of flow is based on relative differences between logs of nearby wells if such logs exist. Although the gradients may be quite different as a result of differing injection history, their relative positions should be obviously consistent. Lithologic effects which show up on one log should show up similarly in other wells at the same site. Failure of logs made at the same site under conditions which should result in thermal stability to compare coherently constitutes an anomaly.

If there are no logs suitable for comparison, then deviations from a predictable geothermal gradient, modified by the effects of injection, are anomalies. These may take the form of a nearly constant temperature between reservoir strata. When more than one log is run, these anomalies are likely to grow (be left behind) as the profile returns toward the natural geothermal while relative differences between the traces elsewhere decrease. In addition areas with active flow will reach a stable temperature more quickly than other areas. If the movement is not related to injection, this temperature should be that of the natural geothermal gradient at the depth of the source reservoir.

If there are anomalies, a failure of MI may be indicated. In such a case, an additional new log may be necessary to show whether forms apparent on the log just made are evolving toward the forms established on the log from another well. Comparison of these two new logs should show increasing parallelism along the cased well bore, if not, then there may be flow along a channel adjacent to the well bore. If this flow results in the movement of liquid into or between USDWs, then the well does not have part 2 of MI. If the well is used to inject hazardous wastes and flow results in movement of fluid from the injection zone into the confining zone, then a release from the solid waste management unit is indicated. In the event that there are unresolved anomalies which might indicate an absence of part 2 of MI, another approved method must be used to confirm the absence of flow into or between USDWs.

Depending on the nature of the liquid movement, radioactive tracer, noise, oxygen activation, or other logs approved by the Region may be used to further define the nature of the fluid movement.

Identification of flow behind the casing is always made from long-term shut-in logs. The resolution of long-term shut-in logs for identifying the presence of flow is greater than that of logs made during injection. The temperature gradient within a well which has been injecting for some time is very shallow. The temperature at the injection zone may be only a few degrees different from that at the surface. The presence of a flow behind the casing will result in a fractional change in this gradient which will be proportional to the ratio of the flow rates within and outside the tubing. Therefore, only a rather substantial flow can be identified using logs made during injection.

ATTACHMENT 6
NOISE LOG (NL)

1 Basis

Channels along well bores are very rarely uniform. When flow is occurring, irregularities in channel cross section usually result in generation of some turbulence which occurs in audible ranges. Sonic energy travels for considerable distances through solids, allowing sensitive microphones to detect the effects of turbulent fluid flow at considerable distances. Different types of turbulence result in sounds having different frequencies. Single phase turbulence results in low frequency sounds, while two phase turbulence usually results in high frequency sounds. High pass filters are used to determine the intensity of detected noise within various frequency ranges.

2 Advantages and Disadvantages of Noise Logs

Advantages:

1. Relative to oxygen activation log, it is practical to increase vertical resolution by increasing spacing density
2. Can identify flow of gas and differentiate it from liquid flow
3. Relative to temperature logs, cannot be used to demonstrate confinement

Disadvantages:

1. Can identify only turbulent flow
2. Relative to temperature logs, cannot be used to demonstrate confinement
3. Requires liquid in well bore through the interval to be tested
4. Injection pressure must be maintained to ensure identification of fluid flow near the injection zone
5. Actual logging time and cost are usually greater than for temperature logging

3 Equipment and Forms

Noise logging tools are wireline tools which are essentially sensitive microphones. Sampling is done in a stationary mode and the time required at each station is approximately 3-4 minutes. Any sounds detected are transmitted to recorders which measure the amount (loudness) of sonic energy received over a period of time. A cumulative measure of the sound energy which has been received is recorded.

Sonic energy travels considerable distances through solids so sampling can be done in a reconnaissance mode, with additional stations run where increases in energy are detected so that exact locations of conditions which cause sonic events can be found. Sonic logs are similar to temperature logs in that they are much more effective in liquid-filled holes because of improved coupling.

The log is the only form which must be submitted. When the level of sound is low, a linear scale is used, and when there are intervals with higher sound, a logarithmic form is used. Either is acceptable. The vertical scale should be small, one or two inches per 100 feet. In addition to the graphical log, a tabulation of sound energy is normally included on the log form and it should also be submitted.

4 Procedure for Producing the Noise Log:

Noise logging may be carried out while injection is occurring in many wells because flow restriction caused by the logging tool is often insufficient to cause turbulence. It is especially desirable to log while injecting when looking for flow resulting from pressure increase near the top of the injection zone. If ambient noise while injecting is greater than 10 mv, injection should be halted. Logging procedures should include the following steps:

1. Make noise measurements at intervals of 100 feet to create a log on a coarse grid;

2. If any anomalies are evident on the coarse log, construct a finer grid by making noise measurements at intervals of 20 feet within the coarse intervals containing high noise levels;
3. Make noise measurements at intervals of 10 feet through the first 50 feet above the injection interval and at intervals of 20 feet within the 100-foot intervals containing: 1) the base of the lowermost bleed-off zone above the injectioninterval, 2) the base of the lowermost USDW, and 3) in the case of varying water quality within the zone of USDW, the top and base of each interval with significantly different water quality from the next interval;
4. Additional measurements may be made to pinpoint depths at which noise is produced; and
5. Use a vertical scale of 1 or 2 inches per 100 feet.

5 Interpretation

The interpretation of noise logs for the purpose of demonstrating part 2 of MI is quite straightforward. The following steps are used:

1. Determine the base noise level in the well (dead well level);
2. Identify departures from this level. An increase in noise near the surface due to equipment operating at the surface is to be expected in many situations;
3. Attempt to determine the extent of any movement, this may be difficult when there are few flow constrictions;
4. If flow is into or between USDWs, a lack of mechanical integrity is indicated. If flow is from the injection zone of a hazardous-waste disposal well into or above the confining zone, failure of containment is indicated.

If the log measurements are ambiguous, the determination should be confirmed using another method.

ATTACHMENT 7
OXYGEN ACTIVATION METHOD

1 Basis

The oxygen activation method is based on the ability of the tool to convert oxygen into Nitrogen 16 (N16) within a short distance of the tool. This is accomplished by emitting high energy neutrons from the tool's neutron source. N16 is an unstable isotope of nitrogen which is referred to as activated oxygen. The half life of activated oxygen is just 7.13 seconds, and the release of gamma rays as the activated oxygen decays into oxygen can be measured. If the tool is stationary and oxygen is activated, detectors placed near the activator device will detect increased gamma radiation. The intensity of the additional radiation will be inversely proportional to the square of the distance of the activated oxygen from the detector. Much of the oxygen near the tool occurs in water. If water containing activated oxygen moves, the measured intensity of radiation will be greater if the slug of activated oxygen moves closer to the detector, and less if it moves away. By comparison of intensity of gamma radiation measured as a result of activation at two detectors, the direction and velocity of water movement can be determined. Studies under controlled conditions have shown that water velocities between two and 120 feet per minute can be measured.

2 Advantages and Disadvantages

Advantages:

1. Interpretation is a simple comparison of a calculated velocity to a minimum velocity which the tool is able to identify reliably
2. Relative to temperature logs, little or no shut-in time is required
3. Does not require a liquid-filled well bore
4. Numerical result eliminates the need for qualitative interpretation

Disadvantages:

1. Can identify flow in a broad, but fixed, velocity range
2. Has a very small range of investigation, smaller than very large well bores

3. Cannot be used to demonstrate the absence of liquid movement through confining layers
4. It is not practical to increase vertical resolution by increasing spacing density
5. Calibration errors may affect tool accuracy, perhaps accounting for false positive indications
6. History includes false positives and missed MIT failures confirmed by one or more other tools
7. Injection pressure must be maintained to ensure identification of fluid flow near the injection zone
8. Actual logging time and cost are usually greater than for other logs

3 Equipment and Forms

The equipment consists of a wireline sonde containing a high- energy neutron generator and gamma ray detectors. By spacing several detectors at increasing distances from the oxygen activation area interpretational accuracy is increased. Although the oxygen which is activated may be present in water which may be moving along the well bore, oxygen is also present in rock and cement. Some of this oxygen is also activated, and its decay products become background radiation which must be accounted for in order to reach a valid measurement of the movement of activated atoms in the fluid passing along the well bore.

The need to account for oxygen which is not in flowing water can be addressed in either of two ways: 1) by making calibration measurements in a representative area of the well bore in which there is thought to be no flow behind the casing, or 2) by extending the measurement period at each station beyond the time during which the activated oxygen in flowing water has been carried away. The rate of decay indicated by the late measurements is used to calculate the theoretical levels of gamma radiation which would have been measured if there were no water movement. The difference between the calculated and measured values is assumed to be the effect of the decay of activated oxygen carried to the vicinity of the detectors as part of moving water.

The first method is used by Western Atlas and the second by Schlumberger. These are the only companies which provide oxygen activation logging service in Region 5.

4 Procedures for Running the Oxygen Activation Log (OAL):

All measurements should be taken for periods of at least five minutes with the well injecting at the maximum normal rate. A total of at least 15 minutes measurement time is required at each station. This total time may be accumulated in one, two, or three episodes. If open-hole caliper logs are available, care should be taken to obtain all readings at depths where the well bore is in gauge. The method for obtaining measurements shall conform to optimum procedures contained in the operator's manual for the tool being used. The following steps are recommended for demonstrating part 2 of MI using the OAL:

1. Secure a log for lithology determination. If no such log is available, run a gamma ray-neutron log to identify porous intervals;
2. If required for tool calibration, background checks will be run with no injection occurring in an interval where no flow is thought to occur. Background calibration should be run for each interval of varying well construction;
3. Take measurements at stations at least 10 feet above the open injection interval;
4. Take measurements at the top of the confining zone and at two or three formation changes between the confining zone and the base of the USDW;
5. Take measurements within 50 feet below the base of each USDW, within 50 feet of the top of the first underlying aquifer, and at least one measurement between these two points;
6. If anomalies are found, additional readings, including readings made while the well is injecting if the original measurements were made while not injecting, or not injecting if the original measurements were made while injecting, should be made above and below the depth of the anomaly to confirm the anomalous reading and discover the extent of fluid movement; and
7. If flow is indicated, another log may be used to confirm the measurement and define the extent of flow. The choice for the confirmation log should be based on all wellbore and

environmental factors, and the tool choice must be approved by Region 5 prior to commencing testing operations.

5 Interpretation

A ratio of the short-spaced flow indicator result to standard deviation of 3-4:1 indicates flow. Indicated water-flow velocities should be in excess of two feet per minute, lower values should be viewed with skepticism. Velocities near and above two feet per minute have been measured at several depths at several sites in Region 5 and other logs did not indicate flow. In some cases the occurrences were repeatable, at least during the period of one logging episode. Although the cause of the false measurements is not known, it is assumed that the logging tool was not properly calibrated for the interval being tested.

To minimize false positives, it is recommended that all measurements be confirmed at several nearby depths and/or measurements be taken under a minimum of 3 varying injection rates, i.e.: 75%, 50%, and 25% of maximum permitted injection rates. Before costly measures are taken to remedy problems, their existence should be confirmed using another approved log.

ATTACHMENT 8
RADIOACTIVE TRACER SURVEYS
FOR DEMONSTRATING PART 2 OF MI

1 Basis

Acceptance of the test as a means for demonstrating part 2 of MI is limited to those wells where there is no aquifer between the injection zone and the base of the lowermost USDW and where there is no significant water quality difference between individual USDWs.

The basis of the test is that flow will follow the well bore upward if the cement seal is poor at and above the base of the casing for open-hole completions or above the uppermost perforation for perforated completions. If the cement at the top of the injection interval is sound and there is no movement upward along the casing at that point, it is assumed that there is no alternate conduit which might allow injected liquids to reach the well bore at a shallower depth and then travel upward through either an uncemented or ineffectively cemented well bore. The analyst is primarily concerned with identifying the uppermost depth at which tracer material can be seen to be moving within and then exiting the well bore.

2 Advantages and Disadvantages

Advantages:

1. Can be run with the well injecting

Disadvantages:

1. Only valid for part 2 when there are no aquifers between the base of the casing and the base of the lowermost USDW and no significant differences between quality of the USDWs
2. Cannot be used to determine interformational flow where the tracer material cannot be introduced into the flow stream outside the casing

3 Equipment and Forms

These are identical to those described for the RTS in Attachment 3.

4 Procedures for Running the Radioactive Tracer Survey (RTS)as a Demonstration of Part 2 of MI

The demonstration of mechanical integrity requires that the packer be seated or the tubing be removed from the well.

Three different test methods are usually employed at each instance of testing: 1) slug tracking, 2) stationary testing, and 3) comparison of logs run before and after the other testing methods are used. Either slug tracking or the stationary tests are adequate tests, but the comparison of logs run before and after the injection is only supplementary, and its use is in identifying the intervals along the well bore where RA material has adhered to the walls as it exited the well bore.

4.1 Recommended procedures for the use of the slug tracking method are:

1. Inject at the maximum rate used for injection unless it is impossible for the tool can be effectively used at that rate. Otherwise inject at the maximum rate at which the winch operator can track the slug;
2. Release a slug of RA tracer far enough above the base of the casing or perforations to allow it to be logged within the casing at least once;
3. Drop the tool down through the slug and then log upward through the slug;
4. Drop the tool down to within 20 feet below the top of the perforations or base of the casing (or tubing tailpipe, if that is lower). Hold the tool at that point until the slug reaches it. As soon as the slug is detected, begin to log upward so that the logging tool passes the top of perforations or the base of the deeper of the casing or tubing just after the slug has passed the same point. This helps to ensure that any upward movement is detected;
5. Drop the tool below the slug, but no more than 50 feet below the perforations/casing/tubing if a split was observed during the previous logging run, and again log upward;
6. Continue making passes to show the upward movement of the slug as long as it is measurable;
7. The procedure (Steps 1 though 6) should be repeated until the highest point to which injectate moved upward is identifiable; and
8. If any slugs are seen to split, the tracer material remaining after all of the planned testing is done should be ejected just above the casing shoe and the resulting slug followed upward as far as possible.

4.2 Recommended procedures for the use of the stationary method are:

1. Injection should be at the maximum rate used to inject waste. The slug of RA material should be ejected some distance above the depth at which the stationary test will be made in order to eliminate electrical effects associated with the ejection which sometimes mask or distort the detection of the downward moving slug. The greater deflection caused by the slug, the better. However, the length of the ejection should not be over a few seconds to avoid producing a long slug.
2. With at least two detectors, one above and one below the ejector, recording in time drive, position the logging tool with the lower detector four feet above the top of the perforations or the deeper of the base of the casing or tubing. When used with slug tracking, position the upper detector about two feet above the highest point reached by the tracked slug;

   The use of at least two detectors has two important advantages: 1) it allows the test to be, in effect, run at two or more depths and may cut the time required to run a test which completely defines the upward distance a slug travels and, more importantly, 2) confirms the direction of travel of any RA material observed after the slug is ejected. Often ejectors leak a small amount of tracer. The direction of movement of extraneous slugs passing by a single detector cannot be determined and may confuse interpretation.

   The scaling should allow the easy calculation of time period and deflections should not be smeared out over so much paper that they are difficult to identify. The time scale should not be compressed so much that determining the time, to at least the minute, at which the increase in radioactivity begins is questionable;
3. The tool is run in time drive for a period sufficient to allow the RA material to reach the perforations, casing shoe, or end of the tailpipe and travel upward to the detectors assuming upward movement at a rate of no more than two feet per minute;

4. If upward moving RA material is detected, following the detection of the slug at the top detector, move the tool upward a short distance and again record in time drive until the RA material is detected. Record the times at which the RA material reaches the detectors to help evaluate how far the detectors should be moved;
5. Continue to monitor the upward movement of the slug until the limit of upward movement is reached. The limit can be considered to be the elevation of a detector which did not record passage of the slug after allowing travel time of two minutes per foot from the point of last detection.

4.3 Recommendations for producing the logs before and after testing are:

1. The log should cover the interval between at least 100 feet below the bottom of the deeper of the casing or tailpipe depth and 200 feet above the shallower of the casing or tailpipe depth.
2. A gamma ray log should be on hand to ensure that the new log reflects background conditions. Occasionally tool leaks cause anomalous results which can be avoided simply by repeating the logging.
3. A presentation including both logs on the same depth scale is helpful. The traces must be coded so as to be clearly identifiable.
4. The log data on disk should be submitted. Having these data allow us to plot various combinations of logging runs at scales which show us what we think we need to see.

5 Interpretation

Each of the three testing methods is interpreted individually.

5.1 The slug tracking records are evaluated by:

1. Reviewing the statistical check performed before testing began to check the sensitivity of the log display, check to be sure the scaling used for the logging is the same as was used for the statistical check;
2. Checking the deflection caused by the slug within the tubing or casing. It should be at least 50 times greater than that caused by lithological background;
3. Checking to see if a slug split occurred at the base of the tubing or casing. Identify any increases of radioactivity along the well bore above the base of the tubing or casing;
4. Evaluating the slug split for upward movement. Turbulence at the base of the tubing often causes some tracer to remain. If only a slow dissipation of the resulting hot spot, with no upward movement, is observed, the split has no significance;
5. If the tubing extends below the casing, upward movement to the base of the casing commonly occurs, this also has no environmental significance;
6. If movement above the base of the casing occurs, its extent must be very carefully determined and recorded. It is not uncommon or of concern if there is some limited movement, particularly where the base of the casing is within a porous, permeable interval. The extent of upward movement should be compared with previous measurements to confirm that the cement seal is not deteriorating.

5.2 The stationary tests are evaluated by:

1. Checking the strength of the slug, often the detector cannot react quickly enough to measure the entire distance of the deflection. The deflection should appear sharp if the total deflection is not measured;
2. Checking the record from the lower detector to see if any increase occurred after the initial passage of the slug;
3. If a second increase in radiation was detected, check the record from the upper detector (above the ejector) to check whether an increase occurred at that detector before the detection of the slug by the lower detector, if so, the detection may be due to an extraneous slug, previously ejected, moving downward past the tool;
4. If no increase in radiation is detected by the upper detector, then the tracer exited the well bore between the lower detector and the upper detector. The maximum upward movement identified through this test is the elevation of the upper detector;
5. If an increase in gamma ray radiation is detected by the upper detector after the detection by the lower detector, the tool should have been moved upward so that the slug had the

opportunity to pass both of the detectors again. If so, repeat steps 2, 3, and 4 until the maximum upward extent of movement of the tracer is established. This depth should be recorded and compared with that for the slug tracking and tests conducted in previous years;

5.3 To evaluate the logs run before and after all other tests are performed:

1. The logs should be printed overlain on the same depth scale. If not, on a light table, light box or back-lighted window, overlay the initial log above the final log. Focus on the interval just above the top of the injection interval;
2.
3. After matching depth and/or collar log features, check to be sure that the gamma ray traces overlay. If they do not, shift one log to the left or right until they generally overlay;
4. Identify regions in which the final log indicates apparent increased radiation. If the magnitude of the increased radiation is greater than the statistical variation, then radioactive tracer material has probably adhered to either the well construction materials or the borehole walls where the waste exited the well bore; and
5. Try to relate all instances of increased radiation above the casing shoe to the results of the previous testing. If unexplained occurrences persist, the results of a recent part 2 MI test should be carefully reviewed to see if upward movement is indicated.

5.4 The result of the testing should be determination of a depth above which no upward movement occurs. The result should be at or below the casing shoe. If it is above the casing shoe, the extent should be tracked and significance determined.

ATTACHMENT 9
CEMENTING RECORDS

1 Basis

A very small span of sound cement surrounding the casing will prevent movement between the well bore and the casing or between casings.

The use of cementing records as a demonstration of part 2 of MI is limited to all Class II wells and those Class III wells in which the nature of the construction precludes the use of temperature or noise logs. The cementing records must indicate that cement is present along the well bore between the injection zone and the base of the lowermost USDW.

2 Advantages and Disadvantages

Advantages:

1. Usually based on existing information
2. A one-time demonstration

Disadvantages:

1. This is an indirect demonstration. The presence of cement does not assure us that it is sound
2. If paper records are not available, they cannot be reconstructed
3. Either the CBL or CET requires that the well bore be water filled to the upper limit of the logged interval

3 Equipment and Forms

1. Forms of Cementing Records

   Cementing records include any acceptable records containing information which allows the calculation of cement placement behind the casings of wells. Cementing records may include

cement bond logs, cement evaluation logs, and temperature logs which give evidence of the location and/or quality of cement along well bores. The most reliable cementing records are job reports from cementing companies, but any records of construction containing information about the placement of cement may be acceptable. Either the original or copies of t hese cementing records must be submitted.

2. Cement Bond and Cement Evaluation Logs

   Cement bond logs (CBLs) use sonic attenuation and travel time to determine whether casing is cemented or free. The more cement which is bonded to casing, the greater will be the attenuation of sounds transmitted along the casing. The Cement Evaluation Tool (CET) operates on a principle similar to the CBL except that the tool uses many sound transmitters and receptors to evaluate the cement in various sectors of the well bore. Instead of an average bond index accounting for the entire circumference of the well bore, the log can identify poor bonding in single 60o segments. This increases the ability to confirm the presence of channels tremendously.

   The logs should include a gamma ray curve, casing collar log, acoustic amplitude and travel time curves, and CBLs should include an acoustic variable density log (VDL). The left hand track should contain the gamma ray and casing collar log. The right hand tracks should contain the acoustic amplitude and travel-time curves in track 2 and the acoustic VDL in track 3. CETs include a graphical depiction of the cemented area of the well bore in track 3. If available, a shop calibration record should be attached. The surface pressure under which the log was run should be noted on the log form.

   In new wells, the cement should be allowed to set for at least 72 hours before logging.

4 Procedures for Recording the Cement Bond Log (CBL) or Logs made Using Cement Evaluation Tool (CET)

1. Centralize the tool. Be sure that the part of the hole to be logged is liquid filled. Calibrate the tool;
2. Record the amplitude and travel time measured by the short- spaced receiver in the fixed gate mode;
3. Run the CBL over the entire cemented length of the casing and through at least two joints of the uncemented portion, if any;
4. Check the travel time. If intervals are found having four microseconds less than travel time in free pipe, check the tool centralization and relog the well if necessary;
5. If the log indicates poor bond, the log can be run under pressure to eliminate any micro-annulus effect. The pressure used should be minimal to prevent enlargement of the micro-annulus. Often reproduction of the pressure used during cement setting is sufficient. For Class I wells (although cement logs are occasionally required at Class I sites, they are not a demonstration of part 2 of MI) pressurizing to the normal annulus pressure may be sufficient to eliminate the micro- annulus; and
6. Check the tool calibration. If significant tool drift has occurred, relog the well with the back-up tool.

5 Interpretation

1. Interpretation of records

   Most cement records document the volume of cement emplaced between the casing and the well bore. For demonstrations of MI for Class II wells, the records must indicate that cement was emplaced at locations which will prevent upward movement from the injection zone. For demonstrations of MI for Class III wells, the records must indicate that cement was emplaced at locations which will prevent upward movement from the injection zone and into or between USDWs.

2. Interpretation of CBLs

   The log is examined to identify the location of cement along the casing. Only a few feet of sound cement are required to prevent flow along the well bore, but in most cases making judgements about the adequacy of a few feet of cement will not be required because there will be more than 10 feet of cement indicated to be sound, or there will be no indications of

sound cement in critical areas. If an initial cement bond log does not indicate the presence of cement, often a second log will be run with pressure on the casing. This may show cement while the earlier log does not. In this case, a microannulus has developed due to past expansion of the casing while it was pressurized during operations or testing. It is sometimes necessary to pressurize the casing above the highest pressure to which it has been subjected. The presence of a microannulus does not indicate a lack of part 2 of MI. Microannuli are very minute. By definition, while they may allow the passage of gas but not liquids.

If there is a question about the adequacy of cement to prevent the movement of liquids into USDWs, then one of the previously described logs, pre-approved by Region 5, should be utilized to demonstrate MI.

ATTACHMENT 10
RADIOACTIVE TRACER SURVEYS FOR
THE INTEGRITY OF CEMENT AT THE TOP OF THE INJECTION INTERVAL

1 Basis

The basis of the use of the RTS for confirming the integrity of the cement at the top of the injection interval is identical to that of demonstrating part 2 of MI. In fact, if there are no aquifers above the injection interval from which the waters might degrade any USDW, the demonstration of cement integrity becomes a demonstration of part 2 of MI.

2 Advantages and Disadvantages

This test is required annually for Class I wells which are used to inject hazardous waste; there is no alternative test. The logs used to demonstrate part 2 of MI may also make a similar demonstration, but such a demonstration cannot be substituted for the RTS for this purpose. Because there is no alternative, and the advantages and disadvantages of the log have been previously listed in Attachment 8, they are not listed here.

3 Equipment and Forms

These are identical to the equipment and forms listed in Attachment 3 for the RTS.

4 Procedures

The procedures for using the RTS to confirm the integrity of cement are identical to those used for the demonstration of part 2 of MI.

5 Interpretation

The interpretation of the RTS used for confirming the integrity of cement is similar to that for demonstrating part 2. If any upward movement is observed, it becomes critical to determine the exact amount of upward movement. The upper limits of upward movement are recorded and compared from year to year to check for any increase.

APPENDIX D-VI

UIC Pressure Falloff Testing Guideline

EPA Region 6

UIC PRESSURE FALLOFF TESTING GUIDELINE

Third Revision

August 8, 2002

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APPENDIX

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EPA Region 6

UIC PRESSURE FALLOFF TESTING GUIDELINE

Third Revision
August 8, 2002

1.0 Background

The Hazardous and Solid Waste Amendments of 1984 to the Resource Conservation and Recovery Act mandated prohibitions on the land disposal of hazardous waste. These prohibitions are known as the land disposal restrictions and EPA promulgated regulations to implement these requirements for injection wells on July 26, 1988. The land disposal restrictions for injection wells are codified in 40 CFR Part 148. In addition to specifying the effective dates of the restrictions on injection of specific hazardous wastes, these regulations outline the requirements for obtaining an exemption to the restrictions.

Facilities that have received an exemption to the land disposal restrictions under 40 CFR Part 148 have demonstrated that, to a reasonable degree of certainty, there will be no migration of hazardous constituents from the injection zone for as long as the waste remains hazardous. As part of this approval, facilities are required by Region 6 to meet approval conditions including annual monitoring in accordance with 40 CFR 148.20(d)(2).

Region 6 has adopted the 40 CFR 146.68(e)(1) requirements for monitoring Class 1 hazardous waste disposal wells. Under 40 CFR 146.68(e)(1), operators are required annually to monitor the pressure buildup in the injection zone, including at a minimum, a shut down of the well for a time sufficient to conduct a valid observation of the pressure falloff curve.

A falloff test is a pressure transient test that consists of shutting in an injection well and measuring the pressure falloff. The falloff period is a replay of the injection preceding it; consequently, it is impacted by the magnitude, length, and rate fluctuations of the injection period. Falloff testing analysis provides transmissibility, skin factor, and well flowing and static pressures. All of these parameters are critical for evaluation of technical adequacy of no migration demonstrations and UIC permits.

2.0 Purpose of Guideline

This guideline has been developed by the Region 6 office of the Evironmental Protection Agency (EPA) to assist operators in planning and conducting the falloff test and preparing the annual monitoring report. Typically, this report should consist of a falloff test and a comparison of the reservoir parameters derived from the test with those of the petition demonstration. Falloff tests provide reservoir pressure data and characterize both the injection interval reservoir and the completion condition of the injection well. Both the reservoir parameters and pressure data are

necessary for no migration and UIC permit demonstrations. Additionally, a valid falloff test is a requirement of a no migration petition condition as well as a monitoring requirement under 40 CFR Part 146 for all Class I injection wells. For no migration purposes, the annual report is viewed not as an enforcement tool, but as an annual confirmation that the petition demonstration continues to be valid.

The main body of this guideline contains general information that pertains to the majority of the facilities impacted. Because each site is unique, one guideline cannot be written to encompass all situations. A more detailed discussion of many topics and equations is included in the attached Appendix.

The ultimate responsibility of conducting a valid falloff test is the task of the operator. Operators should QA/QC the pressure data and test results to confirm that the results "make sense" prior to submission of the report to the EPA for review.

3.0 Timing of Falloff Tests and Report Submission

Falloff tests must be conducted within one year from the date of the original petition approval and annually thereafter. The time interval for each test should not be less than 9 months or greater than 15 months from the previous test. This will ensure that the tests will be performed at relatively even intervals throughout the duration of the petition approval period. Operators can, at their discretion, plan these tests to coincide with the performance of their annual state MIT requirements as long as the time requirements are met. The falloff testing report should be submitted no later than 60 days following the test. Failure to submit a falloff test report will be considered a violation of the applicable petition condition and may result in an enforcement action. Any exceptions should be approved by EPA prior to conducting the test.

4.0 Falloff Test Report Requirements

In general, the report to EPA should provide general information and an overview of the falloff test, an analysis of the pressure data obtained during the test, a summary of the test results, and a comparison of the results with the parameters used in the no migration demonstration. Some of the following operator and well data will not change so once acquired, it can be copied and submitted with each annual report. The falloff test report should include the following information:

1. Company name and address
2. Test well name and location
3. The name and phone number of the facility contact person. The contractor contact may be included if approved by the facility <u>in addition</u> to a facility contact person.

4. A photocopy of an openhole log (SP or Gamma Ray) through the injection interval illustrating the type of formation and thickness of the injection interval. The entire log is not necessary.
5. Well schematic showing the current wellbore configuration and completion information:
   - Wellbore radius
   - Completed interval depths
   - Type of completion (perforated, screen and gravel packed, openhole)
6. Depth of fill depth and date tagged.
7. Offset well information:
   - Distance between the test well and offset well(s) completed in the same interval or involved in an interference test
   - Simple illustration of locations of the injection and offset wells
8. Chronological listing of daily testing activities.
9. Electronic submission of the raw data (time, pressure, and temperature) from all pressure gauges utilized on a floppy disk or CD-ROM. A READ.ME file or the disk label should list all files included and any necessary explanations of the data. A separate file containing any edited data used in the analysis can be submitted as an additional file.
10. Tabular summary of the injection rate or rates preceding the falloff test. At a minimum, rate information for 48 hours prior to the falloff or for a time equal to twice the time of the falloff test is recommended. If the rates varied and the rate information is greater than 10 entries, the rate data should be submitted electronically as well as a hard copy of the rates for the report. Including a rate vs time plot is also a good way to illustrate the magnitude and number of rate changes prior to the falloff test.
11. Rate information from any offset wells completed in the same interval. At a minimum, the injection rate data for the 48 hours preceding the falloff test should be included in a tabular and electronic format. Adding a rate vs time plot is also helpful to illustrate the rate changes.
12. Hard copy of the time and pressure data analyzed in the report.
13. Pressure gauge information: (See Appendix, page A-1 for more information on pressure gauges)
   - List all the gauges utilized to test the well
   - Depth of each gauge
   - Manufacturer and type of gauge. Include the full range of the gauge.
   - Resolution and accuracy of the gauge as a % of full range.
   - Calibration certificate and manufacturer's recommended frequency of calibration
14. General test information:
   - Date of the test
   - Time synchronization: A specific time and date should be synchronized to an equivalent time in each pressure file submitted. Time synchronization should also be provided for the rate(s) of the test well and any offset wells.
   - Location of the shut-in valve (e.g., note if at the wellhead or number of feet from the wellhead)

15. Reservoir parameters (determination):
    - Formation fluid viscosity, μ_f cp (direct measurement or correlation)
    - Porosity, ϕ fraction (well log correlation or core data)
    - Total compressibility, c_t psi^{-1} (correlations, core measurement, or well test)
    - Formation volume factor, rvb/stb (correlations, usually assumed 1 for water)
    - Initial formation reservoir pressure - See Appendix, page A-1
    - Date reservoir pressure was last stabilized (injection history)
    - Justified interval thickness, h ft - See Appendix, page A-15
16. Waste plume:
    - Cumulative injection volume into the completed interval
    - Calculated radial distance to the waste front, r_{waste} ft
    - Average historical waste fluid viscosity, if used in the analysis, μ_{waste} cp
17. Injection period:
    - Time of injection period
    - Type of test fluid
    - Type of pump used for the test (e.g., plant or pump truck)
    - Type of rate meter used
    - Final injection pressure and temperature
18. Falloff period:
    - Total shut-in time, expressed in real time and Δt, elapsed time
    - Final shut-in pressure and temperature
    - Time well went on vacuum, if applicable
19. Pressure gradient:
    - Gradient stops - for depth correction
20. Calculated test data: include all equations used and the parameter values assigned for each variable within the report
    - Radius of investigation, r_i ft
    - Slope or slopes from the semilog plot
    - Transmissibility, kh/μ: md-ft/cp
    - Permeability (range based on values of h)
    - Calculation of skin, s
    - Calculation of skin pressure drop, ΔP_{skin}
    - Discussion and justification of any reservoir or outer boundary models used to simulate the test
    - Explanation for any pressure or temperature anomaly if observed
21. Graphs:
    - Cartesian plot: pressure and temperature vs. time
    - Log-log diagnostic plot: pressure and semilog derivative curves. Radial flow regime should be identified on the plot
    - Semilog and expanded semilog plots: radial flow regime indicated and the semilog straight line drawn
    - Injection rate(s) vs time: test well and offset wells (not a circular or strip chart)
22. A comparison of all parameters with those used in the petition demonstration, including references where the parameters can be found in the petition.

23. A copy of the latest radioactive tracer run to fulfill the annual mechanical integrity testing requirement for the State and a brief discussion of the results.
24. Compliance with any unusual petition approval conditions such as the submission of an annual flow profile survey. These additional conditions may be addressed either in the annual falloff testing report or in an accompanying document.

5.0 Planning

The radial flow portion of the test is the basis for all pressure transient calculations. Therefore the injectivity and falloff portions of the test should be designed not only to reach radial flow, but to sustain a time frame sufficient for analysis of the radial flow period.

General Operational Concerns

Successful well testing involves the consideration of many factors, most of which are within the operator's control. Some considerations in the planning of a test include:

- Adequate storage for the waste should be ensured for the duration of the test
- Offset wells completed in the same formation as the test well should be shut-in, or at a minimum, provisions should be made to maintain a constant injection rate prior to and during the test
- Install a crown valve on the well prior to starting the test so the well does not have to be shut-in to install a pressure gauge
- The location of the shut-in valve on the well should be at or near the wellhead to minimize the wellbore storage period
- The condition of the well, junk in the hole, wellbore fill or the degree of wellbore damage (as measured by skin) may impact the length of time the well must be shut-in for a valid falloff test. This is especially critical for wells completed in relatively low transmissibility reservoirs or wells that have large skin factors.
- Cleaning out the well and acidizing may reduce the wellbore storage period and therefore the shut-in time of the well
- Accurate recordkeeping of injection rates is critical including a mechanism to synchronize times reported for injection rate and pressure data. The elapsed time format usually reported for pressure data does not allow an easy synchronization with real time rate information. Time synchronization of the data is especially critical when the analysis includes the consideration of injection from more than one well.
- Any unorthodox testing procedure, or any testing of a well with known or anticipated problems, should be discussed with EPA staff prior to performing the test.
- Other pressure transient tests may be used in conjunction or in place of a falloff test in some situations. For example, if surface pressure measurements must be used because of a corrosive wastestream and the well will go on vacuum following shut-in, a multi-rate test may be used so that a positive surface pressure is maintained at the well.

- If more than one well is completed into the same reservoir, operators are encouraged to send at least two pulses to the test well by way of rate changes in the offset well following the falloff test. These pulses will demonstrate communication between the wells and, if maintained for sufficient duration, they can be analyzed as an interference test to obtain interwell reservoir parameters.

Site Specific Pretest Planning

1. Determine the time needed to reach radial flow during the injectivity and falloff portions of the test:
   - Review previous welltests, if available
   - Simulate the test using measured or estimated reservoir and well completion parameters
   - Calculate the time to the beginning of radial flow using the empirically-based equations provided in the Appendix. The equations are different for the injectivity and falloff portions of the test with the skin factor influencing the falloff more than the injection period. (See Appendix, page A-4 for equations)
   - Allow adequate time beyond the beginning of radial flow to observe radial flow so that a well developed semilog straight line occurs. A good rule of thumb is 3 to 5 times the time to reach radial flow to provide adequate radial flow data for analysis.

2. Adequate and consistent injection fluid should be available so that the injection rate into the test well can be held constant prior to the falloff. This rate should be high enough to produce a measurable falloff at the test well given the resolution of the pressure gauge selected. The viscosity of the fluid should be consistent. Any mobility issues (k/:) should be identified and addressed in the analysis if necessary.

3. Bottomhole pressure measurements are usually superior to surface pressure measurements because bottomhole measurements tend to be less noisy. Surface pressure measurements can be used if positive pressure is maintained at the surface throughout the falloff portion of the test. The surface pressure gauge should be located at the wellhead. A surface pressure gauge may also serve as a backup to a downhole gauge and provide a monitoring tool for tracking the test progress. Surface gauge data can be plotted during the falloff in a log-log plot format with the pressure derivative function to determine if the test has reached radial flow and can be terminated. Note: Surface pressure measurements are not adequate if the well goes on a vacuum during the test. (See Appendix, page A-2 for additional information concerning pressure gauge selection.)

4. Use two pressure gauges during the test with one gauge serving as a backup, or for verification in cases of questionable data quality. The two gauges do not need to be the same type. (See Appendix, page A-1 for additional information concerning pressure gauges.)

6.0 Conducting the Falloff Test

1. Tag and record the depth to any fill in the test well

2. Simplify the pressure transients in the reservoir
   - C Maintain a constant injection rate in the test well prior to shut-in. This injection rate should be high enough and maintained for a sufficient duration to produce a measurable pressure transient that will result in a valid falloff test.
   - C Offset wells should be shut-in prior to and during the test. If shut-in is not feasible, a constant injection rate should be recorded and maintained during the test and then accounted for in the analysis.
   - C Do not shut-in two wells simultaneously or change the rate in an offset well during the test.

3. The test well should be shut-in at the wellhead in order to minimize wellbore storage and afterflow. (See Appendix, page A-3 for additional information.)

4. Maintain accurate rate records for the test well and any offset wells completed in the same injection interval.

5. Measure and record the viscosity of the injectate periodically during the injectivity portion of the test to confirm the consistency of the test fluid.

7.0 Evaluation of the Falloff Test

1. Prepare a Cartesian plot of the pressure and temperature versus real time or elapsed time.
   - C Confirm pressure stabilization prior to shut-in of the test well
   - C Look for anomalous data, pressure drop at the end of the test, determine if pressure drop is within the gauge resolution

2. Prepare a log-log diagnostic plot of the pressure and semilog derivative. Identify the flow regimes present in the welltest. (See Appendix, page A-6 for additional information.)
   - C Use the appropriate time function depending on the length of the injection period and variation in the injection rate preceding the falloff (See Appendix, page A-10 for details on time functions.)
   - C Mark the various flow regimes - particularly the radial flow period
   - C Include the derivative of other plots, if appropriate (e.g., square root of time for linear flow)
   - C If there is no radial flow period, attempt to type curve match the data

3. Prepare a semilog plot.
   - Use the appropriate time function depending on the length of injection period and injection rate preceding the falloff
   - Draw the semilog straight line through the radial flow portion of the plot and obtain the slope of the line
   - Calculate the transmissibility, kh/:
   - Calculate the skin factor, s, and skin pressure drop, ΔP_{skin}
   - Calculate the radius of investigation, r_i

4. Explain any anomalous results.

8.0 Comparison of Falloff Results to No Migration Petition Data

A comparison between the falloff test results and the parameters used in the no migration petition demonstration should be made. Specifically, the following should be demonstrated:

- Both the flowing and static bottom hole pressures measured during the test should be corrected for skin and be at or below those which were predicted to occur by the pressure buildup model in the approvided no migration petition for the same point in time. (See Appendix, page A-13)

- It should be shown that the (kh/:) parameter group calculated from the current falloff data is the same or greater than that employed in the pressure buildup modeling.

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APPENDIX

Initial Formation Reservoir Pressure from Falloff Testing

For use in the no migration demonstration pressure buildup modeling:

- Some predictive models calculate a pressure buildup while other models calculate a specific pressure based on an initial reservoir pressure assigned to the model. No wellbore skin should be assumed in the demonstration. Historical falloff flowing pressure data used for comparison with model results should be corrected for skin effects
- The initial pressure should represent the initial reservoir pressure prior to initiation of injection in the model.
- Direct bottomhole static measurements are best. If no measurements are available, or are questionable, attempt to correct static surface pressures to bottomhole conditions. Use site specific information if available. Alternatively, the facility can reference a technical paper that may discuss the initial pressure of the injection interval at another location in the same area or an initial static pressure measurement from an offset injection well.
- Review historical measured static pressures. The initial reservoir pressure should be lower than the measured static pressures following injection at the well.

For use in Cone of Influence (COI) calculations in both no migration demonstrations and UIC permits:

- P^* is the false extrapolated pressure obtained from the semilog straight line at a time of 1 hour and is often used as the average reservoir pressure
- P^* is only applicable for a new well in an infinite acting reservoir
- EPA Region 6 does not recommend using P^* for the average reservoir pressure. For long injection periods, P^* will differ significantly from $\overline{P}$, the average reservoir pressure
- Use the final shut-in pressure, if the well reaches radial flow, for the cone of influence calculation

Pressure Gauge Usage and Selection

<u>Usage</u>

- EPA recommends that two gauges be used during the test with one gauge serving as a backup.
- As a general rule, downhole pressure measurements are less noisy and are preferred. Surface pressure measurements can be employed if positive pressure is maintained at the surface throughout the test. Surface gauges are insufficient if the well goes on a vacuum.
- Surface pressure gauges may be impacted by the fluctuations in ambient temperature that can occur over the course of a normal day. If unchecked, this aspect of these gauges can result in erroneous pressure readings. Insulating the gauges appears to be an effective countermeasure for temperature fluctuations in many instances.

- A surface or bottomhole surface readout gauge (SRO) allows tracking of pressures in real time. Analysis of this data can be performed in the field to confirm that the well has reached radial flow prior to ending the test.
- The derivative function plotted on the log-log plot amplifies noise in the data, so the use of a good pressure recording device is critical for application of this curve.
- Mechanical gauges should be calibrated before and after each test using a dead weight tester.
- Electronic gauges should also be calibrated according to the manufacturer's recommendations. The manufacturer's recommended frequency of calibration, and a copy of the gauge calibration certificate should be provided with the falloff testing report demonstrating this practice has been followed.

Selection

- The pressures must remain within the range of the pressure gauge. The larger percent of the gauge range utilized in the test, the better. Typical pressure gauge limits are 2000, 5000, and 10000 psi. Note that gauge accuracy and resolution are typically a function of percent of the full gauge range.
- Electronic downhole gauges generally offer much better resolution and sensitivity than a mechanical gauge but cost more. Additionally, the electronic gauge can generally run for a longer period of time, be programmed to measure pressure more frequently at various intervals for improved data density, and store data in digital form.
- Resolution of the pressure gauge must be sufficient to measure small pressure changes at the end of the test.
- The type of wastestream injected may prevent the use of a downhole gauge unless brine from offsite is brought in and used for the test. This may be cost prohibitive.

Test Design

General Operational Considerations

- The injection period controls what is seen on the falloff since the falloff is replay of the injection period. Therefore, the injection period must reach radial flow prior to shut-in of the well in order for the falloff test to reach radial flow

- Ideally to determine the optimal lengths of the injection and falloff periods, the test should be simulated using measured or estimated reservoir parameters. Alternatively, injection and falloff period lengths can be estimated from empirical equations using assumed reservoir and well parameters.

- The injection rate dictates the pressure buildup at the injection well. The pressure buildup from injection must be sufficient so that the pressure change during radial flow, usually occurring toward the end of the test, is large enough to measure with the pressure gauge selected.

- Waste storage and other operational issues require preplanning and need to be addressed prior to the test date. If brine must be brought in for the injection portion of the test, operators should insure that the fluid injected has a consistent viscosity and that there is adequate fluid available to obtain a valid falloff test. The use of the wastestream as the injection fluid affords several distinct advantages:
  1. Brine does not have to be purchased or stored prior to use.
  2. Onsite waste storage tanks may be used.
  3. Plant wastestreams are generally consistent, i.e., no viscosity variations

- Rate changes cause pressure transients in the reservoir. Constant rate injection in the test well and any offset wells completed in the same reservoir are critical to simplify the pressure transients in the reservoir. Any significant injection rate fluctuations at the test well or offsets must be recorded and accounted for in the analysis using superposition.

- Unless an injectivity test is to be conducted, shutting in the well for an extend period of time prior to conducting the falloff test reduces the pressure buildup in the reservoir and is not recommended.

- Prior to conducting a test, a crown valve should be installed on the wellhead to allow the pressure gauge to be installed and lowered into the well without any interruption of the injection rate.

- The wellbore schematic should be reviewed for possible obstructions located in the well that may prevent the use or affect the setting depth of a downhole pressure gauge. The fill depth in the well should also be reported. The fill depth may not only impact the depth of the gauge, but usually prolongs the wellbore storage period and depending on the type of fill, may limit the interval thickness by isolating some of the injection intervals. A wellbore cleanout or stimulation may be needed prior to conducting the test for the test to reach radial flow and obtain valid results.

- The location of the shut-in valve can impact the duration of the wellbore storage period. The shut-in valve should be located near the wellhead. Afterflow into the wellbore prolongs the wellbore storage period. The injection pipeline leading to the well can act as an extension to the well if the shut-in valve is not located near the wellhead. Operators should report the location of the shut-in valve and its distance from the wellhead, in the test report.

- The area geology should be reviewed prior to conducting the test to determine the thickness and type of formation being tested along with any geological features such as natural fractures, a fault, or a pinchout that should be anticipated to impact the test.

Wellbore and Reservoir Data Needed to Simulate or Analyze the Falloff Test

- Wellbore radius, r_w - from wellbore schematic
- Net thickness, h - See Appendix, page A-15
- Porosity, N - log or core data
- Viscosity of formation fluid, μ_f - direct measurement or correlations
- Viscosity of waste, μ_{waste} - direct measurement or correlations
- Total system compressibility, c_t - correlations, core measurement, or well test
- Permeability, k - previous welltests or core data
- Specific gravity of injection fluid, s.g. - direct measurement
- Injection rate, q - direct measurement

Design Calculations

When simulation software is unavailable the test periods can be estimated from empirical equations. The following are set of steps to calculate the time to reach radial flow from empirically-derived equations:

1. Estimate the wellbore storage coefficient, C (bbl/psi). There are two equations to calculate the wellbore storage coefficient depending on if the well remains fluid filled (positive surface pressure) or if the well goes on a vacuum (falling fluid level in the well):
   a. Well remains fluid filled:

      $C = V_w \cdot c_{waste}$

      where, V_w is the total wellbore volume, bbls

      c_{waste} is the compressibility of the injectate, psi^{-1}

   b. Well goes on a vacuum:

      $$C = \frac{V_u}{\frac{r \cdot g}{144 \cdot g_c}}$$

      where, V_u is the wellbore volume per unit length, bbls/ft

      D is the injectate density, psi/ft

      g and g_c are gravitational constants

2. Calculate the time to reach radial flow for both the injection and falloff periods. Two different empirically-derived equations are used to calculate the time to reach radial flow, $t_{radial\ flow}$, for the injectivity and falloff periods:
   a. Injectivity period:

      $$t_{radial\ flow} > \frac{(200000 + 12000s) \cdot C}{\frac{k \cdot h}{m}} \quad hours$$

   b. Falloff period:

      $$t_{radial\ flow} > \frac{170000 \cdot C \cdot e^{0.14 \cdot s}}{\frac{k \cdot h}{m}} \quad hours$$

   The wellbore storage coefficient is assumed to be the same for both the injectivity and falloff periods. The skin factor, s, influences the falloff more than the injection period.

Use these equations with caution, as they tend to fall apart for a well with a large permeability or a high skin factor. Also remember, the welltest should not only reach radial flow, but also sustain radial flow for a timeframe sufficient for analysis of the radial flow period. As a rule of thumb, a timeframe sufficient for analysis is 3 to 5 times the time needed to reach radial flow.

3. As an alternative to steps 1 and 2, to look a specific distance "L" into the reservoir and possibly confirm the absence or existence of a boundary, the following equation can be used to estimate the time to reach that distance:

$$t_{boundary} = \frac{948 \cdot f \cdot m \cdot c_t \cdot L_{boundary}}{k} \quad hours$$

where, $L_{boundary}$ = feet to boundary
$t_{boundary}$ = time to boundary, hrs

Again, this is the time to reach a distance "L" in the reservoir. Additional test time is required to observe a fully developed boundary past the time needed to just reach the boundary. As a rule of thumb, to see a fully developed boundary on a log-log plot, allow at least 5 times the time to reach it. Additionally, for a boundary to show up on the falloff, it must first be encountered during the injection period.

4. Calculate the expected slope of the semilog plot during radial flow to see if gauge resolution will be adequate using the following equation:

$$m_{semi\log} = \frac{162.6 \cdot q \cdot B}{\frac{k \cdot h}{m}}$$

where, q = the injection rate preceding the falloff test, bpd
B = formation volume factor for water, rvb/stb (usually assumed to be 1)

<u>Considerations for Offset Wells Completed in the Same Interval</u>

Rate fluctuations in offset wells create additional pressure transients in the reservoir and complicate the analysis. Always try to simplify the pressure transients in the reservoir. Do not simultaneously shut-in an offset well and the test well. The following items are key considerations in dealing with the impact of offset wells on a falloff test:

- Shut-in all offset wells prior to the test
- If shutting in offset wells is not feasible, maintain a constant injection rate prior to and during the test
- Obtain accurate injection records of offset injection prior to and during the test
- At least one of the real time points corresponding to an injection rate in an offset well should be synchronized to a specific time relating to the test well

- Following the falloff test in the test well, send at least two pulses from the offset well to the test well by fluctuating the rate in the offset well. The pressure pulses can confirm communication between the wells and can be simulated in the analysis if observed at the test well. The pulses can also be analyzed as an interference test using an Ei type curve.
- If time permits, conduct an interference test to allow evaluation of the reservoir without the wellbore effects observed during a falloff test.

Falloff Test Analysis

In performing a falloff test analysis, a series of plots and calculations should be prepared to QA/QC the test, identify flow regimes, and determine well completion and reservoir parameters. Individual plots, flow regime signatures, and calculations are discussed in the following sections.

Cartesian Plot

- The pressure data prior to shut-in of the well should be reviewed on a Cartesian plot to confirm pressure stabilization prior to the test. A well that has reached radial flow during the injectivity portion of the test should have a consistent injection pressure.

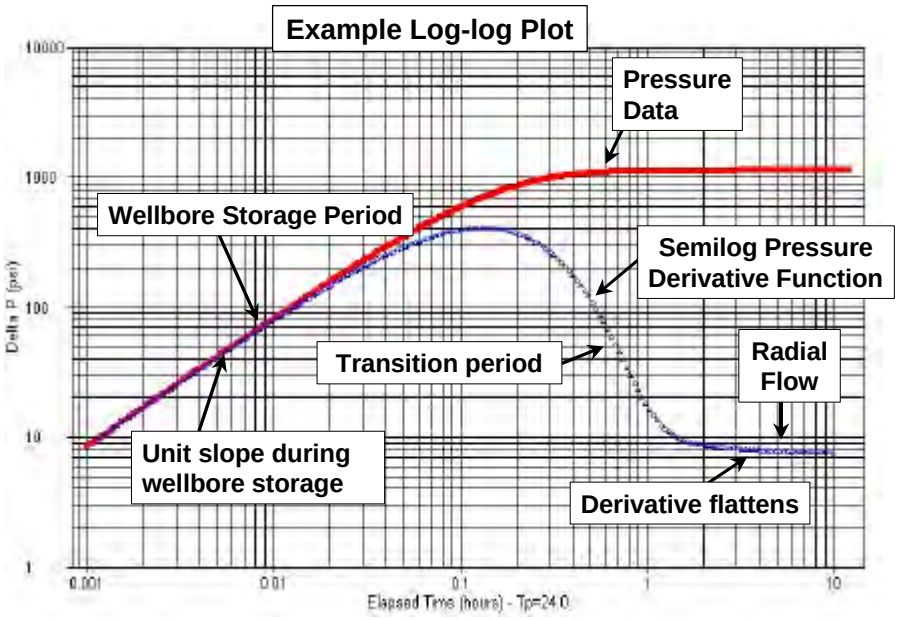
- A Cartesian plot of the pressure and temperature versus real time or elapsed time should be the first plot made from the falloff test data. Late time pressure data should be expanded to determine the pressure drop occurring during this portion of the test. The pressure changes should be compared to the pressure gauges used to confirm adequate gauge resolution existed throughout the test. If the gauge resolution limit was reached, this timeframe should be identified to determine if radial flow was reached prior to reaching the resolution of the pressure gauge. Pressure data obtained after reaching the resolution of the gauge should be treated as suspect and may need to be discounted in the analysis.

- Falloff tests conducted in highly transmissive reservoirs may be more sensitive to the temperature compensation mechanism of the gauge because the pressure buildup response evaluated is smaller. Region 6 has observed cases in which large temperature anomalies were not properly compensated for by the pressure gauge, resulting in erroneous pressure data and an incorrect analysis. For this reason, the Cartesian plot of the temperature data should be reviewed. Any temperature anomalies should be noted to determine if they correspond to pressure anomalies.

- Include the injection rate(s) of the test well 48 hours prior to shut-in on the Cartesian plot to illustrate the consistency of the injection rate prior to shut-in and to determine the appropriate time function to use on the log-log and semilog plots. (See Appendix, page A10 for time function selection)

Log-log Diagnostic Plot

C Plot the pressure and semilog derivative versus time on a log-log diagnostic plot. Use the appropriate time function based on the rate history of the injection period preceding the falloff. (See Appendix, page A-10 for time function selection) The log-log plot is used to identify the flow regimes present in the welltest. An example log-log plot is shown below:



Identification of Test Flow Regimes

C Flow regimes are mathematical relationships between pressure, rate, and time. Flow regimes provide a visualization of what goes on in the reservoir. Individual flow regimes have characteristic slopes and a sequencing order on the log-log plot.

C Various flow regimes will be present during the falloff test, however, not all flow regimes are observed on every falloff test. The late time responses correlate to distances further from the test well. The critical flow regime is radial flow from which all analysis calculations are performed. During radial flow, the pressure responses recorded are representative of the reservoir, not the wellbore.

C The derivative function amplifies reservoir signatures by calculating a running slope of a designated plot. The derivative plot allows a more accurate determination of the radial flow portion of the test, in comparison with the old method of simply proceeding 1½ log cycles from the end of the unit slope line of the pressure curve.

C The derivative is usually based on the semilog plot, but it can also be calculated based on other plots such as a Cartesian plot, a square root of time plot, a quarter root of time plot, and the 1/square root of time plot. Each of these plots are used to identify specific flow

regimes. If the flow regime characterized by a specialized plot is present then when the derivative calculated from that plot is displayed on the log-log plot, it will appear as a "flat spot" during the portion of the falloff corresponding to the flow regime.

C Typical flow regimes observed on the log-log plot and their semilog derivative patterns are listed below:

Flow Regime	Semilog Derivative Pattern
Wellbore Storage	Unit slope
Radial Flow	Flat plateau
Linear Flow	Half slope
Bilinear Flow	Quarter slope
Partial Penetration	Negative half slope
Layering	Derivative trough
Dual Porosity	Derivative trough
Boundaries	Upswing followed by plateau
Constant Pressure	Sharp derivative plunge

Characteristics of Individual Test Flow Regimes

C Wellbore Storage:

1. Occurs during the early portion of the test and is caused by the well being shut-in at the surface instead of the sandface
2. Measured pressure responses are governed by well conditions and are not representative of reservoir behavior and are characterized by both the pressure and semilog derivative curves overlying a unit slope on the log-log plot
3. Wellbore skin or a low permeability reservoir results in a slower transfer of fluid from the well to the formation, extending the duration of the wellbore storage period
4. A wellbore storage dominated test is unanalyzable

C Radial Flow:

1. The pressure responses are from the reservoir, not the wellbore
2. The critical flow regime from which key reservoir parameters and completion conditions calculations are performed
3. Characterized by a flattening of the semilog plot derivative curve on the log-log plot and a straight line on the semilog plot

C Spherical Flow:

1. Identifies partial penetration of the injection interval at the wellbore
2. Characterized by the semilog derivative trending along a negative half slope on the log-log plot and a straight line on the 1/square root of time plot
3. The log-log plot derivative of the pressure vs 1/square root of time plot is flat

- Linear Flow
  1. May result from flow in a channel, parallel faults, or a highly conductive fracture
  2. Characterized by a half slope on both the log-log plot pressure and semilog derivative curves with the derivative curve approximately 1/3 of a log cycle lower than the pressure curve and a straight line on the square root of time plot.
  3. The log-log plot derivative of the pressure vs square root of time plot is flat

- Hydraulically Fractured Well
  1. Multiple flow regimes present including wellbore storage, fracture linear flow, bilinear flow, pseudo-linear flow, formation linear flow, and pseudo-radial flow
  2. Fracture linear flow is usually hidden by wellbore storage
  3. Bilinear flow results from simultaneous linear flows in the fracture and from the formation into the fracture, occurs in low conductivity fractures, and is characterized by a quarter slope on both the pressure and semilog derivative curves on the log-log plot and by a straight line on a pressure versus quarter root of time plot
  4. Formation linear flow is identified by a half slope on both the pressure and semilog derivative curves on the log-log plot and by a straight line on a pressure versus square root of time plot
  5. Psuedo-radial flow is analogous to radial flow in an unfractured well and is characterized by flattening of semilog derivative curve on the log-log plot and a straight line on a semilog pressure plot

- Naturally Fractured Rock
  1. The fracture system will be observed first on the falloff test followed by the total system consisting of the fractures and matrix.
  2. The falloff analysis is complex. The characteristics of the semilog derivative trough on the log-log plot indicate the level of communication between the fractures and the matrix rock.

- Layered Reservoir
  1. Analysis of a layered system is complex because of the different flow regimes, skin factors or boundaries that may be present in each layer.
  2. The falloff test objective is to get a total tranmissibility from the whole reservoir system.
  3. Typically described as commingled (2 intervals with vertical separation) or crossflow (2 intervals with hydraulic vertical communication)

<u>Semilog Plot</u>

- The semilog plot is a plot of the pressure versus the log of time. There are typically four different semilog plots used in pressure transient and falloff testing analysis. After plotting the appropriate semilog plot, a straight line should be drawn through the points located within the equivalent radial flow portion of the plot identified from the log-log plot.

- Each plot uses a different time function depending on the length and variation of the injection rate preceding the falloff. These plots can give different results for the same test, so it is important that the appropriate plot with the correct time function is used for the analysis. Determination of the appropriate time function is discussed below.

- The slope of the semilog straight line is then used to calculate the reservoir transmissibility - kh/:, the completion condition of the well via the skin factor - s, and also the radius of investigation - r_i of the test.

Determination of the Appropriate Time Function for the Semilog Plot

The following four different semilog plots are used in pressure transient analysis:

1. Miller Dyes Hutchinson (MDH) Plot
2. Horner Plot
3. Agarwal Equivalent Time Plot
4. Superposition Time Plot

These plots can give different results for the same test. Use of the appropriate plot with the correct time function is critical for the analysis.

- The MDH plot is a semilog plot of pressure versus)t, where)t is the elapsed shut-in time of the falloff.
    1. The MDH plot only applies to wells that reach psuedo-steady state during injection. Psuedo-steady state means the pressure response from the well has encountered all the boundaries around the well.
    2. The MDH plot is only applicable to injection wells with a *very* long injection period at a constant rate. This plot is not recommended for use by EPA Region 6.

- The Horner plot is a semilog plot of pressure versus $(t_p+)t)/)t$. The Horner plot is only used for a falloff preceded by a single constant rate injection period.
    1. The injection time, $t_p=V_p/q$ in hours, where V_p=injection volume since the last pressure equalization and q is the injection rate prior to shut-in for the falloff test. The injection volume is often taken as the cumulative injection since completion.
    2. The Horner plot can result in significant analysis error if the injection rate varies prior to the falloff.

- The Agarwal equivalent time plot is a semilog plot of the pressure versus Agarwal equivalent time, $)t_e$.
    1. The Agarwal equivalent time function is similar to the Horner plot, but scales the falloff to make it look like an injectivity test.
    2. It is used when the injection period is a short, constant rate compared to the length of the falloff period.
    3. The Agarwal equivalent time is defined as: $)t_e=\log(t_p\ )t)/(t_p+)t)$, where t_p is calculated the same as with the Horner plot.

C The superposition time function accounts for variable rate conditions preceding the falloff.
   1. It is the most rigorous of all the time functions and is usually calculated using welltest software.
   2. The use of the superposition time function requires the operator to accurately track the rate history. As a rule of thumb, at a minimum, the rate history for twice the length of the falloff test should be included in the analysis.

The determination of which time function is appropriate for the plotting the welltest on semilog and log-log plots depends on available rate information, injection period length, and software:

1. If there is not a rate history other than a single rate and cumulative injection, use a Horner time function
2. If the injection period is shorter than the falloff test and only a single rate is available, use the Agarwal equivalent time function
3. If you have a variable rate history use superposition when possible. As an alternative to superposition, use Agarwal equivalent time on the log-log plot to identify radial flow. The semilog plot can be plotted in either Horner or Agarwal time if radial flow is observed on the log-log plot.

<u>Parameter Calculations and Considerations</u>

C Transmissibility - The slope of the semilog straight line, m, is used to determine the transmissibility (kh/∶) parameter group from the following equation:

$$\frac{k \cdot h}{m} = \frac{162.6 \cdot q \cdot \mathrm{B}}{m}$$

where, q = injection rate, bpd (negative for injection)
B = formation volume factor, rvb/stb (Assumed to be 1 for formation fluid)
m = slope of the semilog straight line through the radial flow portion of the plot in psi/log cycle
k = permeability, md
h = thickness, ft (See Appendix, page A-15)
∶ = viscosity, cp

C The viscosity, ∶, is usually that of the formation fluid. However, if the waste plume size is massive, the radial flow portion of the test may remain within the waste plume. (See Appendix, page A-14)
   1. The waste and formation fluid viscosity values usually are similar, however, if the wastestream has a significant viscosity difference, the size of the waste plume and distance to the radial flow period should be calculated.
   2. The mobility, k/∶, differences between the fluids may be observed on the derivative curve.

C The permeability, k, can be obtained from the calculated transmissibility (kh/∶) by

substituting the appropriate thickness, h, and viscosity, :, values.

Skin Factor

C In theory, wellbore skin is treated as an infinitesimally thin sheath surrounding the wellbore, through which a pressure drop occurs due to either damage or stimulation. Industrial injection wells deal with a variety of waste streams that alter the near wellbore environment due to precipitation, fines migration, ion exchange, bacteriological processes, and other mechanisms. It is reasonable to expect that this alteration often exists as a zone surrounding the wellbore and not a skin. Therefore, at least in the case of industrial injection wells, the assumption that skin exists as a thin sheath is not always valid. This does not pose a serious problem to the correct interpretation of falloff testing except in the case of a large zone of alteration, or in the calculation of the flowing bottomhole pressure. The Region has seen instances in which large zones of alteration were suspected of being present.

C The skin factor is the measurement of the completion condition of the well. The skin factor is quantified by a positive value indicating a damaged completion and a negative value indicating a stimulated completion.

1. The magnitude of the positive value indicating a damaged completion is dictated by the transmissibility of the formation.
2. A negative value of -4 to -6 generally indicates a hydraulically fractured completion, whereas a negative value of -1 to -3 is typical of an acid stimulation in a sandstone reservoir.
3. The skin factor can be used to calculate the effective wellbore radius, r_{wa} also referred to the apparent wellbore radius. (See Appendix, page A-13)
4. The skin factor can also be used to correct the injection pressure for the effects of wellbore damage to get the actual reservoir pressure from the measured pressure.

C The skin factor is calculated from the following equation:

$$s = 1.1513\left[\frac{P_{1hr} - P_{wf}}{m} - \log\left(\frac{k \cdot t_p}{\left(t_p + 1\right) \cdot f \cdot m \cdot c_t \cdot r_w^2}\right) + 3.23\right]$$

where, s = skin factor, dimensionless

P_{1hr} = pressure intercept along the semilog straight line at a shut-in time of 1 hour, psi

P_{wf} = measured injection pressure prior to shut-in, psi

: = appropriate viscosity at reservoir conditions, cp (See Appendix, page A-14)

m = slope of the semilog straight line, psi/cycle

k = permeability, md

N = porosity, fraction

c_t = total compressibility, psi^{-1}

r_w = wellbore radius, feet

t_p = injection time, hours

Note that the term $t_p/(t_p + \Delta t)$, where Δt=1 hr, appears in the log term. This term is usually assumed to result in a negligible contribution and typically is taken as 1 for large t. However, for relatively short injection periods, as in the case of a drill stem test (DST), this term can be significant.

Radius of Investigation

- The radius of investigation, r_i, is the distance the pressure transient has moved into a formation following a rate change in a well.

- There are several equations that exist to calculate the radius of investigation. All the equations are square root equations based on cylindrical geometry, but each has its own coefficient that results in slightly different results, (See Oil and Gas Journal, Van Poollen, 1964).

- Use of the appropriate time is necessary to obtain a useful value of r_i. For a falloff time shorter than the injection period, use Agarwal equivalent time function, Δt_e, at the end of the falloff as the length of the injection period preceding the shut-in to calculate r_i.

- The following two equivalent equations for calculating r_i were taken from SPE Monograph 1, (Equation 11.2) and Well Testing by Lee (Equation 1.47), respectively:

$$r_i = \sqrt{0.00105\frac{k \cdot t}{f \cdot m \cdot c_t}} \equiv \sqrt{\frac{k \cdot t}{948 \cdot f \cdot m \cdot c_t}}$$

Effective Wellbore Radius

- The effective wellbore radius relates the wellbore radius and skin factor to show the effects of skin on wellbore size and consequently, injectivity.

- The effective wellbore radius is calculated from the following:

$$r_{wa} = r_w e^{-s}$$

- A negative skin will result in a larger effective wellbore radius and therefore a lower injection pressure.

Reservoir Injection Pressure Corrected for Skin Effects

- The pressure correction for wellbore skin effects, ΔP_{skin}, is calculated by the following:

$$\Delta P_{skin} = 0.868 \cdot m \cdot s$$

where, m = slope of the semilog straight line, psi/cycle
s = wellbore skin, dimensionless

- The adjusted injection pressure, P_{wfa} is calculated by subtracting the ΔP_{skin} from the measured injection pressure prior to shut-in, P_{wf}. This adjusted pressure is the calculated reservoir pressure prior to shutting in the well, Δt=0, and is determined by the following:

$$P_{wfa} = P_{wf} - \Delta P_{skin}$$

- From the previous equations, it can be seen that the adjusted bottomhole pressure is directly dependent on a single point, the last injection pressure recorded prior to shut-in. Therefore, an accurate recording of this pressure prior to shut-in is important. Anything that impacts the pressure response, e.g., rate change, near the shut-in of the well should be avoided.

Determination of the Appropriate Fluid Viscosity

- If the wastestream and formation fluid have similar viscosities, this process is not necessary.

- This is only needed in cases where the mobility ratios are extreme between the wastestream, $(k/\mu)_w$, and formation fluid, $(k/\mu)_f$. Depending on when the test reaches radial flow, these cases with extreme mobility differences could cause the derivative curve to change and level to another value. Eliminating alternative geologic causes, such as a sealing fault, multiple layers, dual porosity, etc., leads to the interpretation that this change may represent the boundary of the two fluid banks.

- First assume that the pressure transients were propagating through the formation fluid during the radial flow portion of the test, and then verify if this assumption is correct. This is generally a good strategy except for a few facilities with exceptionally long injection histories, and consequently, large waste plumes. The time for the pressure transient to exit the waste front is calculated. This time is then identified on both the log-log and semilog plots. The radial flow period is then compared to this time.

- The radial distance to the waste front can then be estimated volumetrically using the following equation:

$$r_{waste\ plume} = \sqrt{\frac{0.13368 \cdot V_{waste\ injected}}{p \cdot h \cdot f}}$$

where, $V_{waste\ injected}$ = cumulative waste injected into the completed interval, gal
$r_{waste\ plume}$ = estimated distance to waste front, ft
h = interval thickness, ft
ϕ = porosity, fraction

- The time necessary for a pressure transient to exit the waste front can be calculated using the following equation:

$$t_w = \frac{126.73 \cdot m_w \cdot c_t \cdot V_{waste\ injected}}{p \cdot k \cdot h}$$

where, t_w= time to exit waste front, hrs
$V_{waste\ injected}$ = cumulative waste injected into the completed interval, gal
h = interval thickness, ft

k = permeability, md

μ_w = viscosity of the historic waste plume at reservoir conditions, cp

c_t = total system compressibility, psi^{-1}

- The time should be plotted on both the log-log and semilog plots to see if this time corresponds to any changes in the derivative curve or semilog pressure plot. If the time estimated to exit the waste front occurs before the start of radial flow, the assumption that the pressure transients were propagating through the reservoir fluid during the radial flow period was correct. Therefore, the viscosity of the reservoir fluid is the appropriate viscosity to use in analyzing the well test. If not, the viscosity of the historic waste plume should be used in the calculations. If the mobility ratio is extreme between the wastestream and formation fluid, adequate information should be included in the report to verify the appropriate fluid viscosity was utilized in the analysis.

Reservoir Thickness

- The thickness used for determination of the permeability should be justified by the operator. The net thickness of the defined injection interval is not always appropriate.

- The permeability value is necessary for plume modeling, but the transmissibility value, kh/μ, can be used to calculate the pressure buildup in the reservoir without specifying values for each parameter value of k, h, and μ.

- Selecting an interval thickness is dependent on several factors such as whether or not the injection interval is composed of hydraulically isolated units or a single massive unit and wellbore conditions such as the depth to wellbore fill. When hydraulically isolated sands are present, it may be helpful to define the amount of injection entering each interval by conducting a flow profile survey. Temperature logs can also be reviewed to evaluate the intervals receiving fluid. Cross-sections may provide a quick look at the continuity of the injection interval around the injection well.

- A copy of a SP/Gamma Ray well log over the injection interval, the depth to any fill, and the log and interpretation of available flow profile surveys run should be submitted with the falloff test to verify the reservoir thickness value assumed for the permeability calculation.

Use of Computer Software

- To analyze falloff tests, operators are encouraged to use well testing software. Most software has type curve matching capabilities. This feature allows the simulation of the entire falloff test results to the acquired pressure data. This type of analysis is particularly useful in the recognition of boundaries, or unusual reservoir characteristics, such as dual porosity. It should be noted that type curve matching is not considered a substitute, but is a compliment to the analysis.

- All data should be submitted electronically with a label stating the name of the facility, the well number(s), and the date of the test(s). The label or READ.Me file should include

the names of all the files contained on the diskette, along with any necessary explanations of the information. The parameter units format (hh:mm:ss, hours, etc.) should be noted for the pressure file for synchronization to the submitted injection rate information. The file containing the gauge data analyzed in the report should be identified and consistent with the hard copy data included in the report. If the injection rate information for any well included in the analysis is greater than 10 entries, it should also be included electronically.

Common Sense Check

- After analyzing any test, always look at the results to see if they "make sense" based on the type of formation tested, known geology, previous test results, etc. Operators are ultimately responsible for conducting an analyzable test and the data submitted to the regulatory agency.

- If boundary conditions are observed on the test, review cross-sections or structure maps to confirm if the presence of a boundary is feasible. If so, the boundary should be considered in the AOR pressure buildup evaluation for the well.

- Anomalous data responses may be observed on the falloff test analysis. These data anomalies should be evaluated and explained. The analyst should investigate physical causes in addition to potential reservoir responses. These may include those relating to the well equipment, such as a leaking valve, or a channel, and those relating to the data acquisition hardware such as a faulty gauge. An anomalous response can often be traced to a brief, but significant rate change in either the test well or an offset well.

- Anomalous data trends have also been caused by such things as ambient temperature changes in surface gauges or a faulty pressure gauge. Explanations for data trends may be facilitated through an examination of the backup pressure gauge data, or the temperature data. It is often helpful to qualitatively examine the pressure and/or temperature channels from both gauges. The pressure data should overlay during the falloff after being corrected for the difference in gauge depths. On occasion, abrupt temperature changes can be seen to correspond to trends in the pressure data. Although the source of the temperature changes may remain unexplainable, the apparent correlation of the temperature anomaly to the pressure anomaly can be sufficient reason to question the validity of the test and eliminate it from further analysis.

- The data that is obtained from pressure transient testing should not collect dust, but be compared to petition or permit parameters. Test derived transmissibilities and static pressures can confirm compliance with no migration and non-endangerment (AOR) conditions.

APPENDIX D-VII

MS IZ 1 Conversion Plan and Schematic

Conversion Plan for Minerva South In-Zone Well No. 001

Stream 34 Well No. 001
SN: 224951, API: 17019219190000
Cameron Parish, LA
(Map ID 1)

RE-ENTER WELL, EVALUATE EXTERNAL CMT ON 7-5/8" & EQUIP AS A MONITOR WELL

RE-ENTER AND TIE-BACK PRODUCTION CSG

1. Locate plugged wellhead and build location
2. After locating csg stub, tie sfc csg back to sfc and install flange and wellhead and BOP equipment.
3. MIRU, pick up workstring and bit to drill out sfc plugs, tagging up on 7-5/8" cut csg @ 2991. (Note one report in file states csg was cut @ 2945.)
4. POOH and pick up shoe to wash over and dress off +/- 15' cut csg.
5. POOH and pick up csg patch and 7-5/8" csg to tie back production csg to surface.
6. Install wellhead & BOP equipment.

CLEAN OUT WELLBORE

7. RIH w/bit to drill out cmt inside cut csg.
8. Continue drilling out cmt inside 7-5/8" csg and RIH to 11,400'.
9. Cir well clean w/KCL & POOH. Pressure test csg and record same.

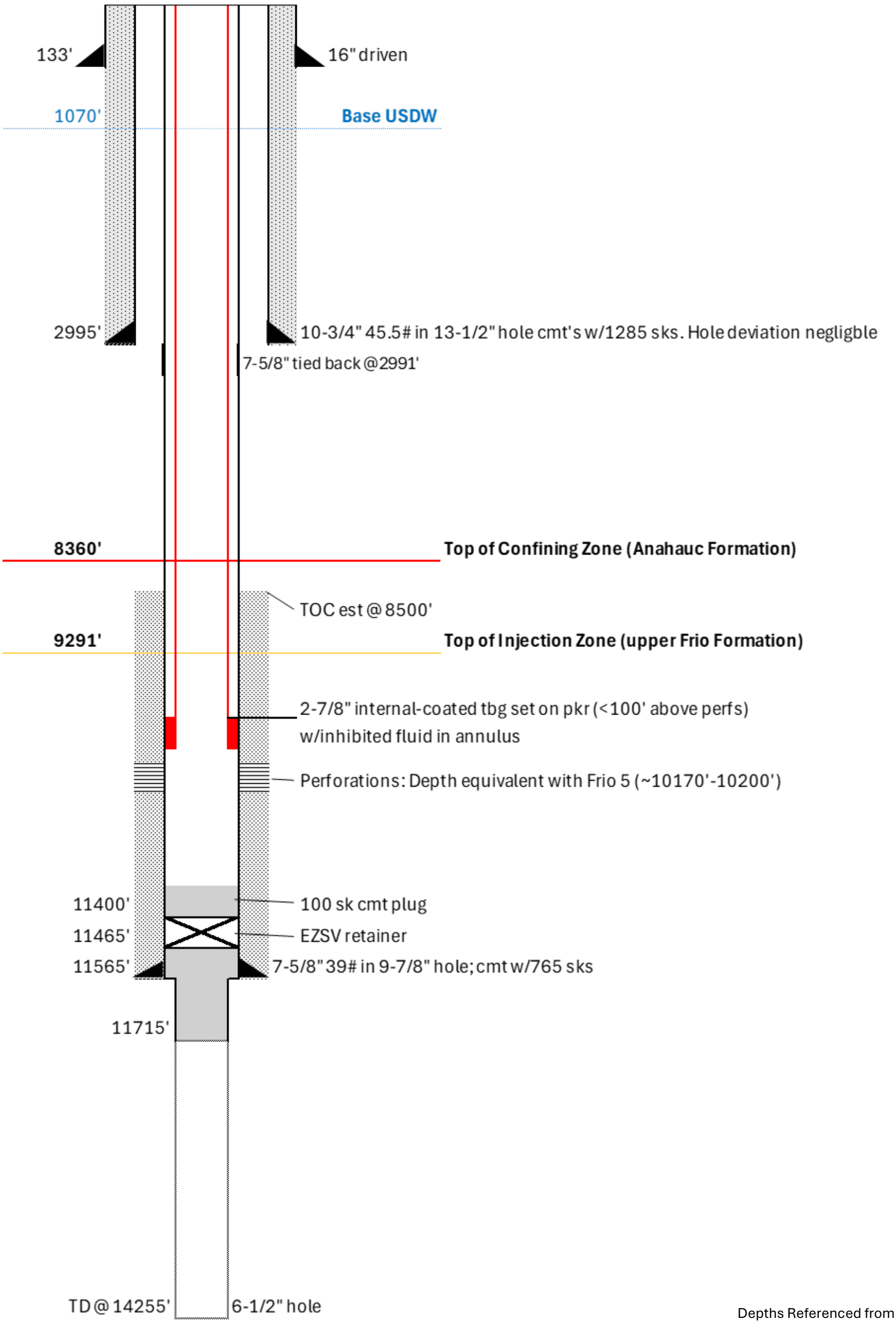
EVALUATE CEMENT BOND

10. Run CBL, temp log and BHP survey.
11. Results from Cmt bond:
    a. If sufficient bonded cmt exists along the base of the Confining Zone (Anahuac Formation), POOH and continue with "in-zone" monitor well plans
    b. If insufficient cmt is bonded along the base of the Confining Zone (Anahuac Formation)
        i. Perforate csg 100' below and above the Confining Zone (Anahuac Formation)/ Injection Zone (Upper Frio Formation) (CZ/IZ) boundary
        ii. Set cmt retainer above lower perforations & attempt a wrap-around sqz extending 100' below and 100' above top of CZ/IZ boundary
        iii. Pull out of retainer and let cmt set up
        iv. Drill out cmt down to the retainer and run CBL to confirm TOC bond with CBL.
        v. If CBL is satisfactory, drill out cmt retainer and cmt. Otherwise, re-sqz and affirm sufficient bond is in place.

COMPLETE AS "IN-ZONE" MONITORING WELL

12. RIH w/ 2-7/8" internally-coated tbg string and 7-5/8" pkr no higher than 100' above initial Injection Zone (Upper Frio Formation) monitoring perforations (TBD).
13. Cir inhibited fluid on tbg/csg annulus.
14. Set pkr and perform and record csg integrity test.
15. Perforate Upper Frio Formation thru-tbg within the initial Injection Zone at a depth TBD. Perforations will be aligned with interval perforated in proposed injection wells.
16. Run temp log, BHP survey and fluid movement survey (to test external mechanical integrity).
17. Install wellhead and tree equipped with isolation & swab valves and pressure recording devices
    a. Monitor wellhead and annulus pressure
    b. Periodically sample air space in wellhead for presence of CO_2 and/or hydrocarbons
    c. Periodically, run suite of logs/surveys to monitor fluid movement behind pipe

Proposed Conversion Wellbore Schematic for Minerva South In-Zone Well No. 001



Depths Referenced from KB

KB= 33 ft above MSL

Gulf Coast Sequestration, LLC (G1037) 5599 San Felipe, Suite 1450, Houston, TX 77056 (713) 997-3145 | www.gcscarbon.com	**Minerva South CCS Well Nos. 001 & 002**	
	Project: **Minerva**	Project ID: **R06-LA-0002**
	Location: **Cameron Parish, LA**	LDENR Appl Nos: **45031 & 45032**

APPENDIX D-VIII

Indirect Monitoring Technology Specifications

Distributed Acoustic Sensing (DAS)



Fiber optic acoustic monitoring for subsea wells

The **SureVIEW™ seismic distributed acoustic sensing (sDAS) interrogator** offers all of the benefits of fiber optic acoustic monitoring—from flow monitoring and optimization, sand detection and stimulation optimization, to seismic and microseismic monitoring—combined in a single interrogator unit.

Unlike other DAS interrogators, SureVIEW sDAS utilizes Baker Hughes SureVIEW **CoreBright™ optical fiber**, a proprietary fiber specifically designed for durable oil and gas deployments. This allows operators to monitor high value assets through the life of the well, from well-centric to reservoir focused scales.

The combination of SureVIEW sDAS with **CoreBright™ enhanced backscatter fiber (EBF)** permits the acquisition of data in subsea wells located long distances from the data acquisition unit. Testing shows that a vertical seismic profile (VSP) can be acquired from the shore, or host facility up to 50 miles (80 km) away.

The SureVIEW sDAS interrogator can output various formats, suitable for various applications, and has the ability to break down the raw data, as well as compute attributes on-the-fly (frequency-band energy, individual spectra). It can also record data either in continuous or trigger mode, and is equipped with an independent global positioning system (GPS)–thus permitting clock synchronization and clock drift control.

SureVIEW sDAS delivers high fidelity data readily available to processing and answer solution teams. The system may also be remotely operated through a connection to the Baker Hughes cloud services, and is compliant with HDF5 data format.

From seismic processing, reservoir characterization, data visualization and advanced modelling and interpretation, we deliver answers, not just data.

Contact a Baker Hughes representative today to learn how we can help you take energy forward.

Applications

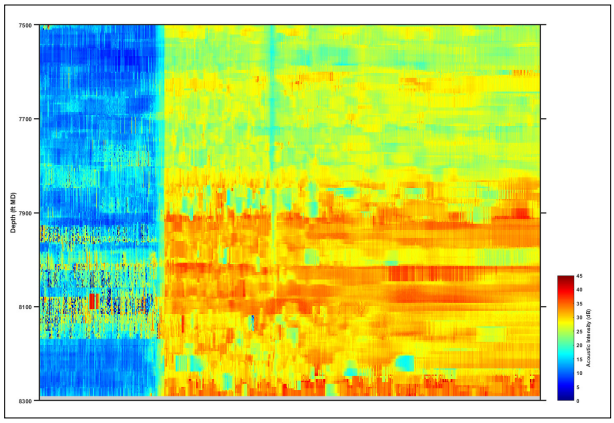
- Subsea and land wells
- Permanent reservoir monitoring
  - Flow monitoring
  - Sand detection
  - Leak detection
  - Stimulation optimization
  - Microseismic monitoring
  - Vertical seismic profiling (VSP)

Benefits

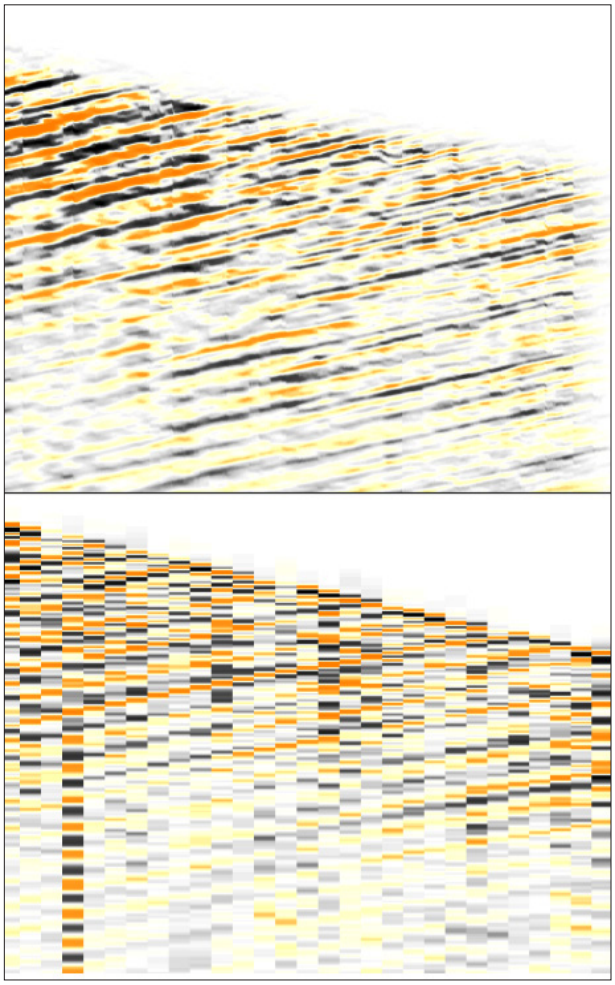
- Delivers an integrated solution from subsurface equipment to remote visualization and analytics that saves time and cost
- Simplifies handling and management of data reducing IT integration time
- Offers a better understanding of the wellbore/reservoir enabling sustained and/or incremental production of your asset
- Enables understanding of the entire completion when coupled with Baker Hughes SureCONNECT™ downhole intelligent wet-connect system
- Provides a long-term well and reservoir monitoring solution while reducing operating costs by minimizing/eliminating unnecessary interventions

Technical Specifications

Technology Supported	SureVIEW DAS VSP
Type	Rackmount
Number of Channels	8
Rack Unit Dimensions	6U
Certifications	CE, TUV
Supply Voltage	110-240 Volts AC, 50 or 60Hz
Typical Power Consumption	Up to 400W
Operating Temperature Range	0°C to +40°C / 32°F to +104°F
Optical Connectors	F3000/APC
Interface Connections	Ethernet, GPS, USB (Geophones) DC Trigger Pulse (GPS Synced)
File Formats	PRODML/HDF5/SEG-Y
Data Storage	960GB (Internal) 8TB (NAS)
Maximum Distance Range	Up to 12 miles (20 km) with CoreBright fiber Up to 50 miles (80 km) with CoreBright EBF
Fiber Type	Single Mode
Spatial Resolution	1.5 meter
Minimum Sampling Interval	0.33 meter
Gauge Length	Selectable 3, 7, 15, 31 meters
Maximum Pulse Rate	10 kHz
Dynamic Range	0.24 nε (over full bandwidth) 1.5pε (narrowband) Up to 1 με



This Distributed Acoustic Sensing (DAS) Frequency Band Energy (FBE) shows acoustic energy acquired in a multi-zone injection well. This information was used to estimate zonal flow allocation.



This comparison shows the upgoing wavefield of a vertical seismic profile (VSP) acquired above the well with a wireline tool (bottom) versus 43 miles (69 km) away from the wellhead (top) with sDAS, and CoreBright™ as lead-in fiber, a 3dB attenuation and a subsea amplifier, and CoreBright™ EBF inside the well.

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Pulse Neutron Capture Log

DCN: W17R008.A2

RESERVOIR PERFORMANCE MONITOR (RPM)

Advancing Reservoir Performance
Formation evaluation and reservoir monitoring

TIER 1

COMPREHENSIVE RESERVOIR EVALUATION AND MANAGEMENT

The Reservoir Performance Monitor (RPM™) platform is an advanced, slimhole, multifunction, pulsed neutron reservoir monitoring instrument. Its instrumentation combines multiple nuclear measurements in one system with industry-leading accuracy and precision. Carbon/oxygen (C/O) and pulsed neutron capture (PNC) measurements acquired with the RPM tool provide water saturation and three-phase holdup determination, while oxygen activation measurements allow detection of water flow and channels.

RPM services address a broad scope of reservoir evaluation and management applications, including reservoir saturation and produced fluids monitoring, formation evaluation, production profiling, workover and well abandonment evaluation, borehole diagnostics, location of bypassed oil, gas detection and quantification, and identification of water production.

The RPM instrument employs three high-resolution gammaray detectors arrayed above an efficient and reliable neutron generator. State-of-the-art detector electronics measure both the arrival time and energy of detected gamma rays. The generator is pulsed at distinct frequencies, and the data acquisition system operates in various timing modes to obtain the different logging measurements. The system hardware is combinable with other production logging instruments; and it is constructed in short, modular sections to facilitate shipping and handling.

ACCURACY IS PARAMOUNT

The accuracy of the RPM service has been ensured by extensive physical characterization in Baker Hughes' Houston Technology Center. The tool's measurements have also been enhanced by 3-D and Monte Carlo modeling to provide accurate response in a wide range of borehole, casing, formation, and fluid conditions; and Baker Hughes' unique Dynamic Response Generator™ feature delivers accuracy and confidence in any borehole geometry.

Unique downhole conditions can be modeled to ensure that analysis of the reservoir is the most accurate available. And extensive pre-job planning tools are available for design of a data acquisition program that optimizes the final answers delivered by the service.

EFFICIENCY IS DESIGNED IN

Flexibility and operating efficiency make the RPM tool a complete multimode, multisensor, solution-based system. All operating modes are selectable by surface commands.

The RPM instrument can be run in combination with conventional production logging sensors to provide a complete picture of a well's production and reserves in a single trip. It can also be combined with Baker Hughes' unique Multi-Capacitance Flow Meter (MCFM™) instrument in the POLARIS™ system for evaluation of highly deviated wells.

WHY THE RPM TOOL WORKS SO WELL

The RPM instrument uses high-energy neutrons to measure both the inelastic and capture gamma rays.

The inelastic gamma rays, produced by fast neutron collisions during the accelerator pulse, are used for carbon/oxygen measurement to determine the formation water saturation in formations with fresh or unknown connate water salinity.

The capture gamma rays, generated by the absorption of slow or "thermal" neutrons after the pulse, are used to measure formation water saturation in formations with saline connate water. The sensitivity of the capture process to salinity produces a log response similar to a conductivity measurement, where the measured thermal neutron absorption cross section (∑) is used to determine water saturation.

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RESERVOIR PERFORMANCE MONITOR (RPM)

TIER 1



APPLICATIONS AND SOLUTIONS

FORMATION EVALUATION

- Cased hole water and gas saturation measurements
  - Through casing (with through-tubing deployment capability)
  - When openhole logs are unavailable or uneconomical
- Quantification of total hydrocarbons in medium- to high-salinity conditions
- Quantification of liquid hydrocarbons in low- and mixed-salinity conditions
- Identification and quantification of gas, independent of salinity
- Evaluation of porosity
- Identification of mineralogy

RESERVOIR MONITORING AND MANAGEMENT

- Monitoring fluid contacts
  - Time-lapse fluid monitoring
  - Gas/oil/water contact levels
  - Production and reservoir depletion
  - Identification of bypassed hydrocarbons
- Reservoir management base logs

BOREHOLE DIAGNOSTICS

- Identification of water channeling and casing leaks
- Production/injection profiling in multiple-string completions
- Multiphase borehole fluid holdup determination

WORKOVER APPLICATIONS

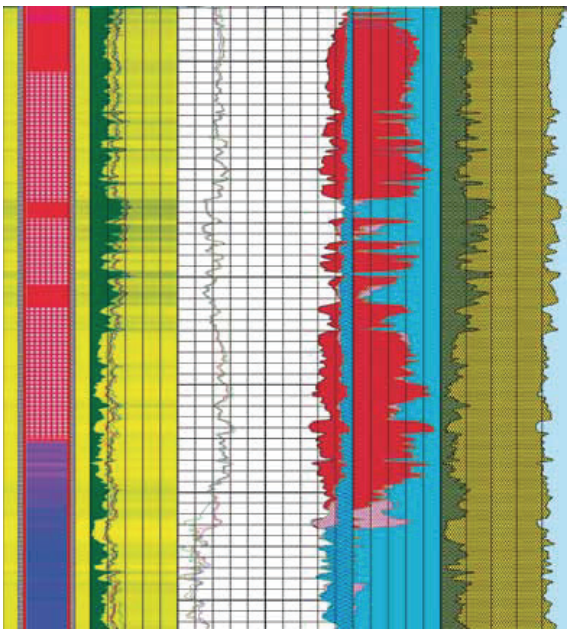
- Location of bypassed hydrocarbons, independent of water salinities
- Evaluation of stimulation operations
- Log-inject-log surveys for determining irreducible hydrocarbons
- Production/injection profiling

The RPM instrument employs three high-resolution gamma-ray detectors arrayed above an efficient and reliable neutron generator.

PULSED NEUTRON CAPTURE

In the Pulsed Neutron Capture (PNC) logging mode, the detectors record the arrival time of the gamma rays, from which the formation ∑ is determined. Time spectra from short-spaced and long-spaced detectors can be processed individually to provide traditional ∑ information. The multiple spectra are processed simultaneously to correct for borehole and diffusion effects, producing a real-time corrected formation ∑ measurement. Multiple additional measurements are provided to measure formation porosity, shale volume, and borehole fluid changes, as well as to identify formation gas.

Advanced interpretation of PNC data is available through Baker Hughes' GEOScience centers using the SEARCH™ analysis program. The identification of gas zones and the measurement of formation gas saturation is performed using the PNC mode. In this application, Baker Hughes combines special instrumentation, response characterization, and an interpretation algorithm to produce a state-of-the-art gas measurement.



Apparent measurements from near and far detectors are combined to produce a real-time corrected formation ∑.

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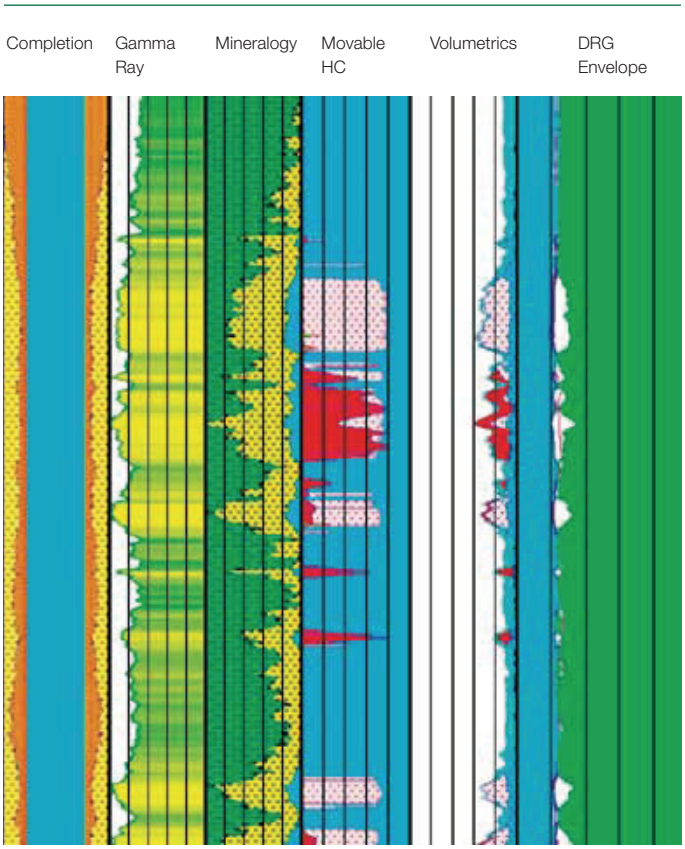
RESERVOIR PERFORMANCE MONITOR (RPM)

TIER 1

CARBON/OXYGEN LOGGING

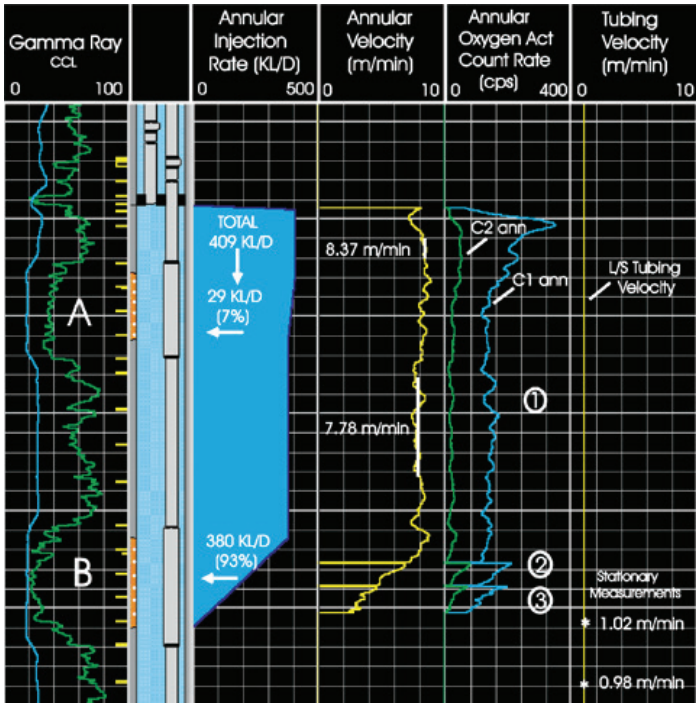
When formation waters are fresh, brackish, or of mixed or unknown salinity, the RPM-C/O acquisition mode is used to detect hydrocarbons. In this mode, direct measurements of the oxygen and carbon content of the reservoir are made, allowing differentiation of hydrocarbon zones from water-bearing zones.

Since chlorine has virtually no inelastic reaction cross section, the C/O measurement can be used to determine formation water saturation independent of salinity.



Interpretation of basic C/O data for monitoring hydrocarbon depletion of a sandstone reservoir.

FOUR MODES FOR OPERATING VERSATILITY



AFL volumetric analysis in a dual-string injection well determined that 7% of the injected fluids were entering zone A and 93% were going into zone B.

WATER FLOW LOGGING

The RPM Annular Flow Log (AFL™) and Hydrolog™ measurements use the principle of oxygen activation to measure water flow. In this application, oxygen is made artificially and temporarily radioactive through the neutronexchange reaction, allowing it to be used as a short-lived tracer. Detection of the movement of the activated oxygen can determine water velocity. These measurements provide a powerful diagnostic tool to identify movement inside the casing, outside the casing, or in the tubing-casing annulus. The measurement techniques allow detection of water movement from 2 to 500 feet per minute in simple and complex completions.

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RESERVOIR PERFORMANCE MONITOR (RPM)

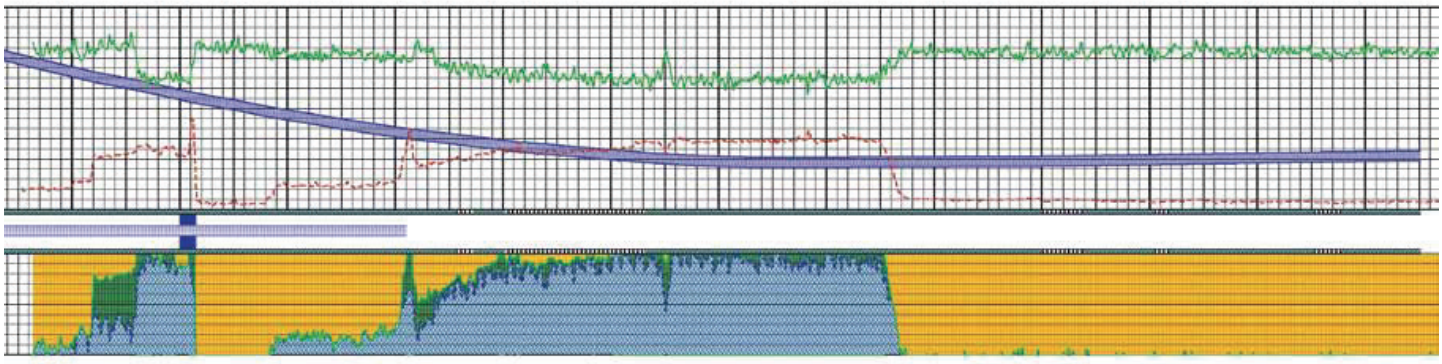
TIER 1

LOG YOUR MOST HOSTILE WELLS

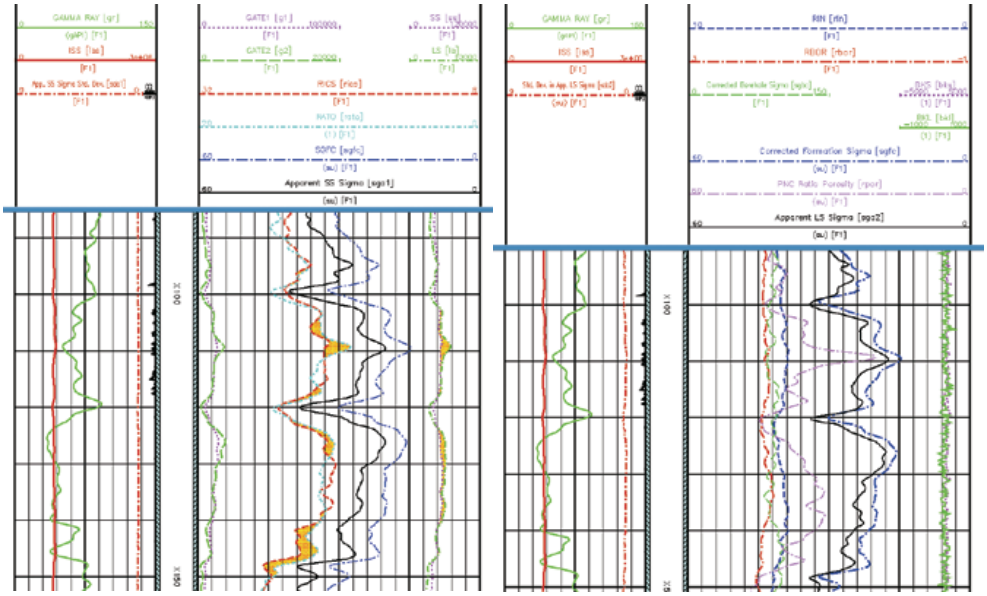
The RPM-C instrument can provide accurate data in wells in which other pulsed neutron tools cannot even survive. It has industry-best standard environmental specifications of 350°F (177°C) and 20,000 psi (138 MPa). Specially modified hardware enables reliable service at temperatures to 500°F (260°C) and pressures to 30,000 psi (207 MPa).

HOLDUP IMAGING

The RPM Pulsed Neutron Holdup Imager (PNHI™) logging mode was designed for measurement of holdups of gas, oil, and water in horizontal boreholes. The PNHI measurement produces a continuous image of the borehole contents, independent of flow regime and unaffected by gravity segregation of the produced fluids.



The PNHI log can determine gas, oil, and water holdups in horizontal boreholes.



Although RPM-PNC data acquisition and processing provide analysis results and statistics that are superior to conventional PDK-100 measurements, the RPM-PNC log display and PDK-100 presentation are similar. In time-lapse studies, an emulation of the PDK-100 curve can be provided with RPM-PNC processing for easy comparison of their measurements.

BUILD ON THE DATA YOU ALREADY HAVE

RPM data can be matched with previous-generation PDK-100™ measurements for easy comparison in mature fields. The RPM service provides real-time emulation of PDK-100 measurements for comparison with historical logs. For remedial work and timelapse monitoring, RPM data can be overlaid with existing log measurements in real time, allowing rapid workover planning.

An advanced feature of the RPM service allows real-time computation of “intrinsic” ∑. Innovative data analysis techniques provide a ∑ measurement that is corrected for borehole and diffusion effects, without prior knowledge of borehole salinity.

Baker Hughes

RESERVOIR PERFORMANCE MONITOR (RPM)

TIER 1

INDUSTRY-BEST STANDARD ENVIRONMENT SPECIFICATIONS

RPM TOOL SPECIFICATIONS		
Temperature (standard)	350°F	177°C
Temperature (NautilusSM service)	Up to 500°F	260°C
Pressure (standard)	20,000 psi	138 MPa
Pressure (Nautilus service)	25,000 psi	172 MPa
Tool OD	1.69 in	42.9 mm
Length (without telemetry)	18.6 ft	5.7 m
Weight	75 lb	34 kg
Minimum restriction	1.80 in	45.7 mm
Maximum hole size	12.25 in	311.2 mm
Tool compressive strength	570 lb	259 kg
Tool tensile strength	22,000 lb	9,979 kg
Depth of investigation	12 in	305 mm
Maximum bend rate	30°/100 ft	30°/30.5 m

OUR EXPERIENCE AT YOUR SERVICE

Expert support at the wellsite and from the Baker Hughes GEOScience Center provide the foundation for superior reservoir surveillance solutions.

Since inception, Tier 1 has provided cased-hole logging services. When required, we work with technology leaders that provide specific logging solutions. The RPM from Baker Hughes is an example of how Tier 1 will provide the best in service quality while deploying logging equipment supported by the experts of the technology.

Baker Hughes

APPENDIX D-IX

VSP Feasibility Study

U Frio VSP Feasibility Study

Scope of Work

Baker Hughes was contracted to assist Gulf Coast Sequestration in evaluating which seismic technique would be optimal for indirect monitoring of a CO_2 plume in the upper Frio Formation within the Minerva south project. All information in this document is based on the reservoir information provided by Gulf Coast Sequestration.

The study's first objective was to determine if appreciable changes in seismic signals would occur from fluid replacement (CO_2 replacing water via injection). When appreciable changes do not occur, false positives (and/or false negatives) obscure seismic methods from interpretating plume geometry. With the information available today, this study suggests that there is high confidence that sufficient changes in the seismic signature will be present within the upper Frio Formation to track the CO_2 plume via VSP and also via other seismic methods. Since appreciable changes were found, the study took on a second objective and investigated what would be the optimal seismic method. The acquisition geometry was optimized for a VSP. The optimal VSP geometry was constrained by a combination of cost, confidence in the 4D response, and size of monitored area. The findings of this optimal VSP acquisition were then placed into the context of other seismic methods and a cost analysis was made between 3D VSP and other seismic methods (2D surface seismic simultaneous with 2D walkaway VSP, 3D surface seismic (high definition), and other new surface monitoring technologies.

Seismic Rock Physics

Rock physics allows us to predict attributes, such as velocity or density from physical properties such as porosity, fluid saturation, and mineralogy (sand, clay, etc.). Our aim within this study was to construct a Rock Physics model to predict how density and velocity will change as fluid changes from water to supercritical CO_2. Figure 1 demonstrates how dry mineral components and porosity were prepared for use in the Xu-White method. This option is used to derive Vp, Vs and Rho using the Xu and White (1995) clay-sand mixture model and the Kuster and Toksoz (1974) differential effective medium (DEM) equations (Keys and Xu, 2002).

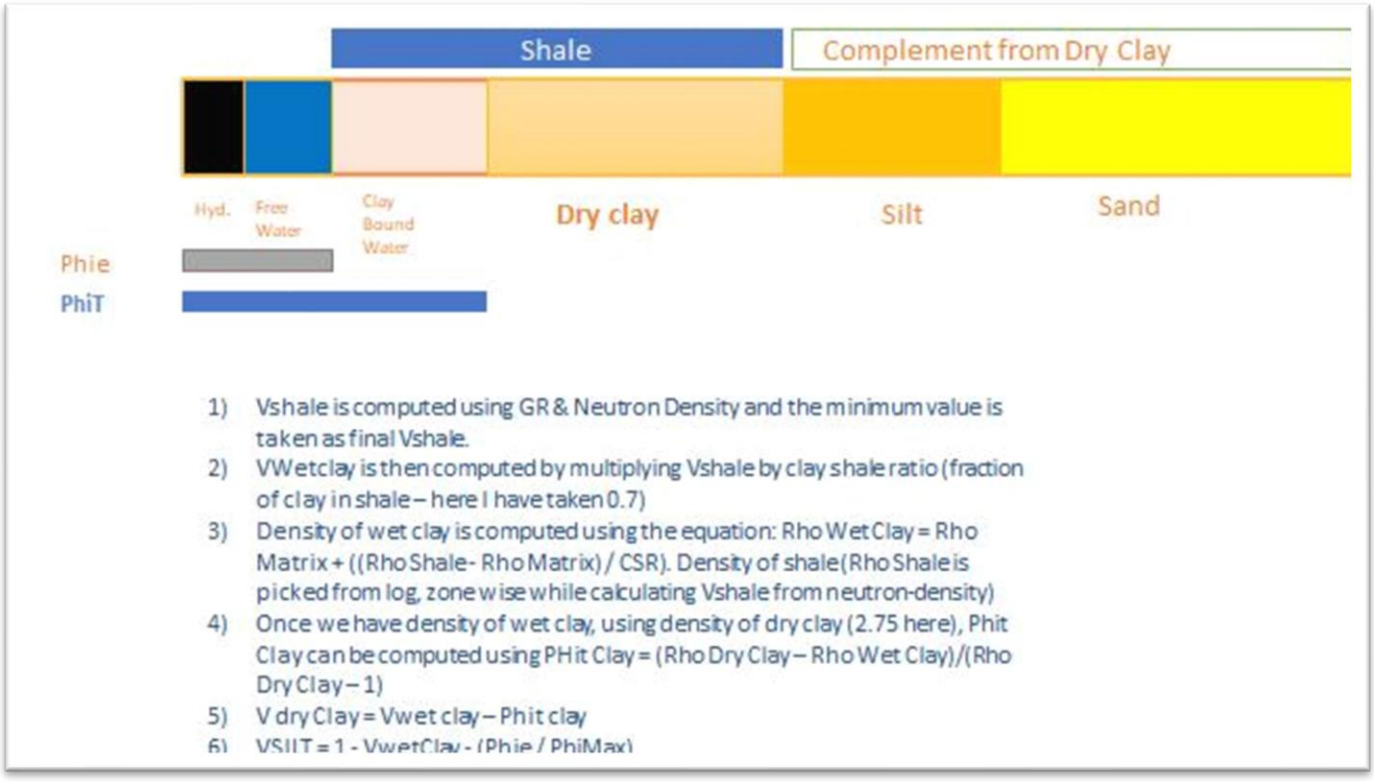


Figure. 1 Rock Physics Model

The Xu-White method allowed us to predict an S-wave velocity, a P-wave, and density using a table of dry minerals properties. As input to this method, total porosity, saturation, and dry clays are necessary. The predicted curves are compared to the measured (p-sonic and density) and table or log analysis are modified until a good match between measured and modeled responses are achieved.

Using the provided log analysis, S-wave and Poisson's ratio were estimated as in-situ. Fluid replacement modelling was carried out using the results as input and 100% water as output. This was done for all the wells; the results below are shown for one well. For the fluid replacement model, CO_2 using 80% was modeled to evaluate the changes in acoustic impedance.

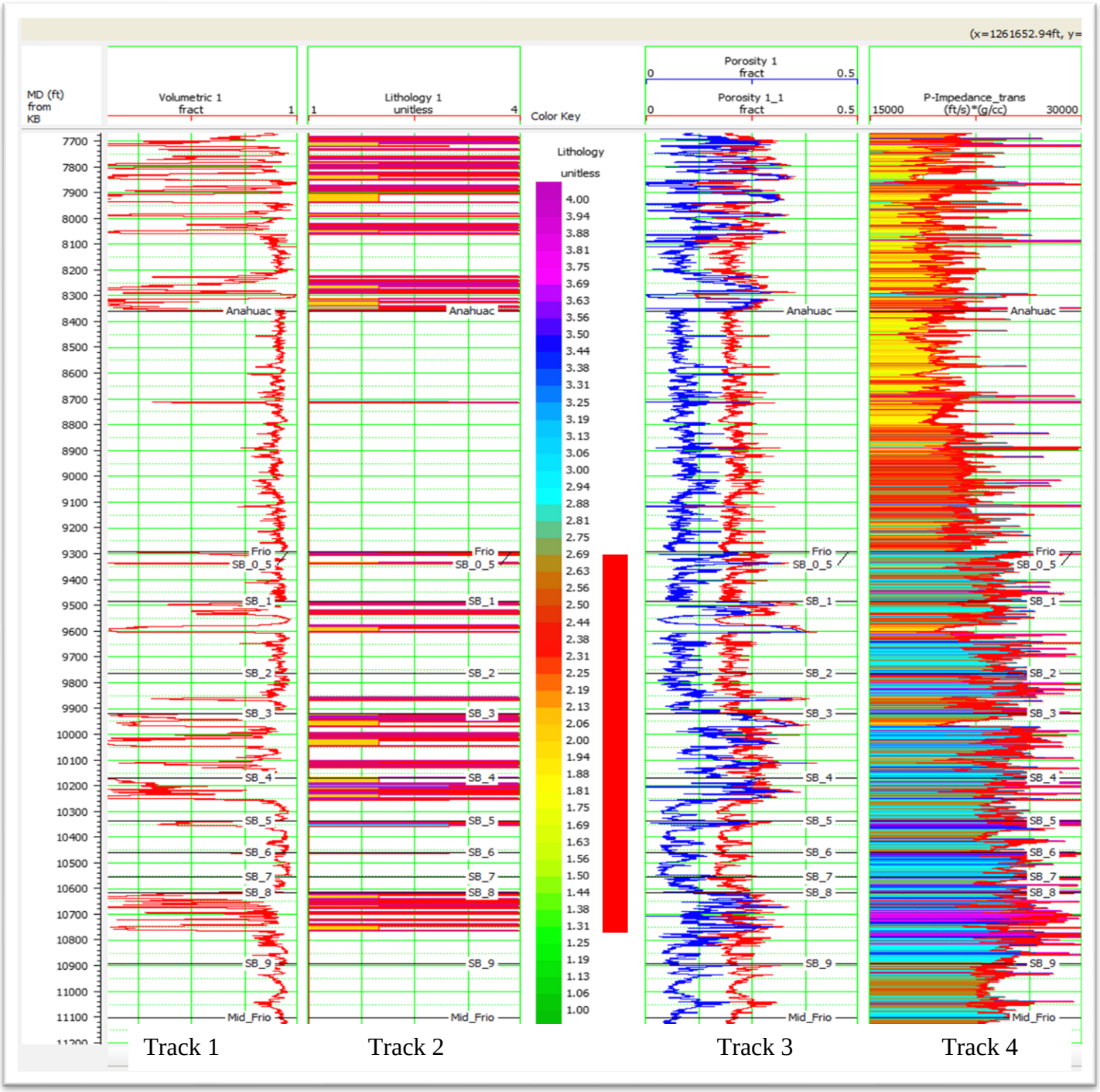


Figure 2. Input curves, supplied by the client and used in rock physics.

The fluid replacement results (Figures 3) confirm that the presence of CO_2 (80%) will change the acoustic impedance on average 15% - track 4- (5% is the noise level detectability in seismic).

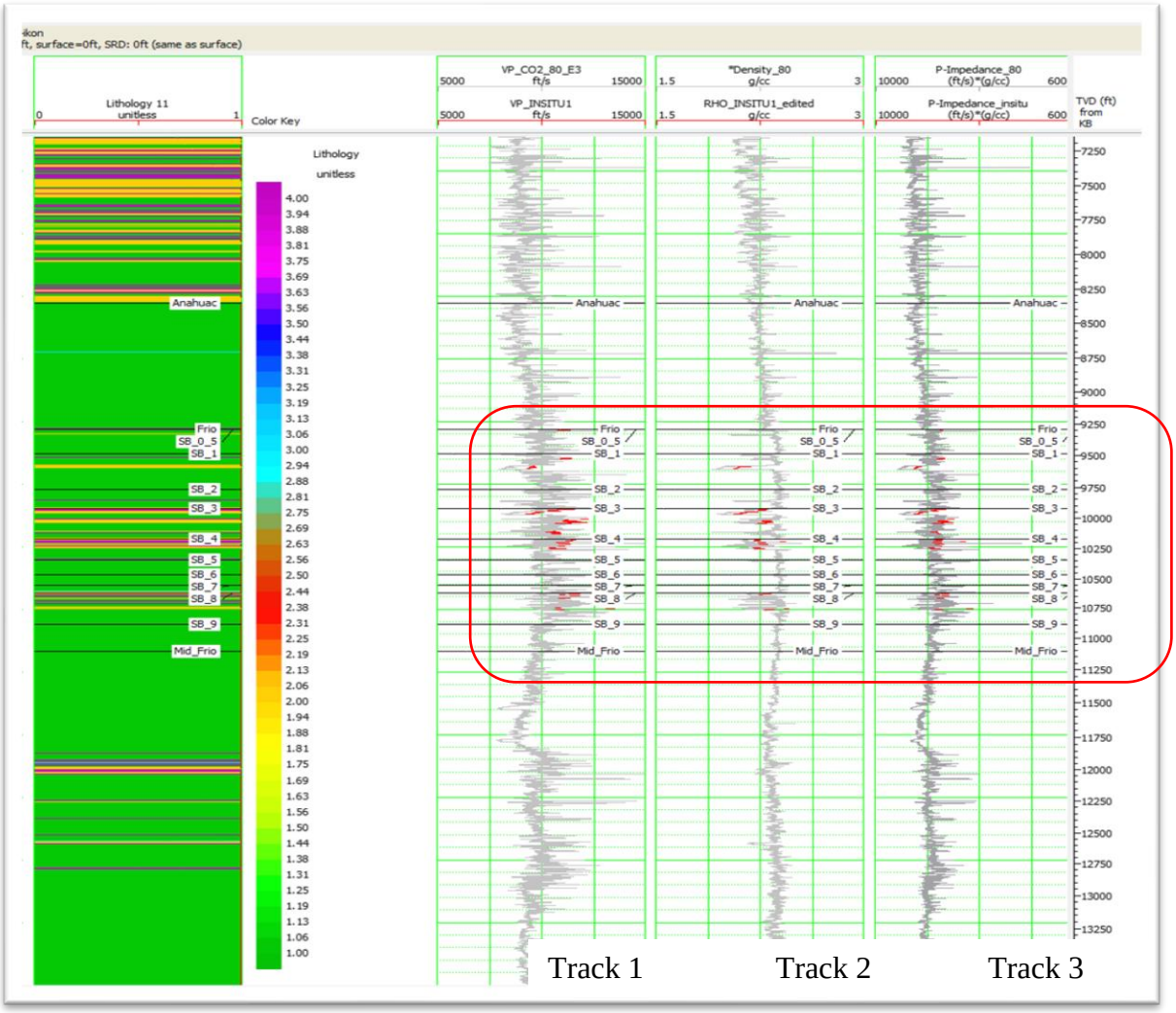


Figure 3: Shows the P-wave (Track 1), density (Track 2), and impedance (Track 3) before and after the fluid substitution. Note where the changes are happening in red shading.

Amplitude versus offset synthetic models were then generated to illustrate these changes (Figure 4), without loss and with loss of energy., Both results indicated that seismic changes are observed with the presence C. Track 1 is the volume of quartz and Track 2 is the lithology facies: red is Quartz. Track 3 is total porosity (red) and effective porosity (blue). Track 4 shows impedance. The red bar indicates the possible injection zones.

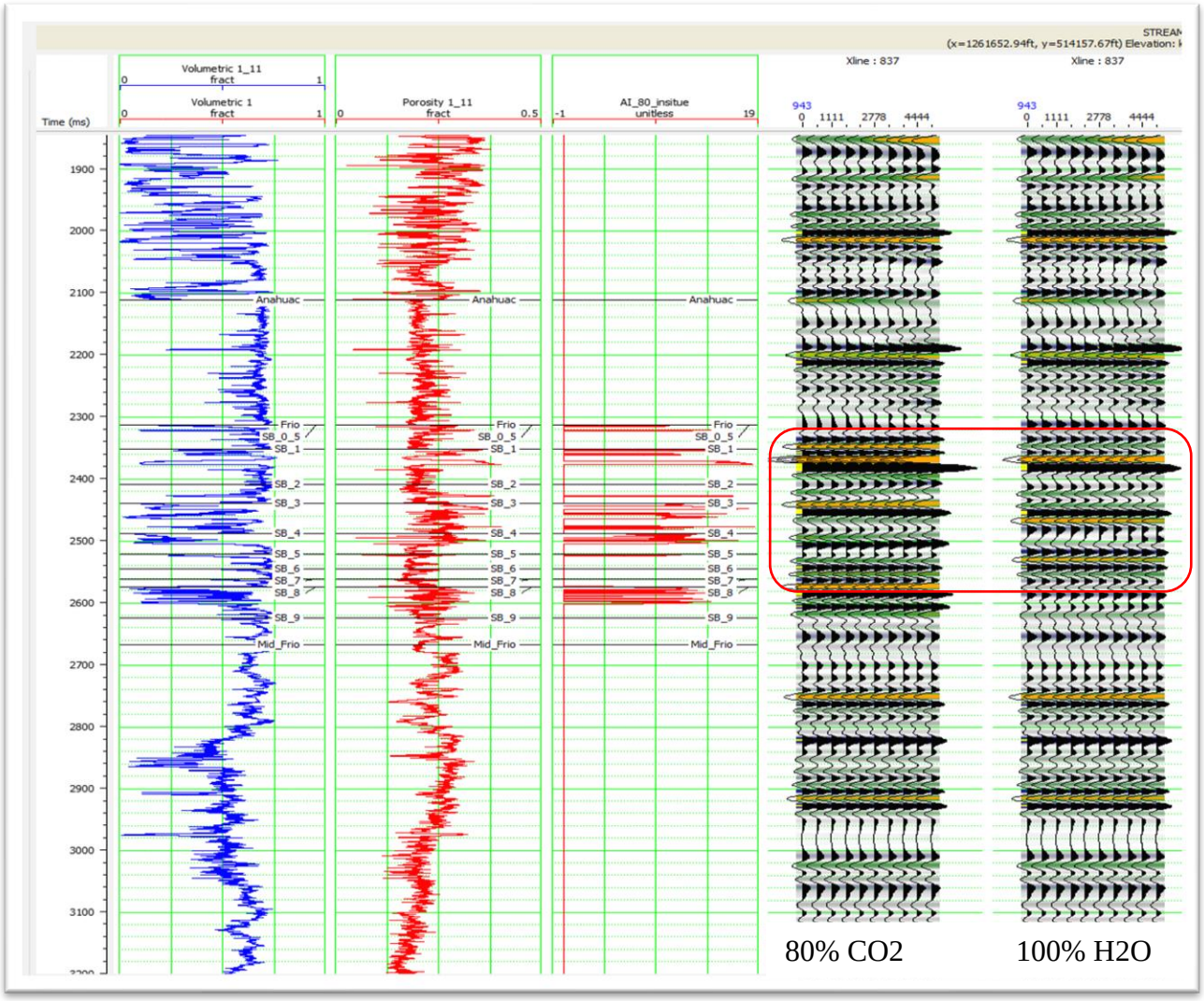


Figure 4. Synthetic AVO Model - results from the fluid substitution 80% CO_2 and 100% H_2O. Note the changes in amplitudes caused by the CO_2.

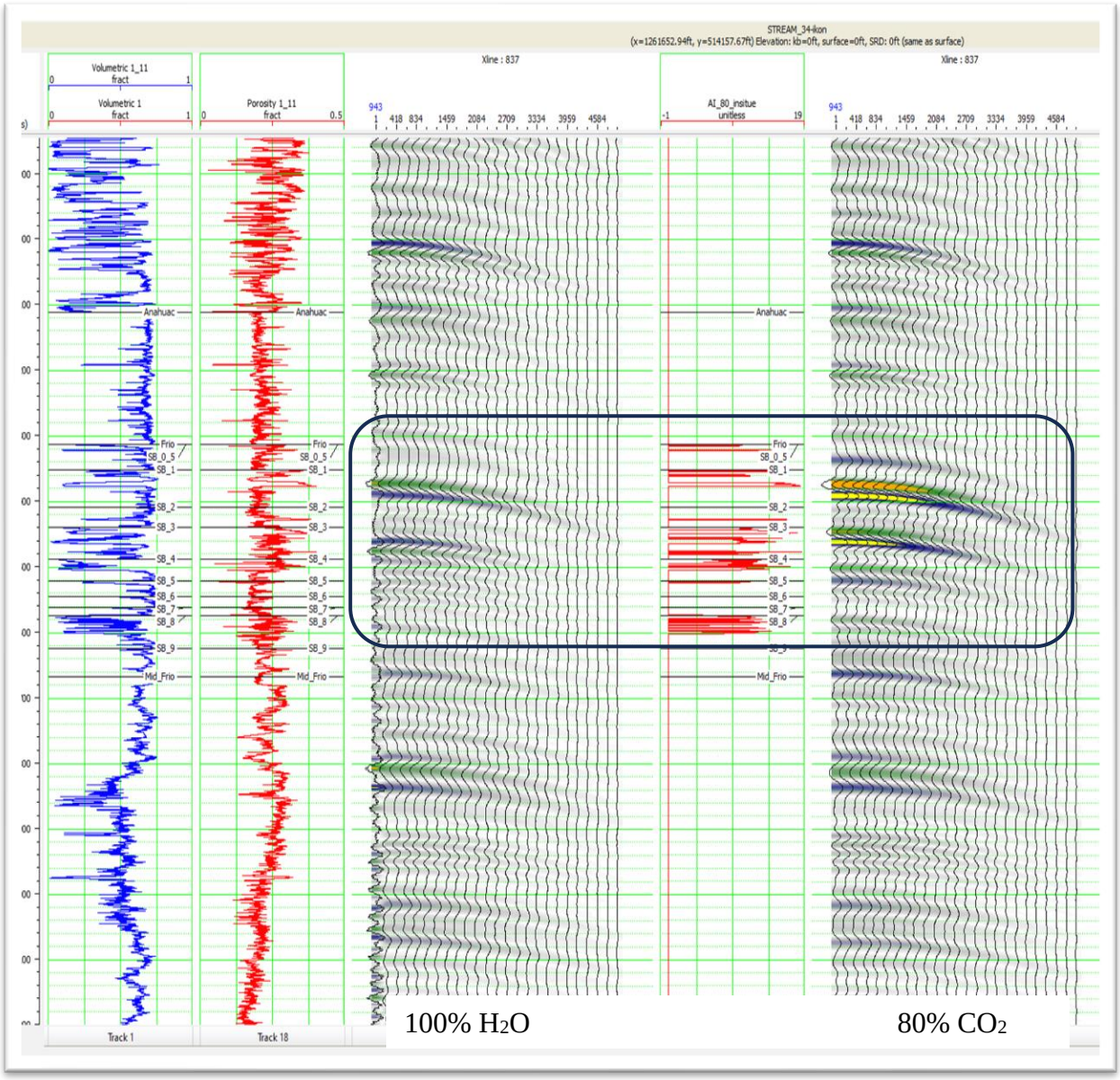


Figure 5. Shows the bright spot cause by CO_2, confirming that the seismic methods will work.

ILLUMINATION 3D VSP FOR MONITORING

Model Building

A 3D P-wave velocity model was build using horizons supplied by the client and the Streamer-34 well (Figure 6).

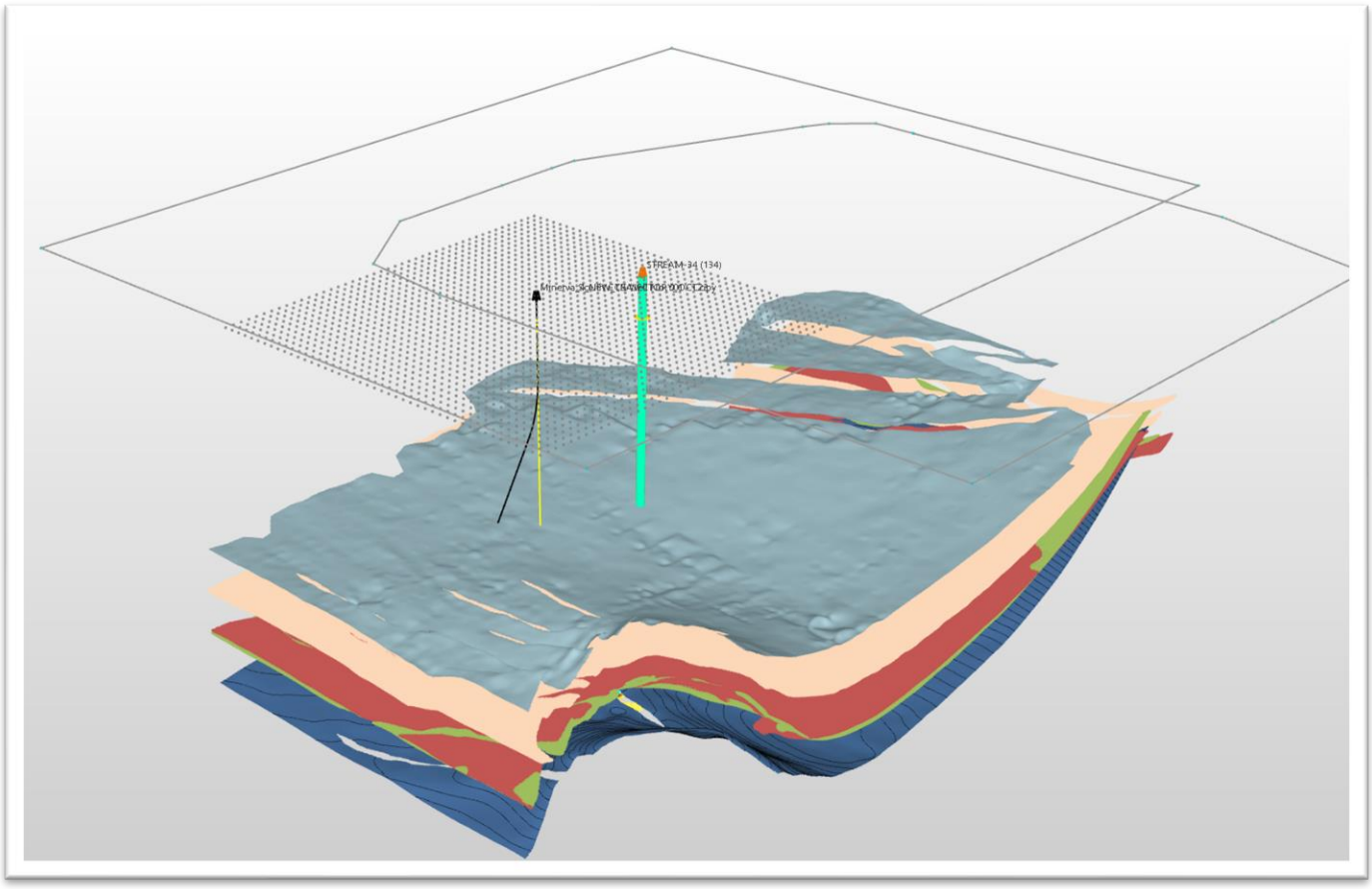


Figure 6- Main horizons for the upper Frio Formation used to build the velocity field. Calibrated well is in green (MS CCS 1).

3D VSP Illumination

Using the proposed well location MS CCS-1 (vertical) and a monitored DAS interval from 500-9,500 ft, an illumination exercise using ray tracing to Mid Frio was ran. The illumination fold is demonstrated for a given acquisition geometry as a Blue-Green-Yellow–Orange-Red surface (Figure 7). This illumination fold counts how many seismic rays impinge upon the upper Frio Formation layer from the set of sources and the set of receivers in the DAS fiber. The higher the fold, the more measurements we have in a particular area and the greater confidence there is in the measurement.

The extent of the upper Frio surface illumination is smaller than the footprint of the receivers. This is due to the critical ray path constraining the distance between the injector well and the plume. Now that the aerial extent of the image is known, we can understand whether this covers the AoR. Given what we understand about the evolution of the plume, this illumination exercise suggests that the usability of the 3D VSP is limited to approximately 10-years for this acquisition geometry. The maximum illumination of the surface using 3D VSP does not allow to extend beyond the 10-years for monitoring purposes of the plume extension. Therefore, after 10-years, the monitoring program will need to be replaced with 2D lines and Walk-Away VSPs. Appreciable changes in source footprint will not substantially improve the overall utility of VSP beyond this 10-year timeframe. Afterwards, conventional 2D lines combined with Walk-Away VSPs will be used to monitor further the changes.

Two extra locations for monitoring were also modeled, but the areas selected cannot be used due to the current surface conditions. As a results, additional seismic techniques have been proposed.

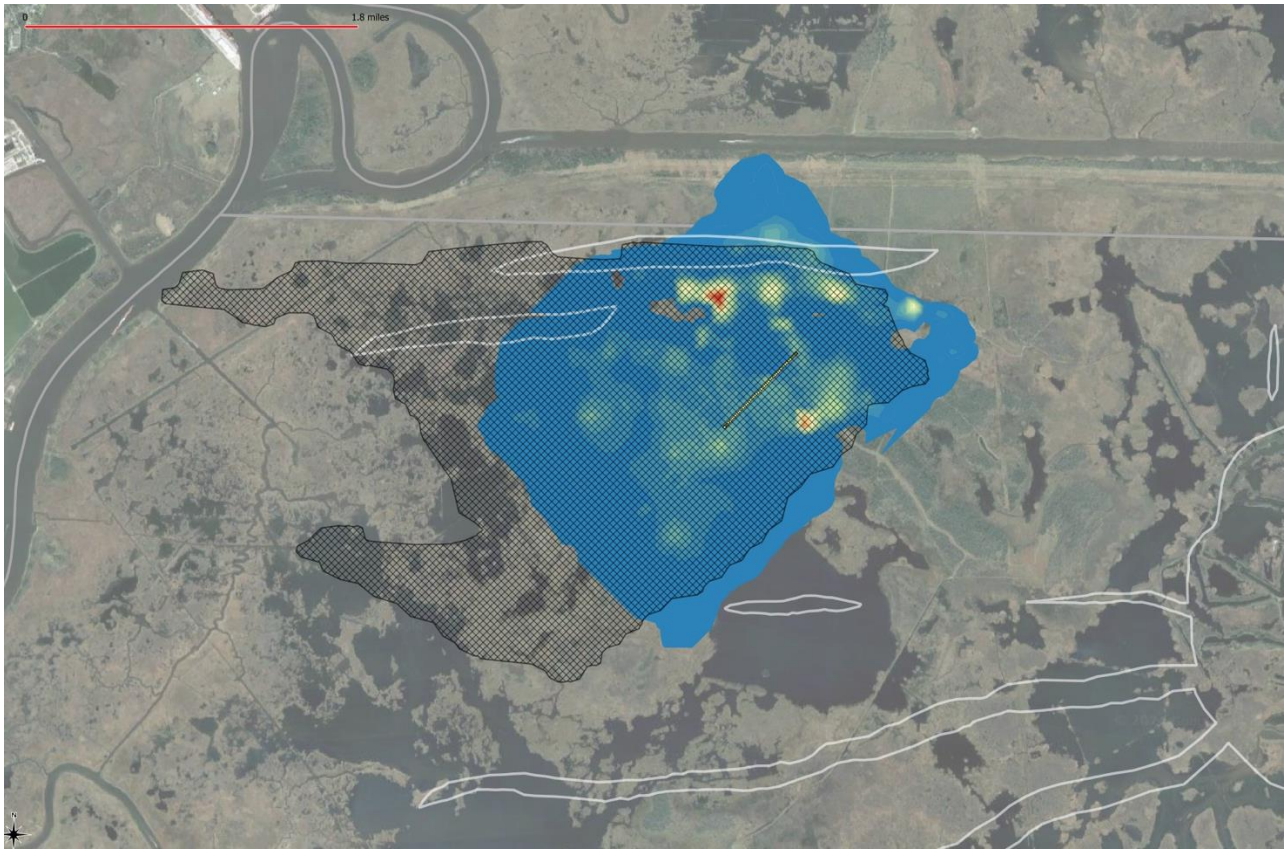


Figure 7. 3D illumination fold is shown in the contour colors– Note: after 10 years another seismic method needs to be used. Dash plume correspond to 75 years.

2D Seismic Illumination

A 2D line was extracted from the existent 3D volume and the center part was replaced with the CO_2 responses (Figure 7.)

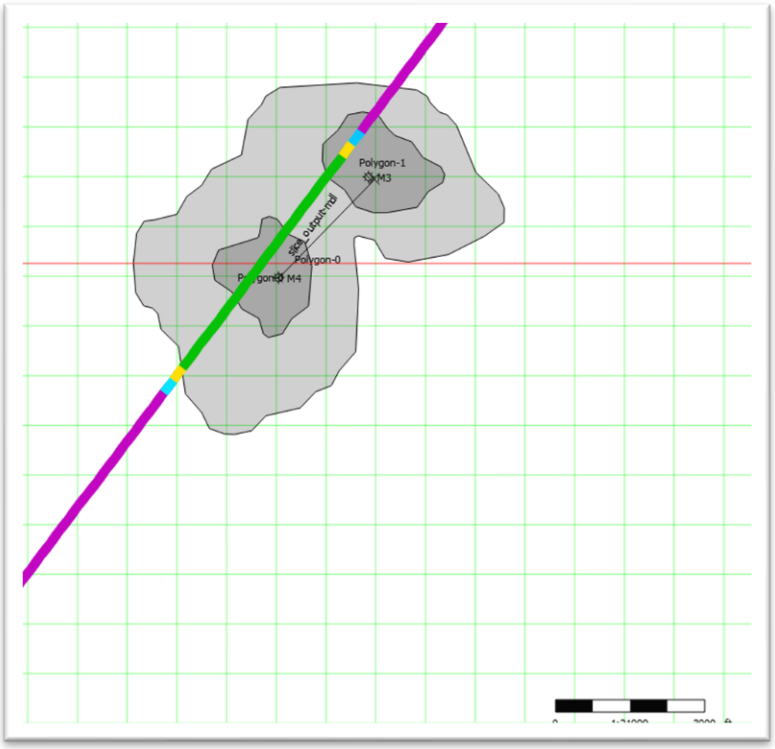


Figure 8. 2D Line extracted from the 3D volume.

Using an acoustic model (P-wave and density, Figure 8.); a normal Incident model was generated with two different frequencies. Note that a 4D effect is observed (Figure 9),.

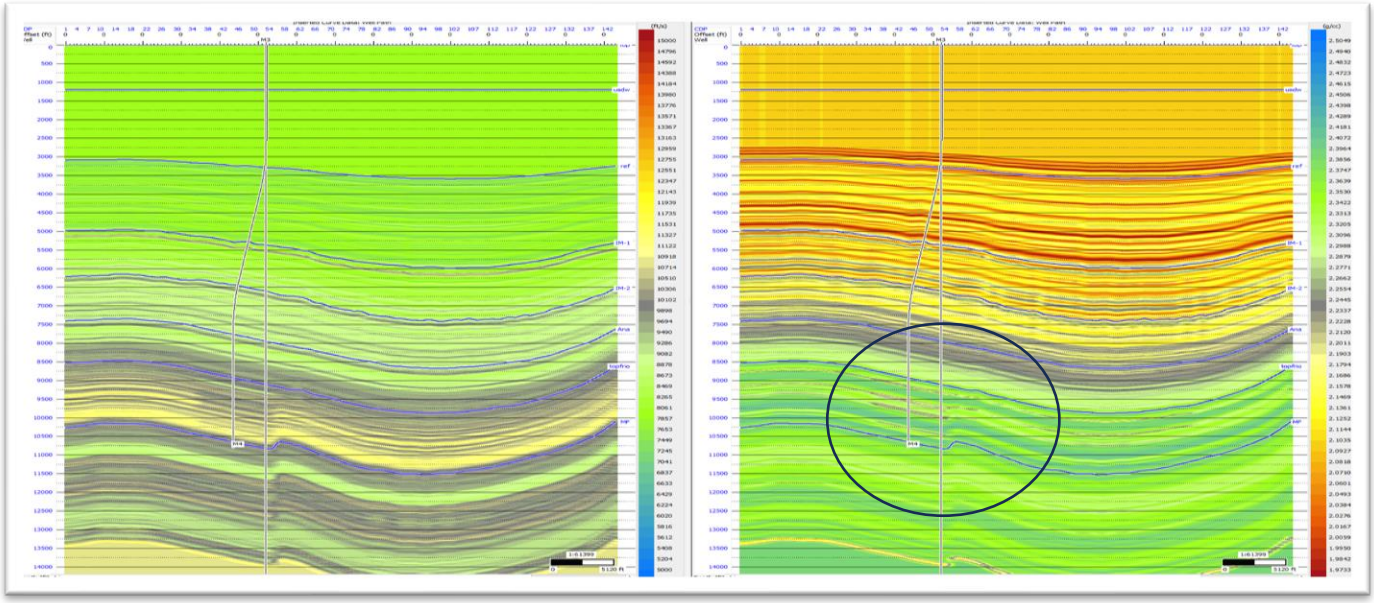


Figure 9. P-wave and Density model used for the Acoustic Model. Injection zone highlighted within the circle.

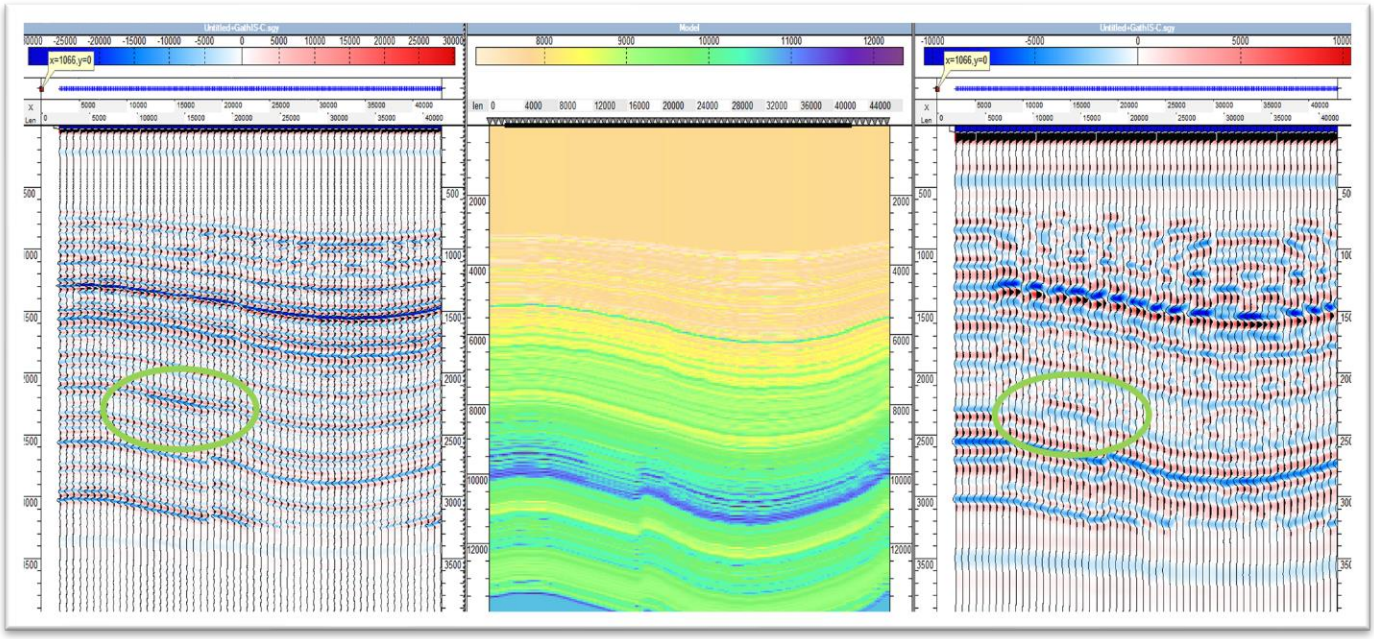


Figure 10. Normal Incident synthetic generated to simulate 2D Seismic line acquisition. The 4D effect is highlighted in the green circle.

Conclusions

1. With the expected plume migration and the reservoir properties provided from the upper Frio Formation, seismic methods can be used to track the CO_2 plume.

2. The injection well can be used to monitor the plume using a 3D VSP with an approximate coverage of no more than 10-years (based on the forecast plume model).

3. 2D conventional seismic methods will work in the area as an alternative method to monitor the plume after year 10.

4. Baseline acquisition of at least the 2 seismic methods listed below is required before the injection starts:

    1. 3D VSP Study (Figurer 10)
    2. 2D surface seismic simultaneous with 2D walkaway VSP (Figure 11)

The costs illustrated below on each acquisition method are preliminary and do not include the cost to lay the receivers, permits, etc. The cost is a guide to illustrate the differences between each method.

3D VSP Survey

Pro: 3D Image, higher vertical resolution.

Cons: Useful for only 10-years of monitoring (from the forecast plume area).

Frequency: Base Line, 5 years, 10 years or at any time that changes do not agree with the prediction triggered/measured by the Walk-Away VSPs.

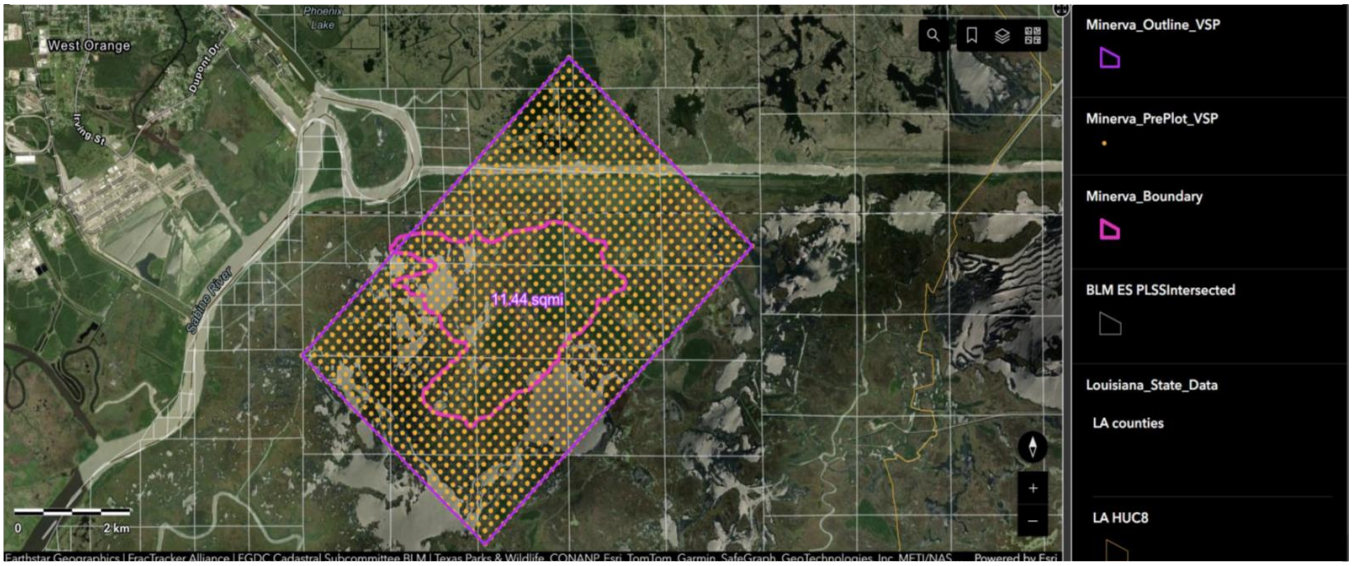


Figure 11. The is 3D VSP shooting in yellow. Pink is the estimated plume size for 10 years. And 11.44 square kilometer area, with sources planned on a 500' x 500' grid with recommended 5.5 lbs pentolite charge loaded 100' deep. With this source only grid, 1,350 source points would be recorded as VSP. The datasets may be used for 3D monitoring in the future. As such, the design and acquisition of the survey must account for repeatability.

2D Surface Seismic Simultaneous with 2D Walkaway VSP

Pros: 2D Image, higher vertical resolution, monitor lifetime of the project; pseudo 3D image can be generated.

Cons: 2D image along the lines - could be mitigated by generating pseudo 3D's

Frequency: Baseline (year 0), every 12 months the WalkAway VSP will be shot and will determine if more detailed monitor information is needed after the model has been calibrated. The more detailed image will come from the 3D VSP. After

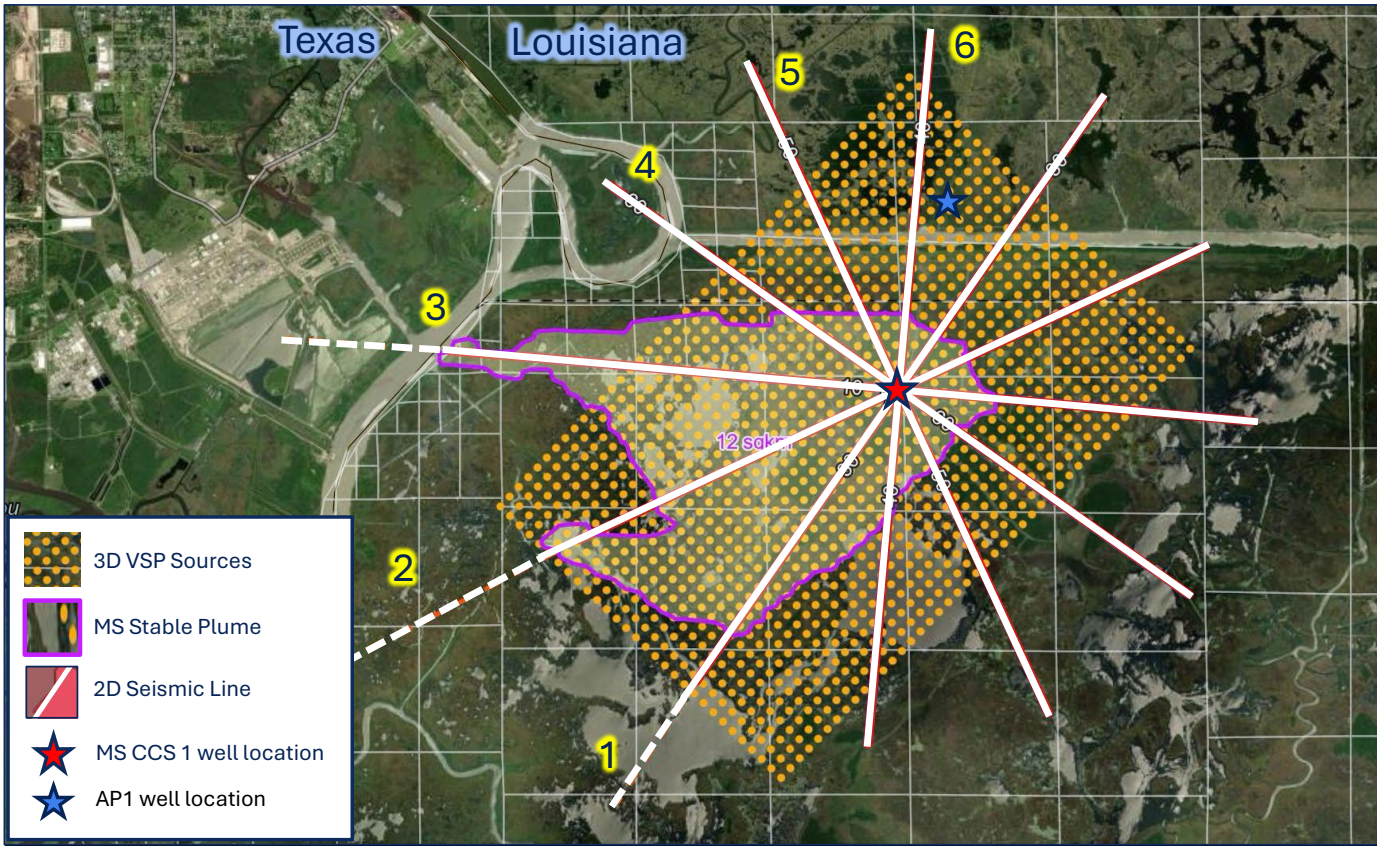


Figure 11: 2D lines program to monitor the plume migration to be acquired simultaneous with VSPs. The 2D star pattern cannot use the same sources as the 3D VSP, as those are sparse and not in line with the receivers, therefore, the 2D lines need its own sources. The star pattern 2D sources and receivers are ONLY along the 2D lines. It is suggested a 27.5' receiver interval and a 55' source interval, which results in ~2,979 source points. The idea here is that the source points will be recorded both by surface sensors that we deploy, and by the downhole receivers that Baker Hughes deploys. The star pattern is achieved by placing 6 walkaway lines, centered on the well, each rotated 30 degrees. VSP data would be acquired using fiber optic cable cemented behind casing in a vertical well. The source point type and the source point interval were not specified, the acquisition company recommends scoping in advance of any testing.

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APPENDIX D-X

Rock Physics, 4D Inversion Feasibility, and 3D Seismic Inversion Study

Minerva Project

Geographic Location: Cameron & Calcasieu, Louisiana

Project Type: Rock Physics, 4D Inversion Feasibility, and 3D Seismic Inversion

Confidential

Technical Report

Client: Gulf Coast Sequestration, LLC
Contract number: OPP-0005403
Date: August 23, 2024
Prepared by: Adriana Pereira, Ikon Science Americas

Reviewed and approved by: Jeremy Gallop, Ikon Science Americas

Ikon SCIENCE

Executive Summary

Gulf Coast Sequestration, LLC (GCS) will build and operate the country's premiere geologic sequestration asset to capture carbon dioxide (CO_2) and safely contain it underground at their Minerva project in Louisiana.

Ikon Science provided Quantitative Interpretation services to allow GCS to have a better understanding of the elastic changes in the subsurface study that can be expected during sequestration, specifically focused on properly monitor the CO_2 plume. In addition, Ikon has provided baseline 3D characterization of the Minerva project area to assist with delineation of the sandstone units.

Ikon Science's technical workflow included petrophysics review, rock physics and seismic modeling, which correspond, respectively, to the 1st, 2nd and 3rd phases of the project.

This report covered the following phases related to the baseline 3D characterization:
Phase 1: Seismic data review and qc, in which three seismic surveys were evaluated.
Phase 6: Seismic data conditioning. seismic to well-ties
Phase 7: Seismic inversion
Phase 8: Reservoir characterization

In Phase1, legacy 3D seismic datasets were analyzed for quality and consistency. Two surveys in the north were reviewed, the Big Island 3D and Alligator Cove Merge 3D. In the south the Black Bayou 3D was reviewed. All surveys contained post-stack processed data, while the Alligator Cove Merge survey also had pre-stack seismic data available.

In Phase 6, seismic data conditioning (SDC) was carried out to the partial angle stacks of Alligator survey. Comparison of the seismic traces before and after SDC showed clear improvement in terms of SNR and lateral continuity of seismic traces. For Black the Bayou survey, data conditioning was applied to the post-stack dataset. Seismic to well ties were carried out for the wells that were part of the Rock Physics Study, as well as for two wells that are in the southern portion of the Black Bayou survey: Gray Matilda-2, Texaco_E_and_P_Etal-3.

Post-stack seismic inversion was subsequently carried out on the Black Bayou survey, which provided the greatest coverage of the sequestration area. Ji-FI (Joint Impedance and Facies Inversion) provided an estimate of the most the most likely facies (sand and shale) from the seismic data, along with the corresponding acoustic impedance. The acoustic impedance volume has a reasonable match with the acoustic logs (AI) for the well Stream-34. A subset of the sandstones at the well were matched by inverted seismic facies. The correlation of well and seismic facies was limited by both seismic resolution and the small difference in the acoustic impedance of sandstones and shales at some depths. There was a fair match with the Texaco_E_and_P_Etal-3 well to the south of the sequestration area.

High amplitude reflections in the post-stack data correlate with some extensive sand bodies from the inversion results extending to the south from the sequestration area. These do not correlate with well control in the south (well Gray Matilda-2) and are considered unlikely to be present in the subsurface. Future characterization with additional wells and/or pre-stack data would provide more constraint on these features.

In the Phase 7, the Ji-Fi inversion acoustic Impedance (AI) was used to create 3D cubes of total porosity (PHIT) and effective porosity (PHIE). To generate reservoir property volumes, total porosity (PHIT) and effective porosity (PHIE) were estimated by a linear transform calibrated using the well log data. Results showed a reasonable match in the north in the main study area for sand bodies that had been correctly classified by the seismic inversion. These volumes can be used assist in the assessment of sand body extent and porosity in the study area.

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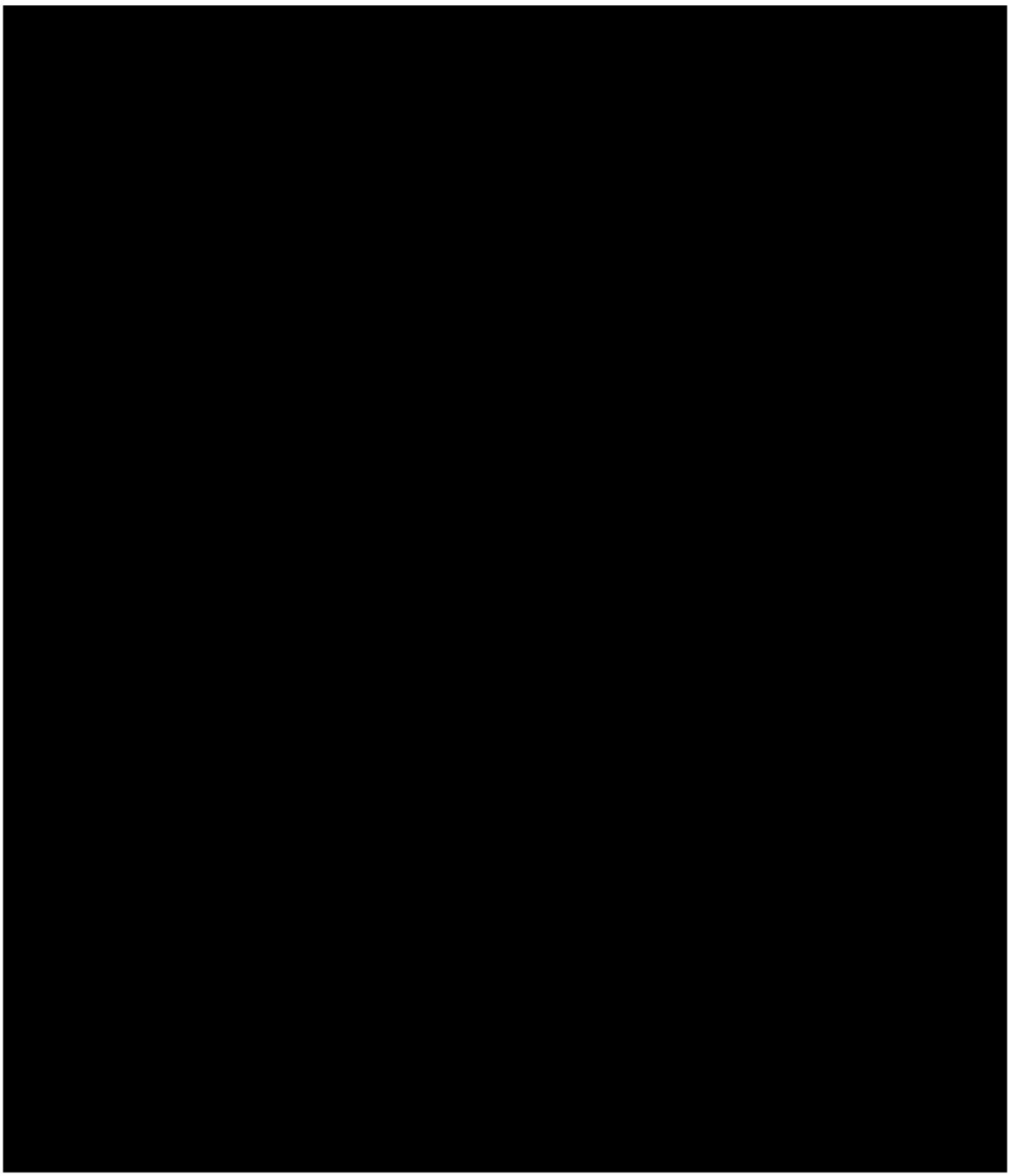
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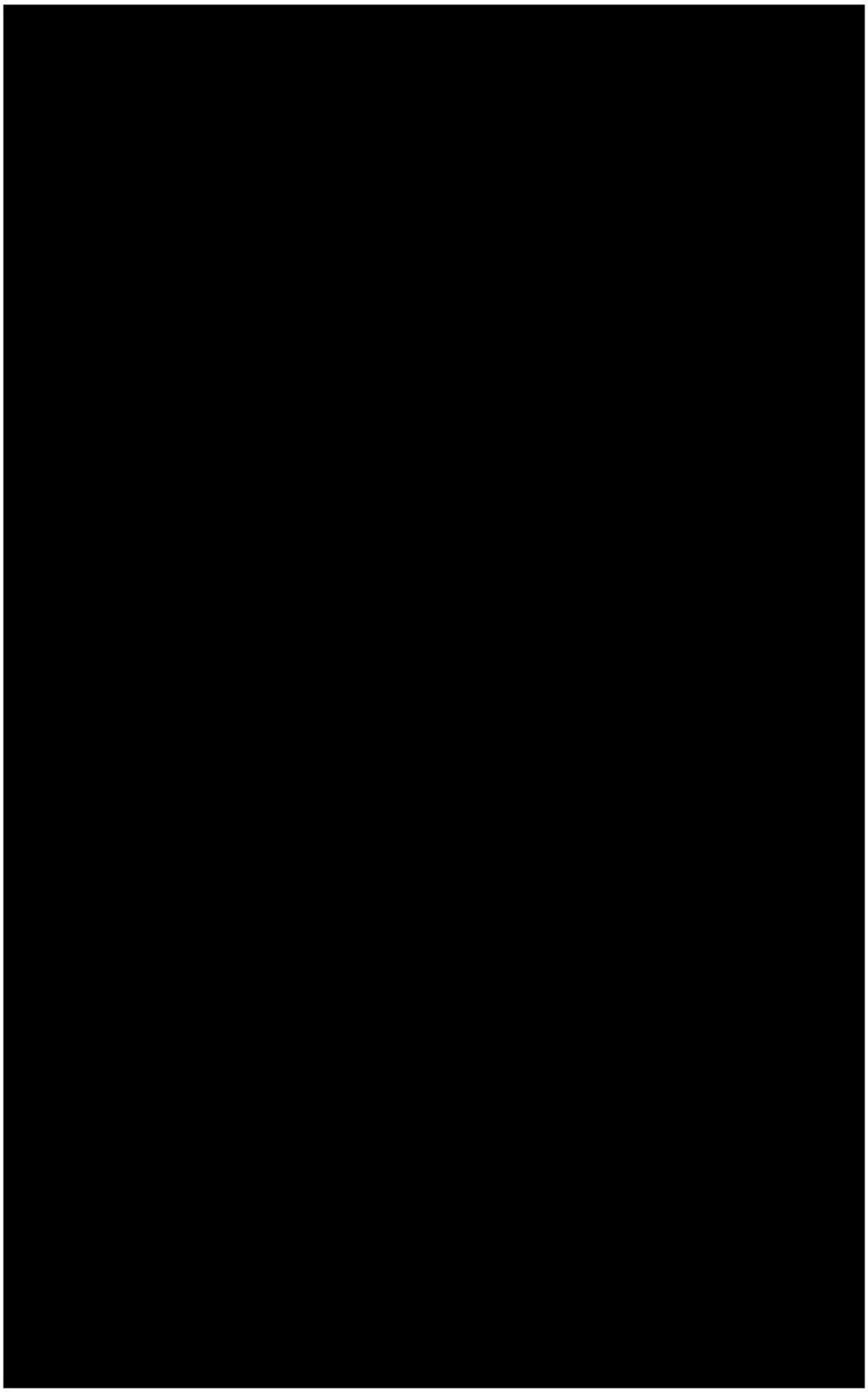
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Table D.I.2-1 QASP Distribution List

Title	Name	Phone	Email	Address
Chief Executive Officer	David Cook	1 (713) 419-6808	dcook@gcscarbon.com	5599 San Felipe Dr., Suite 1450 Houston, Texas 77056
Field Manager	David Richard			2417 Shell Beach Dr. Lake Charles, LA 70601
Site Manager	TBD	TBD	TBD	2417 Shell Beach Dr. Lake Charles, LA 70601
24-7 Control Room Operations	TBD	TBD	TBD	5599 San Felipe Dr., Suite 1450 Houston, Texas 77056
Safety Manager	MaryEllen Roberson	1 (713) 997-3296	mroberson@gcscarbon.com	5599 San Felipe Dr., Suite 1450 Houston, Texas 77056
Audit/Risk Manager	TBD	TBD	TBD	5599 San Felipe Dr., Suite 1450 Houston, Texas 77056

Table D.I.5.1-1 Summary of Testing and Monitoring

Activity	Location(s)	Method	Analytical Technique	Lab/ Custody	Purpose
CO_2 STREAM MONITORING					
Carbon Dioxide Stream Analysis	Comingled inlet pipework to Minerva facility	Sampling Port	Standard gas analysis at lab	Provided by lab	Monitor injectate for accounting
INJECTION AND INTEGRITY MONITORING					
Injection Pressure	Distributed meters at MS CCS 1 & 2	Electronic volumetric flow meter with P/T measurement	Direct measurement	NA	Pressure of CO2 stream
Injection Rate	Distributed meters at MS CCS 1 & 2	Electronic volumetric flow meter with P/T measurement	Direct measurement	N/A	Rate of injection
Injection Volume/Mass	Distributed meters at MS CCS 1 & 2	Electronic volumetric flow meter with pressure & temperature (P/T) measurement	Volume measurements	NA	Volume of CO2 distributed to each well; calculation of mass
Annular Pressure/Temperature	Downhole gauge with transmitter at each wellhead	Electronic P/T gauge in the annulus	Direct measurement	NA	Pressure maintenance in tubing-casing annulus
Annular Volume	Downhole gauge with transmitter at each wellhead	Electronic P/T gauge in the annulus	Calculated measurement	NA	Pressure maintenance in tubing-casing annulus
Downhole Pressure/ Temperature	Downhole gauge with transmitter at each wellhead of MS CCS 1 & 2, MS IZ 1	Downhole P/T gauge run on tubing	Direct measurement	NA	P/T downhole near injection zone
Wellhead Pressure	Pressure gauge on the tubing and annulus of MS CCS 1 & 2, MS IZ 1	Surface pressure gauge at the wellhead	Direct measurement	NA	Wellhead pressure safety
External Mechanical Integrity	MS CCS 1 & 2	DTS fiber optic cables installed in the wellbore annulus	Direct Continuous monitoring	NA	Detect fluid or pressure migration from the injection zone and leakage in casing
Wireline Logging	Conducted at each injection well	Injection profile log	Provided by vendor	NA	Demonstrate External Mechanical Integrity
Corrosion Monitoring	Corrosion Loop	Non-Destructive Testing: Ultrasonic and Radiography equipment	ASTM G1-03	NA	Monitor system integrity
SUBSURFACE MONITORING					
Above Confining Zone Monitoring	MS USDW 1 & 2	Water sampling	Laboratory analysis	Provided by lab	Document groundwater chemistry
	MS CCS 1 & 2	DTS fiber optic cables installed along the long-string	Direct measurement	NA	Monitor for fluid migration from the injection zone
Pressure Fall-Off Testing	MS CCS 1 & 2	EPA Region 6 UIC Pressure Falloff Testing Guideline-Third Revision (August 8, 2002)	Direct Measurement	NA	Assess injectivity
Pressure Front Tracking (Direct)	MS IZ 1, MS CCS 1 & 2	Downhole P/T gauge run on tubing	Direct measurement	NA	In-zone pressure tracking
CO_2 Plume Tracking (Indirect)	MS CCS 1	Walk Away VSP	VSP	NA	Defining the edge of the plume and ensuring it remains within the permitted AoR.
	MS CCS 1	Vertical seismic profile (VSP)	VSP	NA	
	MS CCS 1	2D Seismic Lines	2D Seismic	NA	
	MS IZ 1	PN logs	Wireline logging	NA	Monitor carbon dioxide saturation

Table D.I.6-1 Instrumentation Summary

Instrument Type	Monitoring Location	Monitoring Target	Data Collection Location(s)	Explanation
CO_2 STREAM MONITORING				
Sampling port	CO_2 Stream	Monitor injectate for accounting	Collection at sampling port; analysis via lab	Identify unacceptable impurities, CO_2 accounting
INJECTION AND INTEGRITY MONITORING				
Electronic volumetric flow meter with pressure & temperature (P/T) measurement	MS CCS 1 & 2	Monitor injectate for each well	Computerized control system	Injection volume, rate, and pressure (with mass and density calculations) for surveillance and input to models
Wellhead pressure gauge on tubing	MS CCS 1 & 2, MS IZ 1	Pressure in injection well tubing	Manual reading of gauge	Safety and compliance
Wellhead pressure gauge on annulus	MS CCS 1 & 2, MS IZ 1	Pressure in annulus	Manual reading of gauge	Safety and compliance
Annulus pressure & temperature gauge	MS CCS 1 & 2	Pressure and temperature in tubing-casing annulus	Computerized control system	Monitoring, safety, and compliance
Downhole pressure & temperature gauge	MS CCS 1 & 2	Pressure and temperature in injection interval	Computerized control system	Monitoring, safety, and compliance
DTS fiber optic cable	MS CCS 1 & 2	Surface to Total Depth	Computerized control system	Well integrity
Ultrasonic and Radiography equipment	MS CCS 1 & 2	Corrosion of materials of construction	Loop	Safety and compliance, Well Integrity
SUBSURFACE MONITORING				
Dedicated pump & groundwater level monitoring system	MS USDW 1 & 2	Evangeline Aquifer	Environmental data storage	Installed system or relocated to each of the wells
Downhole pressure & temperature gauge	MS IZ 1	Injection Zone – Pressure	Computerized control system	Track lateral pressure front
Pulse Neutron logging	MS IZ 1	Injection Zone - Plume	Wireline Log	Monitor carbon dioxide saturation within the injection zone
DAS fiber optic cable	MS CCS 1	Surface to Total Depth	Dedicated server, designed as part of VSP array	CO2 Plume Tracking
Walk-Away VSP	MS CCS 1	Injection Zone – Plume	DAS in MS CCS 1 Sources along seismic lines in star pattern	Define the edge of the plume and ensure it remains within the permitted AoR.
3D DAS VSP	MS CCS 1	Injection Zone - Plume	DAS in MS CCS 1 Sources along 500 x 500 foot Grid	Define the edge of the plume and ensure it remains within the permitted AoR.
2D Seismic Lines	Surface	Injection Zone - Plume	Sources and receivers along seismic lines in star pattern	Define the edge of the plume and ensure it remains within the permitted AoR.

Table D.I.6.1-1 Summary of Analytical Parameters for CO_2 Stream

Parameter	Analytical Methods[1]
Carbon Dioxide (CO_2)	ISBT[2] 2.0 Caustic absorption Zahm-Nagel ALI method SAM 4.1 subtraction method (GC/DID) GC/TCD
Water (H_2O)	ISBT 3.0
Oxygen (O_2)	ISBT 4.0 (GC/DID) GC/TCD
Nitrogen (N_2)	ISBT 4.0 (GC/DID) GC/TCD
Hydrogen Sulfide (H_2S)	ISBT 14.0 (GC/SCD)
Argon (Ar)	ISBT 4.0 (GC/DID) GC/TCD
Sulfur dioxide (SO_2)	ISBT 14.0 (GC/SCD)
Methane (CH_4)	ISBT 10.1 (GC/FID)
Total hydrocarbons (C_2H_6, C_3H_8+)	ISBT 10.1 (GC/FID)
Hydrogen (H_2)	ISBT 4.0 (GC/DID) GC/TCD
Carbon Monoxide (CO)	ISBT 5.0 (Colorimetric) ISBT 4.0(GC/DID)
Nitrogen Oxides (any (NO_x)	ISBT 7.0 Colorimetric
δC_{13} and C_{14}	Isotope ratio mass spectrometry Measured once and when a significant new source is added. Used for attribution during monitoring.

Note

[1] An equivalent method may be employed with the prior approval of the Commissioner

[2] International Society of Beverage Technologists (ISBT) Carbon Dioxide Guidelines MBAA TQ vol. 39, no. 1, 2002, pp. 32-35 as cited in ISO/TR 27921:2020(en). Carbon dioxide capture, transportation, and geological storage —Cross Cutting Issues —CO_2 stream composition

Table D.I.6.2-1 Summary of Operational Parameters Measured with Continuous Recording Devices

Parameter	Device(s)	Location
Annular Pressure and Temperature	Electronic pressure & temperature (P/T) gauge in the annulus with transmitter at the surface	Downhole gauge with transmitter at the wellhead
Annular Fluid Volume	Fluid level gauge	Annular Fluid Reservoir
	Electronic P/T gauge in the annulus with	Downhole gauge with transmitter at the wellhead
Injection Pressure	Electronic volumetric flow meter with pressure measurement	Meter with transmitter at wellhead
Injection Rate	Electronic volumetric flow meter with rate measurement	Meter with transmitter at wellhead
Injection Volume/Mass	Electronic volumetric flow meter with P/T measurement	Meter with transmitter at wellhead
Downhole Pressure	Downhole P/T gauge run on tubing	Downhole gauge with transmitter at the wellhead
Downhole Temperature	Downhole P/T gauge run on tubing	Downhole gauge with transmitter at the wellhead

Table D.I.6.2-2 Continuous Recording Device Specifications

Parameter	Value
VOLUMETRIC FLOW METER	
Calibrated working flow rate range	1 - 33 ft/s (0.3 -10 m/s)
Initial flow rate accuracy	< ± 0.15% of measured volume
Flow rate resolution	0.01 m/s
Flow rate zero stability	< 0.003 ft/s (0.0009 m/s)
DOWNHOLE PRESSURE AND TEMPERATURE GUAGE (Reservoir & Annulus)	
Calibrated working pressure range	200 - 10,000 psi
Pressure accuracy	±0.015% 1.5 psi (at full scale)
Pressure resolution	0.0001
Pressure drift stability	±0.02% full scale, 2.0 psi/year
Calibrated working temperature range	77 to 302°F (25 to 302°C)
Temperature accuracy	0.27°F (0.15°C)
Temperature resolution	0.0001°F
Temperature drift stability	0.018°F (<0.01°C) per year
Temperature rating	-99.4 to 302°F (-73 to 302°C)
Instrument calibration frequency	Annual
WELLHEAD PRESSURE GUAGE (Tubing & Annulus)	
Calibrated working pressure range	10-20,000 psi
Pressure accuracy	0.05% full scale accuracy
Pressure resolution	0.001
Pressure drift stability	Limit of 5% full scale for pressure stability

Table D.I.6.2-3 Representative Logging and Testing Tool Specifications

Fiber Optic Cable	Maximum acquisition rate	Minimum spatial resolution	Minimum sampling interval	Sensing /Operating temperature range	Maximum distance range
MECHANICAL INTEGRITY MONITORING					
Distributed Temperature Sensing (DTS)	3.3 sec	~3.3 ft (1.0 m)	1.08 ft (.33 m)	0 – 573°F/300°C	~12.5 mi (20+ km)
PLUME MONITORING					
Distributed Acoustic Sensing (DAS)	10 kHz	~4.9 ft (1.5 m)	1.08 ft (.33 m)	0°C to +40°C / 32°F to +104°F	12 – 50 (EBF) mi (20 – 80 (EBF) km)

Log	Logging speed	Vertical resolution	Investigation	Temperature rating	Pressure rating
MECHANICAL INTEGRITY LOGGING					
Noise Log	0.5 sec	16 bit	10 ms	350°F	20,000 psi
Oxygen Activation Log	2 ft/min	Point of Measurement	12 in	350°F	20,000 psi
Casing Inspection Log	160 ft/min	Point of Measurement	5.5-9.425 in	350°F	15,000 psi
Cement Bond Log	Up to 9 m/min (29.52 ft/min)	3 in	Casing & Cement Interface	350°F for 30 min	20,000 psi
Casing Collar Locator Log	45m/min	Point of Measurement	20 in	400°F for 30 min	20,000 psi
PLUME MONITORING					
Pulsed Neutron Capture Log	2 ft/min	Point of Measurement	12 in	350°F	20,000 psi

Table D.I.6.3-1 Groundwater Analysis Parameters and the Analytical Methods

Parameters	Analytical Methods[1]
FIELD MEASUREMENTS	
Dissolved Oxygen (field)	APHA 2005
Specific Conductance (field)	APHA 2510
Temperature (field)	Thermocouple
Water Density (field)	Oscillating body method
Static Water Level	Sounder
pH (field)	EPA 150.1
LABORATORY ANALYSIS	
Cations (Al, Ba, Mn, As, Cd, Cr, Cu, Pb, Sb, Se, Zn, Tl)	SW846 6010/6020
Cations (Ca, Fe, K, Mg, Na, Si)	SW846 6010/6020
Anions (Br, Cl, F, NO3, SO4)	SM 300
Dissolved CO_2	Coulometric titration, ASTM D513-11
Isotopes δ13C of DIC	Isotope ratio mass spectrometry
Dissolved CH_4 (Methane)	SM 6211 B or 6211 C
Hydrogen Sulfide (H_2S)	ISBT 14.0 (GC/SCD)
Total Dissolved Solids (TDS)	Gravimetry; Method 2540 C
Oxygen, Argon, and Hydrogen	ISBT 4.0 (GC/DID) GC/TCD
Alkalinity	Method 2320B

Notes:

[1] Or similar method

- The listed analytical methods may be revised based on input from the laboratories selected to do the work, and field instruments used during a given event.
- Field duplicates to be collected at rate of 10% (1 for every 10 samples) or 1 per event.
- MS/MSDs to be collected at a rate of 5% (1 for every 20 samples) or 1 per event.
- Field blanks and equipment blanks will be collected as per Section 6.3 of the QASP, Appendix I.

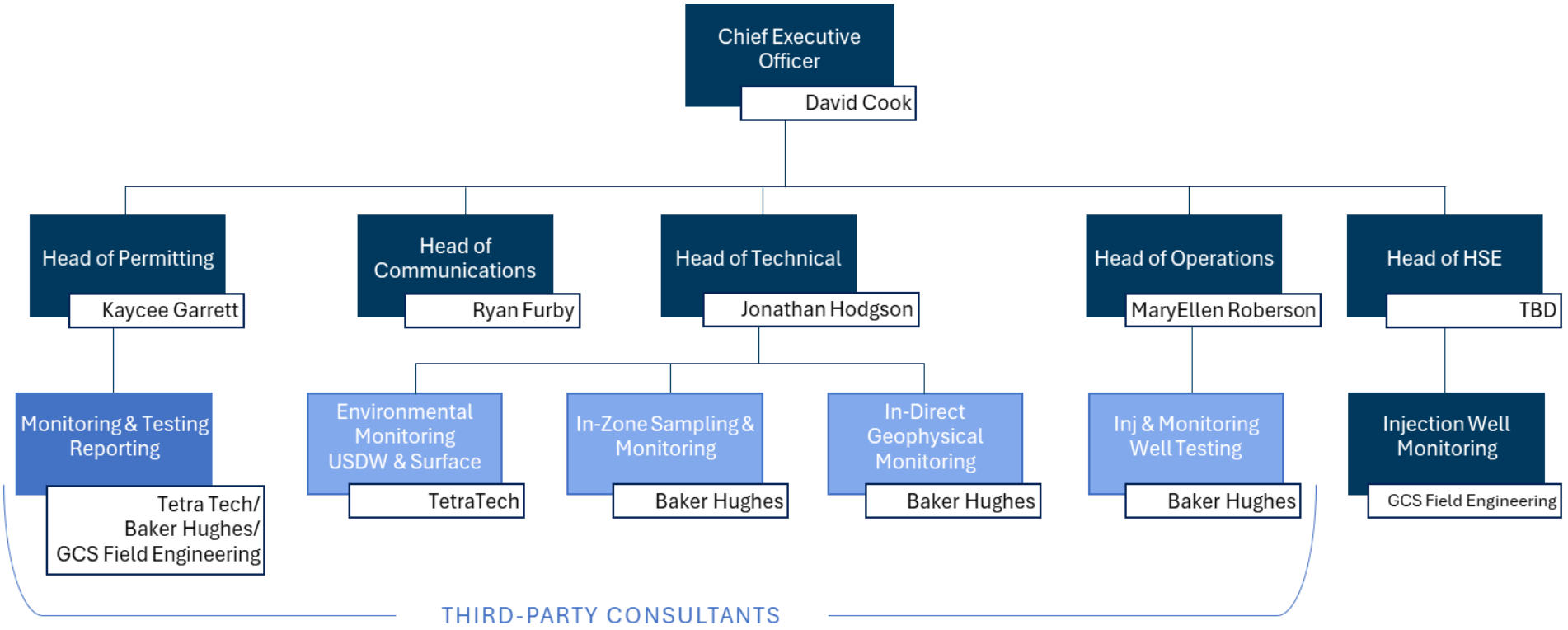
Table D.I.9.4-1 Summary of Analytical Standard Operating Procedures (SOPs)

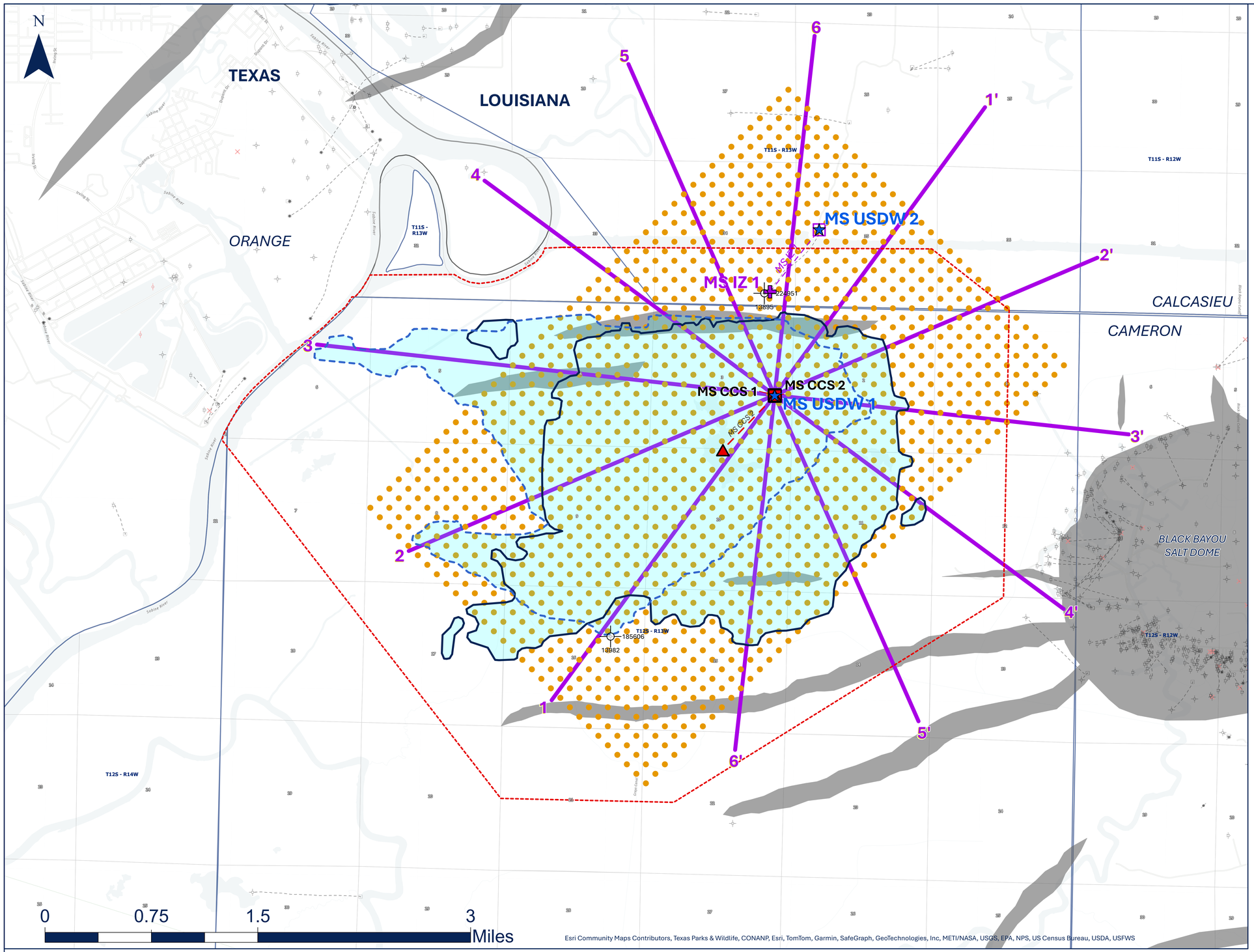
Parameters	Analytical Methods[1]	Detection Limit/ Range	Typical Precisions	QC Requirements
Cations Al, Ba, Mn, As, Cd, Cr, Cu, Pb, Sb Se, & Tl	ICP-MS, EPA Method 6020	0.001 to 0.1 mg/L (analyte, dilution and matrix dependent)	±15%	Daily calibration; blanks, duplicates and matrix spikes at 10% or greater frequency
Cations Ca, Fe, K, Mg, Na, & Si	ICP-OES, EPA Method 6010B	0.005 to 0.5 mg/L (analyte, dilution and matrix dependent)	±15%	Daily calibration; blanks, duplicates and matrix spikes at 10% or greater frequency
Anions Br, Cl, F, NO3, & SO4	Ion Chromatography, EPA Method 300.0	0.02 to 0.13 mg/L (analyte, dilution and matrix dependent)	±15%	Daily calibration; blanks and duplicates at 10% or greater frequency
Dissolved CO_2	Coulometric titration, ASTM D513-11	25 mg/L	±15%	Duplicate measurement; standards at 10% or greater frequency
Isotopes δ13C of DIC	Isotope ratio mass spectrometry[2]	12.2 mg/L HCO3 for δ13C	±0.15‰ for δ13C	10% duplicates; 4 standards/batch
TDS	Gravimetry, APHA 2540C	12 mg/L	±10%	Balance calibration, duplicate analysis
Water Density (field)	Oscillating body method	0.0000 to 2.0000	±0.0002 g/mL	Duplicate measurements
Alkalinity	APHA 2320B	4 mg/L	±3 mg/L	Duplicate analysis
pH (field)	EPA 150.1	2 to 12 pH units	±0.2 pH unit	User calibration per manufacturer recommendation
Specific conductance (field)	APHA 2510	0 to 200 mS/cm	±1% of reading	User calibration per manufacturer recommendation
Temperature (field)	Thermocouple	-5 to 50°C	±0.2°C	Factory calibration

Notes

1 An equivalent method may be employed with the prior approval of the Commissioner.
2 Gas evolution technique by Atekwana and Krishnamurthy (1998), with modifications made by Hackley et al. (2007)

Figure D.I.3.4 GCS Organizational Chart





Gulf Coast Sequestration, LLC (G1037)
5599 San Felipe, Suite 1450, Houston, TX 77056
(713) 997-3145 | www.gcscarbon.com

FIGURE D.I.5.2-1
Monitoring Network for Project Minerva

MAP LEGEND

- 3D VSP Sources
- Injector Bottom Hole
- Injector Well Pad
- Injector Schematic Well Trajectory
- Walk-away VSP / 2D Seismic Line
- Magnetic Survey Flight Area
- Max Extent of Stable CO2 Plume
- Max Extent of Pressure Front
- Delineated Area of Review
- Top Upper Frio Faults
- PLSS Townships & Ranges
- PLSS Sections
- SONRIS Parishes

Monitoring Wells

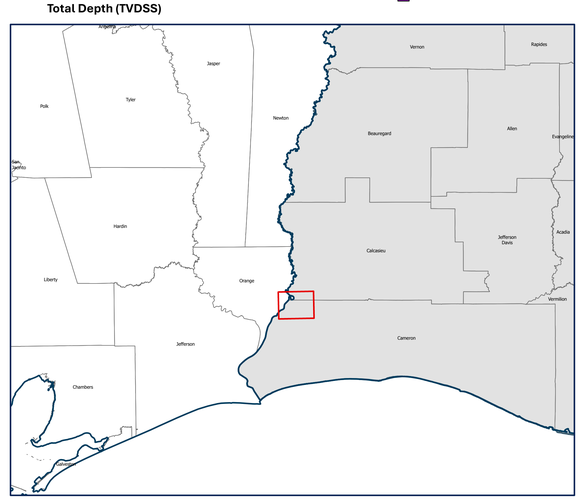
- In-Zone Bottom Location
- In-Zone Surface Location
- USDW Monitoring Well (Vertical)
- In-Zone Well Trajectory

Well Status

- Other
- Active - Producing
- Drilled
- Dry & Plugged
- Inactive
- Orphan
- Permit Expired
- Plugged & Abandoned
- Reverted
- Shut In
- Temporarily Abandoned
- Unable to Locate
- Surface Location
- Well Trajectory

Well Labels

Serial Number
Total Depth (TVDSS)
Monitoring Well Name



MAP DETAILS

PREPARED BY	R WENCEL	**DATE**	11/4/2024 4:14 PM
APPROVED BY	K GARRETT	**DATE**	11/XX/2024
MAP SCALE	1:16,000		
PAGE SIZE	A0 (46.81 W X 33.11 H)		

SPATIAL REFERENCE

PCS	NAD 1927 State Plane Louisiana South (FIPS 1702)
GCS	GCS North American 1927
DATUM	North American 1927
PROJECTION	Lambert Conformal Conic

PROJECT MINERVA DETAILS

WELLS	Minerva South CCS Well Nos. 001 and 002
LOCATION	Cameron Parish, Louisiana
EPA PROJECT ID	R06-LA-0002
LDENR APPL NOS	45031 & 45032

LOUISIANA BOARD OF PROFESSIONAL GEOSCIENTISTS
KAYCEE GARRETT
1325
Est. 2011

Chain of Custody Record

TAT(Check One): ☒ Standard ☐ 24hr ☐ 48hr ☐ 72hr ☐ Other____
(Additional charges may apply for rush TAT. If not specified, standard TAT will apply)

Order ID:_____

Client Name: _____

Address: _____ Phone: _____

_____ Email: _____

Contact Name: _____ P.O. Info:_____

Project Name: _____

Address: _____

_____

Regulatory ID (SDWA/Permit #): _____

Comments:

STL Sample Number	Sample Description / Site ID:	Date Sampled	Time Sampled	Samplers Initials	Test(s) Requested:	Bottle Quantity	See Codes Below				Comments / Field Data:
							Matrix	Sample Type	Bottle Type	Preservative	

Relinquished By:	Count	Date: / Time:	Temp ºC: _____
Received By:		Date: / Time:	Temp ºC: _____ Acceptable: Y / N
Relinquished By:		Date: / Time:	Temp ºC: _____ Acceptable: Y / N
Received in Lab By:		Date: / Time:	Temp ºC: _____ Acceptable: Y / N

Sample Conditions

- Submitted with COC? Y / N
- Number of containers match number on COC? Y / N
- All containers in tact? Y / N
- Tests within holding times? Y / N
- 40 mL VOA vials free of headspace? Y / N

Matrix Key

- NPW = Non-Potable Water
- Solid = Raw Sludge, Dewatered sludge, soil, etc. (reported as mg/kg)
- PW = Potable Water (not for SDWA compliance)
- SDWA = Safe Drinking Water Act Potable Sample

Sample Type Key

- G = Grab
- C = Composite
- 8HC = 8 Hr. Composite
- 24HC = 24 Hr. Composite

SDWA Sample Types

- D=Distribution
- E=Entry Point
- R=Raw
- C=Check
- S=Special
- M=Maximum Residence

Bottle Type Key

- P = Plastic
- G = Glass
- GA = Glass Amber
- VOA = 40mL G or GA
- PP = Sterile Polypropylene
- PS = Sterile Polystyrene
- HDPE = High Density Polyethylene
- O = Other

Preservative Key

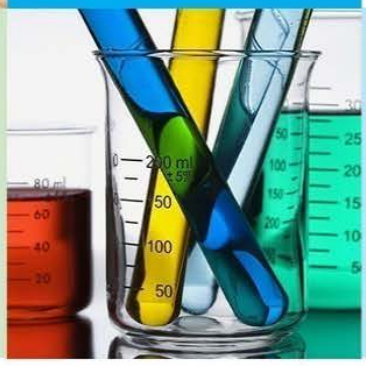
- A = Ascorbic Acid
- C = HCl
- H = HNO_3
- N = Sodium Thiosulfate
- OH = NaOH
- S = H_2SO_4
- O = Other
- NA = None Required

United States Environmental Protection Agency

Sampler's Guide



Contract Laboratory Program Guidance for Field Samplers



Office of Superfund Remediation and Technology Innovation (OSRTI)
United States Environmental Protection Agency (EPA)
Washington, DC 20460

OLEM 9240.0-51
USEPA 540-R-20-005
November 2020

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LIST OF ACRONYMS

ARO	Aroclor
ASB	Analytical Services Branch
BTEX	Benzene, Toluene, Ethylbenzene, and Xylene
CBC	Chlorinated Biphenyl Congener
CDD	Chlorinated Dibenzo-*p*-dioxins
CDF	Chlorinated Dibenzofurans
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CLP	Contract Laboratory Program
CLPSS	Contract Laboratory Program Support System
COC	Chain of Custody
CRQL	Contract Required Quantitation Limit
CVAA	Cold Vapor Atomic Absorption
CWA	Clean Water Act
DMC	Deuterated Monitoring Compound
DOT	Department of Transportation
DQO	Data Quality Objectives
EPA	United States Environmental Protection Agency
ERT	Environmental Response Team (EPA)
ET	Eastern Time
FSP	Field Sampling Plan
GC/MS	Gas Chromatograph/Mass Spectrometer or Gas Chromatography/Mass Spectrometry
GPS	Global Positioning System
HAZWOPER	Hazardous Waste Operations and Emergency Response
HASP	Health and Safety Plan
HCN	Hydrocyanic Acid
HTML	Hypertext Markup Language
IATA	International Air Transport Association
IC	Ion Chromatography
ICP-AES	Inductively Coupled Plasma - Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma - Mass Spectrometry
MA	Modified Analysis
MS	Matrix Spike
MSD	Matrix Spike Duplicate
NIOSH	National Institute for Occupational Safety and Health
NPL	National Priorities List
OLEM	Office of Land and Emergency Management
OSC	On-scene/On-site Coordinator
OSHA	Occupational Safety and Health Administration
OSRTI	Office of Superfund Remediation and Technology Innovation
PCBs	Polychlorinated Biphenyls
PE	Performance Evaluation
PHMSA	Pipeline and Hazardous Materials Safety Administration
ppb	Parts-Per-Billion (e.g., µg/L or µg/kg)
PPE	Personal Protective Equipment

ppm	Parts-Per-Million (e.g., mg/L or mg/kg)
ppt	Parts-Per-Trillion (e.g., ng/L or ng/kg)
PRP	Potentially Responsible Party
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl Chloride
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QATS	Quality Assurance Technical Support
QC	Quality Control
RPM	Remedial Project Manager
RSCC	Regional Sample Control Coordinator
SAM	Site Assessment Manager
SAP	Sampling and Analysis Plan
SARA	Superfund Amendments and Reauthorization Act
SDG	Sample Delivery Group
SIM	Selected Ion Monitoring
SMC	System Monitoring Compound
SMO	Sample Management Office
SOP	Standard Operating Procedure
SOW	Statement of Work
SPLP	Synthetic Precipitation Leaching Procedure
SPP	Site Project Plan
SVOA	Semivolatile Organic Analyte
TCLP	Toxicity Characteristic Leaching Procedure
TIFSD	Technology Innovation and Field Services Division
TOC	Total Organic Carbon
TR/COC	Traffic Report/Chain of Custody
UN	United Nations
UPS	United Parcel Service
USCG	United States Coast Guard
USDA	United States Department of Agriculture
VOA	Volatile Organic Analyte
XML	eXtensible Markup Language

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1.0 INTRODUCTION



The *Contract Laboratory Program Guidance for Field Samplers* (also referred to as the *Sampler's Guide*) describes the organizational roles and responsibilities for those who plan and conduct environmental sample collection for analysis through the U.S. Environmental Protection Agency (EPA) Contract Laboratory Program (CLP).

The following lists the sections of this Guide:

- Section 1, *Introduction*, introduces the structure and purpose of this document.
- Section 2, *General Sampling Information*, describes the general activities associated with environmental sampling.
- Section 3, *CLP Statements of Work*, describes the Statements of Work (SOWs) that define the requirements for CLP sampling.
- Section 4, *CLP Sample Documentation*, lists the types of documentation used to track CLP samples.
- Section 5, *The Scribe Documentation Software Tool*, provides information about Scribe, a software tool used to create sample documentation.
- Section 6, *CLP Sample Containers*, describes the types of containers required for CLP samples.
- Section 7, *CLP Sample Collection*, describes the process by which CLP samples are collected.
- Section 8, *CLP Sample Transportation and Shipping*, outlines the requirements for the packing and shipping of CLP samples.
- Section 9, *Sampler Resources*, provides links to additional information for sampling organizations.

The following lists the appendices of this Guide:

- Appendix A, *Functions within a Sampling Project*, describes the functions within a sampling project which are taken from the Quality Assurance Project Plan (QAPP) requirements.
- Appendix B, *General CLP Sample Collection Guidelines for Aqueous VOA Samples*, provides guidelines for Volatile Organic Analyte (VOA) water samples.
- Appendix C, *CLP Sample Collection Guidelines for Soil VOA Samples by SW-846 Method 5035A, TCLP Extraction by EPA SW-846 Method 1311, and SPLP Extraction by EPA SW-846 Method 1312* provides guidelines for VOA soil samples.
- Appendix D, *CLP Sample Collection Requirements by Analysis Type*, contains the sample collection requirements by SOW.
- Appendix E, *Sampling Techniques and Considerations*, recommends sampling techniques.
- Appendix F, *International Shipping*, contains information regarding shipping samples to laboratories outside the United States.
- Appendix G, *Sampling Checklists*, contains checklists used to help the sampler ensure that all necessary steps are completed.
- Appendix H, *Glossary*, provides definitions for terms used in this document.



If the field sampling team is planning to use the CLP, they should use this Guide to develop the Site Project Plan (SPP), QAPP, and Field Sampling Plan (FSP) documents.

1.1 Overview of the CLP

The CLP is a national network of EPA personnel, commercial laboratories, and support contractors whose fundamental mission is to provide environmental sample collection and analysis under the Superfund program. The Superfund program was established under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) of 1980 and presently exists under the Superfund Amendments and Reauthorization Act (SARA) of 1986. The CLP is directed by the EPA Analytical Services Branch (ASB) of the Technology Innovation and Field Services Division (TIFSD) within the Office of Superfund Remediation and Technology Innovation (OSRTI) under the Office of Land and Emergency Management (OLEM).

The primary responsibility of the CLP is to provide analytical data of known and documented quality to CLP customers through its routine and modified chemical analytical services. The CLP provides a framework that allows data to be produced in a cost-effective and efficient manner. In addition, the CLP has established strict Quality Control (QC) procedures and detailed documentation requirements to ensure the consistent quality of the data. Current CLP data users include the EPA Regions, other EPA Headquarters programs, State and Tribal governments, and other Federal agencies.

1.1.1 Key Participants within the CLP Sampling Process

In coordinating Superfund sampling efforts, ASB is supported by the Sample Management Office (SMO) contractor, Regional Sample Control Coordinators (RSCCs), Site Assessment Managers (SAMs), On-scene/On-site Coordinators (OSCs), and Remedial Project Managers (RPMs). Samplers may work directly with the RSCC, and/or an OSC from the Site Support Personnel during a sampling event. Refer to Table 1-1 for a description of the functions performed by key participants (functions may vary by Region).

Table 1-1. Participants in the CLP Sampling Process

Participants	Responsibilities
Analytical Services Branch (ASB)	ASB directs the CLP within the TIFSD of the OSRTI in the OLEM. ASB's responsibilities include: • Development of the SOWs that define required analytical methods (including QC, detection/quantitation limits, and holding times) for the analytical services procured under the CLP • Development and implementation of policies and budgets for Superfund analytical operations • Development of information management policies and products for analytical data • Management of SMO and Quality Assurance Technical Support (QATS) contracts • National administration, evaluation, and management of the CLP • Direction of CLP Quality Assurance (QA) activities in coordination with overall OLEM QA activities To obtain the most current ASB contact list, refer to the following website: https://www.epa.gov/clp/forms/contact-us-about-superfund-analytical-services-or-contract-laboratory-program#tab-2
CLP Sample Management Office (SMO)	The contractor-operated SMO provides management, operations, and administrative support to the CLP. SMO receives Regional analytical requests, coordinates and schedules sample analyses, and tracks sample shipments. SMO also receives and checks data for completeness and compliance, processes laboratory invoices, and maintains a repository of sampling records and program data.

Table 1-1. (Continued) Participants in the CLP Sampling Process

Participants	Responsibilities
CLP Contract Laboratories	The contractor-operated laboratories within the CLP provide analytical services for the separation, detection, and quantitation of the CLP's target analytes.
Environmental Response Team (ERT)	The ERT is responsible for the development, implementation, and management of the Scribe software system. In addition, the ERT oversees the development of Scribe training webinars and on-site training.
Environmental Response Team (ERT) Support Contractors	The ERT Support Contractors provide technical and administrative support for the development, implementation, and management of the Scribe software system. In addition, the ERT Support Contractors support the development of Scribe training webinars and on-site training.
Regional Sample Control Coordinator (RSCC)	In most Regions, the RSCC coordinates sampling efforts and serves as the central point-of-contact for sampling questions and problems. The RSCC works with SMO to request analytical services and receive laboratory assignments. In addition, the RSCC's activities may include informing SMO of sample shipment, cancellations, special instructions, and sampling issues. To obtain the most current RSCC contact list, refer to the following website: https://www.epa.gov/clp/forms/contact-us-about-superfund-analytical-services-or-contract-laboratory-program#tab-3
Site Support Personnel	The Site Support Personnel consist of the EPA personnel and contractors responsible for developing the QAPP and Sampling Plan for the sampling event at the site. It includes such personnel as the sampling team, QA personnel, OSC, SAM, and RPM. In most Regions, the Site Support Personnel develop Standard Operating Procedures (SOPs) for field sampling and related procedures, and assist sampling teams in adhering to the SOPs. The sampling team determines what type(s) of CLP services will be required for a particular sampling event. The Site Support Personnel review Sampling and Analysis Plans (SAPs) prepared by sampling teams and oversee sampling teams in the field. In addition, the state or territorial environmental protection agency for the location of the site provides support for the sampling event.

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2.0 GENERAL SAMPLING INFORMATION

2.1 Goals of the Sampling Process



Once the U.S. Environmental Protection Agency (EPA) has determined that physical, chemical, and/or biological testing of a site is necessary, samples of material from the site area must be collected. The type of material that must be collected and the analytical method to be used depends upon the physical location of the site, detection level(s), site history (previous sampling), and known or unknown conditions and contaminants. Samples should be collected according to the approved project and site-specific Quality Assurance Project Plan (QAPP) and Sampling and Analysis Plan (SAP). This Guide does not define specific sampling procedures, as these depend upon individual site conditions, Regional requirements, and acceptance and performance criteria. Since Regions may have their own specific requirements for individual sampling programs, they are responsible for generating Region-specific sampling Standard Operating Procedures (SOPs). EPA personnel shall also follow the procedures in CIO 2105-P-02.0 (*EPA QA Field Activities Procedures*).

2.1.1 Follow the Required Sampling Procedures

It is imperative that samplers be aware of the minimum Contract Laboratory Program (CLP) and Regional requirements that directly impact and define how a sampling event will take place. It is important to note that the procedures and guidelines set forth in this document are considered minimum CLP requirements.

The purpose of sampling is to collect representative portions from a suspected contaminated site. Sample collection is critical to determining the presence, type, concentration, and extent of environmental contamination by hazardous substances; thus, it is a crucial part of every sampling and environmental testing effort. Sampling procedures must be consistently followed to mitigate risk of error and the expense of resampling.

Failure to follow proper sampling and shipping procedures could result in samples that are contaminated, in broken containers, mislabeled, lost during shipping, compromised due to improper preservation, or unusable because of a missed holding time. If procedures are inconsistently or improperly followed, any resultant analytical data may be inaccurate and may not be legally defensible.

2.1.2 Maintain Chain of Custody of Samples and Data

Acquiring accurate and legally defensible data is the CLP's primary objective; therefore, the samplers must collect samples according to strict sampling procedures, plans, and guidelines. The Chain of Custody (COC) Records must be generated and the sample COC maintained. EPA and

many other Federal agencies use data resulting from analytical testing of samples for the following activities:

- Site Characterization
- Source Evaluation
- Identification of Potentially Responsible Parties (PRPs)
- Remedial Design
- Assessment of response and remedial priorities
- Remedial Action
- Remedial Investigation/Feasibility Studies
- Assessment of risk to human health and the environment
- Determination of appropriate cleanup actions
- Determination of cleanup achievements

2.1.3 Field Operation Records

Samplers must maintain complete, accurate, and legible field operations records as they perform a sampling activity. The following records are included:

- Field logbooks
- Corrective Action reports
- Sampling trip reports
- Supplemental standardized forms
- Records such as maps or photographs that document each step of each activity performed in the field

Samplers must refer to their project plans for Region-specific field operations record requirements. These records are an important tool because they are considered a part of the official project file when legal issues arise.

2.1.4 Comply with Safety Procedures

Care must be taken to maintain the safety of personnel collecting and handling CLP samples. If sampling requires digging in soil, utility lines (gas, oil, cable, etc.) must be marked to prevent injury or utility outage. Samples must be handled, packed, and shipped in accordance with all applicable Federal [Occupational Safety and Health Administration (OSHA) and Department of Transportation (DOT)] regulations for hazardous materials. Refer to the Health and Safety Plan (HASP) for detailed site safety requirements.

2.2 Obtain Municipal Permits, Licenses, and Clearances

Before starting a sampling event, samplers must obtain the proper municipal permits, access to the property, and any government clearances, if required. Samplers must also contact any appropriate utility companies to ascertain where any underground pipes, cables, etc., may be located.

2.2.1 Request Access to County, State, Tribal, Military, and/or Federal Property

Proper access to perform sampling activities is important not only for legal reasons, but also to eliminate delays in work and possible refusal to allow sampling to take place. It is crucial that the appropriate permits, licenses, and clearances be secured to obtain access for sampling activities that will be performed on County, State, Tribal, military, and/or Federal property. The sampler must contact the appropriate government offices or personnel well in advance to determine what kinds of approval are required. Pre-approval may be required for specific types of sample collection such as drilling or excavation. For example, drilling on a military base requires pre-

approval. Base security may require clearances for all members of the sampling team, including subcontractors. This process may take two or more days.

2.2.2 Contact Private Property Owners

Samplers must obtain written permission from the private property owner(s) before sampling on his/her property, even if verbal permission has been granted. It is recommended that samplers obtain verbal permission prior to their arrival at the sampling location, but written permission can be obtained on the day of sampling. If a property owner refuses to grant access to his/her property, it may be necessary for the sampling organization to contact the appropriate authorities for assistance. A sampler who enters private property without permission may be subject to a charge of trespassing, and samples may be considered part of an illegal search and invalid for legal proceedings.

2.2.3 Contact Utility Companies

The sampler must contact local utility companies (e.g., power, phone, gas, cable, sanitation, etc.) at least one week prior to the sampling event to have underground cables, lines, and pipes flagged and marked. This is required by law. A national one-call directory can be found at: https://call811.com

It may be necessary to turn off the utilities (i.e., electrical wires or gas lines) in order to obtain samples. The utility service(s) disruption dates should be confirmed at least two days prior to sampling activities. Samplers should follow Regional or other appropriate program procedures for the disruption of utilities.



Pre-payment of survey fees to local utility companies may be required.

2.3 Analytical Services Request

To prepare for the sampling event, the samplers should review the “Analytical Services Request Regional Notification” for samples from the CLP. This information may be in the form of the “Analytical Services Request Regional Notification” obtained from the Sample Management Office (SMO) Contract Laboratory Program Support System (CLPSS) Portal, supplied by the Regional Sample Control Coordinator (RSCC), or in other forms of communication from the Region. Information for Modified Analyses may also be obtained from the SMO CLPSS Portal. Field team leaders should contact their RSCC, Remedial Project Manager (RPM), or On-Site Coordinator (OSC) to review this information prior to going into the field, and ensure that this information matches information in the Site Project Plan (SPP), SAP, and/or QAPP. An eXtensible Markup Language (XML) file is provided as part of the laboratory assignment from the SMO CLPSS Portal which can be used for uploading site information into Scribe.

Review the following sources of information for planning:

- **Sample information:** Provides the number of samples requested, the sample matrix, the analysis types, and if Preliminary Results are required. This information is used to determine the equipment and supplies needed for the sampling event.
- **Site location:** Determines whether there are any specific requirements for accessing/exiting the site, or for working at the site.
- **Shipping period:** Establishes the time frame during which the samples are to be shipped to the laboratory/laboratories. This helps determine when sampling should occur.
- **Laboratory information:** Specifies where the samples will be shipped.

2.3.1 Review Sample Request

Review the "Analytical Services Request Notification" and other Regional communication for the following information:

- ☐ The sample request determines some of the preparatory activities for the sampling event.
- ☐ Review and evaluate the sample request to determine the number and types of samples to be collected.
- ☐ Review the required sample collection method(s).
- ☐ Review decontamination procedures necessary for site.
- ☐ Make note of sample holding times and conditions.
- ☐ Determine Performance Evaluation (PE) and Quality Control (QC) sample requirements.
- ☐ Determine whether shipping container temperature blanks are required.

2.4 Review Project Plans

Project plans describe, in detail, the requirements for the sampling event. All field team members should be familiar with the applicable project plans prior to beginning field sampling. These plans may include the following documents.

2.4.1 Site Project Plan (SPP)

The SPP describes the requirements for any activity taking place at the site. It contains information such as site history, potential contaminants, topographical information, etc. that may be integrated into the QAPP.

2.4.2 Health and Safety Plan (HASP)

The HASP describes the measures necessary to maintain the health and safety of the sampling team during the sampling event. It can include topics such as the following:

- Organization structure
- Job hazard analysis
- Site control
- Training
- Medical surveillance
- Personal protective equipment (PPE)
- Exposure monitoring
- Thermal stress
- Decontamination
- Emergency response
- Location of and directions to the nearest Emergency Room or hospital
- Standard Operating Procedures
- Confined space operations
- Spill containment

2.4.3 Quality Assurance Project Plan (QAPP)

The QAPP describes the data quality objectives and data requirements for the project, and is used by samplers to develop any subsequent plans such as the SAP or the Field Sampling Plan (FSP). Refer to Appendix A for more information on QAPP sampling requirements.

2.5 Assemble Sampling Materials

Samplers should prepare for a sampling project by assembling the appropriate sampling materials (equipment, supplies, sample containers, packing materials, and shipping materials). The equipment and supplies must be properly cleaned, calibrated, and tested as necessary to meet the needs of the sampling project prior to sampling.

2.5.1 Equipment and Supplies

Samplers should review the project plans to determine the equipment necessary for sample collection.

The following should be obtained prior to a sampling event:

- Sample containers
- Shipping containers
- Packing material
- Reagent water for decontamination and for preparation of field/equipment blanks
- Access to the Scribe software for creating sample labels, stickers, Traffic Report/COC (TR/COC) Records, and Region-specific Scribe templates
- Custody seals
- Sampling equipment such as bowls, augers, pumps, etc.
- PPE
- Internet access (either at the time of sampling or soon after the samples are shipped)

The QAPP, the SAP, or the CLP Statement of Work (SOW) may also require field samplers to provide the following:

- Shipping container temperature blanks
- Trip blanks for Volatile Organic Analyte (VOA) analysis
- Preservation supplies (e.g., ice or acid)
- Specially prepared sample vials or bottles (e.g., VOA or hexavalent chromium)
- Utensils or equipment for handling tissue samples requested by Modified Analysis

2.6 Perform Readiness Review/Dry Run

A readiness review/dry run is a test run of the proposed sampling event. It is a recommended practice as it affords samplers a chance to review all plans, documentation software (i.e., Scribe), and equipment lists for accuracy and completeness prior to sampling activities. It also provides an opportunity to consult with sampling team members to make sure that all the elements are in place and that everyone understands their tasks before actually going out into the field. Sampling project managers should provide the readiness review or dry run dates and schedules to samplers so that they can prepare accordingly.

2.7 Assess the Status of the Site and the Team

Samplers should consider taking the following actions prior to starting a sampling event:

- ☐ Communicate personnel roles and lines of authority.
- ☐ Verify that HAZWOPER training is up to date for all field staff as required.
- ☐ Ensure that permission has been granted to enter the site and collect samples.
- ☐ Confirm that utility work has been completed (if required).
- ☐ Review local weather forecast to be aware of possible dangerous weather conditions. Ensure that sampling staff are prepared for weather conditions.

- ☐ If the sampling location is inaccessible, contact the appropriate field or Regional personnel for instructions.
- ☐ Verify that the correct sampling equipment is on site.
- ☐ Ensure that personal safety measures are in place.
- ☐ Ensure that a site HASP is in place and includes procedures for emergency medical treatment and first aid, evacuation procedures, emergency contacts, and location of emergency medical facilities.
- ☐ Identify and mark the sampling location with buoys, flags, or stakes according to the sampling plans, maps, and grids.
- ☐ Park the car/van away from the sampling site and turn off the engine. Be aware of car exhaust (BTEX) contamination to volatile organic samples through all procedures, including loading and unloading the containers during shipping.

2.8 Initiate Site Control Measures

The sampling team is responsible for implementing the necessary site control measures during the sampling event, which may include the following:

- ☐ Maintaining a log of authorized personnel entering the site.
- ☐ Preventing unauthorized persons from entering the site.
- ☐ Ensuring that any decontamination equipment or procedures to prevent sample cross-contamination required in the QAPP and/or FSP are in place and carried out.

2.9 Maintain Field Logbook

Samplers must maintain a field logbook that documents the field activities. The information in the field logbooks may be used as evidence in court. The field logbook should meet the following criteria:

- ☐ Use waterproof ink to record all entries.
- ☐ Record the date and time of all entries, and the name of the person recording the information.
- ☐ Correct all errors by drawing a line through the error, initialing and dating the error, and then adding the correct information.
- ☐ Document sampling project information such as:
  - Project name, Project ID, and location
  - Names of samplers
  - Geological observations, including maps and Global Positioning System (GPS) information
  - Atmospheric conditions
  - Field measurements
  - Sampling dates, times, locations, and sample location coordinates
- ☐ Record sampling activity information such as:
  - Sampling dates and times
  - Name(s) of person(s) recording the information
  - Sample identifications
  - Sample matrices
  - Sample descriptions (e.g., odors and/or colors)
  - Number of samples collected
  - Sampling methods/equipment
- ☐ Record any and all deviations from the sampling plan.
- ☐ Record any and all difficulties in sampling and/or any unusual circumstances.

2.10 Preventing Errors

Errors in the sampling process can result in additional costs and delayed sampling results. The following section lists some of the steps that can be taken to avoid common sampling errors.

Document samples correctly:

- ☐ Use the CLP Sample Number and SMO CLPSS Portal-generated CLP Case Number correctly (sample number on each sample).
- ☐ Submit the signed TR/COC Record with the sample(s).
- ☐ Ensure that the TR/COC Record and the sample container information match each other and are accurate.
- ☐ Accurately and legibly complete and attach a custody seal to each shipping container. The project QAPP may also require that custody seals be attached to each sample container or plastic sample bag. Refer to the project QAPP for specific instructions.

Collect and preserve samples correctly:

- ☐ Collect a sufficient volume of sample so that the laboratory can perform the requested analysis and quality controls, such as Matrix Spike (MS), Matrix Spike Duplicate (MSD), and laboratory Duplicate.
- ☐ Ensure that required preservatives have been added to samples.

Ship samples correctly:

- ☐ Pack bottles and containers to prevent breaking or spilling during shipping.
- ☐ For iced samples, evenly distribute bags/packets of ice throughout the cooler and between the sample containers to ensure that all samples are sufficiently cooled to a temperature of $\leq 6°C$, but not frozen, and include a sealed container of water to be used as a temperature blank.
- ☐ Verify that the TR/COC Records have been included prior to sealing the shipping container.
- ☐ Verify that custody seals are attached to the shipping containers.
- ☐ Ensure that the shipping containers are labeled with the designated laboratory address.
- ☐ Include shipping information for United States Department of Agriculture (USDA) Quarantine samples if applicable.
- ☐ If samples are to be shipped internationally, assemble the required additional paperwork or customs authorizations. Refer to Appendix F, International Shipping, for additional information.
- ☐ Upload the electronic TR/COC Record as soon as possible after shipping.

Communicate effectively:

- ☐ It is extremely important that all parties involved in a sampling event remain in contact during the sampling process.
- ☐ The key elements of communication for a sampling event include the relationship between the RSCC, SMO, the samplers in the field, and the laboratories that will be accepting the samples.
- ☐ In instances where there are any changes to the sampling event due to a cancellation or an increase or decrease in the number of samples to be shipped, the sampler should contact the RSCC as soon as possible. The RSCC will work with SMO to resolve any potential capacity, availability, or overbooking issues with the CLP laboratories.

2.11 Exiting the Site

The following activities should be performed before leaving the sampling site:

- ☐ Ensure that all equipment has been collected and removed.
- ☐ Follow Regional guidance regarding decontamination and doffing of PPE, if used.
- ☐ Follow Regional guidance for waste removal and disposal.
- ☐ Ensure that all sampling personnel have cleared the site.
- ☐ If sampling on private property, provide a sample receipt to the property owner for all samples collected and removed from the site.

3.0 CLP STATEMENTS OF WORK

The overall requirements for sample collection, analysis, and handling under the Contract Laboratory Program (CLP) are described in the CLP Statements of Work (SOWs).

3.1 The CLP SOWs

The CLP SOWs are available on the U.S. Environmental Protection Agency (EPA) website at: https://www.epa.gov/clp/superfund-clp-analytical-statements-work-sows. Table 3-1 lists the CLP SOWs.

Table 3-1. CLP Statements of Work

Statement of Work	Analysis Types	Matrix Types
High Resolution	Chlorinated Dibenzo-*p*-Dioxins (CDDs) and Chlorinated Dibenzofurans (CDFs) Chlorinated Biphenyl Congeners (CBCs)	Soil, sediment, biosolids, oil, sludge, ash, tissue, water, and wipe
Organic/Inorganic	Trace Volatile Organic Analytes (Trace VOAs) Trace VOAs Selected Ion Monitoring (SIM) Volatile Organic Analytes (VOAs) Semivolatile Organic Analytes (SVOAs) SVOAs SIM Pesticides Aroclors Metals by Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP - AES), Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) Mercury by Cold Vapor Atomic Absorption (CVAA) Spectrometry Cyanide by Spectrophotometry Anions by Ion Chromatography (IC)* Hexavalent Chromium by IC* Total Organic Carbon (TOC)*	Soil, sediment, water, Toxicity Characteristic Leaching Procedure (TCLP)/ Synthetic Precipitation Leaching Procedure (SPLP) leachate , waste, and wipe

*Anions, Hexavalent Chromium, and TOC will be available by Modified Analysis (MA).

3.2 CLP Sample Definition

A CLP sample is defined as a discrete portion of material to be analyzed from one location for each individual or set of analyses.

A sample consists of all sample aliquots (portions), provided that the analyses are all requested from the same CLP analytical program:

- for each individual or set of analytical methods
- from one location
- for one sample matrix
- for one laboratory

3.2.1 Mixed-matrix Samples

In some instances, a mixed-matrix sample which contains either a supernate (for a sediment/soil sample) or a precipitate (for a water sample) may be collected. The decisions made with regard to the different matrices in such samples can have profound impacts on data usability. In this event, samplers should consult their sampling plans and/or discuss the required procedures with the Remedial Project Manager (RPM), On-Site Coordinator (OSC), or designee.

In general, it is recommended that two individual samples be collected by separating the aqueous layer from the solid/precipitate layer at the point of collection if possible. If the phases or layers cannot be separated effectively in the field at the point of collection, direction should be provided to the receiving laboratory to separate the layers under controlled conditions. In this case, additional sample numbers will be needed for the separate phases. They should be assigned two different sample IDs (e.g., Sample IDs ABC124 and ABC125 for Sample ID ABC123), along with notes in the field sample log and in the Special Instructions section of the Chain of Custody (COC) Record, indicating that the sample IDs are derived or related to the same sample. Refer to Section 5.1.5, Using Scribe for Mixed-matrix Samples, for information on how to use the Scribe software to track mixed-matrix samples.

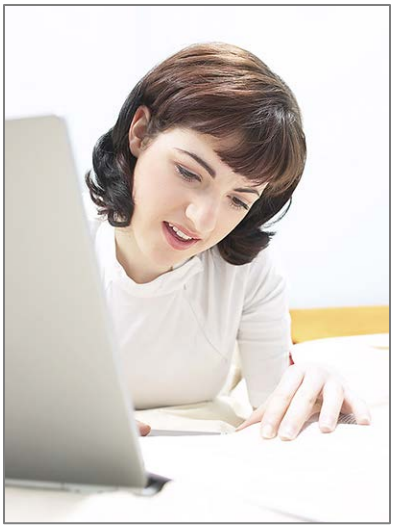


When samples are collected from several locations to form a composite sample, the sample should be assigned either a number from one of the locations used during collection, or a unique number that represents the composite sample, for tracking purposes. The numbering scheme used internally at a sampling event for identifying composite samples should also be documented appropriately (e.g., in the field logbooks).

3.3 CLP Analyses

CLP analysis is generally used for Superfund sites and includes the target analytes. The matrices can be water, leachates derived from the TCLP or SPLP, soil, sediment, waste, wipe, or tissue (non-human) for high resolution analyses. Additional matrices requested under Modified Analysis (MA) for inorganics and organics may include oil, sludge, ash, construction waste, biosolids, or tissue (non-human).

4.0 CLP SAMPLE DOCUMENTATION



The U.S. Environmental Protection Agency (EPA) Contract Laboratory Program (CLP) is required to produce accurate and legally defensible data. Therefore, in order to produce legally defensible data, control of the samples must be maintained to ensure that the samples accurately represent the site and location from which they were collected. Sample documents are tools that allow EPA to maintain the chain of custody of the samples from collection, through shipping, to analysis. The documentation also associates the sample to the sample data. Samplers should review their site-specific project plans and Quality Assurance Project Plans (QAPPs) to determine other types of documentation that must be completed for a sampling project. The following section describes the documents used to maintain the chain of custody and the tools used to create these documents.

The following table summarizes CLP sample documentation.

Table 4-1. CLP Sample Documentation Tracking

Type	Source	Purpose
CLP Sample Number	Assigned by sampling software (Scribe); ranges are supplied by the Regional Sample Control Coordinator (RSCC)	Identifies sample data. Associates the sample to the sample data.
CLP Case Number	Generated by the Sample Management Office (SMO) Contract Laboratory Program Support System (CLPSS) Portal	Identifies groups of samples collected during a single sampling event.
Traffic Report/Chain of Custody (TR/COC) Record	Created in Scribe	Tracks chain of custody of the sample and sample data.
Custody seals	Supplied by the RSCC or field sampling team	Maintains sample integrity; may indicate sample tampering or contamination if broken.
Sample labels	Created in Scribe	Affixed to the sample container to identify an individual sample.
Field operations records (as necessary)	Created and maintained by sampling team	Maintains a record of activities at the site.
Shipping container label (to the laboratory)	Carrier standard form	Used by the carrier to ship the samples to the laboratory.
Shipping container return label (return from the laboratory)	Carrier standard form	Used by the carrier to have the laboratory return the container to the Region.

The documentation required by a Region for a sampling event is outlined in project plans such as the QAPP, Sampling and Analysis Plan (SAP), and Field Sampling Plan (FSP).



EPA recommends that a dedicated field team member be responsible for all sample documentation steps, including reviewing laboratory scheduling information, creating sample labels and TR/COC Records in Scribe, maintaining a field operations log, and relinquishing control of the samples to the laboratory. This person should be identified in the Site Project Plan (SPP) or QAPP.

Under no circumstances should the site name or address appear on any documentation that is sent to the laboratory (for the CLP).

4.1 CLP Sample Numbers

A sample number is a number that is unique per sampling location and identifies each CLP sample. It is used to track samples throughout the sampling and analytical processes, and is recorded on several types of sample and sample documentation (e.g., TR/COC Records and sample labels).

Table 4-2. CLP Sample Number Letter Codes

Region	Letter Code
1	A
2	B
3	C
4	D
5	E
6	F
7	G
8	H
9	Y
10	J

According to the CLP guidelines, each individual inorganic water sample may be analyzed for total metals or filtered metals, but not both. Therefore, water samples collected for total metal and filtered metal analyses from the same sampling location must be assigned separate and unique CLP Sample Numbers. Samples for Toxicity Characteristic Leaching Procedure (TCLP) and Synthetic Precipitation Leaching Procedure (SPLP) may also require separate CLP Sample Numbers.

4.1.1 Requesting Sample Numbers

CLP Sample Numbers are created in Scribe with ranges supplied by the RSCC. The sampler should request a range of sample IDs from the RSCC. Once the initial number is entered into Scribe, the software will auto-generate the additional sample numbers required for the project. Do not re-use CLP sample numbers, as this may create difficulties for Laboratory Information Management Systems.

4.2 CLP Case Numbers

SMO CLPSS Portal-generated Case Numbers are used to track groups of samples from a sampling event throughout the sampling and analytical processes, and are recorded on several types of sample and sample documentation (e.g., TR/COC Records, sample labels). Samplers should correctly assign the Case Number to the appropriate sample bottle or container. CLP Case Numbers are obtained from the “Analytical Services Request Regional Notification” in the Access Assignment Information task in the SMO CLPSS Portal. Samplers should correctly assign the Case Number to the appropriate sample bottle or container.

4.3 CLP TR/COC Records

A TR/COC Record is used as physical evidence of sample custody and as a permanent record for each sample collected. A chain of custody record documents the exchange and transportation of samples from the field to the laboratory.

To meet CLP sample documentation and chain of custody requirements, samplers must attach a separate, signed TR/COC Record to each container shipped. The sampler should consider TR/COC documentation needs when shipping directly from the site.

- ☐ The TR/COC Record must document each sample within the shipping container.
- ☐ The Carrier Name and Airbill Number should be on each COC.
- ☐ Each TR/COC Record **must be signed by the designated field sampler**, documenting that they have relinquished control of the samples.
- ☐ TR/COC Records should be separated and shipped in the containers with the samples listed on them. Attach the TR/COC Record to the inside of the lid of the shipping container. Samples may not be shipped in a container without the corresponding TR/COC Record. This practice maintains the chain of custody for all samples in case of incorrect shipment.
- ☐ The electronic TR/COC Record should be uploaded as soon as possible after shipping.

If more than one TR/COC Record is used for the samples within one shipping container, all of the records must have complete header information and original signatures. Samplers are responsible for the care and custody of samples from the time of collection to the time of shipment to the laboratories for analysis. A sample is considered under custody if the following conditions are met:

- It is in possession or in view after being in possession
- It was in possession and then secured or sealed to prevent tampering
- It was in possession when placed in a secured area

Each time the custody of samples is turned over to another person, the TR/COC Record must be signed off by the former custodian and accepted by the new custodian.

4.4 Chain of Custody Seals

A chain of custody seal is any adhesive label or tape that can be used to seal a sample bottle, container, plastic bag, or shipping container. In the event that a container is opened or tampered with, the seal will be broken. The custody seal is used to maintain the chain of custody, as well as guard against possible sample contamination or tampering during shipping.

- ☐ Custody seals must be placed on each shipping cooler or container, and if required by the project's QAPP or FSP, on each sample bottle, container, or bag (as appropriate).
- ☐ The CLP does not provide custody seals. Custody seals should be obtained from the RSCC or supplied by site personnel.

4.5 Sample Labels

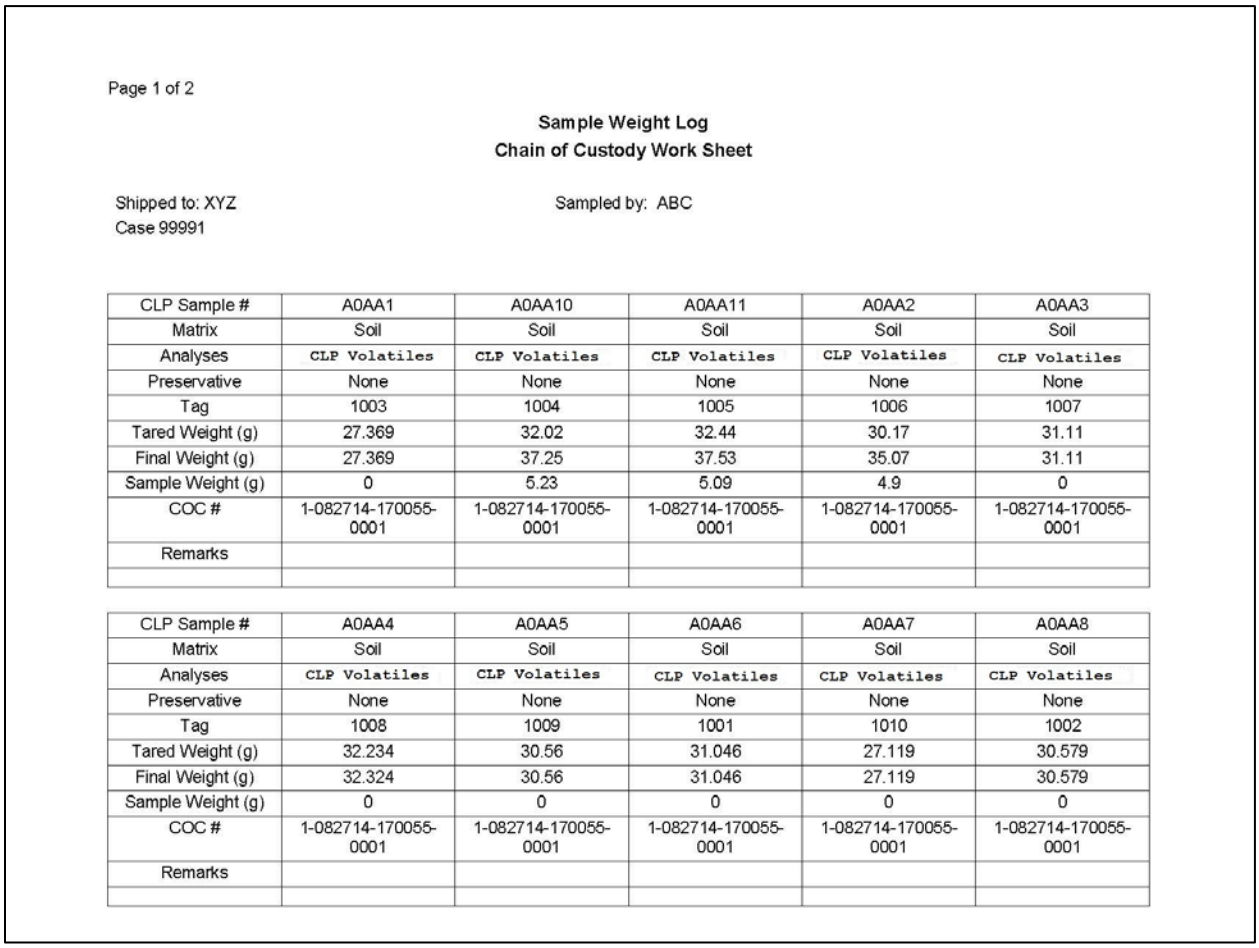
A sample label is a sticker that is attached to a sample bottle or container that contains a field sample or quality control (QC) sample.

- ☐ Sample labels are affixed to each sample container as samples are collected in the field or prior to going in the field.
- ☐ A sample label must contain, at a minimum, the sample number so that the sample can be associated with, and listed on, the associated TR/COC Record.

- Sample labels should also include the required analysis, CLP Case Number, and preservative used (to eliminate confusion at the laboratory). Samplers should refer to their site-specific project plans for Region-specific sample label requirements.
- Site information (e.g., address, site ID) should not be included on the sample label or container.
- Sample tags are NOT required by the CLP.

4.6 Sample Weight Logs

A sample weight log (Figure 4-1) identifies the tared, sample, and final weights per bottle for soil samples for Volatile Organic Analyte (VOA) analysis. In order to support the SOW requirements for VOAs, samplers should enter tared and final weights per bottle in the sample weight log. Sample weight logs are mandatory for VOA soil samples.



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Sample Weight Log
Chain of Custody Work Sheet

Shipped to: XYZ
Case 99991

Sampled by: ABC

CLP Sample #	A0AA1	A0AA10	A0AA11	A0AA2	A0AA3
Matrix	Soil	Soil	Soil	Soil	Soil
Analyses	CLP Volatiles	CLP Volatiles	CLP Volatiles	CLP Volatiles	CLP Volatiles
Preservative	None	None	None	None	None
Tag	1003	1004	1005	1006	1007
Tared Weight (g)	27.369	32.02	32.44	30.17	31.11
Final Weight (g)	27.369	37.25	37.53	35.07	31.11
Sample Weight (g)	0	5.23	5.09	4.9	0
COC #	1-082714-170055-0001	1-082714-170055-0001	1-082714-170055-0001	1-082714-170055-0001	1-082714-170055-0001
Remarks					

CLP Sample #	A0AA4	A0AA5	A0AA6	A0AA7	A0AA8
Matrix	Soil	Soil	Soil	Soil	Soil
Analyses	CLP Volatiles	CLP Volatiles	CLP Volatiles	CLP Volatiles	CLP Volatiles
Preservative	None	None	None	None	None
Tag	1008	1009	1001	1010	1002
Tared Weight (g)	32.234	30.56	31.046	27.119	30.579
Final Weight (g)	32.324	30.56	31.046	27.119	30.579
Sample Weight (g)	0	0	0	0	0
COC #	1-082714-170055-0001	1-082714-170055-0001	1-082714-170055-0001	1-082714-170055-0001	1-082714-170055-0001
Remarks					

Figure 4-1. Scribe Sample Weight Log

5.0 THE SCRIBE DOCUMENTATION SOFTWARE TOOL



The U.S. Environmental Protection Agency (EPA) Analytical Services Branch (ASB) requires samplers to use the Scribe software to create documentation for all Contract Laboratory Program (CLP) sampling efforts. The EPA recommends that a dedicated member of the sampling team be trained in the Scribe software, and be responsible for all uses of Scribe including the sample labels and the Traffic Report/Chain of Custody (TR/COC) Records at the sampling location. For assistance with obtaining or using the Scribe software, contact the Environmental Response Team (ERT) Software Support Help Desk at 800-999-6990 from 9:00 AM – 5:00 PM ET. For additional information regarding Scribe use and training materials, refer to the following website: https://response.epa.gov/scribe. Scribe allows users to create one or more sampling projects, enter data, and create sample documents for that project. Some of the capabilities of Scribe include:

- Tracking sample numbers and Case Numbers
- Associating analysis information to sample numbers
- Creating sample labels
- Setting label size and printing labels
- Selecting sample numbers to add to the chain of custody record
- Printing chain of custody records
- Filtering lists of samples
- Exporting sample data in the following formats: text file (.txt, .csv), spreadsheet (.xls, .wb3), HTML (.htm), XML (.xml), or QuickMap (.kml, .kmz)

The Scribe software tool allows users to track samples electronically. It can be downloaded at no charge from the EPA On-Scene Coordinator (OSC) website at https://www.ertsupport.org/downloads.htm

5.1 Setting Up a Sampling Event in Scribe

Scribe allows the sampler to enter much of the information prior to the event in order to facilitate processing on the day of the event. The following sections describe how to set up the sampling event in Scribe.

5.1.1 Set Up Project

The initial step when using Scribe is to set up the project as follows:

- ☐ Access the Scribe **New Project Wizard** to set up the sampling project.
- ☐ Enter the project **Site Name**, **Site #**, and **Region #** (required).
- ☐ Enter additional project information, if available. The eXtensible Markup Language (XML) file for the Case can be imported from the Sample Management Office (SMO) Contract Laboratory Program Support System (CLPSS) Portal and will customize the analysis and lab lists.

5.1.2 Create Analysis Types

The analysis types to be used for the sampling event must be defined for the project. Refer to the site sampling plan to determine which analyses are to be used.

- Use the **Analyses** table to display a list of all the analysis types available.
- Only analyses with the Program Type of "CLP," such as "CLP ICP-AES Metals," or "CLP Semivolatiles" should be selected for CLP Cases.
- If the required analysis type is missing, it can be added manually using the **Add** button.

5.1.3 Set Default Sample Number Information

Set up the default values for sample number. This allows the samplers to let the system increment sample numbers, rather than hand entering each one.

- Select **File→Options→CLP/Tag Settings** to display the **CLP/Tag Settings** window.
- Enter the new default values and click **OK**.

5.1.4 Indicate Modified Analysis (MA) on Scribe COC Records

When completing a TR/COC Record in Scribe, indicate an MA as follows:

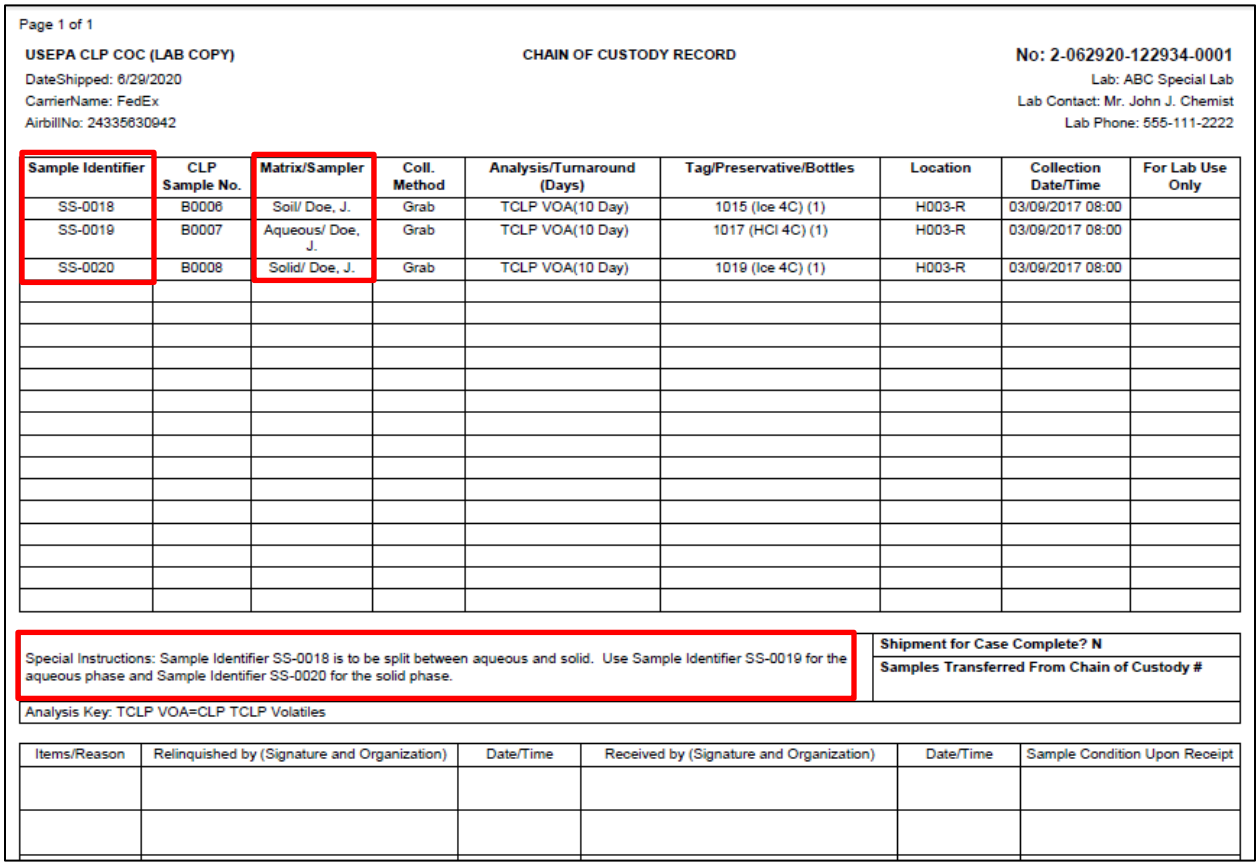
- Identify the samples that will be analyzed using (a) CLP MA(s) by creating a new analysis within the Scribe Analyses table or at the time of entering the Analyses for the sample.
- The MA analysis should contain the Modification Reference Number within the name assigned to the analysis. For example, if a Region submits an MA for an additional analyte, and the SMO assigns the Modification Reference Number 3001.0, the Scribe Analyses could be named "CLP VOA by MA 3001.0.". The associated abbreviation for this analysis could be "VOA MA".

5.1.5 Using Scribe for Mixed-matrix Samples

The Scribe **LinkSampleNo** field links the original sample to the split samples and numbers. Use this field to link to the sample IDs used for the different sample phases as follows:

- Add two (2) additional samples in Scribe indicating in the matrix field which one is the liquid/aqueous phase and which one is the solid phase (i.e., ABC124 and ABC125).
- Tie the two additional samples to the original sample number using the "LinkSampleNo" field.
  - **In Scribe**, in the **Samples** tab, click the **View** button; the **Select Columns** drop-down menu displays. Put a checkmark next to **LinkSampleNo** to make that column visible.
  - Add the "parent" or the original field sample # in the **LinkSampleNo** column (i.e., ABC123).
  - **On the COC Record**, indicate in the **Special Instructions** which of the two new sample numbers the laboratory is to use for the liquid/aqueous phase and which sample number is to be used for the solid phase.

An example of a Scribe COC Record with mixed-matrix samples is shown in Figure 5-1.



Page 1 of 1

USEPA CLP COC (LAB COPY) **CHAIN OF CUSTODY RECORD** **No: 2-062920-122934-0001**

DateShipped: 6/29/2020
CarrierName: FedEx
AirbillNo: 24335630942

Lab: ABC Special Lab
Lab Contact: Mr. John J. Chemist
Lab Phone: 555-111-2222

Sample Identifier	CLP Sample No.	Matrix/Sampler	Coll. Method	Analysis/Turnaround (Days)	Tag/Preservative/Bottles	Location	Collection Date/Time	For Lab Use Only
SS-0018	B0006	Soil/ Doe, J.	Grab	TCLP VOA(10 Day)	1015 (Ice 4C) (1)	H003-R	03/09/2017 08:00	
SS-0019	B0007	Aqueous/ Doe, J.	Grab	TCLP VOA(10 Day)	1017 (HCl 4C) (1)	H003-R	03/09/2017 08:00	
SS-0020	B0008	Solid/ Doe, J.	Grab	TCLP VOA(10 Day)	1019 (Ice 4C) (1)	H003-R	03/09/2017 08:00	

Special Instructions: Sample Identifier SS-0018 is to be split between aqueous and solid. Use Sample Identifier SS-0019 for the aqueous phase and Sample Identifier SS-0020 for the solid phase.

Shipment for Case Complete? N

Samples Transferred From Chain of Custody #

Analysis Key: TCLP VOA=CLP TCLP Volatiles

Items/Reason	Relinquished by (Signature and Organization)	Date/Time	Received by (Signature and Organization)	Date/Time	Sample Condition Upon Receipt

Figure 5-1. Scribe Mixed-Matrix Samples

5.2 Scribe CLP Analysis Codes

The following table lists the analysis codes used for CLP samples in Scribe.

Table 5-1. Scribe CLP Analysis Codes

Analysis Name	Abbreviation
Aroclors	
CLP Aroclors	ARO
High Resolution	
CLP 12 Toxic Congeners	12 Toxic CBCs
CLP 209 Congeners	209 CBCs
CLP Dioxins/Furans	CDD/CDF
Inorganics	
CLP Aluminum	Al
CLP Anions (F, Cl, Br, SO4, NO3, NO2, PO4)	Anions
CLP Anions (F, Cl, Br, SO4)	Anions 28Day
CLP Anions (NO3, NO2, PO4)	Anions 48Hour
CLP Antimony	Sb
CLP Arsenic	As
CLP Barium	Ba
CLP Beryllium	Be

Table 5-1. (Continued) Scribe CLP Analysis Codes

Analysis Name	Abbreviation
CLP Cadmium	Cd
CLP Calcium	Ca
CLP Chromium	Cr
CLP Cobalt	Co
CLP Copper	Cu
CLP Cyanide	CN
CLP Hardness	Hardness
CLP Hexavalent Chromium	Cr+6
CLP ICP-AES Metals	ICP-AES
CLP ICP-MS Metals	ICP-MS
CLP Iron	Fe
CLP Lead	Pb
CLP Magnesium	Mg
CLP Manganese	Mn
CLP Mercury	Hg
CLP Nickel	Ni
CLP Potassium	K
CLP Selenium	Se
CLP Silver	Ag
CLP Sodium	Na
CLP SPLP Aluminum	SPLP Al
CLP SPLP Antimony	SPLP Sb
CLP SPLP Arsenic	SPLP As
CLP SPLP Barium	SPLP Ba
CLP SPLP Beryllium	SPLP Be
CLP SPLP Cadmium	SPLP Cd
CLP SPLP Calcium	SPLP Ca
CLP SPLP Chromium	SPLP Cr
CLP SPLP Cobalt	SPLP Co
CLP SPLP Copper	SPLP Cu
CLP SPLP Cyanide	SPLP CN
CLP SPLP ICP-AES Metals	SPLP ICP-AES
CLP SPLP Iron	SPLP Fe
CLP SPLP Lead	SPLP Pb
CLP SPLP Magnesium	SPLP Mg
CLP SPLP Manganese	SPLP Mn
CLP SPLP Mercury	SPLP Hg
CLP SPLP Nickel	SPLP Ni
CLP SPLP Potassium	SPLP K
CLP SPLP Selenium	SPLP Se
CLP SPLP Silver	SPLP Ag
CLP SPLP Sodium	SPLP Na

Table 5-1. (Continued) Scribe CLP Analysis Codes

Analysis Name	Abbreviation
CLP SPLP Thallium	SPLP Tl
CLP SPLP Vanadium	SPLP V
CLP SPLP Zinc	SPLP Zn
CLP TCLP Arsenic	TCLP As
CLP TCLP Barium	TCLP Ba
CLP TCLP Cadmium	TCLP Cd
CLP TCLP Chromium	TCLP Cr
CLP TCLP ICP-AES Metals	TCLP ICP-AES
CLP TCLP Lead	TCLP Pb
CLP TCLP Mercury	TCLP Hg
CLP TCLP Selenium	TCLP Se
CLP TCLP Silver	TCLP Ag
CLP Thallium	Tl
CLP Total Organic Carbon Water	TOC Water
CLP Total Organic Carbon Soil	TOC Soil
CLP Vanadium	V
CLP Zinc	Zn
Organics	
CLP PAH+PCP	PAH
CLP PAH+PCP by SIM	PAH SIM
CLP Semivolatiles	SVOA
CLP SPLP Semivolatiles	SPLP SVOA
CLP SPLP Volatiles	SPLP VOA
CLP TCLP Semivolatiles	TCLP SVOA
CLP TCLP Volatiles	TCLP VOA
CLP Trace Volatiles	TVOA
CLP Trace Volatiles by SIM	TVOA SIM
CLP Volatiles	VOA
Pesticides	
CLP Pesticides	PEST
CLP SPLP Pesticides	SPLP PEST
CLP TCLP Pesticides	TCLP PEST



To avoid issues with interpretation, ensure that Total Metals and Dissolved Metals are labeled with separate sample IDs.

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6.0 CLP SAMPLE CONTAINERS

The analytical protocol(s) for sample analysis often requires the use of a specific type of sample container. The type of container will also depend on the sample matrix.

It is recommended that samplers use borosilicate glass containers which are inert to most materials when sampling for pesticides and/or other organics, and for Total Organic Carbon (TOC). Borosilicate glass is also recommended for sampling soils for metals. Conventional polyethylene is recommended when sampling for metals and anions in water because of the lower cost and absorption rate of metal ions.



Have extra containers readily available for each sampling event in case of breakage, loss, or contamination.

Containers procured for a sampling event are usually pre-cleaned and shipped ready for use from the manufacturer to the sampling site. Regardless of the type of container used, samplers must ensure that the containers have been analyzed or certified clean to levels below concern for the project based on the specifications in the Quality Assurance Project Plan (QAPP). Certificates must be kept on record. These containers must meet the U.S. Environmental Protection Agency (EPA) container type specifications listed in Tables D-1 through D-4 in Appendix D.



Samplers should document the lot numbers for every lot of cleaned containers used for each project and maintain corresponding certificates of analysis on file and available upon request.

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7.0 CLP SAMPLE COLLECTION

Samplers should determine the types of samples or aliquots to be collected, the volume required for each aliquot, and the preservation requirements by referring to the Site Project Plan (SPP) and Contract Laboratory Program (CLP) sample requirements tables in Appendix D. The following sections describe the types of samples that may be required to be collected.



7.1 Requesting the Scheduling of the Laboratory

Samplers must request that the Regional Sample Control Coordinator (RSCC) schedule the laboratory to be used for the analysis. This should be done as far in advance of the sampling event as possible.

- If one or more Modified Analysis (MA) will be required, scheduling requests should be submitted at least four weeks prior to the start of the sampling event to allow the solicitation process to be completed.
- Samplers should provide information regarding the number of samples, analyses, etc. and if Saturday delivery is likely. If known, additional information regarding weekly shipping frequency is helpful to include.
- When scheduling a sampling event that will last for more than one week, it is recommended that the sampler contact the RSCC (or designee) on a weekly basis to provide updates. Communication between the sampler, the RSCC (or designee), and the Sample Management Office (SMO) is important as it ensures better availability of laboratory capacity.
- If the time frame or number of samples for a sampling event changes, the RSCC and SMO should be notified as soon as possible to maintain capacity at the scheduled laboratory.
- The Region should contact the Analytical Services Branch (ASB) in advance if it is suspected that the samples may contain asbestos.



The CLP has the capability to schedule sampling on an emergency basis; however, the sampler must contact the RSCC (or designee) to obtain details regarding how to handle such a situation.

7.2 Preparing for the Shipping of Samples

Once the samples are collected, they will be shipped to the CLP laboratory for analysis. Samplers must have the necessary shipping supplies on site.

7.2.1 Procure Shipping Supplies

Samplers should refer to the appropriate project plans to determine the types of samples that will be collected during the sampling project to determine the necessary packaging materials to have at the site for all pertinent sample container types and sample matrices.

Samplers should also obtain the appropriate shipping paperwork (e.g., shipping forms required by the delivery service).



The CLP strongly discourages the use of vermiculite and cat litter as sources for packing material. These materials interfere with labeling and documentation and are difficult to remove from sample containers and shipping containers.

7.2.2 Laboratory Assignment Notification

Prior to beginning fieldwork, the samplers may either download an "Analytical Services Request Regional Notification" file via the Access Assignment Information task in the SMO Contract Laboratory Program Support Services (CLPSS) Portal, or obtain it from the RSCC.



The "Analytical Services Request Regional Notification" applies only to activities being performed under the CLP Statements of Work (SOWs).

7.2.3 Verify Laboratory Shipping Information

Samplers should verify the laboratory contact information, including the following:

- Laboratory name
- Laboratory address
- Contact name
- Laboratory phone number

This information, which is provided on the "Analytical Services Request Regional Notification", is used to complete both the Traffic Report/Chain of Custody (TR/COC) Records and shipping paperwork such as address labels and airbills. This file may be accessed through the SMO CLPSS Portal, or can be obtained from the RSCC prior to sampling.

7.2.4 Obtain Shipping Company Information

Samplers should also verify the shipping company information, including the following:

- Company name
- Telephone number
- Account number
- Pickup schedule



Additional guidance will be provided by the U. S. Environmental Protection Agency (EPA) if samples are to be shipped internationally. Also, see Appendix F, International Shipping.

7.2.5 Prepare Sample Container Return Documentation

CLP laboratories must routinely return sample shipping containers to the appropriate sampling office within 14 calendar days following receipt of shipment from the sampler. To ensure that empty sample shipping containers are returned to the appropriate sampling office, samplers must complete the applicable container documentation and work with Regional personnel and government agencies to provide a cost-effective mechanism for this process. The sampling container return documentation should be prepared in advance and provided to samplers before field activities begin.

The sampler (not the CLP laboratory) is responsible for the cost of the return or disposal of the container and should also include shipping airbills bearing the sampler's account number, as well as a return address, to allow for container return.

To maintain consistency across shipping container transportation programs, samplers should proceed as follows:

- Minimize the use of multiple transportation carriers.
- Use multiple-copy labels so the laboratory and the sampling team can each retain a copy for their records.
- Prepare labels in advance so that the laboratory can simply affix a completed shipping label on the container.
- Include third-party billing information (i.e., their shipping account number) on labels so the laboratory will not be billed by the transportation carrier.
- Confirm that the laboratory has been notified of the transportation carrier being used.
- Include the SMO CLPSS Portal-generated CLP Case Number on the return information.

7.3 Collecting Samples

The CLP requirements for sample volumes, preservation, and contractual holding times are defined by the applicable CLP SOWs, and outlined in the tables in Appendix D.

Samplers should follow the sample collection requirements for analyses as provided in the following tables in Appendix D:

- Organic methods (Tables D-1 and D-2)
- Inorganic methods (Table D-3)
- High Resolution methods for Dioxins/Furans and Chlorinated Biphenyl Congeners (CBCs) (Table D-4).

For an explanation of the various sample types and the requirements for collecting and submitting each particular type, refer to Table 7-1.

Table 7-1. Sample Types and CLP Submission Requirements

Sample Type	Purpose	Collection[1]	CLP Sample Number
Field Sample	To analyze for target analytes of interest	Collect from areas that are known or suspected to be contaminated. Collect at the frequency specified in the Quality Assurance Project Plan (QAPP) and Sampling and Analysis Plan (SAP).	Assign CLP Sample Numbers to the sample.
Field Duplicate	To check reproducibility of laboratory and field procedures To indicate non-homogeneity	Collect from areas that are known or suspected to be contaminated. Collect at the frequency specified in the QAPP and SAP.	Assign two separate (unique) CLP Sample Numbers (i.e., one number to the field sample and one to the duplicate). Submit single blind to the laboratory.

Table 7-1. (Continued) Sample Types and CLP Submission Requirements

Sample Type	Purpose	Collection[1]	CLP Sample Number
Field Blank	To check cross-contamination during sample collection, preservation, and shipment, as well as in the laboratory Also to check sample containers and preservatives	Collect for each group of samples of similar matrix at the frequency specified in the QAPP and SAP. Organics - Use water (demonstrated to be free of the contaminants of concern). Inorganics - Use metal-free (deionized or distilled) water or a single clean wipe.	Assign separate CLP Sample Numbers to the field blanks. Submit single blind to the laboratory.
Filter Blank	To check contamination of samples from filtering procedure	Collect when water samples are filtered by filtering blank water using the same procedure and filtering equipment that is used for samples. Use blank water (water demonstrated to be organic-free, deionized or distilled for inorganics) and collect into sample containers.	Assign separate CLP Sample Numbers to the filter blanks. Submit single blind to the laboratory.
Temperature Blank	To provide an accurate measurement of field sample temperature upon arrival to the laboratory Also to establish whether the temperature range has been maintained while in transit	Collect for each shipping container with the frequency specified in the QAPP and SAP.	Ship together with samples from the field to the laboratory. A CLP Sample Number is not required.
Trip Blank [Volatile Organic Analyte (VOA) analysis Only]	To check contamination of VOA samples during handling, storage, and shipment from field to laboratory	Prior to going into the field, prepare and seal one trip blank sample per shipment per matrix. Trip blanks should be matched with respect to matrix and volume of the preservatives used. Prepare trip blank samples with the same preservatives and reagent water used for the corresponding samples. Carry each through the same sampling and handling protocols used for field samples. Aqueous trip blank samples should be prepared using water demonstrated to be free of the contaminants of concern (deionized water is appropriate). Place one trip blank sample for each matrix in each container used to ship VOA samples.	Assign separate CLP Sample Numbers to the trip blanks. Submit single blind to the laboratory.
Equipment Blank or Rinsate Blank	To check field decontamination procedures	Collect when sampling equipment is decontaminated and reused in the field or when a sample collection vessel (bailer or beaker) will be used. Use blank water (water demonstrated to be organic-free, deionized or distilled for inorganics) and pour rinse water into the sample containers.	Assign separate CLP Sample Numbers to the equipment blanks/rinsate. Submit single blind to the laboratory.

Table 7-1. (Continued) Sample Types and CLP Submission Requirements

Sample Type	Purpose	Collection[1]	CLP Sample Number
Matrix Spike (MS) and Matrix Spike Duplicate (MSD) (Organic Analysis Only)	To check accuracy and precision of organic analyses in specific sample matrices	Collect from areas that are known or suspected to be contaminated. MS/MSD are optional per Regional direction.	Assign the same CLP Sample Number to the field sample and the extra volume for MS/MSD. Identify the sample designated for MS/MSD on the TR/COC Record.
Matrix Spike (MS) and Laboratory Duplicate (Inorganic Analysis Only)	To check accuracy and precision of inorganic analyses in specific sample matrices	Collect from areas that are known or suspected to be contaminated. It is recommended that MS and Duplicates be collected in the first round of sampling and included in the first shipment of samples to the laboratory.	Assign the same CLP Sample Number to the field sample and extra volume (if collected). Identify the sample(s) designated for MS and Duplicates on the TR/COC Record.
Performance Evaluation (PE) Samples	Specially-prepared Quality Control (QC) samples used to evaluate a laboratory's analytical proficiency	The PE samples contain analytes with concentrations unknown to the laboratory. Designated Regional or authorized personnel (depending on Regional policy) arrange for Case-specific CLP PE samples to be prepared and shipped by the Quality Assurance Technical Support (QATS) contractor. The PE samples can be shipped to the site, or shipped per Regional direction. QATS provides the appropriate preparation instructions and chain of custody materials.	Samplers must order PE samples and ship them to the laboratory if required by the Region. Assign separate CLP Sample Numbers to the PE samples. Include PE ampule numbers on the TR/COC Record.

[1] Consult Regional or Project Manager Guidance for field QC sample frequencies; laboratory QC sample frequencies are generally fixed in the laboratory contracts or specified in analytical methods.

7.3.1 Field QC Samples

Field QC samples are designed to assess variability of the media being sampled and to detect contamination and sampling errors in the field. The types of field QC samples that are generally collected include the following:

- Field duplicates
- Field blanks (such as equipment, trip, or rinse blanks)

Unless otherwise instructed, field duplicate samples should remain "blind" to the laboratory (i.e., they should have separate CLP Sample Numbers).

7.3.2 Laboratory QC Samples

A laboratory QC sample is an additional analysis of a field sample, as required by the laboratory's contract. There are three types of such samples:

- MS (for organic and inorganic samples)
- MSD (for organic samples only)
- Duplicates (for inorganic samples only)

Samplers should observe the following guidelines when collecting laboratory QC samples:

☐ Follow Regional guidance regarding the collection of laboratory QC samples.

- Regarding Gas Chromatography/Mass Spectrometry (GC/MS) organic analyses, a Region may decide to reference Deuterated Monitoring Compounds (DMCs) rather than MS/MSD for accuracy and precision.

- ☐ Wipe samples do not require laboratory QC samples.
- ☐ When laboratory QC is scheduled for CLP analyses, samplers should select one sample per matrix per Sample Delivery Group (SDG). An SDG closes when 20 samples are received for a Case or one week (3 days for 7-day turnaround samples) has elapsed, whichever comes first. Designate MS/MSD for Pesticides, Aroclors, and GC/MS analyses as directed. For GC/MS, MS/MSD are optional per Regional direction. Designate MS and laboratory Duplicate for metals, mercury, cyanide, anions, hexavalent chromium, and Total Organic Carbon (TOC). Samplers should not select a field blank or a PE Sample for laboratory QC.
- ☐ Designated samples should be identified on the TR/COC Record; the sample(s) designated for laboratory QC should be noted in "Sample Type" column.
- ☐ QC samples should be shipped in the same container as the field samples when possible.



Field QC samples should not be designated as laboratory QC samples.



In the event of multiple sample shipments during a sampling event, it is recommended that the sampler submit laboratory QC samples in the first sample shipment, and as necessary in subsequent shipments to meet laboratory contract requirements.

7.4 Recording Samples

Samplers must use Scribe to record the samples that are collected. To record the samples:

- ☐ Access the Scribe **Sampling** tab to select the type of sampling (Water Sampling, Soil/Sediment Sampling, Wipe Sampling).
- ☐ Enter the detailed information for the sample. Include laboratory analysis for each sample; see tabs for sample details and for analysis.
- ☐ When all information has been entered, click the **Close** button at the bottom of the page to save the entries and close the window.

Refer to Table 5-1 for the CLP analysis codes.

For assistance while using the Scribe software, contact the Environmental Response Team (ERT) Software Support Help Desk at 800-999-6990 from 9:00 AM – 5:00 PM ET. Refer to the following website for information on the use and training of Scribe:
https://response.epa.gov/site/site_profile.aspx?site_id=ScribeGIS

7.4.1 Hardcopy Recording

In the event that Scribe is unavailable, samplers must have backup hardcopy Scribe TR/COC Records. This should be done only in cases of power/equipment failure, and not as a matter of routine during a sampling event.

7.5 Meeting Volume, Preservation, and Holding Time Requirements

Samplers should refer to Tables D-1 through D-4 in Appendix D to obtain the specific sample volumes to be collected, the preservation needed for those samples, and the technical holding times under which they must submit samples to the scheduled CLP laboratory.

7.5.1 Collect Required Sample Volumes

Samplers should ensure that a sufficient volume is collected for each sample. If the sample volume does not meet the requirement set by the project plan, the laboratory may not be able to analyze the sample correctly. Questions regarding collecting lesser volumes than those listed in Tables D-1 through D-4 in Appendix D should be directed to ASB.

Refer to Appendix B for information regarding the collection of aqueous VOA samples. When collecting samples for VOA in soils, samplers must use the SW-846 Method 5035A guidelines included in Appendix C.



If tissue samples are homogenized or processed, it should be performed at a sample processing facility under clean room conditions to reduce potential contamination. Tissue samples should be packed and cooled on ice immediately. Tissue samples should never be sent on Friday for Monday delivery.

7.5.2 Preserve Samples

Without preservation, some samples (e.g., VOAs) may degrade to the point that they will not provide accurate results for the site. The sampler must chemically preserve some water samples for certain analytes prior to shipping them to the laboratory.

Samplers should observe the following procedures:

- ☐ Note any visible reaction between the sample and added chemical preservative in the field record.
- ☐ Preserve and immediately cool all organic, cyanide, hexavalent chromium, and anions (nitrate, nitrite, orthophosphate, and sulfate) water samples to ≤ 6°C, but not frozen, upon collection.
- ☐ Keep samples cooled until shipping (do not freeze water samples).
- ☐ Preservation techniques vary among Regions, so samplers should obtain Region-specific instructions and review the appropriate project plans and Standard Operating Procedures (SOPs).
- ☐ Refer to Appendix B for information regarding the collection of VOA water samples.

7.5.3 Ship Samples within Holding Times

There are two types of holding times: technical and contractual.

- **The technical holding time** is the maximum amount of time allowed between sample collection and the completion of sample extraction and/or analysis.
- **The contractual holding time** is the maximum amount of time that the CLP laboratory can hold a sample prior to extraction and/or analysis. The contractual holding time is the elapsed time expressed in days from the date of receipt of the sample by the laboratory until the date of its extraction and/or analysis, as specified in the applicable CLP SOW.



Contractual holding times are generally set to be two days less than the technical holding times to allow for sample packing and shipping.

Samplers should ship samples to scheduled CLP laboratories as soon as possible after collection.

- Ship samples daily to CLP laboratories whenever possible.
- Samples for certain anions (nitrate, nitrite, and orthophosphate) must ship the same day to meet holding times.
- If samples cannot be shipped on a daily basis, they must be properly preserved and maintained to meet CLP-specified temperatures, holding times, and custody requirements.
- Uploading the electronic TR/COC Record is mandatory and should be performed as soon as possible after shipping.



If samplers are shipping samples after 5:00 PM ET, they should notify the RSCC (or designee) and SMO by 8:00 AM ET on the following business day. When making a Saturday delivery, samplers should notify the RSCC (or designee) and SMO as soon as possible so that SMO will receive the delivery information (including shipping airbill information) by 3:00 PM ET on the Friday prior to delivery. Uploading the electronic TR/COC Record to the SMO CLPSS Portal sends a notification to SMO and to the laboratory that the samples have been shipped.

7.6 Completing the Documentation

The sample documentation required is defined by the project plan. It is highly recommended that samplers provide documentation, even if the Region does not require it.

In general, samplers must complete the following documentation for the samples collected:

- CLP Sample Number (on the sample container or bottle)
- Sample label
- Chain of custody seals (as appropriate)
- TR/COC Record
- Field operations records (as necessary)



Under no circumstances should the site name or address appear on any documentation being sent to the laboratory, unless the laboratory is a Regional EPA laboratory.

An example of a packaged sample is shown in Figure 7-1.

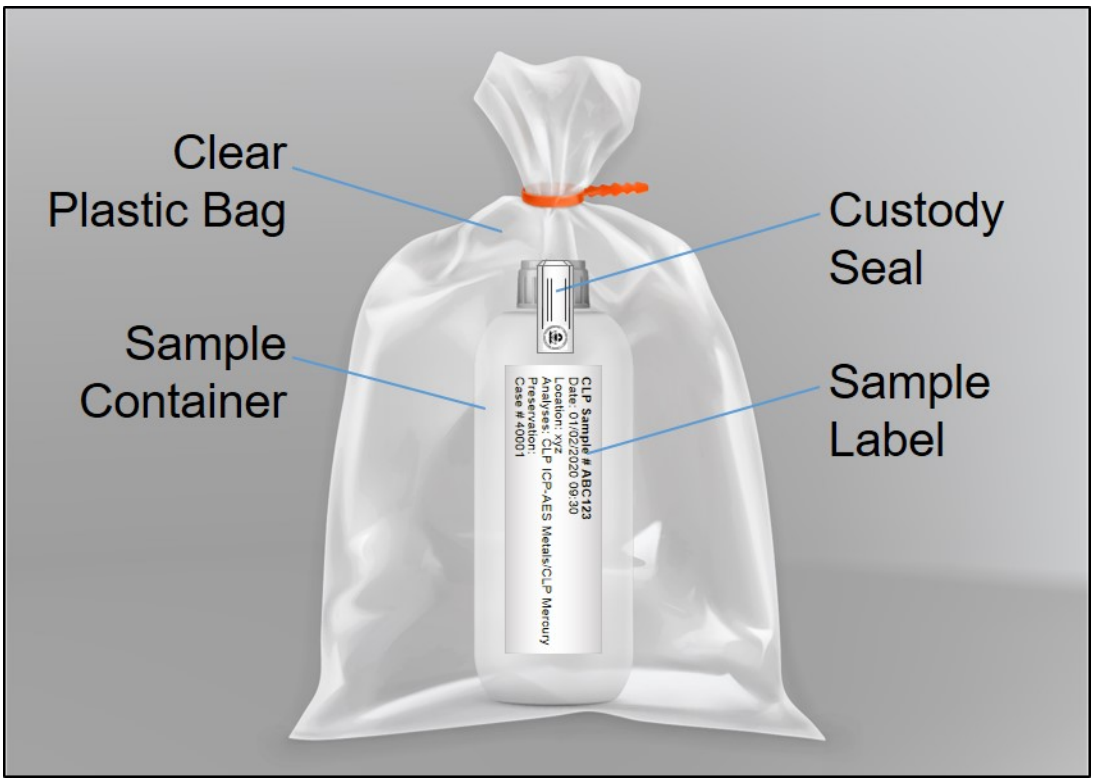


Figure 7-1. Packaged Sample with Identification and Chain of Custody Documentation (Excluding TR/COC Record)

7.6.1 Record and Label the Samples

The sample labels created in Scribe must be affixed to each sample container. A sample label contains the following information:

- Associated CLP Sample Number (either written or pre-printed)
- SMO CLPSS Portal-generated CLP Case Number
- Preservative used
- Analysis
- Additional information such as the location or the date/time of collection

Samplers should record and label the samples collected as follows:

- ☐ Using Scribe, select the **Sampling** tab to select the type of matrix (e.g., Soil/Sediment, Water Sampling).
- ☐ Access the Scribe **Sample Details** page to enter the analysis method, CLP Sample Number, and SMO CLPSS Portal-generated CLP Case Number for each sample.
- ☐ Enter samples associated with an MA by using the MA analysis previously created in Scribe. If the MA does not exist, refer to Section 5.1.2, Create Analysis Types, to create the analysis type for the MA.
- ☐ Print the sample label and place it on the sample container or bottle.
- ☐ If handwriting a sample label, complete the information using waterproof ink, place the label on the outside of the sample bottle or container, then cover the label with clear packaging tape to protect it and maintain legibility.
- ☐ Avoid wrinkles in the tape and labels.
- ☐ Sample tags are NOT required by the CLP.
- ☐ Refer to Figure 7-1 for an example of sample label placement.

Use the following guidelines for these special conditions:

- **Water samples collected for total metals and filtered metals analyses from the same sampling location** - must assign separate (unique) CLP Sample Numbers.
- **Tared VOA sample vials** - must not attach labels to tared VOA sample vials.

7.6.2 Complete the COC Records in Scribe

Samplers should use the Scribe format for CLP projects. Complete the Scribe COC Record as follows:

Access the Scribe COC Page

- Select the **Chain of Custody** link under the **Sample Management** header. The ***Chain of Custody*** page displays.

Create the COC Record

- Click the **Add a Chain of Custody** button at the bottom of the page. The ***COC Details*** pop-up window displays.
- Enter the information for the COC, including selecting the **CLP format** (Inorganic, Organic, or High Resolution).

  Note: It is important that the correct **COC Format** is selected when the COC Record is created. The user should choose the CLP format for the type of samples being submitted, as shown in Figure 7-2.

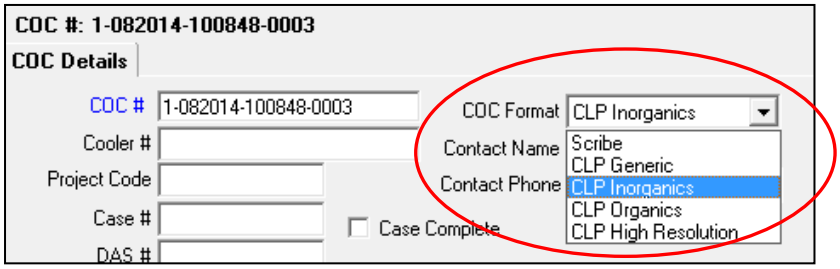


Figure 7-2. COC Details Pop-up Window

- Ensure that the **Case #** is also filled in. (If it was entered in the CLP/Tag Settings, it will automatically be filled in.)

Assign Samples to the COC Record

- Assign samples to the **COC Record** (it will filter based on selected COC format SOW).
- Ensure that all sample information has been entered.
- Enter any additional information, such as sampler name, matrix, and preservation.
- Indicate any samples that will be analyzed using an MA.
- Scribe generates a laboratory and a Regional copy of the COC Record (see Figures 7-3 and 7-4).

Print the COC Record

- Print the **COC Record** by selecting either the **Lab Copy** or **Region Copy**. There will be a QC check; ensure that all information is filled in.
- Print as many copies of the **COC Record** as is necessary.
- Sign and submit original copies of the **COC Record**.



Sampler information, etc., is not added when creating the COC Record; it is added when editing the sample itself.

7.6.3 Making Manual Edits to Printed Scribe COC Records

If a Scribe COC Record has been printed and deletions or edits need to be made, samplers must use the following procedures:

- If making a deletion, delete the incorrect information in Scribe, reprint the COC Record, and discard the original.
- If making an addition, enter the new information in Scribe, reprint the COC Record, and discard the original.
- If corrections occur after shipment, adhere to the Regional procedures and guidelines for handling hardcopy COC Records.

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USEPA CLP COC (LAB COPY) | **CHAIN OF CUSTODY RECORD** | **No: 2-010614-124708-0001**

DateShipped: 1/3/2020 | Lab: EPA Labs

CarrierName: FedEx | Case #: 21490 | Lab Contact: John Smith

AirbillNo: ABC12345 | Cooler #: | Lab Phone:

Sample Identifier	CLP Sample No.	Matrix/Sampler	Coll. Method	Analysis/Turnaround (Days)	Tag/Preservative/Bottles	Location	Collection Date/Time	For Lab Use Only
12345-0001	B0AA0	Soil/ EPA	Grab	SVOA(21)/PR, SVOA 1723.3(21)/PR, PEST(21), ARO(21), VOA(21), VOA MA(21)	(0 C), (0 C), (0 C), (0 C), (0 C), (0 C) (6)	ABC	01/03/2020 08:00	
12345-0002	B0AA1	Soil/ EPA	Grab	ARO(21), PEST(21), SVOA(21)	(0 C), (0 C), (0 C), (0 C) (4)	ABC	01/03/2020 08:00	
12345-0003	B0AA2	Soil/ EPA	Grab	ARO(21), PEST(21), SVOA(21)	(0 C), (0 C), (0 C), (0 C) (4)	DEF	01/03/2020 09:00	
12345-0004	B0AA3	Soil/ EPA	Grab	ARO(21), PEST(21), SVOA(21)	(0 C), (0 C), (0 C), (0 C) (4)	GHI	01/03/2020 10:00	
12345-0005	B0AA4	Soil/ EPA	Grab	ARO(21), PEST(21), SVOA(21)	(0 C), (0 C), (0 C), (0 C) (4)	JKL	01/03/2020 11:00	
12345-0006	B0AA5	Soil/ EPA	Grab	SVOA(21), SVOA 1723.3(21), PEST(21), ARO(21), VOA MA(21)	(0 C), (0 C), (0 C), (0 C), (0 C), (0 C) (6)	DEF	01/03/2020 09:00	
12345-0007	B0AA6	Soil/ EPA	Grab	SVOA(21), SVOA 1723.3(21), PEST(21), ARO(21), VOA MA(21)	(0 C), (0 C), (0 C), (0 C), (0 C), (0 C) (6)	GHI	01/03/2020 10:00	
12345-0008	B0AA7	Soil/ EPA	Grab	ARO(21), PEST(21), SVOA(21)	(0 C), (0 C), (0 C), (0 C) (4)	JKL	01/03/2020 11:00	

Sample(s) to be used for Lab QC: 12345-0001, 12345-0001, 12345-0001, 12345-0001, 12345-0001, 12345-0001

Shipment for Case Complete? Y

Samples Transferred From Chain of Custody #

Analysis Key: SVOA=CLP Semivolatiles, SVOA 1723.3=CLP SVOA MA 1723.3, PEST=CLP Pesticides, ARO=CLP Aroclors, VOA=CLP Volatiles, VOA MA=CLP VOA (MA 1722.4)

Items/Reason	Relinquished by (Signature and Organization)	Date/Time	Received by (Signature and Organization)	Date/Time	Sample Condition Upon Receipt

Figure 7-3. Scribe Chain of Custody Record (Laboratory Copy)

Page 1 of 1

USEPA CLP COC (REGION COPY)
DateShipped: 1/3/2020
CarrierName: FedEx
AirbillNo: ABC12345

CHAIN OF CUSTODY RECORD
Field Sampler's Guide
Case #: 21490
Cooler #:

No: 2-010614-124708-0001
Lab: EPA Labs
Lab Contact: John Smith
Lab Phone:

Sample Identifier	CLP Sample No.	Matrix/Sampler	Coll. Method	Analysis/Turnaround (Days)	Tag/Preservative/Bottles	Location	Collection Date/Time	Sample Type
12345-0001	B0AA0	Soil/ EPA	Grab	SVOA(21)/PR, SVOA 1723.3(21)/PR, PEST(21), ARO(21), VOA(21), VOA MA(21)	(0 C), (0 C), (0 C), (0 C), (0 C), (0 C) (6)	ABC	01/03/2020 08:00	Lab QC
12345-0002	B0AA1	Soil/ EPA	Grab	ARO(21), PEST(21), SVOA(21)	(0 C), (0 C), (0 C), (0 C) (4)	ABC	01/03/2020 08:00	Field Sample
12345-0003	B0AA2	Soil/ EPA	Grab	ARO(21), PEST(21), SVOA(21)	(0 C), (0 C), (0 C), (0 C) (4)	DEF	01/03/2020 09:00	Field Sample
12345-0004	B0AA3	Soil/ EPA	Grab	ARO(21), PEST(21), SVOA(21)	(0 C), (0 C), (0 C), (0 C) (4)	GHI	01/03/2020 10:00	Field Sample
12345-0005	B0AA4	Soil/ EPA	Grab	ARO(21), PEST(21), SVOA(21)	(0 C), (0 C), (0 C), (0 C) (4)	JKL	01/03/2020 11:00	Field Sample
12345-0006	B0AA5	Soil/ EPA	Grab	SVOA(21), SVOA 1723.3(21), PEST(21), ARO(21), VOA MA(21)	(0 C), (0 C), (0 C), (0 C), (0 C), (0 C) (6)	DEF	01/03/2020 09:00	Field Sample
12345-0007	B0AA6	Soil/ EPA	Grab	SVOA(21), SVOA 1723.3(21), PEST(21), ARO(21), VOA MA(21)	(0 C), (0 C), (0 C), (0 C), (0 C), (0 C) (6)	GHI	01/03/2020 10:00	Field Sample
12345-0008	B0AA7	Soil/ EPA	Grab	ARO(21), PEST(21), SVOA(21)	(0 C), (0 C), (0 C), (0 C) (4)	JKL	01/03/2020 11:00	Field Sample

Sample(s) to be used for Lab QC: 12345-0001, 12345-0001, 12345-0001, 12345-0001, 12345-0001, 12345-0001

Shipment for Case Complete? Y

Samples Transferred From Chain of Custody #

Analysis Key: SVOA=CLP Semivolatiles, SVOA 1723.3=CLP SVOA MA 1723.3, PEST=CLP Pesticides, ARO=CLP Aroclors, VOA=CLP Volatiles, VOA MA=CLP VOA (MA 1722.4)

Items/Reason	Relinquished by (Signature and Organization)	Date/Time	Received by (Signature and Organization)	Date/Time	Sample Condition Upon Receipt

Figure 7-4. Scribe Chain of Custody Record (Region Copy)

7.6.4 Complete and Attach Custody Seals

Custody seals are usually pre-printed stickers that are signed (or initialed) and dated by the samplers after sample collection and placed on sample bottles or containers and/or shipping containers (see Figure 7-5).

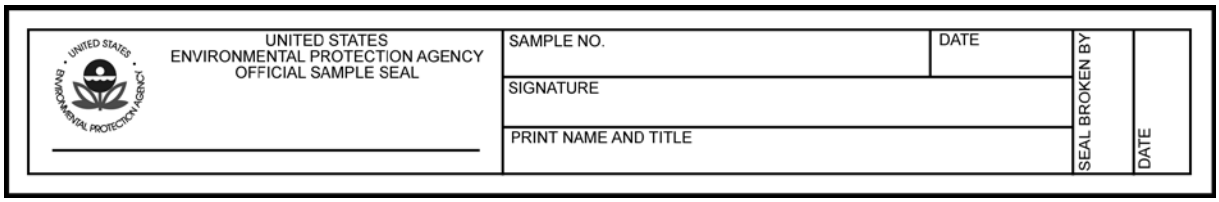


Figure 7-5. Custody Seal

The custody seal documents the individual who sealed the sample container and verifies that the sample has not been tampered with. Custody seals can also be used to maintain custody of other items such as envelopes.

The use and type of custody seals can vary by Region or collecting organization. Samplers should obtain the appropriate custody seals and specific instructions for their use from the RSCC. Note that some Regions require the sampling team to provide their own custody seals.

- Custody seals shall be placed in such a manner that they will break if the sample bottle or container, or the shipping cooler or container is tampered with or opened after leaving custody of the samplers.
- Custody seals should never be placed directly onto a coring tool used as a transport device (e.g., 5 g Sampler) or tared, 40 mL closed-system vials. The seals must be placed on the bag for the coring tool used as a transport device, or on the bag used to enclose the vials. Refer to Table 8-1 for details.

Instructions for completing and attaching a custody seal are included in Table 7-2.

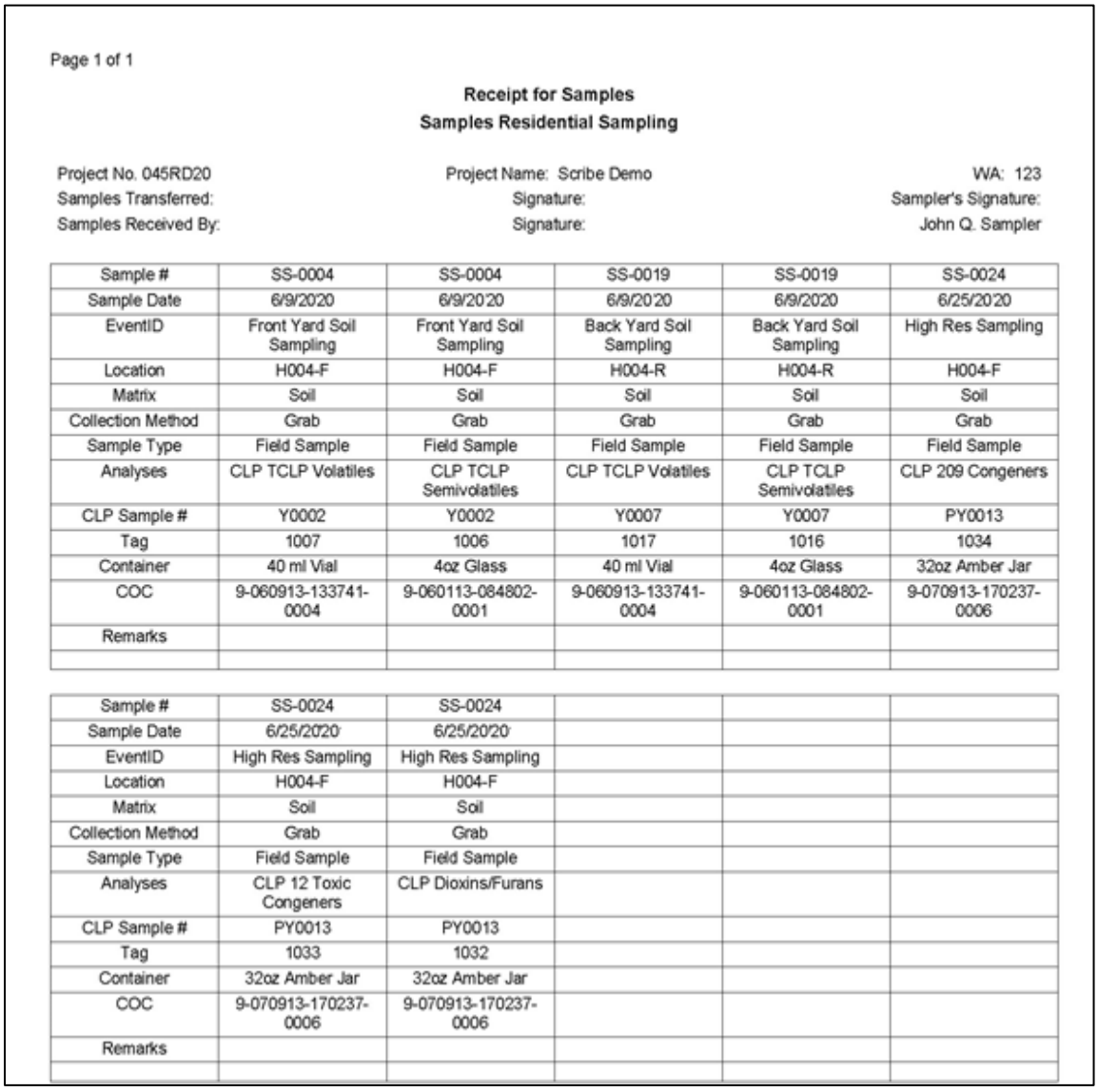
Table 7-2. Completing and Attaching a Custody Seal

Step	Action	Important Notes
1	Record the CLP Sample Number.	The space for the CLP Sample Number does not need to be completed on custody seals being placed on the opening of a shipping container, only on those being placed on the opening of sample bottles or containers.
2	Record the month, day, and year of sample collection.	
3	Sign the seal in the signature field.	
4	Print your name and title in the “Print Name and Title” field.	
5	Place the custody seal over the edge of the sample bottle or container such that it will break if tampered with.	Custody seals can be placed directly on any sample container except for coring tools used as a transport device (e.g., 5 g Samplers) and tared VOA bottles. If packing coring tools used as a transport device or tared VOA bottles, place them in a clear plastic bag and place the custody seal on the outside of the bag.
6	If possible, cover the custody seal with clear plastic tape to protect it.	Take special care to not place the protective tape over the seal in such a way that it can be removed and then re-attached without signs of tampering.

7.7 Providing a Sample Receipt

After samples have been collected on private property, the sampler should prepare a receipt for these samples and provide it to the property owner. This step is especially important when sampling on private property since the analytical results from these samples could be used during future litigation, and the receipt will serve as proof that the owner granted approval for the removal of the samples from the property. An example of a sample receipt created using Scribe is shown in Figure 7-6.

Detailed instructions for generating a Sample Receipt Report are included in Exercise 9 - Section K of the "V 3.10.1 Scribe Training Guide.PDF" which can be obtained from this download: https://response.epa.gov/sites/ScribeGIS/files/Scribe%20V310%20Student%20Files.zip



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Receipt for Samples
Samples Residential Sampling

Project No. 045RD20 | Project Name: Scribe Demo | WA: 123
Samples Transferred: | Signature: | Sampler's Signature:
Samples Received By: | Signature: | John Q. Sampler

Sample #	SS-0004	SS-0004	SS-0019	SS-0019	SS-0024
Sample Date	6/9/2020	6/9/2020	6/9/2020	6/9/2020	6/25/2020
EventID	Front Yard Soil Sampling	Front Yard Soil Sampling	Back Yard Soil Sampling	Back Yard Soil Sampling	High Res Sampling
Location	H004-F	H004-F	H004-R	H004-R	H004-F
Matrix	Soil	Soil	Soil	Soil	Soil
Collection Method	Grab	Grab	Grab	Grab	Grab
Sample Type	Field Sample	Field Sample	Field Sample	Field Sample	Field Sample
Analyses	CLP TCLP Volatiles	CLP TCLP Semivolatiles	CLP TCLP Volatiles	CLP TCLP Semivolatiles	CLP 209 Congeners
CLP Sample #	Y0002	Y0002	Y0007	Y0007	PY0013
Tag	1007	1006	1017	1016	1034
Container	40 ml Vial	4oz Glass	40 ml Vial	4oz Glass	32oz Amber Jar
COC	9-060913-133741-0004	9-060113-084802-0001	9-060913-133741-0004	9-060113-084802-0001	9-070913-170237-0006
Remarks					

Sample #	SS-0024	SS-0024			
Sample Date	6/25/2020	6/25/2020			
EventID	High Res Sampling	High Res Sampling			
Location	H004-F	H004-F			
Matrix	Soil	Soil			
Collection Method	Grab	Grab			
Sample Type	Field Sample	Field Sample			
Analyses	CLP 12 Toxic Congeners	CLP Dioxins/Furans			
CLP Sample #	PY0013	PY0013			
Tag	1033	1032			
Container	32oz Amber Jar	32oz Amber Jar			
COC	9-070913-170237-0006	9-070913-170237-0006			
Remarks					

Figure 7-6. Sample Receipt Created Using the Scribe Software

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8.0 CLP SAMPLE TRANSPORTATION AND SHIPPING

The sampling organization is not only responsible for the transportation and shipping of the Contract Laboratory (CLP) samples to the scheduled recipient laboratory that will be performing the analysis, but it is also responsible for complying with all applicable packaging, labeling, and shipping requirements. Samplers should review the applicable project plans to be aware of all State, Federal, Department of Transportation (DOT), and International Air Transport Association (IATA) regulations governing environmental and hazardous sample packaging.



8.1 Providing Shipment Notification

Some Regions may require that samplers notify their Regional Sample Control Coordinator (RSCC) (or designee) when samples are shipped, while other Regions may allow samplers to contact the Sample Management Office (SMO) directly to provide shipping notification. It is recommended that the electronic Chain of Custody (COC) Record be submitted through the Contract Laboratory Program Support System (CLPSS) (aka "the SMO CLPSS Portal") as soon as possible after shipping. Submitting the COC Record electronically sends a notification to SMO and to the laboratory that the samples have been shipped. It is recommended that samplers contact the RSCC to verify if such notification is necessary. If samplers are shipping samples after 5:00 PM ET, they should notify the RSCC (or designee) and SMO by 8:00 AM ET on the following business day.

It is strongly recommended that samplers provide shipping notification to the RSCC even if they have received approval to directly notify SMO so that the Region is aware of any changes in the final number and timing of samples delivered.

8.2 Packing and Shipping Samples

After collecting the samples, it is important that the samplers properly package them for shipment and ensure that the samples are sent to the appropriate laboratory without delay. Prompt and proper packaging of samples will achieve the following:

- Protect the integrity of samples from changes in composition or concentration caused by bacterial growth or degradation from increased temperatures.
- Reduce the chance of leaking or breaking of sample containers that would result in loss of sample volume, loss of sample integrity, and exposure of personnel to toxic substances.
- Help ensure compliance with shipping regulations.

A single CLP sample may be contained in several different bottles and vials. For example, one water sample may consist of all containers needed for three of the analytical analyses available under this service [i.e., Semivolatile Organic Analyte (SVOA) analysis, Pesticide analysis, and Aroclor analysis], even though the analyses are collected in separate containers. Therefore, the analysis to be performed and the matrix type will determine the type of container(s) that will be used, as well as the volume that should be collected for that particular sample analysis.

8.2.1 Inventory of Samples and Documentation

Samplers should inventory the contents of shipping containers against the corresponding Traffic Report/Chain of Custody (TR/COC) Records when packing samples for shipment to laboratories. Check for the following:

- Ensure that the correct number of containers has been collected for each analysis of the samples.
- Confirm that the required Performance Evaluation (PE) and Quality Control (QC) samples and temperature blanks are included in the shipment.
- Verify that the correct sample numbers and analyses have been assigned to each sample.

8.2.2 Shipping Regulations

Sample shipping personnel are legally responsible for ensuring that sample shipments comply with all applicable shipping regulations. Verify that the following shipping regulations are adhered to if any of the following conditions apply to the samples:

Note: Field Samplers are legally required to know sample characteristics before shipping.

- **Foreign soil movement** - Follow U.S. Department of Agriculture (USDA) soil quarantine and shipping requirements, providing soil permits or required soil import agreements to the laboratory for completion.
- **Chlorinated Dibenzo-*p*-Dioxin (CDD) and Chlorinated Dibenzofuran (CDF)** - Refer to the High Resolution Superfund Method Statement of Work (SOW) for specific information on the safety and handling requirements for samples potentially containing CDD/CDF.
- **Radiological** - Samples suspected to be radioactive must be screened; follow the instructions from the Analytical Services Branch (ASB) Program Manager. Radioactive/Radiological samples are NOT accepted by the CLP.
- **Dry ice** - If dry ice is used to ship tissue samples, follow DOT and IATA regulations. Refer to the Code of Federal Regulations (49 CFR 173.217) classifying dry ice as Hazard Class 9 *UN 1845* (Hazardous Material) and IATA Dangerous Goods regulations or DOT regulations and U.S. Environmental Protection Agency (EPA) guidelines. Refer to Appendix C for detailed shipping guidelines when using SW-846 Method 5035A to preserve and ship frozen samples.



When shipping from remote locations, dry ice may be used with water ice for the purpose of keeping the water ice from melting. Wrap the dry ice in newspaper and place above any water ice. Never place dry ice in an air-tight container.

Access more transportation and shipping information using the following websites:



Dangerous goods regulations
IATA website
https://www.iata.org/en/programs/cargo

DOT/Pipeline and Hazardous Materials Safety Administration (PHMSA)
https://www.phmsa.dot.gov/phmsa-regulations

The nature of the samples collected determines the type of shipping materials to be used.

Refer to the project plan to determine which type of shipping container should be used for each type of sample collected during the sampling event.

8.2.3 Shipping Temperature

Samples must be stored under conditions that maintain sample integrity.

- Samples requiring cold preservation should be placed in shipping containers or other suitable containers with ice to reduce the temperature as soon as possible after collection.
- Ideally, all samples should be shipped the day of collection for overnight delivery to the laboratory.
- If samples requiring cold preservation cannot be shipped on the day of collection, the sample temperature should be maintained at ≤ 6°C, but not frozen, until they are shipped to the laboratory.

8.2.4 Pack Shipping Containers

Packing shipping containers correctly will prevent sample containers from breaking and leaking. Pack shipping containers according to the instructions outlined in Table 8-1.

Table 8-1. Packing Samples for Shipment

Step	Action	Important Notes
1	Seal all drain holes in the shipping container, both inside and out, to prevent leakage in the event of sample breakage.	
2	Check all lids/caps to make sure the samples are tightly sealed and will not leak.	
3	Wipe loose soil residue from containers.	
4	Seal samples in a clear plastic bag.	Custody seals can be placed directly on any sample container except for coring tools used as a transport device (e.g., 5 g Samplers) and tared Volatile Organic Analyte (VOA) bottles. If packing coring tools used as a transport device or tared VOA bottles, place them in a clear plastic bag and affix the custody seal to the outside of the bag.
5	Fully chill those samples that require chilling to ≤ 6°C (but not frozen) prior to placing in the container with suitable packing materials.	
6	It is recommended that samplers line shipping containers with non-combustible, absorbent packing material prior to placing samples in the shipping container.	The CLP strongly discourages the use of vermiculite and cat litter as sources for packing material. These materials interfere with labeling and documentation and are difficult to remove from sample containers and shipping containers.
7	Place samples in CLEAN, sealed, watertight shipping containers (e.g., metal or hard plastic coolers).	
8	Conduct an inventory of the contents of the shipping cooler/container against the corresponding TR/COC Record(s).	
9	Cover samples in double-bagged ice to prevent water damage to packing materials.	Do NOT pour loose ice directly into the sample container. The ice is used to maintain the temperature of the samples in the shipping cooler.
10	It is recommended that a temperature blank be included each shipping container in a location which will allow for easy access by the laboratory upon opening the shipping container.	The temperature blank is generally a 40 mL vial filled with water and labeled “temperature blank” but does not have a CLP Sample Number.
11	Ensure that the site name or other site-identifying information does not appear on any documentation being sent to the laboratory.	

Table 8-1. (Continued) Packing Samples for Shipment

Step	Action	Important Notes
12	Label the outside of the shipping container with any instructions for handling, such as, “This end up,” “Do not Tamper With,” or "Environmental Laboratory Samples."	
13	If shipping samples containing methanol as a preservative (e.g., samples to be analyzed by SW-846 Method 5035A), use a label to indicate the presence of methanol, the United Nations (UN) identification number for methanol (UN 1230), and Limited Quantity.	

VOA soil samples must be placed on their side prior to being placed on ice. Vials are placed on their side so that the septum is wet on the inside, thereby preventing vapor leaks around it, in case any bubbles form. Also, in case the samples freeze, the water will expand into the flexible septum rather than breaking the vial.

8.2.5 Include Required Paperwork

☐ Attach the necessary paperwork to the shipping cooler or container. All paperwork must be placed in a plastic bag or pouch and then secured to the underside of the shipping container lid (Figure 8-1).

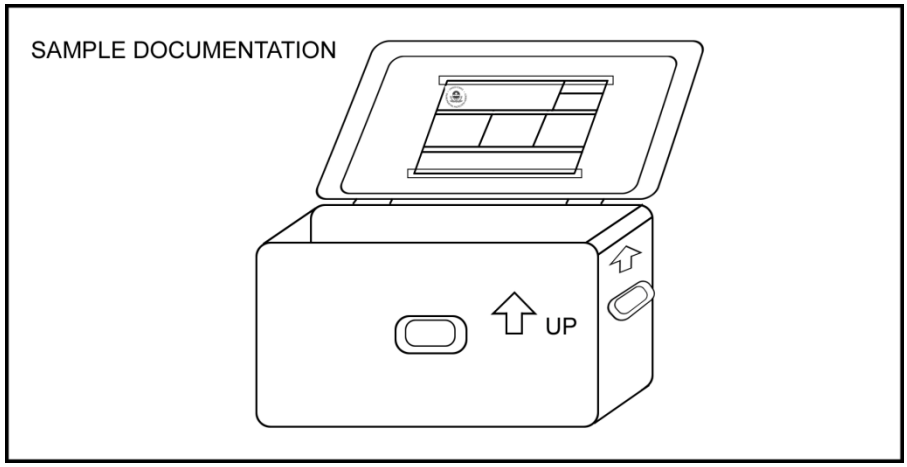


Figure 8-1. Sample Shipping Container with Attached TR/COC Record, PE Sample Instructions (if applicable), and Container Return Documentation

Required paperwork includes:

- TR/COC Records
- Sample weight logs (Figure 4-1), if required for VOA samples
- PE instruction sheets if PE samples are included in the container
- Shipping container return instructions and/or airbills

Contact the RSCC (or designee) for specific paperwork requirements.

8.2.6 Label and Seal Sample Shipping Containers

After packing the samples in the shipping containers, samplers must carefully secure the top and bottom of the containers with tape, place return address labels clearly on the outside of the container, and attach the required chain of custody seals (Figure 8-2).

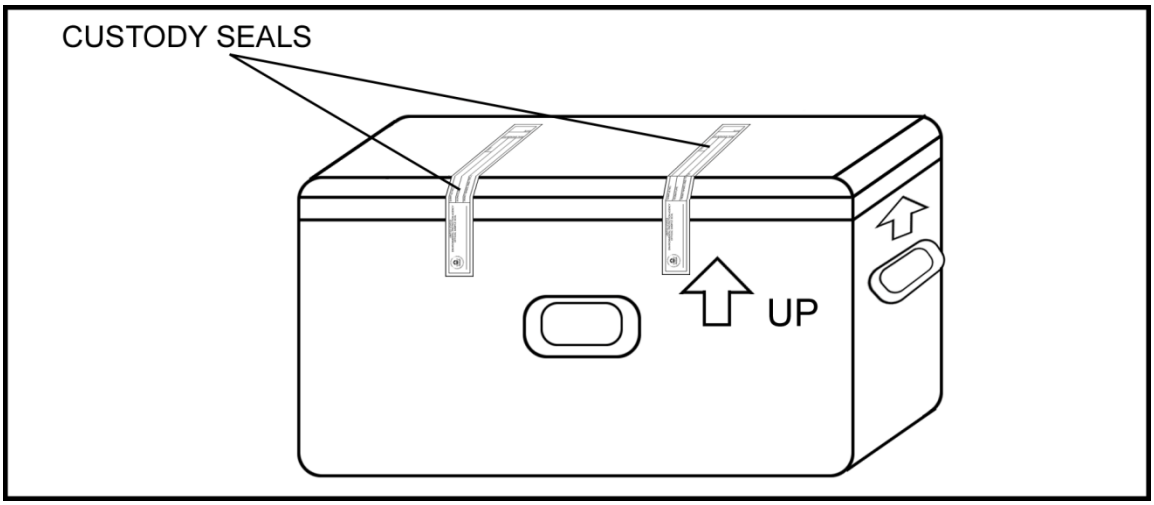


Figure 8-2. Shipping Container with Custody Seals

Use the following guidelines to label shipping containers:

- When shipping more than one container to a laboratory, samplers should mark each container as "1 of 2," "2 of 2," etc.
- An airbill, addressed to the Sample Custodian of the receiving laboratory, must be completed for each container shipped. Samplers should receive the correct name, address, and telephone number of the laboratory to which they must ship samples from the RSCC or the SMO CLPSS Portal.
- To avoid delays in analytical testing, it is critical that for samples associated with multiple types of analyses the correct containers with the correct types of samples are sent to the correct laboratory. For example, inorganic samples may be shipped to one laboratory for analysis, while organic samples may need to be shipped to another laboratory.
- Confirm the shipping company's hours of operation, shipping schedule, and pick-up/drop-off requirements.

8.2.7 Overnight Delivery

It is imperative that samples be sent via overnight delivery. Delays due to longer shipment times may result in missed technical holding times or temperatures rising above the preservation limit, which may destroy sample integrity or require the re-collection of samples for analysis.

8.2.8 Saturday Delivery

Samplers should notify the RSCC (or designee) and SMO as soon as possible when shipping samples for Saturday delivery, so that the delivery information is received by 3:00 PM ET on the Friday prior to delivery.

8.2.9 Shipment Notification

Samplers should upload shipment information to the SMO CLPSS Portal and report all sample shipments to the RSCC (or designee) on the day shipping is completed. **Under no circumstances**

should the sampler contact the laboratory directly. If samplers are shipping samples after 5:00 PM ET, they should notify the RSCC (or designee) or SMO by 8:00 AM ET on the following business day. Samplers should receive the name, phone number, and email address of the appropriate SMO coordinator to notify from the Region/RSCC. Samplers should be aware if the Region requires them to notify the RSCC (or designee) and SMO of sample shipment.

Samplers should provide the following information to the RSCC (or designee):

- Name, phone number, and email address at which they can be reached (preferably closest on-site phone number if still in the field)
- SMO CLPSS Portal-generated Case Number
- Number, matrix and analysis types of samples shipped, and MA number (if required)
- Name of laboratory (or laboratories) to which the samples were shipped
- Airbill number(s)
- Date of shipment
- Case status (i.e., whether or not the Case is complete)
- Problems encountered, special comments, or any unanticipated issues
- Information for the next anticipated shipment



For Saturday delivery, samplers should notify the RSCC (or designee) and SMO as soon as possible so that SMO will receive the delivery information (including shipping airbill information) by 3:00 PM ET on the Friday prior to delivery. Uploading the electronic COC to the SMO CLPSS Portal sends a notification to SMO and to the laboratory that the samples have been shipped.

8.2.10 Uploading the Electronic COC

The electronic COC Record must be uploaded to the SMO CLPSS Portal as soon as possible after sample shipment. The following is an overview of the steps used to upload the electronic COC Record:

☐ Using **Scribe**:

- Under **Sample Management**, click on the **Chain of Custody** link.
- Click the **Export** button on the top of the menu bar.
- Select the **COC XML File (.xml)** option.
- Select the **COC(s)** to be exported.
- Make sure that the **CLP Region Copy COC XML Template** is checked.
- Click **OK**.
- Provide a **filename** for the exported XML file. Per CLP guidance, the XML file name must reference the Region #, Case Number, and the date.
- Click the **Save** button.

☐ Using the SMO **CLPSS Portal**:

- Select the **Submit Chain of Custody** task.
- **Select** the COC file to upload.
- Enter any **comments** associated with the COC file.
- **Submit** the file; CLPSS provides a confirmation page.
- **Print or download** a copy of the submission summary to keep as a record of the submission.



For a detailed description of how to create and upload electronic COC Record files using Scribe and the SMO CLPSS Portal, refer to each system's user documentation.

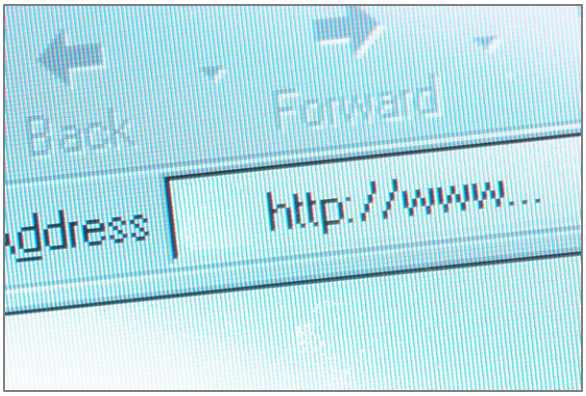
8.2.11 Return of Sample Shipping Containers

CLP laboratories must routinely return sample shipping containers within 14 calendar days following shipment receipt. Therefore, the sampler should also include container return instructions with each shipment. Note that the **samplers** (not the CLP laboratory) are responsible for the costs of return or disposal of these containers and should include shipping airbills bearing the sampler's account number, as well as a return address. **Samplers should use the least expensive return shipping option possible.**

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9.0 SAMPLER RESOURCES

This Guidance document provides a summary of the many resources used to define and manage the sampling process. Samplers may need to refer to the original source documents or websites for further information or clarification. The resources cited herein are listed in this section.



9.1 List of Resources

Table 9-1 provides a list of the resources available to samplers and referenced throughout this Guidance document.

Table 9-1. Resources for Samplers

Resource	Location
U. S. Environmental Protection Agency (EPA) Contract Laboratory Program (CLP) Statements of Work (SOWs)	https://www.epa.gov/clp/superfund-clp-analytical-statements-work-sows
Scribe Software Support	https://ertsupport.org/scribe
Contract Laboratory Program Support System (CLPSS)	https://smoclpss.com/uaa/login
EPA Environmental Response Team (ERT) User Manual for Scribe Contract Laboratory Program (CLP) Sampling	http://www.epaosc.org/sites/ScribeGIS/files/Scribe%20CLP%20User%20Guide.pdf
CLP Guidance Documents	https://www.epa.gov/clp/superfund-clp-analytical-services-guidance-documents-documents
Department of Transportation (DOT) Pipeline and Hazardous Materials Safety Administration (PHMSA) regulations	https://www.phmsa.dot.gov/phmsa-regulations
Use of Dry Ice - Federal Regulations (49CFR 173.217) classified dry ice as Hazard Class 9 *UN 1845* (Hazardous Material).	https://www.gpo.gov/fdsys/pkg/CFR-2004-title49-vol2/xml/CFR-2004-title49-vol2-sec173-217.xml
International Air Transport Association (IATA) transportation regulations	https://www.iata.org
United States Department of Agriculture (USDA) Regulated Organisms and Soil Permits	https://www.aphis.usda.gov/plant_health/permits/organism/soil/
Common Ground Alliance - marking for underground utilities	https://call811.com

Table 9-1. (Continued) Resources for Samplers

Resource	Location
Water Sampling Requirements of Dissolved Metals determinations	***EPA Method SW-846 3005A – Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA or ICP Spectroscopy, Section 2.2:*** Dissolved Metals - The sample is filtered through a 0.45-µm filter at the time of collection and the liquid phase is then acidified at the time of collection with nitric acid. Samples for dissolved metals do not need to be digested as long as the acid concentrations have been adjusted to the same concentration as in the standards. https://www.epa.gov/sites/production/files/2015-12/documents/3005a.pdf
	Clean Water Act (CWA), §136.3 Identification of test procedures. Table II – Required Containers, Preservation Techniques, and Holding Times Footnote 7: For dissolved metals, filter grab samples within 15 minutes of collection and before adding preservatives. For a composite sample collected with an automated sampler (e.g., using a 24-hour composite sampler; see 40 CFR 122.21(g)(7)(i) or 40 CFR Part 403, Appendix E), filter the sample within 15 minutes after completion of collection and before adding preservatives. If it is known or suspected that dissolved sample integrity will be compromised during collection of a composite sample collected automatically over time (e.g., by interchange of a metal between dissolved and suspended forms), collect and filter grab samples to be composited (footnote 2) in place of a composite sample collected automatically. https://www.federalregister.gov/documents/2017/08/28/2017-17271/clean-water-act-methods-update-rule-for-the-analysis-of-effluent
EPA Method SW-846 5035A - Closed-System Purge-and-Trap Extraction for Volatile Organics in Soil and Waste Samples	https://www.epa.gov/sites/production/files/2015-12/documents/5035a_r1.pdf.
NIOSH/OSHA/USCG/EPA Occupational Safety and Health Guidance Manual for Hazardous Waste Site Activities	https://www.osha.gov/Publications/complinks/OSHG-HazWaste/4agency.html
The Roles of Project Managers and Laboratories in Maintaining the Representativeness of Incremental and Composite Soil Samples, EPA/OSWER 9200.1-117FS	https://www.clu-in.org/download/char/RolesofPMsandLabsinSubsampling.pdf

9.2 For More Information

For additional information regarding the CLP or this Guidance document, refer to the Superfund Analytical Services/Contract Laboratory Program website at: https://www.epa.gov/clp

APPENDIX A FUNCTIONS WITHIN A SAMPLING PROJECT

The following table describes Quality Assurance Project Plan (QAPP) sampling requirements based on *EPA Requirements for Quality Assurance Project Plans* (EPA QA/R-5).

Table A-1. QAPP Requirements

Functions Within a Sampling Project	Elements of that Function
Project Management	
Project/Task Organization	Identifies the individuals or organizations participating in the project and defines their specific roles and responsibilities.
Problem Definition/Background	States the specific problem to be solved or decision to be made and includes sufficient background information to provide a historical and scientific perspective for each particular project.
Project/Task Description	Describes the activities to be performed and the schedule for implementation to include: • Measurements to be made during the course of the project. • Applicable technical, regulatory, or program-specific quality standards, criteria, or objectives. • Any special personnel and equipment requirements; assessment tools needed. • A work schedule and any required project and quality records, including types of reports needed.
Quality Objectives and Criteria	Describes the project quality objectives and measurement performance criteria.
Special Training/Certification	Ensures that any specialized training required for modified field sampling techniques, field analyses, laboratory analyses, or data validation should be specified.
Documents and Records	• Itemizes the information and records that must be included in the data report package and specifies the desired reporting format for hardcopy and electronic forms, when used. • Identifies any other records and/or documents applicable to the project such as audit reports, interim progress reports, and final reports that will be produced. • Specifies or references all applicable requirements for the final disposition of records and documents, including location and length of retention period.
Data Generation and Acquisition	
Sampling Process Design (Experimental Design)	• Describes the experimental design or data collection design for the project. • Classifies all measurements as critical or non-critical.
Sampling Methods	• Describes the procedures for collecting samples and identifies sampling methods and equipment. Includes any implementation requirements, support facilities, sample preservation requirements, and materials needed. • Describes the process for preparing and decontaminating sampling equipment to include the disposal of decontamination by-products, selection and preparation of sample containers, sample volumes, preservation methods, and maximum holding times for sampling, preparation, and/or analysis. • Describes specific performance requirements for the method. • Addresses the actions to be taken when a failure in sampling occurs, which party is responsible for corrective action, and how the effectiveness of the corrective action shall be determined and documented.

Table A-1. (Continued) QAPP Requirements

Functions Within a Sampling Project	Elements of that Function
Sample Handling and Custody	• Describes the requirements and provisions for sample handling and custody in the field, transport, and laboratory, taking into account the nature of the samples, the maximum allowable sample holding times before extraction and analysis, and the available shipping options and schedules. • Includes examples of sample labels, custody forms, and sample custody logs.
Analytical Methods	• Identifies the analytical methods and equipment required, including sub-sampling or extraction methods, waste disposal requirements (if any), and specific method performance requirements. • Identifies analytical methods by number, date, and regulatory citation (as appropriate). If a method allows the user to select from various options, the method citations should state exactly which options are being selected. • Addresses the actions to be taken when a failure in the analytical system occurs, who is responsible for corrective action, and how the effectiveness of the corrective action shall be determined and documented. • Specifies the laboratory turnaround time needed, if important to the project schedule. • Specifies whether a field sampling and/or laboratory analysis Case Narrative is required to provide a complete description of any difficulties encountered during sampling or analysis.
Quality Control (QC)	• Identifies required measurement QC checks for both the field and laboratory. • States the frequency of analysis for each type of QC check, and the spike analyte sources and levels. • States or references the required control limits for each QC check and the corrective action(s) required when control limits are exceeded and how the effectiveness of the corrective action shall be determined and documented. • Describes or references the procedures to be used to calculate each of the QC statistics.
Instrument/Equipment Testing, Inspection, and Maintenance	• Describes how inspections and acceptance testing of environmental sampling and measurement systems and their components will be performed and documented. Identifies and discusses the procedure by which final acceptance will be performed by independent personnel. • Describes how deficiencies are to be resolved and when re-inspection will be performed. • Describes or references how periodic preventative and corrective maintenance of measurement or test equipment shall be performed. • Identifies the equipment and/or system requiring periodic maintenance. • Discusses how the availability of spare parts identified in the operating guidance and/or design specifications of the systems will be assured and maintained.
Instrument/Equipment Calibration and Frequency	• Identifies all tools, gauges, instruments, and other sampling, measuring, and test equipment used for data collection activities affecting quality that must be controlled, and at specific times, calibrated to maintain performance within specified limits. • Identifies the certified equipment and/or standards used for calibration. • Describes or references the calibration procedures to be conducted using certified equipment and/or standards with known valid relationships to nationally recognized performance standards. If no such standards exist, documents the basis for calibration. • Indicates how records of calibration shall be maintained and traced to the instrument.
Inspection/Acceptance of Supplies and Consumables	• Describes how and by whom supplies and consumables shall be inspected and accepted for use in the project. • States acceptance criteria for such supplies and consumables.

Table A-1. (Continued) QAPP Requirements

Functions Within a Sampling Project	Elements of that Function
Non-direct Measurements	• Identifies all the types of data needed for project implementation or decision-making that are obtained from non-measurement sources (e.g., computer databases, programs, literature files, historical databases). • Describes the intended use of data. • Defines the acceptance criteria for the use of such data in the project. • Specifies any limitations on the use of the data.
Data Management	• Describes the project data management scheme, tracing the data path from generation in the field or laboratory to their final use or storage. • Describes or references the standard record-keeping procedures, document control system, and the approach used for data storage and retrieval on electronic media.

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APPENDIX B GENERAL CLP SAMPLE COLLECTION GUIDELINES FOR AQUEOUS VOA SAMPLES



Regional guidance and/or specific Project Plan requirements will supersede the guidelines listed below.

Collect the following:

- At least four 40 mL glass containers with polytetrafluoroethylene (PTFE)-lined septa and open top screw-caps that are filled to capacity with no air bubbles, preserved to a pH of 2 with HCl, and cooled to ≤ 6°C, but not frozen, immediately after collection. DO NOT FREEZE THE SAMPLES.

Regular Samples	4 vials (40 mL filled to capacity with no headspace or air bubbles)
Regular Samples Requiring Quality Control (QC) Analysis	4 vials for Sample (40 mL filled to capacity with no headspace or air bubbles) 2 vials for Matrix Spike (MS) (40 mL filled to capacity with no headspace or air bubbles) 2 vials for Matrix Spike Duplicate (MSD) (40 mL filled to capacity with no headspace or air bubbles)

- If Selected Ion Monitoring (SIM) analysis is requested, at least two additional 40 mL glass containers with PTFE-lined septa and open top screw-caps that are filled to capacity with no air bubbles, preserved to a pH of 2 with HCl, and cooled to ≤ 6°C, but not frozen, immediately after collection.

Regular Samples With SIM Analysis	4 vials for Sample (40 mL filled to capacity with no headspace or air bubbles) 2 vials (40 mL filled to capacity with no headspace or air bubbles)

Test for Carbonates, Residual Chlorine, Oxidants, and Sulfides:

- It is important that samplers obtain Regional guidance when testing and ameliorating for:
  - Carbonates;
  - Residual chlorine (e.g., municipal waters or industrial waste waters that are treated with chlorine prior to use or discharge); or
  - Oxidants.
- Volatile Organic Analyte (VOA) samples containing carbonates react with the acid preservative causing effervescence (due to formation of carbon dioxide), which can cause loss of volatile analytes.
- Residual chlorine present in VOA samples can continue to react with dissolved organic matter. This continuous reaction may lead to inaccurate quantitation of certain analytes present in the sample at the time of collection.
- Residual chlorine and oxidants present in VOA samples can cause degradation of certain volatile analytes (e.g., styrene).

Perform the following for *Pre-Preserved* Vials:

1. Pour the sample slowly down the edge of the sample vial to avoid excess aeration or agitation of the sample during filling.
2. Fill the vial completely so that a reverse (convex) meniscus is present and ensure that there are no air bubbles present (either in the body or especially at the top of the vial).
3. Place the septum on the vial so that the PTFE side is in contact with the sample, and then firmly tighten the cap.

4. Gently flip the vial a few times to ensure that the sample is mixed with the acid preservative.
5. While holding the vial inverted, gently tap the sample to check for air bubbles (either in the body or especially at the top of the inverted vial).
6. If air bubbles are present, discard the sample and select a new vial in which to collect a new sample. Repeat Steps 1 - 5 above.
7. Do NOT mix or composite samples for VOAs.
8. Cool sample to a temperature of ≤ 6°C, but not frozen. Samplers should begin the cooling process in the field as samples are being collected. Double-bagged ice should be used. DO NOT FREEZE WATER SAMPLES.
9. Immediately transfer the vial to the sample shuttle (device that contains a "set" of VOA vials) once it has been collected. Do NOT allow ice to touch the vials.

Perform the Following for *Empty* Vials:

1. Rinse the vial with sample water prior to actual sample collection and preservation.



Regions vary in their approach to pre-rinsing and/or re-using sample vials (e.g., some Regions do not recommend pre-rinsing and/or re-use of pre-cleaned containers using sample water). Be sure to follow Regional guidance.

2. Add 1-2 mL of acid preservative to the vial. Check to ensure that the sample requires a preservative (follow Regional guidance).
3. Pour the sample slowly down the edge of the sample vial to avoid excess aeration and agitation of the sample.
4. Fill the vial completely so that a reverse (convex) meniscus is present and ensure that there are no air bubbles present (either in the body or especially at the top of the vial).
5. Place the septum on the vial so that the PTFE side is in contact with the sample, and then firmly tighten the cap.
6. Gently flip the vial a few times to ensure that the sample is mixed with the acid preservative.
7. While holding the vial inverted, gently tap the vial to check for air bubbles (either in the body or especially at the top of the vial).
8. If an air bubble is present that is larger than ~6 mm (pea size), discard the sample and collect a new sample using the same sample vial. Repeat Steps 1 - 7 above.
9. Check the re-collected sample for air bubbles. If there are air bubbles after three consecutive attempts to eliminate air bubbles by the addition of sample water, the entire sample and sample vial should be discarded and a new sample collected without preservative. Note the absence of preservative due to the impact on holding time.
10. Do NOT mix or composite samples for VOAs.
11. Cool sample to a temperature of ≤ 6°C, but not frozen. Samplers should begin the cooling process in the field as samples are being collected. Double-bagged ice should be used. DO NOT FREEZE WATER SAMPLES.
12. Immediately transfer the vial to the sample shuttle (device which contains a "set" of VOA vials) once it has been collected. Do NOT allow ice to touch the vials.

Things to Remember:

- Samples should be shipped as soon as possible, preferably on the same day as sample collection to avoid exceeding sample holding times. If overnight transit is not possible, samples should be maintained at ≤ 6°C, but not frozen, until they are shipped to the laboratory.
- If samples are not preserved (a requirement for certain analyses), the technical holding time is shortened to 7 days.

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APPENDIX C CLP SAMPLE COLLECTION GUIDELINES FOR SOIL VOA SAMPLES BY SW-846 METHOD 5035A, TCLP EXTRACTION BY EPA METHOD SW-846 METHOD 1311, AND SPLP EXTRACTION BY EPA SW-846 METHOD 1312

A. Preferred Options for the Contract Laboratory Program (CLP) are Options 1, 2, 3, and 4:

This analytical method employs sample vials that are filled and weighed in the field and never opened during the analytical process. For this reason, sampling personnel should be equipped with a portable balance capable of weighing to 0.01g.



Soil samples must be placed on their side prior to being frozen or placed on ice. Vials are placed on their side so that the septum is wet on the inside, thereby preventing vapor leaks around it, in case any bubbles form. Also, in case the samples freeze, the water will expand into the flexible septum rather than breaking the vial. Dry ice or field freezers are the only options.

Option 1.

Closed-system Vials:

Container - tared or preweighed 40 mL Volatile Organic Analyte (VOA) Analysis vial containing a magnetic stir bar.

Collect 5 g of soil per vial (iced or frozen in the field). Check the pre-tared weight of the (dry) Volatile Organic Analyte (VOA) vials prior to departure for the sampling event under controlled conditions. Weigh vials and soil samples to the nearest 0.01 g. This check is to ensure that the original weight was properly recorded.

Regular Samples	3 Vials - Dry (5 g soil per vial) 1 Vial - Dry (filled with soil, no headspace) 4 Total Vials
Regular Samples Requiring Quality Control (QC) Analysis	11 Vials - Dry (5 g soil per vial) 1 Vial - Dry (filled with soil, no headspace) 12 Total Vials

Option 2.

Closed-system Vials Containing Water:

Container - tared or pre-weighed 40 mL VOA vial containing a magnetic stir bar and 5 mL water.

Collect 5 g of soil per vial (iced or frozen in the field). Weigh vials and soil samples to the nearest 0.01 g.

Regular Samples	3 Vials with water added (5 g soil and 5 mL water per vial) 1 Vial - Dry (filled with soil, no headspace) 4 Total Vials (3 with water and 1 dry)
Regular Samples Requiring QC Analysis	11 Vials with water added (5 g soil and 5 mL water per vial) 1 Vial - Dry (filled with soil, no headspace) 12 Total Vials (11 with water and 1 dry)

Option 3.

Container - 5 g Samplers or equivalent and coring tool used as a transport device.



All samples should be iced or frozen in the field and bagged individually.

Regular Samples	3 Samplers (5 g soil per Sampler) 1 Vial - Dry (filled with soil, no headspace) 4 Total (3 Samplers and 1 Vial)
Regular Samples Requiring QC Analysis	11 Samplers (5 g soil per Sampler) 1 Vial - Dry (filled with soil, no headspace) 12 Total (11 Samplers and 1 Vial)

Option 4.

Closed-system Vials:

Container - tared or preweighed 40 mL VOA vial.

Collect 25 g of soil per vial (iced or frozen in the field). Check the pre-tared weight of the (dry) VOA vials prior to departure for the sampling event under controlled conditions. Weigh vials and soil samples to the nearest 0.01 g. This check is to ensure that the original weight was properly recorded.

Regular Samples	6 Vials - Dry (25 g soil per vial)

B. Options 5, 6, and 7 are NOT preferred options for the CLP:

Option 5.

Closed-system Vials:

Container - tared or preweighed 40 mL VOA vial containing a magnetic stir bar and preservative.

Collect 5 g of soil per vial and add Sodium bisulfate ($NaHSO_4$) preservative (5 mL water + 1 g $NaHSO_4$) - iced in the field.

Caution: **This option is NOT a Preferred Option for the CLP because:**

$NaHSO_4$ preservation creates low pH conditions that will cause the destruction of certain CLP target analytes (e.g., vinyl chloride, trichloroethene, trichlorofluoromethane, cis- and trans-1,3-dichloropropene). Projects requiring the quantitation of these analytes should consider alternative sample preservation methods. $NaHSO_4$ also cannot be used on carbonaceous soils. Check the soil before using this method of collection! Soils can be checked by placing a test sample in a clean vial, then adding several drops of $NaHSO_4$ solution. If the soil bubbles, use Option 5b and note this issue on the Traffic Report/Chain of Custody (TR/COC) Record.

Option 5a. Samples preserved in the field

Regular Samples	3 Vials with $NaHSO_4$ preservative added (5 g soil per vial) 1 Vial - Dry (filled with soil, no headspace) 4 Total Vials (3 with $NaHSO_4$ preservative and 1 without)
Regular Samples Requiring QC Analyses	6 Vials with $NaHSO_4$ preservative added (5 g soil per vial) 2 Vials - Dry (filled with soil, no headspace) 8 Total Vials (6 with $NaHSO_4$ and 2 without)

Option 5b. Samples to be preserved by the laboratory (No $NaHSO_4$ preservative is added to these samples in the field).

Regular Samples	3 Vials - Dry (5 g soil per vial) 1 Vial - Dry (filled with soil, no headspace) 4 Total Vials
Regular Samples Requiring QC Analyses	6 Vials - Dry (5 g soil per vial) 2 Vials - Dry (filled with soil, no headspace) 8 Total Vials

Option 6.

Methanol Preservation (medium-level analysis only):

Container - tared or pre-weighed 40 mL VOA vials containing 5 mL methanol.

Collect 5 g of soil per vial (iced in the field).

Caution: **This is NOT a preferred option for the CLP because:**

Samples preserved with methanol can only be analyzed by the medium-level method. Low-level Contract Required Quantitation Limits (CRQLs) cannot be achieved when samples are preserved in this manner. If this soil option is used, then samples for low-level analysis by one of the other options should also be collected and accompany the medium-level soil.

Additional problems associated with use of methanol as a preservative in the field include:

- Possible contamination of the methanol by sampling-related activities (e.g., absorption of diesel fumes from sampling equipment);
- Leakage of methanol from the sample vials during shipping, resulting in loss of VOAs prior to analysis.

Regular Samples	2 Vials (5 g soil and 5 mL methanol per vial) 1 Vial - Dry (filled with soil, no headspace) 3 Total Vials (2 with methanol and 1 dry)
Regular Samples Requiring QC Analyses	6 Vials (5 g soil and 5 mL methanol per vial) 1 Vial -Dry (filled with soil, no headspace) 7 Total Vials (6 with methanol and 1 dry)



If shipping samples that contain methanol as a preservative, a shipping label must be used to indicate the presence of methanol. This label must also contain the United Nations (UN) identification number for methanol (UN 1230), and indicate Limited Quantity. Refer to http://www.phmsa.dot.gov for additional information about the safe shipping of methanol.

Option 7.

Glass Containers filled with sample - No Headspace:

Container - 4 oz. Glass Jars.

Glass container filled with soil with no headspace and iced.

Caution: This is NOT a preferred option for the CLP because:

Samples collected in this manner lose most of their volatile analytes prior to analysis when the sample containers are opened and sub-sampled in the laboratory. This option is only available when required by the Region.

Regular Samples	2 Glass Jars (4 oz.) filled with sample, no headspace 1 Vial - Dry (filled with soil, no headspace) 3 Total Containers
Regular Samples Requiring QC Analyses	2 Glass Jars (4 oz.) filled with sample, no headspace 1 Vial - Dry (filled with soil, no headspace) 3 Total Containers

C. Caution:

1. Extreme care should be taken to ensure that frozen or iced samples do not break during shipment.
2. Before adding soil to pre-weighed vials containing a stir bar, weigh the vials to confirm the tared weight. If the weight varies by more than 0.1 g, record the new weight on the label and the sample documentation. Do NOT add labels to these vials once the tared weight has been determined or confirmed.

D. Dry Samples:

Collect in a dry 40 mL VOA vial (or a 4 oz. wide mouth jar) with no headspace. No water, $NaHSO_4$, or methanol is added to this sample. This sample is collected to determine moisture content; therefore, it does not need to be tared or have a stir bar.

E. Iced or Frozen Samples:

1. Iced means cooled to $\leq 6°C$, but not frozen, immediately after collection.
2. Frozen means cooled to $< -7°C$ immediately after collection.
3. Dry ice is not a long-term freezing agent and may contaminate samples.

F. Sample Delivery:

The CLP strongly recommends that all samples arrive at the laboratory by close of business the next day following sample collection.

G. Notes:

1. For Options 2, 5, and 6, check the weight of the pre-tared VOA vials plus liquid in the field due to the possibility that liquid may have leaked out during packing, transit, or deployment in the field just prior to sampling. This check is to ensure that the original weight is properly recorded.
2. For Option 5, samples can be preserved with $NaHSO_4$ either:
   - In the field; or
   - The samplers must evaluate whether $NaHSO_4$ would be compatible with the sample prior to requesting the laboratory to add it to the sample.

3. Regional Quality Assurance Project Plans (QAPPs) may require the use of Option 6. Note that this option is for medium-level analysis ONLY.
4. If water, methanol, or $NaHSO_4$ preservative is added to the vials in the field, a field blank containing the appropriate preservative used in the vials should be sent to the laboratory for analysis.

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APPENDIX D CLP SAMPLE COLLECTION REQUIREMENTS BY ANALYSIS TYPE

The following tables (D-1 through D-4) specify the number of containers of each type necessary for each analysis based on the sampling methodology and QC requirements.

Table D-1. Sample Collection Requirements for CLP Organics [Volatile Organic Analytes (VOAs) Only]

Analysis	Matrix	Sample Type	Container Type[1]	Closure[2]	Minimum Number of Containers Needed				Minimum Volume/Mass[3]	Important Notes	Preservative[4]	Technical Holding Time[5]
					with Water	Dry	% Moisture	TOTAL				
VOAs	Water	Samples Only	40 mL amber or clear glass vial, 24 mm neck finish.	Polypropylene or phenolic, open-top screw-cap, 1.5 cm opening, 24-400 size.	-	-	-	**4**	Fill to capacity	Containers/vials must be filled to capacity with no headspace or air bubbles. Refer to Appendix B for samples requiring QC analyses. If amber containers are not available, the samples should be protected from light.	Preserve to a pH of 2 with HCl and cool to ≤ 6°C, but not frozen, immediately after collection. DO NOT FREEZE water samples.	14 days
		Samples with SIM			-	-	-	**6**				
		Samples with Matrix Spike (MS)/MS Duplicate (MSD)[6]			-	-	-	**8**				
	Soil/ Sediment	Samples Only	**OPTION 1** Closed-system 40 mL amber or clear glass vial containing magnetic stirrer, 24 mm neck finish.	Polypropylene or phenolic, open-top screw-cap, 1.5 cm opening, 24-400 size.	-	3	1	**4**	5g	Place samples on side prior to being iced.[7] Refer to Appendix C for samples requiring QC analyses.	Frozen to < -7°C **OR** Iced to ≤ 6°C, but not frozen.	14 days **OR** 48 hours (unpreserved)[7]
		Samples with MS/MSD[6]			-	11	1	**12**				
		Samples Only	**OPTION 2** Closed-system 40 mL amber or clear glass vial containing magnetic stirrer, 24 mm neck finish and 5 mL water.	Polypropylene or phenolic, open-top screw-cap, 1.5 cm opening, 24-400 size.	3	-	1	**4**	5 g	Place samples on side prior to being iced.[7] Refer to Appendix C for samples requiring QC analyses.	Frozen to < -7°C **OR** Iced to ≤ 6°C, but not frozen.	14 days **OR** 48 hours (unpreserved)[7]
		Samples with MS/MSD[6]			11	-	1	**12**				

Table D-1. (Continued) Sample Collection Requirements for CLP Organics [Volatile Organic Analytes (VOAs) Only]

Analysis	Matrix	Sample Type	Container Type[1]	Closure[2]	Minimum Number of Containers Needed				Minimum Volume/Mass[3]	Important Notes	Preservative[4]	Technical Holding Time[5]
					with Water	Dry	% Moisture	TOTAL				
		Samples Only	**OPTION 3** Coring tool used as a transport device.		-	3	1	**4**	5 g	Refer to Appendix C for samples requiring QC analysis. Place samples on side prior to being iced.[7]	Frozen to < -7°C **OR** Iced to ≤ 6°C, but not frozen.	14 days (frozen) **OR** 48 hours (iced)[7]
		Samples with MS/MSD[6]			-	11	1	**12**				
		Samples for TCLP/SPLP Only	**OPTION 4** Closed-system 40 mL amber or clear glass vial 24 mm neck finish.	Polypropylene or phenolic, open-top screw-cap, 1.5 cm opening, 24-400 size.	-	6	-	**6**	150 g[8]	Place samples on side prior to being iced.[7]	Iced to ≤ 6°C but not frozen.	14 days

Notes

1 Vials for soil analysis are typically pre-labeled and tared. Vials for water analysis are not pre-labeled or tared.

2 Septums for VOA vials 24 mm disc of Polytetrafluoroethylene (PTFE) bonded to silicone for a total thickness of 0.100 - 0.125 in.

3 Minimum volume/mass to be collected in order to ensure sample analysis can be performed. Collect additional volume for MS/MSD samples to allow for sufficient volume for these analyses in the event sample volume is lost as a result of sample containers breaking, leaking, or laboratory accidents.

4 Check Regional guidance regarding use of acid as a preservative of samples that may contain carbonates, residual chlorine, and other oxidants.

5 Technical holding time is calculated from the time of sample collection to sample extraction, and determined as 14 days for preserved (frozen or iced) samples and 48 hours for non-preserved (iced) samples.

6 For Gas Chromatograph/Mass Spectrometer (GC/MS) organic analyses, a Region may decide to reference Deuterated Monitoring Compounds (DMCs) rather than MS/MSD for accuracy and precision.

7 Vials are placed on their side so that the septum is wet on the inside, thereby preventing vapor leaks around it, in case any bubbles form. Also, in case samples freeze, the water will expand into the flexible septum rather than breaking the vial.

8 Samples with low solids content that are scheduled for Toxicity Characteristic Leaching Procedure (TCLP) or Synthetic Precipitation Leaching Procedure (SPLP) may require up to 1000 mL total volume.

Table D-2. Sample Collection Requirements for CLP Organics [Semivolatile Organic Analytes (SVOAs), Pesticides, and Aroclors]

Analysis	Matrix	Sample Type	Container Type	Closure	Minimum Volume/Mass[1]	Important Notes	Preservative/ Collection	Technical Holding Time[2]
SVOAs	Water[3]	Samples Only	1 L amber round glass bottle, 33 mm pour-out neck finish.	Polypropylene or phenolic cap, 33-430 size; 0.015 in. PTFE liner.	2 L (per Test)	If amber containers are not available, the samples should be protected from light.	Cool all samples to ≤ 6°C, but not frozen, immediately after collection. DO NOT FREEZE water samples.	7 days
		Samples with SIM			2 L			
		Samples with MS/MSD			5 L			
		Samples with SIM with MS/MSD			5 L			
	Soil/ Sediment/ Waste[4]	Samples Only	One 8 oz. short, wide mouth, straight-sided, glass jar, 70 mm neck finish or two 4 oz. tall, wide mouth, straight-sided, glass jar, 48 mm neck finish.	Polypropylene or phenolic cap, 70-400 size; 0.015 in. PTFE liner. Or Polypropylene or phenolic cap, 48-400 size; 0.015 in. PTFE liner.	150 g		Cool all samples to ≤ 6°C, but not frozen, immediately after collection.	14 days
		Samples with SIM						
		Samples with MS/MSD	Two 8 oz. short, wide mouth, straight-sided, glass jars, 70 mm neck finish or three 4 oz. tall, wide mouth, straight-sided, glass jar, 48 mm neck finish.		300 g			
		Samples with SIM with MS/MSD						
		Samples for Only TCLP/SPLP	Two 8 oz. short, wide mouth, straight-sided, glass jars, 70 mm neck finish or four 4 oz. tall, wide mouth, straight-sided, glass jar, 48 mm neck finish.		450 g			

Table D-2. (Continued) Sample Collection Requirements for CLP Organics [Semivolatile Organic Analytes (SVOAs), Pesticides, and Aroclors]

Analysis	Matrix	Sample Type	Container Type	Closure	Minimum Volume/Mass[1]	Important Notes	Preservative/ Collection	Technical Holding Time[2]
Pesticides	Water[3, 5]	Samples Only	1 L amber round glass bottle, 33 mm pour-out neck finish.	Polypropylene or phenolic cap, 33-430 size; 0.015 in. PTFE liner.	2 L	If amber containers are not available, the samples should be protected from light.	Cool all samples to ≤ 6°C, but not frozen, immediately after collection. DO NOT FREEZE water samples.	7 days
		Samples with MS/MSD			5 L			
	Soil/ Sediment/ Waste[4]	Samples Only	One 8 oz. short, wide mouth, straight-sided, glass jar, 70 mm neck finish or two 4 oz. tall, wide mouth, straight-sided, glass jar, 48 mm neck finish.	Polypropylene or phenolic cap, 70-400 size; 0.015 in. PTFE liner. Or Polypropylene or phenolic cap, 48-400 size; 0.015 in. PTFE liner.	150 g		Cool all samples to ≤ 6°C, but not frozen, immediately after collection.	14 days
		Samples with MS/MSD	Two 8 oz. short, wide mouth, straight-sided, glass jars, 70 mm neck finish or three 4 oz. tall, wide mouth, straight-sided, glass jar, 48 mm neck finish.		300 g			
		Samples for Only TCLP/SPLP	Two 8 oz. short, wide mouth, straight-sided, glass jars, 70 mm neck finish or four 4 oz. tall, wide mouth, straight-sided, glass jar, 48 mm neck finish.		450 g			
	Wipes	Samples Only	20 mL glass vial.	Polypropylene or phenolic cap, PTFE liner.	1 wipe			14 days
Aroclors	Water[3, 5]	Samples Only	1 L amber round glass bottle, 33 mm pour-out neck finish.	Polypropylene or phenolic cap, 33-430 size; 0.015 in. PTFE liner.	2 L	If amber containers are not available, the samples should be protected from light.	Cool all samples to ≤ 6°C, but not frozen, immediately after collection. DO NOT FREEZE water samples.	7 days
		Samples with MS/MSD			5 L			
	Soil/ Sediment/ Waste[4]	Samples Only	One 8 oz. short, wide mouth, straight-sided, glass jar, 70 mm neck finish or two 4 oz. tall, wide mouth, straight-sided, glass jar, 48 mm neck finish.	Polypropylene or phenolic cap, 70-400 size; 0.015 in. PTFE liner. Or Polypropylene or phenolic cap, 48-400 size; 0.015 in. PTFE liner.	150 g		Cool all samples to ≤ 6°C, but not frozen, immediately after collection.	14 days
		Samples with MS/MSD	Two 8 oz. short, wide mouth, straight-sided, glass jars, 70 mm neck finish or three 4 oz. tall, wide mouth, straight-sided, glass jar, 48 mm neck finish.		300 g			
	Wipes	Samples Only	20 mL glass vial.	Polypropylene or phenolic cap, PTFE liner.	1 wipe			14 days

Table D-2. (Continued) Sample Collection Requirements for CLP Organics [Semivolatile Organic Analytes (SVOAs), Pesticides, and Aroclors]

Notes

1 Minimum volume/mass to be collected in order to ensure sample analysis can be performed.

2 This technical holding time is calculated from the time of sample collection to sample extraction. Sample extracts are to be analyzed within 40 days of extraction. It is recommended that samplers ship samples to the laboratory on the same day that they are collected, or as soon as possible thereafter.

3 An aqueous sample for SVOA analysis would require the field sampler to collect at least 2 L for field samples and at least 3 L for the MS and MSD samples for a total volume of 5 L. If Pesticide or Aroclor MS/MSD analyses are required for the same sample, only two extra 1 L bottles of each sample would be needed, for a total of seven bottles (which includes samples and MS/MSD for both methods). Collect additional volume for MS/MSD samples to allow for sufficient volume for these analyses in the event sample volume is lost as a result of sample containers breaking, leaking, or laboratory accidents.

4 If one or two extractable analyses are required for soil/sediment, only a single 8 oz. or two 4 oz. jars are required. If three extractable analyses are required, two 8 oz. or four 4 oz. jars are required. The number of jars should be doubled if MS/MSD is required.

5 Samplers must test for chlorine in aqueous samples in the field upon collection. Refer to the Sampling and Analysis Plan (SAP) and Appendix E of this document for guidance.

Table D-3. Sample Collection Requirements for CLP Inorganics

Analysis	Matrix	Sample Type	Container Type	Closure	Minimum Volume/ Mass[1]	Important Notes	Preservative/ Collection[2]	Technical Holding Time[3]
Metals/ICP-AES, Metals/ICP-MS, and/or Mercury/CVAA	Water	Samples Only	0.5 L high density polyethylene, cylinder-round bottle, 28 mm neck finish.	Polyethylene cap, ribbed, 28-410 size; F217 polyethylene liner.	0.5 L	DO NOT FREEZE water samples.	Acidify to pH < 2 with HNO_3 immediately after collection.[4]	6 months for all metals except Mercury (28 days)
		Samples with MS/Duplicate			1 L			
	Soil/ Sediment/ Waste[5]	Samples Only	One 8 oz. short, wide mouth, straight-sided, glass jar, 70 mm neck finish.	Polypropylene or phenolic cap, 70-400 size; 0.015 in. PTFE liner.	Fill to capacity		Cool to ≤ 6°C, but not frozen, immediately after collection.	6 months
		Samples with MS/Duplicate						
		Samples for Only TCLP/SPLP	Two 8 oz. short, wide mouth, straight-sided, glass jars, 70 mm neck finish.					
Metals/ICP-AES[6]	Wipe	Samples Only	1 qt. polymer zip-top bag.	Has self-closing mechanism.	N/A		Store at room temperature.	6 months
Cyanide/ Spectrophotometric Determination	Water	Samples Only	0.5 L high density polyethylene, cylinder-round bottle, 28 mm neck finish.	Polyethylene cap, ribbed, 28-410 size; F217 polyethylene liner.	0.5 L	DO NOT FREEZE water samples.	To neutralize residual chlorine, add 0.6 g ascorbic acid for each liter of sample collected, immediately upon collection.[7] Add NaOH until pH > 10 and cool to ≤ 6°C, but not frozen, immediately after collection.	14 days
		Sample with MS/Duplicate			1 L			
	Soil/ Sediment/ Waste[5]	Samples Only	One 8 oz. short, wide mouth, straight-sided, glass jar, 70 mm neck finish.	Polypropylene or phenolic cap, 70-400 size; 0.015 in. PTFE liner.	Fill to capacity		Cool to ≤ 6°C, but not frozen, immediately after collection.	14 days
		Samples with MS/Duplicate						
		Samples for SPLP						

Table D-3. (Continued) Sample Collection Requirements for CLP Inorganics

Analysis	Matrix	Sample Type	Container Type	Closure	Minimum Volume/ Mass[1]	Important Notes	Preservative/ Collection[2]	Technical Holding Time[3]
Anions/Ion Chromatography (IC)[8]	Water	Samples Only	125 mL high density polyethylene, cylinder-round bottle, 28 mm neck finish.	Polyethylene or polypropylene cap, ribbed.	125 mL	DO NOT FREEZE water samples.	For the analysis of nitrate, nitrite, orthophosphate, and sulfate cool to ≤ 6°C, but not frozen, immediately after collection. Do not allow samples for orthophosphate to be held at room temperature more than 12 hours.	48 hours for nitrate, nitrite, and orthophosphate. 28 days for bromide, chloride, fluoride, and sulfate.
		Samples with MS/Duplicate			250 mL			
	Soil	Samples Only	One 8 oz. short, wide mouth, straight-sided, glass jar, 70 mm neck finish.	Polypropylene or phenolic cap, 70-400 size; 0.015 in. PTFE liner.	Fill to capacity		Cool to ≤ 6°C, but not frozen, immediately after collection.	48 hours for nitrate, nitrite, and orthophosphate. 28 days for bromide, chloride, fluoride, and sulfate.
		Samples with MS/Duplicate						
Hexavalent Chromium/Ion Chromatography (IC)[8]	Water	Samples Only	125 mL high density polyethylene or polypropylene, cylinder-round bottle, 28 mm neck finish.	Polyethylene or polypropylene cap, ribbed.	125 mL	DO NOT FREEZE water samples.	Cool to ≤ 6°C, but not frozen, immediately after collection. Field filter. Preserve to pH > 8 using either liquid preservative [NH_4OH/$(NH_4)_2SO_4$ 1 mL per 100 mL sample] or solid mix [13.3 mg Na_2CO_3/10.5 mg $NaHCO_3$/33 mg $(NH_4)_2SO_4$ per sample].	28 days
		Samples with MS/Duplicate			250 mL			
Total Organic Carbon (TOC)[8]	Water	Samples Only	125 m L round glass bottle, 22 mm pour-out neck finish.	Polypropylene or phenolic cap, PTFE liner.	125 mL	DO NOT FREEZE water samples.	Acidify to pH < 2 with H_2SO_4 or H_3PO_4 immediately after collection and cool to ≤ 6°C, but not frozen.	28 days
		Samples with MS/Duplicate			250 mL			
	Soil	Samples Only	4 oz. (120 mL) tall, wide mouth, straight-sided, amber glass jar, 48 mm neck finish.	Polypropylene or phenolic cap, 48-400 size; 0.015 in. PTFE liner.	Fill to capacity		Cool to ≤ 6°C, but not frozen, immediately after collection.	28 days
		Samples with MS/Duplicate						

Table D-3. (Continued) Sample Collection Requirements for CLP Inorganics

Notes

1 Minimum volume/mass to be collected in order to ensure sample analysis can be performed.
2 Check Regional guidance regarding use of acid as a preservative of samples that may contain carbonates, residual chlorine, and other oxidants.
3 This technical holding time is calculated from the time of sample collection to sample analysis.
4 Water samples collected for total metal and filtered metal analyses from the same sampling location must be assigned separate (unique) CLP Sample Numbers.
5 Only one 8 oz. jar is needed for soil/sediment when all metals (including mercury) and cyanide analyses are required for soil/sediment samples. Collect more than one jar when TCLP or SPLP are scheduled.
6 Wipe materials have varied from laboratory tissues (e.g., Kimwipes®) to pre-moistened “baby wipes” from the nearest store.
7 Samplers must test for sulfide and oxidizing agents (e.g., chlorine) in aqueous samples in the field upon collection. Refer to the SAP for guidance. Sulfides adversely affect the analytical procedure. The following can be done to test for and neutralize sulfides. Place a drop of the sample on lead acetate test paper to detect the presence of sulfides. If sulfides are present, treat 25 mL more of the sample than that required for the cyanide determination with powdered cadmium carbonate or lead carbonate. Yellow cadmium sulfide or black lead sulfide precipitates if the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper. Filter the solution through a dry filter paper into a dry beaker, and from the filtrate measure the sample to be used for analysis. Avoid a large excess of cadmium carbonate and a long contact time in order to minimize a loss by complication or occlusion of cyanide on the precipitated material. Sulfide removal should be performed in the field, if practical, prior to pH adjustment with NaOH.
8 Analyses available through Modified Analysis only.

Table D-4. Sample Collection Requirements for CLP Chlorinated Dibenzo-*p*-Dioxins/Chlorinated Dibenzofurans (CDDs/CDFs) and Chlorinated Biphenyl Congeners (CBCs)

Analysis	Matrix	Container Types	Closure	Minimum Volume/Mass[1]	Important Notes	Preservative	Technical Holding Time[2]
CDD/CDF and CBC	Water[3]	1 L amber round glass bottle, 33 mm pour-out neck finish.	Polypropylene or phenolic cap, 33-430 size; 0.015 in. PTFE liner.	2L	If amber containers are not available, the samples should be protected from light.	Cool all samples to ≤ 6°C, but not frozen, immediately after collection. DO NOT FREEZE water samples. If residual chlorine is present, add 80 mg sodium thiosulfate/L of water. If pH is greater than 9, adjust to 7-9 with sulfuric acid.	1 year
	Soil/Sediment/Oil/ Sludge Ash/Biosolids	8 oz. short, wide mouth, straight-sided, glass jar, 70 mm neck finish or 4 oz. (120 mL) tall, wide mouth, straight-sided, amber glass jar, 48 mm neck finish.	Polypropylene or phenolic cap, 70-400 size; 0.015 in. PTFE liner. Or Polypropylene or phenolic cap, 48-400 size; 0.015 in. PTFE liner.	Fill to capacity	If amber containers are not available, the samples should be protected from light.	Cool all samples to ≤ 6°C, but not frozen, immediately after collection.	
	Tissue	Heavy duty aluminum foil as transport device. 8 oz. short, wide mouth, straight-sided, glass jar, 70 mm neck finish or 4 oz. (120 mL) tall, wide mouth, straight-sided, amber glass jar, 48 mm neck finish.	Polypropylene or phenolic cap, 70-400 size; 0.015 in. PTFE liner. Or Polypropylene or phenolic cap, 48-400 size; 0.015 in. PTFE liner.	20 g for each analytical method	If amber containers are not available, the samples should be protected from light.	Cool all samples to ≤ 6°C, or freeze immediately after collection.	

Notes

1 Minimum volume/mass to be collected in order to ensure sample analysis can be performed.

2 This technical holding time is calculated from the time of sample collection to sample extraction. Sample extracts are to be analyzed within 1 year of extraction when sample extracts are stored under the appropriate conditions. It is recommended that samplers ship samples to the laboratory on the same day that they are collected, or as soon as possible thereafter.

3 Samplers must test for chlorine in aqueous samples in the field upon collection. Refer to the SAP for guidance.

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APPENDIX E SAMPLING TECHNIQUES AND CONSIDERATIONS

During a sampling event, samplers are expected to follow prescribed sampling techniques. Samplers should also be aware of any special sampling considerations, contaminant issues, and sample compositing and mixing methods that could affect their sampling efforts.



Regional guidance will take precedence over any of the techniques and considerations listed below.

1. General Sampling Techniques

Information regarding surface water, groundwater, sediment, soil, and surface wipe sampling can be found in many documents including, but not limited to, the following sources:

- *Compendium of ERT Surface Water and Sediment Sampling Procedures*, EPA/540/P-91/005
- *Compendium of ERT Soil Sampling and Surface Geophysics Procedures*, EPA/540/P-91/006
- *Compendium of ERT Groundwater Sampling Procedures*, EPA/540/P-91/007
- *The Roles of Project Managers and Laboratories in Maintaining the Representativeness of Incremental and Composite Soil Samples*, EPA/OSWER 9200.1-117FS
- *Lead in Surface Wipe Samples*, NIOSH Method 9100, August 15, 1994
- *Elements on Wipes*, NIOSH Method 9102, March 15, 2003
- *Surface Wipe Sampling Procedure*, IH75190, Brookhaven National Laboratory, Industrial Hygiene Group, May 10, 2011

When working with potentially hazardous materials, samplers should follow U.S. Environmental Protection Agency (EPA) and Occupational Health and Safety Administration (OSHA) requirements, specific health and safety procedures, and Department of Transportation (DOT) requirements.

2. Special Sampling Considerations

Samplers should refer to the Regional Standard Operating Procedures (SOPs) to obtain specific procedures for proper collection and preservation of samples in the field. For additional guidance regarding sampling for Volatile Organic Analytes (VOAs) Analysis in soil and water, see Appendices B and C. Samplers should obtain Regional guidance when testing and ameliorating for:

- Carbonates in VOA soil and water samples
- Residual chlorine in VOA soil and water samples, or in aqueous cyanide samples
- Oxidants in VOA soil and water samples
- Sulfides and oxidizing agents in aqueous cyanide samples

3. Contaminant Sampling

Certain analytes can be detected in the parts-per-billion (ppb) and/or parts-per-trillion (ppt) range. Extreme care MUST be taken to prevent cross-contamination of these samples. The following precautions should be taken when trace contaminants are a concern:

- Disposable gloves should be worn for each different location sampled.
- When collecting both surface water and sediments, surface water samples should be collected first to reduce the chance of sediment dispersal into the surface water, and the resulting loss of surface water sample integrity.

- Sampling should occur progressively, from the least to the most contaminated area, if this information is known to the sampling team.
- Samplers should use equipment constructed of polytetrafluoroethylene (PTFE), stainless steel, or glass that has been properly pre-cleaned for the collection of samples for trace organic and/or inorganic analyses. Equipment constructed of plastic or polyvinyl chloride (PVC) should NOT be used to collect samples for trace organic analyte analyses.
- Equipment constructed of stainless steel should NOT be used to collect samples for trace metals analyses.

4. Sample Compositing

Sample compositing is a site-specific activity that must be conducted according to the Sampling and Analysis Plan (SAP). Compositing is typically used for large sites to improve the precision (i.e., lower the variance) of the estimated average contaminant concentrations. **Samples for VOA analysis should NOT be composited to minimize loss of analytes.**

Composite samples consist of a series of discrete grab samples that are mixed together to characterize the average composition of a given material. The discrete samples are usually of equal volume, but may be weighted to reflect an increased flow or volume. Nevertheless, all discrete samples must be collected in an identical manner and the number of grab samples forming a composite should be consistent. There are several compositing techniques that may be required, such as:

- Flow-proportioned - Collected proportional to the flow rate during the compositing period by either a time-varying/constant volume or a time-constant/varying volume method. This technique is usually associated with wastewater or storm water runoff sampling.
- Time - Composed of a varying number of discrete samples collected at equal time intervals during the compositing period. This technique is typically used to sample wastewater and streams, and in some air sampling applications.
- Areal - Collected from individual grab samples collected in an area or on a cross-sectional basis. Areal composites are comprised of equal volumes of grab samples where all grabs are collected in an identical manner. This technique is typically used for estimating average contaminant concentrations in soils or sediments. It is also useful when contaminants are present in nugget form (i.e., TNT chunks, lead shot, etc.), thus exhibiting large differences in concentration over a small sample area.
- Vertical - Collected from individual grab samples taken from a vertical cross section. Vertical composites are comprised of equal volumes of grab samples where all grab samples are collected in an identical manner. Examples would include vertical profiles of a soil borehole or sediment columns.
- Volume - Collected from discrete samples whose aliquot volumes are proportional to the volume of sampled material. Volume composites are usually associated with hazardous waste bulking operations where the sample represents combined or bulked waste.

When compositing solid or tissue samples (i.e., sediment, soil, or sludge) for analysis of analytes present in trace quantities, use a stainless steel or PTFE bowl and spatula as applicable.

5. Sample Mixing and Homogenizing

Mixing of the sample for the remaining parameters is necessary to create a representative sample media. It is extremely important that solid samples be mixed as thoroughly as possible to ensure that the sample is representative of the sample location. Refer to the project-specific SAP for instructions on removal of any extraneous materials (e.g., leaves, sticks, rocks, etc.). The mixing technique will depend on the physical characteristics (e.g., particle size, moisture content, etc.) of the solid material. For example, grinding and homogenization of tissue is easier when it is partially frozen. The mixing container should be large enough to hold the sample volume and accommodate the procedures without spilling. Both the mixing container (generally a bowl or tray) and the mixing implement should be properly decontaminated before use. Samples should be homogenized

according to procedures listed in the project-specific SAP. Table E-1 provides a brief procedure for mixing a soil sample with a small particle size (less than 1/4 in.) and filling sample containers in the field.

Table E-1. Mixing a Sample and Filling Sample Containers

Step	Action
1	Roll the contents of the compositing container to the middle of the container and mix.
2	Quarter the sample and move to the sides of the container.
3	Mix each quarter individually, then combine and mix OPPOSITE quarters, then roll to the middle of the container.
4	Mix the sample once more, and then quarter the sample again.
5	Mix each quarter individually, then combine and mix ADJACENT corners, then roll to the middle of the container. The goal is to achieve a consistent physical appearance before sample containers are filled.
6	Flatten piled material into an oblong shape.
7	Using a flat-bottomed scoop, collect a strip of soil across the entire width of the short axis and place it into a sample container.
8	Repeat Step 7 at evenly-spaced intervals until the sample containers are filled.
9	Record the approximate quantity of each subsample in the field logbook.

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APPENDIX F INTERNATIONAL SHIPPING

The following section provides information on shipping Contract Laboratory Program (CLP) samples to laboratories outside the United States.

F.1 United Parcel Service (UPS) Procedure for Shipping to Canada

1. Introduction

Samplers should refer to the Standard Operating Procedure (SOP) for the responsibilities and procedures for shipping to Canadian laboratories. The following sections detail the export shipping process.

2. Overview

UPS will provide pick-up and delivery service for small package (weighing less than 150 lbs. each) shipments to laboratories in Canada.

3. Contact Information

UPS Strategic Support for Government Accounts	https://www.ups.com/us/en/services/government.page
UPS International Customer Service	www.ups.com/international
Preferred Customer Associate Team	https://www.ups.com/us/en/help-support-center.page?

4. Customs Broker

The laboratory should be notified of each shipment so they know to contact their customs broker to have the shipment released. Otherwise, shipments may be held in customs. Laboratories may also act as their own broker.

5. Product Profile

Service Level – EPA receives government pricing for shipments via UPS *Worldwide Express Saver* service. This service provides guaranteed delivery within 1 – 3 business days, by end of day, to Canada. The maximum weight per package is 150 lbs. (70 kg), maximum length is 108 in. (270 cm) per package and the maximum dimensions are 165.0 in. (419.10 cm) per package, length and girth combined.

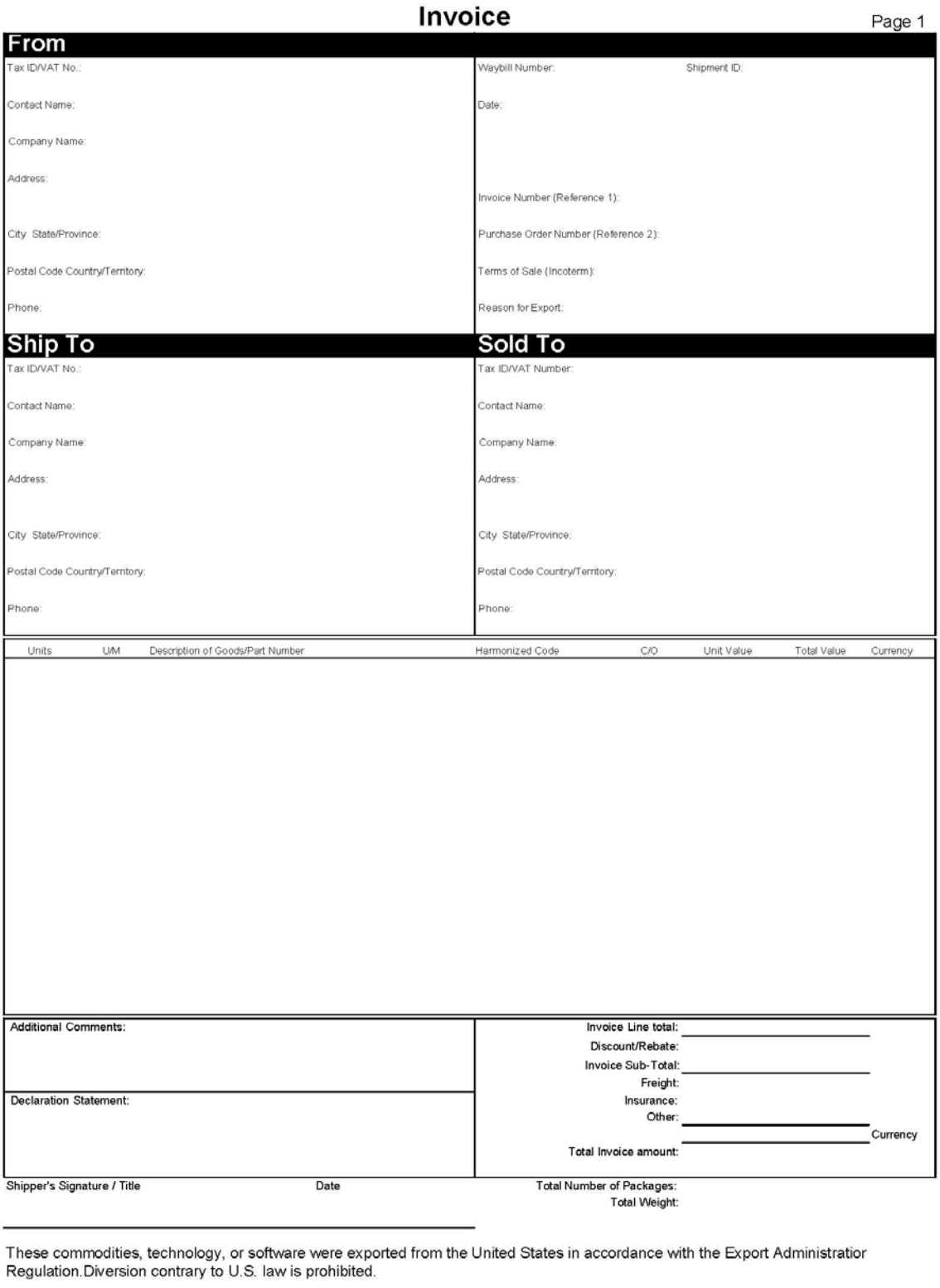
6. Commercial Invoice

A commercial invoice form (see Figure F-1) is used for all shipments containing non-documents. It is the primary document used for importation control, valuation, and duty determination. This document identifies the items in the shipments.

The form should include:

- Complete name and address information for both shipper and consignee
- Phone numbers for shipper and consignee
- Terms of Sale (Incoterm)
- Reason for export
- A complete description of the item
- Type of item
- Item use
- Harmonized Tariff Codes, if known

- Country of origin (where manufactured) for each commodity
- Number of units, unit value, and total value (purchase price) of each item
- Number of packages and total weight
- Shipper’s signature and date
- A nominal or fair market value must be stated for items of no commercial value



Invoice

Page 1

From

Tax ID/VAT No.:

Contact Name:

Company Name:

Address:

City State/Province:

Postal Code Country/Territory:

Phone:

Waybill Number: Shipment ID:

Date:

Invoice Number (Reference 1):

Purchase Order Number (Reference 2):

Terms of Sale (Incoterm):

Reason for Export:

Ship To

Tax ID/VAT No.:

Contact Name:

Company Name:

Address:

City State/Province:

Postal Code Country/Territory:

Phone:

Sold To

Tax ID/VAT Number:

Contact Name:

Company Name:

Address:

City State/Province:

Postal Code Country/Territory:

Phone:

Units	U/M	Description of Goods/Part Number	Harmonized Code	C/O	Unit Value	Total Value	Currency

Additional Comments:

Declaration Statement:

Invoice Line total:

Discount/Rebate:

Invoice Sub-Total:

Freight:

Insurance:

Other:

Currency

Total Invoice amount:

Shipper's Signature / Title Date

Total Number of Packages:

Total Weight:

These commodities, technology, or software were exported from the United States in accordance with the Export Administratior Regulation.Diversion contrary to U.S. law is prohibited.

Figure F-1. Commercial Invoice Template

7. Packing with Coolants and Refrigerants (Dry Ice)

Coolants and refrigerants are used to keep temperature-sensitive items cold or frozen while in transit. Dry ice (frozen carbon dioxide) and ice are the most common types of coolant/refrigerants used for transportation.

International Air Shipments Containing Dry Ice

International Air shipments containing dry ice require the shipper to have a UPS International Special Commodities contract. For additional information, please contact the UPS Hazardous Materials Support Center at 1-800-554-9964, or visit our online UPS Guide for Shipping International Dangerous Goods.

https://www.ups.com/us/en/help-center/packaging-and-supplies/special-care-shipments/international-dangerous-goods/shippers-responsibilities.page

International Dry Ice Packages Shipped via Air Service Require the Following Under International Air Transport Association (IATA):

- Process through WorldShip 2019, CampusShip, or compliant software
- An acceptance audit is performed
- Mark the outer carton with:
  - The words “Dry Ice” of “Carbon Dioxide, Solid” and “UN 1845”
  - The amount of dry ice contained in the package in kg
  - Class 9 Diamond label

Requirements for Preparing Dry Ice Shipments:

- Fill any empty space in the shipping container with appropriate packing material to prevent product movement during transit.
- Wrap temperature-sensitive products in two watertight plastic bags or use absorbent material along with a plastic liner.
- Avoid shipping temperature-sensitive products over the weekend.
- Wrap the refrigerant in paper or another carton to slow the sublimation rate and prevent excess space when using dry ice.
- Do not place the refrigerant at the bottom of the package because cold air will not circulate.
- Do not seal the inner insulated container when using dry ice. Venting is required to allow some carbon dioxide gas to escape the package.

* UPS CampusShip is a web-based, UPS-hosted shipping solution that helps to increase efficiency and reduce costs.

8. Additional Information

Common items that may be hazardous require the shipper to have a UPS International Special Commodities contract. For additional information, contact the UPS Hazardous Materials Support Center at 1-800-554-9964, or visit the online UPS Guide for Shipping International Dangerous Goods.

Descriptions that Indicate Dangerous Goods – watch for any of the following descriptions that could indicate Dangerous Goods or Hazardous Materials:

- Acidic
- Caustic
- Combustible Communicable
- Compressed Gas
- Corrosive
- Explosive
- Flammable
- Infectious
- Inflammable

- Poison
- Radioactive
- Refrigerated
- Toxic
- Volatile

Note: The above is only a sampling of terms which should prompt further questions about a shipment.

9. Tools and Resources

UPS Global

Access UPS Global website to get up-to-date information on everything international, including information on how to prepare an international shipment, track your package, and import/export country regulations and international forms.

Processing International Package using UPS CampusShip

https://www.ups.com/media/en/CampusShip_shipping_QuickStart_Guide.pdf

Step-by-Step Instructions for International Shipping

Step 1. Verify That The Commodity Can Be Shipped

Determine if service restrictions apply to either the United States or Canada.

Check for Embargoed/Suspended Service

Verify that your commodity can be shipped to or from the United States and Canada.

Check List of UPS Export Prohibited Articles

Step 2. Select an International Service If price and time are your primary considerations in selecting an international service, use the Service Comparison tool on UPS CampusShip to find the guaranteed delivery time and price of every service available to and from the United States and Canada.

Step 3. Select an International Billing Option

UPS offers flexible international billing options. Select the applicable option.

Learn More About International Billing Options

Step 4. Create Required Documentation

Determine the export documentation required for the shipment and complete each form.

Learn How to Create Documentation

Step 5. Prepare The Shipment

Use UPS International Shipping Basics to learn more about preparing your shipment.

Learn What Packing Materials to Use for Your International Shipment

Identify Specific Weight and Size Limitations Convert the Weight, Length, Area, and Volume of Your Shipment

Decide whether to declare a value for high value items. If the value of the goods exceeds $100.00 (USD), declare a higher value, up to $50,000.00 (USD) per package. For packages that exceed the maximum declared value, a waiver must be obtained. Refer to the applicable terms and conditions of service for additional limits and restrictions.

Learn More About Declared Value

Step 6. Ship The Package

Use UPS CampusShip or Internet Shipping on ups.com to prepare the international shipping label and the international forms required for certain shipments.

Step 7. Get The Shipment to UPS

In instances where automatic pickup has not been scheduled, UPS On-Call Pickup® may be requested to pick up all ground, air, and international shipments from any location. UPS On-Call Pickup can be scheduled at ups.com or by calling 1-800-PICK-UPS® for same day or future day pickup. Packages can also be shipped from UPS locations including The UPS Store®.

Find Locations

Step 8. Check Shipment Status

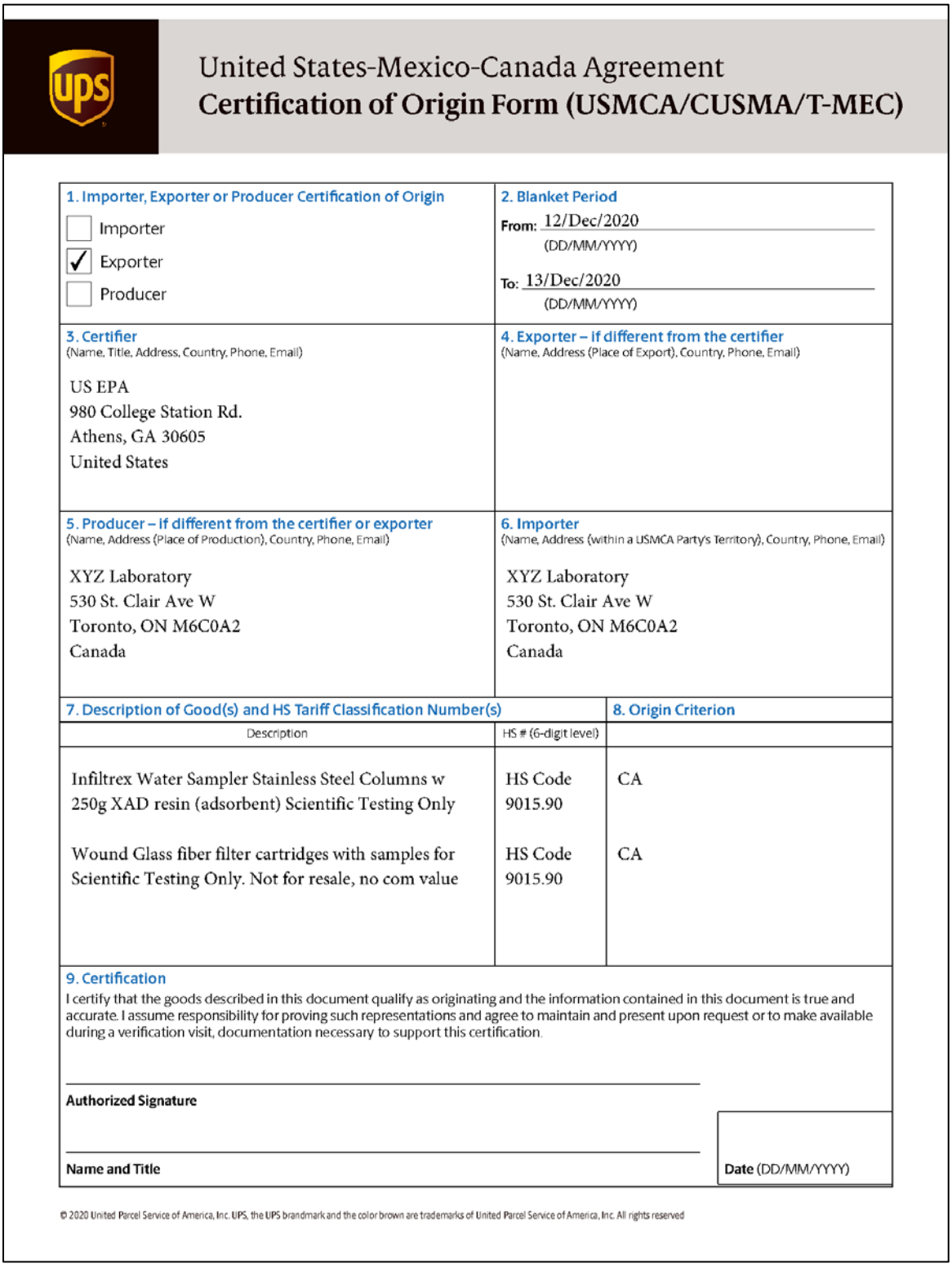
Since each UPS package is assigned a unique tracking number, shipment information is easily accessible. Tracking information is always available at ups.com, by e-mail, and through optional services.

Track Your Shipment

Learn About More Ways to Track

F.2 Completed Customs Forms Example

Shipping samples to an international laboratory requires the completion of a customs form. The following is an example of a correctly completed customs form for shipment to a laboratory in Canada.



United States-Mexico-Canada Agreement
Certification of Origin Form (USMCA/CUSMA/T-MEC)

1. Importer, Exporter or Producer Certification of Origin

- ☐ Importer
- ☑ Exporter
- ☐ Producer

2. Blanket Period

From: 12/Dec/2020 (DD/MM/YYYY)

To: 13/Dec/2020 (DD/MM/YYYY)

3. Certifier
(Name, Title, Address, Country, Phone, Email)

US EPA
980 College Station Rd.
Athens, GA 30605
United States

4. Exporter – if different from the certifier
(Name, Address (Place of Export), Country, Phone, Email)

5. Producer – if different from the certifier or exporter
(Name, Address (Place of Production), Country, Phone, Email)

XYZ Laboratory
530 St. Clair Ave W
Toronto, ON M6C0A2
Canada

6. Importer
(Name, Address (within a USMCA Party's Territory), Country, Phone, Email)

XYZ Laboratory
530 St. Clair Ave W
Toronto, ON M6C0A2
Canada

7. Description of Good(s) and HS Tariff Classification Number(s)

Description	HS # (6-digit level)	8. Origin Criterion
Infiltrex Water Sampler Stainless Steel Columns w 250g XAD resin (adsorbent) Scientific Testing Only	HS Code 9015.90	CA
Wound Glass fiber filter cartridges with samples for Scientific Testing Only. Not for resale, no com value	HS Code 9015.90	CA

9. Certification

I certify that the goods described in this document qualify as originating and the information contained in this document is true and accurate. I assume responsibility for proving such representations and agree to maintain and present upon request or to make available during a verification visit, documentation necessary to support this certification.

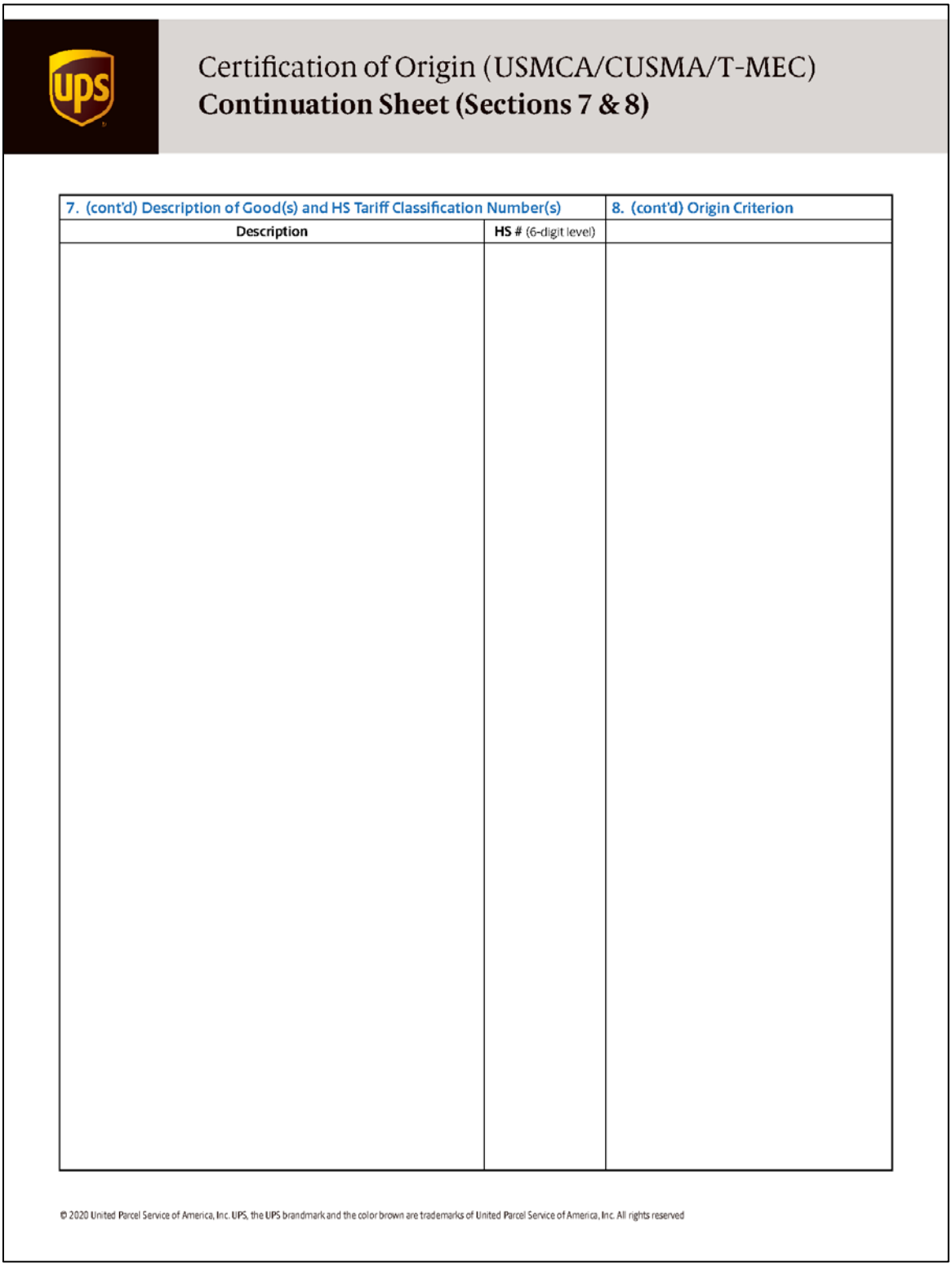
Authorized Signature

Name and Title

Date (DD/MM/YYYY)

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Figure F-2. International Shipping Form (1 of 3)

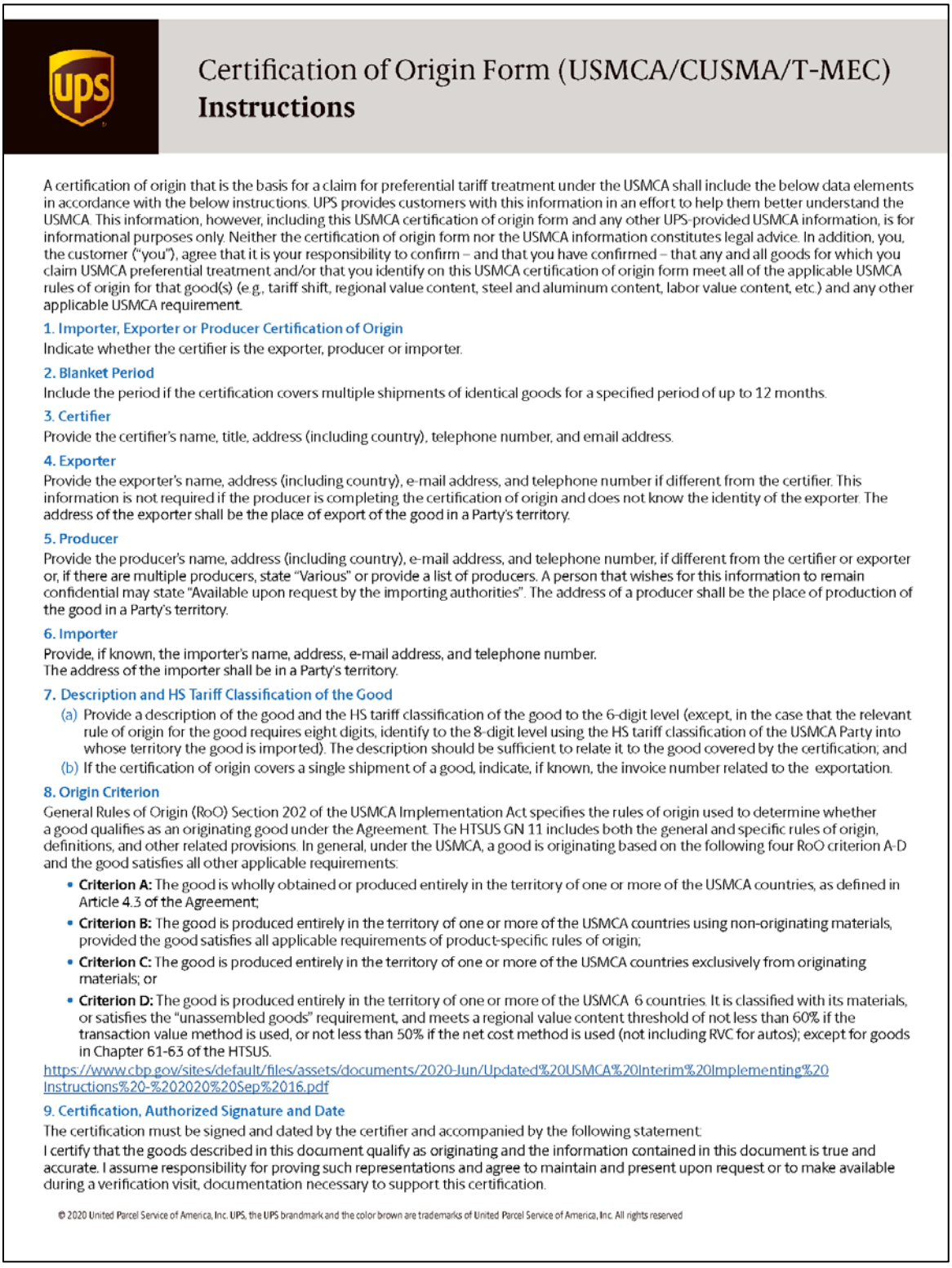


Certification of Origin (USMCA/CUSMA/T-MEC)
Continuation Sheet (Sections 7 & 8)

7. (cont'd) Description of Good(s) and HS Tariff Classification Number(s)		8. (cont'd) Origin Criterion
Description	**HS #** (6-digit level)	

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Figure F-3. International Shipping Form (2 of 3)



Certification of Origin Form (USMCA/CUSMA/T-MEC) Instructions

A certification of origin that is the basis for a claim for preferential tariff treatment under the USMCA shall include the below data elements in accordance with the below instructions. UPS provides customers with this information in an effort to help them better understand the USMCA. This information, however, including this USMCA certification of origin form and any other UPS-provided USMCA information, is for informational purposes only. Neither the certification of origin form nor the USMCA information constitutes legal advice. In addition, you, the customer ("you"), agree that it is your responsibility to confirm – and that you have confirmed – that any and all goods for which you claim USMCA preferential treatment and/or that you identify on this USMCA certification of origin form meet all of the applicable USMCA rules of origin for that good(s) (e.g., tariff shift, regional value content, steel and aluminum content, labor value content, etc.) and any other applicable USMCA requirement.

1. Importer, Exporter or Producer Certification of Origin

Indicate whether the certifier is the exporter, producer or importer.

2. Blanket Period

Include the period if the certification covers multiple shipments of identical goods for a specified period of up to 12 months.

3. Certifier

Provide the certifier's name, title, address (including country), telephone number, and email address.

4. Exporter

Provide the exporter's name, address (including country), e-mail address, and telephone number if different from the certifier. This information is not required if the producer is completing the certification of origin and does not know the identity of the exporter. The address of the exporter shall be the place of export of the good in a Party's territory.

5. Producer

Provide the producer's name, address (including country), e-mail address, and telephone number, if different from the certifier or exporter or, if there are multiple producers, state "Various" or provide a list of producers. A person that wishes for this information to remain confidential may state "Available upon request by the importing authorities". The address of a producer shall be the place of production of the good in a Party's territory.

6. Importer

Provide, if known, the importer's name, address, e-mail address, and telephone number.
The address of the importer shall be in a Party's territory.

7. Description and HS Tariff Classification of the Good

(a) Provide a description of the good and the HS tariff classification of the good to the 6-digit level (except, in the case that the relevant rule of origin for the good requires eight digits, identify to the 8-digit level using the HS tariff classification of the USMCA Party into whose territory the good is imported). The description should be sufficient to relate it to the good covered by the certification; and

(b) If the certification of origin covers a single shipment of a good, indicate, if known, the invoice number related to the exportation.

8. Origin Criterion

General Rules of Origin (RoO) Section 202 of the USMCA Implementation Act specifies the rules of origin used to determine whether a good qualifies as an originating good under the Agreement. The HTSUS GN 11 includes both the general and specific rules of origin, definitions, and other related provisions. In general, under the USMCA, a good is originating based on the following four RoO criterion A-D and the good satisfies all other applicable requirements:

- **Criterion A:** The good is wholly obtained or produced entirely in the territory of one or more of the USMCA countries, as defined in Article 4.3 of the Agreement;
- **Criterion B:** The good is produced entirely in the territory of one or more of the USMCA countries using non-originating materials, provided the good satisfies all applicable requirements of product-specific rules of origin;
- **Criterion C:** The good is produced entirely in the territory of one or more of the USMCA countries exclusively from originating materials; or
- **Criterion D:** The good is produced entirely in the territory of one or more of the USMCA 6 countries. It is classified with its materials, or satisfies the "unassembled goods" requirement, and meets a regional value content threshold of not less than 60% if the transaction value method is used, or not less than 50% if the net cost method is used (not including RVC for autos); except for goods in Chapter 61-63 of the HTSUS.

https://www.cbp.gov/sites/default/files/assets/documents/2020-Jun/Updated%20USMCA%20Interim%20Implementing%20Instructions%20-%202020%20Sep%2016.pdf

9. Certification, Authorized Signature and Date

The certification must be signed and dated by the certifier and accompanied by the following statement:

I certify that the goods described in this document qualify as originating and the information contained in this document is true and accurate. I assume responsibility for proving such representations and agree to maintain and present upon request or to make available during a verification visit, documentation necessary to support this certification.

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Figure F-4. International Shipping Form (3 of 3)

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APPENDIX G SAMPLING CHECKLISTS

Table G-1. Personnel Preparation Checklist

(Page 1 of 2)

Personnel Briefing	Yes	No	Comments
1. Did you review sampling team responsibilities and identify individual(s) responsible for corrective actions?			
2. Did you ensure that you have met the appropriate personal safety and protection requirements?			
3. Did you identify sampling locations and receive permission to access them, as appropriate?			
4. Did you contact the appropriate utility companies PRIOR to the start of sampling?  By law, utility companies must be contacted prior to the start of digging/sampling so that any underground utilities (gas lines, water lines, electrical lines, etc.) can be marked. A list of one-call centers for each state may be found at: https://call811.com			
5. If sampling on private property, do you have sample receipts to provide to the property owner for all samples collected and removed from the property?			
6. Have you determined the number and type of samples to be collected?			
7. Did you review sample collection methods?			
8. Have you reviewed sample container requirements?			
9. Did you review decontamination requirements, procedures, and locations?			
10. Did you determine holding times and conditions?			
11. Did you determine Performance Evaluation (PE) and Quality Control (QC) sample requirements?			
12. Have you obtained shipping container temperature blanks, if required?			
13. Did you review sample label requirements?			
14. Did you review Traffic Report/Chain of Custody (TR/COC) Record and custody seal requirements?			
15. Have you obtained the laboratory name, shipping addresses, and telephone number?			
16. Did you review shipping container return instructions?			
17. Have you obtained shipping company information (name, telephone number, account number, and pickup schedule)?			
18. Have you obtained shipping schedules?			
19. Did you review shipment reporting requirements and the appropriate contact names and telephone numbers for reporting?			

Table G-1. (Continued) Personnel Preparation Checklist

(Page 2 of 2)

Personnel Briefing	Yes	No	Comments
20. Have you included any sampler comments regarding sampling issues (e.g., low volumes, matrix, suspected concentrations based on field measurements)?			

Table G-2. General Sample Collection Checklist

(Page 1 of 1)

General Sample Collection	Yes	No	Comments
1. Did you identify and mark the sampling location with buoys, flags, or stakes according to the sampling plans, maps, and grids?			
2. If the sampling location is inaccessible, did you contact the appropriate field or Regional personnel for instructions?			
3. Did you use the correct sampling equipment?			
4. Did you follow the correct decontamination procedures?			
5. Did you follow the correct collection procedures?			
6. Did you use the correct sample containers for each sample collected?			
7. Did you use certified clean containers for all samples? Are certificates kept on record?			
8. Did you use certified clean water for all field, trip, equipment, and rinsate blanks? Are certificates kept on record?			
9. Did you collect the correct volume for each sample?			
10. Did you collect the correct type of sample, including primary samples and QC samples?			
11. Did you properly preserve each sample collected?			
12. Did you correctly document and label each sample with all necessary information?  Under no circumstances should the site name or address appear on any documentation being sent to the laboratory, unless the laboratory is a Regional U.S. Environmental Protection Agency (EPA) laboratory.			
13. If sampling on private property, did you provide a sample receipt to the owner of the property for all samples collected and removed from the property?			

Table G-3. Completing Field Logbook Checklist

(Page 1 of 1)

Completing Field Logbook	Yes	No	Comments
1. Did you use waterproof ink when writing in the field logbook?			
2. Did you document sampling project information such as: • Project name, Project ID, and location • Names of samplers • Geological observations, including maps • Atmospheric conditions • Field measurements • Sampling dates, times, and locations?  Under no circumstances should the site name or address appear on any documentation being sent to the laboratory, unless the laboratory is a Regional EPA laboratory.			
3. Did you record sampling activity information such as: • Sampling dates and times • Sample identifications • Sample matrices • Sample descriptions (e.g., odors and/or colors) • Number of samples collected • Sampling methods/equipment • Description of QC samples?			
4. Did you document any and all deviations from the sampling plan?			
5. Did you document any and all difficulties in sampling and/or any unusual circumstances?			
6. Were all errors corrected by crossing a line through the error, initialing the error, dating the error, and then adding the correct information?			

Table G-4. Completing Handwritten Sample Labels Checklist

(Page 1 of 1)

Completing Handwritten Sample Labels	Yes	No	Comments
1. Did the Regional Sample Control Coordinator (RSCC) provide Contract Laboratory Program (CLP) Sample Numbers and Sample Management Office (SMO) Contract Laboratory Program Support System (CLPSS) Portal-generated CLP Case Numbers?			
2. If additional CLP Sample Numbers were needed, did you contact the appropriate Regional personnel?			
3. Were the CLP Sample Numbers and SMO CLPSS Portal-generated CLP Case Numbers on the labels correct?			
4. Were samples uniquely numbered and designated to only one sample?  Samples collected for total metal and filtered metal analyses must receive separate, unique, CLP Sample Numbers.			
5. Were QC samples numbered accordingly?			
6. Were the specific requirements followed for total and filtered metals analysis, QC and PE samples, and SW-846 Method 5035A?			
7. Were all temperature blanks labeled with “TEMPERATURE BLANK”?			
8. Was a sample label containing the CLP Sample Number, SMO CLPSS Portal-generated CLP Case Number, location, concentration, preservative, and the analysis, attached to each sample bottle or container as the sample was collected?  Under no circumstances should the site name or address appear on any documentation being sent to the laboratory, unless the laboratory is a Regional EPA laboratory.			
9. Was clear tape placed over the sample labels to protect the labels from moisture and to help the labels adhere to the sample bottle?  Use only CLEAR tape over the sample labels and avoid wrinkles in the tape and the sample labels.			
10. Were all errors corrected by drawing a line through the error, initialing and dating the error, and then adding the correct information?			

Table G-5. Completing Handwritten Custody Seals Checklists

(Page 1 of 1)

Completing Custody Seals	Yes	No	Comments:
1. If required for the project, did you sign and date the custody seal?			
2. Did you attach a completed custody seal to the sample bottle, container, or plastic bag, placing the seal over the cap or lid of each sample bottle or container or on the bag opening such that it will be broken if the sample bottle, container, or bag is opened or tampered with?			
3. As appropriate, did you attach the completed custody seal to the sample shipping container or cooler, placing the seal such that it will be broken if the container or cooler is opened or tampered with?			
4. Were all errors corrected by crossing a line through the error, initialing and dating the error, and then adding the correct information?			

Table G-6. Packing Sample Container Checklist

(Page 1 of 1)

Packing Sample Container	Yes	No	Comments
1. Did you follow all State, Federal, Department of Transportation (DOT), and International Air Transportation Association (IATA) regulations governing the packaging of environmental and hazardous samples?  If samples contain methanol preservation (e.g., samples to be analyzed by SW-846 Method 5035A), refer to the packaging instructions in Appendix C.			
2. Were all CLP Sample Numbers, SMO CLPSS Portal-generated CLP Case Numbers, analyses, labels, and custody seals attached to the correct sample containers?			
3. Is Modified Analysis indicated if requested?			
4. Was an inventory conducted of CLP Sample Numbers, SMO CLPSS Portal-generated CLP Case Numbers, analyses, and containers, and verified against the TR/COC Records?			
5. Were the correct number and type of PE and QC samples collected?			
6. Were all sample containers sealed in clear plastic bags with the sample label and tag (if applicable) visible through the packaging?			
7. Was suitable absorbent packing material placed around the sample bottles or containers?			
8. Were the outsides of metal containers labeled properly with the CLP Sample Number, SMO CLPSS Portal-generated CLP Case Number, and the analysis of the sample inside?			

Table G-7. Packing Shipping Container Checklist

(Page 1 of 2)

Packing Shipping Container	Yes	No	Comments
1. Were shipping samples in a clean waterproof metal or hard plastic ice chest, cooler, or container in good condition?			
2. Were all non-applicable labels from previous shipments removed from the container?			
3. Were all inside and outside drain plugs closed and covered with suitable tape (e.g., duct tape)?			
4. Was the inside of the shipping container lined with plastic (e.g., large heavy-duty garbage bag)?			
5. Was the lined shipping container packed with non-combustible absorbent packing material?			
6. Were sample containers placed in the shipping container in an upright position not touching one another?			
7. Was a shipping container temperature blank included in the cooler?			
8. Did the documentation in the cooler only address the samples in that container?			
9. Was the site name absent from all documentation?  Under no circumstances should the site name or address appear on any documentation being sent to the laboratory, unless the laboratory is a Regional EPA laboratory.			
10. Was there sufficient packing material around and in between the sample bottles to avoid breakage during transport?			
11. If required, was double-bagged ice placed on top and around sample bottles to keep the samples cold at ≤ 6°C?  Do not pack loose ice into the cooler.			
12. Was the top of the plastic liner fastened and secured with tape?			
13. Was a completed custody seal placed around the top of the fastened plastic liner (if required by the Region)?			
14. Were all sample documents enclosed within the shipping container (e.g., TR/COC Record, PE instructions, and container return instructions) in a waterproof plastic bag?			
15. Was the plastic bag, containing the documentation, taped to the underside of the lid?			
16. Were shipping container return instructions and airbills taped to the underside of the cooler lid?			
17. Was the return address of the shipping container written with permanent ink on the underside of the lid?			
18. Was tape placed around the outside of the entire container and over the hinges?			
19. Were the completed custody seals placed over the top edge of the container so the container cannot be opened without breaking the seals?			
20. Was the return address label attached to the top left corner of the container lid?			

Table G-7. Packing Shipping Container Checklist

(Page 2 of 2)

Packing Shipping Container	Yes	No	Comments
21. Were instructional labels attached to the top of the container, as necessary (e.g., "This End Up," "Do Not Tamper With," or "Environmental Laboratory Samples")?			
22. Have all U.S. DOT regulations been met for the shipment when shipping hazardous samples?			
23. If shipping samples containing methanol as a preservative (e.g., samples to be analyzed by SW-846 Method 5035A), was a label used to indicate the presence of methanol, the United Nations (UN) identification number for methanol (UN 1230), and Limited Quantity?			

Table G-8. Shipping & Reporting CLP Samples Checklist

(Page 1 of 1)

Shipping CLP Samples	Yes	No	Comments:
1. Did you follow all State, Federal, DOT, and IATA regulations governing the shipment of environmental and hazardous samples?			
2. Was a separate airbill filled out for each container being shipped?			
3. Was the airbill filled out completely, including correct laboratory name, address, and telephone number, identification of recipient as "Sample Custodian," and appropriate delivery option (e.g., overnight or Saturday)?			
4. Was the completed airbill attached to the top of the container with the correct laboratory address?			
5. If more than one container was being shipped to the same laboratory, were they marked as "1 of 2," "2 of 2," etc.?			
6. Were the samples being shipped "overnight" through a qualified commercial carrier?			
7. Did you export the electronic COC XML file from Scribe?			
8. Did you upload the electronic COC XML file using the Submit Chain of Custody task in the SMO CLPSS Portal?			
Reporting CLP Samples	**Yes**	**No**	**Comments:**
1. Did you contact the RSCC (or designee) and the Contract Laboratory Program Sample Management Office (SMO) on the same day samples were shipped?			
2. If the samples were shipped after 5:00 PM Eastern Time (ET), were they reported to the RSCC (or designee) and to SMO by 8:00 AM ET the following business day?			
3. Did you notify the RSCC (or designee) and SMO so that SMO will receive the delivery information (including shipping airbill information) by 3:00 PM ET on Friday for sample shipments that will be delivered to the laboratory on Saturday?			
4. Did you provide the RSCC (or designee) or the SMO CLPSS Portal with: • Your name, phone number, email address, and Region number; • Case Number of the project; • Modified Analysis Number, if requested; • Exact number of samples, matrix(ces), and type of analysis; • Laboratory(ies) to which the samples were shipped; • Carrier name and airbill number; • Date of shipment; • Date of next shipment; and • Any other information pertinent to the shipment?			

APPENDIX H GLOSSARY

Analyte -- The specific compound, mixture, element, or ion an analysis seeks to determine.

Analytical Services Branch (ASB) -- The branch of the Technology Innovation and Field Services Division (TIFSD) of the United States Environmental Protection Agency's (EPA's) Office of Superfund Remediation and Technology Innovation (OSRTI) responsible for the overall management of the Contract Laboratory Program (CLP) under the Office of Land and Emergency Management (OLEM).

Aroclor -- Polychlorinated biphenyls (PCBs) or a class of organic compounds with 1 to 10 chlorine atoms attached to biphenyl and a general chemical formula of $C_{12}H_{10-x}Cl_x$. PCBs, commercially produced as complex mixtures containing multiple isomers at different degrees of chlorination, were marketed in North America under the trade name Aroclor.

Case -- A finite, usually predetermined, number of samples collected over a given time period from a particular site. Case Numbers are assigned by the Sample Management Office (SMO). A Case consists of one or more Sample Delivery Groups (SDGs).

Chlorinated Dibenzo-*p*-Dioxin/Chlorinated Dibenzofuran (CDD/CDF) -- A group of organic compounds of tetra- through octa-chlorinated dibenzo-*p*-dioxins (CDDs) and dibenzofurans (CDFs).

Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) -- First authorized by Congress in December 1980, and amended in 1986, CERCLA provided broad Federal authority to respond directly to the release or possible release of hazardous substances that may endanger human health or the environment. CERCLA also established a Trust Fund to provide for cleanup when no responsible party could be identified; hence, CERCLA is commonly referred to as "Superfund."

Congener -- Individual compound belonging to a group or class of compounds with a similar general structure.

Contract Laboratory Program (CLP) -- Supports the EPA's Superfund effort by providing a range of state-of-the-art chemical analytical services of known and documented quality. This program is directed by the Analytical Services Branch (ASB) of the Technology Innovation and Field Services Division (TIFSD) Office of the Superfund Remediation and Technology Innovation (OSRTI) of the EPA.

Custody Seal -- An adhesive label or tape that is used to seal a sample bottle or container that maintains chain of custody and that will break if the sample bottle or container is opened or tampered with.

Cyanide (Total) -- Cyanide ion and complex cyanides converted to hydrocyanic acid (HCN) by reaction in a reflux system of a mineral acid in the presence of magnesium ion.

Data Quality Objectives (DQO) -- Qualitative and quantitative statements that clarify technical and quality objectives, define the appropriate type of data, and specify tolerable levels of potential decision errors that will be used as the basis for establishing the quality and quantity of data needed to support decisions.

Data Validation -- Data validation is based on Region-defined criteria and limits, professional judgment of the data validator, and (if available) the Quality Assurance Project Plan (QAPP) and Sampling and Analysis Plan (SAP).

Deuterated Monitoring Compound (DMC) -- Compounds added to every Gas Chromatograph/Mass Spectrometer (GC/MS) calibration standard, blank, and sample to evaluate the efficiency of the extraction/purge-and-trap procedures, and the performance of the GC/MS systems. DMCs are isotopically labeled (deuterated) analogs of native target compounds. DMCs are not expected to be naturally detected in the environmental media.

Duplicate -- Quality Control (QC) sample required by the laboratory's contract to check the accuracy and precision of inorganic analyses. It is a second aliquot of the same sample to determine the precision of the method.

Equipment Blank -- A sample used to check field decontamination procedures. See Field Blank.

Field Blank -- Any sample that is submitted from the field and identified as a blank. A field blank is used to check for cross-contamination during sample collection, sample shipment, and in the laboratory. A field blank includes trip blanks, rinsate blanks, bottle blanks, equipment blanks, preservative blanks, decontamination blanks, etc.

Field Duplicate -- A duplicate sample generated in the field, not in the laboratory. Checks reproducibility of laboratory and field procedures and indicates non-homogeneity.

Field QC Sample -- Any QC samples submitted from the field to the laboratory. Examples include, but are not limited to, field blanks, field duplicates, and field spikes.

Field Sample -- Primary sample material collected from the field from which other samples, such as duplicates or split samples are derived. A field sample can be prepared in the field and sent for analysis in one or multiple containers, and is identified by a unique EPA sample number.

Field Sampling Plan (FSP) -- Developed to outline the actual steps and requirements pertaining to a particular sampling event, and explains, in detail, each component of the event to all involved samplers.

Holding Time -- The elapsed time expressed in hours, days, or months from the date of collection of the sample until the date of its analysis.

> **Contractual** -- The maximum length of time that the CLP laboratory can hold samples prior to extraction and/or analysis, as specified in the CLP analytical services Statements of Work (SOWs).
>
> **Technical** -- The maximum length of time that samples may be held from time of collection to time of preparation and/or analysis and still be considered valid.

Laboratory Blank -- See Method Blank.

Laboratory Duplicate -- A sample required by the laboratory's contract to check the precision of inorganic analyses.

Laboratory QC Sample -- An additional volume of an existing sample, as required by the laboratory's contract, used to detect contamination or error in the laboratory's practices.

Matrix -- The predominant material of which a sample to be analyzed is composed. Matrix is not synonymous with phase (liquid or solid).

Matrix Spike (MS) -- QC sample required by the laboratory's contract to check the accuracy of organic and inorganic analyses. It is an aliquot of a sample (water or soil) that is fortified (spiked) with known quantities of a specific analyte and subjected to the entire analytical procedure to indicate the appropriateness of the method for the matrix by measuring recovery. See Matrix Spike Duplicate.

Matrix Spike Duplicate (MSD) -- QC sample required by the laboratory's contract to check the accuracy and precision of organic analyses. It is a second aliquot of the same matrix as the Matrix Spike (MS) that is spiked to determine the precision of the method. See Matrix Spike.

Method Blank -- An analytical control consisting of all reagents, internal standards and surrogate standards (or DMCs for GC/MS organic analysis), that is carried throughout the entire analytical procedure. The method blank is used to define the level of laboratory, background, and reagent contamination, also referred to as laboratory blank when defining the level of laboratory contamination.

Modified Analysis (MA) -- A contractual document with modified Statement of Work (SOW) requirements that append to the SOW. All contract and analytical SOW requirements remain in effect unless explicitly modified.

Performance Evaluation (PE) Sample -- A sample of known composition to the EPA; however, it is unknown to the Contractor and is provided to evaluate Contractor performance.

Pesticides -- Substances intended to repel, kill, or control any species designated a "pest," including weeds, insects, rodents, fungi, bacteria, and other organisms. Under the CLP, only organochlorine pesticides are analyzed (e.g., DDT, Dieldrin, Endrin, etc.).

Polychlorinated Biphenyls (PCBs) -- A group of toxic, persistent chemicals used in electrical transformers and capacitors for insulating purposes, and in gas pipeline systems as a lubricant. The sale and new use of PCBs were banned by law in 1979.

Quality Assurance (QA) -- An integrated system of management activities involving planning, implementation, assessment, reporting, and quality improvement to ensure that a process, item, or service is of the type and quality needed and expected by the customer.

Quality Assurance Project Plan (QAPP) -- Document written to meet requirements outlined in the document *EPA Guidance for Quality Assurance Project Plans* (EPA QA/R-5). Prepared in advance of field activities and used by samplers to develop any subsequent plans such as the Sampling and Analysis Plan (SAP) or the Field Sampling Plan (FSP).

Quality Control (QC) -- The overall system of technical activities that measures the attributes and performance of a process, item, or service against defined standards to verify that they meet the stated requirements established by the customer; operational techniques and activities that are used to fulfill requirements for quality.

Regional Sample Control Coordinator (RSCC) -- In most Regions, coordinates sampling efforts and serves as the central point of contact for sampling questions and problems. Also assists in coordinating the level of Regional sampling activities to correspond with the monthly projected demand for analytical services.

Regional Site Manager -- Coordinates the development of data quality objectives and oversees project-specific remedial or removal contractors, State officials, or private parties conducting site sampling efforts.

Rinsate Blank -- A sample used to check decontamination procedures. Also see Field Blank.

Sample -- A discrete portion of material to be analyzed that is contained in single or multiple containers, and identified by a unique sample number.

Sample Delivery Group (SDG) -- A unit within a sample Case that is used to identify a group of samples for delivery. An SDG is defined by the following, whichever is most frequent:

- Each Case of field samples received; or
- Each 20 field samples (excluding PE samples) within a Case; or
- Each 7 calendar day period (3 calendar day period for 7-day turnaround) during which field samples in a Case are received (said period beginning with the receipt of the first sample in the SDG).

In addition, all samples and/or sample analyses assigned to an SDG must have been scheduled under the same contractual turnaround time. Preliminary Results have no impact on defining the SDG. Sample may be assigned to SDGs by matrix (e.g., all soil samples in one SDG, all water samples in another) at the discretion of the laboratory.

Sample Label -- An identification label attached to a sample bottle or container to identify the sample.

Sample Management Office (SMO) -- A Contractor-operated facility operated under the SMO contract, awarded and administered by the EPA.

Sample Number -- A unique number used to identify and track a sample. This number can be recorded on a sample label or written on the sample bottle or container using indelible ink.

Sampling and Analysis Plan (SAP) -- A document that explains how samples are to be collected and analyzed for a particular sampling event.

Scribe -- A stand-alone Windows-based desktop application that samplers can use to automatically create and generate sample documentation prior to and during sampling events.

Semivolatile Organic Analyte (SVOA) -- A compound amenable to analysis by extraction of the sample using an organic solvent.

Standard Operating Procedure (SOP) -- A written document that details the method for an operation, analysis, or action with thoroughly prescribed techniques and steps, and that is officially approved as the methods for performing certain routine or repetitive tasks.

Statement of Work (SOW) -- A document that specifies how laboratories analyze samples under a particular Contract Laboratory Program (CLP) analytical program.

Superfund -- The program operated under the legislative authority of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and Superfund Amendments and Reauthorization Act (SARA), that funds and carries out EPA removal and remedial activities at hazardous waste sites. These activities include establishing the National Priorities List (NPL), investigating sites for inclusion on the list, determining their priority, and conducting and/or supervising cleanup and other remedial actions.

Superfund Amendments and Reauthorization Act (SARA) -- The 1986 amendment to the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA).

Traffic Report/Chain of Custody (TR/COC) Record -- A record that is functionally similar to a packing slip that accompanies a shipment of goods. Used as physical evidence of sample custody and functions as a permanent record for each sample collected.

Trip Blank -- A sample used to check for contamination during sample handling and shipment from field to laboratory. Also see Field Blank.

Volatile Organic Analyte (VOA) -- A compound amenable to analysis by the purge-and-trap technique. Used synonymously with the term purgeable compound.

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Interpreting CO_2 Saturation Changes from Pulsed Neutron Logs at the Aquistore Site

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Abstract

The use of repeated pulsed neutron (PN) logging has proved effective in numerous CO_2 storage monitoring portfolios around the world. It is regarded as the go-to technique for interpreting saturation changes at the well-bore and has been routinely used for monitoring saturation changes in hydrocarbon reservoirs since tools appeared in the 1960s. The output from this type of tool that is almost always used for saturation monitoring is the so-called 'Sigma' curve, which can be used to distinguish formation fluids on the basis of how fast thermal neutrons are captured.

Through the AQUISTORE Project in Saskatchewan, Canada, the Petroleum Technology Research Centre (PTRC) is demonstrating time-lapse pulsed neutron logging is an appropriate method to monitor near well CO_2 saturation changes in a highly saline reservoir due to a large Sigma contrast between the saline formation waters and the injected CO_2. PTRC has conducted time-lapsed PN logging at the injection well to observe the saturation in the perforated interval and monitor any above zone migration. In addition, a total of 20 PN logging runs were also undertaken to detect the arrival of CO_2 at the project's observation well, which is located approximately 150 m from the injection well.

Here we present an interpretation of a secondary measurement produced by the tools, which is a measure of the hydrogen index obtained from the total count rates of secondary gamma-rays. We use the Ratio output to determine the suitability of this curve for monitoring CO_2 movement and to see any additional benefits compared to the 'Sigma' curve. We find that the Ratio shows slightly better repeatability than the Sigma curve and could certainly be used in its place to monitor saturation changes. Furthermore, at the Aquistore site the wells were drilled with oil based mud. The Ratio measurement is almost unaffected by the presence of oil, and responds strongly to carbon dioxide thus is more reliable for interpreting saturation.

Keywords: Pulsed Neutron logging; saturation; monitoring; repeatability

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Nomenclature

PN	Pulsed Neutron
Sigma	Used to distinguish formation fluids on the basis of how fast thermal neutrons are captured.
Ratio	A measure of the hydrogen index obtained from the ratio of the "near to far" detector capture count rates.
Job	refers to all the PN logs run on a particular day.
Pass	refers to an individual log. For example the May 2016 Job comprises a Main Pass and three Repeat Passes over the interval of interest.

1. Introduction

Tracking the migration of injected CO_2 in the subsurface is important for effective management of CO_2 storage operations and to meet regulatory requirements. Migration can be tracked using both surface geophysical and well based methods. A variety of wireline logging techniques are available for use in wells but methods that exploit interactions between neutrons and the formation are normally the most accurate and simplest to apply. The most commonly used tools are Pulsed Neutron Logs (PNL) that measure a property known as 'Sigma'. This quantifies the rate that thermal neutrons are captured and it is directly related to the thermal neutron capture cross-section. Sigma measurements have been routinely used for monitoring saturation changes in hydrocarbon reservoirs since tools capable of measuring it appeared in the 1960s. The use of Sigma for CO_2 monitoring is a natural and straightforward extension of that.

PN tools also produce a second measurement which is related to the hydrogen index (hydrogen atoms per unit volume) obtained from the total count rates of secondary gamma-rays (as opposed to their decay rate). The output is often called the "Ratio" as it is obtained by taking the Ratio of counts from two different detectors seeing both the near and far regions of the well-bore. It is a calibrated measurement in as much as the tool response to a source of gamma-rays with a known strength is measured prior to running the log. Nevertheless, the Ratio measurement is strongly dependent on the precise environment of the tool and in particular it is strongly dependent on what fluids are within the well. Because of this, it is most suited to application in dedicated monitoring wells cemented and cased such that no CO_2 surrounds the tool down-hole during logging. In these circumstances it may be the better measurement for monitoring fluid saturation. For example, the Sigma measurement relies on high formation water salinities to give an accurate estimate of water saturation (as this gives a strong contrast in the responses to water and CO_2). The minimum salinity needed to apply the measurement depends on porosity and the accuracy demanded of the saturation estimate, but as a general rule formation waters fresher than a seawater composition (35,000 ppm NaCl (w/w)) are unlikely to be suitable candidates. This obviously can be a major drawback to the use of the Sigma curve in aquifers with relatively fresh water. The Ratio measurement on the other hand needs some chloride in the formation water but can certainly give a satisfactory result at fairly low salinities.

1.1. This Case Study

At the site of the Aquistore Project in Saskatchewan, Canada, CO_2 is injected into brine-saturated Cambro-Ordovician Winnipeg and Deadwood Formations overlying Precambrian basement rocks for the purpose of CO_2 storage [1]. Injection began in April, 2015, using a single vertical injection well which is perforated over intervals ranging from 3170 m to 3370 m depth. Time-lapsed PN logging was conducted at the injection well to observe the saturation in the perforated interval and monitor any above zone migration. In addition, a total of 20 PN logging runs were also undertaken to detect the arrival of CO_2 at the project's observation well, which is located approximately 150 m from the injection well. The observation well is cased and cemented over its entire depth, and no intervals in this well have been perforated. Due to relatively high salinity of the formation water (320,000 ppm), the Sigma output was used in the first instance for the saturation interpretation [2]. Statistically-significant changes in the Sigma log response have been observed, attributed to CO_2 arrival, from February, 2016 (at which time 45

kilotonnes of CO_2 had been injected) onwards until the last logs were acquired in December 2016 (after 104 kilotonnes of CO_2 had been injected) [2].

Here we extend the interpretation to also include the Ratio output to determine the suitability of this curve for monitoring CO_2 movement and to see any additional benefits compared to the 'Sigma' curve. One advantage of the large number of runs means that the saturation state can be seen to change in stages which can be related to changes in both Sigma and Ratio measurements, i.e. to determine the level of noise. We find that the Ratio shows slightly better repeatability than the Sigma curve and responds strongly to carbon dioxide. Moreover, the Ratio measurement is almost unaffected by the presence of oil, making it highly suitable for monitoring wells drilled with oil based mud.

2. Pulsed Neutron logging technology

2.1. Tool Description and Physics of the Measurement

A typical, modern pulsed neutron logging tool comprises a neutron source and two gamma-ray detectors situated approximately 1m from it and 15cm apart. These, together with power supplies and the down-hole instrumentation are located in a slim housing with an outside diameter of the order of 50 mm. This is small enough to allow logging of most production and injection wells without the need to pull the tubing. The neutron source generates intense bursts of fast neutrons by exploiting the fusion of deuterium and tritium nuclei. The bursts last about 0.1 ms and generate 50,000 to 100,000 fast neutrons. The fast neutrons are slowed to thermal velocities as a result of collisions with nuclei in the borehole fluid, completion and formation. Once the neutrons have slowed to thermal energies they can be captured by certain nuclei and in the process a secondary gamma-ray with a characteristic energy is produced. Gamma-rays that are produced in the vicinity of the detectors, and that travel towards the tool, may be detected. Many commonly occurring nuclei are capable of capturing thermal neutrons but normally the most significant is Chlorine-35. This is both abundant and has a high thermal neutron capture cross-section –i.e. it has a strong affinity for thermal neutrons. Other nuclei either tend to be abundant but have a low capture cross-section –ie are less likely to capture neutrons; or have a high capture cross-section but low abundance. So for most intents and purposes the tool responds exclusively to chlorine which is invariably present as chloride ion dissolved in the formation water.

In the Sigma measurement the rate that the secondary gamma-activity decays after the neutron burst is measured. The decay-rate is expressed on a PN log as the quantity Sigma, which is proportional to it and has units simply named 'Capture Units (CU)'. Logging tools are typically designed to be accurate in the range 0-75 CU which covers the range of readings that are likely to be found in reservoir rocks. Each detector can produce a separate Sigma measurement with slightly different depths of investigation (the further the detector is from the source the greater the depth of investigation).

As already noted there is a second type of measurement that the tool can produce which is based on the total number of secondary gamma-rays detected by the tool. For a two detector tool it is actually the Ratio of the two count-rates that is used. Using the Ratio helps to avoid some of the variation caused by changes in environmental factors such as hole size, bore-hole fluid and temperature and pressure. Because the Ratio is not based on the decay rate, there is actually no need for a pulsed source it just happens to be what is needed for the Sigma measurement. The total secondary gamma-ray count-rate is ultimately determined by the population of thermal neutrons in the vicinity of the detectors (providing there is a reasonable concentration of thermal neutron absorbing nuclei). The Ratio measurement is therefore more sensitive to how effective the tool's environment is at slowing fast neutrons than its ability to capture slow neutrons. The naturally occurring substance that is most effective at thermalizing fast neutrons is water (due to its high hydrogen index).

In comparison, both the Sigma and the Ratio measurement respond to water but where Sigma is mainly responding to dissolved chloride, the Ratio responds directly to the water molecules. There are advantages and

disadvantages to both measurements but an important virtue of the Ratio is that it does not need a high salinity to give a good contrast between water saturated and gas bearing formations. This is particularly important in Australia where formation waters are often fresh [3]. On the other hand, because Sigma is a transient measurement it is largely immune to changes in the tool's environment so, for example, changing the contents of a borehole from water to gas should have little or no effect on the measurement and two different tools run in the same well should give the same result. This has an unfortunate practical consequence that the Ratio measurement is considered in some sense inferior and not worthy of the same care and attention devoted to the Sigma. In the case of the Aquistore project, there is a dedicated observation well (named OBS here) which is permanently filled with brine so both measurements are equally applicable. But the injection well (INJ) changed from being filled with brine prior to injection, to being filled with CO_2 once injection was underway.

2.2. Interpretation of the measurements

As noted above both outputs from the tool are indirectly related to water volume. The Sigma measurement is the weighted average of the individual components making up the formation. This simple mixing law is another reason why Sigma is a popular way of monitoring water saturation. If the sand being targeted for injection is modelled as a three component mixture (matrix, water and CO2) then the measured Sigma is given by:

$$\sum = \sum_{ma}(1-Ø) + \sum_{w}Ø.Sw + \sum_{g}Ø.(1-Sw) \qquad 1$$

Where Sw is the water saturation, Ø is the total porosity and suffixes ma, w and g correspond to matrix, water and CO_2. Porosity is known from open-hole log analysis so the equation can be re-arranged to find Sw (assuming the Sigma values for the components are known). In the case of the Aquistore wells the formation water is extremely saline (200 k ppm(w/w) chloride) and the Sigma value has been estimated to be 145 CU. The 'text-book' Sigma value for a sandstone matrix is 4-5 CU. The Aquistore sands have porosities on the order of 10% so that prior to injection (Sw = 1.00) the expected formation Sigma is 18-19 CU. Carbon dioxide has a low Sigma value of about 1.5 CU, this reflects its relatively low density and the weak thermal neutron capturing ability of carbon and oxygen. Even displacing 20% of the water with CO_2 will have an easily detectable effect on the Sigma measurement reducing it to approximately 16 CU. Note that for the fresher formation waters expected in Australia the equivalent change is only about 0.5C U (from about 6.5 to 6 CU).

The Ratio measurement is more difficult to interpret mainly because a) there are no chart books to provide the end point component values; and b) the well-bore contributes to the measurement. Nevertheless, a knowledge of the physics of the measurement can be used to predict how the Ratio depends on water saturation. Recall that the measurement is responding to the effectiveness of the formation and well-bore at slowing the fast neutrons. The well-bore does not change so its contribution should be constant, the same is true of the matrix. Carbon Dioxide has almost no slowing power, because it has a hydrogen index of zero and has a low density, so the Ratio changes in response to changes in formation water volume (or equivalently saturation). In this case a relationship between water volume and Ratio was found by cross-plotting porosity, found from the open hole logs, against the baseline pulsed neutron log (run before injection commenced). This provided a linear relationship between water volume (Ø.Sw) and the Ratio.

$$Ø.Sw = A.(R - B) \qquad 2$$

Where A, B are constants obtained by a fitting process. The values of A, B are unique to the well (OBS) and the specific type of tool used (Weatherford PND), if either of these changes a different relationship is required. The alternative approach would be to model the Ratio using a Monte Carlo technique.

3. Aquistore Project

3.1. Geology

The Aquistore Project is located in the Williston Basin, a large intracratonic basin centred on North Dakota and extending westward into Montana and northwards into Saskatchewan. The basin is approximately oval in shape with the long axis orientated roughly NW to SE. It is underlain by Precambrian basement and is filled with a more or less complete sequence of sediments ranging from Cambrian to Carboniferous and Jurassic to Tertiary. The sediments include clastics, carbonates and evaporates [4]. The CO_2 is being injected into sandstones of Ordovician and Cambrian age. The seal is provided by an organic rich, black shale of Ordovician age. At its deepest point, in western North Dakota, the basin is about 5000 m deep but in the Aquistore area basement is encountered at about 3500 m [5].

This study primarily deals with the sandstones which are being used for injection. These are divided between the Cambrian Deadwood Formation and the Ordovician Black Island Formation. The former lies directly on basement and is approximately 150 m thick in the Aquistore area. The latter lies immediately above the Deadwood and is about 45 m thick. The Black Island is itself capped with the 30 m thick Icebox shale which is the primary seal for the storage complex. Open hole logs have been run to the intermediate casing shoe(s) at about 620 m MDRT and this includes all the sediments older than Tertiary. The pulsed neutron logs were not run above 2500 m, however, and most are terminated at about 2900 m. This is still well above the injection sands and includes several intervals of low porosity limestone and dolomite as well as evaporites that are useful for understanding the tool responses.

3.2. Wells

The two Aquistore wells are operated by the Petroleum Technology Research Centre (of Western Canada) and have the full names PTRC-OBS-5-6-2-8 and PTRC-INJ-5-6-2-8. In this paper they will simply be referred to as OBS and INJ. They are both vertical, drilled to a T.D. of approximately 3400 m and are located approximately 150 m apart. The nature of the geology in the area means that they penetrate almost identical sections and the tops and thicknesses of the various units rarely differ by more than a few metres. Although the wells penetrate very similar stratigraphy they have significantly different designs that reflect their different functions. The southerly well INJ is used for injection. It was drilled through the zone of interest with a 251 mm bit (10 ¼") and was subsequently cased with 193mm (7.5" casing) and cemented. Four sets of perforations at depths between 3170 – 3370m expose the permeable sands into which CO_2 is injected. A Packer was set above these and a 114.3 mm tubing string is used for injection. The second well is the observation well and was drilled with a smaller bit of approximately 216 mm. It has been cased and cemented with 114.3 mm casing meaning that there is a relatively thick cement sheath (compared to a typical hydrocarbon well).

3.3. Pulsed Neutron Logging

Pulsed Neutron logs have been acquired in both wells although this paper concentrates on the results from the OBS well, which was acquired with the Weatherford PND tool. Both wells were drilled in 2012 and the open hole logs were acquired then. A baseline pulsed neutron log was run after the wells had been cased. The tool used for that was the Schlumberger RST. The wells were drilled with oil based mud and open hole log analysis showed they were deeply invaded with oil from the mud. This was still present in all the sands in the OBS well when the baseline RST log was run. The net effect of this was that the Sigma values measured in the sands were lower than expected had they been saturated with formation water.

Injection of CO_2 started with some short duration trials early in 2015 and begun in earnest in October 2015. Twelve PND log surveys have been made between April 2015 and April 2018 (seven of these were made after October 2015). A typical survey involved four individual passes over the Deadwood and Black Island sandstones

up to 3150 m (the target for injection). One pass was normally logged up to a depth of at least 2900 m, approximately 250 m above the top of the zone of interest. This allowed the tool response and repeatability to be checked in formations that were well above the influence of the CO_2. Interpretation of the PND logs showed that most CO_2 was being injected into a 10 m thick sand package within the Deadwood Sandstone (between 3232.5 m and 3242.5 mMDRT).

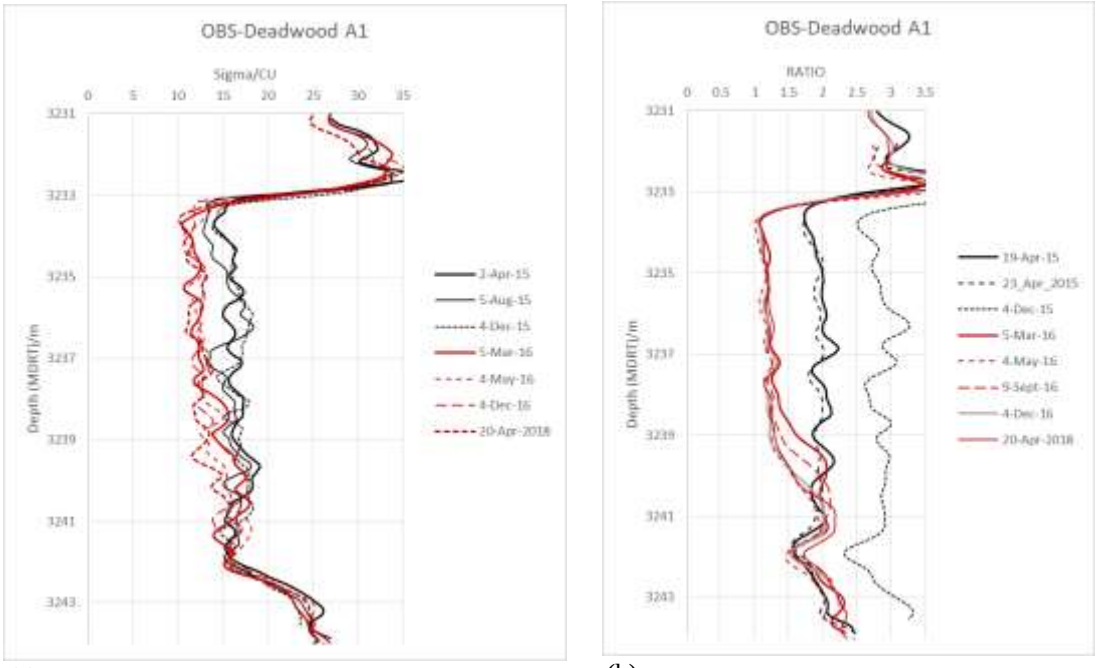
4. Results

4.1. Time-Lapse Results

Sigma and Ratio curves acquired on seven of the surveys are shown in figure 1a and b respectively (several of the earlier surveys have been omitted for clarity). Both measurements show the arrival of the CO_2 plume between December 2015 and March 2016. Sigma falls from approximately 15-16 cu before the arrival of the CO_2 to 10-12 cu after. In the case of the Ratio the equivalent values are 1.8-2.0 and 1-1.2 respectively. A careful examination shows that the base of the sand is still water bearing but that the contact has moved down approximately 2 m between March 2016 and April 2018, this is particularly clear from the Ratio curves.

Agreement between most of the surveys is reasonable until, of course, CO_2 enters the sand. An obvious exception is the Ratio curve acquired in December 2015 which is consistently higher than any of the other surveys and normally exceeds 2.5 in the sand. The curve is in fact offset to higher values for the entire logged interval. The contractor is unable to explain this anomalous response. The Ratio is supposed to be calibrated prior to logging by placing a gamma-ray source of known strength at a fixed position relative to the detectors. Possibly there was an error in this step or possibly the response of the detectors changed at well temperature. Whatever the reason, the log is almost certainly erroneous which is unfortunate as the Sigma curves showed the CO_2 plume passes the OBS well between this survey and the next one.

Both measurements clearly show the arrival of the CO_2 and subsequent downward movement of the contact. The Ratio shows this most clearly partly because the curve is smoother and shows less small scale variation. But in fact the percentage change before and after the arrival of the CO_2 is also greater. The reasons for the differences are discussed below.



(a) (b)

Figure 1: Time-lapse logs over the Deadwood A1 sands in the Observation well (a) Sigma response; (b) Ratio response. Red Curves are post-arrival of the CO_2 plume.

4.2. Repeatability

Some idea of repeatability can be gained by comparing the different surveys before the arrival of the CO_2 plume but it is also possible to compare individual passes made as part of the same survey. The latter is the best way to determine the inherent accuracy of the tool and its detection limits. Figure 2a and b show an example from May 2016. It can be seen that the curves repeat very well. The average Sigma reading and its standard error reading for the four runs is 13.62 (+/-0.02) CU and the equivalent for the Ratio is 1.33 (+/-0.01). These correspond to very small changes in saturation.

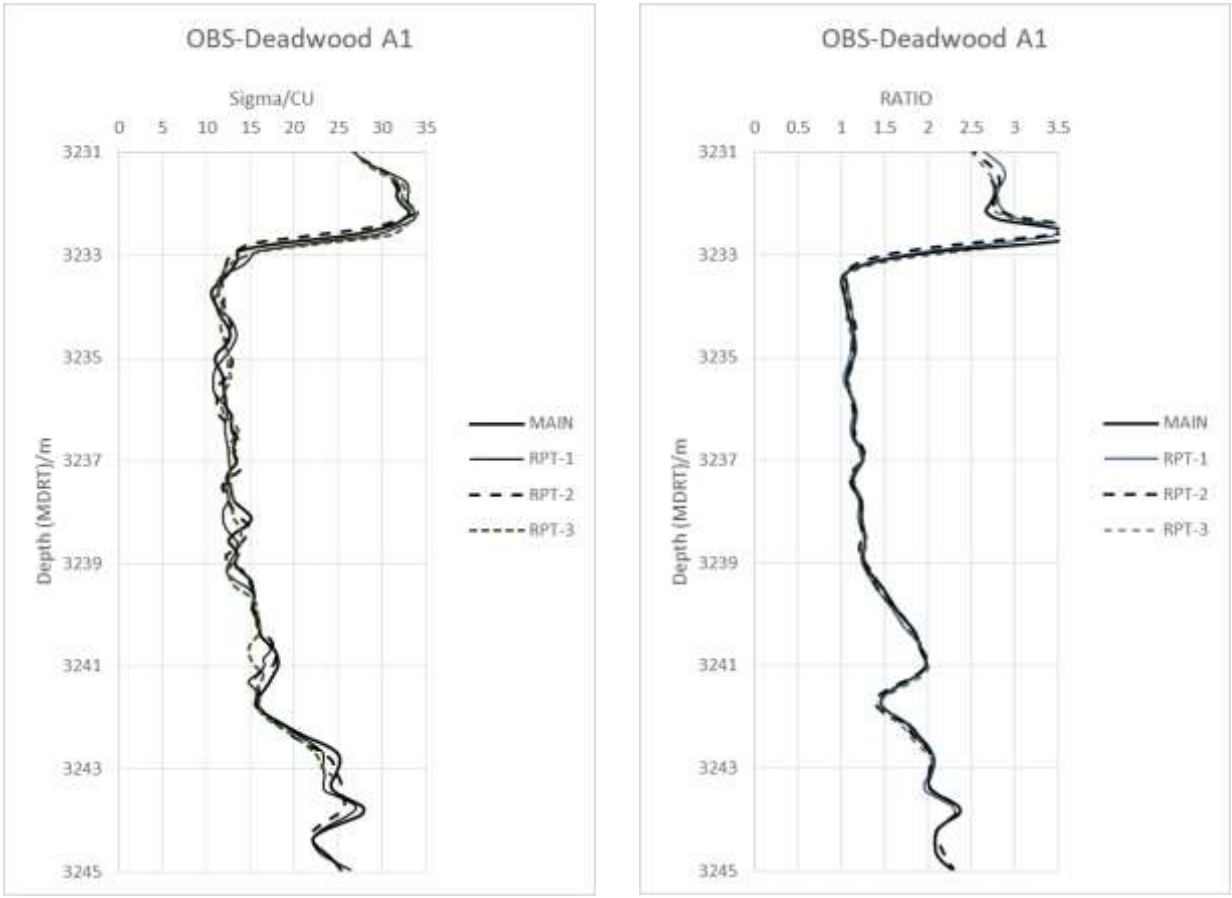


Figure 2: Comparison of repeatability of logging outputs pre-CO_2 arrival (a) Sigma response; (b) Ratio response.

4.3. Oil based mud

As noted earlier the sands were invaded by oil filtrate during drilling and this was still present at the OBS well when the baseline survey was run. In section 2.2 a simple calculation was made that predicted the Sigma reading for the sand saturated with water should be 18 – 19 CU, inspection of figure 2a shows the actual readings varied between 15 – 17 CU. The average Sigma reading for the baseline survey was 15.7 CU whereas the predicted value was 19.1 CU. The reduction is caused by mud filtrate displacing formation water. The Sigma value for the oil is not known but as it contains no chloride (or any other strong thermal neutron absorbers) it will be small. The Schlumberger chart book quotes a value of 22 CU for a 'generic' oil which is far lower than the value for the formation water (estimated at 145CU) [6]. Interestingly for the INJ well the average Sigma reading measured in the baseline survey was very close to the prediction: 17.6 CU predicted vs 17.3 measured. The predicted Sigma at the INJ well is lower because the porosity is lower at that location. In this well water samples were taken using a formation tester and as part of the sampling process the oil had to be pumped out of the formation.

The oil saturation can be found from conventional log analysis and this gave values of 35-40% in the sand considered here. This could be used to predict the Sigma value for the oil invaded sand by substituting into equation

1 but in fact the Sigma curve from the baseline log was used to provide an independent estimate of the oil saturation and this agreed well with the conventional log analysis. The replacement of up to 40% of the water by oil explains the reduced contrast between Sigma logs recorded before and after the arrival of the CO_2. In the case of the Ratio, the effect of replacing formation water with oil is much smaller and potentially non-existent. This is because the hydrogen index of the oil is similar to that of water and therefore a mixture of the two fluids has almost the same ability to thermalize neutrons as water alone. In short, the Ratio measurement is almost insensitive to the presence of oil, and the arrival of the CO_2 produces a much larger change in Ratio than Sigma. As will be discussed below the two measurements together provide strong evidence that the CO_2 has actually removed the oil from the sand.

5. Discussion

Both measurements can be converted to saturation. In the case of Sigma this is achieved by re-arranging equation 1. The accuracy of the saturation depends on the accuracy of the Sigma measurement and properly characterising the Sigma values of the components (the parameters in equation 1). Here the parameters have all been taken from chart-books, but the good agreement between the saturation calculated from open hole log analysis and from the baseline Sigma measurement shows these are reasonable. All of them could be measured in the laboratory if one wanted to remove that element of uncertainty. Figure 3 shows the change in average water saturation (Sw) calculated from Sigma in the sand through time. The presence of the oil in the early surveys can clearly be seen as the Sw is consistently less than 1.

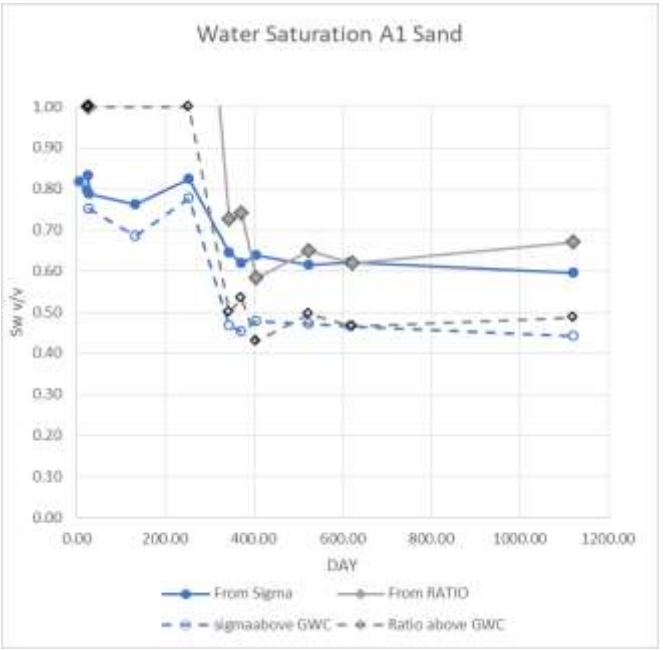


Figure 3: Change in average water saturation (Sw) versus time interpreted from Sigma and Ratio curves (April 2015 is day 0).

Figure 3 also shows the equivalent Sw trend calculated from the Ratio. In this case the calculated Sw for three surveys in April 2015 is 100%. After the arrival of the plume the Sw values fall to similar values to those from the Sigma curve. Unfortunately, the Ratio measured in the survey immediately before the arrival of the plume was the erroneous one discussed above and so has been excluded. The survey before that (August 2015) is also missing because the contractor neglected to provide the Ratio curve. As explained above the Sigma is actually correctly suggesting Sw is less than 100% before the CO_2 arrives, because it is also responding to the oil. The Ratio is almost

insensitive to the oil and so gives the 'expected' Sw of 100%. The good agreement between the Sw values calculated using the two different measurements, after the arrival of the CO_2 actually demonstrates that the oil has largely been removed by the CO_2. This is another aspect of the insensitivity of the Ratio to oil. In effect the Ratio measurement is responding entirely to CO_2 whereas the Sigma responds to CO_2 and oil. If the Sw values agree the oil must have been largely removed. The result is hardly surprising as CO_2 is widely used to mobilize oil in EOR projects but it is interesting to see it in action.

The Sigma curve provides accurate estimates of Sw because of the high salinity and therefore Sigma of the formation water. Analysis of water samples obtained from the INJ well showed it has a chloride ion concentration of 200 kppm (w/w) (this is equivalent to a salinity of 330 kppm although the water contains a high concentration of calcium as well as sodium). This was used to estimate the formation water Sigma value of 145 CU. Even replacing a third of the water with oil still gives a good contrast with the CO_2 bearing formation. For fresher waters the contrast would be less and invasion by oil could seriously compromise the accuracy obtainable. On the other hand, providing there is some chloride ion in the formation water, the Ratio method would still provide good accuracy.

In the previous section it was noted that the Ratio curve has a smoother appearance and amongst other things this makes the contact movement much clearer. The reason for the smoother appearance is due to two factors. Firstly, the measurement combines the outputs from the two detectors and secondly at any point it is based on the sum total of the counts rather than trying to fit a decay to counts accumulated in several short windows. The Sigma measurement is based on the output of one detector –although the two detectors do provide separate measurements which could conceivably be averaged. The disadvantage of the Ratio is that it has inherently lower vertical resolution as it ultimately refers to the whole process from emitting the fast neutrons to detecting the capture gamma-rays. For the Sigma measurement it is the capture process alone that produces the measurement and the source of the neutrons is almost immaterial. Much of the smoother appearance of the Ratio curve is therefore a result of its inherently lower vertical resolution. On the other hand inspection of figure 2a shows that at any depth the Sigma curve can easily vary by 1-2 CU which is simply a reflection of its inherently lower accuracy. As is often the case with logging tools higher vertical resolution comes at a cost of lower accuracy. Accuracy can be improved by making multiple passes and averaging the measurements. By using four passes the signal to noise Ratio can be doubled. An extra pass adds very little additional time to the logging job, particularly if it is limited to the interval of interest.

6. Conclusions

This study confirms that Ratio based measurements provide a valid alternative method to Sigma for monitoring CO_2 plumes. In the case of the Aquistore wells, which are particularly well suited to Sigma monitoring, there is not a great incentive to do this, but where formation water salinities are much lower, Sigma monitoring will at best reveal the passage of the plume and may not even be able to do that. The Ratio measurement on the other hand should be able to quantify CO_2 saturations in even quite fresh water. Thus at deep aquifer sites where formation waters are fresh, e.g. in Australia, the availability of an alternative to Sigma is a major benefit.

Repeated surveys with cased hole Pulsed Neutron Logs in a dedicated observation well have not only allowed the progress of injected CO_2 in this particular facility to be tracked but provide an excellent data set for objectively assessing suitability, accuracy and precision of these tools for use in any geo-sequestration project.

Combining the two measurements brings some additional benefits. In this particular case it was possible to deduce that the CO_2 had succeeded in removing the oil filtrate left over from drilling. In a follow up study we are using the two measurements together to identify and quantify salt precipitation.

Finally, the Ratio measurement should be treated as of equal importance to the Sigma and not simply a by-product. In this particular project the Ratio measurement was clearly in error in a particularly important survey

despite the Sigma measurement being acceptable. Furthermore, for several other surveys it was simply not provided in the initial deliverables.

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