Attachment E.I.4. Laboratory Standard Operating Procedures for Groundwater Analysis

Note: This attachment contains procedures PCC intends to utilize. PCC reserves the right to substitute functionally equivalent procedures to those presented herein.

1.0 Scope And Application

This standard operating procedure (SOP) describes the laboratory procedure for the analysis of drinking water by Inductively Coupled Plasma Mass Spectrometry (ICP/MS). A Thermo Scientific RQ ICP/MS is used in this procedure.

1.1 Target Analyte List and Limits of Quantitation (LOQ)

The target analytes and the normal LOQ that can be achieved with this procedure are provided in Table 1, Appendix A.

LOQ are established in accordance with Pace policy and SOPs for method validation and for the determination of detection limits (DL) and quantitation limits (LOQ). DL and LOQ are routinely verified and updated when needed. The current LOQ for each target analyte that can be determined by this SOP as of the effective date of this SOP is provided in Table 1, Appendix A.

The reporting limit (RL) is the value to which analytes are reported as detected or not detected in the final report. When the RL is less than the lower limit of quantitation (LLOQ), all detects and non-detects at the RL are qualitative. The LLOQ is the lowest point of the calibration curve used for each target analyte.

DL, LOQ, and RL are always adjusted to account for actual amounts used and for dilution.

2.0 Summary of Method

2.1 A representative sample aliquot is tested for turbidity. If the turbidity is less than 1 NTU, the sample is matrix matched to the calibration standards and analyzed without digestion. If turbidity is greater than 1 NTU the sample is digested using an appropriate procedure. Sample material in solution is introduced by pneumatic nebulization into a radio frequency plasma where energy transfer processes cause desolvation, atomization and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio (m/z) by a quadrupole mass spectrometer. The ions transmitted through the quadrupole are detected by an electron multiplier and the ion information processed by a data handling system. Interferences relating to the technique must be recognized and corrected for. Such corrections must include compensation for isobaric elemental interferences and interferences from polyatomic ions derived from the plasma gas, reagents or sample matrix.

2.2 Instrumental drift as well as suppressions or enhancements of instrument response caused by the sample matrix is corrected for by the use of internal standards.

3.0 INTERFERENCES

3.1 Isobaric Elemental Interferences – Isobaric elemental interferences result when isotopes of different elements have the same nominal mass-to-charge ratio and cannot be resolved with the instruments spectrometer. One way to solve this problem is to measure a different isotope for which there is no interference. Alternatively, one can monitor another isotope of the element and subtract an appropriate amount from the element being analyzed, using known isotope ratio information. Corrections for most of the common elemental interferences are programmed into the software.

3.2 Isobaric Polyatomic Interferences – Isobaric polyatomic interferences result when ions containing more than one atom have the same nominal mass-to-charge ratio as an analyte of interest and cannot be resolved by the instrument's spectrometer. Examples include ArCl+ (mass 75), which interferes with As. ClO+ (mass 51), which interferes with V, and must be corrected by measuring ClO+ at mass 53. When possible an interference-free isotope should be chosen for measurement.

3.3 Physical interferences are associated with the sample nebulization and transport processes as well as with ion-transmission efficiencies. Nebulization and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement. Dissolved solids can deposit on the nebulizer tip of a pneumatic nebulizer and on the interface skimmers (reducing the orifice size and the instrument performance). Total solid levels below 0.2% (2,000 mg/L) have been currently recommended to minimize solid deposition. An internal standard can be used to correct for physical interferences, if it is carefully matched to the analyte so that the two elements are similarly affected by matrix changes.

3.4 Memory interferences can occur when there are large concentration differences between samples or standards, which are analyzed sequentially. Sample deposition on the sampler and skimmer cones, spray chamber design, and the type of nebulizer affects the extent of the memory interferences, which are observed. The rinse period between samples must be long enough to eliminate significant memory interference.

3.5 It is important to note that matrix matching acid concentrations between standards, blanks and samples cannot be ignored. ICPMS is more sensitive than ICP in this regard.

3.6 Chromic acid should never be used to clean any container used in ICPMS analysis.

3.7 Standards shall be prepared in class "A" glassware and then stored in clean, plastic containers.

3.8 Interference equations are used to correct for isobaric elemental and polyatomic interferences. All equations can be adjusted if necessary or added if the analyst determines that a particular correction is insufficient or is over correcting the data.

4.0 DEFINITIONS

Refer to the Laboratory Quality Manual for a glossary of common lab terms and definitions.

4.1. Total Recoverable Analyte: The concentration of analyte determined either by "direct analysis" of an unfiltered acid preserved drinking water sample with turbidity of <1 NTU, or by analysis of the solution extract of a solid sample or an unfiltered aqueous sample following digestion by refluxing with hot dilute mineral acid(s) as specified in the method.

4.2. Dissolved Analyte: The concentration of analyte in an aqueous sample that will pass through a 0.45µm membrane filter assembly prior to sample acidification.

4.3. Instrument Detection Limit (IDL): The concentration equivalent to the analyte signal that is equal to the average of the standard deviation of a series of 7 replicate measurements of the calibration blank for 3 non-consecutive days at the selected analytical masses as defined in method SW846-6020B. Method 200.8 defines the IDL as 3 times the standard deviation of 10 replicates run in a single day. We perform these IDL studies as defined by 200.8 because this procedure is more representative of the normal variation of an instrument through a longer period of time than that of 6020B.

4.4. Linear Dynamic Range (LDR): The maximum concentration of the range where the instrument response is linear. The LDR must be determined initially and verified every six months or whenever a significant change in instrument response is observed or expected. The initial demonstration of linearity must use sufficient standards to ensure that the resulting curve is linear. The verification of linearity must use a minimum of a blank and three standards. If any verification data exceeds the initial values by ± 10%, linearity must be reestablished. If any portion of the range is shown to be nonlinear, sufficient standards must be used to clearly define the nonlinear portion. This study will be performed as follows:

4.4.1. A blank and a minimum of three mid-level calibration standards of varied concentrations are plotted on a first order linear curve. The resulting regression coefficient must be ≥ 0.998.

4.4.2. Any additional standards are analyzed using this curve. Their observed concentrations are compared to their known values.

4.4.3. The linear portion of the curve is determined by those standards with observed concentrations that vary by less than 10% from their known values.

4.4.4. Any sample with a concentration over the linear dynamic range must be diluted and reanalyzed until the concentration is within the linear dynamic range.

4.4.5. The linear dynamic range is verified semi-annually by running a multi element standard at the high concentration of the linear range. If the standard recovers within 10% of its true value, it is determined that the element is still linear at that range.

4.5. Autotune/Tune: is a Qtegra software tool that allows the iCAP RQ to be optimized in a consistent, routine manner, giving reproducible levels of performance and saving the operator time and effort. It works by following a pre-defined sequence, optimizing individual instrument parameters in turn. Once the Autotune is completed, an Instrument Setting file is created.

4.6. Instrument calibrations: There are two instrument calibrations that are fundamental for obtaining good quality data on the iCAP RQ: (1) Mass calibration, (2) Detector Cross calibration. Both calibrations may be performed in a single routine, or may be performed separately as needed.

4.7. Mass calibration: Sets the quadrupole scan parameters to give the correct measured mass positions. A mass-calibration must be performed whenever the resolution settings are adjusted, as this will affect the apparent mass position. Mass-calibration must be performed when the Performance Report shows that measured peak positions are >0.1 AMU from their nominal position. Mass-calibrations are best performed using a solution containing as many elements as possible or with every analyte required for analysis at the very least. The solution should contain Li and U as these are used as low and high mass datum points. An appropriate, 1 µg/L, concentration solution should be used and should yield between 100,000-1,500,000 cps for each mass to be calibrated is appropriate.

4.8. Detector Cross Calibration (X-Cal): calculates the correction factor, for each measured mass, between the two detector modes, pulse counting and analogue. These routines can be performed separately, but it is advised to run them simultaneously as described here. The necessary frequency of these calibrations depends upon the amount of signal the detector is exposed to, i.e. how many samples are analyzed, which analytes and what concentrations. This routine must be performed whenever the detector voltages are altered. For most laboratories running a moderate sample load, this procedure may be run weekly. A solution that gives a count rate of between 100,000-1,500,000 cps is appropriate. The default mass used here is indium (m/z 115), so this must be present in the solution for the routine to work. For a iCAP RQ instrument, an appropriate concentration would typically be between 3 and 35 µg/L, depending upon the sensitivity of the system. The solution used must contain all the analytes to be measured as an absolute minimum.

4.9. Tuning Solution: A solution that is used to determine acceptable instrument performance prior to calibration and sample analyses.

4.10. Performance Reports: a PlasmaLab software tool that allows the X Series performance to be checked on a daily basis. The Performance Report can be set-up to give information about instrument sensitivity, stability, background, oxide species, doubly charged species, mass-calibration validity and peak resolution. Like Autotune, the Performance Report is user definable but defaults are provided by the manufacturer during installation.

4.11. Cross Calibration Solution: The cross calibration solution is a standard that allows the ICP-MS to determine the crossover point between the analog and the pulse count detector modes, over the entire mass spectrum. It must contain a large number of isotopes that span the full mass spectrum, at high enough concentrations to trigger the analog detector.

4.12. Interelement Corrections (IEC): Single element standards are prepared and ran at each elements upper linear dynamic range limit. If the standard produces a false positive or negative result for any element other than the target analyte, a correction factor can be calculated and used during calibration and analysis of any samples. However the built-in correction equations in the Qtegra software are usually more accurate than the equations derived from a single analysis run.

4.13. Interference Check Solution (ICSA and ICSAB): A solution of elements that are known as interferants prepared at high concentrations. The results are used to verify the accuracy of the interelement corrections and the absence of interelement spectral interferences.

5.0 HEALTH AND SAFETY

The toxicity or carcinogenicity of each chemical material used in the laboratory has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable.

The laboratory maintains documentation of hazard assessments and OSHA regulations regarding the safe handling of the chemicals specified in each method. Safety data sheets for all hazardous chemicals are available to all personnel. Employees must abide by the health, safety and environmental (HSE) policies and procedures specified in this SOP and in the Pace Chemical Hygiene / Safety Manual.

Personal protective equipment (PPE) such as safety glasses, gloves, and a laboratory coat must be worn in designated areas and while handling samples and chemical materials to protect against physical contact with samples that contain potentially hazardous chemicals and exposure to chemical materials used in the procedure.

Concentrated corrosives present additional hazards and are damaging to skin and mucus membranes. Use these acids in a fume hood whenever possible with additional PPE designed for handing these materials. If eye or skin contact occurs, flush with large volumes of water. When working with acids, always add acid to water to prevent violent reactions. Any processes that emit large volumes of solvents (evaporation/concentration processes) must be in a hood or apparatus that prevents employee exposure.

Contact your supervisor or local HSE coordinator with questions or concerns regarding safety protocol or safe handling procedures for this procedure.

6.0 Sample Collection, Preservation, Holding Time, And Storage

Samples should be collected in accordance with a sampling plan and procedures appropriate to achieve the regulatory, scientific, and data quality objectives for the project.

The laboratory sometimes performs samples collection for samples to be analyzed by this SOP in accordance with laboratory SOP ENV-SOP-LENE-0107, *Field Manual*. Refer to this SOP for these instructions.

The laboratory will provide containers for the collection of samples upon client request for analytical services. Bottle kits are prepared in accordance with laboratory SOP ENV-SOP-LENE-*Assembly of Sample Container Kits*. .

Requirements for container type, preservation, and field quality control (QC) for the common list of test methods offered by Pace are included in the laboratory's quality manual.

General Requirements

Matrix	Routine Container	Minimum Sample Amount[1]	Preservation	Holding Time
Total Aqueous	Plastic 500mL	150 mL	Thermal: None Chemical: pH<2 with Nitric Acid	Collection to Analysis: 180 days
Dissolved Aqueous (lab filtered)	Plastic 500mL	150 mL	Thermal: None Chemical: no preservation	Collection to Analysis: 180 days

Drinking Water	Pre-cleaned, HDPE, glass or PTFE (500 mL)	50 mL	Thermal: NA Chemical: 1:1 HNO3; pH <2	
solid	Glass 4oz	10g	Thermal: ≤6°C Chemical: None	Collection to Analysis: 180 days

[1]*Minimum amount needed for each discrete analysis.*

Field / Matrix QC

Trip Blank	Equipment Blank	MS/MSD	Field Duplicate
NA	As Needed	1/20	1/20

Thermal preservation is checked and recorded on receipt in the laboratory in accordance with laboratory SOP ENV-SOP-LENE-0021, *Sample Management*. Chemical preservation is checked and recorded at time of receipt or prior to sample preparation.

6.1 Sample pH is measured upon receipt to ensure that the pH is <2. If pH is found to be >2, an additional aliquot of 1:1 nitric acid is added by receiving staff (not to exceed 1% of the container's total volume). A label is attached to container noting the time, and date of the addition.

6.2 The sample must now be held for 24 hours and the pH rechecked by the metals staff before digestion may begin. This section does not apply to samples that are received unpreserved for filtration by the laboratory. Failure to achieve proper preservation must be documented on the final report.

6.3 For dissolved elements, sample must be filtered through a 0.45 micron pore diameter membrane filter at collection.

After receipt, samples are stored at room temperature. Prepared samples (extracts, digestates, distillates, other) are stored at room temperature.

After analysis, unless otherwise specified in the analytical services contract, samples are retained for 30 days from date of final report and then disposed of in accordance with Federal, State, and Local regulations.

7.0 EQUIPMENT AND SUPPLIES

7.1 Equipment

Table 7.1 Equipment

Supply	Vendor	Model / Version	Comments
ICP-MS	Thermo Scientific	RQ	or equivalent
Autosampler	Elemental Scientific	SC4DX	or equivalent

7.2 Supplies

Table 7.2 Supplies

Supply	Vendor	Model / Version	Comme
Volumetric Flasks	Various	Various; 5- to1000-mL	Class A
Test tubes	17 x 100mm	Mold Pro / MP-120	or equivalent
Pipettors	Eppendorf	Various	

8.0 REAGENTS AND STANDARDS

8.1 Reagents

Table 8.1 Reagents

Reagent/Standard	Concentration/ Description	Requirements/ Vendor/ Item #
Reagent water	ASTM Type II	SOP S-KS-Q-011
Nitric acid	TraceMetal Grade	Fisher / A509-212 (or equivalent)
Hydrochloric acid	TraceMetal Grade	Fisher / A508-212 (or equivalent)

8.2 Standards

Table 8.2 Standards

Reagent/Standard	Concentration/ Description	Requirements/ Vendor/ Item #
Reagent water	ASTM Type II	SOP S-KS-Q-011
Nitric acid	TraceMetal Grade	Fisher / A509-212 (or equivalent)
Hydrochloric acid	TraceMetal Grade	Fisher / A508-212 (or equivalent)
ICP-1A	200 mg/L: As, Ba, Be, Cd, Co, Cr, Cs, Cu, Li, Mn, Ni, Pb, Se, Sr, U, V, Zn 100 mg/L: Ag, Tl	SPEX / XPACEMN-76-500
ICP-2A	200 mg/L: B, Mo, Pd, Pt, Sb, Sn, Ti, Zr	SPEX / XPACEMN-77-500
ICP-3A	1000 mg/L: Al, Ca, K, Mg, Na, S 500 mg/L Fe, P, Si	SPEX / XPACEMN-75-500
ICP-1B	200 mg/L: As, Ba, Be, Cd, Co, Cr, Cs, Li, Mn, Ni, Pb, Se, Sr, U, V, Zn 100 mg/L: Ag, Tl	High Purity Standards / HP7379-500
ICP-2B	200 mg/L: B, Mo, Pd, Pt, Sb, Sn, Ti, Zr	High Purity Standards / HP7376-500
ICP-3B	1000 mg/L: Al, Ca, K, Mg, Na, S 500 mg/L Fe, P, Si	High Purity Standards / HP7375-500
SPK-STD-1B	200 mg/L: As, Ba, Be, Cd, Co, Cr, Cu, Li, Mn, Ni, P, Pb, Se, Sr, Tl, V, Zn	Inorganic Ventures / PA-STD-1B
SPK-STD-2B	1000 mg/L: Si 200 mg/L: B, Mo, Sb, Sn, Ti, Zr 100 mg/L: Ag	Inorganic Ventures / PA-STD-2B
SPK-STD-3B	2000 mg/L: Al, Ca, Fe, K, Mg, Na	Inorganic Ventures / PA-STD-3B
6020 Internal Standard	10 mg/L Bi, Ho, In, Li6 , Rh, Sc, Tb, Y, Ga, I	Inorganic Ventures / 6020ISS
iCAP Q/RQ TUNE solution	1.0 µg/L Ba, Bi, Ce, Co, In, Li, U	Inorganic Ventures / THERMO-4AREV
iCAP Q/Qnova Calibration solution	35 µg/L Be 20 µg/L Zn 15 µg/L Cu, Ni 10 µg/L Al, Ga, Mg 8 µg/L Co, Li, Sc 6 µg/L Ag, Mn 5 µg/L Sr 4 µg/L Ba, Tl 3 µg/L Bi, Ce, Cs, Ho, In, Rh, Ta, Tb, U, Y	Inorganic Ventures / THERMO-5AREV
Single Element Standards	1-10 mg/L; CRDL, ICSB, STK	Ultra Scientific / Various
ICS-ICPMS	10000 mg/L: Cl 2000 mg/L: C 1000 mg/L: Al, Ca, Fe, K, Mg, Na, P, S 20 mg/L: Mo, Ti	High Purity / CLP-INF-1-500

Reagent/Standard	Concentration/ Description	Requirements/ Vendor/ Item #
Uranium	1000 mg/L	SPEX
Uranium	1000 mg/L	Inorganic Ventures
Mercury - Primary	1000 mg/L	SPEX
Mercury - Secondary	1000 mg/L	Inorganic Ventures

8.3 Storage Conditions

Table 8.3 Storage Conditions

Standard Type	Description	Expiration	Storage
Stock Solutions	▪ Concentrated reference solution purchased directly from approved vendor	▪ Manufacturer's recommended expiration date	▪ Store at room temperature unless manufacturer recommends different storage conditions
Intermediate and Working Standard Solutions	▪ Reference solutions prepared by dilutions of the stock solution	▪ 6 months from preparation or the expiration date listed for the stock source, whichever is sooner. ▪ Working solutions must be checked frequently and replaced if degradation or evaporation is suspected.	▪ Store at room temperature unless stock standard manufacturer recommends different storage conditions

8.4 All working solutions are prepared with an acid matrix of 2% nitric acid and 5% hydrochloric acid. If 1:1 nitric acid and 1:1 hydrochloric acid are used in place of concentrated acids, the final solution must contain 2% nitric acid and 5% hydrochloric acid. If Drinking Water analysis is to be performed, the acid concentration is reduced to 1% nitric and 0.5% hydrochloric.

8.5 Prepare calibration standards according to the table below

Table 8.5 – Working Calibration Standards

Working Standard	Stock(s)	Volume Used (mL)	ICPMS Reagent Blank (or drinking water equivalent) (mL)	Final Volume (mL)
CAL0 (Blk Soln/ICB/CCB)	N/A	N/A	1000	1000
CAL4	ICP-1A ICP-2A ICP-3A Hg Intermediate - 1	0.250 0.250 5.00 5.00	489.5	500

Working Standard	Stock(s)	Volume Used (mL)	ICPMS Reagent Blank (or drinking water equivalent) (mL)	Final Volume (mL)
CAL3	CAL4	100.0	100.0	200
CAL2	CAL4	50.0	150.0	200
CAL1	CAL4	10.0	190.0	200
CCV	ICP-1A ICP-2A ICP-3A Hg Intermediate - 1	0.20 0.20 4.00 4.00	991.6	1000
ICV	SPK-STD-1B SPK-STD-2B SPK-STD-3B U intermediate 2 Hg Intermediate - 2	0.05 0.05 1.00 1.0 2.0	195.90	200
ICPMS Spike (waters)	PA-STD-1B PA-STD-2B PA-STD-3B Zn 1000 mg/L U 1000 mg/L	2.0 2.0 5.0 0.6 0.4	190.0	200
ICPMS Mercury Spike	Mercury - Secondary	0.5	99.5	100
U intermediate – 1 (10mg/L) Primary source	U primary stock	1.0	99.0	100
U working - primary Source (0.1 mg/L)	U intermediate-1	1.0	99.0	100
U intermediate -2	U secondary stock	1.0	99.0	100
Uranium Soil Spike 20 mg/L	U primary stock	2.0	98.0	100
Hg Intermediate – 1	Hg Primary	0.05	99.95	100
Hg Intermediate – 2	Hg Secondary	0.05	99.95	100

8.6 Reporting Limit Standard (CRDL): The CRDL is analyzed prior to any samples after the ICB. Additional CRDLs may be analyzed throughout the analytical sequence at the analyst's discretion. The control limits for the CRDL are ±50% of the true value.

8.6.1 The CRDL 1 Stock Standard is prepared from single element standards. Add 500 mL deionized water to a 1-L volumetric, then add all of the single element standards per the Table 8.6 below, except for Sb, Mo, Pd, Pt, Ti, and Sn. Add 1.0 mL nitric acid. Bring to volume and transfer to a labeled, plastic container.

8.6.2 The CRDL 2 Stock Standard is prepared from Sb, Mo, Pd, Pt, Ti and Sn single element standards. Add 500 mL deionized water to a 1-L volumetric, then add the single element standards per the Table 8.6 below. Add 1.0 mL nitric acid. Bring to volume and transfer to a labeled, plastic container.

8.6.3 CRDL Working Standard – In a 100-mL volumetric flask, add 50 mL deionized water, 2.0 mL nitric acid, 5 mL hydrochloric acid (1.0 mL nitric acid, 0.5 mL hydrochloric if performing drinking water analysis), 1.0 mL each of CRDL1 and CRDL 2 Stock Standards. Bring to volume and transfer to a labeled, plastic container.

Table 8.6 – CRDL 1 and CRDL 2 Stock Standards

Component Standard	Element	Stock Standard Concentration (mg/L)	Volume Used (mL)	Final Volume (mL)	CRDL 1,2 Stock Standard Concentration (ug/L)
Single Element Standard	Al	10,000	0.5	1000	5000
Single Element Standard	Sb	1,000	0.1	1000	100
Single Element Standard	As	1,000	0.1	1000	100
Single Element Standard	Ba	1,000	0.1	1000	100
Single Element Standard	Be	1,000	0.05	1000	50
Single Element Standard	Cd	1,000	0.05	1000	50
Single Element Standard	Cr	1,000	0.1	1000	100
Single Element Standard	Co	1,000	0.1	1000	100
Single Element Standard	Cu	1,000	0.1	1000	100
Single Element Standard	Fe	10,000	0.5	1000	5000
Single Element Standard	Pb	1,000	0.1	1000	100
Single Element Standard	Pd	1,000	0.02	1000	100
Single Element Standard	Pt	1,000	0.1	1000	100
Single Element Standard	Mn	1,000	0.1	1000	100
Single Element Standard	Mo	1,000	0.1	1000	100
Single Element Standard	Ni	1,000	0.1	1000	100
Single Element Standard	Se	1,000	0.1	1000	100
Single Element Standard	Ag	1,000	0.05	1000	50
Single Element Standard	Sr	1,000	0.1	1000	100
Single Element Standard	Tl	1,000	0.1	1000	100
Single Element Standard	Sn	1,000	0.5	1000	100
Single Element Standard	Ti	1,000	0.2	1000	200
Single Element Standard	V	1,000	0.1	1000	100
Single Element Standard	Zn	1,000	1.0	1000	1000

8.6 ICS Interference Check Standards (ICSA and ICSAB). The ICSA and ICSAB are analyzed to demonstrate adequate correction for known interferences. The ICSA and ICSAB are analyzed prior to any samples and every 12 hours thereafter, or at a frequency specified by a project QAPP. Chloride in the ICS provides a means to evaluate software corrections for chloride-related interferences such as $^{35}Cl\ ^{16}O$ on ^{51}V, and $^{40}Ar\ ^{35}Cl$ on $^{75}As^{+}$. Iron is used to demonstrate adequate resolution of the spectrometer for the determination of manganese. Molybdenum serves to indicate oxide effects on cadmium isotopes. The other components are present to evaluate the ability of the measurement system to correct for various polyatomic isobaric interferences. The ICSA(B) recovery limits are ± 20% of the true value or less than 2 times (2X) the RL for non-spiked elements.

8.6.1 The ICSA working standard is prepared by adding 10 mL of ICSA stock and 4.0 mL nitric acid to a 200-mL volumetric half-filled with deionized water. Bring to volume and transfer to a labeled, plastic container.

8.6.2 ICSB-1 Stock Standard – The ICSB stock is prepared from single-element standards. Add 500 mL deionized water to a 1-L volumetric flask, and then add the single elements per the Table 8.7 below. Add 20 mL nitric acid. Bring to volume and transfer to a labeled, plastic container.

Table 8.7 – ICSB-1 Stock Standard

Component Standard	Element	Stock Standard Concentration (mg/L)	Volume Used (mL)	Final Volume (mL)	ICSB Stock Concentration (ug/L)
Single Element Standard	Ag	1000	0.5	1000	500
Single Element Standard	As	1000	1.0	1000	1,000
Single Element Standard	Ba	1000	1.0	1000	1,000
Single Element Standard	Be	1000	0.5	1000	500
Single Element Standard	Cd	1000	0.5	1000	500
Single Element Standard	Cr	1000	1.0	1000	1,000
Single Element Standard	Co	1000	1.0	1000	1,000
Single Element Standard	Cu	1000	1.0	1000	1,000
Single Element Standard	Pb	1000	1.0	1000	1,000
Single Element Standard	Mn	1000	1.0	1000	1,000
Single Element Standard	Ni	1000	1.0	1000	1,000
Single Element Standard	Se	1000	1.0	1000	1,000
Single Element Standard	Sr	1000	1.0	1000	1,000
Single Element Standard	Tl	1000	1.0	1000	1,000
Single Element Standard	V	1000	1.0	1000	1,000
Single Element Standard	Zn	1000	10.0	1000	10,000

8.6.3 ICSB-2 Stock Standard – The ICSB stock is prepared from single-element standards. Add 500 mL deionized water to a 1-L volumetric flask, and then add the single elements per the Table 8.8 below. Add 20 mL nitric acid and 100 mL hydrochloric acid.

Table 8.8 – ICSB-2 Stock Standard

Component Standard	Element	Stock Standard Concentration (mg/L)	Volume Used (mL)	Final Volume (mL)	ICSB Stock Concentration (ug/L)
Single Element Standard	Sb	1000	0.50	1000	500
Single Element Standard	Pd	10,000	0.05	1000	500
Single Element Standard	Pt	1000	0.50	1000	500
Single Element Standard	Sn	1000	0.50	1000	500

8.6.4 The ICSAB standard is prepared by adding 10 mL of ICSA stock, 10 mL ICSB-1, and 10 mL ICSB-2 to a 200-mL volumetric half-filled with deionized water. Add 4.0 mL nitric acid and 10.0 mL hydrochloric acid (2.0 mL nitric, 1.0 mL hydrochloric acid if performing drinking water analysis). Bring to volume and transfer to a labeled, plastic container.

8.7 Carrier Solution - The ESI FAST system autosampler uses a carrier solution since the sample is not continuously pumped to the nebulizer. The Blank Solution is used as the carrier.

8.8 Mass Spectrometer Tuning Standard: A standard containing elements representing all of the mass regions of interest (for example, 10 µg/L of ^{6}Li, ^{115}In and ^{238U} or Pb) must be prepared to verify that the mass resolution and mass calibration of the instrument are within the required specifications. This solution is also used to verify that the instrument has reached thermal stability.

8.8.1 It is preferred to use Tune Standard manufactured by Inorganic Ventured, THERMO-4REV, however, an in-house Tune Standard can be made. See below for instructions.

8.8.2 Stock Tuning Standard (ICPMS Tune Stock) – In a 100-mL volumetric flask, add 1.0 mL nitric acid and 1.0 mL each of the 1,000 mg/L Ba, Bi, Ce, Co, In, Li7, Pb, U single element standards. Bring to volume with deionized water and transfer to a labeled, plastic container.

8.8.3 Working Tuning Standard: In a 1-L volumetric flask, add 500 mL deionized water, 10 mL nitric acid, 5 mL hydrochloric acid, and 0.1 mL ICPMS Tune Stock. Bring to volume and transfer to a labeled, plastic container.

8.9 Cross Calibration Standard (X Cal): contains 50 ug/L of as many elements as possible from ^{6}Li to ^{238}U. This standard is used to calculate the concentration when the detector changes from pulse mode to analog mode. This enables a large linear range while protecting the detector. It is preferred to use a Cross Calibration Standard manufactured by Inorganic Ventures, THERMO-5REV.

8.10 Internal Standards (IS):

8.10.1 Internal standards must be present in all samples, standards and blanks at identical levels. This is achieved by directly adding the internal standard stock by on-line addition prior to nebulization using a second channel of the peristaltic pump and a mixing connector. For full mass range scans, a minimum of six internal standards are suggested. During the analysis, the software uses the ratio of analyte and internal standard intensities to adjust the final concentration values. Ratios are based on the intensities in the sample vs. the calibration blank.

8.10.2 The internal standard should be within 50 amu of the measured mass. The procedure described in this SOP for general applications, details the use of ^{6}Li, ^{45}Sc, ^{71}Ga, ^{89}Y, ^{103}Rh, ^{115}In, ^{159}Tb, ^{165}Ho, ^{193}Ir, and ^{209}Bi. Internal standards may be used per mass, mass range (50 amu) or by interpolation.

8.10.3 The assignment of a particular IS may be dictated by the sample matrix. The concentration of the internal standard should be sufficiently high that good precision is obtained and the possibility of correction errors is minimized if the internal standard is naturally present in the sample. One or more of the internal standards may not be suitable due to matrix interferences. It is up to the analyst to recognize and correct the problem by diluting the sample(s) for reanalysis or selecting an alternative internal standard. The analyst may also enhance the concentration of the IS, however, that procedure requires recalibration with the enhanced IS concentration.

8.10.4 Stock Internal Standard Solution – In a 100-mL volumetric flask, add 10 mL deionized water, 1.0 mL nitric acid, 1.0 mL hydrochloric acid, 3.0 mL 1,000 mg/L ^{209}Bi, 25.0 mL 1,000 mg/L ^{71}Ga, 1.0 mL 1,000 mg/L ^{165}Ho, 3.0 mL 1,000 mg/L ^{115}In, 5.0 mL 1,000 mg/L ^{193}Ir, 5.0 mL 1,000 mg/L ^{6}Li, 1.0 mL 1,000 mg/L ^{103}Rh, 10.0 mL 1,000 mg/L ^{45}Sc, 1.0 mL 1,000 mg/L ^{159}Tb, and 1mL 1,000 mg/L ^{89}Y. Bring to volume and transfer to a labeled, plastic 100-mL container.

8.10.5 Working Internal Standard Solution - In a 1-L volumetric flask, add 500 mL deionized water, 10.0 mL nitric acid, 5.0 mL hydrochloric acid, and 5.0 mL Stock Internal Standard Solution. Bring to volume and transfer to a labeled, plastic 1-L container.

9.0 PROCEDURE

9.1 Equipment Preparation

9.1.1 Verify that the internal standard and carrier lines are in the appropriate containers. Verify that all standards are in the correct positions. Prepare calibration standards, blanks, samples, and QC samples. Build a sequence in the sequence table and apply the repeat run rules to insert the CCV and CCB for every 10 unknowns. Queue the experiment to the Technician queue. Each experiment will require a unique code (e.g. 090511A, 090511B, etc.).

9.1.2 Support Equipment

9.1.3 Instrument

9.1.3.1 Routine Instrument Operating Conditions

Daily – inspect pump tubing, fill internal standard and rinse bottles. Keep immediate area near the instrument clean. As needed based on performance – inspect cones, spray changer and torch. Clean or replace as needed. Quarterly, inspect and clean air filters.

9.2 Initial Calibration

9.2.1 Calibration Design

Calibration consists of a calibration blank and a minimum of three non-zero standards for each mass. The reporting limit is normally the lowest non-blank standard in the calibration curve. The reporting limit may not be less than the lowest non-zero standard in the curve. The ICPMS software uses a linear regression curve fit. Weighting of the curve is allowed. Curve may be forced through zero if acceptance criteria are met. The correlation coefficient must be ≥0.998.

9.2.2 Calibration/Analysis Sequence

1	Instrument Blank
2	CAL0
3	CAL1
4	CAL2
5	CAL3
6	CAL4
7	ICV
8	ICB
9	CRDL
10	ICSA
11	ICSAB
12	CCV
13	CCB
14	10 analytical samples, including QC
15	CCV
16	CCB
17	10 analytical samples, including QC
18	CCV
19	CCB
20	

9.2.3 ICAL Evaluation

Calibration Metric	Parameter / Frequency	Criteria	Comments
Calibration Curve Fit	Performed daily or as needed	Correlation coefficient ≥ 0.998	If not met, determine cause and recalibrate
Initial Calibration Verification Standard (Second Source)	Immediately after each calibration	±10% of true value	Reanalyze ICV once, if ICV is still out, terminate analysis, correct problem, and recalibrate instrument
Calibration Blank (ICB/CCB)	Immediately after the ICV, after each CCV	< PRL or client specified	Samples analyzed with a bracketing CCB that exceeded criteria may be reported if the target analyte(s) in the samples are >10X the amount that was found in the CCB.
CRDL Standard (LLICV/LLCCV)	6020: Immediately after ICB and at the end or as specified per client QAPP 200.8 Immediately after ICB.	Each element tested must be at least between 50-150% of the CRDL value OR As specified per client QAPP	If recoveries are not acceptable, stop analysis for that analyte *Pace Metals 3P Team has determined it is a best practice to use PRL limits of at least 50-150%. Limits may be stricter if required by client.
ICSA	Immediately after the CRDL, or every 12 hours and as specified by client QAPP	Results for non-interference elements = ND ± 2 x CRDL Recovery of interfering elements must be 80-120% of true value	If recoveries are not acceptable, stop analysis for that analyte
ICSAB	Immediately after the CRDL, or every 12 hours and as specified by client QAPP	± 20% of true value	If recoveries are not acceptable, stop analysis for that analyte
Continuing Calibration Verification (CCV)	After the ICSAB, every 10 samples and at the end of analytical sequence	±10% of true value.	If recoveries are not acceptable, stop analysis for that analyte. Samples analyzed with a bracketing CCV that exceeded criteria due to an increase in response may be reported if the target analytes were not detected in the samples.
Internal Standard	Every sample, quality control sample and calibration standard.	6020A: 70-130%. 200.8: 60-125%	If criteria not met, dilute and reanalyze, adjust IS level or select a different internal standard.

9.3 Sample Preparation

9.3.1 Homogenization and Subsampling

Refer to SOP ENV-SOP-LENE-0135

9.4 Drinking Water samples may be tested for turbidity to avoid the digestion step. Samples with turbidity equal to or greater than 1 NTU are digested prior to analysis. Samples with turbidity less than 1 NTU may be analyzed without digestion after matrix matching.

9.5 Digestion Procedure – Applies only to 200.8 Drinking Water samples. All other soils and waters must follow the digestion procedures laid out in ENV-SOP-LENE-0094 and ENV-SOP-LENE-0089 respectively. The digestion is a modified EPA 200.8 procedure as follows:

9.5.1 Shake each sample well and pour 50 mL of sample into a 50-mL digestion tube. LCS, MS and MSD's are spiked with 1.0 mL of ICPMS Spike solution using DI water to bring to volume. Method blanks are not spiked.

9.5.2 Add 1.0 mL of (1:1) HNO_3 and 0.5 mL of (1:1) HCl to the sample. This will be a 1% HNO_3 – 0.5% HCl digestion matrix.

9.5.3 Place the samples in the hot block and cover with a watch glass for 4 hours at 90-95 ºC. Remove from the block and allow to cool.

9.5.4 Bring to volume with reagent water. If digestates are turbid, filter all samples and QC.

9.5.5 Cap and shake each sample as they are diluted, and place them back into the racks while continuing to maintain order.

9.6 Direct Analysis – Allowed for 200.8 Drinking Water analysis only. Add (1:1) HCl to the sample to match standards at 0.5% HCl.

9.6.1 LCS- Spike an aliquot of the CAL0 (Blank).

Method Blank – Use an aliquot of the CAL0 (Blank)

MS/MSD – Spike an aliquot of the matrix-matched sample.

9.7 Aqueous samples – Follow digestion procedure in ENV-SOP-LENE-0089. If samples are turbid, filter all samples and QC.

9.8 Soil samples – Follow the digestion procedure for soils in ENV-SOP-LENE-0094. Dilute digestates 10-fold prior to analysis using a 2% nitric acid solution.

9.9 Instrument Startup:

9.9.1 Verify argon supply and pressure (approx. 85 psi).

9.9.2 Turn on water chiller and verify that the exhaust fan is on.

9.9.3 Ensure that the internal standard solution bottle is filled.

9.9.4 Verify that the auto sampler rinse container is filled.

9.9.5 Empty the waste reservoir if needed.

9.9.6 Ignite the plasma and allow at least 25 minutes of warm-up time while scanning the mass analyzer. Insure that all peristaltic pump tubes are in good condition and correctly clamped onto the peristaltic pumps. Verify that the flow of sample, carrier and internal standard solutions through the uptake lines and into the nebulizer. Verify that the system is free of pulsations by introducing a bubble into each line and observing its progress.

9.9.7 System Operating Conditions

Power	1400W
Pump speed	14 rpm
Uptake time (example)	35 sec
Washout time (example)	15 sec
Carrier pump tubing	Black-black
IS pump tubing	orange-green

9.9.8 Acquisition Parameters

Points per Mass	1
Number of Replicates	3
Integration Time	100 ms (As, Se) 10 ms (all others)
Resolution	Standard

9.10 Performance Reports

9.10.1 A Performance report is run prior to the calibration of the ICPMS.

9.10.1.1 The Standard Mode Performance Report verifies the mass calibration, sensitivity, peak widths, oxides and doubly charged ions and is required to analyze any drinking water samples. If the Standard Mode Performance Report fails, a mass tune may be required.

9.10.1.2 The KED Mode Performance Report verifies the mass calibration, sensitivity, peak widths, oxides and doubly charged ions while utilizing the collision cell and is required to analyze all samples other than drinking water samples. If the KED Mode Performance Report fails, a mass tune may be required.

9.10.1.3 Print and file performance reports with the raw data.

9.10.2 KED Mode: Verify that the instrument is in KED mode indicated by the picklist in the tool bar menu in Instrument Control. Aspirate the tuning solution (place both the carrier and the internal standard lines in the tune solution) and run the Standard Mode performance

9.10.2.1 Mass Resolution (35 Sweeps, 5 Reps)

- Acquisition Parameter: Peak width measured at 10% of peak maximum
- Dwell Time (msec): 1.0
- Point Spacing: 0.05 amu
- Mass Limits: 0.65-0.85 amu (Max error 0.10 amu)

9.10.2.2 Sensitivity (50 Sweeps, 5 Reps)

Element	Limits
$^{4.5}$Bkg	<10 CPS
$^{220.7}$Bkg	<10 CPS
^{59}Co/^{35}Cl.^{16}O	>18.0
^{59}Co	>30,000 CPS
^{238}U	>85,000 CPS
^{209}Bi	>42,500 CPS
^{140}Ce.^{16}O/^{140}Ce	<0.03
^{115}In	>35,000 CPS

9.10.2.3 Stability

Element	%RSD Limit
^{59}Co	2.0
^{238}U	2.0
^{209}Bi	2.0
^{115}In	2.0

9.10.2.4 Mass Resolution (50 Sweeps, 5 Reps)

- Acquisition Parameter: Peak width measured at 10% of peak maximum
- Dwell Time (msec): 0.04
- Point Spacing: 0.02 amu
- Mass Limits: 0.65-0.85 amu (Max error 0.10 amu)

9.10.3 Standard Mode: Verify that the instrument is in standard mode indicated by the picklist in the tool bar menu in Instrument Control. Aspirate the tuning solution (place both the carrier and the internal standard lines in the tune solution) and run the Standard Mode performance report.

9.10.3.1 Mass Resolution (35 Sweeps, 5 Reps)

- Acquisition Parameter: Peak width measured at 10% of peak maximum
- Dwell Time (msec): 1.0
- Point Spacing: 0.05 amu
- Mass Limits: 0.65-0.85 amu (Max error 0.10 amu)

9.10.3.2 Sensitivity (35 Sweeps, 5 Reps)

Element	Limits
$^{4.5}$Bkg	<5.0 CPS
$^{220.7}$Bkg	<5.0 CPS
^{59}Co	>50,000 CPS
^{238}U	>200,000 CPS
^{209}Bi	>42,500 CPS
^{140}Ce.^{16}O/^{140}Ce	<0.03
^{137}Ba++/^{137}Ba	<0.03
^{115}In	>175,000 CPS

9.10.3.3 Stability

Element	%RSD Limit
^{59}Co	2.0
^{238}U	2.0
^{209}Bi	2.0
^{115}In	2.0

9.11 Mass Tuning (if needed): Allow the instrument to achieve thermal stability. Aspirate the 1 ug/L Tuning Solution, inserting both the carrier and internal standard delivery lines into the tune solution so as not to dilute the tune solution. Run the appropriate tune as needed. Tuning events should be logged in the maintenance logbook.

9.11.1 Tune Procedure Summary (Use this order of events, some adjustments may be required after an auto tune)

9.11.1.1 Autotune – Source Tune High Matrix 14.0rpm 3% Oxides

9.11.1.2 Mass Calibration

9.12 Cross-Calibration (Xcal)

9.12.1 The Xcal solution does not need to be run unless a deviation between the pulse counting and analog counting methods is observed in the spectra. The analog counting will appear to sit above the pulse baseline in an observed spectra and indicates that the cross calibration needs to be performed. Also, an indication of when the Xcal needs to be reset is when the calibration loses its linearity (this will likely occur first with High Resolution Mineral elements like Na and K). Aspirate the Xcal solution in Standard Mode, with both the sample delivery and internal standard lines (so as to not dilute the Xcal solution)

9.12.1.1 Cross Calibration Only. This is done when the deviation between the pulse and analog counting methods is observed (from spectra or from linearity observations) and the minimum counts per second listed in the tuning section are achievable. Run the Detector Set-Up wizard in Qtegra when deviation of the analog spectra is observed. The detector cross calibration is selected by default in the wizard. This will reset the detector-gating plateau such that the analog spectra (dashed line in the spectra) will sit directly on top of the pulse baseline (solid line in the spectra).

9.12.1.2 Internal or Labbook Cross Calibration: This can be done during analysis to prevent stopping the current analysis. If, during a run sequence, it is evident that the calibration between pulse and analog is not optimal, the Internal Cross Calibration function can be used. Click the icon in the labbook menu to utilize this functionality. This function uses data within the current labbook to perform and optimize the cross calibration.

9.12.1.3 Detector Setup and Cross Calibration. This is done when the minimum counts per second listed in the tune section are not achievable. Thus, the detector dynode value will be adjusted and a new cross calibration will be performed with the new detector voltage setting. Launch the Instrument Calibration wizard in Qtegra and select detector set up. The detector cross calibration will be checked by default, also select the detector set up portion in the wizard. The voltage applied to the detector will be set first to achieve acceptable sensitivity followed by a detector cross calibration with the new detector setting.

9.13 Analysis

9.13.1 Example Analytical Sequence

See 9.2.2 above.

10.0 Data Analysis And Calculations

10.1 Qualitative Identification

10.2 Quantitative Identification

10.3 Calculations

See the Laboratory Quality Assurance Manual for equations for common calculations.

Manual Calculation of Element Concentrations

Aqueous Samples

$$\text{Concentration } (\mu g/L) = \frac{(A)(V2)(DF)}{(V1)}$$

Solid Samples

$$\text{Concentration } (mg/kg) = \frac{(A)(V2)(DF)}{(W)\times 1000}$$

where:

A = Analyzed concentration of element, ug/L.

V1 = Volume of sample, mL.

V2 = Final digestate volume, mL.

DF = Dilution factor.

W = Weight of sample, g

11.0 Quality Control and Method Performance

11.1 Quality Control

The following QC samples are prepared and analyzed with each batch of samples. Refer to Appendix B for acceptance criteria and required corrective action.

QC Item	Frequency
Method Blank (MB)	1 per batch of 20 or fewer samples. If batch exceeds, 20 samples, every 20.
Laboratory Control Sample (LCS)	1 per batch of 20 or fewer samples. If batch exceeds, 20 samples, every 20.
Internal Standard	Every sample, QC sample and Cal Std.
Matrix Spike (MS)	One per 10 samples
Matrix Spike Duplicate (MSD)	One per batch (20 samples or less)
Sample Duplicate	One per batch of 20 samples or less (Not Required if MSD done.
CRDL Standard (LLICV/LLCCV)	Immediately after ICB and at the end or as specified per client QAP

11.2 Instrument QC

The following Instrument QC checks are performed. Refer to Appendix B for acceptance criteria and required corrective action.

QC Item	Frequency
Initial Calibration	Daily or as needed
Initial Calibration Verification	Immediately after each calibration
Initial Calibration Blank	Immediately after the ICV, after each CCV
Continuing Calibration Verification	Immediately after ICSAB, every 10 samples and at the end of the analytical sequence
Continuing Calibration Blank	Immediately after the ICV after each CCV
ICSA	Immediately after the CRDL, or every 12 hours and as specified by client QAP
ICSAB	Immediately after the CRDL, or every 12 hours and as specified by client QAP
Internal Standard	Every sample, QC sample and Cal Std.

11.3 Method Performance

11.3.1 Method Validation

11.3.1.1 Detection Limits

Detection limits (DL) and limits of quantitation (LOQ) are established at initial method setup and verified on an on-going basis thereafter. Refer to Pace ENV corporate SOP ENV-SOP-CORQ-0011 Method Validation.

11.4 Analyst Qualifications and Training

Employees that perform any step of this procedure must have a completed Read and Acknowledgment Statement for this version of the SOP in their training record. In addition, prior to unsupervised (independent) work on any client sample, analysts that prepare or analyze samples must have successful initial demonstration of capability (IDOC) and must successfully demonstrate on-going proficiency on an annual basis. Successful means the initial and on-going DOC met criteria, documentation of the DOC is complete, and the DOC record is in the employee's training file. Refer to laboratory SOP ENV-SOP-LENE-0110, *Training Procedures* for more information.

12.0 Data Review And Corrective Action

12.1 Data Review

Pace's data review process includes a series of checks performed at different stages of the analytical process by different people to ensure that SOPs were followed, the analytical record is complete and properly documented, proper corrective actions were taken for QC failure and other nonconformance(s), and that test results are reported with proper qualification.

The review steps and checks that occur as employee's complete tasks and review their own work is called primary review.

All data and results are also reviewed by an experienced peer or supervisor. Secondary review is performed to verify SOPs were followed, that calibration, instrument performance, and QC criteria were met and/or proper corrective actions were taken, qualitative ID and quantitative measurement is accurate, all manual integrations are justified and documented in accordance with the Pace ENV's SOP for manual integration, calculations are correct, the analytical record is complete and traceable, and that results are properly qualified.

A third-level review, called a completeness check, is performed by reporting or project management staff to verify the data report is not missing information and project specifications were met.

Refer to laboratory SOP ENV-SOP-LENE-0088, *Data Reduction, Review and Reporting* for specific instructions and requirements for each step of the data review process.

12.2 Corrective Action

Corrective action is expected any time QC or sample results are not within acceptance criteria. If corrective action is not taken or was not successful, the decision/outcome must be documented in the analytical record. The primary analyst has primary responsibility for taking corrective action when QA/QC criteria are not met. Secondary data reviewers must verify that appropriate action was taken and/or that results reported with QC failure are properly qualified.

Corrective action is also required when carryover is suspected and when results are over range.

Samples analyzed after a high concentration sample must be checked for carryover and reanalyzed if carryover is suspected. Carryover is usually indicated by low concentration detects of the analyte in successive samples analyzed after the high concentration sample.

Sample results at concentrations above the upper limit of quantitation must be diluted and reanalyzed. The result in the diluted samples should be within the upper half of the calibration range. Results less than the mid-range of the calibration indicate the sample was over diluted and analysis should be repeated with a lower level of dilution. If dilution is not performed, any result reported above the upper range is considered a qualitative measurement and must be qualified as an estimated value.

Refer to Appendix B for a complete summary of QC, acceptance criteria, and recommended corrective actions for QC associated with this test method.

13.0 Pollution Prevention And Waste Management

Pace proactively seeks ways to minimize waste generated during our work processes. Some examples of pollution prevention include but are not limited to: reduced solvent extraction, solvent capture, use of reusable cycletainers for solvent management, and real-time purchasing.

The EPA requires that laboratory waste management practice to be conducted consistent with all applicable federal and state laws and regulations. Excess reagents, samples and method process wastes must be characterized and disposed of in an acceptable manner in accordance with Pace's Chemical Hygiene Plan / Safety Manual.

14.0 Modifications

A modification is a change to a reference test method made by the laboratory. For example, changes in stoichiometry, technology, quantitation ions, reagent or solvent volumes, reducing digestion or extraction times, instrument runtimes, etc. are all examples of modifications. Refer to Pace ENV corporate SOP ENV-SOP-CORQ-0011 *Method Validation and Instrument Verification* for the conditions under which the procedures in test method SOPs may be modified and for the procedure and document requirements.

The aqueous digestion procedure is a modification of that found in Method 200.8. Samples are digested for a period of four hours, regardless of volume reduction. Sample volume is reduced to 50 mL and acid volumes are reduced to match the method.

15.0 Responsibilities

Pace ENV employees that perform any part this procedure in their work activities must have a signed Read and Acknowledgement Statement in their training file for this version of the SOP. The employee is responsible for following the procedures in this SOP and handling temporary departures from this SOP in accordance with Pace's policy for temporary departure.

Pace supervisors/managers are responsible for training employees on the procedures in this SOP and monitoring the implementation of this SOP in their work area.

16.0 ATTACHMENTS

Attachment 1 -- Internal Standard Assignments

Attachment 2 – Internal Standards

Attachment 3 – Tuning Solution

Attachment 4 – Recommended Elemental Interference Equations

Attachment 5 – Standard True Values

Appendix A – Target Analyte List and Routine

Appendix B – QC Summary

17.0 REFERENCES

17.1. Pace Quality Assurance Manual - most current version.

17.2. National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, "Quality Systems"- most current version.

17.3. The NELAC Institute (TNI); Volume 1, Module 2, "Quality Systems"- most current version.

17.4. Methods for the Determination of Metals in Environmental Samples, Supplement 1 (EPA/600/R-94/111), Method 200.8, Revision 5.4, 1994.

18.0 REVISION HISTORY

This Version: ENV-SOP-LENE-0024, V03

Section	Description of Change
All	combined all ICPMS SOPs and added 6020B

This document supersedes the following document(s):

Document Number	Title	Version
ENV-SOP-LENE-0024	Metals in Drinking Water by EPA 200.8	02

Appendix A: Target Analyte List and Routine LOQ

Table 1: Routine Analyte List and Limits of Quantitation (LOQ)[1]

Element	CAS Number	LOQ (ug/L)	Element	CAS Number	LOQ (ug/L)
Aluminum	7429-90-5	50	Manganese	7439-96-5	1.0
Antimony	7440-36-0	1.0	Molybdenum	7439-98-7	1.0
Arsenic	7440-38-2	1.0	Nickel	7440-02-0	1.0
Barium	7440-39-3	1.0	Selenium	7782-49-2	1.0
Beryllium	7440-41-7	0.5	Silver	7440-22-4	0.5
Cadmium	7440-43-9	0.5	Thallium	7440-28-0	1.0
Chromium	7440-47-3	1.0	Vanadium	7440-62-2	1.0
Cobalt	7440-48-4	1.0	Zinc	7440-66-6	10
Copper	7440-50-8	1.0			
Iron	7439-89-6	50			
Lead	7439-92-1	1.0			

[1] Values in place as of effective date of this SOP. LOQ are subject to change. For the most up to date LOQ, refer to the LIMS or contact the laboratory.

Appendix B: QC Summary QC Item	Frequency	Acceptance Criteria	Corrective Action	Qualification
Internal Standards	Added to all client and QC samples.	200.8: 60-125% 6020: 70-130%	If criteria not met, dilute and reanalyze, adjust IS level or select a different internal standard.	Qualify as needed
ICAL	At instrument set up, daily or after CCV failure	Must meet one of curve fit options presented in Section 9.0. Curve must also pass RSE test at the low and midpoint calibration standard.	Identify and correct source of problem, repeat	None. Do not proceed with analysis
ICV	After Each ICAL	All analytes must be within ± 10% of the true value (%R) or < MDL	Identify source of problem, re-analyze. If repeat failure, repeat ICAL. Analysis may proceed if it can be demonstrated that the ICV exceedance has no impact on analytical measurements. For example, the ICV %R is high, CCV is within criteria, and the analyte is not detected in sample(s).	Qualify analytes with ICV out of criteria.
ICB/CCB	Immediately after the ICV, and after each CCV	< PQL or <10% of the analyte level of associated samples	Samples analyzed with a bracketing CCB that exceeded criteria may be reported if the target analyte(s) in the samples are >10X the amount that was found in the CCB.	Rerun or qualify
CRDL	Immediately after ICB and at the end or as specified per client QAPP	Each element tested must be at least between 50-150% of the CRDL value OR As specified per client QAP	If recoveries are not acceptable, stop analysis for that analyte *Pace Metals 3P Team has determined it is a best practice to use PRL limits of at least 50-150%. Limits may be stricter if required by client.	Rerun
CCV	Daily, before sample analysis, after every 10, and at end of analytical window.	Opening CCV: All analytes within ± 10 %D Ending CCV: All analytes within ± 10 %D	See Section 12 for required corrective actions based on circumstance.	If recoveries are not acceptable, stop analysis for that analyte. Samples analyzed with a bracketing CCV that exceeded criteria due to an increase in response may be reported if the target

Appendix B: QC Summary QC Item	Frequency	Acceptance Criteria	Corrective Action	Qualification
				analytes were not detected in the samples
Method Blank	One per batch of up to 20 samples	Target analytes must be less than one-half the RL.	1)Re-analyze blank to confirm failure.	Qualify results and / or re-digest associated samples. Exceptions: 1)If sample is less than the MDL, report sample qualification 2) If sample result >10x MB detects, report sample with appropriate qualifier indicating blank contamination. 3) If sample result <10x MB detects, re-digest and reanalyze affected samples. If sample cannot be redigested, report sample with appropriate qualifier to indicate an estimated value.
LCS	One per batch of up to 20 samples	85-115%	1) Reanalyze the LCS to verify failure 2) If problem persists, check spike solution 3) Re-digest affected samples where possible	Exception: If LCS recovery > QC limits and target analytes are non-detect in the associated samples, the sample data may be reported with appropriate data qualifiers.
MS/MSD	One per batch of 20 or less samples	70-130%, RPD: Lab-Generated	Perform post digestion spike if required by client	Qualify is outside limits
Dilution Test	1:5 dilution of un-spiked sample digest	PDS failure upon client request; or To verify matrix interference	±10% of undiluted result	Matrix effects are confirmed. Follow client specified actions. NOTE: This test is NOT valid if the original sample is not greater than 50 times the RL.
Post Digestion Spike	Sample spiked with a known amount of standard usually at 1-2 times the amount in the sample	MS/MSD failure upon client request.	80-120%	Follow client specified criteria and /or perform serial dilution test.
Linear Dynamic Range	Whenever a change in instrument hardware or operating conditions or once every 6 months	Upper LDR not more than 10% below the level extrapolated	NA	NA

ATTACHMENT 1 – DEFAULT INTERNAL STANDARD ASSIGNMENTS

ISTD	Analytes
^{45}Sc, Li 6	Be, Al
^{71}Ga, ^{89}Y	As - Sr
^{89}Y, ^{103}Rh	Mo
^{103} Rh, ^{115}In	Ag - Cd
^{115}In, ^{159}Tb, ^{165}Ho	Sn -Ba
^{159}Tb, ^{165}Ho, ^{193} Ir, ^{209}Bi	Tl - Pb

ATTACHMENT 2 – INTERNAL STANDARDS

Mass	ug/L
^{45}Sc	500
^{71}Ga	1250
^{89}Y	50
^{103}Rh	50
^{115}In	150
^{159}Tb	50
^{165}Ho	50
^{193}Ir, Li 6	250
^{209}Bi	150

ATTACHMENT 3 – TUNING SOLUTION

Mass	ug/L
^{7}Li	1
Ba	1
Bi	1
Ce	1
Co	1
In	1
Pb	1
U	1

ATTACHMENT 4 – RECOMMENDED ELEMENTAL INTERFERENCE EQUATIONS

Analyte	Equation
^{43}Ca (1)	-0.00125 * ^{88}Sr
^{45}Sc-KED	-0.06099* ^{31}P
^{51}V (2)	-0.0995 * ^{53}ClO
^{53}ClO	-0.11400 * ^{52}Cr
^{52}Cr (2)	-0.00032 * ^{35}Cl
^{55}Mn	-0.00125 * ^{54}Fe
^{54}Fe	-0.02841 * ^{52}Cr
^{60}Ni	-0.00020 * ^{43}Ca
^{78}Se	-0.03065 * ^{83}Kr
^{111}Cd	-0.00055 * ^{95}Mo
^{115}In	-0.01416 * ^{118}Sn
^{201}Hg	-0.00055 * ^{184}W
^{208}Pb	1.00000 * ^{206}Pb + 1.00000 * ^{207}Pb

(1) Both the ICSAB and the LCS sample are used in the evaluation of this equation. Ca is affected by doubly charged strontium and can vary from day to day plasma conditions. The ICSAB will not fully identify doubly charged conditions based on the ratio of Ca to Sr, whereas the LCS sample for waters and soils have sufficiently large Sr concentrations compared to Ca and will assist in identification of adjustment requirements for the Ca interference equation.

(2) The equation may require periodic adjustment based on the tuning parameters. The mean value in counts per second (cps) for the calibration blank MUST be > 0 cps (ideally, all replicates should be > 0 cps). The normal operating range in cps is 0-1000cps for the calibration blank and must be inspected by the analyst.

ATTACHMENT 5 – STANDARD TRUE VALUES (µG/L)

Mass	ICV	CRDL	CCV	LCS/MS	ICSA	ICSAB
^{9}Be	50	0.5	40	40	0	25
^{27}Al	5000	50	4,000	4,000	50,000	50,000
^{47}Ti	50	2.0	40	40	1,000	1,000
^{51}V	50	1.0	40	40	0	50
^{52}Cr	50	1.0	40	40	0	50
^{54}Fe	2500	50	2,000	2,000	50,000	50,000
^{55}Mn	50	1.0	40	40	0	50
^{89}Co	50	1.0	40	40	0	50
^{60}Ni	50	1.0	40	40	0	50
^{65}Cu	50	1.0	40	40	0	50
^{66}Zn	50	10	40	40	0	500
^{75}As	50	1.0	40	40	0	50
^{78}Se	50	1.0	40	40	0	50
^{88}Sr	50	1.0	40	40	0	50
^{95}Mo	50	1.0	40	40	1,000	1,000
^{105}Pd	50	1.0	40	20	0	50
^{107}Ag	25	0.5	20	20	0	25
^{111}Cd	50	0.5	40	40	0	25
^{118}Sn	50	5.0	40	40	0	50
^{121}Sb	50	1.0	40	40	0	50
^{137}Ba	50	1.0	40	40	0	50
^{195}Pt	50	1.0	40	20	0	50
^{205}Tl	25	1.0	20	20	0	50
^{208}Pb	50	1.0	40	40	0	50
^{238}U	50	0.02	40	40	0	50

1.0 Scope And Application

This standard operating procedure (SOP) describes the laboratory procedure for the determination of metals by inductively coupled plasma atomic emissions spectroscopy in water/soil/wipe samples.

1.1 Target Analyte List and Limits of Quantitation (LOQ)

The target analytes and the normal LOQ that can be achieved with this procedure are provided in Table 1, Appendix A.

LOQ are established in accordance with Pace policy and SOPs for method validation and for the determination of detection limits (DL) and quantitation limits (LOQ). DL and LOQ are routinely verified and updated when needed. The current LOQ for each target analyte that can be determined by this SOP as of the effective date of this SOP is provided in Table 1, Appendix A.

The reporting limit (RL) is the value to which analytes are reported as detected or not detected in the final report. When the RL is less than the lower limit of quantitation (LLOQ), all detects and non-detects at the RL are qualitative. The LLOQ is the lowest point of the calibration curve used for each target analyte.

DL, LOQ, and RL are always adjusted to account for actual amounts used and for dilution.

2.0 Summary of Method

2.1 This method describes the sequential or simultaneous multi-elemental determination of elements by ICP.

2.2 Samples are digested prior to analysis using appropriate sample preparation methods as found in the Metals Prep SOPs (ENV-SOP-LENE-0089(SW-846 3010), ENV-SOP-LENE-0094(SW-846 3050), and ENV-SOP-LENE-0124(wipes).

2.3 Sample digestates are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific atomic-line emission spectra are produced by an inductively-coupled plasma.

2.4 The spectra are dispersed by a grating spectrometer and the intensity of each line is monitored by Charge-Inductive-Device Detector.

3.0 Interferences

3.1 Spectral Interferences

3.1.1 Overlap of a spectral line from another element.

3.1.2 Unresolved overlap of molecular band spectra.

3.1.3 Background contribution from continuous or recombination phenomena.

3.1.4 Stray light from the line emission of high-concentration elements. Spectral overlap can be compensated for by computer-correcting the raw data after monitoring and measuring the

interfering element. Unresolved overlap requires selection of an alternate wavelength. Background contribution and stray light can usually be compensated for by a background correction adjacent to the analyte line. Interelement correction factors are used with the iCAP 6500.

3.2 Physical Interferences

3.2.1 These are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high levels of dissolved solids or high acid concentrations. Physical interferences may be reduced by diluting the sample.

3.2.2 Salt buildup at the tip of the nebulizer can occur when analyzing samples with high dissolved solids, such as soils. Such buildup can affect the aspiration flow rate, resulting in instrument drift. The effects from the aspiration of samples containing high dissolved solids may be controlled by wetting the argon prior to nebulization or diluting the sample.

4.0 DEFINITIONS

Refer to the Laboratory Quality Manual for a glossary of common lab terms and definitions.

5.0 HEALTH AND SAFETY

The toxicity or carcinogenicity of each chemical material used in the laboratory has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable.

The laboratory maintains documentation of hazard assessments and OSHA regulations regarding the safe handling of the chemicals specified in each method. Safety data sheets for all hazardous chemicals are available to all personnel. Employees must abide by the health, safety and environmental (HSE) policies and procedures specified in this SOP and in the Pace Chemical Hygiene / Safety Manual.

Personal protective equipment (PPE) such as safety glasses, gloves, and a laboratory coat must be worn in designated areas and while handling samples and chemical materials to protect against physical contact with samples that contain potentially hazardous chemicals and exposure to chemical materials used in the procedure.

Concentrated corrosives present additional hazards and are damaging to skin and mucus membranes. Use these acids in a fume hood whenever possible with additional PPE designed for handing these materials. If eye or skin contact occurs, flush with large volumes of water. When working with acids, always add acid to water to prevent violent reactions. Any processes that emit large volumes of solvents (evaporation/concentration processes) must be in a hood or apparatus that prevents employee exposure.

Contact your supervisor or local HSE coordinator with questions or concerns regarding safety protocol or safe handling procedures for this procedure.

6.0 SAMPLE COLLECTION, PRESERVATION, HOLDING TIME, AND STORAGE

Samples should be collected in accordance with a sampling plan and procedures appropriate to achieve the regulatory, scientific, and data quality objectives for the project.

The laboratory does not perform sample collection or field measurements for this test method. To assure sample collection and field checks and treatment are performed in accordance with applicable regulations Pace project managers will inform the client of these requirements at the time of request for analytical services when the request for testing is received prior to sample collection. If samples were already collected, the laboratory will record any nonconformance to these requirements in the laboratory's sample receipt record when sufficient information about sample collection is provided with the samples.

The laboratory will provide containers for the collection of samples upon client request for analytical services. Bottle kits are prepared in accordance with laboratory SOP ENV-SOP-LENE-0025, *Assembly of Sample Container Kits*. The bottle kits provided by the laboratory should include field test kits and treatment reagent.

Requirements for container type, preservation, and field quality control (QC) for the common list of test methods offered by Pace are included in the laboratory's quality manual.

General Requirements

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous	250-1L HDPE	Acidified with 1:1 Nitric to pH<2	Room Temperature	Must be analyzed within 180 days of collection.
Aqueous (Pb&Cu)	1L HDPE	Acidified with 1:1 Nitric to pH<2	Room Temperature	Must be analyzed within 180 days of collection.
Soil/Solid	4oz glass jar, or HDPE plastic container	None	0-6°C	Must be analyzed within 180 days of collection.

Field / Matrix QC

Trip Blank	Equipment Blank	MS/MSD	Field Duplicate
N/A	Per QAPP	1 in 20	Per QAPP

Thermal preservation is checked and recorded on receipt in the laboratory in accordance with laboratory SOP ENV-SOP-LENE-0021, *Sample Management*. Chemical preservation is checked and recorded at time of receipt or prior to sample preparation.

After receipt, samples are stored at ≤6°C until sample preparation. Prepared samples (extracts, digestates, distillates, other) are stored at ≤6°C until sample analysis.

After analysis, unless otherwise specified in the analytical services contract, samples are retained for 30 days from date of final report and then disposed of in accordance with Federal, State, and Local regulations.

7.0 Equipment And Supplies

7.1 Equipment

Equipment	Vendor	Model / Version	Description / Comments
Spectrophotometer	Thermo Scientific	iCAP 6500	60ICP03 w/ Iteva or Qtegra Software
Spectrophotometer	Thermo Scientific	iCAP PRO	60ICP06 and 60ICP07 w/ Qtegra Software
Autosampler	Elemental Scientific	SC-FAST	none

7.2 Supplies

Glassware

Glassware	Description	Vendor / Item # / Description
Volumetric Flasks	5-, 10-, 50-, 100-, 500-mL, 1-L	Class A
Test tubes	17 x 100mm	Mold Pro

Miscellaneous

Item	Description	Vendor / Item # / Description
Pipetters	N/A	Eppendorf / various
Kimwipes	Delicate task wipes	Fisher / 06-666A
Filters	Filter-mate screw on filters	Environmental Express / various

8.0 Reagents And Standards

All reagents and standards must be logged into the Epic Pro Standards log and assigned a unique number by the system. See the Standards and Reagents SOP for additional information and requirements pertaining to all standards and reagents. Equivalent materials may be used without violating this SOP. All reagents and stock standards are stored at room temperature.

8.1 The reagents listed below are those currently in use. Other sources or grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

Table 8.1 – Standard Storage Conditions

Standard Type	Description	Expiration	Storage
Stock Standards	Concentrated reference solution purchased directly from approved vendor	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions
Intermediate and Working Standards	Reference solutions prepared by dilutions of the stock solution	Intermediate and working standards – The earliest of six months from the date of preparation or the expiration date of any component standard.	Manufacturer's recommended storage conditions for stock source solution.

Table 8.2 – Reagents and Standards

Standard	Concentration/ Description	Requirements/ Vendor / Item #
ICP-1A	200 mg/L: As, Ba, Be, Cd, Co, Cr, Cs, Cu, Li, Mn, Ni, Pb, Se, Sr, U, V, Zn 100 mg/L: Ag, Tl	SPEX / XPACEMN-76-500
ICP-2A	200 mg/L: B, Mo, Pd, Pt, Sb, Sn, Ti, Zr	SPEX / XPACEMN-77-500
ICP-3A	1000 mg/L: Al, Ca, K, Mg, Na, S 500 mg/L Fe, P, Si	SPEX / XPACEMN-75-500
ICP-1B	200 mg/L: As, Ba, Be, Cd, Co, Cr, Cs, Cu, Li, Mn, Ni, Pb, Se, Sr, U, V, Zn 100 mg/L: Ag, Tl	High Purity Standards / HP7379-500
ICP-2B	200 mg/L: B, Mo, Pd, Pt, Sb, Sn, Ti, Zr	High Purity Standards / HP7376-500
ICP-3B	1000 mg/L: Al, Ca, K, Mg, Na, S 500 mg/L Fe, P, Si	High Purity Standards / HP7375-500
SPK-STD-1B	200 mg/L: As, Ba, Be, Cd, Co, Cr, Cu, Li, Mn, Ni, P, Pb, Se, Sr, Tl, V, Zn	Inorganic Ventures / PA-STD-1B
SPK-STD-2B	1000 mg/L: Si 200 mg/L: B, Mo, Sb, Sn, Ti, Zr	Inorganic Ventures / PA-STD-2B

Standard	Concentration/ Description	Requirements/ Vendor / Item #
	100 mg/L: Ag	
SPK-STD-3B	2000 mg/L: Al, Ca, Fe, K, Mg, Na	Inorganic Ventures / PA-STD-3B
Hydrochloric acid	Baker Instra-Analyzed® Reagent	J.T. Baker / 9530-33
ICSA or Interference Check Standard 1	5000 mg/L: Al, Ca, Mg 2000 mg/L: Fe	High Purity / CLP-INF-1-500
Single Element Standards	1-10 mg/L; CRDL; ICSB	Inorganic Ventures / Various
Yttrium Standard	1000 mg/L	SPEX / PLY2-2X
Reagent water	ASTM Type II	SOP S-KS-Q-011 (latest revision)

8.2 ICP Reagent Blank Solution - Prepare as follows: Add 5000 mL of reagent water to a 20-L carboy. Add 1000 mL of HCl and 400 mL of HNO_3. Bring to volume with reagent water.

8.3 Blank Solution (CAL0) - is a zero standard consisting of 5% HCl and 2% HNO_3. ICP Reagent Blank Solution.

8.4 CAL 5 – Add approximately 100 mL of ICP Reagent Blank Solution to a 1000-mL volumetric flask. Add 4.0 mL ICP-1A, 10.0 mL ICP-2A, and 20.0 mL ICP-3A to the 1000-mL volumetric flask and dilute to volume with ICP Reagent Blank Solution.

8.5 CAL 4 – Add approximately 100 mL of ICP Reagent Blank Solution to a 500-mL volumetric flask. Add 200.0 mL of the CAL 5 solution to the 500-mL volumetric flask and dilute to volume with ICP Reagent Blank Solution.

8.6 CAL 3 – Add approximately 100 mL of ICP Reagent Blank Solution to a 500-mL volumetric flask. Add 50.0 mL of the CAL 5 solution to the 500-mL volumetric flask and dilute to volume with ICP Reagent Blank Solution.

8.7 CAL2 – Add approximately 100 mL of ICP Reagent Blank Solution to a 500-mL volumetric flask. Add 10.0 mL of the CAL 5 solution to the 500-mL volumetric flask and dilute to volume with ICP Reagent Blank Solution.

8.8 CAL 1 - Add approximately 100 mL of ICP Reagent Blank Solution to a 500-mL volumetric flask. Add 5.0 mL of the CAL 5 solution to the 500-mL volumetric flask and dilute to volume with ICP Reagent Blank Solution.

Table 8.3 CAL Standards

Element	CAL 0	CAL 1 (ug/L)	CAL 2 (ug/L)	CAL 3 (ug/L)	CAL 4 (ug/L)	CAL 5 (ug/L)
Ag	Not spiked	5	10	50	200	500
Al	Not spiked	200	400	2000	8000	20000
As	Not spiked	10	20	100	400	1000
B	Not spiked	20	40	200	800	2000
Ba	Not spiked	10	20	100	400	1000
Be	Not spiked	10	20	100	400	1000
Ca	Not spiked	200	400	2000	8000	20000
Cd	Not spiked	10	20	100	400	1000
Co	Not spiked	10	20	100	400	1000
Cr	Not spiked	10	20	100	400	1000
Cs	Not spiked	10	20	100	400	1000
Cu	Not spiked	10	20	100	400	1000
Fe	Not spiked	100	200	1000	4000	10000
K	Not spiked	200	400	2000	8000	20000
Li	Not spiked	10	20	100	400	1000
Mg	Not spiked	200	400	2000	8000	20000
Mn	Not spiked	10	20	100	400	1000
Mo	Not spiked	20	40	200	800	2000
Na	Not spiked	200	400	2000	8000	20000
Ni	Not spiked	10	20	100	400	1000
P	Not spiked	100	200	1000	4000	10000
Pb	Not spiked	10	20	100	400	1000
Pd	Not spiked	20	40	200	800	2000
Pt	Not spiked	20	40	200	800	2000
S	Not spiked	100	200	1000	4000	10000
Sb	Not spiked	20	40	200	800	2000
Se	Not spiked	10	20	100	400	1000
Si	Not spiked	100	200	1000	4000	10000
Sn	Not spiked	20	40	200	800	2000
Sr	Not spiked	10	20	100	400	1000

Element	CAL 0	CAL 1 (ug/L)	CAL 2 (ug/L)	CAL 3 (ug/L)	CAL 4 (ug/L)	CAL 5 (ug/L)
Ti	Not spiked	20	40	200	800	2000
Tl	Not spiked	5	10	50	200	500
U	Not spiked	10	20	100	400	1000
V	Not spiked	10	20	100	400	1000
Zn	Not spiked	10	20	100	400	1000
Zr	Not spiked	20	40	200	800	2000

8.9 Internal Standard - Add approximately 500 mL of ICP Reagent Blank Solution to a 1000-mL volumetric flask. Add 5.0 mL of Yttrium Standard to the 1000-mL volumetric flask and dilute to volume with ICP Reagent Blank Solution.

8.10 Interference Check Sample - The ICS consists of two solutions: Solution A (ICSA) and Solution AB (ICSAB). ICSA consists of the interferents and ICSAB consists of the other target analytes mixed with the interferents.

8.10.1 ICSA - Add approximately ten mL of ICP Reagent Blank Solution to a 400-mL volumetric flask. Add 40.0 mL of ICS1 to the 400-mL volumetric flask and dilute to volume with ICP Reagent Blank Solution. The ICSA contains Al, Ca, Mg at 500 mg/L and Fe at 200 mg/L. These elements should recover within ± 20% of the true value and all other elements should be zero ± 2 x PRL. Due to linear range limitations, it is recommended that this standard be ran at a 10x dilution when analyzed on the iCAP PRO.

8.10.2 ICSB stock - The ICSB stock solution is prepared from single-element standards. In a 1-L volumetric flask add 500 mL of deionized water and 5 mL of concentrated nitric acid. Add the single elements per the table below and bring to volume with deionized water.

Table 8.4 – ICSB Stock Standard

Pace Standard #	Element Components	Single-Element Standard Concentration (µg/mL)	Volume Used (mL)	Final Volume (mL)	ICSB Stock Concentration (µg/L)
Single-Element Standard	Ag	1000	0.50	1000	500
Single-Element Standard	As	1000	1.0	1000	1000
Single-Element Standard	B	1000	5.0	1000	5000
Single-Element Standard	Ba	1000	1.0	1000	1000
Single-Element Standard	Be	1000	0.5	1000	500
Single-Element Standard	Cd	1000	1.0	1000	1000
Single-Element Standard	Co	1000	1.0	1000	1000
Single-Element Standard	Cr	1000	1.0	1000	1000
Single-Element Standard	Cu	1000	1.0	1000	1000
Single-Element Standard	K	10000	5.0	1000	50000
Single-Element Standard	Mn	1000	1.0	1000	1000
Single-Element Standard	Mo	1000	1.0	1000	1000
Single-Element Standard	Na	10000	5.0	1000	50000
Single-Element Standard	Ni	1000	1.0	1000	1000
Single-Element Standard	P	1000	5.0	1000	5000
Single-Element Standard	Pb	1000	1.0	1000	1000
Single-Element Standard	Sb	1000	1.0	1000	1000
Single-Element Standard	Se	1000	1.0	1000	1000
Single-Element Standard	Si	1000	10.0	1000	10000
Single-Element Standard	Sn	1000	1.0	1000	1000
Single-Element Standard	Sr	1000	1.0	1000	1000
Single-Element Standard	Ti	1000	1.0	1000	1000
Single-Element Standard	Tl	1000	1.0	1000	1000
Single-Element Standard	V	1000	1.0	1000	1000
Single-Element Standard	Zn	1000	1.0	1000	1000
Single-Element Standard	Li	1000	1.0	1000	1000
Single-Element Standard	Zr	1000	1.0	1000	1000

8.10.3 ICSAB - Add approximately 100 mL of ICP Reagent Blank Solution to a 400-mL volumetric flask. Add 40.0 mL of ICSA and 40.0 mL of ICSB Stock to the volumetric flask and dilute to volume with ICP Reagent Blank Solution. Results for the ICSAB must recover within the control limit of ±20% of the true value. If analyzing on the iCAP PRO add 4.0 mL of ICSA and 40.0 mL of ICSB Stock solutions.

Table 8.5 ICSAB Concentrations

Element	Concentration (ug/L)
Ag	50
Al	500000
As	100
B	100
Ba	100
Be	50
Ca	500000
Cd	100
Co	100
Cr	100
Cu	100
Fe	200000
K	5000
Mg	500000
Mn	100
Mo	100
Na	5000
Ni	100
P	500
Pb	100
Sb	100
Se	100
Si	1000
Sn	100
Sr	100
Ti	100

Element	Concentration (ug/L)
Tl	100
V	100
Zn	100
Li	100
Zr	100

8.11 Initial Calibration Verification Standard (ICV)

8.11.1 The ICV is a standard from a NIST-traceable, second (independent) source, which contains the same elements that are in the calibration standard. The concentrations are at a level near or equal to the midpoint of the calibration curve. Add approximately 100 mL of ICP Reagent Blank Solution to a 400-mL volumetric flask. Add 1.00 mL ICP-1B, 2.00 mL ICP-2B, and 10.00 mL ICP-3B to the 400-mL volumetric flask and dilute to volume with ICP Reagent Blank Solution.

Table 8.6 ICV Concentrations

Element	Concentration (ug/L)
Ag	250
Al	25000
As	500
B	1000
Ba	500
Be	500
Ca	25000
Cd	500
Co	500
Cr	500
Cu	500
Fe	12500
K	25000
Li	500
Mg	25000
Mn	500
Mo	1000

Element	Concentration (ug/L)
Na	25000
Ni	500
P	12500
Pb	500
Sb	1000
Se	500
Si	12500
Sn	1000
Sr	500
Ti	500
Tl	250
V	500
Zn	500
Zr	1000

8.12 Continuing Calibration Verification Standard (CCV)

8.12.1 The CCV is a standard prepared from the same stock as the calibration standard. Add approximately 100 mL of ICP Reagent Blank Solution to a clean, acid-rinsed 400-mL volumetric flask. Add 1.0 mL ICP-1A, 2.0 mL ICP-2A, and 10.0 mL ICP-3A to the 400-mL volumetric flask and dilute to volume with ICP Reagent Blank Solution.

Table 8.7 CCV Concentrations

Element	Concentration (ug/L)
Ag	250
Al	25000
As	500
B	1000
Ba	500
Be	500
Ca	25000
Cd	500
Co	500
Cr	500

Element	Concentration (ug/L)
Cu	500
Fe	12500
K	25000
Li	500
Mg	25000
Mn	500
Mo	1000
Na	25000
Ni	500
P	12500
Pb	500
Sb	1000
Se	500
Si	12500
Sn	1000
Sr	500
Ti	500
Tl	250
V	500
Zn	500
Zr	1000

8.13 CRDL Stock Standard

8.13.1 The CRDL Stock Solution is prepared from single-element standards and ICP Reagent Blank Solution, in a 1000-mL volumetric flask at the concentrations listed below.

Table 8.8 CRDL Stock Standard

Element	Concentration (ug/L)
Ag	140
Al	1500
As	200
B	2000

Element	Concentration (ug/L)
Ba	100
Be	20
Ca	4000
Cd	100
Co	100
Cr	100
Cu	200
Fe	1000
K	10000
Li	200
Mg	1000
Mn	100
Mo	400
Na	10000
Ni	100
P	2000
Pb	200
Sb	200
Se	300
Si	20000
Sn	1000
Sr	200
Ti	200
Tl	400
V	200
Zn	1000
Zr	200

8.14 CRDL Working Standard

8.14.1 The CRDL Working Standard is prepared from the CRDL Stock solution. In a 400-mL volumetric flask add 100 mL ICP Reagent Blank Solution, 20.0 mL of CRDL Stock Solution and bring to volume with ICP Reagent Blank Solution.

8.15 LCS/MS/MSD Spike True Values

8.15.1 The LCS, MS, and MSD spiking solutions are prepared in accordance with the Metals Preparation SOPs: ENV-SOP-LENE-0089(SW-846 3010), ENV-SOP-LENE-0094(SW-846 3050), and ENV-SOP-LENE-0124(wipes). This solution is made by adding approximately 50 mL DI water to a 400 mL volumetric flask then add 100 mL of each SPK-ICP-1B, SPK-ICP-2B, and SPK-ICP-3B solution, then add 10 mL of Uranium single element standard and fill to the mark with ICP reagent blank.

Table 8.9 – LCS/MS True Values

Element	Concentration (ug/L)
Ag	500
Al	10000
As	1000
B	1000
Ba	1000
Be	1000
Ca	10000
Cd	1000
Co	1000
Cr	1000
Cu	1000
Fe	10000
K	10000
Li	1000
Mg	10000
Mn	1000
Mo	1000
Na	10000
Ni	1000
P	1000
Pb	1000

Element	Concentration (ug/L)
Sb	1000
Se	1000
Si	5000
Sn	1000
Sr	1000
Ti	1000
Tl	1000
V	1000
Zn	1000

9.0 PROCEDURE

9.1 Equipment Preparation

9.1.1 Support Equipment

All support equipment used must be calibrated or verified prior to use according to SOP ENV-SOP-LENE-0030; Support Equipment current revision.

9.1.2 Instrument

9.1.1 Qtegra Methodology and Operation

9.1.1.1 Before startup of the instrument inspect the pump tubing for breakage or uneven wear and replace if necessary. Rotate the pump tubing between thumb and forefinger at the point of contact with the peristaltic pump rollers. Replace any tubing that has a feel of flat spots and does not roll evenly. Replace any tubing that shows any sign of leakage. The peristaltic pump is equipped with a four- position roller assembly, which uses 2-stop pump tubing. Sample delivery tubing coded orange-white. Drain removal tubing is white-white. Internal standard delivery tubing is orange/blue.

9.1.1.2 Check gas supplies. Argon pressure should be regulated to ~90 psi; Check chiller; temperature set point should be at approx.. 20ºC.

9.1.1.3 Turn computer on and log into the network according to instructions given by the IT staff. Confirm main power switch is in the on position.

9.1.1.4 To open the instrument software double-click on the Qtegra icon. In the Dashboard click the "Get Ready" button at the top and center to ignite the plasma. Allow the instrument to warm up for at least 10 minutes however, it is preferable to allow the warm up time to exceed 30 minutes.

9.1.1.5 Create a new labbook from a previous labbook or reference a pre-made template.

9.1.1.6 In the menu option "Sample List" confirm the sample sequence is made in accordance with the quality control requirements of the method and QAAP of the client samples. Type, scan, or copy in any samples needed for analysis.

9.2 Initial Calibration

To perform quantitative measurements, an initial calibration must be established before the analysis of samples. An initial calibration is an evaluation of the relationship between response of the instrument (or process) and the concentration of the target analytes.

9.2.1 The ICP must be calibrated each time it is set up for analysis according to the manufacturer's instructions. Calibration requires analysis of a Calibration Blank and at least one level of calibration solution. Instrument standardization date and time must be recorded in the raw data.

9.2.2 Calibration Design

The standards are prepared according to Section 8.2 and analyzed like samples according to Section 9.3. Final volumes/concentrations of calibration standards may be adjusted as long as there are a minimum of one calibration point and the CRDL/LLOQ must be at or lower than the current reporting limit (LOQ). See Appendix C for concentrations of working standards.

9.2.3 Calibration Sequence

Analyze calibration standards 0 and 1 followed by the ICB, ICV, CRDL, ICSA, and ICSAB, CCV and CCB.

Sequence	Name

1	CAL0
2	CAL1
3	ICB
4	ICV
5	CRDL
6	ICSA
7	ICSAB
8	CCV
9	CCB

9.2.4 ICAL Evaluation

9.2.4.1 Curve Fit

A single point calibration is performed for this method using an instrument zero and one calibration standard.

9.2.4.2 Relative Standard Error (RSE)

For calibrations evaluated using correlation coefficient, the lab evaluates relative error by measurement of the Relative Standard Error (RSE). This calculation shall be performed for 2 calibration levels: the standard at or near the mid-point of the initial calibration and the standard at the lowest level.

Refer to Appendix B for complete RSE acceptance criteria and recommended corrective actions associated with this test method.

9.2.5 Initial Calibration Verification (ICV) / Second Source

9.2.5.1 In addition to meeting the linearity criteria, any new calibration curve must be assessed for accuracy in the values generated. Accuracy is a function of both the "fit" of the curve to the points used and the accuracy of the standards used to generate the calibration points. By meeting the fit criteria, the accuracy relative to the goodness of fit is addressed. However, because all calibration points are from the same source, it is possible that the calibration points may meet linearity criteria but not be accurately made in terms of their true value.

9.2.5.2 Therefore, to assess the accuracy relative to the purity of the standards, a single standard from a secondary source must be analyzed and the results obtained must be assessed relative to the known true value. This step is referred to as *Secondary Source Verification* or, alternatively as *Initial Calibration Verification*. This secondary source must be from an alternative vendor or, in the event an alternative vendor is not available, from a different lot from the same vendor. This standard must be analyzed immediately after the calibration and before any batch QC or client samples. The accuracy of the standard is assessed as a percent difference from the true value according to the following equation:

% Difference = [ResultICV –TrueValueICV] / TrueValueICV * 100

9.2.6 PRL Standard Verification

9.2.6.1 With every ICAL, a standard corresponding to the practical reporting limit (PRL) must also be analyzed and meet established acceptance criteria in Table 9.2.

9.2.7 ICSA (Interference Check Standard) Verification

9.2.7.1 With every ICAL, the inter-element check solution standard must be run to verify the inter-element correction factors. At a minimum, the ICSA standard must be analyzed at the beginning of the run, following the initial calibration, and evaluated against the criteria in Table 9.2. If client-specific requirements dictate that the ICSA must be analyzed at both the beginning and end of the analysis, the ICSA may be analyzed immediately after the completion of those specific samples and is not required to be placed at the very end of the sequence. The ICSAB must be analyzed immediately following the ICSA and meet the criteria in Table 9.2.

9.2.8 Continuing Calibration Verification (CCV)

9.2.8.1 As part of the analytical process, the instrumentation must be checked periodically to determine if the response has changed significantly since the initial calibration was established. This verification process is known as Continuing Calibration Verification. The validity of the initial calibration is checked after every 10 samples and at the end of an analytical sequence by analyzing a midpoint calibration standard (CCV).

9.2.8.2 The values obtained from the analysis of the CCV are compared to the true values. The percent difference must meet the method specified criteria in Table 9.2 for the analysis to proceed.

Table 9.2 – Calibration Acceptance and Verification Criteria

Calibration Metric	Parameter / Frequency	Criteria	Comments
Calibration Curve Fit	Linear Regression for elements requiring multiple calibration levels	Correlation coefficient ≥ 0.995	If not met, remake standards and recalibrate
Initial Calibration Verification Standard (Second Source)	Immediately after each initial calibration	6010B: ≤±10% of true value 200.7: ≤±5% of true value The % RSD between replicate integrations of an ICV std must be <5% (min of 2 integrations).	If 4 or more replicates are used for analysis the RSD must be ≤ 3%
Initial Calibration Verification Standard Low (ICVA)	Immediately after each initial calibration (if required by client- or project-specific QAPP).	≤±10% of true value The % RSD between replicate integrations of an ICV std must be <5% (min of 2 integrations).	If 4 or more replicates are used for analysis the RSD must be ≤ 3%
Calibration Blank	Immediately after each initial calibration (ICB), every 10 samples (CCB), and at the end of the analytical sequence	< PRL	If recoveries are not acceptable, stop analysis and follow corrective actions.
ICSA	Once per ICAL, immediately after verification	Results for non-interference elements = ND ± 2 x PRL Recovery of interfering elements must be 80-120% of true value	If recoveries are not acceptable, stop analysis and follow corrective actions.
ICSAB	Once per ICAL, immediately after ICSA (if required by client- or project-specific QAPP; see Attachments I – IV)	Results = True Value ± 20% (or ± 2 x PRL, whichever is greater).	If recoveries are not acceptable, stop analysis and follow corrective actions.
Continuing Calibration Verification	After every 10 samples and at the end of analytical sequence	≤±10% of true value. The % RSD between replicate integrations of a CCV std must be <5% (min of 2 integrations).	If criteria not met, follow corrective actions.
CRDL	Daily prior to sample analysis (as-needed basis per client- or project-specific QAPP; see Attachments I – IV)	±50% of true value.	If criteria not met, follow corrective actions.
Internal Standard	Every sample, quality control sample and calibration standard.	±30% of true value	If criteria not met, dilute, and reanalyze. Alternatively, Indium may be used if Yttrium is present in the samples.

9.3 Calibration Corrective Actions

9.3.1 Reanalyze the original standard to determine instrument consistency.

9.3.2 Prepare and analyze a new standard to determine preparation consistency / standard integrity.

9.3.3 Perform instrument maintenance, document in instrument maintenance log book.

9.3.4 Recalibrate instrument

9.3.5 Reanalyze any samples affected by unacceptable standard analysis.

9.3.6 If samples were analyzed in spite of verification failures, note the following exceptions for addressing those results. Deviations from this requirement must be noted on the run log with a thorough explanation for the deviation from policy.

Exceptions:

Samples analyzed with a bracketing CCV that exceeded criteria due to an increase in response may be reported if the target analytes were not detected in the samples.

Samples analyzed with a bracketing CCB that exceeded criteria may be reported if the target analyte(s) in the samples are >10x the amount that was found in the CCB.

9.4 Sample Preparation

9.4.1 Follow ICP digestion SOPs (ENV-SOP-LENE-0089(SW-846 3010), ENV-SOP-LENE-0094(SW-846 3050), and ENV-SOP-LENE-0124(wipes) for the sample prep of the samples before analysis.

9.5 Analysis

9.5.1 Example Analytical Sequence

Run No.	Sample ID
1	ICV
3	ICB
4	CRDL
5	ICSA
6	ICSAB
7	CCV1
8	CCB1
9	Sample 1
10	Sample 2
11	Sample 3
12	Sample 4
13	Sample 5
14	Sample 6

Run No.	Sample ID
15	Sample 7
16	Sample 8
17	Sample 9
18	Sample 10
19	CCV2
20	CCB2
21	Sample 11
22	Sample 12
23	Sample 13
24	Sample 14
25	Sample 15
26	Sample 16
27	Sample 17
28	Sample 18
29	CCV3
30	CCB3

10.0 Data Analysis And Calculations

10.1 Calculations

See the Laboratory Quality Assurance Manual for equations for common calculations.

10.2 **Water, TCLP and SPLP leachate:**

$$\text{Concentration (ug/L)} = \frac{(A)(V2)(DF)}{V1}$$

10.3 **Soil:**

$$\text{Concentration (mg/kg)} = \frac{(A)(V2)(DF)}{(W \times 1000)}$$

10.4 **Wipe:**

$$\text{Concentration (ug/wipe)} = \frac{(A)(V2)(DF)}{1000}$$

10.5 **Paint:**

$$\text{Concentration (\%)} = \frac{(A)(V2)(DF)}{(W \times 1E6)}$$

where:
A = Analyzed concentration of element, ug/L.
V1 = Volume of sample, mL.
V2 = Final digestate volume, mL.
DF = Dilution factor.
W = Weight of sample, g.

10.6 **Hardness Calculation**

mg equivalent $CaCO_3$/L = 2.497 [Ca, mg/L] + 4.118 [Mg,mg/L]

11.0 Quality Control and Method Performance

11.1 Quality Control

The following QC samples are prepared and analyzed with each batch of samples. Refer to Appendix B for acceptance criteria and required corrective action.

QC Item	Frequency
Method Blank (MB)	1 per batch of 20 or fewer samples. If batch exceeds, 20 samples, every 20.
Laboratory Control Sample (LCS)	1 per batch of 20 or fewer samples. If batch exceeds, 20 samples, every 20.
Laboratory Control Sample Duplicate (LCSD)	As needed
Matrix Spike (MS)	6010B - One per batch of up to 20 samples. 200.7 - One per 10 samples.
Matrix Spike Duplicate (MSD)	6010B - One per batch of up to 20 samples. 200.7 – if required by QAPP.
Sample Duplicate	200.7 – One Duplicate per batch of up to 20 samples
Post-Digestion Spike (PDS)	QAPP requirements upon MS/MSD failure
Dilution test	QAPP requirements upon PDS failure

11.2 Instrument QC

The following Instrument QC checks are performed. Refer to Appendix B for acceptance criteria and required corrective action.

QC Item	Frequency
Initial Calibration	Performed daily
Initial Calibration Verification	After each ICB
Initial Calibration Blank	After each ICAL

QC Item	Frequency
Lower Limit of Quantitation Check/Contract Required Detection Limit	After each ICV
Interference Check Standard A	After each CRDL
Interference Check Standard B	After each ICSA, if required by QAPP
Continuing Calibration Verification	Daily, before sample analysis, after every 10 samples, and at end of an analytical run
Continuing Calibration Blank	After each CCV

11.3 Method Performance

11.3.1 Method Validation

11.3.1.1 Detection Limits

Detection limits (DL) and limits of quantitation (LOQ) are established at initial method setup and verified on an on-going basis thereafter. Refer to Pace ENV corporate SOP ENV-SOP-CORQ-0011 Method Validation and Instrument Verification.

11.3.1.2 Interfering Element Corrections (IECs)

IECs are checked each quarter for at least the four major interferences, Ca, Mg, Fe, and Al. There is usually not sufficient concentration of the minor interferences to cause a deviation, but once a year, and any time there is a request for other analytes on a sample with a very high concentration of one of the following elements, interferences are updated for Cr, Cu, Mn, Ni, Zn, Mo, V and Co.

Inter-element interferences occur when elements in the sample emit radiation at wavelengths so close to that of the analyte that they contribute to the intensity of the light striking the analyte pixels. If such conditions exist, the calculation will yield an inaccurate concentration for the analyte. Applying inter-element corrections removes the effects of these non-analyte emissions.

Refer to Attachment I for detailed instructions on determining and applying IECs.

11.3.1.3 Linear Dynamic Range (LDR)

The LDR study must be run when the instrument is initially set up and after significant instrument maintenance is performed (i.e. replacing the instrument optics) and at least once annually. The range is determined by running multiple standards (at least 3) approaching the expected range. The highest standard run ±10% of the true value (%R) determines the linear range. The usable range is 90% of that highest standard's true value.

The LDR is verified every 6 months by analyzing a standard at the last established linear range for each analyte, and each analyte must pass ±20% of the true value (%R).

For example, if the current LDR for an analyte is 90,000µg/L, this means that a 100,000µg/L standard previously ran and passed ±10%. To verify that the LDR has not changed, run standards at 80,000µg/L, 90,000µg/L, and 100,000µg/L (or other similar concentrations approaching the previously established range). Use

90% of the true value of the highest standard that passes within ±10% as the new LDR.

Make each standard by adding the appropriate amount of single element stock standard to a 50 mL volumetric, and then bring to volume with matrix blank.

11.4 Analyst Qualifications and Training

Employees that perform any step of this procedure must have a completed Read and Acknowledgment Statement for this version of the SOP in their training record. In addition, prior to unsupervised (independent) work on any client sample, analysts that prepare or analyze samples must have successful initial demonstration of capability (IDOC) and must successfully demonstrate on-going proficiency on an annual basis. Successful means the initial and on-going DOC met criteria, documentation of the DOC is complete, and the DOC record is in the employee's training file. Refer to laboratory SOP ENV-SOP-LENE-0110, *Training Procedures*, for more information.

12.0 Data Review And Corrective Action

12.1 Data Review

Pace's data review process includes a series of checks performed at different stages of the analytical process by different people to ensure that SOPs were followed, the analytical record is complete and properly documented, proper corrective actions were taken for QC failure and other nonconformance(s), and that test results are reported with proper qualification.

The review steps and checks that occur as employee's complete tasks and review their own work is called primary review.

All data and results are also reviewed by an experienced peer or supervisor. Secondary review is performed to verify SOPs were followed, that calibration, instrument performance, and QC criteria were met and/or proper corrective actions were taken, qualitative ID and quantitative measurement is accurate, all manual integrations are justified and documented in accordance with the Pace ENV's SOP for manual integration, calculations are correct, the analytical record is complete and traceable, and that results are properly qualified.

A third-level review, called a completeness check, is performed by reporting or project management staff to verify the data report is not missing information and project specifications were met.

Refer to laboratory SOP ENV-SOP-LENE-088, *Data Reduction, Review and Reporting*, for specific instructions and requirements for each step of the data review process.

12.2 Corrective Action

Corrective action is expected any time QC or sample results are not within acceptance criteria. If corrective action is not taken or was not successful, the decision/outcome must be documented in the analytical record. The primary analyst has primary responsibility for taking corrective action when QA/QC criteria are not met. Secondary data reviewers must verify that appropriate action was taken and/or that results reported with QC failure are properly qualified.

Corrective action is also required when carryover is suspected and when results are over range.

Samples analyzed after a high concentration sample must be checked for carryover and reanalyzed if carryover is suspected. Carryover is usually indicated by low concentration detects of the analyte in successive samples analyzed after the high concentration sample.

Sample results at concentrations above the upper limit of quantitation must be diluted and reanalyzed. The result in the diluted samples should be within the upper half of the calibration range. Results less than the mid-range of the calibration indicate the sample was over diluted and analysis should be repeated with a lower level of dilution. If dilution is not performed, any result reported above the upper range is considered a qualitative measurement and must be qualified as an estimated value.

Refer to Appendix B for a complete summary of QC, acceptance criteria, and recommended corrective actions for QC associated with this test method.

13.0 Pollution Prevention And Waste Management

Pace proactively seeks ways to minimize waste generated during our work processes. Some examples of pollution prevention include but are not limited to: reduced solvent extraction, solvent capture, use of reusable cycletainers for solvent management, and real-time purchasing.

The EPA requires that laboratory waste management practice to be conducted consistent with all applicable federal and state laws and regulations. Excess reagents, samples and method process wastes must be characterized and disposed of in an acceptable manner in accordance with Pace's Chemical Hygiene Plan / Safety Manual.

14.0 Modifications

A modification is a change to a reference test method made by the laboratory. For example, changes in stoichiometry, technology, quantitation ions, reagent or solvent volumes, reducing digestion or extraction times, instrument runtimes, etc. are all examples of modifications. Refer to Pace ENV corporate SOP ENV-SOP-CORQ-0011 *Method Validation and Instrument Verification* for the conditions under which the procedures in test method SOPs may be modified and for the procedure and document requirements.

15.0 Responsibilities

Pace ENV employees that perform any part this procedure in their work activities must have a signed Read and Acknowledgement Statement in their training file for this version of the SOP. The employee is responsible for following the procedures in this SOP and handling temporary departures from this SOP in accordance with Pace's policy for temporary departure.

Pace supervisors/managers are responsible for training employees on the procedures in this SOP and monitoring the implementation of this SOP in their work area.

16.0 Attachments

16.1 Appendix A: Target Analyte List and Routine LOQ

16.2 Appendix B: QC Summary

17.0 REFERENCES

17.1 Pace Quality Assurance Manual – most current version

17.2 National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, "Quality Systems"- most current version.

17.3 The NELAC Institute (TNI); Volume 1, Module 2, "Quality Systems"- most current version.

17.4 Methods for Determination of Metals in Environmental Samples, Supplement I, EPA-600/R-94/111, May 1994, Method 200.7, revision 4.4.

17.5 Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods (SW-846), Third Edition, Method 6010B, revision 2, December 1996.

17.6 ENV-SOP-LENE-0089(SW-846 3010)

17.7 ENV-SOP-LENE-0094(SW-846 3050)

17.8 ENV-SOP-LENE-0124(wipes)

18.0 REVISION HISTORY

This Version: ENV-SOP-LENE-0026, REV. 03

Section	Description of Change
ALL	NEW CORPORATE SOP FORMAT
7.0	NEW ICP INSTRUMENTS ADDED

This document supersedes the following document(s):

Document Number	Reason for Change	Date
S-KS-M-005-rev.9	Section 6 – Changed SOP review frequency Section 9 – Changed instrument make/model. Section 10 – Removed S2 standard and revised procedures for new instrument. Section 11 – Added ICVA and ICSAB standards, changed CRDL to PRL. Section 12 – Revised procedures for new instrument. Section 13 – Updated 200.7 MS requirement and IS recovery limits. Section 14 – Removed 20% nitric acid rinse modification. Section 17 – Added ICSAB table.	August 25, 2009
S-KS-M-005-rev.10	Section 7 – Added Environmental Quality Director. Changed SOP review frequency to annual. Section 15 – Revised SOP reference. Section 16 – Revised method references. Section 17 – Added PRL table.	November 29, 2010

Document Number	Reason for Change	Date
S-KS-M-005-rev.11	SOP - Remove references to Thermo 61E Trace ICP. Section 8 – Removed 24-hour hold period after lab filtration. Table 10.2 – Removed Lithium standard Section 10 – Removed Trace ICP Internal Standard. Revised ICSA prep. Change RDL to CRDL and CRDL to CRDL 2. Table 11.1 – Added Indium as alternative to Yttrium. Section 12 - Added 60ICP04 operating conditions, data storage, and ESI SC-FAST operating conditions. Section 16 – Revised method references.	March 10, 2011
S-KS-M-005-rev.12	General – Converted SOP to new format Table 9.1 – Added Iteva Software Table 13.1 – Added Post Spike and Dilution Test Table 10.1 – Added "or equivalent". Table 11.1 – ICVA/CRDL/CRDL2 if required by client- or project-specific QAPP. Section 18 – Removed Internal Standards and Dilution Test. Redundant info that is now in tables 11.1 and 13.1 Section 20.3 – Added equipment safety Table 24.7 – Updated Si and Ag Solid RLs	July 11, 2012
S-KS-M-005-rev.13	SOP - Updated to latest prescribed format. Adjusted HCl conc in standards. Section 5 – Revised Pb in Soil LOQ from 0.5mg/Kg to 1.0 mg/Kg Section 12 – Eliminated CRDL2 standard. Added Cetac ASXpress operating table. Section 18 – Added MDL verification. Attachments 1-3: Added client-specific criteria.	February 1, 2013
S-KS-M-005-rev.14	Section 1 – Added note that only water samples are analyzed via 200.7 Section 4 – Added note that only water samples are analyzed via 200.7	April 2, 2013
S-KS-M-005-rev.15	Section 10.1 – Increased amount of HCl from 400mL to 1000mL Section 10.2 – Increased concentration of HCl from 2% to 5% Table 11.1 – Added 200.7 ICV criteria Table 12.3 – Updated probe in sample time from 7s to 8s	February 4, 2014
S-KS-M-005-rev.16	Attachment IV - Added client-specific criteria	June 18, 2014
S-KS-M-005-rev.17	SOP - Updated to latest prescribed format. Added sections for Instrument/Equipment Maintenance and Troubleshooting. Section 3.2 Added Hardness to Scope and Application Section 10 – Added equivalency statement. Table 10.1– Updated reagent sources/item #'s Section 14.5 Added formula for Hardness calculation.	April 17, 2015
S-KS-M-005-rev.18	Table 5.1 – Added Li Soil LOQ Table 10.1 – Modified Intermediate and Working Std. Expiration Table 13.1- MSD limits revised to those of MS and RPD of 20.	November 12, 2015
S-KS-M-005-rev.19	Table 9.1 – Updated CETAC model number. Table 12.1 – Revised coolant flow, nebulizer flow, pump speed Table 12.2 – Revised coolant flow, nebulizer flow. Section 12.1.8 – Revised local storage for 60ICP03. Table 13.1 – Added criteria for sample replicates.	June 22, 2016
S-KS-M-005-rev.20	Revised cover to Pace LLC.	September 1, 2017
ENV-SOP-LENE-0026-01	SOP – Removed cover page, TOC and Headers. Tables 10.3 through 10.8 – Added Zirconium Section 18.1 – Revised SOP reference Section 23.1 – Revised SOP reference	January 7, 2018

Document Number	Reason for Change	Date
ENV-SOP-LENE-0026-02	Section 18.3 – Revised SOP reference Section 19 – Added a method modification for 200.7 Table 5.1 – Added TCLP PRLs Sections 10.3 and 10.4 – Revised Table 10.7 — Revised CRDL for some metals Section 12.1.8 – Added file storage instructions	July 18, 2019

Appendix A: Target Analyte List and Routine LOQ

Table 1: Routine Analyte List and Limits of Quantitation (LOQ)[1]

Element	CAS Number	LOQ (ug/L)	LOQ (mg/kg)	TCLP (mg/L)	Element	CAS Number	LOQ (ug/L)	LOQ (mg/kg)	TCLP (mg/L)
Aluminum	7429-90-5	75	7.5	2	Molybdenum	7439-98-7	20	2	0.5
Antimony	7440-36-0	15	1.5	0.3	Nickel	7440-02-0	5	0.5	0.1
Arsenic	7440-38-2	10	1	0.5	Phosphorus	7723-14-0	100	10	10
Barium	7440-39-3	5	0.5	2.5	Potassium	7440-09-7	500	50	50
Beryllium	7440-41-7	1	0.1	0.05	Selenium	7782-49-2	15	1.5	0.5
Boron	7440-42-8	100	10	1	Silicon	7440-21-3	500	50	5
Cadmium	7440-43-9	5	0.5	0.05	Silver	7440-22-4	7	0.7	0.1
Calcium	7440-70-2	200	20	50	Sodium	7440-23-5	500	50	50
Chromium	7440-47-3	5	0.5	0.1	Strontium	7440-26-6	10	1	0.1
Cobalt	7440-48-4	5	0.5	0.1	Thallium	7440-28-0	20	2	0.5
Copper	7440-50-8	10	1	0.2	Tin	7440-31-5	50	5	0.5
Iron	7439-89-6	50	5	1	Titanium	7440-32-6	10	1	0.1
Lead	7439-92-1	10	1	0.5	Vanadium	7440-62-2	10	1	0.1
Lithium	7439-93-2	10	1	0.5	Zinc	7440-66-6	50	10	2.5
Magnesium	7439-95-4	50	5	50	Zirconium	7440-67-7	10	1	0.1
Manganese	7439-96-5	5	0.5	0.1					

[1] Values in place as of effective date of this SOP. LOQ are subject to change. For the most up to date LOQ, refer to the LIMS or contact the laboratory.

Appendix B: QC Summary

QC Item	Frequency	Acceptance Criteria	Corrective Action	Qualification
ICAL	Calibration is done on a daily basis.	Single point calibration	Remake standards, perform maintenance, recalibrate, and verify before sample analysis.	None. Do not proceed with analysis
Lower Limit of Quantitation Check/Contract Required Detection Limit (LLOQ/CRDL)	After each ICV	All analytes must be within ± 50% of the true value. (%R)	Identify source of problem, re-analyze. If repeat failure, repeat ICAL. ***Exceptions:*** Analysis may proceed if it can be demonstrated that the CRDL exceedance has no impact on analytical measurements. If the CRDL %R is high, and the analyte is not detected in sample(s). If the CRDL %R is low, and the analyte is 50x the LOQ.	None.
ICV	After each ICB	**200.7**: All analytes must be within ± 5% of the true value. (%R) **6010B:** All analytes must be within ± 10% of the true value. (%R) with <5% (%RSD) from a minimum of 2 replicate integration	Identify source of problem, re-analyze. If repeat failure, repeat ICAL. ***Exceptions:*** Analysis may proceed if it can be demonstrated that the ICV exceedance has no impact on analytical measurements. If the ICV %R is high, CCV is within criteria, and the analyte is not detected in sample(s).	Qualify analytes with ICV out of criteria.
ICB	After each ICAL	All analytes must be below the LOQ.	Identify source of problem, re-analyze. If repeat failure, repeat ICAL. ***Exceptions:*** Analysis may proceed if it can be demonstrated that the ICB exceedance has no impact on analytical measurements. If the ICB is above the LOQ, and the analyte is not detected in sample(s).	None.
CCV	Daily, before sample analysis, after every 10 samples, and at end of the analytical run.	All analytes within ± 10% of the true value (%R) with <5% (%RSD) from a minimum of 2 replicate integration.	Identify source of problem, re-analyze. If repeat failure, rerun the affected analytes. ***Exceptions:*** Analysis may proceed if it can be demonstrated that the CCV exceedance has no impact on analytical measurements.	Qualify analytes with CCV out of criteria.

QC Item	Frequency	Acceptance Criteria	Corrective Action	Qualification
			If the CCV %R is high and the analyte is not detected in sample(s).	
CCB	After Each CCV	All analytes must be below the LOQ.	Identify source of problem, re-analyze. If repeat failure, repeat the affected analytical sequence or repeat ICAL. ***Exceptions:*** Analysis may proceed if it can be demonstrated that the CCB exceedance has no impact on analytical measurements. If the CCB is above the LOQ, and the analyte is not detected in sample(s) or the analyte is ≥10x the concentration in the blank, report the samples without qualification.	None.
ICSA	Once per calibration	Al, Ca, Fe, and Mg must be within ± 20% of the true value (%R) All other analytes must be below the LOQ	Identify source of problem, re-analyze or adjust the inter-element corrections. Re-analyze until acceptance criteria are met.	None.
ICSAB	Once per calibration if required by QAPP	All analytes must be within ± 20% of the true value (%R)	Identify source of problem, re-analyze or adjust the inter-element corrections. Re-analyze until acceptance criteria are met.	None.
Internal Standards	Every sample, standard and QC sample	Must be within ± 30% of the IS reading for the CAL0 standard.	Associated samples must be diluted and reanalyzed.	Qualify if reanalysis is not possible.
Method Blank	1 per batch of 20 or fewer samples.	All analytes must be below the LOQ.	Identify source of problem, re-analyze. If repeat failure, reanalyze the associated samples. ***Exceptions:*** Analysis may proceed if it can be demonstrated that the MB exceedance has no impact on analytical measurements. If the MB is above the LOQ, and the analyte is not detected in sample(s) or the analyte is ≥10x the concentration in the blank, report the samples without qualification.	Report analytes without qualification and qualify MB for being out of criteria.
LCS	1 per batch of 20 or fewer samples.	**200.7**: All analytes must be within ± 15% of the true value. (%R) **6010B:**	Identify source of problem, re-analyze. If repeat failure, all samples with affected analytes must be removed from the batch, redigested, and reanalyzed. ***Exceptions:***	Report analytes without qualification and qualify LCS for being out of criteria.

QC Item	Frequency	Acceptance Criteria	Corrective Action	Qualification
		All analytes must be within ± 20% of the true value. (%R)	Analysis may proceed if it can be demonstrated that the LCS exceedance has no impact on analytical measurements. If the LCS %R is high, and the analyte is not detected in sample(s).. If samples cannot be redigested (wipes, paint chips, limited volume).	
MS	**200.7:** 1 per batch of 10 or fewer samples. If greater than 10 samples, another MS is required. **6010B:** 1 per batch of 20 or fewer samples.	**200.7**: All analytes must be within ± 30% of the true value. (%R) **6010B:** All analytes must be within ± 25% of the true value. (%R) **Alternative:** In compliance with lab generated limits.	None.	Qualify analytes with MS out of criteria.
MSD	**200.7:** 1 per batch of 10 or fewer samples. If greater than 10 samples, another MSD is required. **6010B:** 1 per batch of 20 or fewer samples.	All analytes must be within ± 20% of the MS. (%RPD) **Alternative:** In compliance with lab generated limits.	None.	Qualify analytes with MSD out of criteria.
Dilution test	6010B Only - Per client request or at analyst discretion. Dilution of samples with analytes 10x the LOQ. Dilution of sample at a 5x or 10x dilution to demonstrate that the analytes are not affected by spectral interference.	All analytes must be within 10% of the initial, undiluted analysis. (%R)	Analyze additional dilutions of the sample digestate until at least two results are within 10% (%R). **Exceptions:** The analyte is less than 10x of the LOQ.	Report from that dilution for the samples in the batch unless they are lower than the LOQ when diluted.

1.0 Scope And Application

This standard operating procedure (SOP) describes the laboratory procedure for the determination of metals by aqueous digestion.

1.1 Target Analyte List and Limits of Quantitation (LOQ)

The target analytes and the normal LOQ that can be achieved with this procedure are provided in the determinative SOP.

LOQ are established in accordance with Pace policy and SOPs for method validation and for the determination of detection limits (DL) and quantitation limits (LOQ). DL and LOQ are routinely verified and updated when needed. The current LOQ for each target analyte that can be determined by this SOP as of the effective date of this SOP is provided in Table 1, Appendix A.

The reporting limit (RL) is the value to which analytes are reported as detected or not detected in the final report. When the RL is less than the lower limit of quantitation (LLOQ), all detects and non-detects at the RL are qualitative. The LLOQ is the lowest point of the calibration curve used for each target analyte.

DL, LOQ, and RL are always adjusted to account for actual amounts used and for dilution.

2.0 Summary of Method

2.1 Sample aliquots are digested for the analysis of metals by heating for an extended period of time in the presence of nitric acid and hydrochloric acid.

3.0 Interferences

3.1 See the analytical SOPs ENV-SOP-LENE-0026 and ENV-SOP-LENE-0024 (or their equivalent revisions or replacements).

4.0 Definitions

Refer to the Laboratory Quality Manual for a glossary of common lab terms and definitions.

5.0 Health and Safety

The toxicity or carcinogenicity of each chemical material used in the laboratory has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable.

The laboratory maintains documentation of hazard assessments and OSHA regulations regarding the safe handling of the chemicals specified in each method. Safety data sheets for all hazardous chemicals are available to all personnel. Employees must abide by the health, safety and

environmental (HSE) policies and procedures specified in this SOP and in the Pace Chemical Hygiene / Safety Manual.

Personal protective equipment (PPE) such as safety glasses, gloves, and a laboratory coat must be worn in designated areas and while handling samples and chemical materials to protect against physical contact with samples that contain potentially hazardous chemicals and exposure to chemical materials used in the procedure.

Concentrated corrosives present additional hazards and are damaging to skin and mucus membranes. Use these acids in a fume hood whenever possible with additional PPE designed for handing these materials. If eye or skin contact occurs, flush with large volumes of water. When working with acids, always add acid to water to prevent violent reactions. Any processes that emit large volumes of solvents (evaporation/concentration processes) must be in a hood or apparatus that prevents employee exposure.

Contact your supervisor or local HSE coordinator with questions or concerns regarding safety protocol or safe handling procedures for this procedure.

6.0 Sample Collection, Preservation, Holding Time, And Storage

Samples should be collected in accordance with a sampling plan and procedures appropriate to achieve the regulatory, scientific, and data quality objectives for the project.

The laboratory does not perform sample collection or field measurements for this test method. To assure sample collection and field checks and treatment are performed in accordance with applicable regulations Pace project managers will inform the client of these requirements at the time of request for analytical services when the request for testing is received prior to sample collection. If samples were already collected, the laboratory will record any nonconformance to these requirements in the laboratory's sample receipt record when sufficient information about sample collection is provided with the samples.

The laboratory will provide containers for the collection of samples upon client request for analytical services. Bottle kits are prepared in accordance with laboratory SOP ENV-SOP-LENE-0025, *Assembly of Sample Container Kits*.

Requirements for container type, preservation, and field quality control (QC) for the common list of test methods offered by Pace are included in the laboratory's quality manual.

General Requirements

Matrix	Routine Container	Minimum Sample Amount[1]	Preservation	Holding Time
Aqueous	Plastic or Glass	50mL	Thermal: Ambient temp or <6°C Chemical: 1:1 HNO3; pH<2	180 days

[1]*Minimum amount needed for each discrete analysis.*

Field / Matrix QC

Trip Blank	Equipment Blank	MS/MSD	Field Duplicate
NA	NA	1/20	1/20

Thermal preservation is checked and recorded on receipt in the laboratory in accordance with laboratory SOP ENV-SOP-LENE-0021, *Sample Management*. Chemical preservation is checked and recorded at time of receipt or prior to sample preparation.

After receipt, samples are stored at ambient temperature until sample preparation. Prepared samples (extracts, digestates, distillates, other) are stored ambient until sample analysis.

After analysis, unless otherwise specified in the analytical services contract, samples are retained for 30 days from date of final report and then disposed of in accordance with Federal, State, and Local regulations.

7.0 Equipment And Supplies

7.1 Equipment and Supplies

Supply	Description	Vendor/ Item # / Description
Analytical balance		Mettler-Toledo / PB3002-S (Or equivalent)
Boiling stones	PTFE	Fisher / 09-191-20 (Or equivalent)
Digestion tubes	50mL, Graduated	Environmental Express / SC475 (Or equivalent)
Filter paper	Whatman #41	Fisher / 09-850-D (Or equivalent)
Filtermate™	2.0 micron	Environmental Express / SC0401 (Or equivalent)
Graduated cylinders	Various sizes	Fisher / 03-007-40 / 03-007-41 (Or equivalent)
Hotblock	Multi-position	Environmental Express / SC154 (Or equivalent)
Pipettors	Various sizes	Eppendorf (Or equivalent)
Watch glasses	Plastic Disposable	Environmental Express / SC505 (Or equivalent)

8.0 Reagents And Standards

8.1 Reagents and Standards

The reagents listed below are those currently in use. Other sources or grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

Table 8.1 – Standard Storage Conditions

Standard Type	Description	Expiration	Storage
Stock Solutions	▪ Concentrated reference solution purchased directly from approved vendor	▪ Manufacturer's recommended expiration date	▪ Manufacturer's recommended storage conditions
Intermediate and Working Standard Solutions	▪ Reference solutions prepared by dilutions of the stock solution	▪ Six months from preparation or the expiration date listed for the stock source, whichever is sooner.	▪ Manufacturer's recommended storage conditions for stock source solution.

Standard Type	Description	Expiration	Storage
		▪ Working solutions must be checked frequently and replaced if degradation or evaporation is suspected.	

Table 8.2 – Reagents and Standards

Reagent/Standard	Concentration/ Description	Vendor/ Item #
Hydrochloric acid	Baker Instra-Analyzed®	J.T. Baker / 9530-33
Hydrogen peroxide	ACS Reagent grade	Macron Fine Chemicals / 5240-05
Nitric acid	Baker Instra-Analyzed®	J.T. Baker / 9598-34
PA-STD-1B (Custom)	200 mg/L: As, Ba, Be, Cd, Co, Cr, Mn, Ni, P, Pb, Se, Sr, Tl, V, Zn	Inorganic Ventures / PA-STD-1B
PA-STD-2B (Custom)	1000 mg/L: Si 200 mg/L: B, Mo, Sb, Sn, Ti, Zr 100 mg/L: Ag	Inorganic Ventures / PA-STD-2B
PA-STD-3B (Custom)	2000 mg/L: Al, Ca, Fe, K, Mg, Na	Inorganic Ventures / PA-STD-3B
Reagent water	ASTM Type II	SOP S-KS-Q-011

Table 8.3 – Working Spike Standards

Working Standard	Stock(s)	Volume Used (mL)	Nitric acid (mL)	Final Volume (mL)
ICP-AES Spike	PA-STD-1B PA-STD-2B PA-STD-3B	50 50 50	**NA**	**200**
ICP-MS Spike	PA-STD-1B PA-STD-2B PA-STD-3B	2.0 2.0 5.0	**2.0**	**200**

8.2 Spike Standard Verification

8.2.1 Dilute ICP Spiking Standard fifty-fold and analyze according to ENV-SOP-LENE-0026, ENV-SOP-LENE-0018, *Metals Determination by ICP-AES* or SOP ENV-SOP-LENE-009, ENV-SOP-LENE-0060 *Metals Determination by ICP-MS* (or their equivalent revisions or replacements). Spike true values are noted in Attachment I.

8.2.2 Spiking Solutions may be used for sample analysis if all element concentrations are ± 15% of the true value.

9.0 PROCEDURE

9.1 Equipment Preparation

9.1.1 Support Equipment

See SOP ENV-SOP-LENE-0030, Support Equipment (or its equivalent revision or replacement) for the calibration of the support equipment used in this procedure

9.1.2 Instrument

9.1.2.1 Routine Instrument Operating Conditions

Not applicable to this SOP

9.2 Initial Calibration

9.2.1 Calibration Design

Not applicable

9.2.2 Calibration Sequence

Not applicable

9.2.3 ICAL Evaluation

9.2.3.1 Curve Fit

Not applicable

9.2.3.2 Relative Standard Error (RSE)

Not applicable

9.2.3.3 Initial Calibration Verification

Not applicable

9.2.4 Continuing Calibration Verification

Not applicable

9.3 Sample Preparation

9.3.1 Homogenization and Subsampling

Not applicable

9.4 Analysis

9.4.1 Filtration of samples for dissolved metals analysis

9.4.1.1 Samples for dissolved metals analysis are normally filtered in the field. In certain instances, the samples are filtered in the laboratory. An aliquot of unpreserved sample is filtered through a 0.45-um, cellulose nitrate filter and preserved with nitric acid.

9.4.1.2 The filtration procedure is as follows:

9.4.1.3 Rinse the filtration apparatus (Erlenmeyer flask, filtration top and bottom) with 20% nitric acid, followed by five rinses with deionized water.

9.4.1.4 A 0.45-um filter is placed on the filtration support with a forceps

9.4.1.5 The filtration top is attached and the pump tubing is attached to the flask

9.4.1.6 150 mL of deionized water is added to the filtration apparatus and the pump is started.

9.4.1.7 After the deionized water has passed through the filter, turn the pump off and disconnect the tubing from the pump. Remove the filter support and pour the filtered aliquot into a pre-certified, HNO_3-preserved, 250-mL sample bottle (obtain from Bottle Prep Department).

9.4.1.8 This aliquot of deionized water serves as the method blank for the batch.

9.4.1.9 Label the bottle with the date, analyst's initials and attach a sample identification label.

9.4.1.10 Repeat steps 1 through 6 for up to twenty samples (substituting the sample for deionized water in Step 4).

9.4.1.11 Record the filter lot number on the filtration batch sheet with the analyst initials and date. Place the batch in the filtration binder.

9.4.1.12 Alternatively, the Flip-mate filters may be used with the filtration manifold to filter multiple samples at once. This system utilizes the 50 mL digestion vessels.

9.4.1.12.1 Fill a digestion tube with 50 mL of sample and screw the flip-mate filter to the tube

9.4.1.12.2 Attach an empty 50 mL digestion tube to the other side of the flip-mate filter.

9.4.1.12.3 Invert the tubes so the sample side is up. Attach the flip-mate filter to the manifold by pressing the male end of the valve to the female end of the flip-mate filter.

9.4.1.12.4 Ensure the pump hose is attached to the manifold. Turn the pump on and open the valve to all ports of the manifold where filters have been attached.

9.4.1.12.5 Allow the sample enough time to filter from the top tube to lower tube.

9.4.1.12.6 Check the volume to ensure no loss of sample.

9.4.1.13 The samples are now ready for digestion. The filtered blank is carried through the digestion process and is the method blank.

9.4.2 Batch samples according to EPIC procedures. Using batch worklist, mark the digestion tube with the sample ID.

9.4.3 Transfer information into Workbench system according to IT staff instructions. Transfer the same information into the prep logbook along with the project number, batch code, QC samples, and spike solution used for the LCS, MS, and MSD.

9.5 Hotblock Digestion

9.5.1 Prepare the Prep Blank and the LCS by measuring out 50 mL of reagent water into an appropriately labeled 50-mL digestion tubes.

9.5.2 Transfer a 50-mL aliquot of a well-mixed sample into a labeled 50-mL digestion tube. For the QC samples (MS/MSD) transfer additional 50-mL aliquots of the same sample into labeled 50-mL digestion tubes.

9.5.3 Spike the LCS, MS and MSD samples with 1.0 mL of the ICP Spiking Standard or 1.0 mL of ICPMS spiking standard.

9.5.4 For analysis by ICP or ICPMS add 2.0 mL of 1:1 HNO_3, 5.0 mL of 1:1 HCl, and place in hotblock maintained at 90-95 °C (do not boil).

9.5.5 Place watch-glasses on the digestion tubes and heat until sample volume has reduced to approximately 10% of the initial sample volume or a minimum of 4 hours.

9.5.6 Remove from heat and allow sample to cool. Wash down sides of digestion tube with reagent water and adjust the final volume to 50 mL with reagent water. Filter only if necessary to remove silicates and other insoluble material.

9.5.7 Complete the digestion logbook page.

10.0 Data Analysis And Calculations

10.1 Qualitative Identification

Not applicable

10.2 Quantitative Identification

Not applicable

10.3 Calculations

See the Laboratory Quality Assurance Manual for equations for common calculations.

11.0 Quality Control and Method Performance

11.1 Quality Control

The following QC samples are prepared and analyzed with each batch of samples. Refer to Appendix B for acceptance criteria and required corrective action.

QC Item	Frequency

Method Blank (MB)	1 per batch of 20 or fewer samples. If batch exceeds, 20 samples, every 20.
Laboratory Control Sample (LCS)	1 per batch of 20 or fewer samples. If batch exceeds, 20 samples, every 20.
Matrix Spike (MS) / Matrix Spike Duplicates (MSD)	1 per batch of 20 or fewer samples. If batch exceeds, 20 samples, every 20.

11.2 Instrument QC

Not applicable. Refer to the determinative SOP.

11.3 Method Performance

11.3.1 Method Validation

11.3.1.1 Detection Limits

Detection limits (DL) and limits of quantitation (LOQ) are established at initial method setup and verified on an on-going basis thereafter. Refer to Pace ENV corporate SOP ENV-SOP-CORQ-0011 Method Validation and Instrument Verification.

11.4 Analyst Qualifications and Training

Employees that perform any step of this procedure must have a completed Read and Acknowledgment Statement for this version of the SOP in their training record. In addition, prior to unsupervised (independent) work on any client sample, analysts that prepare or analyze samples must have successful initial demonstration of capability (IDOC) and must successfully demonstrate on-going proficiency on an annual basis. Successful means the initial and on-going DOC met criteria, documentation of the DOC is complete, and the DOC record is in the employee's training file. Refer to laboratory SOP ENV-SOP-LENE-0110, *Training Procedures*, for more information.

12.0 Data Review And Corrective Action

12.1 Data Review

Pace's data review process includes a series of checks performed at different stages of the analytical process by different people to ensure that SOPs were followed, the analytical record is complete and properly documented, proper corrective actions were taken for QC failure and other nonconformance(s), and that test results are reported with proper qualification.

The review steps and checks that occur as employee's complete tasks and review their own work is called primary review.

All data and results are also reviewed by an experienced peer or supervisor. Secondary review is performed to verify SOPs were followed, that calibration, instrument performance, and QC criteria were met and/or proper corrective actions were taken, qualitative ID and quantitative measurement is accurate, all manual integrations are justified and documented in accordance with the Pace ENV's SOP for manual integration, calculations are correct, the analytical record is complete and traceable, and that results are properly qualified.

A third-level review, called a completeness check, is performed by reporting or project management staff to verify the data report is not missing information and project specifications were met.

Refer to laboratory SOP ENV-SOP-LENE-088, *Data Reduction, Review and Reporting*, for specific instructions and requirements for each step of the data review process.

12.2 Corrective Action

Corrective action is expected any time QC or sample results are not within acceptance criteria. If corrective action is not taken or was not successful, the decision/outcome must be documented in the analytical record. The primary analyst has primary responsibility for taking corrective action when QA/QC criteria are not met. Secondary data reviewers must verify that appropriate action was taken and/or that results reported with QC failure are properly qualified.

Corrective action is also required when carryover is suspected and when results are over range.

Samples analyzed after a high concentration sample must be checked for carryover and reanalyzed if carryover is suspected. Carryover is usually indicated by low concentration detects of the analyte in successive samples analyzed after the high concentration sample.

Sample results at concentrations above the upper limit of quantitation must be diluted and reanalyzed. The result in the diluted samples should be within the upper half of the calibration range. Results less than the mid-range of the calibration indicate the sample was over diluted and analysis should be repeated with a lower level of dilution. If dilution is not performed, any result reported above the upper range is considered a qualitative measurement and must be qualified as an estimated value.

Refer to Appendix B for a complete summary of QC, acceptance criteria, and recommended corrective actions for QC associated with this test method.

13.0 Pollution Prevention And Waste Management

Pace proactively seeks ways to minimize waste generated during our work processes. Some examples of pollution prevention include but are not limited to: reduced solvent extraction, solvent capture, use of reusable cycletainers for solvent management, and real-time purchasing.

The EPA requires that laboratory waste management practice to be conducted consistent with all applicable federal and state laws and regulations. Excess reagents, samples and method process wastes must be characterized and disposed of in an acceptable manner in accordance with Pace's Chemical Hygiene Plan / Safety Manual.

14.0 Modifications

A modification is a change to a reference test method made by the laboratory. For example, changes in stoichiometry, technology, quantitation ions, reagent or solvent volumes, reducing digestion or extraction times, instrument runtimes, etc. are all examples of modifications. Refer to Pace ENV corporate SOP ENV-SOP-CORQ-0011 *Method Validation and Instrument Verification* for the conditions under which the procedures in test method SOPs may be modified and for the procedure and document requirements.

14.1 Method 3010A has been modified to utilize plastic digestion tubes rather than glass Griffin beakers, and acid strengths have been modified. It has been found that the amount of time needed to evaporate samples to method specified volumes exceeds an 8 hour work shift. Therefore, samples are digested until volume is reduced to 10% of the initial sample volume or for a minimum of 4 hours. After which, the samples are considered to be completely digested. Performance Testing (PT) studies support that these modifications do not adversely affect the quality of the analytical data produced by this digestion procedure. (See Attachment II for initial validation data.) Additionally, the method deviates by adding 2 mL Nitric acid per 50 mL final volume instead of the 3 mL Nitric acid per 50 mL.

14.2 Method 200.7, Rev. 4.4 specifies using 1 mL 1:1 HNO_3 and 0.5 mL HCl (when reduced to a 50 mL sample volume). Instead Pace is using 2 mL 1:1 HNO_3 and 5 mL 1:1 HCl, the same ratios used for method 3010A in this SOP.

14.3 Method 200.8 for Total Recoverable metals specifies using 2 mL (1+1) Nitric acid and 1.0 mL of (1+1) HCl to a 100 mL sample. Pace is adding 2 mL of (1+1) Nitric acid and 0.5 mL of (1+1) HCl to a 50 mL sample. The change in HCl concentration is recommended by the Instrument engineers.

15.0 RESPONSIBILITIES

Pace ENV employees that perform any part this procedure in their work activities must have a signed Read and Acknowledgement Statement in their training file for this version of the SOP. The employee is responsible for following the procedures in this SOP and handling temporary departures from this SOP in accordance with Pace's policy for temporary departure.

Pace supervisors/managers are responsible for training employees on the procedures in this SOP and monitoring the implementation of this SOP in their work area.

16.0 ATTACHMENTS

16.1 Attachment I: Spike True Values

16.2 Attachment II: Initial Validation Data

17.0 REFERENCES

17.1 Pace Quality Assurance Manual - most current version.

17.2 National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, "Quality Systems"- most current version.

17.3 The NELAC Institute (TNI); Volume 1, Module 2, "Quality Systems"- most current version.

17.4 "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Analysis and Sampling Procedures; Final Rule" Federal Register Doc. No: 2012-10210.

17.5 EPA Test Methods for Evaluating Solid Waste. SW-846, Third Edition, Update I, Method 3010A, Revision 1, July 1992.

17.6 Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020, Method 200.7, Revision 4.4, 1994.

18.0 REVISION HISTORY

This Version: ENV-SOP-LENE-0089, v02

Section	Description of Change
All	This is a new SOP format

This document supersedes the following document(s):

Document Number	Title	Version
ENV-SOP-LENE-0089	Acid Digestion of aqueous samples	01

Attachment I: Spike True Values (50-mL digestate)

ICP-AES Spike True Values

Element	Concentration (ug/L)	Element	Concentration (ug/L)
Ag	500	Mo	1000
Al	10000	Na	10000
As	1000	Ni	1000
B	1000	P	1000
Ba	1000	Pb	1000
Be	1000	Sb	1000
Ca	10000	Se	1000
Cd	1000	Si	5000
Co	1000	Sn	1000
Cr	1000	Sr	1000
Cu	1000	Ti	1000
Fe	10000	Tl	1000
K	10000	V	1000
Li	1000	Zn	1000
Mg	10000		
Mn	1000		

ICP-MS Spike True Values

Element	Concentration (ug/L)	Element	Concentration (ug/L)
^{9}Be	40	^{105}Pd	20
^{27}Al	4,000	^{107}Ag	20
^{47}Ti	40	^{111}Cd	40
^{51}V	40	^{118}Sn	40
^{52}Cr	40	^{121}Sb	40
^{54}Fe	2,000	^{137}Ba	40
^{55}Mn	40	^{195}Pt	20
^{89}Co	40	^{205}Tl	20
^{60}Ni	40	^{208}Pb	40
^{65}Cu	40	^{238}U	40
^{66}Zn	40	Tin	40
^{75}As	40		
^{78}Se	40		
^{88}Sr	40		
^{95}Mo	40		

Attachment II: Initial Validation Data

Parameter	Analytical Results Obtained (ug/L) Date: 2/4/13 (ICP-AES) Instrument ID: 60ICP04	Analytical Results Obtained (ug/L) Date: 2/4/13 (ICP-MS) Instrument ID: 60ICPM1	ERA WasteWatR Trace Metals (Lot No. P208-500) Certified Value (ug/L)	ERA WasteWatR Trace Metals (Lot No. P208-500) Acceptance Range (ug/L)
Aluminum	467	453.1	456	350-564
Antimony	399	397.4	401	277-484
Arsenic	371	376.5	376	314-441
Barium	1750	1959	1880	1630-2120
Beryllium	539	541.7	544	462-614
Boron	868	Not Evaluated	930	769-1080
Cadmium	672	652	671	573-762
Chromium	796	810.8	779	679-880
Cobalt	289	282.5	276	242-310
Copper	241	240.8	238	214-264
Iron	1026	984.4	1070	946-1210
Lead	321	320.9	305	262-346
Manganese	820	800	767	688-852
Molybdenum	207	208.3	202	168-234
Nickel	813	772	765	688-855
Selenium	631	581.7	652	517-755
Silver	263	264.5	257	220-294
Strontium	213	218.9	217	188-246
Thallium	543	508.9	513	412-616
Vanadium	1462	Not Evaluated	1420	1240-1590
Zinc	255	242.7	253	216-295

1.0 SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the laboratory procedure for the determination of Anions by Ion Chromatography by EPA 300.0 rev 2.1 and SW-846 9056A.

1.1 Target Analyte List and Limits of Quantitation (LOQ)

The target analytes and the normal LOQ that can be achieved with this procedure are provided in Table 1.1.

Table 1.1 – Limits of Quantitation

Anion	Water, mg/L	Soil, mg/kg
Fluoride (F)	0.2	2.0
Chloride (Cl)	1.0	10
Nitrite-N (NO_2-N)	0.1	1.0
Bromide (Br)	1.0	10
Nitrate-N (NO_3-N)	0.1	1.0
Sulfate (SO_4)	1.0	10

LOQ are established in accordance with Pace policy and SOPs for method validation and for the determination of detection limits (DL) and quantitation limits (LOQ). DL and LOQ are routinely verified and updated when needed. The current LOQ for each target analyte that can be determined by this SOP as of the effective date of this SOP is provided in Table 1, Appendix A.

The reporting limit (RL) is the value to which analytes are reported as detected or not detected in the final report. When the RL is less than the lower limit of quantitation (LLOQ), all detects and non-detects at the RL are qualitative. The LLOQ is the lowest point of the calibration curve used for each target analyte.

DL, LOQ, and RL are always adjusted to account for actual amounts used and for dilution.

2.0 SUMMARY OF METHOD

A water sample or a deionized water extract for soil samples are injected into a stream of carbonate-bicarbonate eluent and passed through a series of ion exchangers. The anions of interest are separated on the basis of their relative affinities for a low capacity, strongly basic anion exchanger (guard and separator columns). The separated anions are directed onto a micromembrane suppressor. In the suppressor, the separated anions are converted to their highly conductive acid

forms and the carbonate-bicarbonate eluent is converted to a weakly conductive carbonic acid. The separated anions are measured by conductivity. They are identified on the basis of retention time as compared to standards. Quantitation is by measurement of peak area compared to an external standard calibration curve. Nitrite and nitrate are calculated as nitrogen as N+N.

3.0 INTERFERENCES

- Interferences can be caused by substances with retention times that are like and overlap those of the anion of interest. Large concentrations of one anion can interfere with the peak resolution of an adjacent anion. An initial conductivity reading is recommended prior to analysis, to determine adequate dilution factors. Sample dilution can be used to solve most interference problems.
- Method interferences may be caused by contaminants in the deionized water, reagents, glassware, and other sample processing apparatus that led to discrete artifacts or to elevated baselines in ion chromatograms.
- Any anion that is not retained by the column or only slightly retained will elute in the area of fluoride and interfere. Known co-elution is caused by carbonate, acetate, formate, and other small organic anions.
- The retention times of anions may differ when large amounts of acetate are present. Therefore, this method is not recommended for leachates of solid samples where acetate is used for pH adjustment.
- Samples that contain particulate matter require filtration to prevent damage to instrument columns and flow systems.

4.0 DEFINITIONS

Refer to the Laboratory Quality Manual for a glossary of common lab terms and definitions.

5.0 HEALTH AND SAFETY

Contact your supervisor or local safety coordinator with questions or concerns regarding safety protocol or safe handling procedures for this procedure

The following sections provide general health and safety information about chemicals and materials that may be present in the laboratory.

- The toxicity or carcinogenicity of each chemical material used in the laboratory has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable.
- The laboratory maintains documentation of hazard assessments and OSHA regulations regarding the safe handling of the chemicals specified in each method. Safety data sheets for all hazardous chemicals are available to all personnel. Employees must abide by the health, safety and environmental (EHS) policies and procedures specified in this SOP and in the Pace® Chemical Hygiene / Safety Manual (COR-MAN-0001)

- Personal protective equipment (PPE) such as safety glasses, gloves, and a laboratory coat must be worn in designated areas and while handling samples and chemical materials to protect against physical contact with samples that contain potentially hazardous chemicals and exposure to chemical materials used in the procedure.
- Concentrated corrosives present additional hazards and are damaging to skin and mucus membranes. For procedures that require use of acids, use acids in a fume hood whenever possible with PPE designed for handing these materials. If eye or skin contact occurs, flush with large volumes of water. When working with acids, always add acid to water to prevent violent reactions. For procedures that that emit large volumes of solvents (evaporation/concentration processes), these activities must be performed in a fume hood or apparatus that reduces exposure.

6.0 SAMPLE COLLECTION, PRESERVATION, HOLDING TIME, AND STORAGE

Samples should be collected in accordance with a sampling plan and procedures appropriate to achieve the regulatory, scientific, and data quality objectives for the project.

The laboratory does not always perform sample collection or field measurements for this test method. To assure sample collection and field checks and treatment are performed in accordance with applicable regulations Pace project managers will inform the client of these requirements at the time of request for analytical services when the request for testing is received prior to sample collection. If samples were already collected, the laboratory will record any nonconformance to these requirements in the laboratory's sample receipt record when sufficient information about sample collection is provided with the samples.

The laboratory performs sample collection for samples to be analyzed by this SOP in accordance with laboratory SOP ENV-SOP-LENE-0107. Refer to this SOP for these instructions.

The laboratory will provide containers for the collection of samples upon client request for analytical services. Bottle kits are prepared in accordance with laboratory SOP ENV-SOP-LENE-0025.

Requirements for container type, preservation, and field quality control (QC) for the common list of test methods offered by Pace are included in the laboratory's quality manual.

General Requirements

Matrix	Routine Container	Minimum Sample Amount[1]	Preservation	Holding Time
Aqueous	Plastic; 250mL	10mL	Thermal: ≤6ºC Chemical: None	28 days from Collection (F, Cl, Br, & SO4) 48 hours from Collection (NO2 & NO3)
Solid	Glass; 4oz	10g	Thermal: ≤6ºC Chemical: None	28 days from Collection (F, Cl, Br, & SO4) 48 hours from Extraction (NO2 & NO3)

[1]*Minimum amount needed for each discrete analysis.*

Thermal preservation is checked and recorded on receipt in the laboratory in accordance with laboratory SOP ENV-SOP-LENE-0021.

After receipt, samples are stored at ≤6°C until sample preparation.

After analysis, unless otherwise specified in the analytical services contract, samples are retained for 30 days from date of final report and then disposed of in accordance with Federal, State, and Local regulations.

7.0 EQUIPMENT AND SUPPLIES

7.1 Equipment and Supplies

Table 7.1 – Instrumentation

Equipment	Vendor	Model / Version	Comments
Adjustable pipettor	Eppendorf	Various	
Analytical Balance	Mettler-Toledo	AE-200	
Volumetric(s)	Fisher	various	Class A
Autosampler	Dionex	AS-40, AS-DV	
50 mL Graduated Cylinder	Fisher		Class A
Data Acquisition Software	Dionex	Chromeleon 7.3	
Detector	Dionex	CDM-II	Conductivity
Detector	Dionex	DS6 Heated Cell	Conductivity
Electrolytic pH Modifier	Dionex	063175	
Ion Chromatograph	Dionex	ICS-1600, ICS-2000, ICS-1500, Aquion	
Suppressor	Dionex	AERS 500, 4mm	Or equivalent

Table 7.2 – Chromatographic Supplies

Item	Vendor	Model / ID	Catalog #	Description
Analytical Column	Dionex	Ion Pac AS 22	064141	7 µm, 250 mm x 4 mm
Guard Column	Dionex	Ion Pac AG 22	064139	10 µm, 50 mm x 4 mm
Fast Analytical Column	Thermo	Ion Pac AG 22	079936	150mm x 4 mm

Table 7.3 – General Supplies

Item	Description	Vendor / Item # / Description
Volumetric Flasks	Various sizes	Class A
Centrifuge tubes	50-mL	Fisher
Sample vials	5-mL w/filtering cap	Environmental Express / K1250
Nitrate test strips	For quick dilution testing	Hach/Fisher / 27454-25

Item	Description	Vendor / Item # / Description
Chloride test strips	For quick dilution testing	Hach/Fisher / 27513-40
Filters (0.45 um)	For Luer Lok Syringe	Environmental Express / SF045E
10 mL syringe	Luer Lok	Fisher / 302995

NOTE: All glassware must be rinsed several times with deionized water prior to use. It is recommended that the volumetric flasks be segregated from other use and filled with deionized water during storage.

8.0 REAGENTS AND STANDARDS

8.1 Reagents and Standards

Table 8.1 – Stock Reagents

Reagent	Concentration/ Description	Vendor/ Item #
Deionized water	ASTM Type II	
Sodium carbonate (Na_2CO_3)	ACS Reagent grade	Fisher / S263-500
Sodium bicarbonate ($NaHCO_3$)	ACS Reagent grade	Fisher / S631-3

Table 8.2 – Intermediate Reagents

Reagent	Description
Eluent Stock	Dissolve 5.88g sodium bicarbonate and 23.845g sodium carbonate into a 1-L volumetric flask containing approximately 600 mL deionized water. Dilute to the mark and invert several times to mix. Prepare monthly.

Table 8.3 – Working Reagents

Reagent	Description
Working Eluent	Add 40 mL of Concentrated Eluent into a 2-L volumetric flask. Dilute to the mark with deionized water and invert several times to mix. Prepare daily.

Table 8.4 – Standard Storage Conditions

Standard Type	Description	Expiration	Storage
Stock Solutions	Concentrated reference solution purchased directly from approved vendor	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions
Working Standard Solutions	Reference solutions prepared by dilutions of the stock solution	One week from preparation or the expiration date listed for the stock source, whichever is sooner.	

Standard Type	Description	Expiration	Storage
		▪ Nitrite working standards are prepared daily	

Table 8.5 – Stock Standards

Standard	Concentration	Vendor / Item #
Primary Stock Standard	25 mg/L: , Nitrate-N, Nitrite-N 50 mg/L: Fluoride 100 mg/L: Bromide, Sulfate, Chloride,	Inorganic Ventures / PACEKS-2016
Secondary Stock Standard	250 mg/L: Bromide, Chloride, Sulfate 125mg/L: Fluoride 100 mg/L: Nitrate-N, Nitrite-N	SPEX / VPCLKS-6-250
Soil Spike Standard	400 mg/L Nitrate-N, Nitrite-N 500 mg/L Fluoride 1000 mg/L: Bromide, Sulfate, Chloride	SPEX / VPCLKS-7
MDL Spike Solution	100 mg/L Bromide, Chloride, Sulfate 20 mg/L Fluoride 10 mg/L Nitrate-N, Nitrite-N	SPEX/VPCLKS-5-250

Table 8.6 – Preparation of Calibration, High, Low and CCV Standards

Standard	Stock Standard	Standard Amount	Solvent	Final Total Volume	Calibration Notes R2 value = ≥0.995
CAL0	N/A	0	DI Water	5mL	
CAL1	CAL7	0.05 mL	DI Water	5mL	50% of true value for Fluoride on QAP samples
CAL2	CAL 7	0.1 mL	DI Water	5mL	50% of true value for Fluoride, Nitrate, and Nitrite.
CAL3	CAL7	0.25 mL	DI Water	5mL	50% of true value for Chloride, Bromide, and Sulfate
CAL4CCVB	CAL 7 /Primary	0.625 mL / 2.50mL	DI Water	5mL /50mL	

Standard	Stock Standard	Standard Amount	Solvent	Final Total Volume	Calibration Notes R2 value = ≥0.995
CAL5/CCV	CAL7 / Primary	1.25 mL / 5.00mL	DI Water	5 mL / 50mL	
CCVA	Primary	7.50mL	DI Water	50mL	
CAL6	CAL7	2.5 mL	DI Water	5mL	10% of true value for midpoint of the curve.
CAL7	Primary	10.0 mL	DI Water	50mL	

Table 8.7 – Initial Calibrations Concentrations (mg/L)

Anion	CAL0	CAL1	CAL2	CAL3	CAL4	CAL5	CAL6	CAL7
Fluoride (F)	0	0.1	0.2	0.5	1.25	2.5	5.0	10.0
Chloride (Cl)	0	—	0.4	1.0	2.5	5.0	10.0	20.0
Nitrite-N (NO_2-N)	0	-	0.1	0.25	0.625	1.25	2.5	5.0
Bromide (Br)	0	—	0.4	1.0	2.5	5.0	10.0	20.0
Nitrate-N (NO_3-N)	0	-	0.1	0.25	0.625	1.25	2.5	5.0
Sulfate (SO_4)	0	—	0.4	1.0	2.5	5.0	10.0	20.0

Table 8.8 – ICV/LCS Concentrations

Anion	Stock Concentration (mg/L)	Final Concentration (mg/L)
Fluoride (F)	125.0	2.5
Chloride (Cl)	250.0	5.0
Nitrite-N (NO_2-N)	100.0	2.0
Bromide (Br)	250.0	5.0
Nitrate-N (NO_3-N)	100.0	2.0
Sulfate (SO_4)	250.0	5.0

***prepare ICV/LCS standard by pipetting 2mL of the secondary source into a 100mL volumetric flask. Prepare daily**

Table 8.9 – CCVB CHK Concentrations, 50% true value

Anion	CAL7 Concentration (mg/L)	Final Concentration (mg/L)
Fluoride (F)	50.0	2.5

Anion	CAL7 Concentration (mg/L)	Final Concentration (mg/L)
Chloride (Cl)	100.0	5.0
Nitrite-N (NO_2-N)	25.0	1.25
Bromide (Br)	100.0	5.0
Nitrate-N (NO_3-N)	25.0	1.25
Sulfate (SO_4)	100.0	5.0

***prepare CCVB by pipetting 2.5mL of the primary source into a 50mL volumetric flask. Prepare daily.**

Table 8.10 – CCVA CHK Concentrations, 10% true value

Anion	Stock Concentration (mg/L)	Final Concentration (mg/L)
Fluoride (F)	50.0	7.5
Chloride (Cl)	100.0	15
Nitrite-N (NO_2-N)	25.0	3.75
Bromide (Br)	100.0	15
Nitrate-N (NO_3-N)	25.0	3.75
Sulfate (SO_4)	100.0	15

prepare CCVA by pipetting 7.5mL of the primary source into a 50mL volumetric flask. Prepare daily.

9.0 PROCEDURE

9.1 Equipment Preparation

9.1.1 Support Equipment

Refer to Pace Analytical Services – Kansas SOP ENV-SOP-LENE-0030, Support Equipment, or equivalent replacement, for additional information on calibration requirements for support equipment that may be used in this procedure.

Balances are checked prior to use on each working day with NIST traceable references in the expected range of use, and the results are recorded in the logbook assigned to the balance.

9.1.2 Instrument setup

9.1.2.1 Turn on the PC, suppressor, and pump.

If the instrument is starting from the “off” status, priming the instrument should take place to eliminate air bubbles from the tubing.

To do this, press “Prime” under the pump settings.

Next, follow the instructions on the screen.

Turn the pump head a quarter of a turn (eluent will come out of the hole in the front)

Press “OK” and let instrument prime for 5-10 minutes.

9.1.2.2 Allow the instrument to stabilize for a minimum of 30 minutes before starting the analytical sequence.

9.1.2.3 Enter the sample identifications into Chromeleon.

9.1.2.4 Analyze samples according to specific instrument instructions.

9.1.3 Instrument Operating Conditions (approximate)

9.1.3.1 Eluent flow rate: 1.0 mL/min

9.1.3.2 Suppressor current: 31mA

9.1.3.3 Sample loop: 25 µl

9.1.3.4 Total run time per sample is 7-15 minutes (depending on the type of analytical column) with approximately 2 minutes for loading and injection.

Table 9.1 – Approximate Retention Times

Anion	AS22 Column (Min)
Fluoride (F)	2.72
Chloride (Cl)	4.08
Nitrite-N (NO_2-N)	4.97
Bromide (Br)	5.98
Nitrate-N (NO_3-N)	6.82
Sulfate (SO_4)	10.90

9.2 Initial Calibration

9.2.1 Calibration Design

9.2.1.1 An initial calibration curve using a minimum of five levels and a blank is analyzed prior to the analysis of any client samples. The lowest concentration standard of the initial calibration curve must be at or below the reporting limit, a level below which all reported results must be qualified as estimated values.

9.2.1.2 Allow the instrument to stabilize for a minimum of 30 minutes. Analyze calibration standards 0-7 followed by the ICVand ICB. Process the CAL7 standard and optimize the integration parameters and retention times. Once the integration parameters and retention times are set, reprocess the entire curve, and save.

9.2.1.3 Once the system software’s integration parameters (including retention times) have been optimized and saved, they are not to be adjusted unless the following procedure is completed. Further adjustments to the integration parameters must be approved by the Quality Manager and the Inorganics Manager (or their

designees). If approved, the adjustments need to be applied to the original curve and all analytical sequences to which they apply. This includes all QC/samples. The revised curve and all QC data must be evaluated and reviewed.

9.2.2 Calibration Sequence

Table 9.2 – Example Sequence Beginning with Initial Calibration

Injection	Name
1	CAL0
2	CAL1
3	CAL2
4	CAL3
5	CAL4
6	CAL5
7	CAL6
8	CAL7
10	ICV
11	ICB
12	MB
13	LCS
14	SAMPLE A
15	SAMPLE A MS
16	SAMPLE A MSD
17	SAMPLE B
18	SAMPLE C
19	SAMPLE D
20	SAMPLE E
21	SAMPLE E MS
22	CCV
23	CCB

9.2.3 ICAL Evaluation

9.2.3.1 Curve Fit

Linear Regression – The linear regression calibration curve is derived from a least square's regression analysis of the calibration points. A calibration curve based on this technique will have the format of y=ax+b where "a" is the slope of the line and "b" is the y-intercept. The linear regression is not forced through the origin; therefore, there is a possibility that very low levels of contaminants below the response of the lowest calibration point may

generate erroneous reportable results. A calculation of the correlation coefficient "r" is used to determine the acceptability of a linear regressed curve (see Appendix B).

9.2.3.2 Calibration Linearity Problems

The lowest and/or highest-level calibration standards may be removed from the calibration if the remaining number of concentration levels meets the minimum 5 calibration point requirement. For multi-parameter methods, this may be done on an individual analyte basis. The reporting limit must be adjusted to the lowest concentration remaining in the calibration curve and the upper limit of quantitation must be adjusted to the highest concentration remaining in the calibration curve.

If a calibration point is removed, indicate on the analytical checklist, at the time of calibration, the reason for removing the point. If the removal of a calibration point requires the use of an alternative high daily check standard, document this on the daily run log.

If the calibration problem requires maintenance and recalibration, document the items in the maintenance logbook and recalibrate.

9.2.3.3 Relative Standard Error (RSE)

For any calibration model other than average response, the laboratory shall evaluate Relative Error. This evaluation shall be done on a mid-level calibration point and the lowest calibration point. Refer to Appendix B for acceptance criteria.

Refer to Pace Analytical Services – Corporate POL ENV-POL-CORQ-0005, Acceptable Calibration Practices for Instrument Testing, or equivalent replacement, for additional information and calculations.

9.2.3.4 Initial Calibration Verification

In addition to meeting the linearity criteria, any new calibration curve must be assessed for accuracy in the values generated. Accuracy is a function of both the "fit" of the curve to the points used and the accuracy of the standards used to generate the calibration points. By meeting the fit criteria, the accuracy relative to the goodness of fit is addressed. However, because all calibration points are from the same source, it is possible that the calibration points may meet linearity criteria, but not be accurately made in terms of their true value.

Therefore, to assess the accuracy relative to the purity of the standards, a single standard from a secondary source must be analyzed and the results obtained must be assessed relative to the known true value. This step is referred to as Secondary Source Verification or, alternatively as Initial Calibration Verification. This secondary source must be from an alternative vendor or, in the event an alternative vendor is not available, from a different lot from the same vendor. The accuracy of the standard is assessed as a percent difference from the true value according to the following equation:

$$\%\text{Drift} = \frac{\left(\text{Result}_{\text{ICV}} - \text{True Value}_{\text{ICV}}\right)}{\text{True Value}_{\text{ICV}}} \times 100$$

9.2.4 Continuing Calibration Verification

9.2.4.1 Continuing Calibration Verification (CCV)

As part of the analytical process, the instrumentation must be checked periodically to determine if the response has changed significantly since the initial calibration was established. This verification process is known as Continuing Calibration Verification (CCV). The validity of the initial calibration is checked after every ten samples and at the end of the analytical sequence by analyzing a midpoint calibration standard. The accuracy of the standard is assessed as a percent difference from the true value according to the following equation:

$$\%\text{Drift} = \frac{\left(\text{Result}_{CCV} - \text{True Value}_{CCV}\right)}{\text{True Value}_{CCV}} \times 100$$

9.2.4.2 CCVA and CCVB Standards

If an ICAL is not analyzed the day of analysis, then the validity of the initial calibration is checked by the analysis of both a CCVA check standard and a CCVB check standard. The accuracy of the standard is assessed as a percent difference from the true value according to the following equation:

$$\%\text{Drift} = \frac{\left(\text{Result}_{CHK} - \text{True Value}_{CHK}\right)}{\text{True Value}_{CHK}} \times 100$$

Table 9.3 – Example Sequence NOT Beginning with Initial Calibration

Injection	Name
1	CCVA
2	CCVB
3	CCB
4	MB
5	LCS
6	Sample A
7	Sample A MS
8	Sample A MSD
9	Sample B
10	Sample C
11	Sample D
12	Sample D MS
13	Sample E
14	CCV
15	CCB

9.2.5 Continuing Verification Problems

9.2.5.1 Reanalyze the original CCV standard to determine instrument consistency.

9.2.5.2 Prepare and analyze a new CCV standard to determine preparation consistency / standard integrity.

9.2.5.3 Perform and document instrument maintenance

9.2.5.4 Reanalyze CCV standard to determine if maintenance was effective in restoring performance.

9.2.5.5 Complete recalibration of instrument.

9.2.5.6 If samples were analyzed despite verification failures, note the exception below for addressing those results. Deviations from this requirement must be noted on the injection log with a thorough explanation for the deviation from policy.

9.2.5.7 Exception: If the calibration verification is above the upper control limit for an analyte, non-detect results may be reported without reanalysis.

9.2.6 Retention Time Windows

9.2.6.1 New retention time windows must be established whenever a new IC column is installed.

9.2.6.2 Before establishing retention time windows make sure that the chromatographic system is operating reliably and that the system conditions have been optimized for the anions in the sample matrix to be analyzed.

9.2.6.3 The following process may be used to identify retention times. Make three injections of a standard over the course of a 24-hour period. Serial injections or injections over a period of less than 24 hours may result in retention time windows that are too tight. Record the retention time for each anion to three decimal places (e.g., 0.007). The width of the retention time window for each anion is defined as ± 3 times the standard deviation of the retention times established during the 24-hour period.

9.2.6.4 The width of the retention time windows used to make identifications will be ±10% of the absolute retention time of the CAL6 standard in the initial calibration. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

9.3 Sample Preparation

9.3.1 Homogenization & Subsampling

Refer to Pace Analytical Services – Kansas SOP ENV-SOP-LENE-0135, Sample Homogenization and Sub-Sampling, or equivalent replacement, for information regarding the handling, homogenization, and splitting of samples in order to ensure that a representative aliquot is used for analysis.

9.3.2 **Water samples**: Preparation is not normally needed with “clean” aqueous samples. Turbid aqueous sample may require pre-filtration before they are placed in the autosampler. If any of the samples are pre-filtered, then the MB and the LCS must also be pre-filtered as well. Make sure the sample has been shaken well to mix the sample.

9.3.3 Soil

- Make sure to mix the sample in the jar
- Weigh 5 g of the sample into a 50-mL centrifuge tube and add 50 mL of deionized water. Record the soil weight, in grams, in the preplog.
- Place the centrifuge tubes on a shaker table and shake for 30 minutes.
- Remove tubes from shaker and centrifuge for 10 minutes.
- The supernatant liquid is now ready for analysis.
- Dilute ten-fold prior to sample analysis unless a lower reporting limit is requested for sludges (503). Ex) biosolids, 503 sludges, TWAS etc

9.4 Analysis

9.4.1 Follow the instructions given in Section 9.2 above to calibrate the IC, or to verify the current calibration of the IC.

9.4.2 High conductivities are generally due to chloride or sulfate concentrations. Historical results will also be useful in determining appropriate dilutions. Appropriate dilutions are selected such that the instrument result will fall in the upper half of the calibration curve.

Create a bench sheet (example below) to show the sample number, dilution, and analyte(s) needed. The bench sheet creates an “equation” that pulls in information into LimsLink correctly and efficiently.

CCVA		INSTRUMENT		60WTAU	DATE	9/1/2022	CCVA x	batch worklist notes
CCVB		ANALYST		RKA			CCVB x	
CCB		Q BATCH		90958 / 799254	TEST/METHOD	300.0/9056	CCB x	
BLANK	BLANK						BLANK x	
LCS	LCS				RR 90963		LCS x	
	60408911005	CLIENT	200	CL F SO BR			60408911005 x200	
	60408951003	CLIENT	500	CL			60408951003 x500	
	60408963004	CLIENT	10	SO			60408963004 x10	
	60408990001	CLIENT	200	SO			60408990001 x200	
	60408990002	CLIENT	200	SO			60408990002 x200	
	60408990003	CLIENT	200	SO			60408990003 x200	
	60409011001	CLIENT	10	CL SO			60409011001 x10	
	60409011001	CLIENT	1000	CL SO			60409011001 x1000	
CCV							CCV x	
CCB							CCB x	
	60409032001	CLIENT	200	SO			60409032001 x200	
	60409032002	CLIENT	200	SO (CL F BR)			60409032002 x200	
	3204858	MS	200	CL F SO BR			3204858 x200	
	60409097003	CLIENT	50	SO			60409097003 x50	
	60409103001	CLIENT	5000	CL			60409103001 x5000	
	60409103002	CLIENT	2000	CL			60409103002 x2000	
	60409103003	CLIENT	1000	CL			60409103003 x1000	
	60409103004	CLIENT	4000	CL			60409103004 x4000	
	60409103005	CLIENT	5000	CL			60409103005 x5000	
	60409123001	CLIENT	20	CL			60409123001 x20	
CCV							CCV x	
CCB							CCB x	

9.4.3 Aliquot a portion of the sample into the autosampler cups for analysis.

9.4.4 If the liquid is turbid or has suspended sediment, filter a portion of the liquid into the autosampler cup using a 0.45um syringe filter.

NOTE: If sample filtration is performed, then the quality control samples (MB, LCS, MS/MSD, Sample and Duplicate) must also undergo filtration. Document each filtration on the Batch Worklist; include the lot number of the syringe filters used.

9.4.5 Arrange the autosampler cups on the autosampler tray in the order listed on the benchsheet.

9.4.6 Sample concentrations greater than the highest standard (CAL7) require dilution and reanalysis. Re-analyzed result should be in the upper three-quarters of the curve.

9.5 Example Analytical Sequence - See Tables 9.1 and 9.2

10.0 DATA ANALYSIS AND CALCULATIONS

10.1 Qualitative Identification

10.1.1 Manual Integration

Manual changes to automated integration are called manual integration. Manual integration is sometimes necessary to correct inaccurate automated integrations but must never be used to meet QC criteria or to substitute for proper instrument maintenance and/or method set-up. To assure that all manual integrations are performed consistently and are ethically justified, all manual integrations must be performed, reviewed, and recorded in accordance with corporate SOP ENV-SOP-CORQ-0006, *Manual Integration.*

10.2 Quantitative Identification

10.2.1 When reviewing sample chromatography, the analyst must: note the retention time of the analytes in relation to the retention time windows, identify samples that are greater than the high standard and review peak integrations.

10.2.2 Manual changes to automated integration are called manual integrations. Manual integration is sometimes necessary to correct inaccurate automated integrations but must never be used to meet QC criteria or to substitute for proper instrument maintenance and/or method set-up. To assure that all manual integrations are performed consistently and are ethically justified, all manual integrations must be performed, reviewed, and recorded in accordance with Pace Analytical Services – Corporate SOP ENV-SOP-CORQ-0006, Manual Integration, or equivalent replacement.

10.2.3 Once the system software's integration parameters have been set, they cannot be adjusted unless the adjustments are being made during the processing/review of the initial calibration to optimize the system. After the initial calibration's processing and review is complete, the integration parameters must not be adjusted. Further adjustments to the integration parameters after the initial calibration requires prior approval from the Quality Manager and the Inorganics Manager (or their designees). If approved, then the adjustments need to be applied to the original curve. Then all QC/samples in the analytical

sequence need to be processed with both the updated calibration curve as well as the updated integration parameters.

10.3 EPIC Posting:

10.3.1 Aqueous Samples

- Aqueous samples have one step acodes.
- LIMSLINK is to be utilized for data review and posting to EPIC PRO.
- Post the sample values for each of the anions in mg/L and any applied dilution factor.

10.3.2 Soil/Solid Samples

- Soil/Solid samples have two step acodes.
- Post the actual extracted sample amount in g for the Initial Weight (default is 5 g) and the actual final volume in mL for the Final Volume (default is 50 mL). This information will be autoposted from the prep log in the “leachate soil template”.
- LIMSLINK is to be utilized for data review and posting to EPIC PRO.
- Post the sample value for each of the anions in mg/L and any applied dilution factor.

10.4 Calculations

See the Laboratory Quality Assurance Manual for equations for common calculations.

11.0 Quality Control and Method Performance

11.1 Quality Control

The following QC samples are prepared and analyzed with each batch of samples. Refer to Appendix B for acceptance criteria and required corrective action.

QC Item	Frequency
Method Blank (MB)	1 per batch of 20 or fewer samples. If batch exceeds, 20 samples, every 20.
Laboratory Control Sample (LCS)	1 per batch of 20 or fewer samples. If batch exceeds, 20 samples, every 20.
Matrix Spike (MS)	1 per batch of 10 or fewer samples. If batch exceeds, 10 samples, every 10.
Matrix Spike Duplicate (MSD) or Duplicate	1 per batch of 20 or fewer samples. If batch exceeds, 20 samples, every 20.

11.2 Instrument QC

The following Instrument QC checks are performed. Refer to Appendix B for acceptance criteria and required corrective action.

QC Item	Frequency
Initial Calibration (ICAL)	Quarterly or as needed
Initial Calibration Verification (ICV)	Immediately following ICAL
Continuing Calibration Verification High (CCVA)	Once per analytical run, at the beginning of the run
Reporting Limit Verification Standard/Low (CRDL/CCVB)	Once per analytical run, at the beginning of the run and not to exceed 24 hours
Continuing Calibration Verification (CCV)	After every 10 samples and at end of the sequence.
Continuing Calibration Blank (CCB)	Immediately following each CCV
RT Window (RTW)	Check with ICAL point 7 and with daily CCV

11.3 Method Performance

11.3.1 Method Validation

11.3.1.1 Detection Limits

Detection limits (DL) and limits of quantitation (LOQ) are established at initial method setup and verified on an on-going basis thereafter. Refer to Pace ENV corporate SOP ENV-SOP-CORQ-0011 Method Validation and Instrument Verification.

11.4 Analyst Qualifications and Training

Employees that perform any step of this procedure must have a completed Read and Acknowledgment Statement for this version of the SOP in their training record. In addition, prior to unsupervised (independent) work on any client sample, analysts that prepare or analyze samples must have successful initial demonstration of capability (IDOC) and must successfully demonstrate on-going proficiency on an annual basis. Successful means the initial and on-going DOC met criteria, documentation of the DOC is complete, and the DOC record is in the employee's training file. Refer to laboratory SOP ENV-SOP-LENE-0110, *Training Procedures*, for more information.

12.0 DATA REVIEW AND CORRECTIVE ACTION

12.1 Data Review

The data review process of Pace® Analytical Services includes a series of checks performed at different stages of the process by different people to ensure that SOPs were followed, the analytical record is complete, and properly documented, QC criteria were met, proper corrective actions were taken for QC failure and other nonconformance(s), and test results are reported with proper qualification, when necessary.

The review and checks that are performed by the employee performing the task is called primary review.

All data and test results are also peer reviewed.

This process, known as secondary review is performed to verify SOPs were followed, that calibration, instrument performance, and QC criteria were met and/or proper corrective actions were taken, qualitative ID and quantitative measurement is accurate, all manual integrations are

justified and documented, and approved in accordance with the Pace® Analytical Services SOP for manual integration, calculations are correct, the analytical record is complete and traceable, and that results are properly qualified.

Lastly, a third-level review, called a completeness check, is performed by reporting or project management staff to verify the test report is complete.

Refer to laboratory SOP ENV-SOP-LENE-0088 for specific instructions and requirements for each step of the data review process.

12.2 Corrective Action

Corrective action is required when QC or sample results are not within acceptance criteria.

Refer to Appendix B for a complete summary of QC, acceptance criteria, and recommended corrective actions for QC associated with this test method.

If corrective action is not taken or was not successful, the decision/outcome must be documented in the analytical record. The primary analyst has primary responsibility for taking corrective action when QA/QC criteria are not met. Secondary data reviewers must verify that appropriate action was taken and/or that results reported with QC failure are properly qualified.

Corrective action is also required when carryover is suspected and when results are over range.

Samples analyzed after a high concentration sample must be checked for carryover and reanalyzed if carryover is suspected. Carryover is usually indicated by low concentration detects of the analyte in successive samples analyzed after the high concentration sample.

Sample results at concentrations above the upper limit of quantitation must be diluted and reanalyzed. The result in the diluted samples should be within the upper half of the calibration range. Results less than the mid-range of the calibration indicate the sample was over diluted and analysis should be repeated with a lower level of dilution. If dilution is not performed, any result reported above the upper range is considered a qualitative measurement and must be qualified as an estimated value.

13.0 Pollution Prevention And Waste Management

Pace® proactively seeks ways to minimize waste generated during work processes. Some examples of pollution prevention include but are not limited to reduced solvent extraction, solvent capture, use of reusable cycletainers for solvent management, and real-time purchasing.

The EPA requires that laboratory waste management practices comply with all applicable federal and state laws and regulations. Excess reagents, samples, and method process wastes are characterized and disposed of in an acceptable manner in accordance with the Pace® Chemical Hygiene Plan / Safety Manual. Refer to this manual for these procedures.

14.0 Modifications

The procedures in this SOP have been modified from the reference test method as follows:

Modification	Test Method Procedure	Justification for Modification

LCR is equal to the top point of calibration curve.	Any sample above the calibration curve.	Any sample above the calibration is being diluted and equals doing an LCS every six months.

When applicable, comparability and/or equivalency studies necessary to validate the modification as required per corporate SOP ENV-SOP-CORQ-0011 are retained by local quality personnel for historical reference.

15.0 RESPONSIBILITIES

- All employees of Pace® Analytical Services that perform any part this procedure in their work activities must have a signed Read and Acknowledgement Statement (R&A) in their training file for the version(s) of the SOP that were in effect during the time the employee performed the activity.
- Local quality personnel are responsible for tracking the currency of the R&A on this SOP for employees at the locations they are assigned to and for notifying the General Manager (GM), however named, when R&A are overdue or outstanding. The GM and the employee's direct supervisor are responsible for ensuring the employee completes the R&A assignments as required.
- The supervisors and managers of Pace® Analytical Services, however named, are responsible for training employees on the procedures in this SOP, implementing the SOP in the work area, and monitoring on-going adherence to the SOP the work area(s) they oversee.
- All employees of Pace® Analytical Services are responsible for following the procedures in this SOP. Unauthorized deviations or departures from this SOP are not allowed except with documented approval from the local Quality Manager and only when those deviations do not violate the Pace® Code of Ethics or Professional Conduct (COR-POL-0004) or associated policy and procedure(s). Hand-edits or manual change to the SOP are not permitted. If a change is desired or necessary, Pace® employees must follow the procedures for document revision specified in corporate SOPs ENV-SOP-CORQ-0015 *Document Managemen*t and ENV-SOP-CORQ-0016 *SOP for Creation of SOP and SWI*.
- Local quality personnel are responsible for monitoring conformity to this SOP during routine internal audits of work areas that utilize this SOP and for communicating gaps and deviations found during monitoring to the work area supervisor, who is responsible for correction of the situation.

16.0 ATTACHMENTS

Attachment 1: Method Flow Diagram

Appendix B: QC summary

17.0 REFERENCES

- ENV-SOP-CORQ-0006, *Manual Integration*, current version.
- ENV-SOP-CORQ-0011, *Method Validation*, current version.
- ENV-SOP-CORQ-0015, *Document Management*, current version.

- ENV-SOP-CORQ-0016, *SOP for SOP and SWI,* current version.
- ENV-TMP-CORQ-0007, *Quality Manual Template*, current version.
- COR-POL-0004, *Code of Ethics and Professional Conduct*, current version.
- COR-MAN-001, *Pace® Safety Manua*l, current version.
- EPA Test Methods for Evaluating Solid Waste. SW-846, Third Edition, Final Update IV, Method 9056A, February 2007.
- EPA Methods for Chemical Analysis of Water and Wastes, Revision 2.1 August 1993, Method 300.0

18.0 REVISION HISTORY

Authorship

Primary Author[1]	Job Title	Date Complete
Lenzie Boring	Inorganics Manager	09/12/2022

[1]The primary author is the individual / role responsible for the content of this SOP. Send questions or suggestions for content to the primary author. See the Quality Manager for questions or concerns related to implementation of this SOP.

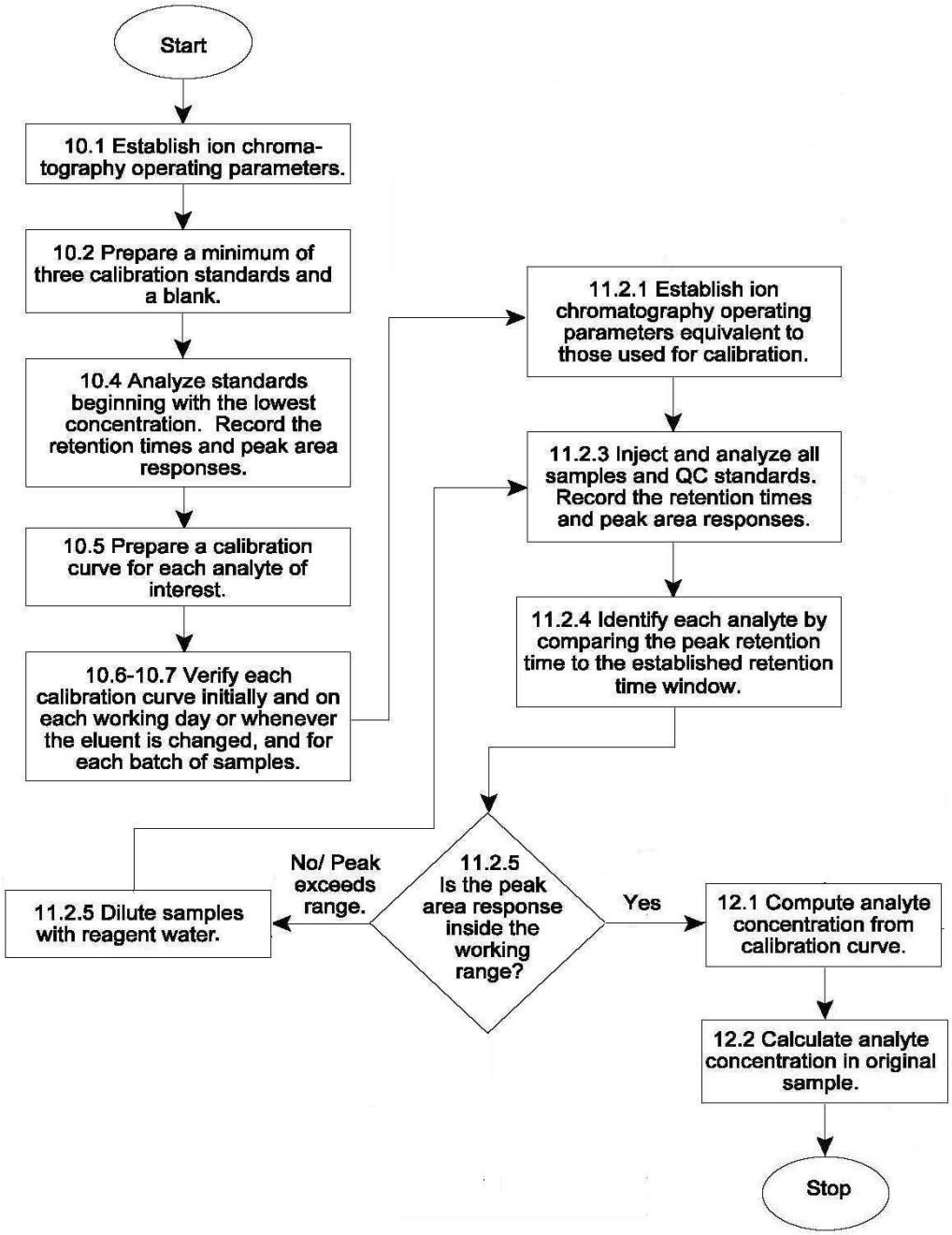
Revisions Made from Prior Version

Section	Description of Change
Various	Updated sections due to SOP template language changing
8.0 & 9.0	Added CAL 7 to SOP
8.0	Updated reagent to ISO 17034 certified

Document Succession: This version replaces the following documents:

Document Number & Version	Document Title	Effective Date:
ENV-SOP-LENE-0075 v0	Anions by Ion Chromatography	09/03/2019

Attachment 1: Method Flow Diagram



Appendix B: QC Summary

Calibration Acceptance and Verification Criteria

Calibration Metric	Parameter / Frequency	Criteria	Comments/Corrective Actions
Calibration Curve Fit	Linear Regression	r ≥ 0.995	If not met, remake standards and recalibrate. Instrument maintenance may be required if problem persists.
CCVA and CCVB Standards	If ICAL is not done on the day of analysis, then these check standards must be analyzed before the samples.	%Drift ±10 % RT ± 10% that of the ICAL 6 standard	Either standard may be reanalyzed once. A second failure confirms and requires corrective action (e.g. re-preparation and/or recalibration).
Initial Calibration Verification Standard (ICV)	Immediately after each initial calibration	%Drift ±10 %	May be reanalyzed once. A second failure confirms and requires re-preparation of standard and/or recalibration. If problem persists an alternative source standards may need to be obtained.
Initial Calibration Verification Blank (ICB)	Immediately after each Initial Calibration Verification Standard	Result should be less than the reporting limit or client QAPP. If results are reported to MDL, the ICB must be evaluated to the MDL.	May be reanalyzed once. A second failure confirms and requires corrective action (e.g. re-preparation of standard(s) and/or recalibration) **Exceptions:** If sample results are reported to MDL and ICB is <RL but >MDL, then corrective action is not necessary other than appropriately qualifying the sample results. Unless the customer's QAPP or technical specification instruct to do otherwise. Samples that are <RL may be reported without qualification. (Not applicable to samples reporting down to MDL) Samples >10x ICB may be reported with appropriate qualification.
Continuing Calibration Verification (CCV)	Immediately after the ICV, prior to the analysis of any samples. Also daily, after every 10 samples and at the end of a run.	%Drift ±10 %	May be reanalyzed once. A second failure confirms and requires corrective action (e.g. re-preparation and/or recalibration). **Exception:** If CCV fails high, then sample(s) that are <RL may be reported with appropriate qualification.
Continuing Calibration Blank (CCB)	Immediately after each Continuing Calibration Verification Standard	Result should be less than the reporting limit or client QAPP.	May be reanalyzed once. A second failure confirms and requires corrective action **Exceptions:** If sample results are reported to MDL and CCB is <RL but >MDL, then corrective action is not necessary other than appropriately qualifying

Calibration Metric	Parameter / Frequency	Criteria	Comments/Corrective Actions
		If results are reported to MDL, the ICB must be evaluated to the MDL.	the sample results. Unless the customer's QAPP or technical specification instruct to do otherwise. Samples that are <RL may be reported without qualification. (Not applicable to samples reporting down to MDL) Samples >10x CCB may be reported with appropriate qualification.

Batch Quality Control Criteria

QC Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Matrix-specific; reagent water or glass beads for soils.	One per batch of up to 20 samples	Result should be less than the reporting limit. If results are reported to MDL, the MB must be evaluated to the MDL.	Re-analyze blank to confirm failure. Qualify results and / or re-analyze associated samples. **Exceptions:** If sample ND, report sample without qualification. If sample result >10x MB report sample with appropriate qualifier indicating blank contamination. If sample result <10x MB and sample cannot be reanalyzed report sample with appropriate qualifier to indicate an estimated value. Client should be alerted of this condition. If sample results are reported to MDL and MB is <RL but >MDL, then corrective action is not necessary other than appropriately qualifying the sample results. Unless the customer's QAPP or technical specification instruct to do otherwise.
Laboratory Control Sample (LCS)	Matrix-specific; reagent water or glass beads for soils spiked with standard	One per batch of up to 20 samples	EPA 300.0: 90-110% EPA 9056A: 80-120%	Reanalyze the LCS to confirm failure Re-prep and reanalyze associated samples. If problem persists, check spike solution **Exceptions:** If LCS > QC limits and these compounds are non-detect in the associated samples, the sample data may be reported with appropriate data qualifiers. If LCS < QC limits and sample cannot be reanalyzed report sample with appropriate qualifier to indicate an estimated value. Client should be alerted to this condition.
Matrix Spike (MS)	Spike standard in client sample(s)	One per 10 samples or 10% per batch of up to 20 samples.	EPA 9056A: 80-120% EPA 300.0: 90-110%	1) No corrective actions necessary. If LCS recovery is in range, the system is considered valid and the out-of-control MS/MSDs are footnoted appropriately by the analyst.
Duplicate	MS Duplicate *OR (alternative)* Sample Dup	One per batch of up to 20 samples.	Max RPD: 15%	1) No corrective actions necessary. Report outliers with comment.

Document Information

Document Number: ENV-SOP-SAL1-0013 **Revision:** 03

Document Title: Inorganic Anions by Ion Chromatography

Department(s): Wet Chemistry

Date Information

Effective Date: 22 Jun 2021

Notes

Document Notes:

All Dates and Times are listed in: Central Time Zone

Signature Manifest

Document Number: ENV-SOP-SAL1-0013 **Revision:** 03

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All dates and times are in Central Time Zone.

ENV-SOP-SAL1-0013 Inorganic Anions by Ion Chromatography

QM Approval

Name/Signature	Title	Date	Meaning/Reason
Kenneth Busch (991414)	Manager - Quality	11 Jun 2021, 09:59:48 AM	Approved

Management Approval

Name/Signature	Title	Date	Meaning/Reason
Charles Girgin (002243)	General Manager 2	14 Jun 2021, 02:19:13 PM	Approved
Melissa Lundgrin (005033)	Supervisor	22 Jun 2021, 08:49:50 AM	Approved

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TEST METHOD STANDARD OPERATING PROCEDURE
TITLE: Inorganic Anions by Ion Chromatography
TEST METHOD EPA 300.0 and EPA 9056A
ISSUER: Pace ENV – Lenexa Quality – LENE

1.0 SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the laboratory procedure for the determination of Fluoride, Chloride, Nitrite, Nitrate, Bromide and Sulfate by Ion Chromatography.

1.1 Target Analyte List and Limits of Quantitation (LOQ)

The target analytes and the normal LOQ that can be achieved with this procedure are provided in Table 1, Appendix A.

LOQ are established in accordance with Pace policy and SOPs for method validation and for the determination of detection limits (DL) and quantitation limits (LOQ). DL and LOQ are routinely verified and updated when needed. The current LOQ for each target analyte that can be determined by this SOP as of the effective date of this SOP is provided in Table 1, Appendix A.

The reporting limit (RL) is the value to which analytes are reported as detected or not detected in the final report. When the RL is less than the lower limit of quantitation (LLOQ), all detects and non-detects at the RL are qualitative. The LLOQ is the lowest point of the calibration curve used for each target analyte.

DL, LOQ, and RL are always adjusted to account for actual amounts used and for dilution.

2.0 SUMMARY OF METHOD

2.1. A water sample is injected into a stream of carbonate-bicarbonate eluent and passed through a series of ion exchangers. The anions of interest are separated based on their relative affinities for a low capacity, strongly basic anion exchanger (guard and separator columns). The separated anions are directed onto a micro membrane suppressor. In the suppressor, the separated anions are converted to their highly conductive acid forms and the carbonate-bicarbonate eluent is converted to a weakly conductive carbonic acid. The separated anions are measured by conductivity. They are identified on the basis of retention time as compared to standards. Quantitation is by measurement of peak area compared to an external standard calibration curve. Nitrite and nitrate are calculated as nitrogen.

3.0 INTERFERENCES

3.1 Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large concentrations of one anion can interfere with the peak resolution of an adjacent anion. An initial conductivity reading is recommended prior to analysis, to determine adequate dilution factors. Sample dilution can be used to solve most interference problems.

3.2 Method interferences may be caused by contaminants in the deionized water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or to elevated baselines in ion chromatograms.

3.3 Any anion that is not retained by the column or only slightly retained will elute in the area of fluoride and interfere. Known co-elution is caused by carbonate, acetate, format, and other small organic anions.

3.4 The retention times of anions may differ when large amounts of acetate are present. Therefore, this method is not recommended for leachates of solid samples where acetate is used for pH adjustment.

3.5 Samples that contain particulate matter require filtration to prevent damage to instrument columns and flow systems.

4.0 DEFINITIONS

Refer to the Laboratory Quality Manual for a glossary of common lab terms and definitions.

5.0 HEALTH AND SAFETY

The toxicity or carcinogenicity of each chemical material used in the laboratory has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable.

The laboratory maintains documentation of hazard assessments and OSHA regulations regarding the safe handling of the chemicals specified in each method. Safety data sheets for all hazardous chemicals are available to all personnel. Employees must abide by the health, safety and environmental (HSE) policies and procedures specified in this SOP and in the Pace Chemical Hygiene / Safety Manual.

Personal protective equipment (PPE) such as safety glasses, gloves, and a laboratory coat must be worn in designated areas and while handling samples and chemical materials to protect against physical contact with samples that contain potentially hazardous chemicals and exposure to chemical materials used in the procedure.

Concentrated corrosives present additional hazards and are damaging to skin and mucus membranes. Use these acids in a fume hood whenever possible with additional PPE designed for handing these materials. If eye or skin contact occurs, flush with large volumes of water. When working with acids, always add acid to water to prevent violent reactions. Any processes that emit large volumes of solvents (evaporation/concentration processes) must be in a hood or apparatus that prevents employee exposure.

Contact your supervisor or local HSE coordinator with questions or concerns regarding safety protocol or safe handling procedures for this procedure.

6.0 SAMPLE COLLECTION, PRESERVATION, HOLDING TIME, AND STORAGE

Samples should be collected in accordance with a sampling plan and procedures appropriate to achieve the regulatory, scientific, and data quality objectives for the project.

The laboratory does not perform sample collection or field measurements for this test method. To assure sample collection and field checks and treatment are performed in accordance with applicable

regulations Pace project managers will inform the client of these requirements at the time of request for analytical services when the request for testing is received prior to sample collection. If samples were already collected, the laboratory will record any nonconformance to these requirements in the laboratory's sample receipt record when sufficient information about sample collection is provided with the samples.

The laboratory will provide containers for the collection of samples upon client request for analytical services. Bottle kits are prepared in accordance with laboratory SOP ENV-SOP-LENE-0025, *Assembly of Sample Container Kits.*

Requirements for container type, preservation, and field quality control (QC) for the common list of test methods offered by Pace are included in the laboratory's quality manual.

General Requirements

Matrix	Routine Container	Minimum Sample Amount[1]	Preservation	Holding Time
Aqueous	Plastic, 120 or 250 or 500 ml	5 ml	Thermal: ≤6ºC Chemical: None	28 days from collection for fluoride, chloride, bromide, and sulfate. 48 hours from collection for nitrate, and nitrite.

[1]*Minimum amount needed for each discrete analysis.*

Field / Matrix QC

Trip Blank	Equipment Blank	MS/MSD	Field Duplicate
NA	NA	1/20	1/20

Thermal preservation is checked and recorded on receipt in the laboratory in accordance with laboratory SOP ENV-SOP-LENE-0021, *Sample Management*. Chemical preservation is checked and recorded at time of receipt or prior to sample preparation.

After receipt, samples are stored at ≤6°C until sample preparation. Prepared samples (extracts, digestates, distillates, other) are stored at ≤6°C until sample analysis.

After analysis, unless otherwise specified in the analytical services contract, samples are retained for 30 days from date of final report and then disposed of in accordance with Federal, State, and Local regulations.

7.0 EQUIPMENT AND SUPPLIES

7.1 Equipment

Equipment	Vendor	Model / Version	Comments
Adjustable pipettor	Eppendorf	Various	
Analytical Balance	Mettler-Toledo	XS205	
Volumetric(s)	Fisher	various	

Autosampler	Dionex	AS-DV	
50 mL Graduated Cylinder	Fisher		Class A
Conductivity electrode	Fisher	09-327-1	
Conductivity meter	Fisher	09-328	Or equivalent
Data Acquisition Software	Dionex	Chromeleon® 6.80	
Detector	Dionex	CDM-II	Conductivity
Detector	Dionex	DS6 Heated Cell	Conductivity
Electrolytic pH Modifier	Dionex	063175	
Ion Chromatograph	Dionex	ICS-1600	
Suppressor	Dionex	AERS 500, 4mm	Or equivalent

7.2 Supplies

Item	Vendor	Model / ID	Catalog #	Description
Analytical Column	Dionex	Ion Pac AS14A	NC9314210	7 µm, 250 mm x 4 mm
Guard Column	Dionex	Ion Pac AG	056897	7µm, 50 mm x 4 mm
Volumetric Flasks		Various sizes		Class A
Sample Vials	Environmental Express	5 mL vials w/ filtering cap	K1250	
Centrifuge Tubes	Fisher	50 mL and 15 mL	22-170-199/ 22-170-194	

NOTE: All glassware must be rinsed several times with deionized water prior to use. It is recommended that the volumetric flasks be segregated from other use and filled with deionized water during storage.

8.0 Reagents And Standards

8.1 Reagents

Reagent	Concentration/ Description	Vendor/ Item #
Deionized water	ASTM Type II	ENV-SOP-SAL1-0027 (current revision)
Sodium carbonate (Na_2CO_3)	ACS Reagent grade	Fisher / S263-500
Sodium bicarbonate ($NaHCO_3$)	ACS Reagent grade	Fisher / S631-3
Hydrochloric acid (HCl)	ACS Reagent grade	Fisher / A508-212
Intermediate Reagent: Eluent Stock	Dissolve 8.4g sodium bicarbonate and 84.8g sodium carbonate into a 1-L volumetric flask containing approximately 600 mL deionized	

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ISSUER: Pace ENV – Lenexa Quality – LENE

	water. Dilute to the mark and invert several times to mix. Prepare as needed or every 6 months.	
Working Eluent	Add 20 mL of Concentrated Eluent into a 2-L volumetric flask. Dilute to the mark with deionized water and invert several times to mix. Prepare as needed.	

8.2 Standard Storage Conditions

Standard Type	Description	Expiration	Storage
Stock Solutions	▪ Concentrated reference solution purchased directly from approved vendor	▪ Manufacturer's recommended expiration date	▪ Manufacturer's recommended storage conditions
Working Standard Solutions	▪ Reference solutions prepared by dilutions of the stock solution	▪ One week from preparation or the expiration date listed for the stock source, whichever is sooner	

8.3 Stock Standards

Standard	Concentration	Vendor / Item #
Primary Stock Standard	25 mg/L: , Nitrate-N, Nitrite-N 50 mg/L: Fluoride 100 mg/L: Bromide, Sulfate, Chloride,	Inorganic Ventures / PACEKS-2016
Secondary Stock Standard	250 mg/L: Bromide, Chloride, Sulfate 125mg/L: Fluoride 100 mg/L: Nitrate-N, Nitrite-N	SPEX / VPCLKS-6-250
MDL Spike Solution	100 mg/L Bromide, Chloride, Sulfate 20 mg/L Fluoride 10 mg/L Nitrate-N, Nitrite-N	SPEX/VPCLKS-5-250

8.4 Preparation of Calibration, High, Low and CCV Standards

Standard	Stock Standard	Standard Amount	Solvent	Final Total Volume
CAL0	N/A	0	DI Water	50mL
CAL1	Primary	1 mL	DI Water	500mL
CAL2	Primary	2 mL	DI Water	500mL
CAL3	Primary	5 mL	DI Water	500mL
CAL4/Low check	Primary	5 mL	DI Water	100mL

CAL5/CCV	Primary	5.00mL	DI Water	50mL
CAL6	Primary	10.0mL	DI Water	50mL
High check	Primary	15.0mL	DI Water	100mL

8.5 ICV Concentrations

Anion	Stock Concentration (mg/L)	Final Concentration (mg/L)
Fluoride (F)	125.0	2.5
Chloride (Cl)	250.0	5.0
Nitrite-N (NO_2-N)	100.0	2.0
Bromide (Br)	250.0	5.0
Nitrate-N (NO_3-N)	100.0	2.0
Sulfate (SO_4)	250.0	5.0

8.6 Low Check Standard Concentrations

Anion	Stock Concentration (mg/L)	Final Concentration (mg/L)
Fluoride (F)	50.0	2.5
Chloride (Cl)	100.0	5.0
Nitrite-N (NO_2-N)	25.0	1.25
Bromide (Br)	100.0	5.0
Nitrate-N (NO_3-N)	25.0	1.25
Sulfate (SO_4)	100.0	5.0

8.7 High Check Standard Concentrations

Anion	Stock Concentration (mg/L)	Final Concentration (mg/L)
Fluoride (F)	50.0	7.5
Chloride (Cl)	100.0	15
Nitrite-N (NO_2-N)	25.0	3.75
Bromide (Br)	100.0	15
Nitrate-N (NO_3-N)	25.0	3.75
Sulfate (SO_4)	100.0	15

8.8 CCV Concentrations

Anion	Stock Concentration (mg/L)	Final Concentration (mg/L)
Fluoride (F)	50.0	5
Chloride (Cl)	100.0	10
Nitrite-N (NO_2-N)	25.0	2.5
Bromide (Br)	100.0	10
Nitrate-N (NO_3-N)	25.0	2.5
Sulfate (SO_4)	100.0	10

9.0 PROCEDURE

9.1 Equipment Preparation

9.1.1 Support Equipment

9.1.2 Instrument

9.1.2.1 Routine Instrument Operating Conditions

9.1.2.1.1 Allow the instrument to stabilize for a minimum of 30 minutes. Analyze calibration standards 0-6 followed by the ICV, ICB, CCV and ICB. Process the CAL6 standard and optimize the integration parameters and retention times. Once the integration parameters and retention times are set, reprocess the entire curve and save.

9.1.2.1.2 Once the system software's integration parameters (including retention times) have been optimized and saved, they are not to be adjusted unless the following procedure is completed. Further adjustments to the integration parameters must be approved by the Quality Manager and the Inorganics Manager (or their designees). If approved, the adjustments need to be applied to the original curve and all analytical sequences to which they apply. This includes all QC/samples. The revised curve and all QC data must be evaluated and reviewed

9.2 Initial Calibration

9.2.1 Calibration Design

Linear Regression – The linear regression calibration curve is derived from a least squares regression analysis of the calibration points. A calibration curve based on this technique will have the format of y = ax + b where "a" is the slope of the line and "b" is the y-intercept. The linear regression is not forced through the origin; therefore, there is a possibility that very low levels of contaminants below the response of the lowest calibration point may generate erroneous reportable results. A calculation of the correlation coefficient "r" is used to determine the acceptability of a linear regressed curve.

An initial calibration curve using a minimum of five levels and a blank is analyzed prior to the analysis of any client samples. The lowest concentration standard of the initial

calibration curve must be at or below the reporting limit, a level below which all reported results must be qualified as estimated values.

9.2.2 Calibration Sequence

Anion	S0	S1	S2	S3	S4	S5	S6	Stock
Fluoride (F)	0	0.1	0.2	0.5	2.5	5	10	50
Chloride (Cl)	0	—	0.4	1.0	5.0	10	20	100
Nitrite-N (NO_2-N)	0	-	0.1	0.25	1.25	2.5	5	25
Bromide (Br)	0	—	0.4	1.0	5.0	10	20	100
Nitrate-N (NO_3-N)	0	-	0.1	0.25	1.25	2.5	5	25
Sulfate (SO_4)	0	—	0.4	1.0	5.0	10	20	100

9.2.3 ICAL Evaluation

9.2.3.1 Curve Fit

The correlation coefficient must be >0.995. If the curve passes, print the data and continue with the run. If the curve fails, determine the problem and recalibrate.

9.2.3.2 Relative Standard Error (RSE)

Initial calibrations using linear regression must be evaluated for their relative error using the following equation:

$$\% \text{ Relative Error} = \frac{\text{Calculated Value} - \text{True Value}}{\text{True Value}} \times 100$$

9.2.3.3 The procedure used is to quantitate calibration standards against the curve. All except the low standard must recover within 90-110% and the low-level stand must recover at 50-150%.

9.2.3.4 Initial Calibration Verification

In addition to meeting the linearity criteria, any new calibration curve must be assessed for accuracy in the values generated. Accuracy is a function of both the "fit" of the curve to the points used and the accuracy of the standards used to generate the calibration points. By meeting the fit criteria, the accuracy relative to the goodness of fit is addressed. However, because all calibration points are from the same source, it is possible that the calibration points may meet linearity criteria, but not be accurately made in terms of their true value.

Therefore, to assess the accuracy relative to the purity of the standards, a single standard from a secondary source must be analyzed and the results obtained must be assessed relative to the known true value. This step is referred to as Secondary Source Verification or, alternatively as Initial Calibration Verification. This secondary source must be from an alternative vendor or, in the event an alternative vendor is not available, from a different lot from the same vendor. The accuracy of the standard is assessed as a percent difference from the true value according to the following equation:

$$\%\text{Drift} = \frac{\left(\text{Result}_{ICV} - \text{True Value}_{ICV}\right)}{\text{True Value}_{ICV}} \times 100$$

9.2.4 Continuing Calibration Verification

As part of the analytical process, the instrumentation must be checked periodically to determine if the response has changed significantly since the initial calibration was established. This verification process is known as Continuing Calibration Verification (CCV). The validity of the initial calibration is checked after every ten samples and at the end of the analytical sequence by analyzing a midpoint calibration standard. The accuracy of the standard is assessed as a percent difference from the true value according to the following equation:

$$\%\text{Drift} = \frac{\left(\text{Result}_{CCV} - \text{True Value}_{CCV}\right)}{\text{True Value}_{CCV}} \times 100$$

9.3 Sample Preparation

9.3.1 Homogenization and Subsampling

Refer to the SOP ENV-SOP-LENE-0135, Sample Homogenization and Sub-Sampling.

9.4 Analysis

9.4.1 Example Analytical Sequence Beginning with an Initial Calibration

Injection	Name
1	CAL0
2	CAL1
3	CAL2
4	CAL3
5	CAL4
6	CAL5
7	CAL6
8	ICV
9	ICB
10	CCV
11	CCB
12	MB
13	LCS
14	Sample A
15	Sample B
16	Sample B MS
17	Sample B MSD
18	Sample C

Injection	Name
19	Sample D
20	Sample E
21	Sample E MS
22	CCV
23	CCB

9.4.2 Example Sequence NOT Beginning with Initial Calibration

Injection	Name
1	CCVA (High Check)
2	CCVB (Low Check)
3	CCB
4	MB
5	LCS
6	Sample A
7	Sample A MS
8	Sample A MSD
9	Sample B
10	Sample C
11	Sample D
12	Sample D MS
13	Sample D MSD
14	CCV
15	CCB

10.0 DATA ANALYSIS AND CALCULATIONS

10.1 Qualitative Identification

10.1.1 Manual Integration

Manual changes to automated integration is called manual integration. Manual integration is sometimes necessary to correct inaccurate automated integrations but must never be used to meet QC criteria or to substitute for proper instrument maintenance and/or method set-up. To assure that all manual integrations are performed consistently and are ethically justified, all manual integrations must be performed, reviewed, and recorded in accordance with corporate SOP ENV-SOP-CORQ-0006, *Manual Integration.*

10.2 Quantitative Identification

The curve is used to quantitate the concentration of an unknown based on its response and this known relationship.

10.3 Calculations

See the Laboratory Quality Assurance Manual for equations for common calculations.

11.0 QUALITY CONTROL AND METHOD PERFORMANCE

11.1 Quality Control

The following QC samples are prepared and analyzed with each batch of samples. Refer to Appendix B for acceptance criteria and required corrective action.

QC Item	Frequency
Method Blank (MB)	1 per batch of 20 or fewer samples. If batch exceeds, 20 samples, every 20.
Laboratory Control Sample (LCS)	1 per batch of 20 or fewer samples. If batch exceeds, 20 samples, every 20.
Matrix Spike (MS)	2per batch of 20 or fewer samples. If batch exceeds, 20 samples, every 20
Matrix Spike Duplicate (MSD)	2 per batch of 20 or fewer samples. If batch exceeds, 20 samples, every 20

11.2 Instrument QC

The following Instrument QC checks are performed. Refer to Appendix B for acceptance criteria and required corrective action.

QC Item	Frequency
Initial Calibration	As needed
Initial Calibration Verification (ICV)	Immediately following an Initial Calibration
Initial Calibration Blank (ICB)	Immediately following the ICV
Continuing Calibration Verification (CCV)	Immediately after the ICB, prior to the analysis of any samples. Also, daily, after every 10 samples and at the end of a run.
Continuing Calibration Blank (CCB)	Immediately after each Continuing Calibration Verification Standard

11.3 Method Performance

11.3.1 Method Validation

11.3.1.1 Detection Limits

Detection limits (DL) and limits of quantitation (LOQ) are established at initial method setup and verified on an on-going basis thereafter. Refer to Pace ENV corporate SOP ENV-SOP-CORQ-0011 Method Validation and Instrument Verification.

11.4 Analyst Qualifications and Training

Employees that perform any step of this procedure must have a completed Read and Acknowledgment Statement for this version of the SOP in their training record. In addition, prior to unsupervised (independent) work on any client sample, analysts that prepare or analyze samples must have successful initial demonstration of capability (IDOC) and must successfully demonstrate on-going proficiency on an annual basis. Successful means the initial and on-going DOC met criteria, documentation of the DOC is complete, and the DOC record is in the employee's training file. Refer to laboratory SOP ENV-SOP-LENE-0110, *Training Procedures*, for more information.

12.0 Data Review And Corrective Action

12.1 Data Review

Pace's data review process includes a series of checks performed at different stages of the analytical process by different people to ensure that SOPs were followed, the analytical record is complete and properly documented, proper corrective actions were taken for QC failure and other nonconformance(s), and that test results are reported with proper qualification.

The review steps and checks that occur as employee's complete tasks and review their own work is called primary review.

All data and results are also reviewed by an experienced peer or supervisor. Secondary review is performed to verify SOPs were followed, that calibration, instrument performance, and QC criteria were met and/or proper corrective actions were taken, qualitative ID and quantitative measurement is accurate, all manual integrations are justified and documented in accordance with the Pace ENV's SOP for manual integration, calculations are correct, the analytical record is complete and traceable, and that results are properly qualified.

A third-level review, called a completeness check, is performed by reporting or project management staff to verify the data report is not missing information and project specifications were met.

Refer to laboratory SOP ENV-SOP-LENE-088, *Data Reduction, Review and Reporting*, for specific instructions and requirements for each step of the data review process.

12.2 Corrective Action

Corrective action is expected any time QC or sample results are not within acceptance criteria. If corrective action is not taken or was not successful, the decision/outcome must be documented in the analytical record. The primary analyst has primary responsibility for taking corrective action when QA/QC criteria are not met. Secondary data reviewers must verify that appropriate action was taken and/or that results reported with QC failure are properly qualified.

Corrective action is also required when carryover is suspected and when results are over range.

Samples analyzed after a high concentration sample must be checked for carryover and reanalyzed if carryover is suspected. Carryover is usually indicated by low concentration detects of the analyte in successive samples analyzed after the high concentration sample.

Sample results at concentrations above the upper limit of quantitation must be diluted and reanalyzed. The result in the diluted samples should be within the upper half of the calibration range. Results less than the mid-range of the calibration indicate the sample was over diluted and analysis should be repeated with a lower level of dilution. If dilution is not performed, any result reported above the upper range is considered a qualitative measurement and must be qualified as an estimated value.

Refer to Appendix B for a complete summary of QC, acceptance criteria, and recommended corrective actions for QC associated with this test method.

13.0 POLLUTION PREVENTION AND WASTE MANAGEMENT

Pace proactively seeks ways to minimize waste generated during our work processes. Some examples of pollution prevention include but are not limited to: reduced solvent extraction, solvent capture, use of reusable cycletainers for solvent management, and real-time purchasing.

The EPA requires all laboratory waste management practice to be conducted consistent with all applicable federal and state laws and regulations. Excess reagents, samples and method process wastes must be characterized and disposed of in an acceptable manner in accordance with Pace's Chemical Hygiene Plan / Safety Manual.

14.0 MODIFICATIONS

A modification is a change to a reference test method made by the laboratory. For example, changes in stoichiometry, technology, quantitation ions, reagent or solvent volumes, reducing digestion or extraction times, instrument runtimes, etc. are all examples of modifications. Refer to Pace ENV corporate SOP ENV-SOP-CORQ-0011 *Method Validation and Instrument Verification* for the conditions under which the procedures in test method SOPs may be modified and for the procedure and document requirements.

15.0 RESPONSIBILITIES

Pace ENV employees that perform any part this procedure in their work activities must have a signed Read and Acknowledgement Statement in their training file for this version of the SOP. The employee is responsible for following the procedures in this SOP and handling temporary departures from this SOP in accordance with Pace's policy for temporary departure.

Pace supervisors/managers are responsible for training employees on the procedures in this SOP and monitoring the implementation of this SOP in their work area.

16.0 ATTACHMENTS

Attachment 1: Method Flow Diagram

17.0 REFERENCES

17.1 Pace Quality Assurance Manual- most current version.

17.2 National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, "Quality Systems"- most current version.

17.3 The NELAC Institute (TNI); Volume 1, Module 2, "Quality Systems"- most current version.

17.4 EPA Test Methods for Evaluating Solid Waste. SW-846, Third Edition, Final Update IV, Method 9056A, February 2007.

17.5 EPA Methods for Chemical Analysis of Water and Wastes, Revision 2.1 August 1993, Method 300.0

18.0 REVISION HISTORY

This Version:

Section	Description of Change
All	This is and SOP reformat

This document supersedes the following document(s):

Document Number	Title	Version
ENV-SOP-SAL1-0013	Inorganic Anions by Ion Chromatography	02

Pace Analytical®

TEST METHOD STANDARD OPERATING PROCEDURE
TITLE: Inorganic Anions by Ion Chromatography
TEST METHOD EPA 300.0 and EPA 9056A
ISSUER: Pace ENV – Lenexa Quality – LENE

Appendix A: Target Analyte List and Routine LOQ

Table 1: Routine Analyte List and Limits of Quantitation (LOQ)[1]

Analyte	Aqueous (mg/L)
Fluoride (F)	0.1
Chloride (Cl)	1.0
Nitrite-N (NO_2-N)	0.1
Bromide (Br)	0.5
Nitrate-N (NO_3-N)	0.1
Sulfate (SO_4)	1.0

[1] *Values in place as of effective date of this SOP. LOQ are subject to change. For the most up to date LOQ, refer to the LIMS or contact the laboratory.*

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Appendix B: QC Summary

QC Item	Frequency	Acceptance Criteria	Corrective Action	Qualification
ICAL	At instrument set up, after CCV failure	Must meet one of curve fit options presented in Section 9.0. For any curve fit other than Average RF (RSD), curve must also pass RSE test at the low and midpoint calibration standard.	Identify and correct source of problem, repeat	None. Do not proceed with analysis
ICV	After Each ICAL	All analytes must be within ± 10% of the true value. (%R)	Identify source of problem, re-analyze. If repeat failure, repeat ICAL. Analysis may proceed if it can be demonstrated that the ICV exceedance has no impact on analytical measurements. For example, the ICV %R is high, CCV is within criteria, and the analyte is not detected in sample(s).	Qualify analytes with ICV out of criteria.
RT Window Study	At method set-up and after major instrument maintenance	Window is ±10% of the absolute retention time of the Ccalib6	NA	NA
CCV	Daily, before sample analysis, after every 10, and at end of analytical window.	Opening CCV: All analytes within ± 10 %D Ending CCV: All analytes within ± 10 %D RT ± 10% that of the ICAL 6 standard	See Section 12 for required corrective actions based on circumstance.	Qualify analytes with CCV out of criteria.
Method Blank	1 per batch of 20 or fewer samples. If batch exceeds, 20 samples, every 20	Result should be less than the reporting limit. If results are reported to MDL, the MB must be evaluated to the MDL.	1) Re-analyze blank to confirm failure. 2) Qualify results and / or re-analyze associated samples.	1) If sample ND, report sample without qualification. 2) If sample result >10x MB report sample with appropriate qualifier indicating blank contamination. 3) If sample result <10x MB and sample cannot be reanalyzed report sample with appropriate qualifier to indicate an estimated value.

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				Client should be alerted of this condition. 4) If sample results are reported to MDL and MB is <RL but >MDL, then corrective action is not necessary other than appropriately qualifying the sample results. Unless the customer's QAPP or technical specification instruct to do otherwise.
LCS	1 per batch of 20 or fewer samples. If batch exceeds, 20 samples, every 20	EPA 300.0: 90-110% EPA 9056A: 80-120%	1) Reanalyze the LCS to confirm failure 2) Re-prep and reanalyze associated samples. 3) If problem persists, check spike solution	1) If LCS > QC limits and these compounds are non-detect in the associated samples, the sample data may be reported with appropriate data qualifiers. 2) If LCS < QC limits and sample cannot be reanalyzed report sample with appropriate qualifier to indicate an estimated value. Client should be alerted to this condition.
MS/MSD	2 per batch of 20 or fewer samples. If batch exceeds, 20 samples, every 20	EPA 9056A: 80-120% EPA 300.0: 80-120%	1) No corrective actions necessary. If LCS recovery is in range, the system is considered valid and the out-of-control MS/MSDs are footnoted appropriately by the analyst.	
Sample Duplicate	1 per batch of 20 or fewer samples if no MSD. If batch exceeds, 20 samples, every 20	Max RPD: 15%	1) No corrective actions necessary. Report outliers with comment.	
LLCCV		%Drift ±10 % RT ± 10% that of the ICAL 6 standard	Either standard may be reanalyzed once. A second failure confirms and requires corrective action (e.g. re-preparation and/or recalibration).	

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ICB	Immediately after each Initial Calibration Verification Standard	Result should be less than the reporting limit or client QAPP. If results are reported to MDL, the ICB must be evaluated to the MDL.	May be reanalyzed once. A second failure confirms and requires corrective action (e.g. re-preparation of standard(s) and/or recalibration)	If sample results are reported to MDL and ICB is <RL but >MDL, then corrective action is not necessary other than appropriately qualifying the sample results. Unless the customer's QAPP or technical specification instruct to do otherwise. Samples that are <RL may be reported without qualification. (Not applicable to samples reporting down to MDL) Samples >10x ICB may be reported with appropriate qualification.
CCB	Immediately after each Continuing Calibration Verification Standard	Result should be less than the reporting limit or client QAPP. If results are reported to MDL, the ICB must be evaluated to the MDL.	May be reanalyzed once. A second failure confirms and requires corrective action	If sample results are reported to MDL and CCB is <RL but >MDL, then corrective action is not necessary other than appropriately qualifying the sample results. Unless the customer's QAPP or technical specification instruct to do otherwise. Samples that are <RL may be reported without qualification. (Not applicable to samples reporting down to MDL) Samples >10x CCB may be reported with appropriate qualification.

Document Information

Document Number: ENV-SOP-LENE-0014 **Revision:** 04

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All Dates and Times are listed in: Central Time Zone

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ENV-SOP-LENE-0014 - Alkalinity by Automation by SM2320B

QM Approval

Name/Signature	Title	Date	Meaning/Reason
Kenneth Busch (991414)	Manager - Quality	07 Apr 2021, 11:37:11 AM	Approved

Management Approval

Name/Signature	Title	Date	Meaning/Reason
Kenneth Busch (991414)	Manager - Quality	07 Apr 2021, 11:37:22 AM	Approved
Charles Girgin (002243)	General Manager 2	07 Apr 2021, 12:58:55 PM	Approved
Joshua Cunningham (003261)	Manager	20 Apr 2021, 12:27:16 PM	Approved

1.0 SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the laboratory procedure for the determination of Alkalinity by an automated Titration.

1.1 Target Analyte List and Limits of Quantitation (LOQ)

The target analytes and the normal LOQ that can be achieved with this procedure are 20 mg/L for water and 200 mg/kg for solid alkalinity samples.

LOQ are established in accordance with Pace policy and SOPs for method validation and for the determination of detection limits (DL) and quantitation limits (LOQ). DL and LOQ are routinely verified and updated when needed. The current LOQ for each target analyte that can be determined by this SOP as of the effective date of this SOP is provided in Table 1, Appendix A.

The reporting limit (RL) is the value to which analytes are reported as detected or not detected in the final report. When the RL is less than the lower limit of quantitation (LLOQ), all detects and non-detects at the RL are qualitative. The LLOQ is the lowest point of the calibration curve used for each target analyte.

DL, LOQ, and RL are always adjusted to account for actual amounts used and for dilution.

2.0 SUMMARY OF METHOD

An unpreserved sample is titrated with a standardized sulfuric acid solution to an endpoint that is determined electrometrically. The endpoint for total alkalinity is pH 4.5, with extrapolation to pH 4.2 if alkalinity is low. The endpoint for phenolphthalein alkalinity is pH 8.3. The results obtained from the phenolphthalein and total alkalinity determinations offer a means for classification of bicarbonate, carbonate, hydroxide, and total alkalinity.

This method is applicable to most water and solid samples, regardless of moisture content. Common matrices are ground and surface water, wastewater, aqueous sludge, sediment, soils, and other solid samples.

The method is not applicable for alkalinity in samples that contain a significant amount of oils, greases, and petroleum products.

3.0 INTERFERENCES

3.1 Substances, such as salts of weak organic and inorganic acids present in large amounts, may cause interference in the electrometric pH measurements.

3.2 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.

4.0 DEFINITIONS

Refer to the Laboratory Quality Manual for a glossary of common lab terms and definitions.

5.0 HEALTH AND SAFETY

The toxicity or carcinogenicity of each chemical material used in the laboratory has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable.

The laboratory maintains documentation of hazard assessments and OSHA regulations regarding the safe handling of the chemicals specified in each method. Safety data sheets for all hazardous chemicals are available to all personnel. Employees must abide by the health, safety and environmental (HSE) policies and procedures specified in this SOP and in the Pace Chemical Hygiene / Safety Manual.

Personal protective equipment (PPE) such as safety glasses, gloves, and a laboratory coat must be worn in designated areas and while handling samples and chemical materials to protect against physical contact with samples that contain potentially hazardous chemicals and exposure to chemical materials used in the procedure.

Concentrated corrosives present additional hazards and are damaging to skin and mucus membranes. Use these acids in a fume hood whenever possible with additional PPE designed for handing these materials. If eye or skin contact occurs, flush with large volumes of water. When working with acids, always add acid to water to prevent violent reactions. Any processes that emit large volumes of solvents (evaporation/concentration processes) must be in a hood or apparatus that prevents employee exposure.

Contact your supervisor or local HSE coordinator with questions or concerns regarding safety protocol or safe handling procedures for this procedure.

6.0 SAMPLE COLLECTION, PRESERVATION, HOLDING TIME, AND STORAGE

Samples should be collected in accordance with a sampling plan and procedures appropriate to achieve the regulatory, scientific, and data quality objectives for the project.

The laboratory does not perform sample collection or field measurements for this test method. To assure sample collection and field checks and treatment are performed in accordance with applicable regulations Pace project managers will inform the client of these requirements at the time of request for analytical services when the request for testing is received prior to sample collection. If samples were already collected, the laboratory will record any nonconformance to these requirements in the laboratory's sample receipt record when sufficient information about sample collection is provided with the samples.

The laboratory will provide containers for the collection of samples upon client request for analytical services. Bottle kits are prepared in accordance with laboratory SOP ENV-SOP-LENE-0025, *Assembly of Sample Container Kits*. For this test method, immediately after sample collection, samples should be checked for X and X and field treated. The bottle kits provided by the laboratory should include field test kits and treatment reagent.

Requirements for container type, preservation, and field quality control (QC) for the common list of test methods offered by Pace are included in the laboratory's quality manual.

General Requirements

Matrix	Routine Container	Minimum Sample Amount[1]	Preservation	Holding Time
Aqueous	Plastic or Glass 1L	60mL	Thermal: ≤6°C, but not freezing Chemical: None	14 days
Solid	4oz glass jar	10g	Thermal: ≤6°C, but not freezing Chemical: None:	14 days

[1]*Minimum amount needed for each discrete analysis.*

Field / Matrix QC

Trip Blank	Equipment Blank	MS/MSD	Field Duplicate
NA	NA	1 per 20	Per client request

Thermal preservation is checked and recorded on receipt in the laboratory in accordance with laboratory SOP ENV-SOP-LENE-0021, *Sample Management*. Chemical preservation is checked and recorded at time of receipt or prior to sample preparation.

After receipt, samples are stored at ≤6°C until sample preparation. Prepared samples (extracts, digestates, distillates, other) are stored at ≤6°C until sample analysis.

After analysis, unless otherwise specified in the analytical services contract, samples are retained for 30 days from date of final report and then disposed of in accordance with Federal, State, and Local regulations.

7.0 EQUIPMENT AND SUPPLIES

7.1 Equipment and Supplies

Table 7.1 – Equipment and Supplies

Supply	Vendor	Model / Version	Comments
Autosampler	Mantech	PC-1000-681	AutoMax73 Beaker Sampler
Rinse Pump	Mantech	PC-1000-475	
Titration Module	Mantech	PC-1040-00	QC-Titrate™
Analytical balance	Mettler-Toledo	AE200	or equivalent capable of weighing
Volumetric Flasks	Various	Class A	2-L, 1-L, and 500-mL.
Graduated cylinder	Fisher	08-561A	50-mL, Class A, TD

8.0 REAGENTS AND STANDARDS

8.1 Reagents and Standards

Table 8.1 – Standard Storage Conditions

Standard Type	Description	Expiration	Storage
Stock Solutions	▪ Concentrated reference solution purchased directly from approved vendor	▪ Manufacturer's recommended expiration date	▪ Manufacturer's recommended storage conditions
Working Standard Solutions	▪ Reference solutions prepared by dilutions of the stock solution	▪ Working Alkalinity standards are stored for no more than a week.	▪ Ambient temperature or manufacturer's recommended storage conditions for stock source solution.

Table 8.2 – Reagents and Standards

Reagent/Standard	Concentration/ Description	Vendor/ Item #
Reagent water	ASTM Type II	SOP S-KS-Q-011
Sodium carbonate, anhydrous	ACS reagent grade	Fisher / S263
Ampulated Alkalinity Standard	25,000 mg/L	Fisher / NC9308291
Sulfuric acid, concentrated	Fisher TraceMetal grade	Fisher / A510
Buffer Solution, pH 4.00	Color-coded Red	Fisher / SB-101
Buffer Solution, pH 7.00	Color-coded Yellow	Fisher / SB-107
Buffer Solution, pH 10.00	Color-coded Blue	Fisher / SB-115
0.02N Sulfuric acid	0.02N Sulfuric acid	Fisher/AA35649K7

8.2 H_2SO_4 (1.0N): Measure 28 mL concentrated H_2SO_4 into a 1-L volumetric flask containing approximately 700 mL of reagent water, dilute to the mark and invert several times to mix.

8.3 H_2SO_4 (0.02N): Measure 40 mL of the 1.0 N H_2SO_4 solution into a 2-L volumetric flask containing approximately 1500 mL of reagent water, dilute to the mark and invert several times to mix. Depending on concentration of sample alkalinity, higher concentration of titrant may be necessary.

8.4 ICV/LCS Solution: Add the contents of one Alkalinity Standard ampoule to a 500mL volumetric flask containing approximately 350mL of reagent water, dilute to the mark and invert several times to mix. This will yield a concentration of 500 mg/L. Do not store for more than one week. (Alternatively, the contents of two Alkalinity Standard ampoules can be diluted to a final volume of 1000mL using a 1-L volumetric flask if additional available volume is needed.)

8.5 CCV: Dry approximately 1 g of sodium carbonate at 180ºC for 4 hours in an oven and cool in a desiccator. Weigh out 0.5 g (to the nearest mg) of the dried sodium carbonate, Na_2CO_3, and place into a 1-L volumetric flask containing approximately 500 mL of reagent water, invert several times to dissolve and dilute to the mark with reagent water. Do not store for more than a week.

9.0 PROCEDURE

9.1 Sample Analysis Set-up

9.1.1 Return to the Main Menu. Select the “prism: button, then “OK”. Select load template. Enter the sample ID’s using the following convention: 60121234001_x1.

9.1.2 The x1 denotes the dilution based on 30 mL of sample.

9.1.3 Save the template using today’s date. Click the “start” button to begin the run. NEVER use the “STOP” button. It will erase all run data.

9.1.4 To add samples or dilutions to the run, select “Priority” and add at the end of the sample list.

9.1.5 The data file will be saved automatically to the G: drive on the network. When the run is complete a dialog box will appear. The raw data will print when exiting this dialog box.

9.2 Reporting Data

9.2.1 Use Limslink create a runlog. Include the LCS, CCV,ICV, titrant and pH ID’s on the runlog. The runlog should match the dilutions on the raw data. Also indicate on the runlog if any data is not being reported. Save the runlog to G:/WET/RUNLOGS/ALK/. Print the runlog and include with the raw data.

9.2.2 Import data to EPIC Pro. Submit the data for peer review.

9.3 Calibration

9.3.1 Calibration must be performed daily prior to sample analysis or Titrant Standardization.

9.3.2 Load freshly poured, 30-mL aliquots of the 4.0, 7.0, and 10.0 pH buffers into autosampler positions one through three, respectively. Fill the titrant bottle and the rinse bottle as needed. Verify that the waste bottle is empty. pH Buffers should be replaced daily.

9.3.3 Verify that the power is active to all QC-Titrate components. Click on the QC-Titrate icon. This will bring you to the main menu. Select the pH cal button. Click start. The unit will calibrate and print a report automatically. Record the pH buffer ID’s on the calibration report or add to the run log.

9.3.4 Calibration Criteria

	Minimum	Maximum
Slope	-65	-53
Intercept	-100	100
Correlation Coeff.	0.990	1.00

9.4 Standardization of the Alkalinity Titrant (if needed)

9.4.1 Standardize the titrant each time a new batch is prepared, if purchased 0.02N sulfuric acid is not used. Section 11.2 is not needed when purchased 0.02N sulfuric is used.

9.4.2 Quantitatively measure two 30-mL aliquots of the Normality check solution (ICV/LCS) into separate cups.

9.4.3 At the Main Menu. Select the “prism: button, then “OK”. Select load template. Load the ALK NORM CHECK. Autotitrate the two aliquots with the (0.02 N) H_2SO_4 solution to pH 4.2.

9.4.4 Print and submit the titrant standardization for peer review.

9.4.5 Determine the normality of acid by use of the following equation:

$$\text{Normality (N)} = \frac{A \times B}{53.00 \times C}$$

where:

A = grams of Na_2CO_3 weighed in to 1-L flask

B = mL of Na_2CO_3 solution taken for titration

C = average of the two titrant volumes in mL.

9.4.6 Update the H_2SO_4 normality in the Alkalinity templates.

9.5 Initial Calibration Verification (ICV) and LCS: Measure 30 mL of the ICV/LCS Solution into a 100-mL cup. The final concentration of the ICV is 500 mg $CaCO_3$/L. An ICV sample must be analyzed at the beginning of the tray. ICV acceptability is ± 10%. An LCS is included for every batch and the acceptability is ±10%. (Note: Since there is no separate preparation step for aqueous samples in this procedure, the ICV can also be used for the aqueous LCS for the first analytical batch of samples.)

9.6 Continuing Calibration Verification (CCV): Measure 30 mL of the sodium carbonate solution from Section 10.4 into a 100-mL cup. Prepare a sufficient number of CCVs to be analyzed every 10 titrations and at the end of the tray. CCV acceptability is ± 10%.

9.7 Calibration Blanks (ICB/CCB): Measure 30 mL of reagent water into a 100-mL cup. Prepare a sufficient number of CCBs to be analyzed after every ICV and CCV. Calibration blanks must not contain any alkalinity above the reporting limit. (Note: Since there is no separate preparation step for aqueous samples in this procedure, the ICB can also be used for the aqueous MB for the first analytical batch of samples.)

9.8 Sample Preparation

9.8.1 Homogenization and Subsampling

Samples: Measure 30 mL of a water sample or 5 g of a soil sample plus 30 mL reagent water into a 100-mL cup (mix soil and water to form a slurry). Any sample that requires greater than 30 mL titrant must be analyzed using stronger titrant. Batch QC and verification standards may also need to be made at higher concentration to better represent the concentration of the samples and to increase the likelihood of passing QC.

9.9 Analysis

9.9.1 Example Analytical Sequence

Run Number	Sample Description
1	ICAL Standard 1
2	ICAL Standard 2
3	ICAL Standard 3
4	ICAL Standard 4
5	ICAL Standard 5
6	ICAL Standard 6
7	ICAL Standard 7
8	ICV Standard
9	ICB
10	CCV
11	MB
12	LCS
13	Sample 1
14	Sample 2
15	Sample 3
16	Sample 3 Matrix Spike
17	Sample 3 Duplicate
18	Sample 4
19	Sample 5
20	Sample 6
21	CCV
22	CCB
23	Sample 7
24	Sample 8
25	Sample 9
26	CCV
27	CCB

10.0 DATA ANALYSIS AND CALCULATIONS

10.1 Aqueous sample:

$$\text{Alkalinity (mg } CaCO_3\text{/L)} = \frac{A \times N \times 50000}{\text{mL of sample}}$$

10.2 Soil/ Solid sample:

$$\text{Alkalinity (mg } CaCO_3\text{/kg)} = \frac{A \times N \times 50000}{\text{g of sample}}$$

Where:
A = mL of standard acid.
N = Normality of standard acid.

10.3 Alkalinity Relationships

10.3.1 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.

10.3.2 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.

10.3.3 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:

- Carbonate ($CO3^{2-}$) alkalinity is present when phenolphthalein alkalinity is not zero, but is less than total alkalinity.
- Hydroxide (OH^-) alkalinity is present if phenolphthalein alkalinity is more than half the total alkalinity.
- Bicarbonate ($HCO3^-$) alkalinity is present if phenolphthalein alkalinity is less than half the total alkalinity.

Table 10.1 – Alkalinity Relationships*

Result of Titration	Hydroxide Alkalinity (as $CaCO_3$)	Carbonate Alkalinity (as $CaCO_3$)	Bicarbonate Alkalinity (as $CaCO_3$)
P = 0	0	0	T
P < ½T	0	2P	T-2P
P = ½T	0	2P	0
P > ½T	2P-T	2(T-P)	0
P = T	T	0	0

*P=phenolphthalein alkalinity (pH 8.3 endpoint); T= total alkalinity (pH 4.5 endpoint).

10.4 Calculations

See the Laboratory Quality Assurance Manual for equations for common calculations.

11.0 QUALITY CONTROL AND METHOD PERFORMANCE

11.1 Quality Control

The following QC samples are prepared and analyzed with each batch of samples. Refer to Appendix B for acceptance criteria and required corrective action.

QC Item	Frequency
Method Blank (MB)	1 per batch of 20 or fewer samples. If batch exceeds, 20 samples, every 20.
Laboratory Control Sample (LCS)	1 per batch of 20 or fewer samples. If batch exceeds, 20 samples, every 20.
Matrix Spike (MS)	1 per batch of 20 or fewer samples. If batch exceeds, 20 samples, every 20.
Matrix Spike Duplicate (MSD)	1 per batch of 20 or fewer samples. If batch exceeds, 20 samples, every 20.

11.2 Instrument QC

The following Instrument QC checks are performed. Refer to Appendix B for acceptance criteria and required corrective action.

QC Item	Frequency
Initial Calibration	Run every batch
Initial Calibration Verification	Run after Calibration
Initial Calibration Blank	Run after ICV
Continuing Calibration Verification	Run after every 10 samples
Continuing Calibration Blank	Run after CCV

11.3 Method Performance

11.3.1 Method Validation

11.3.1.1 Detection Limits

Detection limits (DL) and limits of quantitation (LOQ) are established at initial method setup and verified on an on-going basis thereafter. Refer to Pace ENV corporate SOP ENV-SOP-CORQ-0011 Method Validation and Instrument Verification.

11.4 Analyst Qualifications and Training

Employees that perform any step of this procedure must have a completed Read and Acknowledgment Statement for this version of the SOP in their training record. In addition, prior to unsupervised (independent) work on any client sample, analysts that prepare or analyze samples must have successful initial demonstration of capability (IDOC) and must successfully demonstrate on-going proficiency on an annual basis. Successful means the initial and on-going DOC met criteria, documentation of the DOC is complete, and the DOC record is in the employee's training file. Refer to laboratory SOP ENV-SOP-LENE-0110, *Training Procedures*, for more information.

12.0 DATA REVIEW AND CORRECTIVE ACTION

12.1 Data Review

Pace's data review process includes a series of checks performed at different stages of the analytical process by different people to ensure that SOPs were followed, the analytical record is complete and properly documented, proper corrective actions were taken for QC failure and other nonconformance(s), and that test results are reported with proper qualification.

The review steps and checks that occur as employee's complete tasks and review their own work is called primary review.

All data and results are also reviewed by an experienced peer or supervisor. Secondary review is performed to verify SOPs were followed, that calibration, instrument performance, and QC criteria were met and/or proper corrective actions were taken, qualitative ID and quantitative measurement is accurate, all manual integrations are justified and documented in accordance with the Pace ENV's SOP for manual integration, calculations are correct, the analytical record is complete and traceable, and that results are properly qualified.

A third-level review, called a completeness check, is performed by reporting or project management staff to verify the data report is not missing information and project specifications were met.

Refer to laboratory SOP ENV-SOP-LENE-088, *Data Reduction, Review and Reporting*, for specific instructions and requirements for each step of the data review process.

12.2 Corrective Action

Corrective action is expected any time QC or sample results are not within acceptance criteria. If corrective action is not taken or was not successful, the decision/outcome must be documented in the analytical record. The primary analyst has primary responsibility for taking corrective action when QA/QC criteria are not met. Secondary data reviewers must verify that appropriate action was taken and/or that results reported with QC failure are properly qualified.

Corrective action is also required when carryover is suspected and when results are over range.

Samples analyzed after a high concentration sample must be checked for carryover and reanalyzed if carryover is suspected. Carryover is usually indicated by low concentration detects of the analyte in successive samples analyzed after the high concentration sample.

Sample results at concentrations above the upper limit of quantitation must be diluted and reanalyzed. The result in the diluted samples should be within the upper half of the calibration range. Results less than the mid-range of the calibration indicate the sample was over diluted and analysis should be repeated with a lower level of dilution. If dilution is not performed, any result reported above the upper range is considered a qualitative measurement and must be qualified as an estimated value.

Refer to Appendix B for a complete summary of QC, acceptance criteria, and recommended corrective actions for QC associated with this test method.

13.0 POLLUTION PREVENTION AND WASTE MANAGEMENT

Pace proactively seeks ways to minimize waste generated during our work processes. Some examples of pollution prevention include but are not limited to: reduced solvent extraction, solvent capture, use of reusable cycletainers for solvent management, and real-time purchasing.

The EPA requires that laboratory waste management practice to be conducted consistent with all applicable federal and state laws and regulations. Excess reagents, samples and method process wastes must be characterized and disposed of in an acceptable manner in accordance with Pace's Chemical Hygiene Plan / Safety Manual.

14.0 MODIFICATIONS

A modification is a change to a reference test method made by the laboratory. For example, changes in stoichiometry, technology, quantitation ions, reagent or solvent volumes, reducing digestion or extraction times, instrument runtimes, etc. are all examples of modifications. Refer to Pace ENV corporate SOP ENV-SOP-CORQ-0011 *Method Validation and Instrument Verification* for the conditions under which the procedures in test method SOPs may be modified and for the procedure and document requirements.

14.1 Method 2320B has been modified to analyze soils by performing a DI Leach and analyzing the

15.0 RESPONSIBILITIES

Pace ENV employees that perform any part this procedure in their work activities must have a signed Read and Acknowledgement Statement in their training file for this version of the SOP. The employee is responsible for following the procedures in this SOP and handling temporary departures from this SOP in accordance with Pace's policy for temporary departure.

Pace supervisors/managers are responsible for training employees on the procedures in this SOP and monitoring the implementation of this SOP in their work area.

16.0 ATTACHMENTS

Attachment 1: Batch and Instrument QC summary

17.0 REFERENCES

17.1 Pace Quality Assurance Manual - most current version.

17.2 National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, "Quality Systems"- most current version.

17.3 The NELAC Institute (TNI); Volume 1, Module 2, "Quality Systems"- most current version.

17.4 Standard Methods for the Examination of Water and Wastewater, Online Edition, Method 2320B (1997).

18.0 REVISION HISTORY

This Version:

Section	Description of Change
17	Added attachment for QC summaries

This document supersedes the following document(s):

Document Number	Reason for Change	Date
S-KS-I-050-rev.0	New Procedure	January 10, 2013
S-KS-I-050-rev.1	Table 10.1 – Added Section 10.3 – Reworded ICV/LCS prep so that either one or two ampoules can be used. Sections 11.3 and 11.5 – Added note about ICV/ICB can also be used as LCS/MB Table 11.1 – Reworded for clarity Table 13.1 – Reworded for clarity	August 7, 2013
S-KS-I-050-rev.2	SOP – Updated to latest prescribed format. Added sections for Instrument/Equipment Maintenance and Troubleshooting. Section 12 – Added path for runlog and additional information for sample IDs.	November 18, 2014
S-KS-I-050-rev.3	Table 10.2 – Added 0.02N Sulfuric Acid Section 11.2 – Modified to include purchased 0.02N Sulfuric Acid	December 29, 2015
S-KS-I-050-rev.4	SOP – Minor grammatical changes. Section 12.1 – Soils are mixed before titration.	April 10, 2017
S-KS-I-050-rev.5	SOP – Revised date and minor formatting changes	June 20, 2018
ENV-SOP-LENE-0014	Published to Master Control, no changes	October 8, 2018
ENV-SOP-LENE-0014-02	Section 12.1 – Revised to add using a stronger titrant if needed. Dilution of a sample is not allowed.	March 1, 2019
ENV-SOP-LENE-0014-03	NEW SOP format	March 23, 2021
ENV-SOP-LENE-0014-04	Addition of QC limits chart Attachment 1	April 7, 2021

Attachment 1: Batch and Instrument QC summary

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Matrix-specific; reagent water or glass beads for soils.	One per batch of up to 20 samples	Result should be less than the reporting limit. If results are reported to MDL, the MB must be evaluated to the MDL.	1) Re-analyze blank to confirm failure. 2) Qualify results and / or reanalyze associated samples. ***Exceptions:*** 1) If sample ND, report sample without qualification 2) If sample result >10x MB report sample with appropriate qualifier indicating blank contamination. 3) If sample result <10x MB and sample cannot be reanalyzed report sample with appropriate qualifier to indicate an estimated value. Client should be alerted of this condition.
Laboratory Control Sample (LCS)	Matrix-specific; reagent water or glass beads for soils spiked with standard	One per batch of up to 20 samples	90-110%	1) Reanalyze the LCS to confirm failure 2) Re-prep and reanalyze associated samples. 3) If problem persists, check spike solution ***Exceptions:*** 1) If LCS > QC limits and these compounds are non-detect in the associated samples, the sample data may be reported with appropriate data qualifiers. 2) If LCS < QC limits and sample cannot be reanalyzed report sample with appropriate qualifier to indicate an estimated value. Client should be alerted to this condition.
Duplicate	Sample Dup	One per every 10 samples (10%)	Water Max RPD: 10% Soil Max RPD: 20%	1) No corrective actions necessary. Report outliers with comment.

Calibration Metric	Parameter / Frequency	Criteria	Comments
Initial Calibration Verification	Daily, prior to sample analysis.	90-110%	May be reanalyzed once. A second failure confirms and requires re-preparation of standard and/or recalibration. If problem persists an alternative source standards may need to be obtained.

Calibration Metric	Parameter / Frequency	Criteria	Comments
Initial Calibration Verification Blank	Immediately after each Initial Calibration Verification	Result should be less than the reporting limit. If sample results are reported to MDL, the ICB must be evaluated to the MDL.	May be reanalyzed once. A second failure confirms and requires corrective action (e.g. re-preparation of standard(s) and/or recalibration) **Exceptions:** If sample results are reported to MDL and ICB is <RL but >MDL, then corrective action is not necessary other than appropriately qualifying the sample results. Unless the customer's QAPP or technical specification instruct to do otherwise. Samples that are <RL may be reported without qualification. (Not applicable to samples reporting down to MDL) Samples >10x ICB may be reported with appropriate qualification.
Continuing Calibration Verification	Every 10 titrations thereafter and at the end of the analytical sequence. Samples need to be bracketed with an acceptable CCV standard	90-110%	May be reanalyzed once. A second failure confirms and requires corrective action (e.g. re-preparation and/or recalibration). **Exception:** If CCV fails high, then sample(s) that are <RL may be reported with appropriate qualification.
Continuing Calibration Blank	Immediately after each Continuing Calibration Verification. Samples need to be bracketed with an acceptable CCB standard	Result should be less than the reporting limit. If sample results are reported to MDL, the ICB must be evaluated to the MDL.	May be reanalyzed once. A second failure confirms and requires corrective action **Exceptions:** If sample results are reported to MDL and ICB is <RL but >MDL, then corrective action is not necessary other than appropriately qualifying the sample results. Unless the customer's QAPP or technical specification instruct to do otherwise. Samples that are <RL may be reported without qualification. (Not applicable to samples reporting down to MDL) Samples >10x CCB may be reported with appropriate qualification.

Pace ANALYTICAL SERVICES	DC#_Title: ENV-SOP-LENE-0036 v04_Total Dissolved Solids (TDS)	
	Effective Date: 11/29/2022	

Management Approval:
Charles Girgin Approved on 11/23/2022 1:27:07 PM
Kenneth Busch Approved on 11/29/2022 1:50:23 PM

1.0 SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the laboratory procedure for the determination of Total Dissolved Solids (TDS) by gravimetry by SM 2540 C 1997 and 2015. Applicable matrices are aqueous samples which include drinking water, surface waters and saline waters as well as domestic and industrial wastes.

1.1 Target Analyte List and Limits of Quantitation (LOQ)

The target analytes that can be determined by this SOP and the associated LOQ is provided in Table 1, Appendix A.

2.0 SUMMARY OF METHOD

A well-mixed sample is filtered through a standard glass fiber filter. The filtrate is then evaporated and dried to constant weight at 180°C.

3.0 INTERFERENCES

Highly mineralized waters containing significant concentrations of calcium, magnesium, chloride, and/or sulfate may be hygroscopic and will require prolonged drying, desiccation and rapid weighing.

Samples containing high concentrations of bicarbonate will require careful and prolonged drying at 180°C to ensure that all the bicarbonate is converted to carbonate.

Too much residue in the evaporating dish will crust over and entrap water that will not be driven off during drying. Total residue must be limited to less than 200 mg. . Sample results with residue greater than 200 mg must be reanalyzed using less sample volume. Any results reported with residue greater than 200 mg must be noted as such.

4.0 DEFINITIONS

Refer to the Laboratory Quality Manual for a glossary of common lab terms and definitions.

5.0 HEALTH AND SAFETY

Contact your supervisor or local safety coordinator with questions or concerns regarding safety protocol or safe handling procedures for this procedure

The following sections provide general health and safety information about chemicals and materials that may be present in the laboratory.

- The toxicity or carcinogenicity of each chemical material used in the laboratory has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as achievable.

- The laboratory maintains documentation of hazard assessments and OSHA regulations regarding the safe handling of the chemicals specified in each method. Safety data sheets for all hazardous chemicals are available to all personnel. Employees must abide by the health, safety and environmental (EHS) policies and procedures specified in this SOP and in the Pace® Chemical Hygiene / Safety Manual (COR-MAN-0001)
- Personal protective equipment (PPE) such as safety glasses, gloves, and a laboratory coat must be worn in designated areas and while handling samples and chemical materials to protect against physical contact with samples that contain potentially hazardous chemicals and exposure to chemical materials used in the procedure.
- Concentrated corrosives present additional hazards and are damaging to skin and mucus membranes. For procedures that require use of acids, use acids in a fume hood whenever possible with PPE designed for handing these materials. If eye or skin contact occurs, flush with large volumes of water. When working with acids, always add acid to water to prevent violent reactions. For procedures that emit large volumes of solvents (evaporation/concentration processes), these activities must be performed in a fume hood or apparatus that reduces exposure.

6.0 SAMPLE COLLECTION, PRESERVATION, HOLDING TIME & STORAGE

The laboratory provides containers for the collection of samples upon client request. Refer to laboratory SOP ENV-SOP-LENE-0107 for procedures related to preparation of bottle kits for the test method(s) associated with this SOP.

The laboratory performs samples collection for samples to be analyzed by this SOP in accordance with laboratory SOP ENV-SOP-LENE-0025. Refer to this SOP for these instructions.

Container Type, Minimum Sample Amount, Preservation, and Holding Time Requirements:

Matrix	Container Size & Type	Required Sample Amount[1]	Preservation	Holding Time
Aqueous	Plastic or Glass: 500mL	200mL	Thermal: ≤6°C, but not frozen Chemical: N/A	Collection to Analysis: 7 days

[1] *Amount of sample required for each discrete test.*

Thermal preservation is checked and recorded on receipt in accordance with laboratory SOP ENV-SOP-LENE-0021. Chemical preservation is checked and recorded at time of receipt or prior to sample preparation.

After receipt, samples are stored at ≤6°C until sample preparation. Prepared samples (extracts, digestates, distillates, other) are stored at ≤6C until sample analysis.

After analysis, samples are retained as stated in the Pace® standard terms and conditions, unless otherwise specified in the analytical services contract. Samples are then disposed of in accordance with Federal, State, and Local regulations.

7.0 EQUIPMENT & SUPPLIES

7.1 Equipment

- Analytical Balance by Mettler-Toledo, Model AE-240 or equivalent
- Stable Weigh Station by Environmental Express, Model TDS600F; 6 Place filtration system

7.2 Supplies

- Graduated cylinders: 10, 25, 50, 100, 250-mL, Class A, To Deliver (TD): Catalog #'s Fisher / 07-250 (-067, -068, -069)
- Volumetric flask: 1-liter, Class A: Catalog #'s Fisher / 10-209H
- TDS Vessels: TDS Pre-weighed bags and filters: Catalog #'s Env. Exp. / TDS111
- Drying Oven Maintains 180 ± 2°C , 104 ± 1°C Fisher / 15-103-0520
- Desiccator Cabinet Four-shelf, acrylic Fisher / 08-642-23C
- Desiccant Drierite, non-indicating, 8 mesh Fisher / 07-577-3B
- Desiccant Drierite, indicating, 10-20 mesh Fisher / 07-578-4B
- Vacuum pump Edwards Amazon
- Tubing PVC, 5/16" ID Fisher / 14-169-7F

8.0 REAGENTS & STANDARDS

8.1 Reagents

- Reagent water that is ASTM Type II, refer to SOP ENV-SOP-LENE-0131

8.2 Standards

- Potassium chloride (KCl): ACS Reagent Grade; crystalline: Catalog #'s: Fisher / P-217

8.3 Formulations

- LCS Working Standard – Add 1.00g of potassium chloride to a 1-liter volumetric flask containing approximately 400 mL of reagent water. Bring to volume and invert several times to mix. Assign a three-month expiration date from the preparation date (not to extend beyond the expiration dates of the source reagents). Store at ambient temperature.

9.0 PROCEDURE

9.1 Equipment Preparation

9.1.1 Support Equipment

Refer to Pace Analytical Services – SOP ENV-SOP-LENE-0030, Support Equipment, or equivalent replacement, for additional information on calibration requirements for support equipment that may be used in this procedure.

Balances are checked prior to use on each working day with NIST traceable references in the expected range of use, and the results are recorded in the logbook assigned to the balance.

9.1.2 **Instrument Set Up**

9.1.2.1 Balance

Check balance calibration daily before use. The balance must be clean and level (level indicator bubble in circle) before use. The balance is calibrated and serviced annually by a qualified technician.

9.1.2.2 Desiccators

Check the desiccant to determine if re-drying or replacing desiccant is needed (pink color).

9.1.2.3 Ovens

Check the oven temperatures each day of use. Perform corrective action if oven temperature acceptance criteria are not met.

9.1.2.4 Vacuum Filtration Device and Filter Maintenance

Periodically inspect the vacuum filtration device for leaks. Maintain the oil level in the vacuum pump and periodically change the oil. Change the Whatman Vacu-guard Filter on the vacuum line when necessary. Soak filter funnels in soap and water weekly. Clean or change the tubing as needed.

9.2 Sample Preparation

9.2.1 **Homogenization & Subsampling**

Refer to Pace Analytical Services – ENV-SOP-LENE-0135, Sample Homogenization and Sub-Sampling, or equivalent replacement, for information regarding the handling, homogenization, and splitting of samples in order to ensure that a representative aliquot is used for analysis.

9.3 Sample Batch Creation

9.3.1 Create a batch (per 20 samples) in Epic-Pro for each TDS test code required. Each batch must include 1 LCS, 1MB, and 2 DUP (or 1 DUP per ten samples).

9.3.2 Print the batch worklist report and use this to search the scannable locations of samples. Once all samples have been found scan them out to your location or cart.

9.3.3 Open prep log 2540C | TDS (Stable Weigh) template. NOTE: If beakers are use 2540C | TDS template

9.3.4 Under “Search by Batch” on the workbench, enter the HBN of the TDS batch (this can be found in the upper left-hand corner of the batch worklist) and use this workbench to record the sample volumes filtered below.

9.3.5 Populate the Standard Sequence IDs for the TDS Stable Weigh vessels and TDS filters used under the corresponding column.

9.3.6 TDS Stable Weigh vessels have a scannable barcode allowing simultaneous population of vessel traceability under the “ID” column and “Beaker Wt. 1 (g)” fields.

9.3.7 Note: The run date/time is automatically entered into the electronic log when the vessel barcode is scanned. This time needs to be changed to the “Oven temp 1 date/time” (the time that the samples are placed into the drying oven).

9.3.8 All samples require a specific conductance measurement to be determined and recorded.

9.3.9 After the specific conductance measurements have been recorded, return to data software, and transcribe them into the appropriate fields.

9.3.10 The volume to be filtered is dependent upon the range of the conductivity (see table below).

Conductance (µmho/cm)	Filtration Volume (mL)
0-500	200
500-1000	100
1000-1500	75
1500-2000	50
2000-2500	25
2500-3500	15
3500-4500	10
4500-5500	8
5500-6500	7
6500-7500	6
7500-9000	5
9000-11000	4
11000-13000	3
13000-16000	2
16000-20000	1
>20000	0.5-1

Note: If you have insufficient sample, change the volume in the column to the amount used. This must be done to allow the sample to be calculated correctly. If the conductivity is greater than 8,000, then you will need to use less sample by performing stepwise dilutions.

9.4 Sample Vessel Weight Determination/Verification (Initial)

9.4.1 Tare the balance.

9.4.2 Place an empty Stable Weigh vessel on the balance using the weighing bracket and close the door.

9.4.3 While the balance is equilibrating, confirm the Stable Weigh vessel trace number in column labeled “ID.”

9.4.4 Record or confirm the weight of the TDS vessel/pre-weighed vessel in the data software

9.4.5 Place the vessels on their aluminum tray. This will allow for a much faster process from this point forward.

9.4.6 Resave the electronic log (recommended to save often).

9.4.7 If beakers are used record ID and weigh of the empty beaker into appropriate columns, beakers must have been previously dry at 180 ± 2°C for a minimum of one hour.

9.5 Sample Filtration

9.5.1 Assemble the 6-Place filling station.

9.5.2 Thoroughly mix the sample by vigorous hand shaking (or stirring).

9.5.3 Using the conductivity measurement determined in Section 9.3.8, transfer the specified sample volume to the filtration apparatus. Use a graduated cylinder for volumes of 10 mL or greater, and a pipette for volumes less than 10mL.

9.5.4 Place the filter on the apparatus with the wrinkled side facing up. Wash the filter with 3 successive volumes of ≥10 mL of DI water. Allow complete drainage between washings and continue suction until all traces of water are removed.

9.5.5 Collect the sample and washings into the appropriate beaker/vessel and place beakers/vessels on trays to be placed into the drying oven.

9.5.6 DI water is filtered for the MB, and a potassium chloride solution is used for the LCS.

9.6 Sample Vessel Weight Determination/Verification (Final)

9.6.1 Place the vessel into the 104 ± 1°C oven, until the liquid has evaporated to dryness from all vessels (usually overnight). Record time in/time out and temperature reading in the TDS worksheet for each drying cycle. This will complete the drying process and convert all bicarbonates to carbonates.

9.6.2 Once the samples have evaporated, place them into the 180 degree oven for 1 hour.

9.6.3 Remove the trays and vessels from the 180 ± 2°C oven and let cool on the counter for about 2 minutes, until they will not melt the plastic desiccator shelves. Do not allow samples to cool to room temperature! The residue will absorb water from the air, requiring an additional drying cycle for removal.

9.6.4 Place the vessels into the desiccator while maintaining the order to allow them to finish cooling without absorbing any humidity.

9.6.5 Tare the balance.

9.6.6 Place beaker/vessel on balance and record weight on the data software.

9.6.7 Repeat the drying (at 180 ± 2°C) and weighing process for all the samples until the weight change between successive measurements is <0.5 mg of the previous weight.

9.6.8 Evaluate the data and identify any samples that do not meet the QC objectives outlined in Section 11.1.

9.6.9 When finished, save the electronic log template.

Pace Prep Log Report

Batch Information: WET TDS 105492 **Template Version: F-KANS-I-011-Rev.01 (17Oct2021)**

Analysis Method	SM 2540C	Analyzed By	JDS	Instrument	60BL12	Oven ID	60OV03
Acceptance Range	178-182 C	Oven Correction Factor (C)	-2.7	Oven Temp In1 (C) | Corr | Date/Time | Init	182.7 | 180.0 | 02/14/2022 15:26 | JDS	Oven Temp Out1 (C) | Corr | Date/Time | Init	182.7 | 180.0 | 02/15/2022 08:11 | JDS
Desic. In 1 ID | Date/Time | Init	02/15/2022 08:11:28:007 | 02/15/2022 08:11 | JDS	Desic. Out 1 Date/Time | Init	02/15/2022 09:14 | JDS	Oven Temp In2 (C) | Corr | Date/Time | Init	182.7 | 180.0 | 02/15/2022 09:25 | JDS	Oven Temp Out2 (C) | Corr | Date/Time | Init	182.7 | 180.0 | 02/15/2022 10:25 | JDS
Desic. In 2 ID | Date/Time | Init	02/15/2022 10:25:14:732 | 02/15/2022 10:25 | JDS	Desic. Out 2 Date/Time | Init	02/15/2022 13:17 | JDS	Oven Temp In3 (C) | Corr | Date/Time | Init		Reviewed By	BLA
Reviewed By Date	02/15/2022 14:48	Batch Notes					

Sample Information:

QC Rule	Sample Type	Lab Sample ID	Select	ID	Conductivity (uS/cm)	TDS Residue (g)	TDS Posted (mg/L)	TDS Final (mg/L)	Run Date/Time	Cont. Wt 1 (g)	Cont. Use 1	Initial Volume (mL)	Oven Wt 1 (g)	Oven Use 1
2540C W	BLANK	**3078772**	Y	B0391913		0.0000	0.0000	0.0000	02/14/2022 14:40:57	3.9137	M	200	3.9138	N
2540C W	LCS	**3078773**	Y	B0391914		0.1000	500.00	1000.0	02/14/2022 14:41:03	3.7326	M	100	3.8328	N
2540C W	PS	**60392305002**	Y	B0391915	1037	0.0781	390.50	1041.3	02/14/2022 14:41:09	3.7003	M	75	3.7784	N
2540C W	DUP	**3078774**	Y	B0391916	1037	0.0799	399.50	1065.3	02/14/2022 14:41:15	3.8062	M	75	3.8856	N
2540C W	PS	**60392461001**	Y	B0391917	108.3	0.0136	68.000	68.000	02/14/2022 14:41:21	3.6884	M	200	3.7025	N
2540C W	PS	**60392291003**	Y	B0391918	4000	0.0502	251.00	5020.0	02/14/2022 14:41:27	3.9781	M	10	4.0284	N
2540C W	PS	**60392293001**	Y	B0391919	7010	0.0477	238.50	7950.0	02/14/2022 14:41:35	3.7935	M	6	3.8407	N
2540C W	PS	**60392331001**	Y	B0391920	1149	0.0888	444.00	1184.0	02/14/2022 14:41:42	3.8674	M	75	3.956	N
2540C W	PS	**60392331002**	Y	B0391921	659	0.0621	310.50	621.00	02/14/2022 14:41:48	3.8395	M	100	3.9013	N
2540C W	PS	**60392331003**	Y	B0391922	869	0.0452	226.00	452.00	02/14/2022 14:41:55	3.7056	M	100	3.7503	N
2540C W	PS	**60392331004**	Y	B0391923	665	0.2405	1202.5	2405.0	02/14/2022 14:42:01	3.6879	M	100	3.9283	N
2540C W	PS	**60392331005**	Y	B0391924	1567	0.0909	454.50	1818.0	02/14/2022 14:42:08	3.7056	M	50	3.7963	N
2540C W	PS	**60392331006**	Y	B0391925	1337	0.1100	550.00	1466.7	02/14/2022 14:42:15	3.7879	M	75	3.8975	N
2540C W	PS	**60392331007**	Y	B0391926	1481	0.1207	603.50	1609.3	02/14/2022 14:42:22	3.8346	M	75	3.9553	N
2540C W	DUP	**3078775**	Y	B0391927	1481	0.1297	648.50	1729.3	02/14/2022 14:42:28	3.9209	M	75	4.0503	N

Tue, 1 Mar 2022 16:32:38 -0600

10.0 DATA ANALYSIS & CALCULATIONS

10.1 Calculations

Refer to the Laboratory Quality Assurance Manual, Lab Calculations, or equivalent replacement, for equations used to perform common calculations.

10.1.1 **Total Dissolved Solids (TDS)**

Total Dissolved Solids (mg/L) = ((A-B) ×1,000)/C

Where:

A (grams) = Weight of vessel + residue

B (grams) = Weight of vessel

C (mL) = Volume of sample filtered

11.0 QUALITY CONTROL & METHOD PERFORMANCE

11.1 Quality Control

Prepare the following QC samples with each batch of samples. Refer to Appendix B for acceptance criteria and required corrective action(s).

QC Check	Acronym	Frequency
Method Blank	MB	1 per batch of 20 or fewer samples. If batch exceeds 20 samples, every 20 samples.
Laboratory Control Sample	LCS	1 per batch of 20 or fewer samples. If batch exceeds 20 samples, every 20 samples.
LCS Duplicate	LCSD	As Required.
Sample Duplicate	SD	1 per 10 or fewer samples

11.2 Method Performance

11.2.1 Method Validation

Refer to corporate SOP ENV-SOP-CORQ-0011 for general requirements and procedures for method validation.

Establish detection limits (DL) and limits of quantitation (LOQ) at initial method set up and verify the DL and LOQ on an on-going basis thereafter. Refer to corporate policy and/or SOP for DL and LOQ requirements and procedures.

12.0 DATA REVIEW & CORRECTIVE ACTION

12.1 Data Review

The data review process of Pace® Analytical Services includes a series of checks performed at various stages of the process by different people to ensure that SOPs were followed, the analytical record is complete, and properly documented, QC criteria were met, proper corrective actions were taken for QC failure and other nonconformance(s), and test results are reported with proper qualification, when necessary.

The review and checks that are performed by the employee performing the task is called primary review.

All data and test results are also peer reviewed.

This process, known as secondary review is performed to verify SOPs were followed, that calibration, instrument performance, and QC criteria were met and/or proper corrective actions were taken, qualitative ID and quantitative measurement is accurate, all manual integrations are justified and documented, and approved in accordance with the Pace® Analytical Services SOP

for manual integration, calculations are correct, the analytical record is complete and traceable, and that results are properly qualified.

Lastly, a third-level review, called a completeness check, is performed by reporting or project management staff to verify the test report is complete.

Refer to laboratory SOP ENV-SOP-LENE-0088 for specific instructions and requirements for each step of the data review process.

12.2 Corrective Action

Corrective action is required when QC or sample results are not within acceptance criteria.

Refer to Appendix B for a complete summary of QC, acceptance criteria, and recommended corrective actions for QC associated with this test method.

If corrective action is not taken or was not successful, the decision/outcome must be documented in the analytical record. The primary analyst has primary responsibility for taking corrective action when QA/QC criteria are not met. Secondary data reviewers must verify that appropriate action was taken and/or that results reported with QC failure are properly qualified.

Corrective action is also required when carryover is suspected and when results are over range.

Samples analyzed after a high concentration sample must be checked for carryover and reanalyzed if carryover is suspected. Carryover is usually indicated by low concentration detects of the analyte in successive samples analyzed after the high concentration sample.

Sample results at concentrations above the upper limit of quantitation must be diluted and reanalyzed. The result in the diluted samples should be within the upper half of the calibration range. Results less than the mid-range of the calibration indicate the sample was over diluted and analysis should be repeated with a lower level of dilution. If dilution is not performed, any result reported above the upper range is considered a qualitative measurement and must be qualified as an estimated value.

13.0 Pollution Prevention & Waste Management

Pace® proactively seeks ways to minimize waste generated during work processes. Some examples of pollution prevention include but are not limited to reduced solvent extraction, solvent capture, use of reusable cycletainers for solvent management, and real-time purchasing.

The EPA requires that laboratory waste management practices comply with all applicable federal and state laws and regulations. Excess reagents, samples, and method process wastes are characterized and disposed of in an acceptable manner in accordance with the Pace® Chemical Hygiene Plan / Safety Manual. Refer to this manual for these procedures.

14.0 Modifications

The procedures in this SOP have not been modified from the reference test method(s) cited.

When applicable, comparability and/or equivalency studies necessary to validate the modification as required per corporate SOP ENV-SOP-CORQ-0011 are retained by local quality personnel for historical reference.

15.0 RESPONSIBILITIES

- All employees of Pace® Analytical Services that perform any part this procedure in their work activities must have a signed Read and Acknowledgement Statement (R&A) in their training file for the version(s) of the SOP that were in effect during the time the employee performed the activity.
- Local quality personnel are responsible for tracking the currency of the R&A on this SOP for employees at the locations they are assigned to and for notifying the General Manager (GM), however named, when R&A are overdue or outstanding. The GM and the employee's direct supervisor are responsible for ensuring the employee completes the R&A assignments as required.
- The supervisors and managers of Pace® Analytical Services, however named, are responsible for training employees on the procedures in this SOP, implementing the SOP in the work area, and monitoring on-going adherence to the SOP the work area(s) they oversee.
- All employees of Pace® Analytical Services are responsible for following the procedures in this SOP. Unauthorized deviations or departures from this SOP are not allowed except with documented approval from the local Quality Manager and only when those deviations do not violate the Pace® Code of Ethics or Professional Conduct (COR-POL-0004) or associated policy and procedure(s). Hand-edits or manual change to the SOP are not permitted. If a change is desired or necessary, Pace® employees must follow the procedures for document revision specified in corporate SOPs ENV-SOP-CORQ-0015 *Document Managemen*t and ENV-SOP-CORQ-0016 *SOP for Creation of SOP and SWI*.
- Local quality personnel are responsible for monitoring conformity to this SOP during routine internal audits of work areas that utilize this SOP and for communicating gaps and deviations found during monitoring to the work area supervisor, who is responsible for correction of the situation.

16.0 ATTACHMENTS

- Appendix A: Routine Analyte List and LOQ
- Appendix B: QC Summary & Corrective Action Table

17.0 REFERENCES

- ENV-SOP-CORQ-0006, *Manual Integration*, current version.
- ENV-SOP-CORQ-0011, *Method Validation*, current version.
- ENV-SOP-CORQ-0015, *Document Management*, current version.
- ENV-SOP-CORQ-0016, *SOP for SOP and SWI,* current version.
- ENV-TMP-CORQ-0007, *Quality Manual Template*, current version.
- COR-POL-0004, *Code of Ethics and Professional Conduct*, current version.
- COR-MAN-001, *Pace® Safety Manua*l, current version.
- Standard Methods 2540 C – 1997 and 2015 published editions

18.0 REVISION HISTORY

Authorship

Primary Author[1]	Job Title	Date Complete
Lenzie Boring	Inorganics Manager	11/22/2022

[1]The primary author is the individual / role responsible for the content of this SOP. Send questions or suggestions for content to the primary author. See the Quality Manager for questions or concerns related to implementation of this SOP.

Revisions Made from Prior Version

Section	Description of Change
Various	Updated to SOP Template language
9.5.4	Added language as to which way the filter should face on the filtering apparatus
9.6.1	Updated procedure to add drying the sample to dryness before placing in 180 oven.

Document Succession: This version replaces the following documents:

Document Number & Version	Document Title	Effective Date:
ENV-SOP-LENE-0036 v03	Total Dissolved Solids (TDS)	04/11/2022

Appendix A: Target Analyte List and LOQ

Table 1: Routine Analyte List and Limits of Quantitation (LOQ)[1]

Analyte	Water (mg/L)
Total Dissolved Solids	5

[1]Values in place as of effective date of this SOP. LOQ are subject to change. For the most up to date LOQ, refer to the LIMS or contact the laboratory.

Appendix B: QC Summary and Corrective Action Table

QC Item	Frequency	Acceptance Criteria	Corrective Action	Qualification
Constant Weight Check	All QC and samples	Weight change of less than 0.5 mg.	Put the samples back in the oven for an additional hour and reweigh. If constant weight cannot be achieved, samples must be reanalyzed. If constant weight cannot be achieved due to the sample matrix, the sample must be qualified as estimated.	Reportable Comment "Constant weight could not be obtained. The reported result should be considered an estimated value."
Method Blank (MB)	1 per batch of 20 or fewer samples.	TDS < RL	Reanalyze batch with associated MB and/or re-prepare batch of samples with a new MB, unless the original result meets the exceptions stated below: **Exceptions:** 1) If sample is ND or > 10x MB result, report sample without qualifier. 2) If sample result <10x MB result and the samples cannot be reanalyzed, report the associated samples with appropriate qualifier.	Qualify samples with MB out of criteria. Refer to Footnotes in EPIC.
Laboratory Control Sample (LCS)	1 per batch of 20 or fewer samples.	TDS must be within ± 10% of the true value. (%R)	Reanalyze batch with associated LCS and/or re-prepare batch of samples with a new LCS, unless the original result meets the exception stated below: **Exceptions:** If LCS recovery is > QC limits, and the associated samples are ND, then the sample data may be reported with the appropriate data qualifier.	Qualify samples with LCS out of criteria. Refer to Footnotes in EPIC.
Sample Duplicate (DUP)	1 per 10 or fewer samples	TDS must have RPD ≤ 10% (%D)	Qualify duplicated sample.	Qualify sample with DUP out of criteria. Refer to Footnotes in EPIC.
Maximum Dried Residue Yield	All samples	Max. Residue < 200 mg	If there is an excess of residue, or filtration time exceeds 10 minutes, the sample must be prepared at a reduced initial volume. Identify any sample that yields >200 mg of dried residue, and if necessary, report the value the appropriate qualifier.	Refer to Section 9.6 Reportable Comment "Result estimated. Sample residue is greater than 200 mg at a volume of X mL."
Minimum Dried Residue Yield	All samples	Min. Residue > 2.5 mg	Identify any sample that yields <2.5 mg **of dried residue** and report the value and qualify accordingly.	Refer to Section 9.6

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the laboratory procedure for the determination of Mercury by CVAA

1.1. Target Analyte List and Limits of Quantitation (LOQ)

The target analytes and the normal LOQ that can be achieved with this procedure:

Analyte	LOQ
MERCURY (AQUEOUS)	0.2 ug/L
MERCURY (NON-AQUEOUS)	0.5 mg/Kg

LOQ are established in accordance with Pace policy and SOPs for method validation and for the determination of detection limits (DL) and quantitation limits (LOQ). DL and LOQ are routinely verified and updated when needed. The current LOQ for each target analyte that can be determined by this SOP as of the effective date of this SOP is provided in Table 1, Appendix A.

The reporting limit (RL) is the value to which analytes are reported as detected or not detected in the final report. When the RL is less than the lower limit of quantitation (LLOQ), all detects and non-detects at the RL are qualitative. The LLOQ is the lowest point of the calibration curve used for each target analyte.

DL, LOQ, and RL are always adjusted to account for actual amounts used and for dilution.

2. SUMMARY OF METHOD

2.1. Aqueous - A sample aliquot is digested in diluted potassium permanganate, potassium persulfate, sulfuric acid, and nitric acid and oxidized for 2 hours at 95 ± 3°C. The mercury is then reduced with stannous chloride to elemental mercury and measured by automated cold vapor atomic absorption technique at a wavelength of 253.7 nm.

2.2. Solid - A weighed portion of sample is digested in nitric and hydrochloric acids for 2 minutes at 95 ± 3°C. The sample is diluted, and potassium permanganate solution added. The sediment sample is then oxidized for 30 minutes at 95 ± 3°C. The mercury is reduced with stannous chloride to elemental mercury, aerated from solution in a closed system, and measured by automated cold vapor atomic absorption technique at a wavelength of 253.7 nm.

3. INTERFERENCES

3.1. Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from reagent water.

3.2. Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.

3.3. Seawaters, brines, and industrial effluents high in chlorides require additional permanganate because during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation at 253.7 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the spectrometer.

3.4. Certain volatile organic materials that absorb at this wavelength may also cause interference. Letting the samples vent before analysis can help to reduce this interference.

4. DEFINITIONS

Refer to the Laboratory Quality Manual for a glossary of common lab terms and definitions.

5. HEALTH AND SAFETY

The toxicity or carcinogenicity of each chemical material used in the laboratory has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable.

The laboratory maintains documentation of hazard assessments and OSHA regulations regarding the safe handling of the chemicals specified in each method. Safety data sheets for all hazardous chemicals are available to all personnel. Employees must abide by the health, safety and environmental (HSE) policies and procedures specified in this SOP and in the Pace Chemical Hygiene / Safety Manual.

Personal protective equipment (PPE) such as safety glasses, gloves, and a laboratory coat must be worn in designated areas and while handling samples and chemical materials to protect against physical contact with samples that contain potentially hazardous chemicals and exposure to chemical materials used in the procedure.

Concentrated corrosives present additional hazards and are damaging to skin and mucus membranes. Use these acids in a fume hood whenever possible with additional PPE designed for handing these materials. If eye or skin contact occurs, flush with large volumes of water. When working with acids, always add acid to water to prevent violent reactions. Any processes that emit large volumes of solvents (evaporation/concentration processes) must be in a hood or apparatus that prevents employee exposure.

Caution: Mercury compounds are highly toxic if swallowed, inhaled, or absorbed through the skin. All analyses should be conducted under an exhaust hood. Safety glasses and chemical resistant gloves should always be worn when handling concentrated mercury standards.

Contact your supervisor or local HSE coordinator with questions or concerns regarding safety protocol or safe handling procedures for this procedure.

6. SAMPLE COLLECTION, PRESERVATION, HOLDING TIME, AND STORAGE

Samples should be collected in accordance with a sampling plan and procedures appropriate to achieve the regulatory, scientific, and data quality objectives for the project.

The laboratory performs samples collection for samples to be analyzed by this SOP in accordance with laboratory SOP ENV-SOP-LENE-0107, *Field Manual*. Refer to this SOP for these instructions.

The laboratory will provide containers for the collection of samples upon client request for analytical services. Bottle kits are prepared in accordance with laboratory SOP ENV-SOP-LENE-0025, *Assembly of Sample Container Kits*. The bottle kits provided by the laboratory should include field test kits and treatment reagent.

Requirements for container type, preservation, and field quality control (QC) for the common list of test methods offered by Pace are included in the laboratory's quality manual.

General Requirements

Matrix	Routine Container	Minimum Sample Amount[1]	Preservation	Holding Time
Aqueous	Plastic or glass (500-mL).	90mL	Thermal: N/A Chemical: HNO3; pH<2	Collection to Analysis: 28 Days.
Solid	Wide-mouth glass jar (4-oz).	1 g	Thermal: ≤6ºC Chemical: HNO3; pH<2	Collection to Analysis: 28 Days.
Wipe	One Ghost Wipe™ per digestion tube or glass vial w/PTFE-lined septum.	1 wipe	Thermal: N/A Chemical: HNO3; pH<2	Collection to Analysis: 28 Days.
Leachate	Plastic or glass (500-mL).	90mL	Thermal: N/A Chemical: HNO3; pH<2	Filtration to Analysis: 28 Days.

[1]*Minimum amount needed for each discrete analysis.*

Field / Matrix QC

Trip Blank	Equipment Blank	MS/MSD	Field Duplicate
If client requested	If client requested	1/20 (or MS per 10 for 245.1)	If requested

Thermal preservation is checked and recorded on receipt in the laboratory in accordance with laboratory SOP ENV-SOP-LENE-0021, *Sample Management*. Chemical preservation is checked and recorded at time of receipt or prior to sample preparation.

After receipt, samples are stored at ≤6°C until sample preparation. Prepared samples (extracts, digestates, distillates, other) are stored at ≤6°C until sample analysis.

After analysis, unless otherwise specified in the analytical services contract, samples are retained for 30 days from date of final report and then disposed of in accordance with Federal, State, and Local regulations.

7. EQUIPMENT AND SUPPLIES

Table 7.1 Equipment and Supplies

Supply	Vendor	Model / Version	Comments
Boiling Stones	Fisher	09-191-20	PTFE
Cellulose Nitrate Filters	Fisher	09-905-17	Whatman, 47 um x 47mm
Digestion Tubes	Environmental Express	SC475/SC415	68-mL, graduated to 50-mL, 15mL
Ghost Wipes™	Environmental Express	SC4200	15 x 15 cm
HDPE Sample bottles, 250-m	Fisher	NC9095184	Preserved with 2.5 mL 20% HNO_3.
Hotblock	Environmental Express	SC154/196	54-or 96 position
Mercury Analyzer	Perkin-Elmer	FIMS-400	or equivalent
Mercury Analyzer	Cetac	QuickTrace™ M-76	or equivalent
Pipettor	Fisher	05-403-121	Eppendorf

8. REAGENTS AND STANDARDS

8.1. The reagents listed below are those currently in use. Other sources or grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

Table 8.1 – Standard Storage Conditions

Standard Type	Description	Expiration	Storage
Stock Standards	▪ Concentrated reference solution purchased directly from approved vendor	▪ Manufacturer's recommended expiration date	▪ Manufacturer's recommended storage conditions
Intermediate and Working Standards	▪ Reference solutions prepared by dilutions of the stock solution	▪ Intermediate standards – two weeks from preparation or the expiration date listed for the stock source, whichever is sooner. ▪ Working Standards – Prepared directly at the time of use.	▪ Manufacturer's recommended storage conditions for stock source solution.

Table 8.2 – Stock Reagents and Standards

Reagent/Standard	Concentration/ Description	Vendor/ Item #
1000 ppm Mercury	Primary Standard, ISO 17034 certified	Spex, PLHG4-2Y
1000 ppm Mercury (2nd Source)	Secondary Standard, ISO 17034 certified	Inorganic Ventures CGHC1-500mL
Hydrochloric acid	Baker Instra-Analyzed®	J.T. Baker / 9530-33
Hydroxylamine HCl	ACS Reagent Grade	J.T. Baker / 2196-01

Reagent/Standard	Concentration/ Description	Vendor/ Item #
Nitric acid	Baker Instra-Analyzed®	J.T. Baker / 9598-34
Potassium permanganate	ACS Reagent Grade	J.T. Baker / 3227-01
Potassium persulfate	Baker Instra-Analyzed®	J.T. Baker / 3239-01
Reagent water	ASTM Type II	
Stannous chloride dihydrate	ACS Reagent Grade	J.T. Baker / 3980-01
Sulfuric acid	Baker Instra-Analyzed®	J.T. Baker / 9673-33

Table 8.3 – Intermediate Standards

Standard	Source Standard	Standard Amount (mL)	Solvent	Final Total Volume (mL)	Final Concentration (ug/L)
Primary Intermediate (Working) Standard (ICAL Spike Solution)	Primary Stock Standard	0.075	Water	500	150
Secondary Intermediate (Working) Standard (ICV Spike Solution)	Secondary Stock Standard	0.075	Water	500	150

8.2. Intermediate preparation: Add 5 mL of concentrated HNO_3 to a 500-mL volumetric flask containing ~250 mL of reagent water, followed by 0.075 mL of the 1000 ppm Mercury primary standard or secondary standard. Dilute to the mark with reagent water and invert the flask to mix the standard. Assign a fourteen day expiration date.

8.3. Since some programs require the verification of the spike solutions prior to use, the intermediates are prepared weekly and overlap so that the solutions can be verified prior to use. After weekly intermediate preparation, dilute as a CCV or ICV respectively. Analyze as a sample. The recovery must be 90-110%. Note the verification date in the Mercury standards logbook.

Table 8.4 – Working Standards for Aqueous Calibration Curve

Standard	Source Standard	Standard Amount (mL)	Solvent	Final Total Volume (mL)	Final Concentration (ug/L)
CAL0 Standard 1/ICB/CCB*	NA	N/A	Water	30	0
CAL1 Standard 2/Low CHK	ICAL Spike Solution	0.040	Water	30	0.20
CAL2 Standard 3	ICAL Spike Solution	0.20	Water	30	1.0
CAL3 Standard 4	ICAL Spike Solution	0.40	Water	30	2.0
CAL4 Standard 5/CCV	ICAL Spike Solution	1.0	Water	30	5.0
CAL5 Standard 6	ICAL Spike Solution	2.0	Water	30	10
ICV Standard	ICV Spike Solution	1.0	Water	30	5.0

*Reagent water only.

Note: The working standards for the aqueous calibration curve get the same amounts of reagents added to them just like the samples (see section 9.6 below). For EPA method 245.1, the calibration standards skip the heating step. When preparing EPA method 7470A, the calibration standards are heated like the samples.

Table 8.5 – Working Standards for Soil/Wipe Calibration Curve

Standard	Source Standard	Standard Amount (mL)	Solvent	Starting Volume (mL)	Final Concentration (ug/L)
ICAL0 Standard 1/ICB/CCB*	NA	N/A	Water	10	0
CAL1 Standard 2/Low CHK	ICAL Spike Solution	0.10	Water	10	0.50
CAL2 Standard 3	ICAL Spike Solution	0.20	Water	10	1.0
CAL3 Standard 4	ICAL Spike Solution	0.40	Water	10	2.0
CAL4 Standard 5/CCV	ICAL Spike Solution	1.0	Water	10	5.0
CAL5 Standard 6	ICAL Spike Solution	2.0	Water	10	10
ICV Standard	ICV Spike Solution	1.0	Water	10	5.0

*Reagent water only.

Note: The working standards for the soil/wipe calibration curve undergo the same digestion procedures as the samples (see section 9.5 below).

Table 8.6 – Working Reagents

Working Reagent	Description
Hydroxylamine Hydrochloride Solution	Dissolve 120 g of hydroxylamine hydrochloride in a 1-L volumetric flask containing about 500mL of reagent water. Dilute to the mark with reagent water and invert several times to mix.
Potassium Permanganate Solution	Dissolve 50 g of potassium permanganate in a 1-L volumetric flask containing about 500mL of reagent water. Dilute to the mark with reagent water and invert several times to mix.
Potassium Persulfate Solution	Dissolve 50 g of potassium persulfate in a 1-L volumetric flask containing about 500mL of reagent water. Dilute to the mark with reagent water and invert several times to mix.
Stannous Chloride Solution	Add 60 mL of concentrated HCl to a 2-L volumetric flask containing 500-1000 mL reagent water. Add 22.2 g of stannous chloride and dissolve. Dilute to the mark with reagent water and invert several times to mix. Store in refrigerator at ≤6°C, but not freezing.
Hg Carrier Solution	In a 2-L volumetric flask, add 500 mL of reagent water and 60 mL of concentrated HCl. Dilute to the mark with reagent water and invert several times to mix.
QuickTrace Rinse Solution	Add 1000 mL of reagent water to the 2-L rinse bottle, followed by 100 mL concentrated HCl and 40 mL concentrated HNO_3. Dilute to the mark with reagent water and invert several times to mix.

9. PROCEDURE

9.1. Equipment Preparation

9.1.1. Support Equipment

All support equipment (balances, pipettors, thermometers, etc.) must be calibrated or verified prior to use according to SOP ENV-SOP-LENE-0030, *Support Equipment*, current revision or replacement.

9.1.2. **Instrument**

9.1.2.1 **Routine Instrument Operating Conditions**

1.1.1.1.1 Refer to instrument manual (manufacturer recommendations).

- *Gas Flow (mL/min): 100*
- *Sample Uptake (s): 40*
- *Rinse (s): 95*
- *Read Delay (s): 51 (adjusted as needed at start of each day)*
- *Replicates (s): 4*
- *Replicate Time (s): 1.5*
- *Pump Speed (%): 50*
- *Wavelength (nm): 253.7*

1.1.1.1.2 Allow the instrument to warmup for a minimum of 30 minutes for the lamp and pump to stabilize. See the manufacturer's instruction manual for maintenance and troubleshooting.

9.1.2.2 **Maintenance**

- Replace the Hg lamp every 6 months or when a noticeable loss in stability is observed.
- Replace the Perma Pure® Dryer Cartridge every 3-6 months or when the mercury absorbance for a given standard drops to 50% or more of its original value.
- Inspect the block digestors on a daily basis and report any problems to the supervisor. Send digestors back to manufacturer if repairs are needed.
- On a daily basis check the LED on the DI water still and ensure that it reads no less than 10 MΩ. Let the Department Manager know if the reading falls below 10 MΩ.
- Periodically clean the GLS and replace the drain tube.
- Change tubing on the peristaltic pump regularly.
- Recalibrate the thermometers in the Hotblocks annually.
- All maintenance is recorded in the Maintenance Log for the Teledyne Leeman Labs QuickTrace® M-7600 Mercury Analyzer.

9.2. **Initial Calibration**

To perform quantitative measurements, an initial calibration must be established before the analysis of samples. An initial calibration is an evaluation of the relationship between response of the instrument (or process) and the concentration of the target analytes.

All samples, where applicable, must be associated with an acceptable initial calibration. In general, if an initial calibration is not acceptable, corrective actions must be performed and all associated samples re-analyzed. If the sample re-analysis is not possible, data

associated with an unacceptable initial calibration must be reported with appropriate data qualifiers.

See the Pace *Acceptable Calibration Practices for Instrument Testing* Policy, ENV-POL-CORQ-0005, current revision or equivalent, for additional information regarding acceptable calibration practices.

9.2.1. **Calibration Design**

An initial calibration curve using five calibration standards and a blank (method requirement is a blank and three calibration standards) is prepared and analyzed each working day (24 hour clock) or when CCVs do not meet acceptance criteria. The lowest concentration standard of the initial calibration curve must be at or below the reporting limit, a level below which all reported results must be qualified as estimated values.

9.2.2. **Calibration Sequence**

Run Number	Sample Description
1	HG-CAL0
2	HG -CAL1
3	HG -CAL2
4	HG -CAL3
5	HG -CAL4
6	HG -CAL5
7	ICV Standard (from 2nd source)
8	CRDL
9	CCV (as required by EPA 245.1)
10	ICB

9.2.3. **ICAL Evaluation**

9.2.3.1 **Curve Fit**

The calibration curve is a representation of the relationship of the instrument response and analyte concentration. The curve is used to quantitate the concentration of an unknown based on its response and this known relationship. A linear calibration curve is produced by this method.

Linear Regression – The linear regression calibration curve is derived from a least square's regression analysis of the calibration points. A calibration curve based on this technique will have the format of y= ax+b where "a" is the slope of the line and "b" is the y-intercept. The linear regression is not forced through the origin; therefore, there is a possibility that very low levels of contaminants below the response of the lowest calibration point may generate erroneous reportable results. A calculation of the correlation coefficient "r" is used to determine the acceptability of a linear regressed curve.

9.2.3.2 **Relative Standard Error (RSE)**

Initial calibrations using linear regression must be evaluated for Relative Error. Relative error can be calculated and evaluated by either of two options. The Mercury curve is evaluated using Relative Standard Error (%RSE). %RSE is analogous to %RSD. In fact, both SW-846 8000 and 40CFR Part 136 allow %RSE to be used in place of correlation coefficient (R) or coefficient of determination (r^2) for the acceptability determination of the curve.

The Mercury curve is evaluated using the following equation for Relative Standard Error (%RSE):

$$\%\ RSE = 100 \times \sqrt{\sum_{i=1}^{n} \left[\frac{x'i - xi}{xi}\right] \Big/ (n-p)}$$

xi = True Value of the Calibration Standard

x'i = Measured Concentration of the Calibration Standard

p = Number of terms in fitting equation

n = number of calibration points.

The % RSE is calculated by the instrument software and can be found on the results printout. In the absence of method defined criteria, the %RSE must be ≤ 20%.

When criteria for relative standard error are not met, the calibration is not acceptable for use. The source of the problem must be determined and corrected, or recalibration is required. If recalibration does not meet acceptance criteria, notify the department manager and Quality Manager to determine how to proceed.

9.2.3.3 **Initial Calibration Verification**

Because all calibration points are from the same source, it is possible that the calibration points may meet linearity criteria but not be accurately made in terms of their true value.

To assess the accuracy relative to the purity of the standards, a single standard from a secondary source must be analyzed and the results obtained must be assessed relative to the known true value. This verification process is performed using the standard referred to as the Initial Calibration Verification Standard (ICV). This secondary source must be from an alternative manufacturer or, in the event an alternative manufacturer is not available, from a different lot prepared independently by the same manufacturer. Prepare the ICV as specified in Section 8.2.9 and analyze immediately after the last initial calibration standard. The accuracy of the standard is assessed as a percent difference from the true value according to the following equation:

$$\%\ Difference = \frac{Result\ ICV - True\ Value\ ICV}{True\ Value\ ICV} \times 100$$

The ICV must be within ± 10% of its true value. ICV failure indicates that the working standards used for initial calibration or verification may not have been prepared correctly or are no longer adequate for use. When criteria are not met, investigation and corrective action is expected regardless of whether the ICV fails high or low.

If the ICV does not meet acceptance criteria, examine the data to determine the cause for failure:

Inspect the calibration and ICV standard preparation records to verify the parent materials used were not expired and/or have not degraded and verify the standard(s) were made properly in accordance with the test method SOP.

If no problems are found, remake and reanalyze the ICV. If the second ICV fails, remake the calibration standards and recalibrate the instrument.

Notify the department manager and Quality Manager if the additional calibration curve does not meet acceptance criteria.

Decisions to proceed with use of the calibration without resolution of the ICV failure, whether the failure is high or low, must be documented in the technical record by the individual making the decision with the rationale for which the decision was made.

Any test result reported for an analyte that did not meet ICV criteria must be qualified in the final test report to alert the end user of the data of the nonconformance.

Primary, secondary and tertiary data reviewers must confirm that any results reported for analyte(s) that did not meet ICV acceptance criteria are qualified in the final test report, regardless of level of type or level of report.

An Initial Calibration Blank (ICB) must be run after the ICV to verify the instrument is working correctly (i.e., there is no drift). The ICB should meet acceptance criteria of < ½ the Reporting Limit (RL/LOQ) for methods EPA 7470A/7471B and < the MDL for method EPA 245.1.

9.2.4. **Continuing Calibration Verification**

As part of the analytical process, the instrumentation must be checked daily to determine if the response has changed significantly since the initial calibration was established. The Continuing Calibration Verification Standard (CCV) is analyzed to check the validity of the initial calibration. The CCV is run prior to the analysis of any sample, after every ten samples, and at the end of the analytical sequence by analyzing a midpoint calibration standard. EPA 245.1 also requires a CCV to be run following the calibration curve. The accuracy of the standard is assessed as percent difference from the true value according to the following equation:

$$\%\ Difference = \frac{Result\ ICV - True\ Value\ ICV}{True\ Value\ ICV} \times 100$$

For EPA 245.1, a CCV must be run immediately following the calibration curve and must be within ± 5% of the true value. Subsequent CCVs must be within ± 10% of the true value. EPA 7470A and 7471B require CCVs to be within ± 10% of the true value. If the CCV does not meet acceptance criteria, examine the data to determine the cause for failure and impact to results.

If the identified cause of failure is known and affects only the CCV standard (such as improper standard preparation), then document corrective action and proceed if reanalysis of the CCV passes.

If the cause of the failure is unknown, then all samples analyzed prior to the failing CCV must be re-analyzed following corrective action and a passing CCV. If the source of the problem cannot be determined and corrected, recalibration is required.

See the Pace *Acceptable Calibration Practices for Instrument Testing* Policy, ENV-POL-CORQ-0005, current revision or equivalent, for additional information regarding continuing calibration verification corrective action.

A Continuing Calibration Blank (CCB) must be run after every CCV. The CCB should meet acceptance criteria of < ½ the Reporting Limit (RL/LOQ) for methods EPA 7470A/7471B and < the MDL for method EPA 245.1.

9.2.5. **Reporting Limit Verification Sample**

During daily sample analysis, a reporting limit verification standard (CRDL) must be run prior to running any samples.

The CRDL should be within ± 50% of the true value. If the CRDL does not meet acceptance criteria, it may be re-prepared and re-analyzed to determine if improper standard preparation occurred. If it still fails acceptance criteria, see the Department Manager and Quality Manager.

9.2.6. **Initial and Daily Calibration Acceptance Criteria**

The calibration criteria listed below must be met for each calibration curve/batch or additional actions must be performed.

Calibration Acceptance and Verification Criteria

Calibration Metric	Parameter / Frequency	Criteria	Comments/Corrective Actions
Calibration Curve Fit	Linear Regression	$r \geq 0.995$	If not met, remake standards and recalibrate. Instrument maintenance may be required if problem persists.
Initial Calibration Verification Standard (ICV) **[Known as QCS in 245.1]**	Immediately after each initial calibration	7470/7471: 90-110% 245.1: 95-105%	May be reanalyzed once. A second failure confirms and requires re-preparation of standard and/or recalibration. If problem persists an alternative source standard may need to be obtained.
Low Level Check Standard (CRDL or RL)	Immediately after each initial calibration	50-150%	May be reanalyzed once. A second failure confirms and requires re-preparation of standard and/or recalibration
Initial Calibration Verification Blank (ICB)	Immediately after each Initial Calibration Verification Standard	Result should be less than the reporting limit. If results are reported to MDL, the ICB must be evaluated to the MDL.	May be reanalyzed once. A second failure confirms and requires corrective action (e.g., re-preparation of standard(s) and/or recalibration) **Exceptions:** If sample results are reported to MDL and ICB is <RL but >MDL, then corrective action is not necessarily other than appropriately qualifying the sample results. Unless the customer's QAPP or technical specification instruct to do otherwise. Samples that are <RL may be reported without qualification. (Not applicable to samples reporting down to MDL) Samples >10x ICB may be reported with appropriate qualification.
Continuing Calibration Verification (CCV)	Prior to the analysis of any samples and every 10 samples thereafter. Samples need to be bracketed with CCVs	7470/7471: 80-120% 245.1: 90-110%	May be reanalyzed once. A second failure confirms and requires corrective action (e.g. re-preparation and/or recalibration). **Exception:** If CCV fails high, then sample(s) that are <RL may be reported with appropriate qualification.

9.3. **Sample Preparation**

9.3.1. **Homogenization and Subsampling**

Refer to the current SOP ENV-SOP-LENE-0135, Sample Homogenization and Sub-sampling.

9.3.2. **Sample Batch Preparation**

1. Before beginning the digestion, obtain a batch number and fill in the electronic logbook for each set of samples of a similar matrix and analytical requirements using the assigned HBN number.
2. The electronic logbook for the scheduled batch is examined prior to beginning the digestion process to ensure that no more than 20 samples are scheduled for the batch and that all samples require the scheduled digestion. If an error is detected in the scheduled batch, the error is fixed before proceeding with the digestion. The scheduled samples are batched in Epic and all digestion data (sample volumes, spiking information, etc.) is entered directly into the electronic logbook.
3. Obtain all the samples from their respective places on the storage shelves. Log them out from the EPIC using the barcode reader.
4. Set out the number of digestion cups required for the sample batch. All samples in the batch must be digested in the same type of digestion cup.
5. Labels printed from Epic Pro are attached on the upper side of each digestion cup. Also label digestion cups to be used for QC samples and calibration standards (if first digestion batch of the day). Make sure the labels match the corresponding sample or QC.

9.4. **Filtration for dissolved metals analysis (Total mercury samples are not filtered for EPA Method 245.1, Rev. 3.0).**

9.4.1. Dissolved samples are normally filtered in the field; however, samples are filtered in the laboratory in certain instances. The dissolved sample is prepared by filtering an aliquot of unpreserved sample through a 0.45-um, cellulose nitrate filter and preserving with nitric acid.

9.4.1.1 Rinse the filtration apparatus (Erlenmeyer flask, filtration top and bottom) with 20% nitric acid, followed by five rinses with reagent water.

9.4.1.2 A 0.45-um filter is placed on the filtration support with a forceps

9.4.1.3 The filtration top is attached, and the pump tubing is attached to the flask

9.4.1.4 Add 150 mL of reagent water to the filtration apparatus and start the pump.

9.4.1.5 After the reagent water has passed through the filter, turn the pump off and disconnect the tubing from the pump. Remove the filter support and pour the filtered aliquot into a pre-certified, HNO_3-preserved, 250-mL sample bottle (obtain from Bottle Prep Department).

9.4.1.6 This aliquot of reagent water serves as the method blank for the batch.

9.4.1.7 Label the bottle with the date, analyst's initials and attach a sample identification label.

9.4.1.8 Repeat steps 1 through 6 for up to twenty samples (substituting the sample for reagent water in Step 4).

9.4.1.9 Record the filter lot number in the digestion logbook.

9.4.1.10 The samples are now ready for digestion. The filtered blank is carried through the digestion process and takes the place of the method blank.

9.5. **Soil Digestion**

9.5.1. Begin by preparing the working standards as outlined in Table 10.5 above.

9.5.2. Method Blank: Add 0.3-0.4 g of boiling stones to a digestion tube. Bring volume to 10 mL with reagent water.

9.5.3. LCS: Add 0.3-0.4 g of boiling stones to a digestion tube, and spike with 1.0 mL of the Working Calibration Standard. After the spike has been added, bring volume to 10 mL with reagent water.

9.5.4. MS/MSD: Weigh into a digestion tube 0.3-0.4 g (soil) of a well homogenized portion of the selected sample. (Homogenization procedures can be found in S-KS-Q-046-rev.1, Sample Homogenization and Sub-Sampling, or its equivalent revision or replacement.) Spike with 1.0 mL of the Working Calibration Standard. After the spike has been added, bring volume to 10 mL with reagent water.

9.5.5. Client samples: Weigh into a digestion tube 0.3-0.4 g (soil) of a well homogenized portion of the selected sample. (Homogenization procedures can be found in S-KS-Q-046, Sample Homogenization and Sub-Sampling, or its equivalent revision or replacement.) Bring volume to 10 mL with reagent water.

9.5.5.1 Sludge samples: use 1 to 2 g.

9.5.6. Add 1.25 mL HNO_3 and 3.75 mL HCl to all digestion tubes including calibration curve, ICV/CCV, Method Blank, LCS, MS/MSD, and Client Samples. CAUTION: Perform this step inside a fume hood.

9.5.7. Heat all the digestion tubes in a hot block at 90-95°C for 2 minutes.

9.5.8. Remove the tubes from the hot block and allow them to cool to room temperature.

9.5.9. Bring volume of each tube to 25mL with reagent water. Add 5.0 mL of potassium permanganate solution to each tube and allow them to stand at least 15 minutes. Note: If the samples do not maintain their purple color at this step, add an additional 5.0mL of the $KMnO_4$ solution and wait an additional 15 minutes. If the purple color is still not maintained, use less sample volume and repeat this process. Also notify the department supervisor about this situation.

- Note: If additional $KMnO_4$ is added to a sample, then additional $KMnO_4$ also needs to be added to the Method Blank and the LCS. In this event, it is imperative to maintain the same final volume for all tubes processed together.

9.5.10. Place each tube back into the 90-95°C hot block, cover with watch glass, and allow them to digest for at least 30 minutes.

9.5.11. Remove the tubes and allow them to cool to room temperature.

9.5.12. Verify that the volume of each tube is 30mL and bring volume up to 30mL with reagent water if needed.

9.5.13. Add 1.8 mL of hydroxylamine hydrochloride solution to remove the excess permanganate. Note: Perform this step in a fume hood, as chlorine gas may evolve.

9.5.14. The samples are then ready for analysis. Note: A basis of 30mL is used to calculate the final results of the samples.

9.6. **Digestion of Water, TCLP and SPLP Leachates**

9.6.1. Begin by preparing the working standards as outlined in Table 10.4 above.

9.6.2. Method Blank: Measure 30 mL of reagent water into a digestion tube. Note: For TCLP use 10 mL of the leachate blank and 20 mL of reagent water. For SPLP use 30 mL of leachate blank.

9.6.3. LCS: Measure approximately 10 mL of reagent water into a digestion tube. Add 1.0 mL of the Working Calibration Standard to the digestion tube and dilute to 30 mL with reagent water. Note: For TCLP use 10 mL of the leachate blank and 19 mL of reagent water. Extra permanganate is necessary to reduce positive chloride interference from TCLP fluid.

9.6.4. MS/MSD: Measure 30 mL of the selected water sample or SPLP leachate into each of two digestion tubes. Add 1.0 mL of the Working Calibration Standard to each digestion tube. Note: For TCLP use 10 mL of the sample leachate and 20 mL of reagent water.

9.6.5. Client samples: Measure 30 mL of the water sample or SPLP leachate into a digestion tube. Note: For TCLP use 10 mL of the sample leachate and 20 mL of reagent water.

9.6.6. Add 1.5 mL of concentrated H_2SO_4 and 0.75 mL of concentrated HNO_3 to each digestion tube.

9.6.7. Add 5.0 mL of $KMnO_4$ solution to each of the digestion tubes and allow them to stand at least 15 minutes. Note: If the samples do not maintain their purple color at this step, add an additional 5.0mL of the $KMnO_4$ solution and wait an additional 15 minutes. If the purple color is still not maintained, use less sample volume and repeat this process. Also notify the department supervisor about this situation.

- Note: If additional $KMnO_4$ is added to a sample, then additional $KMnO_4$ also needs to be added to the Method Blank and the LCS. In this event, it is imperative to maintain the same final volume for all tubes processed together.

9.6.8. Add 2.5 mL of potassium persulfate solution to each digestion tube.

9.6.9. Heat the tubes for 2 hours in a 90-95°C hot block. (Note: Calibration standards used for EPA 245.1 skip this heated step. This includes the ICV, CCV, and RL standards. Calibration standards used for 7470A are heated just like the samples.)

9.6.10. Remove the tubes from the hot block and allow them to cool to room temperature.

9.6.11. Verify that the volume of each tube is 40mL and bring volume up to 40mL with reagent water if needed.

9.6.12. Add 1.8 mL of hydroxylamine hydrochloride solution to remove the excess permanganate. NOTE: Perform this step in a fume hood, as chlorine gas may evolve.

9.6.13. The samples are now ready for analysis. Note: A basis of 30mL is used to calculate the final results of the samples.

9.7. **Optional reduced volume digestion**

9.7.1. Pour 10 mL of sample (or 3.3 mL of a TCLP leachate) into a 15-mL digestion tube.

9.7.2. Add 0.5 mL of sulfuric acid and 0.3 mL of nitric acid to each digestion tube.

9.7.3. Add 1.7 mL of potassium permanganate solution to each of the digestion tubes and allow them to stand at least 15 minutes. Note: If the samples do not maintain their purple color at this step, add an additional 1.0mL of the $KMnO_4$ solution and wait an additional 15 minutes. If the purple color is still not maintained, use less sample volume and repeat this process. Also notify the department supervisor about this situation.

- Note: If additional $KMnO_4$ is added to a sample, then additional $KMnO_4$ also needs to be added to the Method Blank and the LCS. In this event, it is imperative to maintain the same final volume for all tubes processed together.

9.7.4. Add 0.8 mL of potassium persulfate to each digestion tube.

9.7.5. Cap and place digestion tubes in the hot block for 2 hours at 90-95ºC.

9.7.6. Remove the tubes from the hot block and allow them to cool to room temperature

9.7.7. Add 0.6 mL of hydroxylamine hydrochloride solution to remove the excess permanganate. NOTE: Perform this step in a fume hood, as chlorine gas may evolve.

9.8. **Ghost Wipe™ Digestion**

9.8.1. Begin by preparing the working standards as outlined in Table 10.5 above.

9.8.2. Method Blank: Place one unused Ghost Wipe™ in a digestion tube.

9.8.3. LCS: Place one unused Ghost Wipe™ in a digestion tube and spike with 1.0 mL of the Working Calibration Standard.

9.8.4. Add 5 mL of reagent water to all digestion tubes including calibration curve, ICV/CCV, Method Blank, LCS, MS/MSD, and Client Samples.

9.8.5. Add 5 mL of concentrated HNO_3 to all digestion tubes and place them into a hot block at 90-95 °C for a minimum of 15 minutes. NOTE: It is necessary to continue heating until the Ghost Wipes™ have completely dissolved.

9.8.6. Remove the tubes from the hot block and allow them to cool to room temperature.

9.8.7. Add 5 mL of 1:1 HCl, 10 mL of reagent water and 5 mL of potassium permanganate solution to each tube and cover with cap. Place each tube back into the 90-95 °C hot block and allow them to digest for 15 minutes.

9.8.8. Remove the tubes and allow them to cool to room temperature.

9.8.9. Add 1.8 mL of hydroxylamine hydrochloride solution to remove the excess permanganate. NOTE: Perform this step in a fume hood, as chlorine gas may evolve.

9.8.10. The samples are then ready for analysis.

9.9. **Analysis by Perkins Elmer FIMS 400**

9.9.1. Before startup of the instrument, inspect the pump tubing for signs of wear and replace if necessary.

9.9.2. Check gas supply. Argon pressure should be regulated to 50 psi.

9.9.3. Turn computer on and log in according to instructions given by the IT staff. Confirm FIMS main power switch is in the on position. After confirmation of the switch setting, double click on the WinLab icon to initialize the instrument setup routine. After routine is complete go to toolbar at the top of the screen and double click on the Method window. Select the correct operating method (See the supervisor) and double click to load the method.

9.9.4. Allow the instrument to warm up for at least one hour. This allows the instrument to stabilize before analysis begins and will eliminate instrument drift as analysis occurs.

9.9.5. Place the standards in the autosampler cups in the following sequence: Calibration Blank-Position 1, RL(0.2 for Waters, 0.5 for Soils)-Position 2, 1.0 ug/L-Position 3, 2.0 ug/L-Position 4, 5.0 ug/L-Position 5, 10.0 ug/L-Position 6, Low Level CHK-Position 7 and ICV/CCV-Position 8.

9.9.6. Place the Reductant line into the Stannous Chloride solution and the Carrier line into the Hg Carrier solution prior to analysis. The Reductant line has a red connector and uses the red-red pump tubing while the Carrier line uses the yellow-blue tubing. Verify that these lines are properly connected according to the diagram on the instrument manifold.

9.9.7. The autosampler table is set up as follows. At one of the computer workstations, double click on the Limslink icon. Follow the instructions for creating a Lims autosampler for the FIMS. Close and exit the Lims spreadsheet. Return to the FIMS WinLab menu. Locate the File menu on the toolbar and click. Go to Open Autosampler and double-click. Locate the autosampler table created and identified in the Lims method. Double click. Autosampler table is now loaded into the FIMS autosampler method.

9.9.8. Load samples in the positions indicated on the autosampler menu. Return to FIMS WinLab menu. Locate Auto icon on the toolbar. Click and the automated analysis window opens. Double click on gray SET UP tab and click on correct method, hit ok. Double click on the Results Data Set. Type in the date of the analysis and hit enter. This saves the data to this results file.

9.9.9. Click on the Analyze tab on the automated analysis window. Click the Analyze All button. The instrument will now perform the automated analysis in the sequence indicated by Table 4.

9.10. **Analysis by Cetac M-7500/M7600 QuickTrace Mercury Analyzer**

9.10.1. Open Quicktrace software and turn on the lamp. Allow 30 minutes for the unit to stabilize. Verify that the gas pressure is between 110 and 120 psi. Empty drain bottle if needed. Fill the reagent bottle with stannous chloride and verify that the rinse bottle is filled adequately..

9.10.2. Click on Instrument tab in the toolbar, set the carrier gas to 100mL/min. Inspect pump tubing, replace any worn tubing and then lock into place. Place rinse tubing and recirculator into rinse bottle and stannous line into the reagent bottle. Do not lock shoe clamps on the pump tubing at this time.

9.10.3. In the Instrument tab click on the auto-sampler button, turn on the rinse pumps and lower sipper into rinse station. Verify that the vents are open on the waste container.

9.10.4. Open the method template appropriate to the run by clicking on File-Open-QuickTrace-Templates-Pace Templates.

9.10.5. Lock down shoe clamps, click on the analyzer button. Set pump speed to 35% and start pumps. Verify a smooth flow in both the auto-sampler line and the stannous line.

9.10.6. Open the optical cabinet door by loosening the thumbscrew on the front of the instrument. Verify sample flowing over the center post in the Gas Liquid Separator (GLS). Place Chemwipe™ by exhaust port on top of GLS. Increase gas to 350 mL/min and pump speed to 100%, pinch drain tubing allowing several bubbles to rise up the center post to wet it fully. Center post should change from a frosted look to clear. Remove Chemwipe™ and allow GLS to drain fully. Reduce carrier gas back to 100mL/min as well as setting pump speed to 35%.

9.10.7. Attach the naphyion to the exhaust port at the top of the GLS and close the optical cabinet door. Allow several minutes to stabilize and click on the lamp status button located in the analyzer tab and record the lamp current in the logbook.

9.10.8. Click on the Sequence button in the toolbar and enter the sample information into the table. Place the standards in the appropriate slot on the auto-sampler; 0=S:1, RL(0.2 for Waters, 0.5 for Soils)=S:2, 1.0=S:3, 2.0=S:4, 5.0=S:5, 10.0=S:6, ICV/CCV=S:7. Pour samples and place in appropriate slots on the auto-sampler. Then go to File→Save As MMDDYYMethod(i.e.-040112S for Soil run on 04/01/16). Save file to QuickTrace\Data.

9.10.9. Click the GO button in the toolbar to begin analysis. The QuickTrace will perform an autozero and a calibration designated by the method selected, followed by an analysis of the samples entered into the sequence table. Record the absorbance of the 10 ug/L standard in the log book.

9.10.10. Upon completion of analysis place the stannous tubing in a 10% Nitric acid solution and allow to rinse for 10 minutes. Disconnect the GLS exhaust tubing from the top. Increase carrier gas to 350mL/min and pump speed to 100%. Place Chemwipe by exhaust port and pinch drain tubing. Allow solution to bubble up over the center post and drain out completely to clean the GLS. Repeat 2-3 times to ensure full cleaning of the post. If pumps stop due to overflow sensor just restart and continue.

9.10.11. Place stannous line in reagent water to rinse and remove rinse tubing from rinse bottle and place in plastic bag, leave recirculator tubing in the rinse bottle.

9.10.12. Allow autosampler rinse station to dry fully and no more rinse should be seen in the recirculator tubing. Remove the stannous line from reagent water and raise the sipper. Remove recirculator line from rinse bottle and place in bag with the rest of the rinse tubing. Allow all lines to run dry, when nothing can be seen moving through the waste line close the vents on the waste container.

9.10.13. Click Instrument Tab, Analyzer. Stop pumps and release shoe clamps. Loosen the tubing to prevent further wear. Set carrier gas to 0 mL/min, close gas off at regulator as well, and turn off the lamp.

9.10.14. Software should be closed if the unit will not be used for an extended period of time (>1day).

9.11. **Example Analytical Sequence**

Typical Sequence with Continuing Calibration

Run Number	Sample Description
1	CRDL
2	CCV
3	CCB
4	Method Blank
5	LCS
6	Sample 1
7	Sample 1-MS (or MS1; 245.1 only)*
8	Sample 1-MSD (7470A and 7471B)
9	Post Digestion Spike
10	Sample 2
11	Sample 3
12	Sample 4
13	Sample 5 (or Sample 4 Dup if requested)
14	CCV
15	CCB
16	Sample 6
17	Sample 7
18	Sample 8
19	Sample 9
20	Sample 10
21	Sample 11
22	Sample 12 (or Sample 11 MS2; 245.1 only)*
23	Sample 13
24	Sample 14
25	Sample 15
26	CCV
27	CCB
28-32	Sample 16-20
33	CCV
34	CCB

*MS required for 10% of samples for 245.1

10. DATA ANALYSIS AND CALCULATIONS

10.1. Quantitative Identification

10.1.1. The instrument software automatically calculates the Mercury concentration of the sample from a comparison of the sample absorbance reading and the calibration curve.

10.2. **Calculations**

See the Laboratory Quality Assurance Manual for equations for common calculations.

Quantitative results are calculated as shown in Equation 10-1, -2, and -3:

Equation 10-1:

$$\text{Mercury aqueous}\left(\frac{\mu g}{L}\right) = \frac{\boldsymbol{ppb\ Hg\ x\ 60\ mL}}{\boldsymbol{40\ mL}} \times \mathbf{D}$$

where: 60 mL is the final volume of the sample

40 mL is the initial sample volume.

D is any dilution factor required.

Equation 10-2:

$$\text{Mercury TCLP}\left(\frac{\mu g}{L}\right) = \frac{\boldsymbol{ppb\ Hg\ x\ 60\ mL}}{\boldsymbol{6\ mL}} \times \mathbf{D}$$

where: 60 mL is the final volume of the sample

6 mL is the initial sample volume.

D is any dilution factor required.

Equation 10-3:

$$\text{Mercury solid}\left(\frac{\mu g}{kg}\right) = \frac{\boldsymbol{ppb\ Hg\ x\ Vf}}{\boldsymbol{weight\ of\ sample}} \times \mathbf{D}$$

where: Vf is the final volume of the sample

D is any dilution factor required.

10.3. **Epic Pro Reporting**

Digestion prep data is recorded in the electronic logbook and saved as the batch ID and analysis. The analyst must document any sample or batch information determined to be outside normal procedure in either the Sample Notes or Batch Notes (including adding additional Potassium Permanganate if needed).

Review all digestion data for data entry errors and Save the finished data in the logbook. Send batch for secondary review. Clone the MPRP batch to create an analytical batch for the instrument analyst. Post data from the Electronic logbook into Epic Pro.

Go to Epic Pro and open the batch to check the validation report. Check for data entry errors and quality control issues before exiting the screen. Submit batch paperwork for secondary review Quality Control and Method Performance

11.0 Quality Control and Method Performance

11.1 Batch QC

The following QC samples are prepared and analyzed with each batch of samples. Refer to Appendix A for acceptance criteria and required corrective action.

QC Item	Frequency per batch
Method Blank (MB)	1 per batch of 20 or fewer samples.
Laboratory Control Sample (LCS)	1 per batch of 20 or fewer samples.
Matrix Spike/Duplicate (MS/MSD)	1 MS/MSD pair per batch of 20 or fewer samples for EPA 7470A and EPA 7471B. 1 MS per 10 samples for EPA 245.1.
Sample Duplicate	Sample/Sample Dup run if requested by a client or for verification purposes.

11.2 Instrument QC

The following Instrument QC checks are performed. Refer to Appendix A for acceptance criteria and required corrective action.

QC Item	Frequency
Initial Calibration	Every 24 hours.
Initial Calibration Verification (ICV)	Immediately after each Initial Calibration.
Initial Calibration Blank (ICB)	Immediately after each Initial Calibration Verification (ICV) Standard.
Continuing Calibration Verification (CCV)	After the ICV as part of the Initial Calibration (required for EPA 245.1). (Referred to as the IPC solution in the EPA 245.1 method.) Prior to the analysis of any samples, after every 10 samples, and at the end of a run.
Continuing Calibration Blank (CCB)	Prior to the analysis of any samples, after every 10 samples, and at the end of a run. Immediately following each Continuing Calibration Verification Standard.
Reporting Limit Verification/Lower Limit of Quantitation Check/Contract Reporting Detection Limit (CRDL)	At the beginning of the batch, before any samples including QC are run.

11.3 Method Performance

11.3.1 Method Validation

11.3.1.1 Detection Limits

Detection limits (DL) and limits of quantitation (LOQ) are established at initial method setup and verified on an on-going basis thereafter. Refer to Pace ENV corporate SOP ENV-SOP-CORQ-0011 Method Validation.

11.4 Analyst Qualifications and Training

Employees that perform any step of this procedure must have a completed Read and Acknowledgment Statement for this version of the SOP in their training record. In addition, prior to unsupervised (independent) work on any client sample, analysts that prepare or analyze samples must have successful initial demonstration of capability (IDOC) and must successfully demonstrate on-going proficiency on an annual basis. Successful means the initial and on-going DOC met criteria, documentation of the DOC is complete, and the DOC record is in the employee's training file. Refer to laboratory SOP ENV-SOP-LENE-0110, *Training Procedures* for more information.

12. DATA REVIEW AND CORRECTIVE ACTION

12.1. Data Review

Pace's data review process includes a series of checks performed at different stages of the analytical process by different people to ensure that SOPs were followed, the analytical record is complete and properly documented, proper corrective actions were taken for QC failure and other nonconformance(s), and that test results are reported with proper qualification.

The review steps and checks that occur as employee's complete tasks and review their own work is called primary review.

All data and results are also reviewed by an experienced peer or supervisor. Secondary review is performed to verify SOPs were followed, that calibration, instrument performance, and QC criteria were met and/or proper corrective actions were taken, qualitative ID and quantitative measurement is accurate, all manual integrations are justified and documented in accordance with the Pace ENV's SOP for manual integration, calculations are correct, the analytical record is complete and traceable, and that results are properly qualified.

A third-level review, called a completeness check, is performed by reporting or project management staff to verify the data report is not missing information and project specifications were met.

Refer to laboratory SOP ENV-SOP-LENE-088, *Data Reduction, Review and Reporting*, for specific instructions and requirements for each step of the data review process.

12.2. Corrective Action

Corrective action is expected any time QC or sample results are not within acceptance criteria. If corrective action is not taken or was not successful, the decision/outcome must be documented in the analytical record. The primary analyst has primary responsibility for taking corrective action when QA/QC criteria are not met. Secondary data reviewers must verify that appropriate action was taken and/or that results reported with QC failure are properly qualified.

Corrective action is also required when carryover is suspected and when results are over range.

Samples analyzed after a high concentration sample must be checked for carryover and reanalyzed if carryover is suspected. Carryover is usually indicated by low concentration detects of the analyte in successive samples analyzed after the high concentration sample.

Sample results at concentrations above the upper limit of quantitation must be diluted and reanalyzed. The result in the diluted samples should be within the upper half of the calibration range. Results less than the mid-range of the calibration indicate the sample was over diluted and analysis should be repeated with a lower level of dilution. If dilution is not performed, any result reported above the upper range is considered a qualitative measurement and must be qualified as an estimated value.

Refer to Appendix B for a complete summary of QC, acceptance criteria, and recommended corrective actions for QC associated with this test method.

13. POLLUTION PREVENTION AND WASTE MANAGEMENT

Pace proactively seeks ways to minimize waste generated during our work processes. Some examples of pollution prevention include but are not limited to: reduced solvent extraction, solvent capture, use of reusable cycletainers for solvent management, and real-time purchasing.

The EPA requires that laboratory waste management practice to be conducted consistent with all applicable federal and state laws and regulations. Excess reagents, samples and method process wastes must be characterized and disposed of in an acceptable manner in accordance with Pace's Chemical Hygiene Plan / Safety Manual.

14. MODIFICATIONS

A modification is a change to a reference test method made by the laboratory. For example, changes in stoichiometry, technology, quantitation ions, reagent or solvent volumes, reducing digestion or extraction times, instrument runtimes, etc. are all examples of modifications. Refer to Pace ENV corporate SOP ENV-SOP-CORQ-0011 *Method Validation and Instrument Verification* for the conditions under which the procedures in test method SOPs may be modified and for the procedure and document requirements.

14.1. Hydrochloric acid is used in place of sulfuric acid in making the stannous chloride solution. This modification is used to keep the stannous chloride from precipitating out. This precipitation would cause the instrument lines to clog and force the instrument to be inoperable. Using the HCl eliminates this and ensures longer stability of the stannous chloride solution.

14.2. For solid samples, well homogenized portions are weighed as per 7471B. Triplicate portions of solid samples are not taken as per 7471A.

15. RESPONSIBILITIES

Pace ENV employees that perform any part this procedure in their work activities must have a signed Read and Acknowledgement Statement in their training file for this version of the SOP. The employee is responsible for following the procedures in this SOP and handling temporary departures from this SOP in accordance with Pace's policy for temporary departure.

Pace supervisors/managers are responsible for training employees on the procedures in this SOP and monitoring the implementation of this SOP in their work area.

16. ATTACHMENTS

None.

17. REFERENCES

17.1. Methods for the Determination of Metals in Environmental Samples, Supplement 1 (EPA/600/R-94/111), Revision 3.0, Method 245.1.

17.2. EPA Test Methods for Evaluating Solid Waste. SW-846, Third Edition, Update IV, 2/2007, Methods 7000B and 7471B.

17.3. EPA Test Methods for Evaluating Solid Waste. SW-846, Third Edition, Update II, 9/1994, Methods 7470A and 7471A.

17.4. EPA Test Methods for Evaluating Solid Waste. SW-846, Third Edition, Update I, 7/1992, Method 7000A.

17.5. Federal Register, Volume 72, Page 11200, Method Update Rule.

17.6. Pace Quality Assurance Manual - most current version.

17.7. National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, "Quality Systems"- most current version.

18. REVISION HISTORY

This Version: ENV-SOP-LENE-0059_V2

Section	Description of Change
All	New SOP template

This document supersedes the following document(s):

Document Number	*Reason for Change*	*Date*
S-KS-M-006-rev.11	Section 10 – Converted standard and reagent prep into table format Table 10.2 – Added standard expiration and storage Section 10.4.1 – Added note about water ICAL prep. 245.1 no heat and 7470 w/ heat Section 10.5.1 – Added note about soil ICAL prep. Same as samples Section 11 – Reworded and added general descriptions Section 12.2.9 – Revised add 10mL of DI to bring volume to 25mL with DI. Revised note to add additional KMnO4 solution instead of adding neat crystals. Section 12.2.12 – Added verify 30mL volume and bring to 30mL if necessary before the hydroxylamine addition. The 30mL final volume was after the hydroxylamine addition in previous revision. Section 12.2.14 – Added note about 30mL basis Section 12.3.7 – Revised note to add additional KMnO4 solution instead of adding neat crystals. Section 12.3.9 – Revised note. 245.1 ICAL no heat and 7470 ICAL w/ heat Section 12.3.11 – Added 40mL volume verification, and bring to 40mL if necessary Section 12.3.13 – Added note about 30mL basis Section 12.4.3 – Added 15min wait to see if purple color sticks Table 13.1 – Reworded and removed Replicate Table 13.2 – Added sample QC table for Replicate Section 14 – Added note about 30mL final volume basis used to calc results Section 17 – Removed 7470 mod about no heat ICAL Attachments II, III, and IV - Added	February 3, 2014
S-KS-M-006-rev.12	SOP - Updated to latest prescribed format. Added sections for Instrument/Equipment Maintenance and Troubleshooting. Section 10 – Added equivalency statement. Table 10.1– Updated reagent sources/item #'s Section 12.7.9 – Removed Autozero step and replaced with following section.	February 23, 2015
S-KS-M-006-rev.13	Section 12.2.4-Corrected reference to Sample Homogenization SOP Section 10.2, 10.3 – Intermediate (Working) Spike Solution verification added.	September 18, 2015
S-KS-M-006-rev.14	Table 13.1, Error correction; "Phosphorus" removed as the element spiked.	October 5, 2015

Document Number	*Reason for Change*	*Date*
S-KS-M-006-rev.15	SOP – Revised formatting and Pace Inc. to Pace LLC Section 2.0 – Removed reference to FIMS, sentences restructured. Table 7.1 – Added Method 245.1 samples held for 24 hours after preservation and before prep begins. Section 12.1 – Added not filtering Method 245.1 samples for Total Mercury. Section 12.2.2 – Weight range of boiling stones changed. Section 12.2.5.1 – Added Section 12.2.9 – Added to maintain same final volumes for all tubes processed. Section 12.3.7 – Added to maintain same final volumes for all tubes processed. Section 12.7.7 – Added clarification to exhaust line connections.	December 20, 2016
S-KS-M-006-rev.16	SOP – Revised cover. Table 13.1 – Revised for MS/MSD recovery using 7471B is 80-120%. Section 12.7 – Revised instrument pump speed from 50% to 35%.	September 5, 2017
S-KS-M-006-rev.17	Table 13.1—Added RSD criteria.	January 5, 2018
S-KS-M-006-rev.18	SOP – Revised cover to 2018 dates Section 11.1.2 and 11.1.3 from rev. 17 removed (Not Applicable Calibration techniques) Section 18.3.2 – Changed RSD criteria to 20%.	July 18, 2018
SOP-LENE-0059-01	Master Control Published	October 8, 2018
ENV-SOP-LENE-0059-02	Table 10.4 and Table 10.5 – Revised for terminology Section 12.3.3 – Revised LCS instructions Section 12.3.4 – Revised MS/MSD instructions	September 4, 2019

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Notes

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Pace Analytical™

STANDARD OPERATING PROCEDURE

SEMIVOLATILE ORGANICS BY GC/MS

Reference Methods: SW-846, Method 8270C

Local SOP Number:	S-KS-O-013-rev.16
Effective Date:	Date of Final Signature
Supersedes:	S-KS-O-013-rev.15

Approvals

Laboratory General Manager — Date: 5/10/18

Laboratory Quality Manager — Date: 5-10-18

Department Manager — Date: 5-10-18

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
Signature	Title	Date
Signature	Title	Date

S-KS-O-013-rev.16

TABLE OF CONTENTS

1. Purpose/Identification of Method

1.1. This Standard Operating Procedure (SOP) documents the procedures used by PASI – Kansas to determine the concentration of semivolatile organic compounds (SVOCs) in environmental samples. The laboratory utilizes GC/MS and bases these documented procedures on those listed SW-846 Method 8270C.

2. Summary of Method

2.1. Sample extracts are prepared for analysis by an appropriate sample preparation method. The semivolatile organic compounds are introduced into the gas chromatograph (GC) by injecting an aliquot of the sample extract. The GC conditions are programmed to separate the analytes. The GC effluent is directly introduced to a mass spectrometer (MS) for both identification and quantification of analytes. Analytes are identified by comparison of their mass spectra with spectra of authentic standards. Analytes are quantified by comparing the response of a selected major (quantitation) ion relative to an internal standard using a multi-point calibration curve.

3. Scope and Application

3.1. Personnel: The policies and procedures contained in this SOP are applicable to all personnel involved in the analytical method or non-analytical process.

3.2. This procedure may be used to determine concentrations of neutral, acidic, and basic semivolatile organic compounds in extracts prepared from many types of water samples, soil samples and wastes. Analytes must be soluble in dichloromethane and amenable to capillary gas chromatography. Specific compound classes include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols.

4. Applicable Matrices

4.1. This SOP is applicable to water and most solid samples, regardless of moisture content. Common matrices are ground and surface water, wastewater, aqueous sludge, sediment, soils, oils and other solid samples. Procedures may need to be adapted to address limits in the method or equipment that might hinder or interference with sample analysis. All adaptations made to address matrix related modifications must be documented within the analytical data.

5. Limits of Detection and Quantitation

5.1. The reporting limit (LOQ) for all analytes is shown in the table below for this method. All current MDLs are listed in the LIMS and are available by request from the Quality Manager.

Table 5.1 Limits of Quantitation

Analyte	PQL water (ug/L)	PQL soil (ug/kg)	Analyte	PQL water (ug/L)	PQL soil (ug/kg)
1,2,4-Trichlorobenzene	10	330	Benzo(b)fluoranthene	10	330
1,2-Dichlorobenzene	10	330	Benzo(g,h,i)perylene	10	330
1,2-Diphenylhydrazine	10	330	Benzo(k)fluoranthene	10	330
1,3-Dichlorobenzene	10	330	Benzoic acid	50	1670
1,4-Dichlorobenzene	10	330	Benzyl alcohol	20	660
2,4,5-Trichlorophenol	50	1600	Bis (2-Chloroethoxy)methane	10	330
2,4,6-Trichlorophenol	10	330	Bis (2-Chloroethyl) ether	10	330
2,4-Dichlorophenol	10	330	Bis (2-Chloroisopropyl) ether	10	330
2,4-Dimethylphenol	10	330	bis(2-Ethylhexyl)phthalate	10	330
2,4-Dinitrophenol	50	1670	Butylbenzylphthalate	20	330
2,4-Dinitrotoluene	10	330	Chrysene	10	330
2,6-Dinitrotoluene	10	330	Dibenz (a,h) anthracene	10	330
2-Chloronaphthalene	10	330	Dibenzofuran	10	330
2-Chlorophenol	10	330	Diethylphthalate	10	330
2-Methylnaphthalene	10	330	Dimethylphthalate	10	330
2-Methylphenol	10	330	Di-n-butylphthalate	10	330
2-Nitroaniline	50	660	Di-n-octylphthalate	10	330
2-Nitrophenol	10	330	Fluoranthene	10	330
3&4-Methylphenol	10	330	Fluorene	10	330
3,3'-Dichlorobenzidine	20	660	Hexachloro-1,3-butadiene	10	330
3-Nitroaniline	50	660	Hexachlorobenzene	10	330
4,6-Dinitro-2-methylphenol	50	1670	Hexachlorocyclopentadiene	10	330
4-Bromophenylphenyl ether	10	330	Hexachloroethane	10	330
4-Chloro-3-methylphenol	20	660	Indeno(1,2,3-cd)pyrene	10	330
4-Chloroaniline	20	660	Isophorone	10	330
4-Chlorophenylphenyl ether	10	330	Naphthalene	10	330
4-Nitroaniline	50	660	Nitrobenzene	10	330
4-Nitrophenol	50	1670	N-Nitroso-di-n-propylamine	10	330
Acenaphthene	10	330	N-Nitrosodiphenylamine	10	330
Acenaphthylene	10	330	Pentachlorophenol	50	1670
Aniline	10	330	Phenanthrene	10	330
Anthracene	10	330	Phenol	10	330
Benz(a)anthracene	10	330	Pyrene	10	330
Benzo(a)pyrene	10	330			

Table 5.2 Other Amenable Compounds

Analyte	PQL water (ug/L)	PQL soil (ug/kg)		Analyte	PQL water (ug/L)	PQL soil (ug/kg)
2,3,4,5-Tetrachlorophenol	10	330		Benzenethiol (Thiophenol)	50	1670
2,3,5,6-Tetrachlorophenol	10	330		Benzidine	50	1670
3,4,5-Trichlorophenol	10	330		Benzo(j)fluoranthene	10	330
2,5-Dichlorophenol	10	330		Benzothiophene	50	1670
2,6-Dichlorophenol	10	330		bis(2-Ethylhexyl)adipate	10	330
3,4-Dichlorophenol	10	330		Carbazole	10	330
1-Methylnaphthalene	10	330		Dibenz(a,h)acridine	50	1670
1-Methylnaphthalene	10	330		Indene	50	330
2,3,4,6-Tetrachlorophenol	50	1670		N-Nitrosodimethylamine	10	330
2-Chlorobenzyl chloride	10	330		Pyridine	10	330
6-Methylchrysene	50	1670		Quinoline	10	330
7,12-Dimethylbenz(a)anthracene	10	330		Terpineol	10	330
Azobenzene	10	330				

6. Interferences

6.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks.

6.2. Interferences by phthalate esters can pose a major problem in all analyses. Common flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials during laboratory operations. Cross-contamination of clean glassware occurs when plastics and samples are handled by personnel. Interferences from phthalates can best be minimized by avoiding the use of plastics in the laboratory. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination.

6.3. Matrix interferences may be caused by high concentration contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the site being sampled.

6.4. Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent (methylene chloride) between sample injections. When a concentrated sample is injected, a solvent blank should follow to ensure there is no carryover.

6.5. N-Nitrosodiphenylamine and 1, 2-Diphenylhydrazine decompose in the GC injection port forming Diphenylamine and Azobenzene, respectively. As a result, it is these decomposition products that are present in the calibration standards and LCS/MS spiking solution.

7. Sample Collection, Preservation, Shipment and Storage

Table 7.1 Sample Collection, Preservation, Shipment and Storage

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous	1-liter amber glass	N/A	≤6ºC, but not freezing.	7 days from collection.
Solid	4-oz. glass jar	N/A	≤6ºC, but not freezing.	14 days from collection.
Extracts	2-5mL glass vials, same as used for standard storage	N/A	≤–10°C	40 days from extraction.

8. Definitions

8.1. Definitions of terms found in this SOP are described in the Pace Analytical Services Quality Manual, Glossary Section.

9. Equipment and Supplies

Table 9.1 Equipment and Supplies

Supply	Vendor	Model / Version	Comments
Gas Chromatograph	Agilent	7890A	or equivalent
Mass Spectrometer	Agilent	5975	or equivalent
Data System	Thruput Systems, Inc.	Target, version 3.4	
Vacuum Pump (Rough)	Edwards	E2M2	or equivalent
Autosampler	Hewlett-Packard	7683	or equivalent
Analytical Column	Supelco	SLB-5ms	30m, 0.25mm, 0.25 um, or equivalent
Electron Multiplier	Agilent	G1099-80001	High Energy Dynode, or equivalent
EI Filament	Agilent	G2590-60053	High Temp filament for 5973, or equivalent
Volumetric Flasks	Various	Class A	5mL, 10mL, 50mL, 100mL
Glass Autosampler Vials	Fisher	03-375-2S	2mL, amber
Borosilicate Inserts	Fisher	03-375-3B	400uL low volume vial inserts
Gas tight syringes	Hamilton	1700 Series	10-, 25-, 100-, 500-, 1000-uL
Microdispensers	Fisher	21-176E	100 uL
Replacement Bores	Fisher	21-175-25	

10. Reagents and Standards

Table 10.1 Reagents and Standards

Reagent/Standard	Concentration/ Description	Vendor/ Item #
Methylene chloride	Pesticide analysis grade	Fisher / D151 or equivalent
Methanol	Pesticide analysis grade	Fisher / A451 or equivalent

10.1. Preparation Procedures

10.1.1. Standards for injection into the GC/MS are prepared in methylene chloride. Standards for addition into samples prior to extraction are prepared in methanol. A label containing the concentration, standard log ID number, and expiration date must be affixed to the outside of every standard container. Do not assign expiration dates that exceed the manufacturer's recommended expiration date.

10.2. 8270C Surrogate Spiking solution

10.2.1. Surrogate standards are added to all samples and QC samples before extraction. The compounds specified for this purpose are:

Table 10.2 Surrogate Compounds

Acid Surrogates	Base/Neutral Surrogates
Phenol-d_6	Nitrobenzene-d_5
2,4,6-Tribromophenol	Terphenyl-d_{14}
2-Fluorophenol	2-Fluorobiphenyl

10.2.2. Prepare a single surrogate standard spiking solution in methanol that contains the acid surrogates at a concentration of 75 ug/mL and the base/neutral surrogates at 50 ug/mL and assign a six-month expiration date. Verify the solution prior to use according to SOP S-KS-O-003, Organic Extraction Spike Fortification, and store in amber glass vials at ≤6°C. Spike all QC and client samples with a 1.0 mL aliquot prior to extraction.

10.3. 8270C Laboratory Control Sample/Matrix Spike (LCS/MS) solution

10.3.1. Prepare the 8270C LCS/MS spiking solution in methanol at the concentrations are listed in Attachment I and assign a six-month expiration date. Verify the solution prior to use according to SOP S-KS-O-003, Organic Extraction Spike Fortification, and store in amber glass vials at ≤6°C. Spike the LCS, MS and MSD with a 1.0 mL aliquot prior to extraction.

10.4. TCLP/SPLP Laboratory Control Sample/Matrix Spike (LCS/MS) solution

10.4.1. Prepare the TCLP/SPLP LCS/MS spiking solution in methanol at the concentrations are listed in Attachment II and assign a six-month expiration date. Verify the solution prior to use according to SOP S-KS-O-003, Organic Extraction Spike Fortification, and store in amber glass vials at ≤6°C. Spike the TCLP/SPLP LCS, MS and MSD with a 1.0 mL aliquot prior to extraction.

10.5. Internal Standard Solution

10.5.1. Prepare the internal standard solution in methylene chloride containing the following compounds at a concentration of 200 ug/mL: 1,4- Dichlorobenzene-d4, Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12, and Perylene-d12. Assign a six-month expiration date and store in amber glass vials at ≤–10°C.Add 10 uL of internal standard solution to 100 uL of every standard, sample and QC sample injected. This will yield and internal standard concentration of 20 ug/mL.

10.6. DFTPP Tuning Standard:

10.6.1. Prepare the tuning standard solution in methylene chloride containing the following compounds at a concentration of 50 ug/mL: decafluorotriphenylphosphine (DFTPP), 4,4'-DDT, pentachlorophenol, and benzidine. Assign a six-month expiration date and store in amber vials at at ≤–10°C.

10.6.2. 1 ul is injected to give an on column amount of 50 ng.

10.7. Working Calibration Standards

10.7.1. Prepare calibration standards in methylene chloride at a minimum of five (nine is suggested) concentration levels for each analyte of interest (5,10, 20, 40, 50, 60, 70, 80, 100 ug/mL). Assign a six-month expiration date and store in amber vials at ≤–10°C. These solutions must be replaced after six months, or sooner, if comparison with quality control check standards indicates a problem.

10.8. Second-Source Verification Standard (SSV)

10.8.1. Prepare the SSV standard in methylene chloride containing all analytes of interest, purchased from a source independent of the Calibration Standard supplier, at a concentration of 50 ug/mL. Assign a six-month expiration date and store in amber vials at ≤–10°C.

11. Calibration and Standardization

11.1. Tune Verification

11.1.1. The mass spectrometer tune status must be verified prior to initial calibration and at the beginning of each analytical sequence. If the current tune status does not meet the ion abundance criteria (Table 12.2), take corrective actions as outlined in the equipment manufacturers' instructions for re-tuning the mass spectrometer. The tune status must be re-verified after the tuning procedures.

11.2. Analysis of Standards

11.2.1. An initial calibration curve using a minimum of five points is analyzed prior to analyzing client samples. The lowest concentration must be at or below the equivalence of the standard reporting limit. The lowest calibration point reflects the practical quantitation limit for that compound, a level below which all reported results must be qualified as estimated values. Refer to Table 11.1 for compound concentrations.

11.2.2. An analyte must be present and calibration curve in control in order to be reported on the target analyte list. Analytes identified by mass spectral match but not present and in control in the calibration table may be reported as Tentatively Identified Compounds (TICs). Guidelines for identification are listed in Section 12.7.3. Results for these TICs should be reported only on a present/absent basis. However, quantitative results may be reported provided they are qualified as estimated values.

Table 11.1 Target Analyte Initial Calibration Concentrations

Analyte	Std 1 (ug/mL)	Std 2 (ug/mL)	Std 3 (ug/mL)	Std 4 (ug/mL)	Std 5 (ug/mL)	Std 6 (ug/mL)	Std 7 (ug/mL)	Std 8 (ug/mL)	Std 9 (ug/mL)
1,2,4-Trichlorobenzene	5	10	20	40	50	60	70	80	100
1,2-Dichlorobenzene	5	10	20	40	50	60	70	80	100
1,2-Diphenylhydrazine	5	10	20	40	50	60	70	80	100
1,3-Dichlorobenzene	5	10	20	40	50	60	70	80	100
2,4,5-Trichlorophenol	5	10	20	40	50	60	70	80	100
2,4,6-Trichlorophenol	5	10	20	40	50	60	70	80	100
2,4-Dichlorophenol	5	10	20	40	50	60	70	80	100
2,4-Dimethylphenol	5	10	20	40	50	60	70	80	100
2,4-Dinitrophenol	5	10	20	40	50	60	70	80	100
2,4-Dinitrotoluene	5	10	20	40	50	60	70	80	100
2,6-Dinitrotoluene	5	10	20	40	50	60	70	80	100
2-Chloronaphthalene	5	10	20	40	50	60	70	80	100
2-Chlorophenol	5	10	20	40	50	60	70	80	100
2-Methylnaphthalene	5	10	20	40	50	60	70	80	100
2-Methylphenol	5	10	20	40	50	60	70	80	100
2-Nitroaniline	5	10	20	40	50	60	70	80	100
2-Nitrophenol	5	10	20	40	50	60	70	80	100
3&4-Methylphenol	5	10	20	40	50	60	70	80	100
3,3'-Dichlorobenzidine	5	10	20	40	50	60	70	80	100
3-Nitroaniline	5	10	20	40	50	60	70	80	100
4,6-Dinitro-2-methylphenol	5	10	20	40	50	60	70	80	100
4-Bromophenylphenyl ether	5	10	20	40	50	60	70	80	100
4-Chloro-3-methylphenol	5	10	20	40	50	60	70	80	100
4-Chloroaniline	5	10	20	40	50	60	70	80	100
4-Chlorophenylphenyl ether	5	10	20	40	50	60	70	80	100
4-Nitroaniline	5	10	20	40	50	60	70	80	100
4-Nitrophenol	5	10	20	40	50	60	70	80	100
Acenaphthene	5	10	20	40	50	60	70	80	100
Acenaphthylene	5	10	20	40	50	60	70	80	100
Aniline	5	10	20	40	50	60	70	80	100
Anthracene	5	10	20	40	50	60	70	80	100
Benz(a)anthracene	5	10	20	40	50	60	70	80	100
Benzo(a)pyrene	5	10	20	40	50	60	70	80	100
Benzo(b)fluoranthene	5	10	20	40	50	60	70	80	100
Benzo(g,h,i)perylene	5	10	20	40	50	60	70	80	100
Benzo(k)fluoranthene	5	10	20	40	50	60	70	80	100
Benzoic acid	5	10	20	40	50	60	70	80	100
Benzyl alcohol	5	10	20	40	50	60	70	80	100
bis(2-Chloroethoxy)methane	5	10	20	40	50	60	70	80	100
bis(2-Chloroethyl) ether	5	10	20	40	50	60	70	80	100
bis(2-Chloroisopropyl) ether	5	10	20	40	50	60	70	80	100
bis(2-Ethylhexyl)phthalate	5	10	20	40	50	60	70	80	100
Butylbenzylphthalate	5	10	20	40	50	60	70	80	100
Chrysene	5	10	20	40	50	60	70	80	100
Dibenz(a,h)anthracene	5	10	20	40	50	60	70	80	100

Analyte	Std 1 (ug/mL)	Std 2 (ug/mL)	Std 3 (ug/mL)	Std 4 (ug/mL)	Std 5 (ug/mL)	Std 6 (ug/mL)	Std 7 (ug/mL)	Std 8 (ug/mL)	Std 9 (ug/mL)
Dibenzofuran	5	10	20	40	50	60	70	80	100
Diethylphthalate	5	10	20	40	50	60	70	80	100
Dimethylphthalate	5	10	20	40	50	60	70	80	100
Di-n-butylphthalate	5	10	20	40	50	60	70	80	100
Di-n-octylphthalate	5	10	20	40	50	60	70	80	100
Fluoranthene	5	10	20	40	50	60	70	80	100
Fluorene	5	10	20	40	50	60	70	80	100
Hexachloro-1,3-butadiene	5	10	20	40	50	60	70	80	100
Hexachlorobenzene	5	10	20	40	50	60	70	80	100
Hexachlorocyclopentadiene	5	10	20	40	50	60	70	80	100
Hexachloroethane	5	10	20	40	50	60	70	80	100
Indeno(1,2,3-cd)pyrene	5	10	20	40	50	60	70	80	100
Isophorone	5	10	20	40	50	60	70	80	100
Naphthalene	5	10	20	40	50	60	70	80	100
Nitrobenzene	5	10	20	40	50	60	70	80	100
N-Nitroso-di-n-propylamine	5	10	20	40	50	60	70	80	100
N-Nitrosodiphenylamine	5	10	20	40	50	60	70	80	100
Pentachlorophenol	5	10	20	40	50	60	70	80	100
Phenanthrene	5	10	20	40	50	60	70	80	100
Phenol	5	10	20	40	50	60	70	80	100
Pyrene	5	10	20	40	50	60	70	80	100

Table 11.2 Non-standard compounds amenable to analysis by this method

Analyte	Std 1 ug/mL	Std 2 ug/mL	Std 3 ug/mL	Std 4 ug/mL	Std 5 ug/mL	Std 6 ug/mL	Std 7 ug/mL	Std 8 ug/mL	Std 9 ug/mL
2,3,4,5-Tetrachlorophenol	5	10	20	40	50	60	70	80	100
2,3,5,6-Tetrachlorophenol	5	10	20	40	50	60	70	80	100
3,4,5-Trichlorophenol	5	10	20	40	50	60	70	80	100
2,6-Dichlorophenol	5	10	20	40	50	60	70	80	100
3,4-Dichlorophenol	5	10	20	40	50	60	70	80	100
2,5-Dichlorophenol	5	10	20	40	50	60	70	80	100
1-Methylnaphthalene	5	10	20	40	50	60	70	80	100
2,3,4,6-Tetrachlorophenol	5	10	20	40	50	60	70	80	100
1-Methylnaphthalene	5	10	20	40	50	60	70	80	100
2-Chlorobenzyl chloride	5	10	20	40	50	60	70	80	100
6-Methylchrysene	5	10	20	40	50	60	70	80	100
7,12-Dimethylbenz(a)anthracene	5	10	20	40	50	60	70	80	100
Azobenzene	5	10	20	40	50	60	70	80	100
Benzenethiol (Thiophenol)	5	10	20	40	50	60	70	80	100
Benzidine	5	10	20	40	50	60	70	80	100
Benzo(j)fluoranthene	5	10	20	40	50	60	70	80	100
Benzothiophene	5	10	20	40	50	60	70	80	100
bis(2-Ethylhexyl)adipate	5	10	20	40	50	60	70	80	100
Carbazole	5	10	20	40	50	60	70	80	100
Dibenz(a,h)acridine	5	10	20	40	50	60	70	80	100
Indene	5	10	20	40	50	60	70	80	100
N-Nitrosodimethylamine	5	10	20	40	50	60	70	80	100
Pyridine	5	10	20	40	50	60	70	80	100
Quinoline	5	10	20	40	50	60	70	80	100
Terpineol	5	10	20	40	50	60	70	80	100

11.3. Calibration Response Factors

11.3.1. Response factors (RF) establish the relationship of the instruments response in comparison with the concentration of any given analyte. The RF includes the concentration and response of the internal standard as well. By relating the IS concentration and response in an inverse manner, the target analyte concentration is adjusted to account for drift in the instrument on a per injection basis. As instrument response increases as indicated by the response of the internal standard, the concentration of the target is mathematically decreased, and vice versa.

11.3.2. To calculate the RF for any given calibration standard (or calibration verification standard), tabulate the area response of the characteristic ions against concentration for each compound and each internal standard. Calculate response factors (RF) for each compound relative to one of the internal standards. The internal standard selected for the calculation of the RF for a compound should be the internal standard that has a retention time closest to the compound being measured. Response factors are calculated using the following equation.

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

Where:
Ax = Area of the characteristic ion for the compound being measured.

Ais = Area of the characteristic ion for the specific internal standard.
Cis = Concentration of the specific internal standard (ug/mL).
Cx = Concentration of the compound being measured (ug/mL).

11.3.3. Most, if not all modern chromatography data systems are capable of calculating this factor and using it to quantify analyte concentrations. The 8270C method has minimum requirements that these response factors must meet in order to be considered valid. The method uses a subset of the target analyte list to evaluate the performance of the system. These compounds are referred to as the System Performance Check Compounds or the SPCCs. The SPCCs serve as an indicator of instrument sensitivity and, by meeting a minimum value, ensure that the laboratory has adequate sensitivity to analyze and reliably report data for environmental samples.

11.4. Calibration Curve Fit

11.4.1. The calibration curve is a representation of the relationship of the instrument response and analyte concentration. The curve is used to quantitate the concentration of an unknown based on its response and this known relationship. The curve is produced in several ways depending on the nature of the "goodness of fit".

11.4.2. Average Response Factor ($\overline{RF}$): The average response factor is determined by averaging the response factors calculated for each calibration level for each target analyte. The average RF can be used to calculate the concentration of target analytes in samples provided the criteria are met for consistency in the RFs for any given analyte. An average response factor is the default curve fitting option for calibrations. It is in the most basic sense, a linear regression that is forced through zero at the origin. Because of its simplicity and the interception of the y-axis at the origin, this is the preferred technique for curve fitting. A calculation of the percent relative standard deviation (%RSD) is used to determine the acceptability of the use of the $\overline{RF}$ (see Table 11.3).

The % RSD is calculated as follows: $\%RSD = \frac{SD \times 100}{\overline{RF}}$

Where:
SD = Standard deviation of the averaged RFs for a given compound

11.4.3. The average response factor is also used to diagnose the integrity of the chromatography system as it relates to calibration linearity. The Calibration Check Compounds (CCCs) are a subset of the target analyte list that must meet specific criteria (see Table 11.3) for the calibration to be acceptable. For the CCCs, the %RSD for each is compared to the method criteria. If that of any CCC exceeds the criteria, the system needs to be inspected for potential sources of errors and recalibrated.

11.4.4. Linear Regression: The linear regression calibration curve is derived from a least squares regression analysis of the calibration points. A calibration curve based on this technique will have the format of y = ax + b, where "a" is the slope of the line and "b" is the y intercept. In order to use this curve fit technique, a minimum of 5 calibration points must be available and the origin cannot be included as one of the points. This technique works well for calibrations where the response of the instrument is linear in nature but does not necessarily intercept the y-axis at the origin. However, because the linear regression is not forced through the origin, very low levels of contaminants below the response of the lowest calibration point may generate erroneous reportable results. A calculation of the correlation coefficient "r" is used to determine the acceptability of a linear regressed curve (see Table 11.3).

11.4.5. Non-linear Regression: The non-linear regression calibration curve is derived from a least squares regression analysis of the calibration points. A calibration curve based on this technique will have the format of $y= ax^2+bx+c$. In order to use this curve fit technique, a minimum of 6 calibration points must be available and the origin cannot be included as one of the points. This technique works well for calibrations where the response of the instrument gradually decreases with increasing concentrations. Using this technique, an analyst may be able to generate calibration curves with correlation coefficients very close or equivalent to 1.000. However, because the non-linear regression is not forced through the origin, very low levels of contaminants below the response of the lowest calibration point may generate erroneous reportable results. Likewise, high levels of contamination may not be able to be calculated due to regression equations with multiple intercepts of either axis on the calibration plot.

11.4.6. A calculation of the coefficient of determination (COD) is used to determine the acceptability of a non-linear regressed curve (see Table 11.3). Either the low or high calibration points may be dropped to meet linearity criteria provided the laboratory meets the minimum 6 calibration point requirements. Points within the center of the curve may not be dropped unless an obvious problem is discovered and documented. The point must be dropped in its entirety and reanalyzed. Re-analysis should be within the same 12-hour time window and must occur within 8 hours of the original analysis.

11.5. Calibration Verification

11.5.1. Second Source Verification (SSV)

11.5.1.1. In addition to meeting the linearity criteria, any new calibration curve must be assessed for accuracy in the values generated. Accuracy is a function of both the "fit" of the curve to the points used and the accuracy of the standards used to generate the calibration points. By meeting the fit criteria, the accuracy relative to the goodness of fit is addressed. However, because all calibration points are from the same source, it is possible that the calibration points may meet linearity criteria but not be accurately made in terms of their true value.

11.5.1.2. Therefore, to assess the accuracy relative to the purity of the standards, a single standard from a secondary source must be analyzed and the results obtained must be assessed relative to the known true value. This step is referred to as ***Secondary Source Verification*** or, alternatively as ***Initial Calibration Verification***. This secondary source must be from an alternative vendor or, in the event an alternative vendor is not available, from a different lot from the same vendor. The accuracy of the standard is assessed as a percent difference from the true value according to the following equation:

$$\%\text{Difference} = \frac{\left(\text{Result}_{SSV} - \text{True Value}_{SSV}\right)}{\text{True Value}_{SSV}} \times 100$$

11.5.2. Continuing Calibration Verification (CCV)

11.5.2.1. As part of the analytical process, the instrumentation must be checked periodically to determine if the response has changed significantly since the initial calibration was established. This verification process is known as ***Continuing Calibration Verification***. The validity of the initial calibration is checked at the beginning of every analytical sequence and every 12 hours thereafter for as long as the instrument is

analyzing samples and is accomplished by analyzing a midpoint calibration standard (CCV).

11.5.2.2. The values obtained from the analysis of the CCV are compared to the true values and a percent change calculated. The percent change must meet the method specified criteria for the analysis to proceed for an additional 12 hours.

11.5.2.3. The actual determination of change in instrument response is based on the type of curve fit used for each analyte. Calibration curves based on an average response factor are assessed based on the percent difference of the RF calculated for the CCV from the average RF established in the initial calibration. Calibration curves based on a linear or non-linear regression are assessed based on the percent drift of the calculated result from the known true value of the standard. The equations for these calculations are as follows:

$$\%\text{Difference} = \frac{\left(\text{RF}_{\text{CCV}} - \overline{\text{RF}}\right)}{\overline{\text{RF}}} \times 100 \text{ (curves based on } \overline{\text{RF}}\text{)}$$

$$\%\text{Drift} = \frac{\left(\text{Result}_{\text{CCV}} - \text{True Value}_{\text{CCV}}\right)}{\text{True Value}_{\text{CCV}}} \times 100 \text{ (curves based on linear or quadratic regression)}$$

Table 11.3 Calibration Criteria

Calibration Metric	Parameter / Frequency	Criteria	Comments
Calibration Curve Fit	Average Linear Regression Non-linear Regression Percent Relative Error Check on Linear and Non-linear Regression curve fits.	%RSD ≤15% r ≥ 0.99 COD ≥ 0.99 20% of true value of both low curve point (report limit) and midlevel curve point.	If not met, try linear regression fit, then non-linear regression fit. If still not met, take corrective action and recalibrate before analyzing samples. If this criteria is not meet then only non-detects can be reported, all detected amounts must be re-analyzed following a proper curve fit.
System Performance Check Compounds (SPCCs)	N-Nitroso-di-n-propylamine Hexachlorocyclopentadiene 2,4-Dinitrophenol 4-Nitrophenol	Avg RF ≥0.05	Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system.
Calibration Check Compounds (CCCs)	Acenaphthene 1,4-Dichlorobenzene Hexachlorobutadiene N-Nitrosodiphenylamine Di-n-octylphthalate Fluoranthene Benzo(a)pyrene 4-Chloro-3-methylphenol 2,4-Dichlorophenol 2-Nitrophenol Phenol Pentachlorophenol 2,4,6-Trichlorphenol	%RSD ≤30%	%RSD for the calibration check compounds (CCC's) must be ≤30% regardless of curve fit used. If the CCCs are not included on a list of analytes for a project, and therefore not included in the calibration standards, then all compounds of interest must meet a ≤15% RSD criterion.
Second Source Verification Standard	Immediately after each initial calibration	% Diff ±30%	Reprepare and reanalyze the ICV once. If it fails a second time a new initial calibration should be rerun.
Continuing Calibration Verification	Prior to the analysis of any samples and every 12 hours thereafter		If the requirements for continuing calibration are not met, these corrective actions must be taken prior to reanalysis of standards. Only two injections of the same standard are permitted back to back. Note: If two injections are analyzed back to back, both must be reviewed and the latest injection must be used.
	SPCCs	Must meet response criteria listed above	
	Internal Standard RT Internal Standard Response	RT ±30 sec 50 – 200%	Use mid-point standard level of the most recent initial calibration sequence.
	CCCs	RF ± 20% Diff. Result ± 20% Drift	Use for Avg RF calibration curves Use for linear and non-linear calibration curves
	Non-CCC Targets	RF ± 40% Diff. Result ± 40% Drift	Some programs may require control over non-CCC target analytes. In the absence of specified criteria, use those listed here.

11.6. Calibration Corrective Actions

11.6.1. Calibration Linearity Problems

11.6.1.1. Certain target analytes are difficult to chromatograph and behave erratically. The compounds are benzyl alcohol, 4-chloroaniline, hexachlorocyclopentadiene, 2-nitroaniline, 3-nitroaniline, 4-nitroaniline, 3,3'-dichlorobenzidine, pyridine, benzoic acid, and benzidine. These compounds will not be subject to the linearity criteria,

however they must be detectable at the RL as a minimum. In addition, if these analytes are detected the result must be qualified or reanalyzed with an acceptable initial calibration.

11.6.2. Continuing Verification Problems

11.6.2.1. Reanalyze the original CCV standard to determine instrument consistency.

11.6.2.2. Prepare and analyze a new CCV standard to determine preparation consistency / standard integrity.

11.6.2.3. Document instrument maintenance

11.6.2.4. Reanalyze CCV standard to determine if maintenance was effective in restoring performance.

11.6.2.5. Complete recalibration of instrument.

11.6.2.6. If samples were analyzed in spite of verification failures, note the following exceptions for addressing those results. Deviations from this requirement must be noted on the injection log with a thorough explanation for the deviation from policy.

Exception: If calibration verification is above the upper control limit, samples non-detected for those analytes may be reported without reanalysis. Quantitation of spiked QC samples requires an acceptable calibration without exception.

12. Procedure

12.1. GC/MS System Preparation

12.1.1. Configure the GC/MS system to match the following operating parameters based on instrument configuration. The parameters themselves are saved as a method on the chromatography data system. By loading the last method used, the instrument will auto-configure to match the parameters from the last time the system was operated under that method. Verify that the settings in the software match the appropriate configuration.

Table 12.1 Instruments and Operating Parameters

Instrument IDs	Component	Settings and Consumables	
60MSS4	Gas Chromatograph	Column: Supelco SLB-5ms, 30m, 0.25mm, 0.25 um df Inlet Liner: Restek #22401 Inlet Seal: Restek #21306 Column Ferrules: Agilent #5062-3508	Flow: Helium, 1.8 mL/min (constant) Initial Temperature: 50 ºC Initial Time: 2 min. Rate: 22 ºC/min Final Temperature: 320 ºC Final Time: 1.9 min. Injector Temperature: 255 ºC Transfer Line Temperature: 305 ºC MS Source Temperature: 230 ºC MS Quad Temperature: 150 ºC Split Purge On: 0.1 min.
	Mass Spectrometer	Tune File: dftpp.u	
	Autosampler	Sample Washes: 0 Sample Pump: 2 Injection Volume 1.0 uL Syringe Size: 10 uL	PostInj Solvent A Washes: 3 PostInj Solvent B Washes: 2 Viscosity Delay: 0 sec. Plunger Speed: Fast PreInjection Dwell: 0 min PostInjection Dwell: 0 min

12.2. Tune Status Verification

12.2.1. At the beginning of each analytical sequence, prior to the analysis of any samples, the mass spectrometer tune status must be verified by analyzing the DFTPP Tuning Standard.

12.2.2. To evaluate the tune spectra, following the operating instructions for the chromatography data system to access the data file and obtain mass spectra for DFTPP. If the software has a program or macro for automatically selecting the spectra and evaluating the response ratios, use this option. Otherwise, the spectra must be obtained in one the following manners, in the listed order.

1. **Using an average of three scans, centered on the apex of the peak; or,**
2. **Using an average of all scans across the width of the peak, taken at half height; or,**
3. **Using an average of all scans taken across the width of the peak from baseline to baseline.**

A background scan taken immediately before, but not including the peak, must be subtracted.

12.2.3. Evaluate the ion ratios against the criteria below. If the ratios meet the criteria, then analysis may proceed for 12 hours. The window for analysis is 12 hours from the injection time of the DFTPP Tuning Standard. After that, the tune status must be verified again to establish a new analytical window. The same ion abundance criteria used for the DFTPP tune verification coupled with the initial calibration must be used for all subsequent analyses associated with that initial calibration.

Table 12.2 DFTPP Tuning Criteria

Mass (m/z)	Ion Abundance Criteria
51	30.0-80.0% of m/z 198
68	<2.0% of m/z 69
69	Present
70	<2.0% of m/z 69
127	25.0-75.0% of m/z 198
197	<1.0% of m/z 198
198	Base peak, 100% relative abundance
199	5.0-9.0% of m/z 198
275	10.0-30.0% of m/z 198
365	>0.75% of m/z 198
441	Present, but less than m/z 443
442	40.0-110.0% of m/z 198
443	15.0-24.0% of m/z 442

12.2.4. Any changes made to the system must be followed with the reanalysis of the tune verification standard. Any maintenance performed on the physical mass spec components requires recalibration. "Autotunes" may be performed as long as the following CCV meets all criteria for response, retention time and sensitivity.

12.3. Breakdown Verification

12.3.1. Tailing Factor Verification

12.3.1.1. Benzidine and pentachlorophenol should be present at their normal responses, and no peak tailing should be visible. Corrective action must be taken if poor chromatography is noted. Corrective action may include replacing the injection port liner and/or removing the first 6"-12" of the capillary column. Document any instrument maintenance performed in the maintenance log. After corrective action is taken, reinject the DFTPP Tuning Standard.

12.3.2. GC/MS system inertness should also be assessed by calculating the percent breakdown of DDT into the products DDD and DDE. The calculation is performed as follows:

$$\text{DDT degradation} = 100 \times \frac{\text{Sum of Peak Areas for (DDE + DDD)}}{\text{Sum of Peak Areas for (DDT + DDE + DDD)}}$$

12.3.3. Breakdown of DDT should not exceed 20%. See the sections below if DDT breakdown is greater than 20%.

12.3.4. If any organochlorine pesticides are target analytes and the breakdown exceeds 20%, then corrective action must be taken. Corrective action may include replacing the injection port liner and/or removing the first 6"-12" of the capillary column. Document any instrument maintenance performed in the maintenance log. After corrective action is taken, reinject the DFTPP Tuning Standard.

12.3.5. If organochlorine pesticides are <u>not</u> target analytes and the breakdown exceeds 20%, then corrective action may not be necessary as long as all SPCC and CCC criteria are met. (See Table 11.3 for SPCC and CCC criteria.) If all SPCC and CCC criteria are met, then the GC/MS system will be considered sufficiently inert.

12.4. Calibration Verification

12.4.1. After the instrument tune conditions are verified and the system meets tune criteria, the instrument must undergo calibration verification. If it has already been determined that the instrument needs to be recalibrated, follow the procedures listed in Section 11.2 (Analysis of Standards). Otherwise, analyze a Continuing Calibration Verification Standard to determine the current calibration status.

12.4.2. If the CCV meets control criteria, the system is deemed to be in control and analysis of samples may commence. If the CCV does not meet control criteria, follow the corrective action procedures listed Section 11.6 (Calibration Corrective Actions). If the tune verification has been combined with the CCV, the 12-hour analysis window begins from the analysis date / time of the CCV.

Note: In situations where the instrument will run unattended (i.e. overnight), the analyst may load sequential (back-to-back) CCVs in anticipation of that the first in the series may fail due to carry over from a previous sample. If so, both CCVs must be evaluated according

to the protocol set forth in the Quality Assurance Manual within Section 6 – Equipment and Measurement Traceability.

12.5. Sample Preparation

12.5.1. Aqueous samples are prepared according to EPA 3510C. These procedures are contained in a separate standard operating procedure. Refer to SOP S-KS-O-029 for details on the preparation of aqueous samples.

12.5.2. Soil/Solid samples are prepared according to EPA 3546. These procedures are contained in a separate standard operating procedure. Refer to SOP S-KS-O-032 for details on the preparation of soil or solid samples.

12.6. Sample Analysis

12.6.1. Withdraw 100 uL of sample extract and add to a low-volume vial insert that had been placed in an autosampler vial.

12.6.2. Add 10 uL of Internal Standard Solution to the low-volume insert, cap and crimp.

12.6.3. Place on autosampler tray, load ChemStation method '8270', and start instrument.

12.6.4. Process all runs with Target software.

12.6.5. View sample chromatograms and verify analyte identifications (Section 12.7.1)

12.6.6. Post data to EPIC Pro.

12.7. Data Reduction

12.7.1. Qualitative Analysis

12.7.1.1. Retention Time Comparison: The relative retention time (RRT) of the sample component must be within ±0.06 RRT units of the component in the calibration verification standard. Extracted Ion Current Plots (EICPs) may be used to provide a more reliable assignment of RT in the presence of coeluting components.

- Mass Spectrum Comparison: The characteristic ions from the reference mass spectrum are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds are identified as present when the following criteria are met. Note; There are many compounds analyzed by this method that do not display three ions with relative intensity's of over 30% for the compounds. Therefore it is extremely important to review as aspects of the compound for positive detection. Ions, Ion Ratios, Retention Times and spectra. The compounds in attachment III & IV display the primary ion used in this method and various secondary ions in which not all are 30% or greater.

12.7.1.2.

- The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other.
- The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum.
- Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times.

12.7.2. Quantitative Analysis

12.7.2.1. Quantitation is based on the integrated abundance of the target analyte's quantitation ion using the internal standard technique. The GC/MS data system will calculate the concentration of each analyte in the sample extract. If supplied with the preparation parameters, the system may be able to calculate the results back to the original matrix. The calculation for the concentration of the target analyte in the original matrix is listed below and is based on the calibration table in units of ppm (ug/mL).

12.7.2.2. If the initial analysis of the sample or a dilution of the sample has a concentration that exceeds the calibration range, the sample must be analyzed at a higher dilution. Dilutions should be made such that the target analyte is roughly the equivalent of the mid calibration point whenever possible. Sample aliquots are measured in volumetric syringes and brought to volume by the addition of solvent via an appropriate syringe. If dilutions are made on extracts that already contain internal standards, a proportional aliquot of internal standard solution must be added to the diluted extract based on the volume of diluent used.

13. Quality Control

Table 13.1 Batch Quality Control

QC Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Matrix-specific; Reagent water or Ottawa sand	One per 20 samples	1) Target analytes must be less than reporting limit. 2) If results are reported to MDL, target analytes in MB should be non-detect.	1) Re-analyze blank to confirm failure. 2) Qualify results and / or re-extract associated samples. ***Exceptions:*** 1) If sample ND, report sample without qualification 2) If sample result >10x MB detects and sample cannot be reanalyzed, report sample with appropriate qualifier indicating blank contamination. 3) If sample result <10x MB detects, report sample with appropriate qualifier to indicate an estimated value.
Laboratory Control Sample (LCS)	Matrix-specific; Reagent water or Ottawa sand spiked with Method specified compounds: Base / Neutrals 1,2,4-Trichlorobenzene Acenapthene 2,4-Dinitrotoluene Pyrene N-Nitroso-di-n-propylamine 1,4-Dichlorobenzene *OR (alternative)* Full Target List	One per batch of up to 20 samples Acids Pentachlorophenol Phenol 2-Chlorophenol 4-Chloro-3-methylphenol 4-Nitrophenol	Laboratory derived limits Method Specified List: All compounds must pass control criteria, with no exceptions. Full Target List: Marginal exceedances allowed according to NELAC 2003 Chap. 5 D.1.1.2.1.e.	1) Reanalyze the LCS to verify failure 2) If LCS passes, review samples for potential injection problems 3) If problem persists, check spike solution 4) Re-extract samples where possible ***Exceptions:*** 1) If LCS rec > QC limits and these compounds are non-detect in the associated samples, the sample data may be reported with appropriate data qualifiers.
Matrix Spike (MS)	Client sample spiked with all target compounds	One per 10 samples	Laboratory generated limits	If LCS and MBs are acceptable, the MS/MSD chromatogram should be reviewed and it may be reported with appropriate footnote indicating matrix interferences
MSD / Duplicate	MS Duplicate *OR (alternative)* Sample Dup	One for every 10% of samples.	Laboratory generated limits	Report results with an appropriate footnote.

Table 13.1 Sample Quality Control

QC Metric	Components	Frequency	Acceptance Criteria	Corrective Action
Internal Standard	1,4 Dichlorobenzene-d4 Naphthalene-d8 Acenaphthene-d10 Phenanthrene-d10 Chrysene-d12 Perylene-d12	Added to all samples, spikes, control samples and method blanks prior to analysis.	IS peak area within 50-200% of the associated CCV standard. IS retention time within ±30 seconds of the associated CCV standard.	**Recovery Failure:** 1) Re-analyze sample to confirm failure 2) Assess impact of sample matrix 3) In the absence of obvious matrix interference, reanalyze sample. **Retention Time Failure:** 1) If matrix interference is NOT probable, the analytical system must be checked for source of retention time shifting. 2) Affected samples should be reanalyzed in the absence of an obvious instrument or matrix related interference.
Surrogate Standards	Nitrobenzene-d5 2-Fluorobiphenyl Terphenyl-d14 Phenol-d6 2-Fluorophenol 2,4,6-Tribromophenol	Added to all samples, spikes, control samples and method blanks prior to analysis.	Laboratory derived limits	1) Re-analyze extract to confirm failure 2) Assess impact of sample matrix 3) In the absence of obvious matrix interference (high background, extremely dark extract), re-extract sample. ***Exceptions:*** 1) Surr rec above criteria and target compounds < RL, result may be reported with appropriate footnote. 2) Surr rec out of control due to obvious sample matrix interference (i.e. co-elution), report results with appropriate footnote.

14. Data Analysis and Calculations

14.1. Aqueous Sample:

$$\text{Concentration (ug/L)} = \frac{(C_x)(V_x)(DF)}{(V_s)}$$

Where:
C_x= Concentration in extract (ug/mL).
V_v= Volume of final extract (mL).
DF = Dilution factor.
V_s = Volume of water sample extracted (mL).

14.2. Soil/Solid sample:

$$\text{Concentration (ug/kg)} = \frac{(C_x)(V_x)(1000)(DF)}{(W_s)}$$

Where:
C_x = Concentration in extract (ug/mL).
V_v = Volume of final extract (mL).
DF = Dilution factor.
W_s = Weight of soil sample extracted (g).

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. See Table 13.1.

16. Corrective Actions for Out-of-Control Data

16.1. See Tables 11.3 and 13.1.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. See Table 13.1. If there is no additional sample volume to perform re-analyses, all data will be reported as final with applicable qualifiers. If necessary, an official case narrative will be prepared by the Quality Manager or Project Manager.

18. Method Performance

18.1. All applicable personnel must read and understand this SOP with documentation of SOP review maintained in their training files.

18.2. Method Detection Limit (MDL) Study: An MDL study must be conducted annually per S-ALL-Q-004, Method Detection Limit Studies for each matrix per instrument.

18.3. Demonstration of Capability (DOC): Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC) per S-ALL-Q-020, Training Procedures.

18.3.1. Analysis of 4 replicates of reagent water spiked with 1 mL of the 8270C LCS/MS Spiking Solution at a concentration of 50 ug/L or equivalent to the LCS.

18.3.2. Analysis of 4 replicates of Ottawa sand spiked with 1 mL of 8270C LCS/MS Spiking Solution at a concentration of 1670 ug/kg or equivalent to the LCS.

18.3.3. If the recoveries are within the matrix-specific LCS recovery limits and the RSDs are <30%, system performance is acceptable and analysis of samples may begin. If any recovery falls outside the acceptance range, or an RSD exceeds the precision limit, system performance is unacceptable. In this event, correct the problem and repeat the test.

19. Method Modifications

19.1. DFTPP tuning criteria are taken from the USEPA CLP Statement of Work for Organics Analysis, Multi-Media, Multi-Concentration OLM04.2, 5/1999.

20. Instrument Maintenance

20.1 There is relatively low instrument maintenance. The maintenance that needs to be checked routinely is gas pressure for column flow (helium tank). The pressure needs to be monitored and when below 200 PSI needs to be changed. Other maintenance is done on an as needed basis, such as changing the injection port liner, trim column, change septa and gold seal, change out column and clean MS source. Please inform supervisor of issues and your plans for repairing these issues.

21. Trouble Shooting

21.1 No detection of peaks:

21.1.1 Check to make sure that the gases is at sufficient levels above 200 PSI.

21.1.2 Check to make sure that MS is seeing PFTBA (tuning solution), if not switch filaments and try again.

21.1.3 Check to make sure that autosampler is pulling up sample into the needle.

If all of these are OK, then check with supervisor for review of column issues.

22. Safety

22.1. Standards and Reagents: The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Material Safety Data Sheets (MSDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood whenever possible.

22.2. Samples: Take precautions when handling samples. Samples should always be treated as potentially hazardous “unknowns”. The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples. In the event a sample container must be opened, it is recommended to perform this in a hood whenever possible.

22.3. Equipment

22.3.1. Portions of the analytical instrumentation operate at high temperature. Instruments should be turned off or the heated zone temperatures lowered to reduce the risk of thermal burns. Allow adequate time for the equipment to cool prior to working on these specific zones.

22.3.2. The instrument also uses gas under high pressure. These high pressures introduce the risk of injury due to flying objects should a vessel or line rupture. Safety glasses are mandatory at all times when working in, on or around these pieces of equipment. Even instrumentation that is not operating may contain portions of the system under pressure.

23. Waste Management

23.1. Procedures for handling waste generated during this analysis are addressed in S-ALL-KS-002, Waste Handling.

23.2. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (e.g., before a reagent expires).

24. Pollution Prevention

24.1. The company wide Chemical Hygiene and Safety Manual contains information on pollution prevention.

25. References

25.1. Pace Quality Assurance Manual - most current version.

25.2. National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, “Quality Systems”- most current version.

25.3. The NELAC Institute (TNI); Volume 1, Module 2, “Quality Systems”- most current version.

25.4. EPA Test Methods for Evaluating Solid Waste, SW-846, Methods 8000B, 8081A and 8270C, Third Edition, Update III, 12/1996.

25.5. USEPA CLP Statement of Work for Organics Analysis, Multi-Media, Multi-Concentration OLM04.2, 5/1999.

26. Tables, Diagrams, Flowcharts, and Validation Data

26.1. Attachment I: 8270C LCS/MS Solution.

26.2. Attachment II: TCLP/SPLP LCS/MS Solution.

26.3. Attachment III: Characteristic Ions for 8270C Compounds.

26.4. Attachment IV: Characteristic Ions for Amenable Compounds

26.5. Attachment V: Client-Specific Criteria (Internal Use Only).

26.6. Attachment VI: Client-Specific Criteria (Internal Use Only).

27. Revisions

Document Number	Reason for Change	Date
S-KS-O-013-rev.11	Section 7 – Changed Revision and Distribution Table 8.l – Revised temperatures Section 10 – Changed surrogate storage temperature. Removed duplicate documentation requirements. Table 11.3 – Revised calibration requirements. Section 12 – Removed extraction methods no longer performed Table 12.1 – Revised operating parameters. Section 13 – Removed sample duplicate. Table 13.1 – Revised blank matrix. Section 14 – Revised precision limit. Section 15 – Revised SOP reference. Section 16 – Revised reference.	September 15, 2010
S-KS-O-013-rev.12	SOP – Updated to latest prescribed format. Section 12 – Revised DDT breakdown criteria. Section 19 – Documented tuning modification. Attachment IV- Added amenable compound info Attachment V- Added client-specific criteria. Attachment VI- Added client-specific criteria.	August 21, 2012
S-KS-O-013-rev.13	Table 11.3 updated comments for CCV	September 26, 2014
S-KS-O-013-rev.14	Added section 20 – Instrument maintenance Added section 21 – Trouble Shooting Updated Attachment III Updated Attachment IV Updated section 12.7.1.1	March 17, 2015
S-KS-O-013-rev.15	SOP-Cover page changed to Pace LLC Table 11.1 -- Calibration table to have 9 points instead of 8 points added 5 ug/ml Std. Section 10.6.2 -- Added Section to injection 1 µl of DFTPP solution for 50 ng on column Section 10.7.1 -- Calibration levels to include level 5 Section 20.1 -- Removed reference to Purge and Trap system.	April 18, 2017
S-KS-O-013-rev.16	SOP – Revised Rev. numbers and dates Table 5.1 – Added analytes Section 11.4.6 – Revised minimum number of curve points from 5 to 6 Table 11.1 – Added analytes Attachment I – Added analytes Table 11.3 – Added Percent Relative Error Check on Linear and Non-linear Table 11.3 -- Regression curve fits criteria added	May 9, 2018

Attachment I - 8270C LCS/MS Solution

Analyte	CASRN	Conc. (ug/mL)	Analyte	CASRN	Conc. (ug/mL)
1,2,4-Trichlorobenzene	120-82-1	50	Benzidine	92-87-5	50
1,2-Dichlorobenzene	95-50-1	50	Benzo(a)anthracene	56-55-3	50
1,3-Dichlorobenzene	541-73-1	50	Benzo(a)pyrene	50-32-8	50
1,4-Dichlorobenzene	106-46-7	50	Benzo(b)fluoranthene	205-99-2	50
2,4,5-Trichlorophenol	95-95-4	50	Benzo(g,h,i)perylene	11-24-2	50
2,4,6-Trichlorophenol	88-06-2	50	Benzo(k)fluoranthene	207-08-9	50
2,3,4,5-Tetrachlorophenol	4901-51-3	50	Benzoic Acid	65-85-0	50
2,3,4,6-Tetrachlorophenol	58-90-2	50	Benzyl alcohol	100-51-6	50
2,3,5,6-Tetrachlorophenol	935-95-5	50	Bis(2-Chloroethoxy)methane	111-91-1	50
2,4-Dichlorophenol	87-65-0	50	Bis(2-chloroethyl) ether	111-44-4	50
2,4-Dimethylphenol	105-67-9	50	Bis(2-chloroisopropyl)ether	108-60-1	50
2,5-Dichlorophenol	583-78-8	50	Bis(2-ethylhexyl)phthalate	117-81-7	50
2,6-Dichlorophenol	87-65-0	50	Butyl benzyl phthalate	85-68-7	50
3,4-Dichlorophenol	95-77-2	50	Carbazole	86-74-8	50
2,4-Dinitrophenol	51-28-5	50	Chrysene	218-01-9	50
2,4-Dinitrotoluene	121-14-2	50	Dibenz(a,h)anthracene	53-70-3	50
2,6-Dinitrotoluene	606-20-2	50	Dibenzofuran	132-64-9	50
2-Chloronaphthalene	91-58-7	50	Diethyl phthalate	84-66-2	50
2-Chlorophenol	95-57-8	50	Dimethylphthalate	131-11-3	50
1-Methylnaphthalene	90-12-0	50	Di-n-butyl phthalate	84-74-2	50
2-Methylnaphthalene	91-57-6	50	Di-n-octyl phthalate	117-84-0	50
2-Methylphenol (o-Cresol)	95-48-7	50	Diphenylamine	122-39-4	50
2-Nitroaniline	88-74-4	50	Fluoranthene	206-44-0	50
2-Nitrophenol	88-75-5	50	Fluorene	86-73-7	50
3,3'-Dichlorobenzidine	91-94-1	50	Hexachlorobenzene	118-74-1	50
3-Methylphenol (m-Cresol)	108-39-4	25	Hexachlorobutadiene	87-68-3	50
3-Nitroaniline	99-09-2	50	Hexachlorocyclopentadiene	77-47-4	50
4,6-Dinitro-2-methylphenol	534-52-1	50	Hexachloroethane	67-72-1	50
4-Bromophenyl phenyl ether	101-55-3	50	Indeno(1,2,3-cd)pyrene	193-39-5	50
4-Chloro-3-methylphenol	59-50-7	50	Isophorone	78-59-1	50
4-Chloroaniline	106-47-8	50	Naphthalene	91-20-3	50
4-Chlorophenyl phenyl ether	7005-72-3	50	Nitrobenzene	98-95-3	50
4-Methylphenol (p-Cresol)	106-44-5	25	N-Nitrosodimethylamine	62-75-9	50
4-Nitroaniline	100-01-6	50	N-Nitrosodi-n-propylamine	621-64-7	50
4-Nitrophenol	100-02-7	50	Pentachlorophenol	87-86-5	50
Acenaphthene	83-32-9	50	Phenanthrene	85-01-8	50
Acenaphthylene	208-96-8	50	Phenol	108-95-2	50
Aniline	62-53-3	50	Pyrene	129-00-0	50
Anthracene	120-12-7	50	Pyridine	110-86-1	50
Azobenzene	103-33-3	50			

Attachment II - TCLP/SPLP LCS/MS Solution

Analyte	CASRN	Conc. (ug/mL)
4-Methylphenol (p-Cresol)	106-44-5	100
3-Methylphenol (m-Cresol)	108-39-4	100
2-Methylphenol (o-Cresol)	95-48-7	100
1,4-Dichlorobenzene	106-46-7	100
Hexachlorobutadiene	87-68-3	100
Hexachlorobenzene	118-74-1	100
Hexachloroethane	67-72-1	100
Nitrobenzene	98-95-3	100
Pentachlorophenol	87-86-5	100
Pyridine	110-86-1	100
2,4,6-Trichlorophenol	88-06-2	100
2,4,5-Trichlorophenol	95-95-4	100
2,4-Dinitrotoluene	121-14-2	100

Attachment III - Characteristic Ions for 8270C Compounds

Compounds	Primary Ion	Secondary Ion(s)	Internal Standard
Phenol	94	65,66	1
bis(2-Chloroethyl)ether	93	63,95	1
2-Chlorophenol	128	65,130	1
1,3-Dichlorobenzene	146	148,111	1
1,4-Dichlorobenzene	146	148,111	1
Benzyl alcohol	108	79,77	1
1,2-Dichlorobenzene	146	148,111	1
2-Methylphenol (o-Cresol)	108	107,77.79,90	1
bis(2-Chloroisopropyl)ether	45	77,121	1
4-Methylphenol (p-Cresol)	108	107,77,79,90	1
N-Nitroso-di-n-propylamine	70	42,101,130	1
Hexachloroethane	117	201,199	1
3-Methylphenol (m-Cresol)	108	107,77,79,90	1
1,2-Diphenylhydrazine	77	105,82	1
N-Nitrosodimethylamine	42	74,44	1
Aniline	93	66,65	1
Nitrobenzene	77	123,65	2
Isophorone	82	95,138	2
2-Nitrophenol	139	65,109	2
2,4-Dimethylphenol	122	121,107	2
Benzoic acid	122	105,77	2
2,5-Dichlorophenol	162	164, 99	2
2,6-Dichlorophenol	162	164 , 63	2
3,4-Dichlorophenol	162	164 ,99	2
bis(2-Chloroethyoxy)methane	93	95,123	2
2,4-Dichlorophenol	162	164,98	2
1,2,4-Trichlorobenzene	180	182,145	2
Naphthalene	128	129,127	2
4-Chloroaniline	127	65,92,129	2
Hexachlorobutadiene	225	223,227	2
4-Chloro-3-methylphenol	107	144,142	2
2-Methylnaphthalene	142	141, 115	2
1-Methylnaphthalene	142	141,115	2
Hexachlorocyclopentadiene	237	235,272	3
2,4,6-Trichlorophenol	196	198,200	3
2,4,5-Trichlorophenol	196	198, 200	3
2,3,4,5-Tetrachlorophenol	232	230, 131	3
2,3,4,6-Tetrachlorophenol	232	230,131	3
2,3,5,6-Tetrachlorophenol	232	230,234	3
2-Chloronaphthalene	162	164,127	3
2-Nitroaniline	65	92,138	3
Dimethylphthalate	163	194,164	3

Compounds	Primary Ion	Secondary Ion(s)	Internal Standard
Acenaphthylene	152	151,153	3
2,6-Dinitrotoluene	165	63,89	3
3-Nitroaniline	138	108,92	3
Acenaphthene	154	152,153	3
2,4-Dinitrophenol	184	63,154	3
2,4-Dinitrotoluene	165	63,89	3
Diethylphthalate	149	177,150	3
4-Nitrophenol	109	139,65	3
Dibenzofuran	168	139	3
4-Chlorophenyl phenyl ether	204	206,141	3
Fluorene	166	165,167	3
4-Nitroaniline	138	65,108,80	3
4,6-Dinitro-2-methylphenol	198	51,105	4
N-Nitrosodiphenylamine	169	168,167	4
4-Bromophenyl phenyl ether	248	250,141	4
Hexachlorobenzene	284	142,249	4
Pentachlorophenol	266	264,268	4
Phenanthrene	178	179,176	4
Anthracene	178	179,176	4
Di-n-butylphthalate	149	150,104	4
Fluoranthene	202	101,203	4
Pyrene	202	200,203	5
Butylbenzylphthalate	149	91,206	5
3,3'-Dichlorobenzidine	252	254,126	5
Benzo(a)anthracene	228	229,226	5
Chrysene	228	226,229	5
bis(2-Ethylhexyl)phthalate	149	167,279	5
Indeno(1,2,3-cd)pyrene	276	138,227	5
Benzidine	184	92,185	5
7,12-Dimethylbenz(a)anthracene	256	241,239,120	5
Di-n-octylphthalate	149	167,43	6
Benzo(b)fluoranthene	252	253,125	6
Benzo(k)fluoranthene	252	253,125	6
Benzo(a)pyrene	252	253,125	6
Dibenz(a,h)anthracene	278	139,279	6
Benzo(g,h,i)perylene	276	138,277	6
Surrogates			
Phenol-d6	99	42,71	1
2-Fluorophenol	112	64	1
Nitrobenzene-d5	82	128,54	2
2,4,6-Tribromophenol	330	332,141	3
2-Fluorobiphenyl	172	171	3

Compounds	Primary Ion	Secondary Ion(s)	Internal Standard
Terphenyl-d14	244	122,212	5
Internal Standards			
1,4-Dichlorobenzene-d4	152	115,150	1
Naphthalene-d6	136	68	2
Acenaphthene-d10	164	162,160	3
Phenanthrene-d10	188	94,80	4
Chrysene-d12	240	120,236	5
Perylene-d12	264	260,265	6

Attachment IV - Characteristic Ions for Amenable Compounds

Compounds	Primary Ion	Secondary Ion(s)	Internal Standard	Compounds	Primary Ion	Secondary Ion(s)	Internal Standard
1-Methylnaphthalene	142	141	2	Benzothiophene	134	89	2
2,3,4,6-Tetrachlorophenol	232	131,230,166,168	3	bis(2-Ethylhexyl)adipate	129	112	5
2-Chlorobenzyl chloride	125	127	3	Carbazole	167	166,139	4
6-Methylchrysene	242	241	5	Dibenz(a,h)acridine	279	139	6
7,12-Dimethylbenz(a)anthracene	256	241,239,120	6	Indene	116	115	2
Azobenzene	77	105	3	N-Nitrosodimethylamine	42	74	1
Benzenethiol (Thiophenol)	110	66	1	Pyridine	79	52	1
Benzidine	184	185,92	5	Quinoline	129	102	2
Benzo(j)fluoranthene	252	253	6	Terpineol	93	59	2

Attachment V – BP-Specific Criteria (Internal Use Only)

Calibration Metric	Frequency	Criteria	Corrective Action
Initial calibration	Each time the instrument is set up and when CCCs and SPCCs in the calibration do not meet criteria. Established initially at five concentration levels - low standard at or below project-required quantitation limit (PRQL).	Ave RRF for each SPCC, surrogate and PAH compound ≥0.050. %RSD for each CCC, surrogate and PAH compound ≤30%. %RSD for all target and surrogate compounds ≤15% or generate a calibration curve. The calibration curve must have a correlation coefficient (R) ≥0.99 or a coefficient of determination (COD) ≥0.99.	If a target compound does not meet the acceptance criteria, a new initial calibration must be performed. If SPCC or CCC criteria are not met, a new initial calibration must be performed.
Initial Calibration Verification	Immediately following the initial calibration and prior to sample analyses. Must be at or near the mid-point calibration range for all target compounds, SPCCs, CCCs, and surrogates.	RRF for each SPCC, surrogate and PAH compound ≥0.050. %D for RRFs of all target analytes and surrogates ≤20%; with the exception that up to 10 non-CCCs can be out but must be ≤40% (exception does not apply to PAH compounds). All TCL compounds (listed below) must have RRF ≥0.05.	Reprepare and reanalyze the ICV once. If it fails a second time a new initial calibration should be rerun.
Continuing Calibration Verification	Every 12 hours. Must be at or near the mid-point calibration range for all target compounds, SPCCs, CCCs, and surrogates.	RRF for each SPCC, surrogate and PAH compound ≥0.050. %D for RRFs of all target analytes and surrogates ≤20%; with the exception that up to 10 non-CCCs can be out but must be ≤40% (exception does not apply to PAH compounds). All TCL compounds must have RRFs 0.05.	Correct system, if necessary, and recalibrate. Criteria must be met before sample analysis may begin.
Internal standards	Added to all blanks, standards, QC samples, and samples.	Peak area within -50% to +100% of area in associated continuing calibration standard. Retention time (RT) within 30 sec of RT for associated continuing calibration standard.	Inspect instrument for malfunctions; correct identified malfunctions, then reanalyze samples. If no instrument malfunction is identified, proceed as follows: Reanalyze sample. If reanalysis is out, report both sets of data. If in, report only second set.
Surrogate Compounds	Calibrated and quantitated as target compounds. Added to all standards, blanks, samples, and QC samples.	All recoveries must be within acceptance limits.	If recovery acceptance criteria are not within limits: Check to be sure that there are no errors in calculations, surrogate solutions, and internal standards. Also, check instrument performance. If no problem is found, prepare and analyze the sample a second time. If the reanalysis is within limits and holding times, then report only the reanalysis. If the reanalysis is within limits, but out of hold, then report both sets of data. If the reanalysis is still out of limits, then report both sets of data. If the sample was chosen for the MS/MSD analysis, and the MS and/or MSD are outside limits, then no reanalysisis required.
Method Blank	One per extraction batch of 20 or fewer samples per matrix per day. Must undergo all sample preparative procedures. Must be run on each instrument used for sample analysis.	Target phthalate esters ≤5x PRQL. All other target compounds <1/2 PRQL. Must meet surrogate and internal standard criteria.	Reanalyze to determine if instrument contamination was the cause. If the method blank is still noncompliant, reextract and reanalyze all samples unless >10x the blank, or there are no positive results.

Calibration Metric	Frequency	Criteria	Corrective Action
Laboratory Control Sample (LCS)	One per matrix per extraction batch (if applicable) per set of 20 samples per day. Must undergo all sample preparative procedures. Must contain all target compounds at concentrations at the mid-point of the calibration range.	% Recoveries (and RPDs, if applicable) within laboratory-generated limits; with the exception that the following compounds may recover outside limits, but at least ≥10%: Hexachlorocyclopentadiene N-Nitrosodimethylamine Pentachlorophenol 2,4-Dinitrophenol 4-Nitrophenol Benzoic acid 4-Chloro-3-methylphenol 2-Nitroaniline 3-Nitroaniline 4-Chloroaniline Four additional non-PAH compounds.	Reanalyze the LCS to determine if instrumental conditions or analytical preparation was the cause. If still out reprepare and reanalyze associated samples and LCS. Exception: If LCS recovery is high and no associated positive results are reported, then address the issue in the SDG Narrative and no further action is needed.
Matrix Spike/Matrix Spike Duplicate	One per matrix per extraction batch (if applicable) per set of 20 samples per day. Must undergo all sample preparative procedures. Must be spiked with all target compounds at concentrations at or near the midpoint of the calibration range.	% Recoveries within laboratory- generated limits. RPDs within laboratory-generated limits.	If LCS is acceptable, then report in the SDG Narrative that there was probable matrix interference.
Qualitative/ Quantitative Issues	If instrument level of any compound in a sample exceeds the instrument level of that compound in the highest level standard, the sample must be diluted to approximately mid-level of the calibration range and reanalyzed If the concentration of the target analyte that exceeded the calibration range is present in the high-level sample and in the sample analyzed immediately after at a level greater than the PRQL, but ≤5x PRQL, then that second sample must be reanalyzed to determine if carryover occurred.	The instrument level of all compounds must be within the calibration range for all samples. The sample analyzed immediately after a high-level sample must display concentrations of the high-level target compounds < the PRQL or greater than 5x PRQL.	Dilute the sample to bring the level of the highest concentration of target compounds within the calibration range. A sample displaying concentrations of target compounds between the PRQL and 5x the PRQL which was analyzed immediately after a high-level sample must be reanalyzed. If the results do not agree within the PRQL, report only the second analysis.
Compound Identification	In addition to the criteria listed in 12.7.1, all ions present in the reference mass spectrum at a relative intensity >10% must be present in the sample spectrum. The analyst making the comparison and using their professional judgment must carefully consider ions greater than 10 percent in the sample spectrum, but not present in the standard spectrum.	All ions present in the standard mass spectra at a relative intensity greater than 10.0 percent (most abundant ion in the spectrum equals 100.0 percent) must be present in the sample spectrum. Ions greater than 10 percent in the sample spectrum, but not present in the standard spectrum may indicate a false identification.	Required for definitive identification. Identification requires peer- or supervisory review.
TCL Compounds	2,3,4,6-Tetrachlorophenol 2,4,5-Trichlorophenol 2,4,6-Trichlorophenol 2,4-Dichlorophenol 2,4-Dimethylphenol 2,4-Dinitrophenol 2,4-Dinitrotoluene 2,6-Dinitrotoluene 2-Chloronaphthalene 2-Chlorophenol 2-Methylnaphthalene 2-Methylphenol 2-Nitroaniline 2-Nitrophenol 3,3'-dicholorobenzidine 3-Nitroaniline 4,6-Dinitro-2-methylphenol 4-Bromophenyl-phenylether 4-Chloro-3-methylphenol 4-Chloroaniline	4-Chlorophenyl-phenyl ether 4-Methylphenol 4-Nitroaniline 4-Nitrophenol Acenaphthene Acenaphthylene Anthracene Benzo(a) pyrene Benzo(a)anthracene Benzo(b) fluoranthene Benzo(g,h,i) perylene Benzo(k) fluoranthene Bis(2-chloroethoxy) methane Bis(2-chloroethyl) ether Bis(2-chloroisopropyl)ether Bis(2-ethylhexyl) phthalate Butylbenzylphthalate Carbazole Chrysene Dibenzo(a,h) anthracene	Dibenzofuran Diethylphthalate Dimethylphthalate Di-n-butylphthalate Di-n-octylphthalate Fluoranthene Fluorene Hexachlorobenzene Hexachlorobutadiene Hexachlorocyclopentadiene Hexachloroethane Indeno(1,2,3,-cd) pyrene Isophorone Naphthalene Nitrobenzene N-Nitroso-di-n propylamine N-Nitrosodiphenylamine Pentachlorophenol Phenanthrene Phenol Pyrene

Attachment VI – ConocoPhillips-Specific Criteria (Internal Use Only)

Calibration Metric	Frequency	Criteria	Corrective Action
Initial calibration	Each time the instrument is set up and when calibration verification criteria are not met. A minimum of five calibration standards is required for linear calibration (at least six standards are required for nonlinear calibration). The low-level calibration standard must be at or below the reporting limit.	%RSD must be <15% for each target analyte or a calibration curve must be generated. The "Grand Mean" approach is unacceptable. All PAHs and surrogate compounds are considered CCCs and SPCCs and must meet method criteria.	When the minimum RRF is not met, a new calibration must be performed. A linear or nonlinear calibration curve (with r >0.99) must be generated when the RSD criterion is not met. A new calibration must be performed when SPCC and CCC criteria are not met.
Initial Calibration Verification	Second-source calibration verification standard must be analyzed after every initial calibration.	% Drift or % Difference must be ≤20% for all target compounds and surrogates.	Correct system and reanalyze ICV. If second ICV fails, recalibrate system.
Continuing Calibration Verification	At the beginning of each 12-hour shift (following the DFTPP tune check).	% Drift or % Difference must be ≤20% for all target compounds and surrogates.	Correct system and reanalyze CCV. If second CCV fails, recalibrate system and reanalyze all associated project samples.
Internal standards	Added to every standard, sample, and QC sample. Sample internal standard area counts and RTs must be compared to the internal standard area counts and RTs of the associated CCV standard. CCV internal standard area counts and RTs must be compared to the area counts and RTs of the ICV standard.	Area counts of the internal standard peaks must be 50-200% of the internal standard area observed in the reference. Retention time (RT) of the internal standard must not vary more than ± 30 seconds from the RT of the internal standards observed in associated CCV standard.	Correct system, if necessary; reanalyze sample.
Surrogate Recovery	Calibrated as target compounds. Added to blanks, samples, and QC samples.	All recoveries meet laboratory-generated acceptance limits.	Check to be sure that there are no errors in the calculations, surrogate solutions, or internal standards. Check instrument performance. Correct the problem and reanalyze the extract if a problem is identified. If no problems are identified, reextract and reanalyze sample. If surrogate recovery criteria are met upon reextraction/reanalysis, report the reanalysis results. If surrogate recovery criteria are not met upon reextraction/reanalysis, report both sets of data. If the reextraction/reanalysis is performed outside of holding time, provide both the original and reanalysis results to the data user.
Method Blank	One per extraction batch of 20 or fewer samples analyzed on each instrument used for analysis of ConocoPhillips samples. A method blank is required for each extraction method.	Target compound results <½ the RL. If samples are reported to the MDL, target compounds must not be present above the MDL.	Reanalyze to determine if instrument contamination was the cause. If the method blank is still noncompliant, reextract and reanalyze all samples unless >10x the blank, or there are no positive results.
Laboratory Control Sample (LCS)	One per extraction batch of up to 20 samples. LCS must undergo all sample preparation procedures and must contain all target compounds at the midpoint of the calibration range.	% Recoveries within laboratory-generated limits.	Reanalyze LCS to confirm results. If LCS results are outside acceptance criteria upon reanalysis, reextract and reanalyze associated project samples. If high recoveries are observed and "not-detected" results are reported for the associated samples, reanalysis is not necessary.
Matrix Spike/Matrix Spike Duplicate	One per matrix per extraction batch of up to 20 samples.	% Recoveries and RPDs within laboratory-generated limits.	If LCS results meet acceptance criteria, report probable matrix interference in the SDG Narrative. Do not reanalyze the MSIMSD samples unless laboratory error is confirmed (e.g., non-spiked).

Calibration Metric	Frequency	Criteria	Corrective Action
Qualitative/ Quantitative Issues	If the instrument level of any target compound in a sample exceeds the calibration range, the sample must be diluted and reanalyzed.	The instrument level of all target compounds must be within the calibration range. Solvent lot numbers must be recorded for all samples reanalyzed at dilutions.	Dilute the sample to bring the target compound level within the calibration range.
Manual Integrations	Manual integrations may not be performed for the purpose of meeting calibration or QC criteria.	Manual integrations must be performed in accordance with the associated laboratory SOP. Manual integrations must be reviewed and approved by a supervisor.	N/A

Document Information

Document Number: ENV-SOP-LENE-0039 **Revision:** 03

Document Title: Separatory Funnel Extraction

Department(s): Organic Prep

Date Information

Effective Date: 07 Apr 2021

Notes

Document Notes:

All Dates and Times are listed in: Central Time Zone

Signature Manifest

Document Number: ENV-SOP-LENE-0039 **Revision:** 03
Title: Separatory Funnel Extraction

All dates and times are in Central Time Zone.

ENV-SOP-LENE-0039 Separatory Funnel Extraction

QM Approval

Name/Signature	Title	Date	Meaning/Reason
Gregory Busch (003971)	Manager - Quality	21 Feb 2020, 10:32:25 AM	Approved

Management Approval

Name/Signature	Title	Date	Meaning/Reason
Charles Girgin (002243)	General Manager 2	24 Feb 2020, 12:29:34 PM	Approved
Harry Borg (005736)	Manager	03 Mar 2020, 08:17:33 AM	Approved

ENV-SOP-LENE-0039_Separatory Funnel Extraction

QM Approval

Name/Signature	Title	Date	Meaning/Reason
Kenneth Busch (991414)	Manager - Quality	31 Mar 2021, 12:27:30 PM	Approved

Management Approval

Name/Signature	Title	Date	Meaning/Reason
Kenneth Busch (991414)	Manager - Quality	31 Mar 2021, 12:27:42 PM	Approved
Harry Borg (005736)	Manager	31 Mar 2021, 04:39:11 PM	Approved
Charles Girgin (002243)	General Manager 2	01 Apr 2021, 07:55:19 AM	Approved

Pace Analytical®

TEST METHOD STANDARD OPERATING PROCEDURE
TITLE: Separatory Funnel Extraction for semi-volatile analysis
TEST METHOD SW-846 3510, EPA 508
ISSUER: Pace ENV – Lenexa Quality – LENE

1.0 SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the laboratory procedure for the determination of extracting non-volatile and semi-volatile organic compounds from aqueous samples in a separatory funnel while meeting the requirements specified in EPA Method 3510C and EPA Method 508.

1.1 Target Analyte List and Limits of Quantitation (LOQ)

The target analytes and the normal LOQ that can be achieved with this procedure are provided in the respective determinative methods and are available by request from the Quality Manager.

LOQ are established in accordance with Pace policy and SOPs for method validation and for the determination of detection limits (DL) and quantitation limits (LOQ). DL and LOQ are routinely verified and updated when needed.

The reporting limit (RL) is the value to which analytes are reported as detected or not detected in the final report. When the RL is less than the lower limit of quantitation (LLOQ), all detects and non-detects at the RL are qualitative. The LLOQ is the lowest point of the calibration curve used for each target analyte.

DL, LOQ, and RL are always adjusted to account for actual amounts used and for dilution.

2.0 SUMMARY OF METHOD

2.1 A measured volume of sample (usually about 1L for regular volume, 500ml for Kansas TPH, 500ml for Iowa OA2 and about 100mL for reduced volume) is serially extracted with solvent in a separatory funnel. Some extractions also require the monitoring and adjusting of the pH of the sample. The extract is separated from the sample and is concentrated, followed by cleanup or analysis.

3.0 INTERFERENCES

3.1 Solvents, reagents, and glassware can all contribute to compound artifacts or raised baselines; both conditions that can affect chromatography. Analyzing method blanks is therefore crucial in determining the presence of contaminants.

3.2 Phthalate esters are common contaminant products in many products in the lab. All plastic products should be avoided when performing this method.

4.0 DEFINITIONS

Refer to the Laboratory Quality Manual for a glossary of common lab terms and definitions.

5.0 HEALTH AND SAFETY

The toxicity or carcinogenicity of each chemical material used in the laboratory has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable.

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The laboratory maintains documentation of hazard assessments and OSHA regulations regarding the safe handling of the chemicals specified in each method. Safety data sheets for all hazardous chemicals are available to all personnel. Employees must abide by the health, safety and environmental (HSE) policies and procedures specified in this SOP and in the Pace Chemical Hygiene / Safety Manual.

Personal protective equipment (PPE) such as safety glasses, gloves, and a laboratory coat must be worn in designated areas and while handling samples and chemical materials to protect against physical contact with samples that contain potentially hazardous chemicals and exposure to chemical materials used in the procedure.

Concentrated corrosives present additional hazards and are damaging to skin and mucus membranes. Use these acids in a fume hood whenever possible with additional PPE designed for handing these materials. If eye or skin contact occurs, flush with large volumes of water. When working with acids, always add acid to water to prevent violent reactions. Any processes that emit large volumes of solvents (evaporation/concentration processes) must be in a hood or apparatus that prevents employee exposure.

Contact your supervisor or local HSE coordinator with questions or concerns regarding safety protocol or safe handling procedures for this procedure.

6.0 SAMPLE COLLECTION, PRESERVATION, HOLDING TIME, AND STORAGE

Samples should be collected in accordance with a sampling plan and procedures appropriate to achieve the regulatory, scientific, and data quality objectives for the project.

The laboratory does not perform sample collection or field measurements for this test method. To assure sample collection and field checks and treatment are performed in accordance with applicable regulations Pace project managers will inform the client of these requirements at the time of request for analytical services when the request for testing is received prior to sample collection. If samples were already collected, the laboratory will record any nonconformance to these requirements in the laboratory's sample receipt record when sufficient information about sample collection is provided with the samples.

The laboratory will provide containers for the collection of samples upon client request for analytical services. Bottle kits are prepared in accordance with laboratory SOP ENV-SOP-LENE-0025, *Assembly of Sample Container Kits*. For this test method, immediately after sample collection, samples should be checked for X and X and field treated. The bottle kits provided by the laboratory should include field test kits and treatment reagent.

Requirements for container type, preservation, and field quality control (QC) for the common list of test methods offered by Pace are included in the laboratory's quality manual.

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General Requirements

Matrix[2]	Routine Container	Minimum Sample Amount[1]	Preservation	Holding Time
Aqueous (8270)/(8270LV)	1L/100ml Amber	100mL	Thermal: <6°C Chemical: Not Applicable	Collection to Prep: 7days Prep to Analysis: 40 days
Aqueous (625.1)/(/625.1LV)	1L/100ml Amber	100mL	Thermal: <6°C Chemical: 80mg sodium thiosulfate if residual chlorine is present	Collection to Prep: 7days Prep to Analysis: 40 days
Aqueous (8082)/(8082LV)	1L/100ml Amber	100mL	Thermal: <6°C Chemical: Not Applicable	Collection to Prep: 1 year Prep to Analysis: 1 year
Aqueous (608.3PCB)/(608.3PCBLV)	1L/100ml Amber	100mL	Thermal: <6°C Chemical: 80mg sodium thiosulfate if residual chlorine is present	Collection to Prep: 1 year Prep to Analysis: 1 year
Aqueous (KS TPH)	500ml Amber	500mL	Thermal: <6°C Chemical: Not Applicable	Collection to Prep: 14days Prep to Analysis: 40 days
Aqueous (508)	1L Amber	1L	Thermal: <6°C Chemical: 80mg sodium thiosulfate if residual chlorine is present	Collection to Prep: 7days Prep to Analysis: 14 days
Aqueous (8121)	1L Amber	1L	Thermal: <6°C Chemical: Not Applicable	Collection to Prep: 7days Prep to Analysis: 40 days
8015DRO/ORO	1L/100ml Amber	100mL	Thermal: <6°C Chemical: Not Applicable	Collection to Prep: 7days Prep to Analysis: 40 days
Iowa OA2	500mL/100ml Amber	100mL	Thermal: <6°C Chemical: Not Applicable	Collection to Prep: 7days Prep to Analysis: 40 days
Oklahoma DRO	1L Amber	1L	Thermal: <6°C Chemical: HCL preserved pH<2	Collection to Prep: 7days Prep to Analysis: 40 days

[1]*Minimum amount needed for each discrete analysis.*

[2]*LV indicates low volume 100ml extraction volume*

Field / Matrix QC

Trip Blank	Equipment Blank	MS/MSD	Field Duplicate
NA	NA	Per extraction batch	NA

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Thermal preservation is checked and recorded on receipt in the laboratory in accordance with laboratory SOP ENV-SOP-LENE-0021, *Sample Management*. Chemical preservation is checked and recorded at time of receipt or prior to sample preparation.

After receipt, samples are stored at ≤6°C until sample preparation. Prepared samples (extracts, digestates, distillates, other) are stored at ≤6°C until sample analysis.

After analysis, unless otherwise specified in the analytical services contract, samples are retained for 30 days from date of final report and then disposed of in accordance with Federal, State, and Local regulations.

7.0 EQUIPMENT AND SUPPLIES

7.1 Equipment and Supplies

Supply	Vendor	Model / Version	Comments
N-EVAP™	Organomation Associates	112	Nitrogen Evaporator
S-EVAP™	Organomation Associates	120	Solvent Evaporator
ExcelVap	Horizon / Biotage	ExcelVap	24/8 place concentration work station
200mL Tube w/ 1.0mL	Biotage	ExcelVap® II / 45817	ExcelVap® sample stem tube or equivalent
Clear Bath®	Fisher	105535 / 15-459-20	Water treatment for ExcelVap
Shaker table	Eberbach	6010	
3-D Floor Shaker	Glas-Col, LLC	099A VS5504	
Analytical Balance	Ohaus	SP202	Capable of measuring ±0.01g
Boiling Chips	Fisher	09-191-20	PTFE
Concentrator tubes	Fisher	K570051-1025	10-mL capacity
Funnels	Fisher	10-371C	HDPE
Glass beakers	Fisher	02-539K	Kimax; 250-mL.
Pasteur pipettes	Fisher	22-378-893	5.75”
Screw Top Glass Vials	Fisher	Various	1 mL, 4 mL, 12 mL,
Separatory Funnels	Fisher	10-437-25E	2-L, PTFE
Separatory Funnels	Fisher	10-437-25B	250-mL, PTFE
Test tubes	Fisher	14-959-35AA	16x100mm, threaded w/marking spot
Autosampler vials	Fisher	03-391-9	Fisher Brand; ~2mL, amber glass.

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Supply	Vendor	Model / Version	Comments
Micro-syringes	Fisher	Various	Hamilton; gas-tight, various sizes.
Funnels	Fisher	10-371C	Polypropylene
Graduated cylinders	Fisher	Various	Class A, 1000-, 250-, 100-mL.
Kuderna-Danish (K-D) flasks	Fisher	NC9599012 or equivalent	500-mL with ground glass joints.
K-D concentrator tubes	Fisher	K570012-0500 or equivalent	with ground glass fitting.
Snyder columns	Fisher	K503000-0121 or equivalent	3-ball variety.
Keck clip	Fisher	05-880D	For securing K-D joints
Filter paper	Fisher	09-790-12G	P-8
pH paper	Fisher	Type CF / 09-876-17	Whatman; 0-14 range.
Glass stirring rods	Fisher	11-380D	For breaking up emulsions.
200ml Glass Extraction tubes	Quark	QTU-200-V	Used with table shaker
Chlorine Test Strips	Fisher /(Aquachek)	STK#501311420 or equivalent	Measuring free chlorine is sample

8.0 REAGENTS AND STANDARDS

8.1 Reagents & Standards

Reagent/Standard	Concentration/ Description	Vendor/ Item #
Acetone	Fisher Optima™ grade	Fisher / A929 or equivalent
Hexane	Fisher Optima™ grade	Fisher / H303 or equivalent
Methylene chloride	Pesticide grade	MG Scientific / B&J-CS299AC-200 or equivalent
Methanol	MG Scientific Absolute™ ACS grade	MG Scientific / M1240-4L or equivalent
MTBE (methyl tert-Butyl ether)	Supra Solv	Sigma Aldrich /101995,1000
Reagent water	ASTM Type II water	SOP S-KS-Q-011 (latest revision)
Sodium chloride	USP/FCC	Fisher / S640 or equivalent
Sodium hydroxide pellets	ACS Reagent grade	Fisher/ S318 or equivalent
Sodium sulfate, anhydrous	ACS Reagent grade	MG Scientific / 3375-09-4692437 or equivalent
Sulfuric acid solution	1:1 solution; Ricca Chemical	Fisher / 8180-16 or equivalent
Potassium Phosphate Dibasic Anhydrous	ACS 99+	Fisher/ P288-100 or equivalent

- Phosphate Buffer, pH 7 -- Prepare by mixing 29.6 mL 0.1 N HCl and 50 mL 0.1 M dipotassium phosphate.

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9.0 PROCEDURE

9.1 Equipment Preparation

9.1.1 Support Equipment

See SOP ENV-SOP-LENE-0030, Support Equipment (or its equivalent revision or replacement) for the calibration of the support equipment used in this procedure.

9.1.2 Instrument

9.1.2.1 Routine Instrument Operating Conditions

Not applicable to this prep SOP.

9.2 Initial Calibration

9.2.1 Calibration Design

Not applicable to this prep SOP.

9.2.2 Calibration Sequence

Not applicable to this prep SOP.

9.2.3 ICAL Evaluation

9.2.3.1 Curve Fit

Not applicable to this prep SOP.

9.2.3.2 Relative Standard Error (RSE)

Not applicable to this prep SOP.

9.2.3.3 Initial Calibration Verification

Not applicable to this prep SOP.

9.2.4 Continuing Calibration Verification

Not applicable to this prep SOP.

9.3 Sample Preparation

9.3.1 Homogenization and Subsampling

Not applicable to this prep SOP.

9.4 Analysis

9.4.1 Extraction of Regular Volume (>100mL) Samples

9.4.1.1 Inspect all required glassware to ensure it is clean and undamaged.

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9.4.1.2 If the glassware is wet rinse first with methanol, this step is not necessary if the glassware is already dry. Then rinse the glassware three rinses with methylene chloride followed by a final rinse with methanol.

9.4.1.3 Allow the samples to warm to room temperature. Prepare two additional sample aliquots to serve as an MS and MSD.

9.4.1.4 Prior to measurement of the water sample volume, perform a visual inspection of the sample. There are three different sample types that you are likely to encounter:

- Sample with minimal sediment content.
- Sample with more than one-quarter inch of sediment on the bottom of the container.
- Bi-phasic or multi-phasic sample containing two or more layers.

9.4.2 Water sample with minimal sediment

9.4.2.1 Mark the level of sample on the outside of the bottle with a marker, briefly shake each sample to re-suspend settled solids.

NOTE: If only a portion of the contents of the sample container is going to be extracted, and not the entire contents of the sample container, then briefly shake the container to homogenize the contents and measure the portion used in a graduated cylinder.

(508/608.3/625.1/8121/8270) – Then need to verify if residual chlorine is present by the use of chlorine test strips and if present, treat with 80mg of sodium thiosulfate, prior proceeding any further.

9.4.2.2 Pipet 1.0 mL of the appropriate surrogate spiking solution into the sample bottle for all Method 3510 extractions with the exception of methods: EPA 508, 625.1 and 608.3 which are to be spiked into the separatory funnels.(also add 1.0 mL of the matrix spiking standard if this is a matrix spike sample). Attention: When containers are filled to the top or poured into a graduated cylinder, The surrogate and matrix spikes needs to be spiked into the separatory funnel instead of the sample bottle container and must be done prior to addition of any solvent.

9.4.2.3 Pour sample into the 2-L separatory funnel (if the sample volume is ≤500 mL, then adjust to 1-L with reagent water). Iowa OA2 & Kansas TPH uses only 500ml for all samples and QC.

Use this step only if catechol, 3- or 4-methylcatechol are to be determined: Add sufficient sodium chloride (NaCl) to the 1 liter of sample to fully saturate the liquid (this will be approximately 300 grams of sodium chloride per liter of sample). There should be sufficient NaCl added such that, after shaking to dissolve, the separatory funnel still contains some NaCl crystals. If no NaCl crystals can be detected add more NaCl. This same process must be completed for the Blank, LCS, MS and MSD.

Proceed to pH adjustment step.

9.4.2.4 Check and record the pH of any sample aliquots that will be analyzed for Methods 508,608.3,625.1, and 8270C and Kansas TPH by removing a few drops with a

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disposable pipette for application to pH strips. Refer to Tables in section 24 for the proper extraction pH.

9.4.2.5 Adjust and record sample aliquot pH (if necessary) with 1:1 sulfuric acid solution or 10N sodium hydroxide solution. Method 508 will require the addition of 50mls of potassium phosphate buffering solution and then pH rechecked if not at a pH of 7 adjust with either the sulfuric acid or sodium hydroxide solution.

Note for Method 508: Requires that 100g of NaCL be added to the sample and shaken until dissolved. This is to be done after pH adjustment to 7 pH units.

9.4.2.6 Add 60 mL of methylene chloride to the sample container, cap, and briefly shake. Transfer the solvent to the 2-L separatory funnel.

NOTE: If only a portion of the contents of the sample container was measured out in a graduated cylinder, and not the entire contents of the sample container, then add 60 mL of methylene chloride to the graduated cylinder by pouring down the side while rotating the cylinder.

9.4.2.7 Refill the sample bottle to the mark with water and then measure the volume of sample that was in the bottle with a graduated cylinder.

9.4.2.8 Proceed with further procedures as described in sections 9.4.4 through 9.4.9.

9.4.3 Water sample with more than one-quarter inch of sediment

9.4.3.1 Immediately notify your Supervisor and the Project Manager to determine if the sediment must be analyzed separately.

9.4.3.2 (508/608.3/625.1/8121/8270) – Then need to verify if residual chlorine is present by the use of chlorine test strips and if present, treat with 80mg of sodium thiosulfate, prior proceeding any further.

9.4.3.3 Carefully decant the water from the container to the 1-L graduated cylinder ensuring minimal sediment is transferred.

9.4.3.4 Record the volume at the bottom of the meniscus up to a maximum volume of 1-L. and pour the sample into the separatory funnel (if the sample volume is ≤500 mL, then adjust to 1-L with reagent water, with the exception of the Iowa OA2 or Kansas TPH method leave all at 500ml).

9.4.3.5 Pipet 1.0 mL of the surrogate spiking solution into the separatory funnel (also add 1.0 mL of the matrix spiking standard if this is a matrix spike). This must be done prior to the addition of any solvent.

Use this step only if catechol, 3- or 4-methylcatechol are to be determined: Add sufficient sodium chloride (NaCl) to the sample to fully saturate the liquid (this will be approximately 300 grams of sodium chloride per liter of sample). There should be sufficient NaCl added such that, after shaking to dissolve, the separatory funnel still contains some NaCl crystals. If no NaCl crystals can be detected add more NaCl. This same process must be completed for the Blank, LCS, MS and MSD.

Proceed to pH adjustment step.

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9.4.3.6 Check and record the pH of any sample aliquots that will be analyzed for Methods 508,608.3,625.1, and 8270C by removing a few drops with a disposable pipette for application to pH strips. Refer to Tables in section 24 for the proper extraction pH. Method 508 will require the addition of 50mls of potassium phosphate buffering solution and then pH rechecked if not at a pH of 7 adjust with either the sulfuric acid or sodium hydroxide solution.

Note for Method 508: Requires that 100g of NaCL be added to the sample and shaken until dissolved. This is to be done after pH adjustment to 7 pH units.

9.4.3.7 Adjust and record sample aliquot pH (if necessary) with 1:1 sulfuric acid solution or 10N sodium hydroxide solution.

9.4.3.8 Add 60 mL of methylene chloride to the graduated cylinder by pouring down the side while rotating the cylinder. Finally, transfer the solvent to the separatory funnel.

9.4.3.9 Proceed with further procedures as described in sections 9.4.4 through 9.4.9.

9.4.3.10 Bi-phasic or multi-phasic sample

9.4.3.11 Immediately notify your Supervisor and Project Manager and determine which phase(s) is to be tested.

9.4.3.12 (508/608.3/625.1/8121/8270) Need to verify if residual chlorine is present by the use of chlorine test strips and if present, treat with 80mg of sodium thiosulfate, prior proceeding any further.

9.4.3.13 Carefully pour the sample from the container to a pre-rinsed 2-L separatory funnel. For the bi-phasic sample, the top layer will typically contain the lower density organics and the lower layer the aqueous. If more than one phase is present, a series of miscibility evaluations may be necessary in order to determine the phase types present.

9.4.3.14 Drain the lower or aqueous phase into the 1-L graduated cylinder, record the volume to the bottom of the meniscus and pour the sample into the separatory funnel (if the sample volume is ≤500 mL, then adjust to 1-L with reagent water).

9.4.3.15 Pipet 1.0 mL of the surrogate spiking solution into the separatory funnel (also add 1.0 mL of the matrix spiking standard if this is a matrix spike).

Use this step only if catechol, 3- or 4-methylcatechol are to be determined: Add sufficient sodium chloride (NaCl) to fully saturate the liquid (this will be approximately 300 grams of sodium chloride per liter of sample). There should be sufficient NaCl added such that, after shaking to dissolve, the separatory funnel still contains some NaCl crystals. If no NaCl crystals can be detected add more NaCl. This same process must be completed for the Blank, LCS, MS and MSD.

Proceed to pH adjustment step.

9.4.3.16 Check and record the pH of any sample aliquots that will be analyzed for Methods 508,608.3,625.1, and 8270C by removing a few drops with a disposable pipette for application to pH strips. Refer to Tables in section 26 for the proper extraction pH.

9.4.3.17 Adjust and record sample aliquot pH (if necessary) with 1:1 sulfuric acid solution or 10N sodium hydroxide solution. Method 508 will require the addition of 50mls of potassium phosphate buffering solution and then pH rechecked if not at a pH of 7 adjust with either the sulfuric acid or sodium hydroxide solution.

Note for Method 508: Requires that 100g of NaCL be added to the sample and shaken until dissolved. This is to be done after pH adjustment to 7 pH units.

9.4.3.18 Add 60 mL of methylene chloride to the graduated cylinder by pouring down the side while rotating the cylinder. Finally, transfer the solvent to the 2-L separatory funnel.

9.4.3.19 From the first 2-L separatory funnel used, drain the remaining top layer or organic phase into the original sample container and cap. Keep for possible further testing.

9.4.3.20 Proceed with further procedures as described in sections 9.4.4 through 9.4.8.

9.4.4 Add (2) 1-L aliquots of reagent water to separatory funnels to serve as the Method Blank and LCS. Add 1.0 mL of the surrogate spiking solution to the MB and LCS and 1.0 mL of the matrix spiking standard to the LCS. Adjust and record pH's (if necessary) with 1:1 sulfuric acid solution or 10N sodium hydroxide solution and add 60 mL of methylene chloride to each.

9.4.5 Shake each sample by hand for approximately 10-30 seconds with periodic venting into a hood to release gas pressure.

9.4.6 Extract the sample by shaking the funnel for three minutes on the 3-D Floor Shaker at 150 rpm for the 2 liter separatory funnels and 170 rpm for the 250 ml separatory funnels. Allow the organic layer to separate from the water phase the recommended time is 10 minutes. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, and may include: stirring, filtration of the emulsion through glass wool, centrifugation, or other physical means such as gently knock the outside of the separatory funnel with a small aluminum rod, or centrifuge the samples in 40-mL VOA vials.

9.4.7 Drain the methylene chloride extract through a funnel containing filter paper and sodium sulfate into a Kuderna-Danish/ concentrator tube setup.

9.4.8 Add a second 60-mL volume of methylene chloride to the separatory funnel and repeat the extraction procedure a second time, combining the extracts in the K-D flask. Perform a third extraction in the same manner.

9.4.9 If the sample requires a 2nd pH adjustment (such as 625.1 and 8270C), adjust the sample pH and perform three more 60ml methylene chloride extractions and combine with the original methylene chloride extractions.

9.5 Extraction of TCLP/SPLP Leachates

9.5.1 Inspect all required glassware to ensure it is clean and undamaged.

9.5.2 If the glassware is wet rinse first with methanol, this step is not necessary if the glassware is already dry. Then rinse the glassware three rinses with methylene chloride followed by a final rinse with methanol.

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9.5.3 Allow the leachates to warm to room temperature. The leachates are collected in 500 mL amber glass bottles; only 100 mL is used for extraction, with the remainder of the leachate held in reserve and for QC samples.

9.5.4 Place 250-mL separatory funnels onto a ring stand and label appropriately, allowing one funnel for each sample leachate and one each for the MB, LCS, MS.

9.5.5 Pour 100 mL of the TCLP (or SPLP) Extraction Fluid (same lot as was used to leach the samples) into the separatory funnels marked MB and LCS. Note: Since the sample leachate bottle contains more volume than is processed, spiking cannot be done into those bottles.

9.5.6 Pour 100 mL of each sample leachate into its respective separatory funnel and 100 mL of the sample leachate selected for spiking into the separatory funnel labeled MS.

9.5.7 Inject 1.0 mL of TCLP surrogate spiking solution into all sample leachates, MB, LCS, and MS.

9.5.8 Inject 1.0 mL of TCLP matrix spiking standard into the separatory funnels labeled LCS and MS.

9.5.9 Adjust and record pH's to <2 with 1:1 sulfuric acid solution (approx. 1-2 mL), check after addition to verify pH is still at <2 pH units incase of sample buffering.

9.5.10 Add 60 mL of methylene chloride to each 100-mL graduated cylinder used to measure samples by pouring down the side while rotating the cylinder then transfer to the respective separatory funnel.

9.5.11 Shake each sample by hand for approximately 30 seconds with periodic venting into a fume hood to release gas pressure.

9.5.12 Extract the sample by shaking the funnel for three minutes on the 3-D Floor Shaker at 170 rpm. Allow the organic layer to separate from the water phase the recommended time is 10 minutes. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, and may include: stirring, filtration of the emulsion through glass wool, centrifugation, or other physical means such as gently knock the outside of the separatory funnel with a small aluminum rod, or centrifuge the samples in 40-mL VOA vials.

9.5.13 Drain the methylene chloride extract through a funnel containing filter paper and sodium sulfate into a Kuderna-Danish/concentrator tube setup.

9.5.14 After draining the samples, rinse the sodium sulfate in each funnel with approx. 10-15 mL of methylene chloride.

9.5.15 Add a second 60-mL volume of methylene chloride to the separatory funnel and repeat the extraction procedure a second time, combining the extracts in the K-D flask. Perform a third extraction in the same manner.

9.5.16 Using 10N NaOH, adjust and record the pH to >11 on all samples.

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9.5.17 Serially extract three times with 60 mL of methylene chloride, as outlined in Section 9.5.12 – 9.5.15.

9.6 Extraction of Reduced Volume (≤100mL) Samples

9.6.1 Inspect all required glassware to ensure it is clean and undamaged.

9.6.2 If the glassware is wet rinse first with methanol, this step is not necessary if the glassware is already dry. Then rinse the glassware three rinses with methylene chloride followed by a final rinse with methanol.

9.6.3 Allow the samples to warm to room temperature. Prepare two additional sample aliquots to serve as an MS and MSD.

9.6.4 Prior to measurement of the water sample volume, perform a visual inspection of the sample. There are three different sample types that you are likely to encounter:

- Sample with minimal sediment content.
- Sample with more than one-quarter inch of sediment on the bottom of the container.
- Bi-phasic or multi-phasic sample containing two or more layers.

9.6.5 Water sample with minimal sediment

9.6.6 Mark the level of sample on the outside of the bottle with a marker, briefly shake each sample to re-suspend settled solids. NOTE: If only a portion of the contents of the sample container is going to be extracted, and not the entire contents of the sample container, then briefly shake the container to homogenize the contents and measure the portion used in a graduated cylinder.

(625.1/8270) – Then need to verify if residual chlorine is present by the use of chlorine test strips and if present, treat with 8mg of sodium thiosulfate, prior proceeding any further.

9.6.6.1 Pipet 1.0 mL(when using separatory funnels) or Pipet 0.1ml (when using 200ml glass extraction vessels) of the appropriate surrogate spiking solution into the sample bottle for all Method 3510 extractions with the exception of methods: EPA 625.1 and 608.3 which are to be spiked into the separatory funnels.(also add 1.0 mL or 0.1ml of the matrix spiking standard depending is separatory funnel or glass vessel, if this is a matrix spike sample). Attention: When containers are filled to the top or are poured from a graduated cylinder, the surrogate and matrix spikes needs to be spiked into the separatory funnel instead of the sample bottle container and must be done prior to addition of any solvent.

9.6.6.2 Pour the sample (or sample with spikes) into the 250-mL separatory funnel (if the sample volume is ≤50 mL, then adjust to 100 mL with reagent water). For methods 608.3/625.1/8082 & 8270C use special 200ml glass shaker table extraction vessel instead of separatory funnels.

9.6.6.3 Add 15 mL of methylene chloride to the sample container, cap, and briefly shake. Transfer the solvent to the 250-mL separatory funnel. Add 6ml if using the 200ml glass shaker table extraction vessels.

9.6.6.4 Refill the sample bottle to the mark with water and measure the volume of sample that was in the bottle with a graduated cylinder.

9.6.6.5 Proceed with further procedures as described in sections 9.6.9 through 9.6.12

9.6.7 Water sample with more than one-quarter inch of sediment

9.6.7.1 Immediately notify your Supervisor and the Project Manager to determine if the sediment must be analyzed separately.

9.6.7.2 (625.1/8270) – Need to verify if residual chlorine is present by the use of chlorine test strips and if present, treat with 8mg of sodium thiosulfate, prior proceeding any further.

9.6.7.3 Carefully decant the water from the container to a 100-mL graduated cylinder ensuring minimal sediment is transferred.

9.6.7.4 Record the volume at the bottom of the meniscus.

9.6.7.5 Pour sample into the separatory funnel or glass extraction tube (if the sample volume is ≤50 mL, then adjust to 100 mL with reagent water). Pipet 1.0 mL if into separatory funnel or 0.1ml if into glass vessel of the surrogate spiking solution. (also add 1.0 mL or 0.1ml of the matrix spiking standard depending is separatory funnel or glass vessel, if this is a matrix spike sample).

9.6.7.6 Add 15 mL of methylene chloride to the graduated cylinder by pouring down the side while rotating the cylinder, 6mls if using glass extraction vessels. Transfer the solvent to the separatory funnel.

9.6.7.7 Proceed with further procedures as described in sections 9.6.9 through 9.6.12.

9.6.8 Bi-phasic or multi-phasic samples

9.6.8.1 Immediately notify your Supervisor and Project Manager and determine which phase(s) is to be tested.

9.6.8.2 (625.1/8270) – Need to verify if residual chlorine is present by the use of chlorine test strips and if present, treat with 8mg of sodium thiosulfate, prior proceeding any further.

9.6.8.3 Carefully pour the sample from the container into a 250-mL separatory funnel. Bi-phasic samples will typically have the lower-density organics in the top layer and the lower layer will be aqueous. If more than one phase is present, a series of miscibility evaluations may be necessary in order to determine the phase types present.

9.6.8.4 Drain the lower or aqueous phase into the 250-mL graduated cylinder, record the volume to the bottom of the meniscus and pour the sample into the separatory funnel or glass extraction vessel(if the sample volume is ≤50 mL, then adjust to 100 mL with reagent water).

9.6.8.5 Pipet 1.0 mL of the surrogate spiking solution into the separatory funnel or 0.1ml of surrogate if into the glass extraction vessel.(also add 1.0 mL or 0.1ml of the matrix spiking standard depending is separatory funnel or glass vessel, if this is a matrix spike sample).

9.6.8.6 Add 15 mL of methylene chloride to the graduated cylinder by pouring down the side while rotating the cylinder, 6ml if using glass extraction vessels. Finally, transfer the solvent to the separatory funnel or glass extraction vessel.

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9.6.8.7 From the first 250-mL separatory funnel used, drain the remaining top layer or organic phase into the original sample container and cap. Keep for possible further testing.

9.6.8.8 Proceed with further procedures as described in sections 9.6.9 through 9.6.12

9.6.9 Add (2) 100-mL aliquots of reagent water to separatory funnels or glass extraction vessels to serve as the Method Blank and LCS. Add 1.0 mL of the surrogate spiking solution is separatory funnel or 0.1ml if glass vessel to the MB and LCS and 1.0 mL if separatory funnel and 0.1ml if glass vessel of the matrix spiking standard to the LCS. Add 15 mL of methylene chloride to each separatory funnel, if using glass extraction vessels add 6ml of methylene chloride to each glass vessel.

9.6.10 Shake each sample by hand for approximately 10-30 seconds with periodic venting into a hood to release gas pressure.

9.6.11 Extract the sample by shaking the funnel for three minutes on the 3-D Floor Shaker at 170 rpm. If using Glass Extraction Vessels, shake for three minutes on Table Shaker. Allow the organic layer to separate from the water phase the recommended time is 10 minutes. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, and may include: stirring, filtration of the emulsion through glass wool, centrifugation, or other physical means such as gently knock the outside of the separatory funnel with a small aluminum rod, or centrifuge the samples in 40-mL VOA vials.

9.6.12 Drain the methylene chloride extract through a funnel containing filter paper and sodium sulfate into a Kuderna-Danish/ concentrator tube setup for reduced volume 8270SIM samples. (Use ExcelVap tubes for reduced volume OA2, 8015, and MO TPH-DRO/ORO samples and all samples done on the table shaker with glass extraction vessels.)

9.6.13 Add a second 15-mL volume of methylene chloride to the separatory funnel or 6 mls if using glass extraction vessels and repeat the extraction procedure a second time, combining the extracts in the K-D flask or ExcelVap tube. Perform a third extraction in the same manner.

9.6.14 Methods that require changing the pH and doing a 2nd series of extractions such as 625.1 and 8270, repeat the methylene extraction step 3 more times after changing the pH. Using 15mls each time if using separatory funnels and 6ml each time if using the glass extraction vessels.

9.7 Extract Concentration (Kuderna-Danish Method)

9.7.1 Quantitatively transfer the extract to a Kuderna-Danish (K-D) flask, fitted with a concentrator tube, and add 1-2 clean boiling chips. Attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL methylene chloride to the top.

9.7.2 Place the K-D apparatus on a hot water bath (~70ºC) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 20 to 25 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. Note: The K-D temperature range should be set between 60 to 80 degrees with a target of

70 degrees C. At the target range of 70 the concentrator balls should have sufficient chatter and not be flooding. If there is not sufficient chatter or the balls are flooding contact the appropriate supervisor for guidance.

9.7.3 When the apparent volume of liquid reaches approximately 10 mL, disconnect the K-D apparatus (Snyder column) from the methylene chloride collection device.

9.7.4 and allow K-D volumes to come down to ~ 5mls.

9.7.5 If a solvent exchange is required (as indicated in Tables 26.1 or 26.2):

- concentrate the extract to approximately 5 mL and add 10 mL of hexane or MTBE for Method 508,
- repeat the process of concentration and exchange solvent addition,
- concentrate to approximately 5ml

9.7.6 Rinse in a circular motion, the Snyder column with 2-3 mL of the final solvent. Remove the entire K-D flask apparatus and let cool for approximately 10 minutes, must be cool to the touch.

9.7.7 Remove Snyder column and KD flask and extract is now ready for final concentration step.

9.7.8 Final Extract Concentration (N-EVAP)

9.7.9 Place the concentrator tube in a warm water bath (~35 ºC) and further evaporate the solvent volume to approximately ½ of the target final volume (Tables in section 24) with a gentle stream of nitrogen. The extract must never be allowed to become dry. If it does, contact your supervisor immediately.

9.7.10 Rinse down sides of concentrator tube with extract and transfer to final vial type (2ml or 10ml) as appropriate for the target final volume. Add more final solvent to the concentrator tube and again rinse the sides and transfer this to the final vial type (try to keep original extract and extra solvent below final solvent volume. Adjust final extract volume to the appropriate volume by either adding more solvent or using N-EVAP to blow down to final volume is you over shot the true final volume. (It is critical that this volume is precise)

9.7.11 If the final extract will not be analyzed immediately, it must be stored in accordance with the determinative method.

9.8 ExcelVap Extract Concentration

9.8.1 The concentrator tubes are rinsed with methylene chloride prior to use.

9.8.2 Verify that the ExcelVap is set to the appropriate program.

9.8.3 Micro-Vessel Units: Program A (40ml volumes or less and a final volume of 1ml). Program B (40ml volumes or less and a final volume of 5ml).

9.8.4 Macro-Vessel Units: Program A (40ml volumes or less and a final volume of 1ml). Program B (40ml volumes or less and a final volume of 5ml or 10ml).

9.8.5 The ExcelVap temperature must be recorded on the laboratory bench sheet.

9.8.6 While under the fume hood, quantitatively transfer the entire sample extract into a labeled ExcelVap tube (Take care as not to fill the tube full, it must have at a minimum 1 ¾ inch of

head space. This will insure that during the ExcelVap process splashing and cross contamination does not occur.) Note: Do not pour sample extract into the tubes while they are in the ExcelVap.

9.8.7 Ensure that the nitrogen flow has been turned on and has enough pressure in the tank.

9.8.8 Place tubes into the ExcelVap and close the lid.

9.8.9 Select the appropriate program in the ExcelVap and turn on all the rows of tubes that you have samples in and start the program.

9.8.10 The programs have set times and when the timer sounds, you must check the volume in the ExcelVap tubes and from this point on you must not leave unattended. It is important to remove the tubes when the volumes get just below the expected final volumes. The majority of these final volumes is 1ml and methylene chloride will evaporate rapidly in the ExcelVap below this level. This may cause extract to go dry or extremely low, which will result in low analyte recoveries.

9.8.11 Using a 9" disposable pipette, remove the solvent from the excelVap tube and place into the final extract vessel to be sent to the analytical laboratory.

9.8.12 Add small amounts of fresh solvent and rinse down the side walls of the ExcelVap tube in a swirling motion at the point just above where the tube narrows. Add the solvent to the final extract vessel do not go over expected volume.

9.8.13 Repeat the above technique until you reach your final extract volume.

9.8.14 Adjust final extract volume to the appropriate volume by either adding more solvent or using N-EVAP to blow down to final volume if you over shot the true final volume. (It is critical that this volume is precise)

9.8.15 Securely tighten the sample extract cap and store all extracts according to the determinative method.

9.9 ExcelVap Maintenance

9.9.1 ExcelVap Nozzles

9.9.1.1 The nozzles in the ExcelVap are removeable and should be replaced in the event that they get bent or no longer deliver the expected flow.

9.9.2 ExcelVap Water Bath

9.9.2.1 ExcelVap's that are used for 40mL volumes (Micro Vessels) need to have the water checked daily and verified that they are at the proper level. This level should be at the 10 L volume mark located on the inside back panel of the water reservoir. Note: Only deionize water is to be used.

9.9.2.2 ExcelVap's that are used for 150mL volumes (Macro Vessels) need to have the water checked daily and verified that they are at the proper level. This level should be at the 9 L level, half-way between the 8L and 10L marks located on the inside back panel of the water reservoir. Note: Only deionize water is to be used.

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10.0 DATA ANALYSIS AND CALCULATIONS

10.1 Qualitative Identification

Not Applicable

10.2 Quantitative Identification

Not Applicable

10.3 Calculations

See the Laboratory Quality Assurance Manual for equations for common calculations.

11.0 QUALITY CONTROL AND METHOD PERFORMANCE

11.1 Quality Control

The following QC samples are prepared and analyzed with each batch of samples. Refer to Appendix B for acceptance criteria and required corrective action.

QC Item	Frequency
Method Blank (MB)	1 per batch of 20 or fewer samples.
Laboratory Control Sample (LCS)	1 per batch of 20 or fewer samples.
Laboratory Control Sample Duplicate (LCSD)	As needed; KS MRH/HRH required
Matrix Spike (MS)	1 per batch of 20 or fewer samples.
Matrix Spike Duplicate (MSD)	1 per batch of 20 or fewer samples.
Surrogate Spike	Added to all QC and samples

11.2 Instrument QC

Not Applicable.

11.3 Method Performance

11.3.1 Method Validation

11.3.1.1 Detection Limits

Detection limits (DL) and limits of quantitation (LOQ) are established at initial method setup and verified on an on-going basis thereafter. Refer to Pace ENV corporate SOP ENV-SOP-CORQ-0011 Method Validation and Instrument Verification.

11.4 Analyst Qualifications and Training

Employees that perform any step of this procedure must have a completed Read and Acknowledgment Statement for this version of the SOP in their training record. In addition, prior to unsupervised (independent) work on any client sample, analysts that prepare or analyze samples must have successful initial demonstration of capability (IDOC) and must successfully

demonstrate on-going proficiency on an annual basis. Successful means the initial and on-going DOC met criteria, documentation of the DOC is complete, and the DOC record is in the employee's training file. Refer to laboratory SOP ENV-SOP-LENE-0110, *Training Procedures*, for more information.

12.0 Data Review And Corrective Action

12.1 Data Review

Pace's data review process includes a series of checks performed at different stages of the analytical process by different people to ensure that SOPs were followed, the analytical record is complete and properly documented, proper corrective actions were taken for QC failure and other nonconformance(s), and that test results are reported with proper qualification.

The review steps and checks that occur as employee's complete tasks and review their own work is called primary review.

All data and results are also reviewed by an experienced peer or supervisor. Secondary review is performed to verify SOPs were followed, that calibration, instrument performance, and QC criteria were met and/or proper corrective actions were taken, qualitative ID and quantitative measurement is accurate, all manual integrations are justified and documented in accordance with the Pace ENV's SOP for manual integration, calculations are correct, the analytical record is complete and traceable, and that results are properly qualified.

A third-level review, called a completeness check, is performed by reporting or project management staff to verify the data report is not missing information and project specifications were met.

Refer to laboratory SOP ENV-SOP-LENE-088, *Data Reduction, Review and Reporting*, for specific instructions and requirements for each step of the data review process.

12.2 Corrective Action

Corrective action is expected any time QC or sample results are not within acceptance criteria. If corrective action is not taken or was not successful, the decision/outcome must be documented in the analytical record. The primary analyst has primary responsibility for taking corrective action when QA/QC criteria are not met. Secondary data reviewers must verify that appropriate action was taken and/or that results reported with QC failure are properly qualified.

Corrective action is also required when carryover is suspected and when results are over range.

Samples analyzed after a high concentration sample must be checked for carryover and reanalyzed if carryover is suspected. Carryover is usually indicated by low concentration detects of the analyte in successive samples analyzed after the high concentration sample.

Sample results at concentrations above the upper limit of quantitation must be diluted and reanalyzed. The result in the diluted samples should be within the upper half of the calibration range. Results less than the mid-range of the calibration indicate the sample was over diluted and analysis should be repeated with a lower level of dilution. If dilution is not performed, any result

reported above the upper range is considered a qualitative measurement and must be qualified as an estimated value.

Refer to Appendix B for a complete summary of QC, acceptance criteria, and recommended corrective actions for QC associated with this test method.

13.0 POLLUTION PREVENTION AND WASTE MANAGEMENT

Pace proactively seeks ways to minimize waste generated during our work processes. Some examples of pollution prevention include but are not limited to: reduced solvent extraction, solvent capture, use of reusable cycletainers for solvent management, and real-time purchasing.

The EPA requires that laboratory waste management practice to be conducted consistent with all applicable federal and state laws and regulations. Excess reagents, samples and method process wastes must be characterized and disposed of in an acceptable manner in accordance with Pace's Chemical Hygiene Plan / Safety Manual.

14.0 MODIFICATIONS

A modification is a change to a reference test method made by the laboratory. For example, changes in stoichiometry, technology, quantitation ions, reagent or solvent volumes, reducing digestion or extraction times, instrument runtimes, etc. are all examples of modifications. Refer to Pace ENV corporate SOP ENV-SOP-CORQ-0011 *Method Validation and Instrument Verification* for the conditions under which the procedures in test method SOPs may be modified and for the procedure and document requirements.

14.1 Surrogate and matrix spikes are not spiked into the sample containers if the containers are full or if not all the sample is being used. The surrogate and matrix spikes are spiked into the extraction separatory funnels or glass extraction vessels prior to any solvent being added. This will work in the same manner as spiking into the containers which is to give surrogates and spikes the ability to disperse into sample prior to solvent addition.

14.2 The addition of 8mg of sodium thiosulfate is used instead of 80mg of sodium sulfate when residual chlorine is present when doing the 100ml extractions vs the 1liter extractions. Amount is reduced by the same factor as the volume of sample being extracted**.**

15.0 RESPONSIBILITIES

Pace ENV employees that perform any part this procedure in their work activities must have a signed Read and Acknowledgement Statement in their training file for this version of the SOP. The employee is responsible for following the procedures in this SOP and handling temporary departures from this SOP in accordance with Pace's policy for temporary departure.

Pace supervisors/managers are responsible for training employees on the procedures in this SOP and monitoring the implementation of this SOP in their work area.

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16.0 ATTACHMENTS

Table 26.1 – Extraction conditions regular volume

Table 26.2 – Extraction conditions reduced volume

17.0 REFERENCES

17.1 Pace Quality Assurance Manual – most current version.

17.2 National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, "Quality Systems"- most current version.

17.3 The NELAC Institute (TNI); Volume 1, Module 2, "Quality Systems"- most current version.

17.4 EPA Test Methods for Evaluating Solid Waste, SW-846, Third Edition, Update III, 12/96, Method 3510C.

17.5 Method 508, Determination of Chlorinated Pesticides in Water by Gas Chromatography with an Electron Capture Detector, Rev. 3.1, 1995.

18.0 REVISION HISTORY

This Version:

Section	Description of Change
All	NEW SOP format

This document supersedes the following document(s):

TEST METHOD STANDARD OPERATING PROCEDURE
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Document Number	Reason for Change	Date
S-KS-O-029-rev.0	New	October 8, 2007
S-KS-O-029-rev.1	Grammatical/Removal of outdated information.	September 18, 2009
S-KS-O-029-rev.2	Section 7 – Revised Distribution Section 10 - Removed spike and surrogate preparation. Section 12 - Removed reference to Method 8081. Samples to be spiked before addition of bottle rinsates.	January 26, 2011
S-KS-O-029-rev.3	Section 9 – Added TurboVap Section 12 – Added the TurboVap® II Extract concentration procedure Section 12.10 - removed 10 min. time limit, allow to separate before proceeding.	September 28, 2011
S-KS-O-029-rev.4	SOP – Deleted Responsibilities and Distribution section. Section 6 – Substituted reference to Quality Manual. Section 11 – Added spent sample disposal. Section 13 – Added LOD language.	November 4, 2011
S-KS-O-029-rev.5	General – Updated to latest prescribed format and combined reduced volume and regular volume extraction procedures into one SOP Section 7 – Removed analytical holding time. Section 12 – Revised criteria for sample volume adjustments. Added salting out procedure for catechols. Moved solvent exchange procedure to S-EVAP. Revised glassware rinsing procedure to match lab practice. Biphasic samples transferred to separatory funnels before surrogate spiking. Revised TurboVap instructions. 12.3.10 – Revised extraction of reduced volume to use table shaker instead of floor shaker and added extra hand shake out step for OA2 reduced volume 12.3.12 – Revised KD use for reduced volume SIM only. Other reduced volume analyses use TurboVap. Section 13 – Reworded tables for clarity Section 24 – Revised final volume to 1.0mL for reduced volume OA2, 8015, and MODRO	November 15, 2013
S-KS-O-029-rev.6	SOP -- Revised to latest prescribed format. 12.2.12- add floor shake r and make shaker table an option 12.3.10 – add floor shaker and make shaker table an option 12.4.2 – change K-D water batch to set 70 degrees 19.2 – add method modification to spike surrogates and spikes into separatory funnel and not container or grad cylinder.	March 2, 2015
S-KS-O-029-rev.7	Section 2.0 – Inserted "500ml for Kansas TPH" Sections 12.1.5 and 12.1.6 – Kansas TPH 500 mL volume added. Section 12.1.10 – Added rpm specifications. Added Headers of Table 26.1 and Table 26.2 Table 26.1 – Added Kansas TPH Method	April 15, 2016
S-KS-O-029-rev.8	Table 26.1 – Added 1,4-Dioxane (SIM)	November 08,2016
S-KS-O-029-rev.9	SOP – Cover page changed to Pace LLC. Section : 3.2 Added Chlorinated Hydrocarbons Table 26.1 – Added 8121, Chlorinated Hydrocarbons	April 16, 2018
ENV-SOP-LENE-0039-01	SOP – Removed Cover page, Table of Contents and headers Sections 12.1, 12.2 and 12.3 – Revised instruction for methanol rinse Section 18.2 – Revised SOP reference Section 18.3 – Revised SOP reference	November 2, 2018

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Document Number	Reason for Change	Date
ENV-SOP-LENE-0039-02	Section 12.1.5.2 – Revised to spike into the sample bottle. Section 12.1.6.4 – Revised to spike into the sample bottle Section 12.1.6.7 – Removed original section (transferring sediment into different container). Section 12.2.3 and 12.2.5 – Revised to add additional information Section 12.3.5 – Revised to spike into the sample bottle Section 12.3.6.5 – Removed original section (transferring sediment into different container). Section 19.2 – Removed method modification on spiking in separatory funnel.	January 9, 2019
ENV-SOP-LENE-0039-02	Section 1.0 – Added EPA Method 508 Section 26.0 --Added method 508 to table 26.1 Section 12.0 -- Added MTBE to table 12.4.4 Section 25.0 – Added EPA Method 508 reference	January 30,2020
ENV-SOP-LENE-0039-03	Updated sections to include the reduced volume process for all extraction methods.	March 31, 2021
ENV-SOP-LENE-0039-03	Updated the equipment from turbo vaps to excel vaps	March 31, 2021
ENV-SOP-LENE-0039-03	Updated 508 extraction to follow closer to the method per KDHE audit	March 31, 2021

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Appendix A: Target Analyte List and Routine LOQ

Table 1: Routine Analyte List and Limits of Quantitation (LOQ)[1]

Refer to Analytical SOPs.

[1] Values in place as of effective date of this SOP. LOQ are subject to change. For the most up to date LOQ, refer to the LIMS or contact the laboratory.

Table 26.1

Extraction Conditions for Various Methods (Regular ≥500mL Volume)

Method	Initial Extraction pH	Secondary Extraction pH	Exchange Solvent	Final Extract Volume (mL)
8015B/C	as received	N/A	N/A	5.0
8082	5-9	N/A	hexane	10.0
8270C	<2	>11	N/A	1.0
8270C (PAH SIM)	as received	N/A	N/A	1.0
OA-2	as received	N/A	N/A	5.0
Oklahoma DRO	as received	N/A	N/A	5.0
TCLP 8270C	<2	>11	N/A	1.0
MO TPH-DRO/ORO	as received	N/A	N/A	10.0
Kansas TPH	< 2	N/A	N/A	5.0
1,4-Dioxane (SIM)	< 2	N/A	N/A	1.0
8121 Chlorinated Hydrocarbons.	As received	N/A	hexane	10.0
EPA 508	Phosphate buffered at 7	N/A	MTBE	10.0

Table 26.2

Extraction Conditions for Various Methods (100mL Volume)

Method	Initial Extraction pH	Secondary Extraction pH	Exchange Solvent	Final Extract Volume (mL)
8015B/C	as received	N/A	N/A	1.0
8082	5-9	N/A	hexane	5
8270C	<2	>11	N/A	1.0
8270C (PAH SIM)	as received	N/A	N/A	1.0
OA-2	as received	N/A	N/A	1.0
TCLP 8270C	<2	>11	N/A	1.0

Document Information

Document Number: ENV-SOP-LENE-0023 **Revision:** 02

Document Title: Conductivity

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Notes

Document Notes:

All Dates and Times are listed in: Central Time Zone

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Document Number: ENV-SOP-LENE-0023 **Revision:** 02

Title: Conductivity

All dates and times are in Central Time Zone.

ENV-SOP-LENE-0023 (Conductivity & Salinty)

QM Approval

Name/Signature	Title	Date	Meaning/Reason
Kenneth Busch (991414)	Manager - Quality	23 Aug 2021, 10:51:08 AM	Approved

Management Approval

Name/Signature	Title	Date	Meaning/Reason
Kenneth Busch (991414)	Manager - Quality	23 Aug 2021, 10:51:20 AM	Approved
Joshua Cunningham (003261)	Manager	23 Aug 2021, 11:09:09 AM	Approved
Charles Girgin (002243)	General Manager 2	25 Aug 2021, 11:05:10 AM	Approved

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TEST METHOD STANDARD OPERATING PROCEDURE
TITLE: Specific Conductivity and Salinity
TEST METHOD SM 2510B and SM 2520B
ISSUER: Pace ENV – Lenexa Quality – LENE

1.0 SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the laboratory procedure for the determination of Conductivity and Salinity by electrode meter.

1.1 Target Analyte List and Limits of Quantitation (LOQ)

The target analytes and the normal LOQ that can be achieved with this procedure are provided in achieved with this procedure is 1.0 µmhos/cm for Conductivity and 1.0 ppth (part per thousand). MDLs are not applicable to this procedure.

LOQ are established in accordance with Pace policy and SOPs for method validation and for the determination of detection limits (DL) and quantitation limits (LOQ). DL and LOQ are routinely verified and updated when needed. The current LOQ for each target analyte that can be determined by this SOP as of the effective date of this SOP is provided in Table 1, Appendix A.

The reporting limit (RL) is the value to which analytes are reported as detected or not detected in the final report. When the RL is less than the lower limit of quantitation (LLOQ), all detects and non-detects at the RL are qualitative. The LLOQ is the lowest point of the calibration curve used for each target analyte.

DL, LOQ, and RL are always adjusted to account for actual amounts used and for dilution.

2.0 SUMMARY OF METHOD

2.1 The specific conductance or salinity of a sample is measured using a self-contained conductivity meter, Wheatstone Bridge type, or equivalent.

2.2 Samples are preferably analyzed at 25°C. If not, the instrument will apply a Temperature Compensation factor of 2% per ºC

3.0 INTERFERENCES

3.1 Coatings of oily material or particulate matter can impair electrode response. The electrode should be thoroughly rinsed and cleaned between samples.

4.0 DEFINITIONS

Refer to the Laboratory Quality Manual for a glossary of common lab terms and definitions.

5.0 HEALTH AND SAFETY

The toxicity or carcinogenicity of each chemical material used in the laboratory has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable.

The laboratory maintains documentation of hazard assessments and OSHA regulations regarding the safe handling of the chemicals specified in each method. Safety data sheets for all hazardous

chemicals are available to all personnel. Employees must abide by the health, safety and environmental (HSE) policies and procedures specified in this SOP and in the Pace Chemical Hygiene / Safety Manual.

Personal protective equipment (PPE) such as safety glasses, gloves, and a laboratory coat must be worn in designated areas and while handling samples and chemical materials to protect against physical contact with samples that contain potentially hazardous chemicals and exposure to chemical materials used in the procedure.

Concentrated corrosives present additional hazards and are damaging to skin and mucus membranes. Use these acids in a fume hood whenever possible with additional PPE designed for handing these materials. If eye or skin contact occurs, flush with large volumes of water. When working with acids, always add acid to water to prevent violent reactions. Any processes that emit large volumes of solvents (evaporation/concentration processes) must be in a hood or apparatus that prevents employee exposure.

Contact your supervisor or local HSE coordinator with questions or concerns regarding safety protocol or safe handling procedures for this procedure.

6.0 SAMPLE COLLECTION, PRESERVATION, HOLDING TIME, AND STORAGE

Samples should be collected in accordance with a sampling plan and procedures appropriate to achieve the regulatory, scientific, and data quality objectives for the project.

The laboratory performs samples collection for samples to be analyzed by this SOP in accordance with laboratory SOP ENV-SOP-LENE-0107, *Field Manual*. Refer to this SOP for these instructions.

The laboratory will provide containers for the collection of samples upon client request for analytical services. Bottle kits are prepared in accordance with laboratory SOP ENV-SOP-LENE-0025, *Assembly of Sample Container Kits*.

Requirements for container type, preservation, and field quality control (QC) for the common list of test methods offered by Pace are included in the laboratory's quality manual.

General Requirements

Matrix	Routine Container	Minimum Sample Amount[1]	Preservation	Holding Time
Aqueous	Plastic or glass, 250 or 500 mL	50 mL	Thermal: ≤6°C (not frozen) Chemical: None	28 days
Soil	2 or 4 oz. glass jar	20 g	Thermal: ≤6°C (not frozen) Chemical: None	Collection to Prep:28 days Prep to Analysis: Same Day

[1]*Minimum amount needed for each discrete analysis.*

Field / Matrix QC

Trip Blank	Equipment Blank	MS/MSD	Field Duplicate
NA	NA	NA	As Needed

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Thermal preservation is checked and recorded on receipt in the laboratory in accordance with laboratory SOP ENV-SOP-LENE-0021, *Sample Management*. Chemical preservation is checked and recorded at time of receipt or prior to sample preparation.

After receipt, samples are stored at ≤6°C until sample preparation. Prepared samples (extracts, digestates, distillates, other) are stored at ≤6°C until sample analysis.

After analysis, unless otherwise specified in the analytical services contract, samples are retained for 30 days from date of final report and then disposed of in accordance with Federal, State, and Local regulations.

7.0 EQUIPMENT AND SUPPLIES

7.1 Equipment

Supply	Vendor	Model / Version	Comments
Conductivity meter	Thermo-Fisher	Orion Star A212	With automatic temperature compensation
Analytical balance	Mettler-Toledo	AE240	Or equivalent
Magnetic stirrer	Fisher	Various	

7.2 Supplies

Supply	Vendor	Model / Version	Comments
Disposable cups, 100-mL	Fisher	N/A	N/A
Stirbars	Fisher	14-513-94	8x25mm
Wash bottle	Fisher	03-409-11E	Nalgene®
Graduated cylinders	Fisher	08-553B	100-mL, Class A
Volumetric flask	Fisher	10-209H	1-L, Class A
Laboratory wipe tissues	Fisher	06666A	Kimwipes

8.0 REAGENTS AND STANDARDS

8.1 Reagents

Reagent/Standard	Concentration/ Description	Vendor/ Item #
Reagent water	ASTM Type II	SOP ENV-SOP-LENE-0131 (latest revision)
Probe storage solution	Redi-Stor® Probe Storage Solution	Fisher / 09-330-1

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8.2 Standards

Reagent/Standard	Concentration/ Description	Vendor/ Item #
Primary standard (high)	30,100 µmho/cm; Ricca Chemical	Fisher / 2247.30-32
Primary standard (mid)	4,500 µmho/cm; Ricca Chemical	Fisher / R5888420-1A
Primary standard (mid)	1409 µmho/cm; Ricca Chemical	Fisher / 589532
Primary standard (mid)	718 µmho/cm; Ricca Chemical	Fisher / 58877232
Primary standard (low)	15 µmho/cm; Ricca Chemical	Fisher / 22360316
Secondary check standard	447 µmho/cm; Cole-Parmer	Fisher / 13-300-117

9.0 PROCEDURE

9.1 Initial Calibration

9.1.1 Turn the conductivity meter on and let it warm up for 10 minutes. Ensure that all standards are at room temperature.

9.1.2 Fill a disposable cup with approximately 50 mL of each primary standard.

9.1.3 Press the “Cal” button. Immerse the conductivity probe into the 15 µmho/cm solution up to the immersion level.

9.1.4 While stirring, select the “Start” button. Allow sufficient time for conductivity value to stabilize.

9.1.5 If the displayed concentration differs from the actual concentration press the “Edit” button and adjust the value. Once entered, press the “done” button to establish the value then the “next” button to move to the next standard.

9.1.6 Repeat steps 9.2.4 – 9.2.5 for each remaining primary standard.

9.1.7 Once the last standard is read select the “cal done” button followed by the “measure” button to return to the main screen.

9.2 Measure the 5 primary standards to verify proper operation over the entire range. Note: This is equivalent to performing the cell constant (K). The cell constant is determined by dividing the measured value by the true value of the reference standard.

9.3 Results must be within ±10% of the solution true values to begin analysis.

9.4 Recalibrate when any of the calibration check standards, ICV or CCV’s are verified outside of the control limits.

9.4.1 Calibration Standard Concentrations

Standard Concentration (µmho/cm)	Standard Type	Lower Control Limit	Upper Control Limit
15	Primary	13.5	16.5
718	Primary	646	790
1408	Primary	1267	1549
4500	Primary	4050	4950
30100	Primary	27090	33110

9.4.2 ICAL Evaluation

9.4.2.1 Curve Fit

The instrument response to the standards is checked to verify the response is accurate. No external curve is produced.

9.4.2.2 Relative Standard Error (RSE)

Not applicable to this procedure.

9.4.2.3 Initial Calibration Verification

9.4.2.4 Initial Calibration Verification (ICV) must be performed using the secondary check standard (447 µmho/cm).

9.4.2.5 The values obtained from the analysis of the ICV are compared to the true values and a percent difference calculated. The percent difference must meet the method specified criteria for the analysis to proceed for an additional 20 samples.

9.4.3 Continuing Calibration Verification

9.4.3.1 The values obtained from the analysis of the CCV are compared to the true values and a percent difference calculated. The percent difference must meet the method specified criteria for the analysis to proceed for an additional 20 samples.

9.5 Sample Preparation

9.5.1 Homogenization and Subsampling

Refer to the SOP ENV-SOP-LENE-0135, *Sample Homogenization and Sub-Sampling*.

9.6 Analysis

A daily calibration check is performed prior to analysis. Read each of the standards listed in Calibration Concentrations table and record the values in the electronic logbook. If all are in control, proceed with sample analysis. If any are out of control, recalibrate.

9.7 Sample Analysis

9.7.1 Allow samples to warm to room temperature prior to analysis.

9.7.2 Water Samples: Fill the disposable cup with about 50 mL of sample. Verify that the probe is fully immersed.

9.7.3 Soil Samples: Weigh 20 g of sample into a centrifuge tube, add 20 mL reagent water and cap. Place the centrifuge tube on a shaker and shake for about 15 minutes. Centrifuge the mixture for about 10 minutes. Decant the supernatant into a disposable cup.

9.7.4 Rinse the probe with reagent water and immerse the probe into the sample, up to the immersion level. Press the “measure” button. Stir and allow reading to stabilize.

9.7.5 Rinse the probe with reagent water and return to step 12.1.4.

9.7.6 Record all results in the Conductivity or Salinity Workbench template.

9.7.7 If performing Salinity analysis, perform daily QC checks in the same manner as conductivity analysis. Once instrument performance is verified, change the measured units from mS/cm to psu. The acceptable range is 2 to 42 psu. If greater than 42 psu, the result must be qualified as estimated.

9.7.8 Example Analytical Sequence

Lab Sample ID	Sample Type
CAL0	CAL 0
CAL1	CAL 1
CAL2	CAL 2
CAL3	CAL 3
CAL4	CAL 4
CAL5	CAL 5
ICV	Calibration Verification
Method blank	Blank
Sample	PS
Sample Duplicate	DUP
Sample	PS
Sample	PS
Sample	PS
Sample	PS
Sample	PS

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Lab Sample ID	Sample Type
Sample	PS
Sample	PS
CCVA	CCVA
Repeat cycle of Samples alternating CCVA and CCVB	

10.0 DATA ANALYSIS AND CALCULATIONS

10.1 Quantitative Identification

Results are read directly from the instrument.

10.2 Calculations

See the Laboratory Quality Assurance Manual for equations for common calculations.

11.0 QUALITY CONTROL AND METHOD PERFORMANCE

11.1 Quality Control

The following QC samples are prepared and analyzed with each batch of samples. Refer to Appendix A for acceptance criteria and required corrective action.

QC Item	Frequency
Method Blank (MB)	1 per batch of 20 or fewer samples. If batch exceeds, 20 samples, every 20.
Sample Duplicate	1 per batch of 20 or fewer samples. If batch exceeds, 20 samples, every 20.
Laboratory Control Sample (Salinity only)	1 per batch of 20 or fewer samples. If batch exceeds, 20 samples, every 20.

11.2 Instrument QC

The following Instrument QC checks are performed. Refer to Appendix A for acceptance criteria and required corrective action.

QC Item	Frequency
Initial Calibration	Every 6 months or if daily calibration verification fails. Whichever is sooner.
Initial Calibration Verification	After calibration prior to the analysis of samples.
Initial Calibration Blank	With each calibration
Continuing Calibration Verification	Every 10 samples or QC

11.3 Method Performance

11.3.1 Method Validation

11.3.1.1 Detection Limits

Detection limits (DL) and limits of quantitation (LOQ) are established at initial method setup and verified on an on-going basis thereafter. The Method Detection Limit procedure does not apply to this test. Refer to Pace ENV corporate SOP ENV-SOP-CORQ-0011 Method Validation and Instrument Verification and to the laboratory's SOP ENV-SOP-LENE-0117, *Limit of Detection*, for these procedures.

11.4 Analyst Qualifications and Training

Employees that perform any step of this procedure must have a completed Read and Acknowledgment Statement for this version of the SOP in their training record. In addition, prior to unsupervised (independent) work on any client sample, analysts that prepare or analyze samples must have successful initial demonstration of capability (IDOC) and must successfully demonstrate on-going proficiency on an annual basis. Successful means the initial and on-going DOC met criteria, documentation of the DOC is complete, and the DOC record is in the employee's training file. Refer to laboratory SOP ENV-SOP-LENE-010, *Training Procedures*, for more information.

12.0 Data Review And Corrective Action

12.1 Data Review

Pace's data review process includes a series of checks performed at different stages of the analytical process by different people to ensure that SOPs were followed, the analytical record is complete and properly documented, proper corrective actions were taken for QC failure and other nonconformance(s), and that test results are reported with proper qualification.

The review steps and checks that occur as employee's complete tasks and review their own work is called primary review.

All data and results are also reviewed by an experienced peer or supervisor. Secondary review is performed to verify SOPs were followed, that calibration, instrument performance, and QC criteria were met and/or proper corrective actions were taken, qualitative ID and quantitative measurement is accurate, all manual integrations are justified and documented in accordance with the Pace ENV's SOP for manual integration, calculations are correct, the analytical record is complete and traceable, and that results are properly qualified.

A third-level review, called a completeness check, is performed by reporting or project management staff to verify the data report is not missing information and project specifications were met.

Refer to laboratory SOP ENV-SOP-LENE-088, *Data Reduction, Review and Reporting*, for specific instructions and requirements for each step of the data review process.

12.2 Corrective Action

Corrective action is expected any time QC or sample results are not within acceptance criteria. If corrective action is not taken or was not successful, the decision/outcome must be documented in the analytical record. The primary analyst has primary responsibility for taking corrective action when QA/QC criteria are not met. Secondary data reviewers must verify that appropriate action was taken and/or that results reported with QC failure are properly qualified.

Corrective action is also required when carryover is suspected and when results are over range.

Samples analyzed after a high concentration sample must be checked for carryover and reanalyzed if carryover is suspected. Carryover is usually indicated by low concentration detects of the analyte in successive samples analyzed after the high concentration sample.

Sample results at concentrations above the upper limit of quantitation must be diluted and reanalyzed. The result in the diluted samples should be within the upper half of the calibration range. Results less than the mid-range of the calibration indicate the sample was over diluted and analysis should be repeated with a lower level of dilution. If dilution is not performed, any result reported above the upper range is considered a qualitative measurement and must be qualified as an estimated value.

Refer to Appendix B for a complete summary of QC, acceptance criteria, and recommended corrective actions for QC associated with this test method.

13.0 Pollution Prevention And Waste Management

Pace proactively seeks ways to minimize waste generated during our work processes. Some examples of pollution prevention include but are not limited to: reduced solvent extraction, solvent capture, use of reusable cycletainers for solvent management, and real-time purchasing.

The EPA requires that laboratory waste management practice to be conducted consistent with all applicable federal and state laws and regulations. Excess reagents, samples and method process wastes must be characterized and disposed of in an acceptable manner in accordance with Pace's Chemical Hygiene Plan / Safety Manual.

14.0 Modifications

A modification is a change to a reference test method made by the laboratory. For example, changes in stoichiometry, technology, quantitation ions, reagent, or solvent volumes, reducing digestion or extraction times, instrument runtimes, etc. are all examples of modifications. Refer to Pace ENV corporate SOP ENV-SOP-CORQ-0011 *Method Validation and Instrument Verification* for the conditions under which the procedures in test method SOPs may be modified and for the procedure and document requirements.

15.0 Responsibilities

Pace ENV employees that perform any part this procedure in their work activities must have a signed Read and Acknowledgement Statement in their training file for this version of the SOP. The employee is responsible for following the procedures in this SOP and handling temporary departures from this SOP in accordance with Pace's policy for temporary departure.

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Pace supervisors/managers are responsible for training employees on the procedures in this SOP and monitoring the implementation of this SOP in their work area.

16.0 ATTACHMENTS

Attachment 1: Electronic Logbook example for Conductivity

17.0 REFERENCES

17.1 Pace Quality Assurance Manual - most current version.

17.2 National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, "Quality Systems"- most current version.

17.3 The NELAC Institute (TNI); Volume 1, Module 2, "Quality Systems"- most current version.

17.4 Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Analysis and Sampling Procedures, Federal Register Doc. No: 2012-10210.

17.5 Methods for the Chemical Analysis of Water and Wastes, EPA/600/4-79/020, Method 120.1, Revised 1982.

17.6 Standard Methods for the Examination of Water and Wastewater, Method 2510 B – 2011 and 2520 B – 2011.

17.7 Test Methods for Evaluating Solid Waste; SW-846, Method 9050A, Revision 1, December 1996.

18.0 REVISION HISTORY

This Version: ENV-SOP-LENE-0023, Rev 02

Section	Description of Change
All	New SOP format and added salinity 2520.

This document supersedes the following document(s):

Document Number	Reason for Change	Date
KS-I-2340-E	Grammatical/Removal of outdated information.	June 4, 2001
KS-I-2340-F	Grammatical/Removal of outdated information.	February 11, 2003

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Document Number	Reason for Change	Date
KS-I-025-rev.6	Section 9.1 – Changed definition of deionized water. Section 9.2 – Changed upper range of conductivity meter. Added catalog number. Section 9.3 – Added probe description, catalog number and strorage instructions. Section 10 – Changed 10.2 umho to ~10 umho*. Section 11 – Deleted reference to sample screening. Changed 10.2 umho to ~10 umho. Section 11.11 – Changed Range switch setting for reading 447 standard. Section 12.2.1 – Changed 30 grams and 30 mL to 20 grams and 20 mL. Section 12.2.2 – Added 'approximately'. Section 12.2.3 – Added 'approximately'. Section 13 – Deleted references to ½ PRL, LCS and MS/MSD. Section 14 – Deleted references to MDL studies. Added cell constant determination.	11May2006
KS-I-025-rev.7	Title Page – Added Standard Method method number. Section 9.2 – Removed duplicate supplies. Table 10.1 – Updated table with current order #'s. Table 10.2 – Updated table with current order #'s. Section 11 – Changed thought to throughout. Table 11.1 – Updated table to include secondary standards. Table 12.1 – Updated table to include instrument Pace ID# and levels of conductivity meter. Section 13.4.3 – Corrected equation used to determine cell constant.	30September2008
S-KS-I-025-rev.8	Section 6 – Added unit definitions. Section 7 – Revised SOP review frequency, official version and added Environmental Quality Director. Section 10 – Changed standard sources and values.	November 30, 2010
S-KS-I-025-rev.9	SOP – Deleted Responsibilities and Distribution section. Section 10 – Revised Calibration Verification Section 14 – Revised SOP reference. Section 15 – Added MUR reference.	January 11, 2012

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Document Number	Reason for Change	Date
S-KS-I-025-rev.10	SOP - Updated to latest prescribed format. Table 9.1 – Added new instrument. Section 11 – Revised for new instrument. Section 12 – Revised for new instrument. Section 23 – Revised references. Attachment 1 – Added client-specific criteria.	March 5, 2013
S-KS-I-025-rev.11	Revised standard concentration. Added 12.1.5.4	June 11, 2014
S-KS-I-025-rev.12	SOP – Updated to latest prescribed format. Table 10-- Revised primary standard conc. Section 11.1-- Revised wording and added a warning. Section 11.5.2 -- Revised CCV corrective actions Section 12.1.5 – Revised to dilute the sample if reading is high (overload at high setting).	June 23, 2015
S-KS-I-025-rev.13	Section 11.2 – Revised to specify the secondary standard as an "ICV". Section 11.4 – Initial Calibration Verification (ICV) must be the secondary check standard. Section 12.1.5.4 – Results should be from the minimum dilution needed.	May 6, 2016
S-KS-I-025-rev.14	SOP – Updated cover page to Pace LLC Table 9.1 – Updated with new instrument.t Table 10.1 – Two new high standards added. Section 11.0 – Revised calibration instructions. Section 11.2 – Added cell constant reference. Table 11.1 – Revised to add high standards. Section 12.0 – Removed selecting the range of sample measurement. Table 13.1 – Added Table 13.1 header. Section 14.0 – Removed cell constant. Added reference to Section 11 tables. Section 16.0 – Changed to reference Table 11.2.	May 31, 2017
ENV-SOP-0023, Rev 01	New SOP format	September 03, 2019

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Attachment 1: Electronic logbook example for Conductivity

Prep Log Report

Batch Information: WET COND/RESIST 101083 101084 **Template Version: F-KANS-I-003-Rev.00 (25Apr2019)**

Analysis Method	EPA 9050	Instrument	60WETM	Balance ID	60BAL11	Analyzed By	BLA
Reviewed By	LDB	Reviewed By Date	08/03/2021 13:08	Batch Notes			

Sample Information:

QC Rule	Sample Type	Lab Sample ID	Select	Run Date/Time	Meter Specific Conductance	Units	Sample Temp (C)	Posted Specific Conductance	Units	Resistivity (ohms-cm)	Final Resistivity (ohms-cm)	Matrix	Sample Weight (g)	Sample Notes
WET COND_Q	CAL1	**CAL1**	Y	08/02/2021 10:32:28	14.13	uS/cm	18.6	14.13	uS/cm			Water		
WET COND_Q	CAL2	**CAL2**	Y	08/02/2021 10:33:07	694.8	uS/cm	18.6	694.8	uS/cm			Water		
WET COND_Q	CAL3	**CAL3**	Y	08/02/2021 10:33:25	1368	uS/cm	18.6	1368	uS/cm			Water		
WET COND_Q	CAL4	**CAL4**	Y	08/02/2021 10:36:24	4350	uS/cm	18.6	4350	uS/cm			Water		
WET COND_Q	CAL5	**CAL5**	Y	08/02/2021 10:36:52	28940	uS/cm	18.6	28940	uS/cm			Water		
WET COND_Q	ICV	**ICV**	Y	08/02/2021 10:37:19	432.5	uS/cm	18.6	432.5	uS/cm			Water		
9050 S	BLANK	**2950511**	Y	08/02/2021 10:37:43	0.496	uS/cm	18.6	0.496	uS/cm			Solid		
9050 S	PS	**60375467001**	Y	08/02/2021 10:38:16	231.9	uS/cm	18.6	231.9	uS/cm			Solid	20.09	
9050 S	DUP	**2950512**	Y	08/02/2021 10:38:19	231.9	uS/cm	18.6	231.9	uS/cm			Solid	20.09	
9050 S	PS	**60375467003**	Y	08/02/2021 10:38:53	175.8	uS/cm	18.6	175.8	uS/cm			Solid	20.24	
9050 S	PS	**60375467005**	Y	08/02/2021 10:39:25	27.27	uS/cm	18.6	27.27	uS/cm			Solid	20.29	
9050 S	PS	**60375467007**	Y	08/02/2021 10:39:56	28.71	uS/cm	18.6	28.71	uS/cm			Solid	20.36	
RESIST	PS	**40230596001**	Y	08/02/2021 10:40:30	168.3	uS/cm	18.6	168.3	uS/cm	5942	5942	Solid	19.95	
RESIST	PS	**60375831001**	Y	08/02/2021 10:40:59	897.5	uS/cm	18.6	897.5	uS/cm	1114	1114	Solid	20.28	
WET COND_Q	CCVA	**CCVA**	Y	08/02/2021 10:41:30	14.09	uS/cm	18.6	14.09	uS/cm			Water		

Prep Log Report

QC Rule	Sample Type	Lab Sample ID	CAL-STD
WET COND_Q	CAL1	**CAL1**	42458 (1)
WET COND_Q	CAL2	**CAL2**	42459 (1)
WET COND_Q	CAL3	**CAL3**	42464 (1)
WET COND_Q	CAL4	**CAL4**	42460 (1)
WET COND_Q	CAL5	**CAL5**	42461 (1)
WET COND_Q	ICV	**ICV**	42462 (1)
9050 S	BLANK	**2950511**	
9050 S	PS	**60375467001**	
9050 S	DUP	**2950512**	
9050 S	PS	**60375467003**	
9050 S	PS	**60375467005**	
9050 S	PS	**60375467007**	
RESIST	PS	**40230596001**	
RESIST	PS	**60375831001**	
WET COND_Q	CCVA	**CCVA**	42458 (1)

Standard Notes:

42458: WET Specific Conductivity 15 uS/cm
42459: WET Specific Conductivity 718 uS/cm
42460: WET Specific Conductivity 4500 uS/cm
42461: WET Specific Conductivity 30,100 uS/cm
42462: WET Specific Conductivity ICV 447 uS/cm
42464: WET Specific Conductivity 1409 uS/cm

Document Information

Document Number: ENV-SOP-LENE-0061 **Revision:** 02

Document Title: Oil and Grease/TPH by 1664A

Department(s): Wet Chemistry

Date Information

Effective Date: 01 Feb 2021

Notes

Document Notes:

All Dates and Times are listed in: Central Time Zone

Signature Manifest

Document Number: ENV-SOP-LENE-0061 **Revision:** 02

Title: Oil and Grease/TPH by 1664A

All dates and times are in Central Time Zone.

ENV-SOP-LENE-0061 Oil and Grease/TPH by 1664

QM Approval

Name/Signature	Title	Date	Meaning/Reason
Gregory Busch (003971)	Manager - Quality	22 Dec 2020, 01:44:34 PM	Approved

Management Approval

Name/Signature	Title	Date	Meaning/Reason
Charles Girgin (002243)	General Manager 2	23 Dec 2020, 07:59:34 AM	Approved
Joshua Cunningham (003261)	Manager	22 Jan 2021, 09:28:07 AM	Approved

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TEST METHOD STANDARD OPERATING PROCEDURE
TITLE: Oil and Grease/TPH by 1664
TEST METHOD EPA 1664A, EPA 1664B, SW846-9070A
ISSUER: Pace ENV – Lenexa Quality – LENE

1.0 SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the laboratory procedure for the determination of n-hexane extractable material (HEM: oil and grease) and n-hexane extractable material that is not adsorbed by silica gel (SGT-HEM; non-polar material) meeting the requirements specified in method EPA 1664: Revision A and Revision B by liquid/liquid extraction and gravimetric analysis.

1.1 Target Analyte List and Limits of Quantitation (LOQ)

The target analytes and the normal LOQ that can be achieved with this procedure is 5 mg/L in aqueous samples.

LOQs are established in accordance with Pace policy and SOPs for method validation and for the determination of detection limits (DL) and quantitation limits (LOQ). DL and LOQ are routinely verified and updated when needed.

The reporting limit (RL) is the value to which analytes are reported as detected or not detected in the final report. When the RL is less than the lower limit of quantitation (LLOQ), all detects and non-detects at the RL are qualitative. The LLOQ is the lowest point of the calibration curve used for each target analyte.

DL, LOQ, and RL are always adjusted to account for actual amounts used and for dilution.

2.0 SUMMARY OF METHOD

2.1 A 1-L sample is acidified to pH <2 and serially extracted three times with n-hexane in a separatory funnel. The extract is dried over sodium sulfate.

2.2 The solvent is evaporated from the extract and the HEM is desiccated and weighed. If the HEM is to be used for determination of SGT-HEM, the HEM is re-dissolved in n-hexane.

2.3 For SGT-HEM determination, an amount of silica gel proportionate to the amount of HEM is added to the solution containing the re-dissolved HEM to remove polar materials. The solution is filtered to remove the silica gel, the solvent is distilled, and the SGT-HEM is desiccated and weighed.

3.0 INTERFERENCES

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts that affect results in a positive manner. All materials used will be demonstrated to be free from interferences by the extraction of a method blank.

3.2 Wash all glassware in hot water using Neutrad® liquid detergent to remove possible oil and grease contamination.

3.3 Sodium sulfate and silica gel fines have the potential to inflate results for HEM and SGT-HEM by passing through the filter paper. Inadequate filtration may be supplemented by use of a 0.45 um filter.

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3.4 Samples consisting of complex matrices can contain substances (such as particulates or detergents) that may require the analysis of a smaller sample.

3.5 Some samples may present with emulsions. The optimum technique for emulsions depends on the sample, but may include stirring, filtration through glass wool, use of solvent phase separation paper, centrifugation, use of an ultrasonic bath with ice, addition of NaCl, or other physical methods. Saturation of the sample with salt (NaCl) prior to extraction may aid in preventing emulsion formation.

4.0 DEFINITIONS

Refer to the Laboratory Quality Manual for a glossary of common lab terms and definitions.

4.1 HEM (n-Hexane Extractable Material) - Material that is extracted from a sample and determined by this method (Oil and Grease). This material includes relatively non-volatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases, and related matter.

4.2 SGT-HEM (Silica Gel Treated n-Hexane Extractable Material) - Components of HEM that are not adsorbed by silica gel (non-polar material).

5.0 HEALTH AND SAFETY

The toxicity or carcinogenicity of each chemical material used in the laboratory has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable.

The laboratory maintains documentation of hazard assessments and OSHA regulations regarding the safe handling of the chemicals specified in each method. Safety data sheets for all hazardous chemicals are available to all personnel. Employees must abide by the health, safety and environmental (HSE) policies and procedures specified in this SOP and in the Pace Chemical Hygiene / Safety Manual.

Personal protective equipment (PPE) such as safety glasses, gloves, and a laboratory coat must be worn in designated areas and while handling samples and chemical materials to protect against physical contact with samples that contain potentially hazardous chemicals and exposure to chemical materials used in the procedure.

Concentrated corrosives present additional hazards and are damaging to skin and mucus membranes. Use these acids in a fume hood whenever possible with additional PPE designed for handing these materials. If eye or skin contact occurs, flush with large volumes of water. When working with acids, always add acid to water to prevent violent reactions. Any processes that emit large volumes of solvents (evaporation/concentration processes) must be in a hood or apparatus that prevents employee exposure.

Contact your supervisor or local HSE coordinator with questions or concerns regarding safety protocol or safe handling procedures for this procedure.

6.0 SAMPLE COLLECTION, PRESERVATION, HOLDING TIME, AND STORAGE

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Samples should be collected in accordance with a sampling plan and procedures appropriate to achieve the regulatory, scientific, and data quality objectives for the project.

The laboratory may perform samples collection for samples to be analyzed by this SOP in accordance with laboratory SOP ENV-SOP-LENE-0107, *Field Manual*. Refer to this SOP for these instructions.

The laboratory will provide containers for the collection of samples upon client request for analytical services. Bottle kits are prepared in accordance with laboratory SOP ENV-SOP-LENE-0025, *Assembly of Sample Container Kits*.

Requirements for container type, preservation, and field quality control (QC) for the common list of test methods offered by Pace are included in the laboratory's quality manual.

General Requirements

Matrix	Routine Container	Minimum Sample Amount[1]	Preservation	Holding Time
Aqueous	1-L glass	1 Liter	Thermal: ≤6°C (not frozen) Chemical: HCl or H2SO4 to pH <2.	Collection to Prep and Analysis: 28 days

[1]*Minimum amount needed for each discrete analysis.*

Field / Matrix QC

Trip Blank	Equipment Blank	MS/MSD	Field Duplicate
NA	NA	1/20	1/20

Thermal preservation is checked and recorded on receipt in the laboratory in accordance with laboratory SOP ENV-SOP-LENE-0021, *Sample Management*. Chemical preservation is checked and recorded at time of receipt or prior to sample preparation.

After receipt, samples are stored at ≤6°C until sample preparation. Prepared samples (extracts, digestates, distillates, other) are stored at ≤6°C until sample analysis.

After analysis, unless otherwise specified in the analytical services contract, samples are retained for 30 days from date of final report and then disposed of in accordance with Federal, State, and Local regulations.

7.0 EQUIPMENT AND SUPPLIES

7.1 Equipment

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Equipment	Vendor	Model / Version	Comments
Analytical balance	Mettler-Toledo	AE240	Or equivalent
Desiccator	Sanplatec	Dry Keeper	Or equivalent
Filter funnel	Fisher	10-322E	75-mm diameter with short stem
Slide Warmer	Premiere	XH-2001	25″ x 8″ Surface
Centrifuge			
Ultrasonic Bath			
Pipette	Fisher	Eppendorf	Various
Separatory funnel	Fisher	10-437-25E	PTFE, 2-L with stopcock
Volumetric flask, 200-mL	Fisher	FB-400-200	Class A
10 mL volumetric pipet	Fisher	Class A glass	

7.2 Supplies

Supplies	Vendor	Model / Version	Comments
Drierite (Indicating)	Fisher	07-578-4B	10-20 mesh
Drierite (Non-indicating)	Fisher	07-577-3B	8 mesh
Filter paper	Fisher	09-795E	11-cm diameter
Weighing tins	Fisher	08-732-104	105-mm diameter

8.0 REAGENTS AND STANDARDS

8.1 Reagents

Reagents	Concentration/ Description	Vendor/ Item #
Acetone	ACS Reagent grade	Fisher / A18
Hexadecane	Certified	Fisher / 03035-500
n-Hexane	ACS Reagent grade, 95% n-Hexane	Fisher / H306
Reagent water	ASTM Type II	SOP S-KS-Q-011
Sodium sulfate	ACS Reagent grade	Fisher / S421

8.2 Standards

Standards	Concentration/ Description	Vendor/ Item #
Silica gel	Davisil Grade 636, 60 Å, 35-60 mesh	Sigma / 236802-1KG
Stearic acid	Grade I, ≥98.5%	Sigma / S-4751
Sulfuric acid	ACS Reagent grade	Fisher / A510

8.1 Spiking Standard Solution, 4 mg HEM/mL (2 mg SGT-HEM/mL).

8.1.1 Measure the following reagents and place into a clean, 500-mL volumetric flask: 1000 ± 10 mg stearic acid and 1000 ± 10 mg hexadecane.

8.1.2 Add approximately 100 mL acetone and swirl to mix and dissolve. Once dissolved, dilute to the mark with acetone and invert several times. Transfer the solution to a 500-mL amber flask with a PTFE-lined cap. Store the solution in the dark at ambient temperature. The solution must be replaced after 6 months or sooner if degradation has occurred.

8.1.3 Prior to use each day, verify that the standard has not precipitated. If needed warm to re-dissolve. The test noted below must be performed if the LCS recovery fails or if the concentration of the spike solutions is in doubt.

8.1.3.1 Note: if the spike solution concentration is in doubt, pipet 10 +/- 0.1 mL with a volumetric pipet. Place in a tared pan and evaporate to dryness in a fume hood. The residue weight must be 40 +/-1 mg. If not prepare a fresh solution.

8.2 Silica gel

8.2.1 Silica gel must be dried at 200–250°C for a minimum of 24 hours and stored in a tightly sealed container.

8.2.2 Determine the n-hexane soluble material content of each manufacturer's lot of silica gel by extracting 30 g of silica gel with n-hexane and evaporating the n-hexane to dryness. The silica gel must contain less than 5 mg of n-hexane soluble material per 30 g (< 0.17 mg/g). Attach results of this verification to the Certificate of Analysis on file.

8.3 Sodium sulfate

Sodium sulfate must be dried at 200–250°C for a minimum of 24 hours and stored in a tightly sealed container.

9.0 PROCEDURE

9.1 Equipment Preparation

9.1.1 Support Equipment

9.1.1.1 The calibration of the analytical balance must be verified each day of use, prior to sample measurements, and the results of the verification must be documented in the balance calibration logbook.

9.1.1.2 Verify calibration of the balance before and after each day or after measurement of the analytical batch. If calibration is not verified, recalibrate the balance and reweigh the batch.

9.1.2 Instrument

9.1.2.1 Routine Instrument Operating Conditions

There is no instrument for this test beyond the analytical balance.

9.2 Initial Calibration

9.2.1 Calibration Design

The balance calibration is verified each day of use, prior to sample measurements and the results of the verification must be documented in the electronic log.

9.2.2 Calibration Sequence

9.2.3 ICAL Evaluation

9.2.3.1 Curve Fit

Not applicable.

9.2.3.2 Relative Standard Error (RSE)

Not applicable.

9.2.3.3 Initial Calibration Verification

Not applicable.

9.2.4 Continuing Calibration Verification

Not applicable.

9.3 Sample Preparation

9.3.1 Homogenization and Subsampling

The entire contents of the 1 liter sample are used

9.4 Analysis

9.4.1 Inspect all required glassware to ensure it is clean, dry and undamaged. Rinse all glassware 2-3 times using n-hexane before use. Allow the samples to warm to room temperature.

9.4.2 Preparation for the analysis:

9.4.2.1 Select a maximum of (24) 120-mL tins and number them with a marker.

9.4.2.2 Create an EPIC QC batch for the samples.

9.4.2.3 Include a MB, LCS, MS, and Duplicate for the Batch QC. As an alternate, an MS/MSD may be performed with each batch if there is enough sample volume available.

9.4.2.4 The analytical balance must be verified each day of use, prior to sample measurements, and the results of the verification must be documented in the balance calibration logbook.

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9.4.2.5 Weigh the tins using the analytical balance and LimsLink to record the tin Initial Weights.

9.4.3 Quality Control Samples

9.4.3.1 Method Blank (MB): Prepare the MB by adding 1000 mL of DI water to a clean 1-L amber bottle containing 5 mL of concentrated sulfuric acid. Cover and mix. After mixing, verify that the pH is < 2 by dipping a clean stir rod into the container and transferring a drop to a pH strip. Rinse the stir rod into a separatory funnel with hexane. Record the pH on your bench sheet. Transfer the bottle to a separatory funnel.

9.4.3.2 Laboratory Control Sample (LCS): Prepare the LCS by adding 1000 mL of DI water to a clean 1-L amber bottle containing 5 mL of concentrated sulfuric acid. Cover and mix. After mixing, verify that the pH is < 2 by dipping a clean stir rod into the container and transferring a drop to a pH strip. Rinse the stir rod into a separatory funnel with hexane. Record the pH on your bench sheet. Transfer the bottle to the separatory funnel add 10 mL of spike to the separatory funnel; the final concentration of the LCS is 40 mg/L HEM or 20 mg/L SGT-HEM.

9.4.3.3 Matrix Spike (MS): Prepare the MS by choosing a client sample (if enough sample has been submitted) and marking the level of the water meniscus in the bottle with a pen for later volume determination.

9.4.3.3.1 Mix the sample by inverting the container 3 times. After mixing the sample dip a clean stir rod into the sample and transfer a drop to a pH strip, rinse the stir rod back into the separatory funnel that the sample will be poured. Ensure that the pH is less than 2. If the pH is not less than 2, add 5 mL of concentrated sulfuric acid to the sample bottle, invert three times and check the pH again. Continue this procedure until the pH is less than 2. Record the pH on your bench sheet for each sample.

9.4.3.3.2 Pour the sample into a separatory funnel using a pre-cleaned filter funnel, rinsing down the sides with n-hexane. Add 10 mL of the HEM Standard. The final concentration of the MS is 40 mg/L HEM or 20 mg/L SGT-HEM.

9.4.3.3.3 If, as in compliance monitoring, the concentration of Hem or SGT-HEM in the sample is being checked against a regulatory concentration limit, the spiking level shall be at that limit, at 1 to 5 times the background concentration of the sample (pre-determined) or at the concentration of the OPR (LCS).

9.4.3.3.4 If the concentration of HEM or SGT-HEM in a sample is not being checked against a limit, the spike shall be at the concentration of the LCS or at 1 to 5 times higher than the background concentration, whichever concentration is higher.

- NOTE: Sample containing high concentrations (>100 mg/L) of HEM will require a large volume of spiking solution for the MS. If the concentration of HEM is expected to exceed 1,000 mg/L, smaller sample volumes should be collected for the background measurement and MS so that the amount of HEM plus the amount spiked does not exceed 1,000 mg/L.

9.4.4 Client Samples

9.4.4.1 Mark the level of the water meniscus in the bottle with a pen for later volume determination.

9.4.4.2 Mix the sample by inverting the container 3 times. After mixing the sample, dip a clean stir rod into the sample and transfer a drop to a pH strip, rinse the stir rod back into the separatory funnel that the sample will be poured. Ensure that the pH is less than 2. If the pH is not less than 2, add 5 mL of concentrated sulfuric acid to the sample bottle, invert three times and check the pH again. Continue this procedure until the pH is less than 2. Record the pH on your bench sheet for each sample.

9.4.4.3 Pour the sample into a separatory funnel using a pre-cleaned filter funnel and rinse down the funnel sides.

9.4.4.4 Add 30 mL of n-hexane directly into the sample bottle. Cap and shake to remove any adhered oil and grease to the bottle walls. Note: Vent the bottle carefully to release the pressure. Repeat this for the MB, LCS, MS, DUP, and remaining batch samples.

9.4.4.5 Transfer the solvent into the separatory funnel. Extract by shaking vigorously on mechanical shaker (if available), or by hand for a minimum of 2 minutes. Vent the separatory funnel after 15 seconds to release the pressure by pointing the tip up and into the fume hood and slowly opening the valve. Caution: Shake the funnel gently at first and vent under a hood by tilting the bottom of the funnel upward and away from you while slowly opening the stopcock. Ensure the cap is firmly tight to avoid leakage during this process. Repeat this process frequently during the mixing process.

9.4.4.6 Return the separatory funnel to the rack and repeat this for the remainder of the samples and QC. Allow the layers to separate at least 10 minutes.

9.4.4.7 Line the bench with clean paper towels directly under the separatory funnel to prevent any residue from adhering to the tins.

9.4.4.8 Prepare the glass funnels by folding a piece of filter paper so that it fits into the funnel and add sodium sulfate to fill half of the funnel, minimum of 10 g. Rinse the sodium sulfate and funnel with n-hexane and discard the rinsate. Suspend the glass funnel under the separatory funnel.

9.4.4.9 Place the pre-weighed tin under the glass funnel.

9.4.4.10 Drain the water (bottom) layer back into the original sample container for the next extraction.

9.4.4.11 Filter the n-hexane (top) layer through the filter funnel containing solvent-moistened sodium sulfate and filter paper and collect in the pre-weighed tin. Note: An emulsion that fails to dissipate can be broken by adding sodium chloride or sodium sulfate to the separatory funnel and mixing well. Centrifugation is another option. If a portion of the emulsion gets into the filter funnel, add about 1 g sodium sulfate into the filter paper cone and slowly drain the emulsion through the salt. Additional 1-g portions can be added to the cone as required.

9.4.4.12 Repeat the extraction twice more with additional portions of fresh n-hexane adding to the sample bottle first for bottle rinsing.

9.4.4.13 Rinse the tip of each separatory funnel, the filter paper, and then the funnel with a total of 10-20 mL n-hexane, collecting the rinsates in the tin.

9.4.4.14 Determine the volume of each sample by adjusting the amount of water in the bottle to the mark made in Step 9.4.4.1. Pour the water into a 1-L graduated cylinder. Measure the volume of the sample and record on the bench sheet.

9.4.4.15 Turn on slide warmer (set to achieve 70°C). Record the observed and corrected temperature of the slide warmer.

9.4.4.16 NOTE: The Method 1664A refers to a distilling head for solvent collection and approximately 70C (11.4.1). The lab is not using a distillation head to recapture solvent. The temperature must not be so high as to cause loss of target analytes but must be high enough to evaporate the hexane solvent. EPA has noted in a technical document that the procedure for drying the boiling flask at 70° C for 30-45 minutes followed by desiccation for 30 minutes was suggested by the American Petroleum Institute as a means for assuring that residual water or n-hexane would not affect the measurement. If this problem is experienced, we suggest a lower temperature or a shorter drying time.

9.4.4.17 Place tins on the slide warmer leaving the sash open about one foot.

9.4.4.18 The tins must be observed carefully so that the hexane does not evaporate to complete dryness; once a “dry spot” forms remove the tin from the hotplate and allow evaporation to continue in the fume hood.

9.4.4.19 Remove the tin from the hotplate and place into a desiccator for a minimum of 15-30 minutes.

9.4.4.20 Inspect the residue in the tin for crystals. Crystal formation is an indication that sodium sulfate may have dissolved and passed into the tin. This may happen if the drying capacity of the sodium sulfate is exceeded or if the sample is not adjusted to low pH. If crystals are observed, re-dissolve the extract in n-hexane, quantitatively transfer through a filter into another pre-weighed tin and repeat the evaporation step.

9.4.5 Determining the final weights of the HEM samples:

9.4.5.1 The analytical balance must be verified each day of use, prior to sample measurements, after sample measurements and the results of the verifications must be documented in the balance calibration logbook.

9.4.5.2 Remove the tins from the desiccator. Use the analytical balance and LimsLink to record the tin Final Weights. Return tins to a desiccator for 30 minutes and reweigh to determine constant weight (must be within 4% of the previous weight or less than 0.5 mg, whichever is less. If not, tins will be returned to the desiccator for 30 minutes and reweighed again. If determining SGT-HEM, continue onto Section 9.4.6, otherwise, proceed to post the data.

9.4.6 Determining SGT-HEM

9.4.6.1 If the HEM exceeds 1000 mg, the sample is to be split per the following procedure.

9.4.6.1.1 Add approx. 90 mls of hexane to the pan containing the HEM residue and re-dissolve. Transfer to a 100 ml volumetric flask; bring to volume with hexane and mix.

9.4.6.1.2 Based on the mg of HEM present, pipet (to a pan) an appropriate amount of Hexane from the 100ml volumetric flask that will result in HEM-that is less than 1000 mg.

9.4.6.2 Re-dissolve the HEM sample back into n-hexane and add 3 g silica gel per 100 mg of HEM. If necessary, transfer the tin to the hotplate and apply heat to completely dissolve the HEM.

9.4.6.3 Let the mixture sit for 10 minutes with occasional swirling.

9.4.6.4 Prepare the glass funnels by folding a piece of Fisher P8 filter paper so that it fits into the funnel wet with n-hexane.

9.4.6.5 Number a new set of clean tins with a marker and weigh them. Use an analytical balance and LimsLink to record the tin Initial Weights.

9.4.6.6 Quantitatively transfer the extract, filtering through the funnel and filter paper, to the pre-weighed 120-mL tin.

9.4.6.7 Turn on slide warmer and verify it is set to achieve 70 ºC. Place a thermometer on the heating surface. The temperature should rise to approximately 70ºC.

9.4.6.8 Place tins on the hotplate. The temperature should now drop to approximately 40ºC; do not attempt to adjust the hotplate's temperature setting.

9.4.6.9 The tins must be observed carefully so that the hexane does not evaporate to complete dryness; once a "dry spot" forms remove the tin from the hotplate and allow evaporation to continue in the fume hood.

9.4.6.10 Remove the tin from the fume hood and place into a desiccator for a minimum of 15 minutes.

9.4.6.11 Remove the tins from the desiccator. Use the analytical balance and LimsLink to record the tin Final Weights. Proceed with the constant weighing procedure listed above in the HEM Section 9.4.5.2.

9.4.6.12 If the SGT-HEM result is greater than 100mg and the ratio of 3 g silica gel/100g HEM was not maintained, the residue must be re-dissolved in hexane and the process repeated with the proper ratio. Record the amount of silica gel used if greater than 3 grams is used. The ratio must be maintained to insure accurate data (high bias).

9.4.7 EPIC Pro Posting:

9.4.7.1 The extracted sample volume, 1000, in mL, is posted for the Initial Volume and the 1 mL for the Final Volume; or a ratio of the same 1000/1 ratio (i.e. 800 mL initial and 0.8 mL for final).

9.4.7.2 Post the sample final gravimetric result, in mg/L. You should be able to auto post everything directly.

10.0 DATA ANALYSIS AND CALCULATIONS

10.1 Qualitative Identification

The analyte extracted is the detectable analyte.

10.2 Quantitative Identification

$$\text{HEM or SGT-HEM} = \frac{W_h}{V_s}$$

where,

W_h = Residue weight, gross weight of extraction flask minus the tare weight, in milligrams.
V_S = Sample volume extracted, in liters (L).

10.3 Calculations

See the Laboratory Quality Assurance Manual for equations for common calculations.

11.0 QUALITY CONTROL AND METHOD PERFORMANCE

11.1 Quality Control

The following QC samples are prepared and analyzed with each batch of samples. Refer to Appendix A for acceptance criteria and required corrective action.

QC Item	Frequency
Method Blank (MB)	1 per batch of 20 or fewer samples. If batch exceeds, 20 samples, every 20.
Laboratory Control Sample (LCS)	1 per batch of 20 or fewer samples. If batch exceeds, 20 samples, every 20.
Matrix Spike (MS)	1 per batch of 20 or fewer samples. If batch exceeds, 20 samples, every 20.
Sample Duplicate	1 per batch of 20 or fewer samples. If batch exceeds, 20 samples, every 20.

11.2 Instrument QC

Not applicable.

11.3 Method Performance

11.3.1 Method Validation

11.3.1.1 Detection Limits

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Detection limits (DL) and limits of quantitation (LOQ) are established at initial method setup and verified on an on-going basis thereafter. Refer to Pace ENV corporate SOP ENV-SOP-CORQ-0011 Method Validation and Instrument Verification.

11.4 Analyst Qualifications and Training

Employees that perform any step of this procedure must have a completed Read and Acknowledgment Statement for this version of the SOP in their training record. In addition, prior to unsupervised (independent) work on any client sample, analysts that prepare or analyze samples must have successful initial demonstration of capability (IDOC) and must successfully demonstrate on-going proficiency on an annual basis. Successful means the initial and on-going DOC met criteria, documentation of the DOC is complete, and the DOC record is in the employee's training file. Refer to laboratory SOP ENV-SOP-LENE-0110, *Training Procedures*, for more information.

11.5 Demonstration of Capability (DOC): Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC) per ENV-SOP-LENE-0110, Training Procedures.

11.5.1 Analysis of four replicates of reagent water, spiked with 10 mL of the Spiking Standard Solution, at a concentration of 40 mg/L HEM (20 mg/L SGT-HEM).

11.5.2 Using the results of the set of four analyses, compute the average percent recovery (X) and the standard deviation of the percent recoveries for HEM and for SGT-HEM.

11.5.3 Compare s and X with the corresponding limits for initial precision and recovery in the table below. If s and X meet the acceptance criteria, system performance is acceptable, and analysis of samples may begin. If, however, s exceeds the precision limit or X falls outside the range for recovery, system performance is unacceptable. In this event, correct the problem and repeat the test.

Demonstration of Capability Criteria

HEM Recovery (X)	83-101
HEM Precision (s)	11
SGT-HEM Recovery (X)	83-116
SGT-HEM Precision (s)	28

12.0 DATA REVIEW AND CORRECTIVE ACTION

12.1 Data Review

Pace's data review process includes a series of checks performed at different stages of the analytical process by different people to ensure that SOPs were followed, the analytical record is complete and properly documented, proper corrective actions were taken for QC failure and other nonconformance(s), and that test results are reported with proper qualification.

The review steps and checks that occur as employee's complete tasks and review their own work is called primary review.

All data and results are also reviewed by an experienced peer or supervisor. Secondary review is performed to verify SOPs were followed, that calibration, instrument performance, and QC criteria were met and/or proper corrective actions were taken, qualitative ID and quantitative measurement is accurate, all manual integrations are justified and documented in accordance with the Pace ENV's SOP for manual integration, calculations are correct, the analytical record is complete and traceable, and that results are properly qualified.

A third-level review, called a completeness check, is performed by reporting or project management staff to verify the data report is not missing information and project specifications were met.

Refer to laboratory SOP ENV-SOP-LENE-088, *Data Reduction, Review and Reporting*, for specific instructions and requirements for each step of the data review process.

12.2 Corrective Action

Corrective action is expected any time QC or sample results are not within acceptance criteria. If corrective action is not taken or was not successful, the decision/outcome must be documented in the analytical record. The primary analyst has primary responsibility for taking corrective action when QA/QC criteria are not met. Secondary data reviewers must verify that appropriate action was taken and/or that results reported with QC failure are properly qualified.

Corrective action is also required when carryover is suspected and when results are over range.

Samples analyzed after a high concentration sample must be checked for carryover and reanalyzed if carryover is suspected. Carryover is usually indicated by low concentration detects of the analyte in successive samples analyzed after the high concentration sample.

Sample results at concentrations above the upper limit of quantitation must be diluted and reanalyzed. The result in the diluted samples should be within the upper half of the calibration range. Results less than the mid-range of the calibration indicate the sample was over diluted and analysis should be repeated with a lower level of dilution. If dilution is not performed, any result reported above the upper range is considered a qualitative measurement and must be qualified as an estimated value.

Refer to Appendix A for a complete summary of QC, acceptance criteria, and some recommended corrective actions for QC associated with this test method.

12.2.1 If the results of the spike fail the acceptance criteria, and the recovery of the QC standard in the ongoing precision and recovery test (LCS) for the analytical batch is within the acceptance criteria in Appendix A, an interference is present. In this case, the result may not be reported or used for purposes regulatory compliance purposes and the laboratory must assess the potential cause for the interference. If the interference is attributable to sampling, the site or discharge/waste stream should be resampled. If the interference is attributable to a matrix problem, the laboratory must modify the method, repeat the tests required for an IDOC, and repeat the analysis of the sample and the MS (and MSD, if performed). Most matrix interference problems are attributable to the formation of emulsions in the extraction. Section 11.3.5 of method 1664A provides suggestions for overcoming emulsion problems.

12.2.2 If the results of both the spike and the ongoing precision and recovery test fail the acceptance criteria, the analytical system is judged to be out of control, and the problem shall be identified and corrected, and the sample batch reanalyzed. All samples must be associated with a valid MS (and MSD, if performed).

13.0 POLLUTION PREVENTION AND WASTE MANAGEMENT

Pace proactively seeks ways to minimize waste generated during our work processes. Some examples of pollution prevention include but are not limited to: reduced solvent extraction, solvent capture, use of reusable cycletainers for solvent management, and real-time purchasing.

The EPA requires that laboratory waste management practice to be conducted consistent with all applicable federal and state laws and regulations. Excess reagents, samples and method process wastes must be characterized and disposed of in an acceptable manner in accordance with Pace's Chemical Hygiene Plan / Safety Manual.

14.0 MODIFICATIONS

A modification is a change to a reference test method made by the laboratory. For example, changes in stoichiometry, technology, quantitation ions, reagent or solvent volumes, reducing digestion or extraction times, instrument runtimes, etc. are all examples of modifications. Refer to Pace ENV corporate SOP ENV-SOP-CORQ-0011 *Method Validation and Instrument Verification* for the conditions under which the procedures in test method SOPs may be modified and for the procedure and document requirements.

14.1 Sample duplicates are used to check method precision.

14.2 Concentrated sulfuric acid is used to adjust pH.

14.3 A slide warmer is used instead of an oven. See the Note in Section 12.4.15 above. Method 1664B does not require an oven drying step at 70 ± 2 ºC (1.7.1.3) in the final weighing sequence, which means it is unnecessary.

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14.4 A lower Precision and Recovery standard concentration such as 20 mg/L (instead of the 40 mg/L noted above) may be used to spike matrix samples provided the concentration of the spike : (a) greater than the background concentration, or (b) less than or equal to the regulatory compliance level and (c) all quality control requirements are achieved.

14.5 Collection and analysis of a smaller sample volume is permitted provided all the quality control requirements of 1664B, Section 9 are met. If smaller sample volumes are used, all QC and initial and ongoing demonstration of performance samples must use the same volume as the smaller volume samples. To achieve a proportionately smaller matrix spike at the recommended OPR concentration of 40 mg/L, i.e., spike 0.1 mL of the 4 mg/mL PAR standard for every 10 mL of proportionately smaller sample volume or fraction thereof. To report the most accurate HEM and SGT-HEM values in mg/L, subtract the smaller volume method blank value from the smaller volume sample value provided the recovery value of the smaller volume matrix spike is equal to or greater than the MDL for the modified method. Multiply this proportionately smaller sample value by the appropriate dilution factor and express the final sample result in mg/L. For example, if 4.4 mg/100 mL was the result for the proportionately smaller sample and 0.6 mg/100mL was the result for the method blank, the reported concentration of the sample should be 38.0 mg/L ([4.4 mg/100 mL – 0.6 mg/100 mL] x 10 = 38.0 mg/L). Additionally, all samples must be associated with an uncontaminated, 1-L method blank before the results may be reported for regulatory compliance purposes.

15.0 RESPONSIBILITIES

Pace ENV employees that perform any part this procedure in their work activities must have a signed Read and Acknowledgement Statement in their training file for this version of the SOP. The employee is responsible for following the procedures in this SOP and handling temporary departures from this SOP in accordance with Pace's policy for temporary departure.

Pace supervisors/managers are responsible for training employees on the procedures in this SOP and monitoring the implementation of this SOP in their work area.

16.0 ATTACHMENTS

17.0 REFERENCES

17.1 Pace Quality Assurance Manual - most current version.

17.2 National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, "Quality Systems"- most current version.

17.3 The NELAC Institute (TNI); Volume 1, Module 2, "Quality Systems"- most current version.

17.4 Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Analysis and Sampling Procedures, Federal Register Doc. No: 2012-10210.

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17.5 Method 1664: n-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated n-Hexane Extracted Material (SGT-HEM; Non-polar Material) by Extraction and Gravimetry. EPA 821-R98-002, Revision A, February 1999.

17.6 Method 1664, Revision B: n-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated n-Hexane; Non-polar Material) by Extraction and Gravimetry, EPA 821-R-10-001, February 2010

17.7 EPA Test Methods for Evaluating Solid Waste, SW-846, Third Edition, Update IIIB, Method 9070A, Rev. 1, November 2004.

18.0 REVISION HISTORY

This Version:

Section	Description of Change
All	This is an SOP reformat

This document supersedes the following document(s):

Document Number	Title	Version
ENV-SOP-LENE-0061	Oil and Grease/TPH by 1664A and 1664B	01

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Appendix A: QC Summary

QC Item	Frequency	Acceptance Criteria	Corrective Action	Qualification
Method Blank	1 per batch of 20 or fewer samples. If batch exceeds, 20 samples, every 20.	<PQL	Analysis of samples is halted until the source of contamination is eliminated and a blank shows no evidence of contamination.	Exceptions: If sample ND, report sample without qualification
LCS	1 per batch of 20 or fewer samples. If batch exceeds, 20 samples, every 20.	HEM: 78-114% SGT-HEM: 64-132%	Correct the problem and re-extract the analytical batch.	Exceptions: 1) If LCS rec > QC limits and these compounds are non-detect in the associated samples, the sample data may be reported with appropriate data qualifiers.
MS	1 per batch of 20 or fewer samples. If batch exceeds, 20 samples, every 20.	HEM: 78-114% SGT-HEM: 64-132%	Repeat the analysis with additional sample. MS must be within acceptance range for regulatory acceptance. Refer to Section 9.3 of the analytical method and Section 12 above.	Report results with an appropriate footnote.
Sample Duplicate	1 per batch of 20 or fewer samples. If batch exceeds, 20 samples, every 20.	HEM: 18% SGT-HEM: 34%	Report results with an appropriate footnote.	

1.0 SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the laboratory procedure for the determination of Ferrous Iron by SM 3500 Fe B - 2011.

1.1 Target Analyte List and Limits of Quantitation (LOQ)

The target analyte that can be determined by this SOP and the associated LOQ is 0.2 mg/L.

2.0 SUMMARY OF METHOD

A well-mixed sample is acidified with hydrochloric acid and buffered with ammonium acetate at a pH of 3.2 to 3.3. Ferrous iron forms a colored complex with 1, 10-phenanthroline that is then measured spectrophotometrically at 510 nm.

To determine dissolved ferrous iron the sample is filtered through a 0.45 um membrane filter. The filtrate is then treated in the same manner as for the total determination.

3.0 INTERFERENCES

Excessive color and/or turbidity interfere.

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.

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.

4.0 DEFINITIONS

Refer to the Laboratory Quality Manual for a glossary of common lab terms and definitions.

5.0 HEALTH AND SAFETY

Contact your supervisor or local safety coordinator with questions or concerns regarding safety protocol or safe handling procedures for this procedure

The following sections provide general health and safety information about chemicals and materials that may be present in the laboratory.

- The toxicity or carcinogenicity of each chemical material used in the laboratory has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable.

- The laboratory maintains documentation of hazard assessments and OSHA regulations regarding the safe handling of the chemicals specified in each method. Safety data sheets for all hazardous chemicals are available to all personnel. Employees must abide by the health, safety and environmental (EHS) policies and procedures specified in this SOP and in the Pace® Chemical Hygiene / Safety Manual (COR-MAN-0001)
- Personal protective equipment (PPE) such as safety glasses, gloves, and a laboratory coat must be worn in designated areas and while handling samples and chemical materials to protect against physical contact with samples that contain potentially hazardous chemicals and exposure to chemical materials used in the procedure.
- Concentrated corrosives present additional hazards and are damaging to skin and mucus membranes. For procedures that require use of acids, use acids in a fume hood whenever possible with PPE designed for handing these materials. If eye or skin contact occurs, flush with large volumes of water. When working with acids, always add acid to water to prevent violent reactions. For procedures that that emit large volumes of solvents (evaporation/concentration processes), these activities must be performed in a fume hood or apparatus that reduces exposure.

6.0 .SAMPLE COLLECTION, PRESERVATION, HOLDING TIME & STORAGE

Samples should be collected in accordance with a sampling plan and procedures appropriate to achieve the regulatory, scientific, and data quality objectives for the project.

The laboratory does not always perform sample collection or field measurements for this test method. To assure sample collection and field checks and treatment are performed in accordance with applicable regulations Pace project managers will inform the client of these requirements at the time of request for analytical services when the request for testing is received prior to sample collection. If samples were already collected, the laboratory will record any nonconformance to these requirements in the laboratory's sample receipt record when sufficient information about sample collection is provided with the samples.

The laboratory performs sample collection for samples to be analyzed by this SOP in accordance with laboratory SOP ENV-SOP-LENE-0107. Refer to this SOP for these instructions.

The laboratory will provide containers for the collection of samples upon client request for analytical services. Bottle kits are prepared in accordance with laboratory SOP ENV-SOP-LENE-0025.

Requirements for container type, preservation, and field quality control (QC) for the common list of test methods offered by Pace are included in the laboratory's quality manual.

Container Type, Minimum Sample Amount, Preservation, and Holding Time Requirements:

Matrix	Container Size & Type	Required Sample Amount[1]	Preservation	Holding Time
Aqueous	250mL amber with no headspace	25mL	Thermal: Cool ≤6°C Chemical: HCl	Collection to Analysis: 15mins

[1] *Amount of sample required for each discrete test.*

Thermal preservation is checked and recorded on receipt in the laboratory in accordance with laboratory SOP ENV-SOP-LENE-0021.

After receipt, samples are stored at ≤6°C until sample preparation.

After analysis, unless otherwise specified in the analytical services contract, samples are retained for 30 days from date of final report and then disposed of in accordance with Federal, State, and Local regulations.

7.0 EQUIPMENT & SUPPLIES

7.1 Equipment

Equipment	Description	Vendor / Item#
Spectrophotometer	UV-Visible	Shimadzu / UV-1800
Volumetric flasks	5mL, 10mL, 50mL, 100mL	Fisher / Various
Cuvettes	Polystyrene, 1-cm, 4.5 mL	Fisher / 14-955-125
Pipetters	N/A	Eppendorf / various

7.2 Supplies

Supplies	Description	Vendor / Item#
Centrifuge tubes	50-mL	Fisher / 06-443-19
Syringe Filters	Polyethersulfone, 25 mm, 0.45 um	Environmental Express / SF045E

8.0 REAGENTS & STANDARDS

8.1 Reagents

Reagents	Concentration/ Description	Vendor/ Item #
1,10-Phenanthroline, monohydrate	ACS Reagent Grade	Fisher / P70
Ammonium acetate	ACS Reagent Grade	Fisher / A639
Deionized water	ASTM Type II	SOP S-KS-Q-011
Hydroxylamine	ACS Reagent Grade	JT Baker / 2196-01
Hydrochloric acid	Fisher TraceMetal™ Grade	Fisher / A508

8.2 Standards

Standards	Concentration/ Description	Vendor/ Item #
Iron Standard	1000 mg/L, primary standard	Spex / PLFE2-2Y
Iron Reference Standard Solution	1000 mg/L, secondary standard	Absolute / 54141

Standard Type	Description	Expiration	Storage
Stock Solutions	▪ Concentrated reference solution purchased directly from approved vendor	▪ Manufacturer's recommended expiration date	▪ Manufacturer's recommended storage conditions
Working Standard Solutions	▪ Reference solutions prepared by dilutions of the stock solution	▪ Working solutions are not stable and must be prepared daily.	▪ Not applicable

8.3 Formulations

Ammonium acetate buffer: Dissolve 250 g ammonium acetate in a one-liter beaker containing 150 mL of deionized water. Add 700 mL of glacial acetic acid. Assign a one-year expiration date from the preparation date (not to extend beyond the expiration dates of the source reagents). Store in a tightly stoppered container at ambient temperature. Because even a good grade of ammonium acetate contains a significant amount of iron, prepare new reference standards with each buffer preparation.

Hydroxylamine solution: Dissolve 10 g hydroxylamine in 50 mL deionized water. Dilute to 100 mL and mix. Solution is stable for six months. Assign a one-year expiration date from the preparation date (not to extend beyond the expiration dates of the source reagents). Store at ambient temperature.

Phenanthroline solution: Dissolve 1.g 1, 10-phenanthroline monohydrate in 1000mL water by stirring and heating to 80°C. Do not boil. Discard the solution if it darkens. Heating is unnecessary if 2 drops concentrated HCl are added to the water. NOTE: One milliliter of this reagent is sufficient for no more than 100 ug Fe. Solution is stable for six months, and store at ambient temperature.

Iron Intermediate Standard: Add 50 mL of deionized water to a 100-mL volumetric flask followed by 10 mL of the Iron Standard (primary). Bring to volume and invert several times to mix.

Working Standard Preparation: Begin preparing standards by placing 25 mL of deionized water into 50-mL beakers. Pipet the appropriate volumes of standard and deionized water listed in Table 8.4. Proceed to Section 9 for digestion and color development steps.

Table 8.3 – Working Standard Preparation

Pace Standard ID	Standard Used	Concentration (mg/L)	Volume Used (mL)	Final Volume (mL)	Standard Concentration (mg/L)
CAL0	N/A	N/A	N/A	N/A	0
CAL1	Intermediate	100	0.05	50	0.1
CAL2 / CCVB	Intermediate	100	0.25	50	0.5
CAL3	Intermediate	100	0.5	50	1.0
CAL4/CCV	Intermediate	100	0.75	50	1.5

Pace Standard ID	Standard Used	Concentration (mg/L)	Volume Used (mL)	Final Volume (mL)	Standard Concentration (mg/L)
CAL5 / CCVA	Intermediate	100	1.	50	2.0
CAL6	Intermediate	100	1.5	50	3.0
ICV Standard	Secondary Stock	1000	0.05	50	1.0
ICB/CCB*	N/A	N/A	N/A	N/A	0

9.0 PROCEDURE

9.1 Equipment Preparation

Allow the instrument to stabilize for a minimum of 30 minutes.

9.1.1 Support Equipment

Refer to Pace Analytical Services – Kansas SOP ENV-SOP-LENE-0030, Support Equipment, or equivalent replacement, for additional information on calibration requirements for support equipment that may be used in this procedure.

Balances are checked prior to use on each working day with NIST traceable references in the expected range of use, and the results are recorded in the logbook assigned to the balance.

9.1.2 Instrument Set Up

9.1.2.1 Routine Instrument Operating Conditions

Load the ferrous iron method on the spectrophotometer and ensure the wavelength is set to 510 nm.

9.2 Calibration

9.2.1 Calibration Frequency

Calibration occurs at initial setup, CCV failure, and at a minimum every six months.

9.2.2 Calibration Levels

Refer to Table 8.3

9.2.3 Calibration Sequence

Run Number	Sample Description
1	CAL0

Run Number	Sample Description
2	CAL1
3	CAL2
4	CAL3
5	CAL4
6	CAL5
7	CAL6
8	ICV Standard
9	ICB

9.2.4 Calibration Evaluation

9.2.4.1 Curve Fit

Linear Regression – The linear regression calibration curve is derived from a least squares regression analysis of the calibration points. A calibration curve based on this technique will have the format of y = ax + b where “a” is the slope of the line and “b” is the y-intercept. The linear regression is not forced through the origin; therefore, there is a possibility that very low levels of contaminants below the response of the lowest calibration point may generate erroneous reportable results. A calculation of the correlation coefficient “r” is used to determine the acceptability of a linear regressed curve.

Determine the correlation coefficient, r, using the instrument’s software. The correlation coefficient must be greater than 0.995 to begin sample analysis.

9.2.4.2 Relative Error

Back calculate the concentration of each calibration point in the calibration curve. The back-calculated and true concentrations should agree within ±10%. At the lower limit of the operational range, acceptance criteria are ±50%.

9.2.4.3 Initial Calibration Verification

After each ICAL the ICV is run and must be within ± 10% of the true value.

9.2.4.4 Continuing Calibration Verification

Run daily before samples are run and then every 10 samples and at the end of the analytical run. The analyte must be within ± 10% of the true value.

9.3 Sample Preparation

9.3.1 Homogenization & Subsampling

Refer to Pace Analytical Services – Kansas SOP ENV-SOP-LENE-0135, Sample Homogenization and Sub-Sampling, or equivalent replacement, for information regarding

the handling, homogenization, and splitting of samples in order to ensure that a representative aliquot is used for analysis.

9.4 Analysis

9.4.1 Analysis

Method Blank (MB)

- Place 25 mL of deionized water into a 50-mL centrifuge tube.

Laboratory Control Sample (LCS)

- Place 25 mL of deionized water into a 50-mL beaker and spike with 0.5mL of the Iron Intermediate Solution.

Sample Duplicate

- Randomly select a sample from the analytical batch for duplicate analysis. Place 25 mL of the selected sample into a centrifuge tube.

Client Sample

- Place 25 mL of the sample to be tested into a 50-mL centrifuge tube.
- The Calibration standards and the LCS must be digested to reduce the spiked iron to the ferrous state. Add 1 mL of concentrated hydrochloric acid and 0.5 mL of hydroxylamine solution, place them on a hotplate to boil and reduce the volume to 15–20 mL. Cool and transfer quantitatively to 50-mL centrifuge tubes. Add 5 mL of ammonium acetate buffer and 10 mL of phenanthroline solution. Dilute to 50 mL with deionized water and invert to mix.
- Add 1 mL concentrated hydrochloric acid, 5 mL of ammonium acetate buffer and 10 mL of phenanthroline solution to the Method Blank, Client Samples, and Sample Duplicate. Dilute to 50 mL with deionized water and invert to mix.
- Color development is rapid. Read the color within 5–10 minutes, but no longer than 15 minutes.
- Transfer appropriate portions of the solutions to a 1-cm cuvette and place in the instrument's measurement cell, measure its absorbance at 510 nm with an aliquot of a color-developed water blank in the reference cell. From the corrected absorbance at 510 nm, determine the concentration of ferrous iron present by quantitation against the calibration curve.
- In the event of a turbid sample, an aliquot of the sample containing all reagents except phenanthroline should be prepared and placed in the reference cell to correct the sample for turbidity (i.e., a turbidity blank).
- If the sample absorbance/concentration is greater than the highest standard, dilute the raw sample and re-analyze. DO NOT dilute sample aliquot that has undergone color development. The response of the diluted sample must be between that of the midpoint and high standards.

9.4.2 Example Analytical Sequence

Run Number	Sample Description
1	CCVA _ Hi
2	CCVB _ Low
3	CCB
4	MB
5	LCS
6	Sample 1
7	Sample 2
8	Sample 3
9	Sample 3 Duplicate
10	Sample 4
11	Sample 5
12	Sample 6
13	Sample 7
14	CCV
15	CCB
16	Sample 8
17	Sample 9
18	Sample 10
19	CCV
20	CCB

10.0 DATA ANALYSIS & CALCULATIONS

10.1 Qualitative Identification

Ferrous iron present in the sample and standards will form a color with the reagents.

The color formed will be measured using a spectrophotometer at 510 nm wavelength.

11.0QUALITY CONTROL & METHOD PERFORMANCE

11.1 Quality Control

Prepare the following QC samples with each batch of samples. Refer to Appendix B for acceptance criteria and required corrective action(s).

QC Check	Acronym	Frequency
Method Blank	MB	1 per batch of 20 or fewer samples. If batch exceeds 20 samples, every 20 samples.
Laboratory Control Sample	LCS	1 per batch of 20 or fewer samples. If batch exceeds 20 samples, every 20 samples.
LCS Duplicate	LCSD	Per client request
Sample Duplicate	SD	1 per batch of 20 or fewer samples. If batch exceeds 20 samples, every 20 samples.

11.2 Instrument QC

Perform the following checks to verify instrument performance. Refer to Appendix B for acceptance criteria and required corrective action.

Instrument Check	Acronym	Frequency
Initial Calibration Verification	ICV	Immediately following Calibration
Initial Calibration Blank	ICB	Immediately following ICV
Continuing Calibration Verification	CCV	Immediately after the ICV, prior to the analysis of any samples. Also daily, after every 10 samples and at the end of a run.
Continuing Calibration Blank	CCB	Immediately after each Continuing Calibration Verification Standard
High (CCVA) and Low (CCVB) Check Standards	CCVA / CCVB	If ICAL is not performed on the day of analysis, then these check standards should be analyzed before the samples.

11.3 Method Performance

11.3.1 Method Validation

Refer to corporate SOP ENV-SOP-CORQ-0011 for general requirements and procedures for method validation.

Establish detection limits (DL) and limits of quantitation (LOQ) at initial method set up and verify the DL and LOQ on an on-going basis thereafter. Refer to corporate policy and/or SOP for DL and LOQ requirements and procedures.

12.0 Data Review & Corrective Action

12.1 Data Review

The data review process of Pace® Analytical Services includes a series of checks performed at different stages of the process by different people to ensure that SOPs were followed, the analytical record is complete, and properly documented, QC criteria were met, proper corrective actions were taken for QC failure and other nonconformance(s), and test results are reported with proper qualification, when necessary.

The review and checks that are performed by the employee performing the task is called primary review.

All data and test results are also peer reviewed.

This process, known as secondary review is performed to verify SOPs were followed, that calibration, instrument performance, and QC criteria were met and/or proper corrective actions were taken, qualitative ID and quantitative measurement is accurate, all manual integrations are justified and documented, and approved in accordance with the Pace® Analytical Services SOP for manual integration, calculations are correct, the analytical record is complete and traceable, and that results are properly qualified.

Lastly, a third-level review, called a completeness check, is performed by reporting or project management staff to verify the test report is complete.

Refer to laboratory SOP ENV-SOP-LENE-0088 for specific instructions and requirements for each step of the data review process.

12.2 Corrective Action

Corrective action is required when QC or sample results are not within acceptance criteria.

Refer to Appendix B for a complete summary of QC, acceptance criteria, and recommended corrective actions for QC associated with this test method.

If corrective action is not taken or was not successful, the decision/outcome must be documented in the analytical record. The primary analyst has primary responsibility for taking corrective action when QA/QC criteria are not met. Secondary data reviewers must verify that appropriate action was taken and/or that results reported with QC failure are properly qualified.

Corrective action is also required when carryover is suspected and when results are over range.

Samples analyzed after a high concentration sample must be checked for carryover and reanalyzed if carryover is suspected. Carryover is usually indicated by low concentration detects of the analyte in successive samples analyzed after the high concentration sample.

Sample results at concentrations above the upper limit of quantitation must be diluted and reanalyzed. The result in the diluted samples should be within the upper half of the calibration range. Results less than the mid-range of the calibration indicate the sample was over diluted and analysis should be repeated with a lower level of dilution. If dilution is not performed, any result reported above the upper range is considered a qualitative measurement and must be qualified as an estimated value.

13.0 POLLUTION PREVENTION & WASTE MANAGEMENT

Pace® proactively seeks ways to minimize waste generated during work processes. Some examples of pollution prevention include but are not limited to reduced solvent extraction, solvent capture, use of reusable cycletainers for solvent management, and real-time purchasing.

The EPA requires that laboratory waste management practices comply with all applicable federal and state laws and regulations. Excess reagents, samples, and method process wastes are characterized and disposed of in an acceptable manner in accordance with the Pace® Chemical Hygiene Plan / Safety Manual. Refer to this manual for these procedures.

14.0 MODIFICATIONS

The procedures in this SOP have not been modified from the reference test method(s) cited.

When applicable, comparability and/or equivalency studies necessary to validate the modification as required per corporate SOP ENV-SOP-CORQ-0011 are retained by local quality personnel for historical reference.

15.0 RESPONSIBILITIES

- All employees of Pace® Analytical Services that perform any part this procedure in their work activities must have a signed Read and Acknowledgement Statement (R&A) in their training file for the version(s) of the SOP that were in effect during the time the employee performed the activity.
- Local quality personnel are responsible for tracking the currency of the R&A on this SOP for employees at the locations they are assigned to and for notifying the General Manager (GM), however named, when R&A are overdue or outstanding. The GM and the employee's direct supervisor are responsible for ensuring the employee completes the R&A assignments as required.

- The supervisors and managers of Pace® Analytical Services, however named, are responsible for training employees on the procedures in this SOP, implementing the SOP in the work area, and monitoring on-going adherence to the SOP the work area(s) they oversee.
- All employees of Pace® Analytical Services are responsible for following the procedures in this SOP. Unauthorized deviations or departures from this SOP are not allowed except with documented approval from the local Quality Manager and only when those deviations do not violate the Pace® Code of Ethics or Professional Conduct (COR-POL-0004) or associated policy and procedure(s). Hand-edits or manual changes to the SOP are not permitted. If a change is desired or necessary, Pace® employees must follow the procedures for document revision specified in corporate SOPs ENV-SOP-CORQ-0015 *Document Managemen*t and ENV-SOP-CORQ-0016 *SOP for Creation of SOP and SWI*.
- Local quality personnel are responsible for monitoring conformity to this SOP during routine internal audits of work areas that utilize this SOP and for communicating gaps and deviations found during monitoring to the work area supervisor, who is responsible for correction of the situation.

16.0 ATTACHMENTS

- Appendix B: QC Summary & Corrective Action Table

17.0 REFERENCES

- ENV-SOP-CORQ-0006, *Manual Integration*, current version.
- ENV-SOP-CORQ-0011, *Method Validation*, current version.
- ENV-SOP-CORQ-0015, *Document Management*, current version.
- ENV-SOP-CORQ-0016, *SOP for SOP and SWI,* current version.
- ENV-TMP-CORQ-0007, *Quality Manual Template*, current version.
- COR-POL-0004, *Code of Ethics and Professional Conduct*, current version.
- COR-MAN-001, *Pace® Safety Manua*l, current version.
- Standard Methods for the Examination of Water and Wastewater, Online Edition, 3500–Fe B–2011.

18.0 REVISION HISTORY

Authorship

Primary Author[1]	Job Title	Date Complete
Lenzie Boring	Inorganics Manager	10/18/2022

[1]The primary author is the individual / role responsible for the content of this SOP. Send questions or suggestions for content to the primary author. See the Quality Manager for questions or concerns related to implementation of this SOP.

Revisions Made from Prior Version

Section	Description of Change
All	New SOP template

Document Succession: This version replaces the following documents:

Document Number & Version	Document Title	Effective Date:
ENV-SOP-LENE-0010 V02	Ferrous Iron	07/07/2020

Appendix B: QC Summary and Corrective Action Table

QC Item	Frequency	Acceptance Criteria	Corrective Action	Qualification
ICAL	At instrument set up, after CCV failure	Must meet one of curve fit options presented in Section 9.0. For any curve fit other than Average RF (RSD), curve must also pass RSE test at the low and midpoint calibration standard.	Identify and correct source of problem, repeat	None. Do not proceed with analysis
ICV	After Each ICAL	All analytes must be within ± 15% of the true value. (%R)	Identify source of problem, re-analyze. If repeat failure, repeat ICAL. Analysis may proceed if it can be demonstrated that the ICV exceedance has no impact on analytical measurements. For example, the ICV %R is high, CCV is within criteria, and the analyte is not detected in sample(s).	Qualify analytes with ICV out of criteria.
CCV / High CCV	Daily, before sample analysis, after every 10, and at end of analytical window.	Opening CCV: All analytes within ± 10 %D Ending CCV: ± 10 %D	See Section 12 for required corrective actions based on circumstance.	Qualify analytes with CCV out of criteria.
Method Blank	One per batch of up to 20 samples	Result should be less than the reporting limit. If results are reported to MDL, the MB must be evaluated to the MDL.	1) Re-analyze blank to confirm failure. 2) Qualify results and / or re-analyze associated samples.	1) If sample ND, report sample without qualification 2) If sample result >10x MB report sample with appropriate qualifier indicating blank contamination. If sample result <10x MB and sample cannot be reanalyzed report sample with appropriate qualifier to indicate an estimated value. Client should be alerted of this condition.

QC Item	Frequency	Acceptance Criteria	Corrective Action	Qualification
LCS	One per batch of up to 20 samples	90-110% Recovery	1) Reanalyze the LCS to confirm failure 2) Re-prep and reanalyze associated samples. 3) If problem persists, check spike solution	1) If LCS > QC limits and these compounds are non-detect in the associated samples, the sample data may be reported with appropriate data qualifiers. 2) If LCS < QC limits and sample cannot be reanalyzed report sample with appropriate qualifier to indicate an estimated value. Client should be alerted to this condition.
Sample Duplicate	One per batch of up to 20 samples.	Max RPD: 10%	No corrective actions necessary. Report outliers with comment..	
Low CCV Check	Whenever an Initial Calibration is not done	50-150% Recovery (See Section 9)	May be re-analyzed once. A second failure confirms and requires corrective action(s).	Samples cannot be reported without a valid curve
ICB	Immediately after each CCV	Result should be less than one-half the reporting limit. If results are reported to MDL, the ICB must be evaluated to the MDL.	May be re-analyzed once. A second failure confirms and requires corrective action(s).	If sample results are reported to MDL and CCB is <RL but >MDL, then corrective action is not necessary other than appropriately qualifying the sample results. Unless the customer's QAPP or technical specification instruct to do otherwise. Samples that are <RL may be reported without qualification. (Not applicable to samples reporting down to MDL) Samples >10x CCB may be reported with appropriate qualification.
CCB	Immediately after each CCV	Result should be less than one-half the reporting limit. If results are reported to MDL, the ICB must be evaluated to the MDL.	May be re-analyzed once. A second failure confirms and requires corrective action(s).	If sample results are reported to MDL and CCB is <RL but >MDL, then corrective action is not necessary other than appropriately qualifying the sample results. Unless the customer's QAPP or technical specification instruct to do otherwise. Samples that are <RL may be reported without qualification. (Not applicable to samples reporting down to MDL) Samples >10x CCB may be reported with appropriate qualification.

1.0 SCOPE & APPLICATION

This standard operating procedure (SOP) describes the laboratory procedure for the determination of total, amenable to chlorination and weak acid dissociable cyanide in water, soil, and reactive scrubber solution samples by colorimetry by methods EPA 9010B, 9012A/B, SM 4500 CN E & G(1999 & 2016), and SM 4500 CN I (2011 & 2016)

1.1 Target Analyte List and Limits of Quantitation (LOQ)

The target analytes that can be determined by this SOP and the associated LOQ is provided in Table 1, Appendix A.

2.0 SUMMARY OF METHOD

Cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a reflux-distillation operation and absorbed in a scrubber solution containing sodium hydroxide. The cyanide ion in the absorbing solution is then determined colorimetrically using a Seal Discrete Analyzer. The cyanide is converted to cyanogen chloride, CNCl, by reaction with Chloramine-T at a pH of less than 8 without hydrolyzing the cyanate. After the reaction is complete, a reddish color is formed with the addition of pyridine-barbituric acid reagent. The absorbance is read at 570 nm.

To determine cyanide amenable to chlorination a portion of the sample is chlorinated at a pH >11 to decompose the cyanide. Cyanide levels in the chlorinated sample are then determined as well as the total cyanide. Cyanides amenable to chlorination are then calculated by the difference between the two results.

Weak acid dissociable (WAD) cyanide is determined from a slightly acidified (pH 4.5 to 6.0) sample under this procedure's distillation conditions. The method does not recover cyanide from tight complexes that would not be amenable to oxidation by chlorine. The acetate buffer used contains zinc salts to precipitate iron cyanide as a further assurance of the selectivity of the method.

3.0 INTERFERENCES

Sulfides, oxidizing agents, nitrites, and nitrates are removed by pre-treatment procedures. Most other interfering substances are removed by distillation.

Oxidizing agents, such as chlorine, decompose most cyanides during storage. Oxidizing agents need to be removed prior to sample preservation and storage. Ascorbic acid is no longer being recommended for preservation of samples for cyanide analysis. Ascorbic acid functions as a carbon donor in the presence of nitrite or nitrate and generates cyanide during the distillation. Sodium thiosulfate is an adequate dechlorinating agent if it is not used in excess. Sodium arsenite also may be used, but it is a hazardous material.

Sulfide will distill over with cyanide and therefore, adversely affect the colorimetric procedures. Precipitation of sulfide with cadmium salts should be avoided since the formation of insoluble cadmium

cyanide complexes can result in loss of cyanide. In this SOP sulfide inference is mitigated by precipitating out sulfide with powdered lead carbonate as per method SM4500-CN. It should be noted that some studies have shown that sulfide and cyanide can form thiocyanate in the presence of lead sulfide causing decreased cyanide recoveries.

High bias cyanide results may be obtained for samples that contain nitrate and/or nitrite. During the distillation nitrate and nitrite will form nitrous acid that will react with some organic compounds to form oximes. These oximes will decompose under test conditions to generate HCN. The interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid.

4.0 DEFINITIONS

Refer to the Laboratory Quality Manual for a glossary of common lab terms and definitions.

- **Amenable Cyanide** – Cyanide that is amenable to chlorination. This is determined by analyzing both chlorinated and unchlorinated portions of sample. Amenable cyanide is calculated by the difference between the total cyanide in the unchlorinated portion and the total cyanide in the chlorinated portion.
- **Weak Acid Dissociable (WAD) Cyanide** – Cyanide that is liberated from a slight acidification (pH 4.5 to 6.0) under the prescribed distillation conditions. WAD cyanide typically does not include cyanide that is bound in tight complexes.

5.0 HEALTH & SAFETY

Contact your supervisor or local safety coordinator with questions or concerns regarding safety protocol or safe handling procedures for this procedure

The following sections provide general health and safety information about chemicals and materials that may be present in the laboratory.

- The toxicity or carcinogenicity of each chemical material used in the laboratory has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable.
- The laboratory maintains documentation of hazard assessments and OSHA regulations regarding the safe handling of the chemicals specified in each method. Safety data sheets for all hazardous chemicals are available to all personnel. Employees must abide by the health, safety and environmental (EHS) policies and procedures specified in this SOP and in the Pace® Chemical Hygiene / Safety Manual (COR-MAN-0001)
- Personal protective equipment (PPE) such as safety glasses, gloves, and a laboratory coat must be worn in designated areas and while handling samples and chemical materials to protect against physical contact with samples that contain potentially hazardous chemicals and exposure to chemical materials used in the procedure.
- Concentrated corrosives present additional hazards and are damaging to skin and mucus membranes. For procedures that require use of acids, use acids in a fume hood whenever possible with PPE designed for handing these materials. If eye or skin contact occurs, flush with large volumes of water. When working with acids, always add acid to water to prevent violent reactions.

For procedures that that emit large volumes of solvents (evaporation/concentration processes), these activities must be performed in a fume hood or apparatus that reduces exposure.

6.0 .SAMPLE COLLECTION, PRESERVATION, HOLDING TIME & STORAGE

The laboratory provides containers for the collection of samples upon client request. Refer to laboratory SOP ENV-SOP-LENE-0107 for procedures related to preparation of bottle kits for the test method(s) associated with this SOP.

The laboratory performs samples collection for samples to be analyzed by this SOP in accordance with laboratory SOP ENV-SOP-LENE-0025. Refer to this SOP for these instructions.

Container Type, Minimum Sample Amount, Preservation, and Holding Time Requirements:

Matrix	Container Size & Type	Required Sample Amount[1]	Preservation	Holding Time
Aqueous	Plastic, 250 mL	50 mL	Thermal: ≤6°C (not frozen) Chemical: NaOH to pH ≥12	Collection to Prep: 14 days Prep to Analysis: Immediate
Soil/Solid	Glass jar, 4 or 8 oz	0.4 g	Thermal: ≤6°C (not frozen) Chemical: None	Collection to Prep: 14 days Prep to Analysis: Immediate

[1] *Amount of sample required for each discrete test.*

Thermal preservation is checked and recorded on receipt in accordance with laboratory SOP ENV-SOP-LENE-0021. Chemical preservation is checked and recorded at time of receipt or prior to sample preparation.

After receipt, samples are stored at ≤6°C until sample preparation. Prepared samples (extracts, digestates, distillates, other) are stored at ≤6C until sample analysis.

After analysis, samples are retained as stated in the Pace® standard terms and conditions, unless otherwise specified in the analytical services contract. Samples are then disposed of in accordance with Federal, State, and Local regulations.

7.0 EQUIPMENT & SUPPLIES

7.1 Equipment

Equipment	Vendor	Model / Version	Description / Comments
Discrete Analyzer	Seal	AQ400	or equivalent
Analytical Balance	Mettler-Toledo	AE200	0.0001g resolution
Distillation block	Micro-Dist®	Hach / MDD001	or equivalent

7.2 Supplies

Supply	Description	Vendor/ Item # / Description
Volumetric Flasks	Various sizes	Class A
Pipetters	Various sizes	Eppendorf / various / or equivalent
Distillation tubes	Micro-Dist® Cyanide-1	Hach / A17001/ or equivalent
pH paper	Wide-range	Fisher / 14-850-11B
KI starch paper	N/A	Fisher / 14-860
Lead acetate paper	N/A	Fisher / 14-862
Reaction Segments	18 Reaction wells/segments	Seal/ 5000
Reagent Containers	43mL – Reagent Wedge	Seal/ 5010
2mL Sample Cups	2 mL Vail for 80 position tray	Seal/ 6015
5mL Sample Cups	5 mL Vial for 80 position tray	Seal/ 171-0354-01
Reagent Container Caps	43 mL Reagent Container Caps	Seal/ 5050-50
Lamp Assembly	N/A	Seal/ 6100
Aspiration Probe	N/A	Seal/ 5110
Sampler Probe	N/A	Seal/ 6125-S
Complete Tubing Set	N/A	Seal/ 57002
Peristaltic Tubing Set	N/A	Seal/ 2-0021
Syringe Glass Body, Piston and O'Ring	N/A	Seal/ 5195-1
3 Month Maintenace Kit	N/A	Seal/ AQ3M-4
6 Month Maintenace Kit	N/A	Seal/ AQ6M-4
12 Month Maintenance Kit	N/A	Seal/ AQ12M-4
Barbed Fitting	Peristaltic tubing	Seal/ 5720
Sample Probe Washer Assembly	N/A	Seal/ MA000102
1 cm Cuvette	N/A	Seal/ 5670-1
Cuvette Inlet Tubing	N/A	Seal/ 5671
Cuvette Outlet Tubing	N/A	Seal/ 5672

8.0 REAGENTS & STANDARDS

8.1 Reagents

Reagent	Concentration/ Description	Requirements/ Vendor / Item #
Reagent water	ASTM Type II	SOP S-KS-Q-011
Hydrogen Peroxide	30%	Fisher / H325-500
Sodium Thiosulfate	Anhydrous, ACS Grade	Fisher / S446-500
Barbituric acid	≥98%	Fisher / O3108-100
Lead carbonate	≥99.99%	Fisher / 50-343-042
Chloramine-T Trihydrate	≥12% active chlorine	Fisher / O1779-250
Glacial acetic acid	ACS Reagent Grade	Fisher / A38
Hydrochloric acid	ACS Reagent Grade	Fisher / A508-SK-212
Pyridine	ACS Reagent Grade	Fisher / P368-4
Sodium acetate trihydrate	ACS Reagent Grade	Fisher / S209-500
Sodium phosphate monobasic monohydrate	ACS Reagent Grade	Fisher / S-369-500
Sodium hydroxide	ACS Reagent Grade	Fisher / S318-3
Sodium hypochlorite solution (5.25%)	Consumer-grade, unscented	Clorox or equivalent
Sulfamic acid	ACS Reagent Grade	Fisher / A295-500
Sulfuric acid	ACS Reagent Grade	Fisher / A510-SK-212
Zinc acetate dihydrate	ACS Reagent Grade	Acros / 207645000
Cuvette Cleaning Solution	N/A	SEAL /5676
0.1N Sodium Arsenite	ACS Reagent Grade	Fisher/ LC229002

8.2 Standards

Standard	Concentration/ Description	Requirements/ Vendor / Item #
Primary stock standard	HPS / 1000 mg/L CN^-	Environmental Express / IC-CN-M
Secondary stock standard	Spex / 1000 mg/L CN^-	Spex / RSCN9-2Y

8.3 Formulations

8.3.1 Working Reagents

Reagent	Description
Sodium hydroxide, 0.25N	Dissolve 10g NaOH in one liter of reagent water.
Sodium hydroxide, 0.025N	Dilute 10mL of 0.25N NaOH in 100mL of reagent water.
Phosphate Buffer	Dissolve 138 g sodium phosphate monobasic monohydrate in 900 mL DI water and dilute to the mark. Store at ≤ 6ºC. Remake solution every 3 months or as needed.
Color Reagent (Pyridine-Barbituric acid)	Place 15 g barbituric acid in a 1L volumetric flask and add enough DI water to wash the sides of the flask and wet the barbituric acid. Add 75 mL pyridine and mix. Add 15 mL concentrated hydrochloric acid and swirl to mix. Add additional DI water and stir to dissolve the barbituric acid. Dilute to the mark with DI water and invert to mix. For lowest detection limits, chill this reagent and perform gravity filtration. Every two weeks filter a portion of reagent for use. Stable for 6 months. Store at ≤ 6ºC
Chloramine-T Solution	Dissolve 1.0 g chloramine-T trihydrate in 100 mL DI water and store at ≤ 6ºC. Prepare fresh daily.
Releasing Agent (7.11M Sulfuric acid / 0.79M Magnesium chloride solution)	Completely dissolve 32.2g of magnesium chloride hexahydrate in a glass container containing 110.8g of reagent water. Slowly add 75 mL conc. sulfuric acid (CAUTION: HCl fumes are released in this step; must be performed in a fume hood!). Solution is ready for use when cool.
Sulfamic acid, 0.4N	Dissolve 40g of sulfamic acid in 1 liter of reagent water.
WAD distillation solution	Add 136g of sodium acetate and 40g of zinc acetate to a 1-L volumetric flask containing 500 mL of reagent water. Add 50 mL of glacial acetic acid and bring to volume with reagent water.
Sodium Thiosulfate ($Na_2S_2O_3$) solution, 500g/L	Dissolve 25g of Sodium Thiosulfate ($Na_2S_2O_3$) in 50mL of reagent water.
Hydrogen Peroxide (H_2O_2) solution, (3%)	Perform a ten-fold (10x) dilution of the 30% Hydrogen Peroxide Solution with reagent water. (e.g. 5mL of 30% H_2O_2 diluted to a final volume of 50mL)

8.3.2 Intermediate Standards

Standard	Stock Standard	Standard Amount	Solvent	Final Total Volume	Final Concentration
Primary Cyanide Intermediate Standard	Primary Stock Standard	0.100mL	0.25N NaOH	100mL	1.0 mg/L
Secondary Intermediate Standard	Secondary Stock Standard	0.100mL	0.25N NaOH	100mL	1.0 mg/L

8.3.3 Working Standards

Standard	Intermediate Standard	Standard Amount	Solvent	Solvent Volume in Distillation Tube	Final Concentration
Calibration Standard	Primary Int Standard	1.20mL	Reagent Water	4.8mL	0.2 mg/L
ICV Working Standard	Secondary Int Standard	0.600mL	Reagent Water	5.4mL	0.1 mg/L
CCV Working Standard	Primary Int Standard	0.600mL	Reagent Water	5.4mL	0.1 mg/L
MDL	Primary Int. Standard	0.03mL	Reagent Water	5.97mL	0.005mg/L

All Working Standards are prepared in distillation tubes and undergo the distillation process.

9.0 PROCEDURE

9.1 Equipment Preparation

9.1.1 Support Equipment

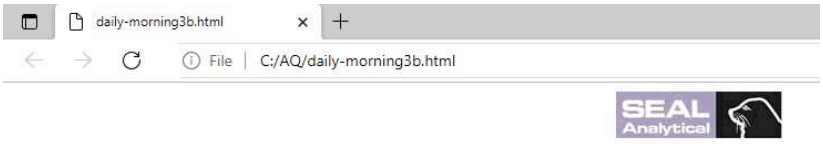
Refer to Pace Analytical Services – Kansas SOP ENV-SOP-LENE-0030, Support Equipment, or equivalent replacement, for additional information on calibration requirements for support equipment that may be used in this procedure.

Balances are checked prior to use on each working day with NIST traceable references in the expected range of use, and the results are recorded in the logbook assigned to the balance.

9.1.2 Instrument Set Up

9.1.2.1 Routine Instrument Operating Conditions:

9.1.2.2 Set up based on the Seal Daily Tasks as shown below:



AQ400 Daily (Morning) Tasks

	Daily (Morning) Tasks	
☐	Empty and Refill Wash Water Reservoir	
☐	Empty the Waste Container	
☐	Replace Reaction Segments as Required	
Maintenance Menu		
	☐	Observe movements during initialization • Movements should be smooth and they should be the same each initialization
	☐	**DILUTER:** Prime Syringe (5-10 times) • Verify no air remains in syringe and operating smoothly.
	☐	**DILUTER:** Check operation of Probe Washer • Turn on Waste Pump and Wash Valve • Verify water movement through chamber
	☐	**CUVETTE:** Perform 1-5 Auto Washes • Observe Wash Bath is Filling and Clean
	☐	**CUVETTE**: Check/Adjust Aspiration for both Inner and Outer Wells • Verify that there is 1-2" of water (no bubbles) in the outlet tubing of cuvette
☐	Run "Daily Startup" Procedure. Water baseline voltages for filters 1 through 9 should range from 0.7 to 4.85 V. Filter 10/Dark should be near 0.027 V.	
☐	Inspect reagents for particulates or excessive color. Filter or replace reagents as needed. Check the method documents for information on reagent stability and symptoms of reagent degradation.	
☐	Cadmium Coil checks as required. See Cadmium Coil Care section of "Technical Tips" in the Customer Support Manual	

**See Customer Support Manual or Operator Manual for more information of above items.

9.1.2.3 Periotic Operator Maintenance:

Daily:

1. Check the cuvette aspiration and adjust as necessary.
2. Check the operation of the probe washer. Confirm proper flow and check for contamination and/or leaking/dripping. Clean, or replace as necessary.
3. Run daily start-up and compare water baselines. Adjust gain if required.
4. Run Hypochlorite solution clean using the extra wash function from the maintenance screen.
5. Clean the cuvette with seal cuvette cleaning solution using the extra wash function from the maintenance screen.

Weekly:

1. Check the peristaltic pump tubing for damage. Replace, as necessary.
2. Check the cuvette aspiration tubing and waste tubing for kinks, damage, or blockages. Replace as necessary.
3. Check that the waste pump functions correctly (i.e., operates to empty sampler wash well and pull water through the probe washer).
4. Using a swab, clean the walls of the inner and outer sections of the sampler wash bath and aspiration wash bath.
5. Inspect the sample probe and aspiration probe for cleanliness, leaking, dripping or damage. Clean, adjust, or replace as necessary.

Monthly:

1. Replace laspiration pump tub and check cuvette aspiration.
2. Replace wash pump tubes.
3. Clean and lubricte the pump rollers on the two peristaltic pumps.
4. Clean the lamp filter.

6 Months:

1. Replace the probe wash assembly and check the sample probe.
2. Replace the syringe barrel, plunger and o-ring. Clean and lubricate the syringe screw drive.
3. Replace the lame and optimize the gain and offset.
4. Inspect cuvette aspiration probe, aspiration inlet and outlet tubing, and waste tubing for kinks, damage or blockages. Replace as necessary.

Yearly:

1. Schedule instruments yearly Preventive Maintenace with Seal Tech.

9.2 Calibration

9.2.1 Calibration Frequency

Calibration will occur daily

9.2.2 Calibration Levels

The Seal instrument will autodilute the calibration standard and will analyze all points of the initial calibration according to the method loaded. The high standard and ICV are digested with each digestion group. The curve points are 0, 0.004, 0.025, 0.05, 0.1, 0.2 mg/L.

9.2.3 Calibration Sequence

Run Number	Sample Description
1	ICAL Standard 0
2	ICAL Standard 1
3	ICAL Standard 2
4	ICAL Standard 3
5	ICAL Standard 4
6	ICAL Standard 5
7	Standard 0
8	ICV Standard
9	CCV
10	CCB
11	Sample 1
12	Sample 2
13	Sample 3
14	Sample 3 Duplicate
15	Sample 4
16	Sample 5
17	Sample 6
18	Sample 7
19	CCV
20	CCB
21	Sample 8
22	Sample 9
23	Sample 10
24	CCV
25	CCB

9.2.4 Calibration Evaluation

9.2.4.1 Curve Fit

The curve fit used is linear.

9.2.4.2 Relative Error

Refit curve points with acceptance criteria of ± 10% of True Value, except for the low standard with a criterion of ± 50% of True Value.

9.2.4.3 Initial Calibration Verification

In addition to meeting the linearity criteria, any new calibration curve must be assessed for accuracy in the values generated. Accuracy is a function of both the "fit" of the curve to the points used and the accuracy of the standards used to generate the calibration points. By meeting the fit criteria, the accuracy relative to the goodness of fit is addressed. However, because all calibration points are from the same source, it is possible that the calibration points may meet linearity criteria, but not be accurately made in terms of their true value.

Therefore, to assess the accuracy relative to the purity of the standards, a single standard from a secondary source must be analyzed and the results obtained must be assessed relative to the known true value. This step is referred to as Secondary Source Verification or, alternatively as Initial Calibration Verification. This

secondary source must be from an alternative vendor or, in the event an alternative vendor is not available, from a different lot from the same vendor. The accuracy of the standard is assessed as a percent difference from the true value according to the following equation:

$$\%\text{Drift} = \frac{(\text{Result}_{ICV} - \text{True Value}_{ICV})}{\text{True Value}_{ICV}}$$

9.2.4.4 Continuing Calibration Verification

As part of the analytical process, the instrumentation must be checked periodically to determine if the response has changed significantly since the initial calibration was established. This verification process is known as Continuing Calibration Verification (CCV). The validity of the initial calibration is checked after every ten samples and at the end of the analytical sequence by analyzing a midpoint calibration standard. The accuracy of the standard is assessed as percent drift from the true value according to the following equation:

$$\%\text{Drift} = \frac{(\text{Result}_{CCV} - \text{True Value}_{CCV})}{\text{True Value}_{CCV}}$$

9.3 Sample Preparation

9.3.1 Homogenization & Subsampling

Refer to Pace Analytical Services – Kansas SOP ENV-SOP-LENE-0135, Sample Homogenization and Sub-Sampling, or equivalent replacement, for information regarding the handling, homogenization, and splitting of samples in order to ensure that a representative aliquot is used for analysis.

9.4 Analysis

9.4.1 Amenable Cyanide Sample Pretreatment (Use only if determining cyanide amenable to chlorination.)

Distillation of two samples is required, one that has been chlorinated to destroy all amenable cyanide present and the other unchlorinated. Analyze distillates from both tests for total cyanide. The observed difference equals cyanides amenable to chlorination.

Select the samples that require amenable cyanide analysis for this pretreatment. No QC samples are required for amenable cyanide per the method. A method blank and duplicate may be performed.

The pretreatment step should be performed in a hood.

9.4.2 Amenable Cyanide Waters:

Measure 50 mL of sample, or a portion diluted to 50 mL, and add sodium hypochlorite (bleach) dropwise to the sample while agitating. Check pH and maintain the pH between 11 and 12 by adding NaOH solution if necessary.

Test for chlorine by placing a drop of treated sample on a strip of KI starch paper. A distinct blue color indicates sufficient chlorine (approximately 50 to 100 mg Cl2/L) Maintain excess residual chlorine for 1 hour while agitating. If necessary, add more bleach and/or NaOH.

In the fume hood gradually add 0.6mL of Sodium Arsenite until no residual chlorine is present. Test residual chlorine with KI starch paper. The KI starch paper should no longer turn blue if all the chlorine has been removed. Minimize sample exposure to ultraviolet radiation before distillation by storing it in the dark.

9.4.3 Amenable Cyanide Soils:

Measure 1.0g of sample and 50mL of DI water into aluminum covered sample cup. Add stir bar and let spin for 15 minutes to homogenize soil and water mixture. Add sodium hypochlorite (bleach) dropwise to the sample while agitating. Check pH and maintain the pH between 11 and 12 by adding NaOH solution if necessary.

Test for chlorine by placing a drop of treated sample on a strip of KI starch paper. A distinct blue color indicates sufficient chlorine (approximately 50 to 100 mg Cl2/L). Maintain excess residual chlorine for 1 hour while agitating. If necessary, add more bleach and/or NaOH.

In the fume hood gradually add 0.6mL of Sodium Arsenite until no residual chlorine is present. Test residual chlorine with KI starch paper. The KI starch paper should no longer turn blue if all the chlorine has been removed.

After dechlorinating the sample. Pipette 6mLs of the dechlorinated sample into the distillation tube. Follow the sample distillation below.

Minimize sample exposure to ultraviolet radiation before distillation by storing in the dark.

9.4.4 **Sulfide Screening** – All water samples are screened at the time of sample receipt for the presence of Sulfide by pipetting a drop of sample onto lead acetate paper. If the lead acetate paper turns dark this indicates the presence of Sulfide. Samples demonstrating the presence of Sulfide will be marked as such by sample receiving and treated as follows:

Treat 25 mL more of the stabilized sample (pH ≥12) than that required for the cyanide determination (6 mL) with powdered lead carbonate. 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. Avoid a large excess of lead and a long contact time in order to minimize a loss by complexation or occlusion of cyanide on the precipitated material.

Filter the solution through dry filter paper into a dry beaker and, from the filtrate, measure the sample to be used for analysis.

9.4.5 **Chlorine Screening –** Chlorine screening is performed at the time of sample receipt. Samples are treated immediately with Sodium Arsenite if the presence of chlorine is detected.

9.4.6 Distillation

Set controller on micro distillation block to 120°C. Allow approximately 40 min. for heater block to warm up.

With the M end of the distillation tube facing upwards, put as many of the collector tubes as there are samples in the collector tube rack.

Put as many sample tubes into the sample tube rack as you have samples to distill; up to 21 for one block.

Prepare the method blank by placing 6 mL of reagent water (0.2 g of boiling stones for soils) into a sample tube.

Prepare the laboratory control sample by placing 5.4 mL of reagent water and 0.6 mL of the Working Standard solution (0.2 g of boiling stones for soils) into a sample tube.

Randomly select a sample from the analytical batch for matrix spiking. Place 5.4 mL of the selected sample (0.2 g for soils) and 0.6 mL of the Working Standard solution into a sample tube.

Place 6 mL of sample (0.2 g for soils) into each sample tube. Randomly select a sample from the analytical batch for duplicate analysis.

Add 0.6 mL of sulfamic acid solution to each sample tube.

Total or amenable cyanide: Add 0.75 mL of 7.11 M sulfuric acid / 0.79 M magnesium chloride solution to each sample tube and immediately push the D end of the collector tube over the open end of each sample tube to start the seal.

Weak acid dissociable cyanide: Add 0.75 mL of WAD digestion solution to each sample tube and immediately push the D end of the collector tube over the open end of each sample tube to start the seal.

Place the assembly in the press, putting the sample tube through the hole in the white base. Before pressing, grip the collector tube firmly at the breakaway point to keep the tube from shifting during the pressing procedure.

Put on the heat-resistant gloves. Push the sample tube and D end of each tube all the way into the preheated block so that the collector tube stop ring touches the block.

Set timer for 30 min.

When 30 min. is up, put on heat-resistant gloves. Remove the first tube from the block and immediately pull off its sample tube using a downward, twisting motion as opposed to a sideways motion. You must remove the sample tube within seconds of removing it from the block or a suck-back of the sample will occur. Dispose of the sample tube and the hot solution left in it by dropping it into the sink or waste container..

Invert each collector tube and place it into the collector tube rack, now with the D end up.

Allow to cool for approximately 10 min. Then, for each collector tube, hold horizontally and rinse its walls with the distillate in order to homogenize. Slowly roll distillate around in the tube to gather all droplets into the bulk of the distillate.

With D end up, break the collector tube in half by polling the D end towards yourself. Rinse the D end with reagent water to collect any left-over droplets and pour into M end. Break off and dispose of the D end.

In the remaining M end of the collector tube, dilute to the 6.0 mL mark with reagent water. Push the second cap onto the open end of the tube as far as it will go and shake the tube with a gentle whipping motion to mix. Do not invert.

Record all distillation information in the distillation logbook.

Sample is then ready for analysis on the Seal™ Discrete Analyzer.

9.4.7 Sample Analysis

Open the method in the Seal™ Operation menu to run the Cyanide method.

Calibrate the Seal™ as per Section 11 above.

Using .45 micron filters. Filter the samples into the autosampler cups and arrange them in the order they are on the worklist.

Ensure that the DQM is enabled to run the CCV/CCB first, after each group of 10 samples, at the end of the sequence.

If the sample absorbance/concentration is greater than the highest standard dilutes the extract and re-analyze. The response to the diluted sample must be between the mid and high standards. NOTE: If the auto dilutor is activated this step is not necessary.

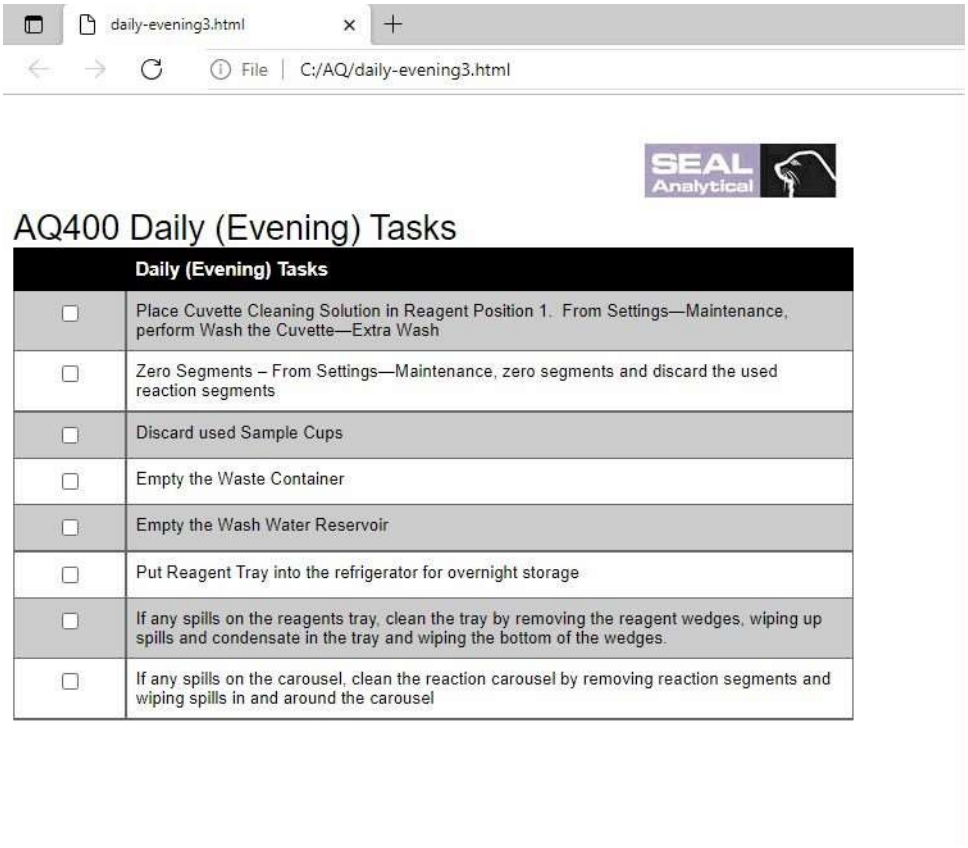
When running Amenable samples make sure they are reading lower than the Total Cyanide counterpart.

Reporting for amenable solids is done under the (Amenable Soil Calculation) in the logbook.

9.4.8 Example Analytical Sequence

See the Sequence in Section 9.2.3.

9.4.9 Seal shut down procedure:



	Daily (Evening) Tasks
☐	Place Cuvette Cleaning Solution in Reagent Position 1. From Settings—Maintenance, perform Wash the Cuvette—Extra Wash
☐	Zero Segments – From Settings—Maintenance, zero segments and discard the used reaction segments
☐	Discard used Sample Cups
☐	Empty the Waste Container
☐	Empty the Wash Water Reservoir
☐	Put Reagent Tray into the refrigerator for overnight storage
☐	If any spills on the reagents tray, clean the tray by removing the reagent wedges, wiping up spills and condensate in the tray and wiping the bottom of the wedges.
☐	If any spills on the carousel, clean the reaction carousel by removing reaction segments and wiping spills in and around the carousel

10.0 DATA ANALYSIS & CALCULATIONS

10.1 Qualitative Identification

Cyanide ion present in the sample and standards will form a color with the reagents. The color formed will be measured using a spectrophotomer at 570 nm wavelength.

10.1.1 Manual Integration

Manual integration is sometimes necessary to correct inaccurate automated integrations but must never be used to meet QC criteria or to substitute for proper instrument maintenance and/or method set-up. To assure that all manual integrations are justified and proper all manual integrations must be performed, documented, reviewed, and approved in accordance with corporate SOP ENV-SOP-CORQ-0006, *Manual Integration.* Refer to this SOP for guidance on manual integration techniques and required procedures.

11.0 QUALITY CONTROL & METHOD PERFORMANCE

11.1 Quality Control

Prepare the following QC samples with each batch of samples. Refer to Appendix B for acceptance criteria and required corrective action(s).

QC Check	Acronym	Frequency
Method Blank	MB	1 per batch of 20 or fewer samples. If batch exceeds 20 samples, every 20 samples.
Laboratory Control Sample	LCS	1 per batch of 20 or fewer samples. If batch exceeds 20 samples, every 20 samples.
LCS Duplicate	LCSD	Per client request.
Matrix Spike	MS	One per batch of up to 20 samples.
Matrix Spike Duplicate	MSD	One per batch of up to 20 samples.
Sample Duplicate	SD	One per batch of up to 20 samples.

11.2 Instrument QC

Perform the following checks to verify instrument performance. Refer to Appendix B for acceptance criteria and required corrective action.

Instrument Check	Acronym	Frequency
Initial Calibration	ICAL	Every Day
Initial Calibration Verification	ICV	Immediately after each Initial Calibration
Initial Calibration Blank	ICB	Immediately after each Initial Calibration Verification Standard
Continuing Calibration Verification	CCV	Prior to the analysis of any samples and every 10 samples thereafter. Samples need to be bracketed with CCVs
Continuing Calibration Blank	CCB	Immediately after each Continuing Calibration Verification Standard

11.3 Method Performance

11.3.1 Method Validation

Refer to corporate SOP ENV-SOP-CORQ-0011 for general requirements and procedures for method validation.

Establish detection limits (DL) and limits of quantitation (LOQ) at initial method set up and verify the DL and LOQ on an on-going basis thereafter. Refer to corporate policy and/or SOP for DL and LOQ requirements and procedures.

12.0 DATA REVIEW & CORRECTIVE ACTION

12.1 Data Review

The data review process of Pace® Analytical Services includes a series of checks performed at different stages of the process by different people to ensure that SOPs were followed, the

analytical record is complete, and properly documented, QC criteria were met, proper corrective actions were taken for QC failure and other nonconformance(s), and test results are reported with proper qualification, when necessary.

The review and checks that are performed by the employee performing the task is called primary review.

All data and test results are also peer reviewed.

This process, known as secondary review is performed to verify SOPs were followed, that calibration, instrument performance, and QC criteria were met and/or proper corrective actions were taken, qualitative ID and quantitative measurement is accurate, all manual integrations are justified and documented, and approved in accordance with the Pace® Analytical Services SOP for manual integration, calculations are correct, the analytical record is complete and traceable, and that results are properly qualified.

Lastly, a third-level review, called a completeness check, is performed by reporting or project management staff to verify the test report is complete.

Refer to laboratory SOP ENV-SOP-LENE-0088 for specific instructions and requirements for each step of the data review process.

12.2 Corrective Action

Corrective action is required when QC or sample results are not within acceptance criteria.

Refer to Appendix B for a complete summary of QC, acceptance criteria, and recommended corrective actions for QC associated with this test method.

If corrective action is not taken or was not successful, the decision/outcome must be documented in the analytical record. The primary analyst has primary responsibility for taking corrective action when QA/QC criteria are not met. Secondary data reviewers must verify that appropriate action was taken and/or that results reported with QC failure are properly qualified.

Corrective action is also required when carryover is suspected and when results are over range.

Samples analyzed after a high concentration sample must be checked for carryover and reanalyzed if carryover is suspected. Carryover is usually indicated by low concentration detects of the analyte in successive samples analyzed after the high concentration sample.

Sample results at concentrations above the upper limit of quantitation must be diluted and reanalyzed. The result in the diluted samples should be within the upper half of the calibration range. Results less than the mid-range of the calibration indicate the sample was over diluted and analysis should be repeated with a lower level of dilution. If dilution is not performed, any result reported above the upper range is considered a qualitative measurement and must be qualified as an estimated value.

13.0 POLLUTION PREVENTION & WASTE MANAGEMENT

Pace® proactively seeks ways to minimize waste generated during work processes. Some examples of pollution prevention include but are not limited to reduced solvent extraction, solvent capture, use of reusable cycletainers for solvent management, and real-time purchasing.

The EPA requires that laboratory waste management practices comply with all applicable federal and state laws and regulations. Excess reagents, samples, and method process wastes are characterized and disposed of in an acceptable manner in accordance with the Pace® Chemical Hygiene Plan / Safety Manual. Refer to this manual for these procedures.

14.0 MODIFICATIONS

The procedures in this SOP have been modified from the reference test method as follows:

Modification	Test Method Procedure	Justification for Modification
Chloramine-T and the color reagent are prepared in accordance with SEAL method	All methods	Manufacturer recommendation

When applicable, comparability and/or equivalency studies necessary to validate the modification as required per corporate SOP ENV-SOP-CORQ-0011 are retained by local quality personnel for historical reference.

15.0RESPONSIBILITIES

- All PAS employees that perform any part of this procedure in their work activities must have a signed Read and Acknowledgement Statement (R&A) in their training file.
- PAS supervisors and managers are responsible for training employees on the procedures in this SOP, implementing the SOP in the work area, and monitoring on-going adherence to the SOP the work area(s) they oversee.
- Local quality personnel are responsible for tracking the currency of the R&A on this SOP for employees at the locations they are assigned to and for notifying the department leaders of overdue assignments.
- All employees of PAS are responsible for following the procedures in this SOP. Unauthorized deviations or departures from this SOP are not allowed except with documented approval from the local Quality Manager and only when those deviations do not violate the Pace® Code of Ethics or Professional Conduct (COR-POL-0004) or associated policy and procedure(s). Hand-edits or manual change to the SOP are not permitted. If a change is desired or necessary, employees must follow the procedures for document revision specified in corporate SOPs ENV-SOP-CORQ-0015, *Document Management* and ENV-SOP-CORQ-0016, *SOP for Creation of SOP and SWI*.
- Local quality personnel are responsible for monitoring conformity to this SOP during routine internal audits of work areas that utilize this SOP and for communicating gaps and deviations found during monitoring to the work area supervisor, who is responsible for correction of the situation.

16.0 ATTACHMENTS

- Appendix A: Routine Analyte List and LOQ
- Appendix B: QC Summary & Corrective Action Table

17.0 REFERENCES

- ENV-SOP-CORQ-0006, *Manual Integration*, current version.
- ENV-SOP-CORQ-0011, *Method Validation*, current version.
- ENV-SOP-CORQ-0015, *Document Management*, current version.
- ENV-SOP-CORQ-0016, *SOP for SOP and SWI,* current version.
- ENV-TMP-CORQ-0007, *Quality Manual Template*, current version.
- COR-POL-0004, *Code of Ethics and Professional Conduct*, current version.
- COR-MAN-001, *Pace® Safety Manua*l, current version.
- Standard Methods for the Examination of Water and Wastewater, Online Edition, 4500-CN- A, B, C, E, G, and I (1999, 2011, & 2016).
- EPA Test Methods for Evaluating Solid Waste. SW-846, Third Edition, Update IV, 2/2007, Methods 9010B and 9012A/B.
- MICRO-DIST™ Operation and Applications Manual, Lachat instruments, Part No. 01304, Revised May 2002, Method Cyanide-1.

18.0 REVISION HISTORY

Authorship

Primary Author[1]	Job Title	Date Complete
Lenzie Boring	Inorganics Manager	11/22/2022

[1]The primary author is the individual / role responsible for the content of this SOP. Send questions or suggestions for content to the primary author. See the Quality Manager for questions or concerns related to implementation of this SOP.

Revisions Made from Prior Version

Section	Description of Change
Various	Updated to new SOP template format and language
7.2	Updated Supplies needed for the Cyanide analysis
8.1	Updated Standards to reflect ISO certified standards
8.3.1	Added work solutions used at bench
8.3.3	Added the MDL check reagent
9.1.2	Added better operating conditions and maintenance for the SEAL
9.4	Amenable prep steps added more instructions and other minor edits

Document Succession: This version replaces the following documents:

Document Number & Version	Document Title	Effective Date:
ENV-SOP-LENE-0007 v02	Cyanide	11/30/2020

Appendix A: Target Analyte List and LOQ

Table 1: Standard Analyte List and LOQ

Analyte	CAS #	LOQ[1] Aqueous (mg/L)	LOQ[1] Solid (mg/Kg)
Cyanide (Total, WAD, and Amenable)		**0.005**	**0.015**

[1] Values as of effective date of this SOP. LOQ are subject to change, contact quality personnel for most current information.

Appendix B: QC Summary and Corrective Action Table

QC Item	Frequency	Acceptance Criteria	Corrective Action	Qualification
ICAL	At instrument set up, after CCV failure	r ≥ 0.005 Curve must also pass RSE test at the low and midpoint calibration standard.	Identify and correct source of problem, repeat	None. Do not proceed with analysis
ICV	After Each ICAL	All analytes must be within ± 10 % of the true value. (%R)	Identify source of problem, re-analyze. If repeat failure, repeat ICAL. Analysis may proceed if it can be demonstrated that the ICV exceedance has no impact on analytical measurements. For example, the ICV %R is high, CCV is within criteria, and the analyte is not detected in sample(s).	Qualify analytes with ICV out of criteria.
CCV	Daily, before sample analysis, after every 10, and at end of analytical window.	Opening CCV: All analytes within ± 10 %D Ending CCV: All analytes within ± 10 %D	See Section 12 for required corrective actions based on circumstance.	Qualify analytes with CCV out of criteria.
Method Blank	Matrix-specific; reagent water or inert material such as glass beads or Ottawa sand for soils. One per batch of up to 20 samples	Result should be less than the reporting limit. If results are reported to MDL, the MB must be evaluated to the MDL.	1) Re-analyze blank to confirm failure. 2) Qualify results and / or reanalyze associated samples.	Exceptions: 1) If sample ND, report sample without qualification 2) If sample result >10x MB report sample with appropriate qualifier indicating blank contamination. 3) If sample result <10x MB and sample cannot be reanalyzed report sample with appropriate qualifier to indicate an estimated value. Client should be alerted of this condition.

QC Item	Frequency	Acceptance Criteria	Corrective Action	Qualification
LCS	Matrix-specific; reagent water or inert material such as glass beads or Ottawa sand for soils. One per batch of up to 20 samples	Lab generated	1) Reanalyze the LCS to confirm failure 2) Re-prep and reanalyze associated samples. 3) If problem persists, check spike solution	Exceptions: 1) If LCS > QC limits and these compounds are non-detect in the associated samples, the sample data may be reported with appropriate data qualifiers. 2) If LCS < QC limits and sample cannot be reanalyzed report sample with appropriate qualifier to indicate an estimated value. Client should be alerted to this condition.
MS	One per batch of up to 20 samples.	Lab generated	No corrective actions necessary. If LCS recovery is in range, the system is considered valid and the out-of-control MS/MSDs are footnoted appropriately by the analyst.	
Sample Duplicate	One per batch of up to 20 samples.	Lab generated	No corrective actions necessary. Report outliers with comment.	
ICB	Immediately after each Initial Calibration Verification Standard	Result should be less than the reporting limit. If sample results are reported to MDL, the ICB must be evaluated to the MDL.	May be reanalyzed once. A second failure confirms and requires corrective action (e.g. re-preparation of standard(s) and/or recalibration)	Exceptions: If sample results are reported to MDL and ICB is <RL but >MDL, then corrective action is not necessary other than appropriately qualifying the sample results. Unless the customer's QAPP or technical specification instruct to do otherwise. Samples that are <RL may be reported without qualification. (Not applicable to samples reporting down to MDL) Samples >10x ICB may be reported with appropriate qualification.

QC Item	Frequency	Acceptance Criteria	Corrective Action	Qualification
CCB	Immediately after each Continuing Calibration Verification Standard	Result should be less than the reporting limit. If sample results are reported to MDL, the ICB must be evaluated to the MDL.	May be reanalyzed once. A second failure confirms and requires corrective action	Exceptions: If sample results are reported to MDL and ICB is <RL but >MDL, then corrective action is not necessary other than appropriately qualifying the sample results. Unless the customer's QAPP or technical specification instruct to do otherwise. Samples that are <RL may be reported without qualification. (Not applicable to samples reporting down to MDL) Samples >10x CCB may be reported with appropriate qualification.

1.0 SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the laboratory procedure for the determination of sulfide in water samples by colorimetry by SM 4500 S2 D - 2000.

1.1 Target Analyte List and Limits of Quantitation (LOQ)

The target analytes and the normal LOQ that can be achieved with this procedure is 0.05 mg/L.

2.0 SUMMARY OF METHOD

Sulfide reacts with N,N-dimethyl-p-phenylenediamine in the presence of ferric chloride to produce methylene blue, a dye whose absorbance is measured at wavelength maximum of 664 nm using a spectrophotometer.

3.0 INTERFERENCES

The sample must be collected with minimum aeration. Sulfide may be volatilized by aeration and any oxygen inadvertently added to the sample may convert the sulfide to an immeasurable form. Dissolved oxygen should not be present in any water used to dilute standards.

Color and turbidity may interfere with the observation of color or with the photometric readings.

Strong reducing agents interfere by preventing the formation of the blue color. Thiosulfate at concentrations of about 10 mg/L may retard color formation or completely prevent it. Sulfide itself prevents the reaction if its concentration is very high, in the range of several hundred milligrams per liter.

Ferrocyanide can interfere by producing a blue color similar to that of methylene blue.

4.0 DEFINITIONS

Refer to the Laboratory Quality Manual for a glossary of common lab terms and definitions.

5.0 HEALTH AND SAFETY

Contact your supervisor or local safety coordinator with questions or concerns regarding safety protocol or safe handling procedures for this procedure

The following sections provide general health and safety information about chemicals and materials that may be present in the laboratory.

- The toxicity or carcinogenicity of each chemical material used in the laboratory has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable.

- The laboratory maintains documentation of hazard assessments and OSHA regulations regarding the safe handling of the chemicals specified in each method. Safety data sheets for all hazardous chemicals are available to all personnel. Employees must abide by the health, safety and environmental (EHS) policies and procedures specified in this SOP and in the Pace® Chemical Hygiene / Safety Manual (COR-MAN-0001)
- Personal protective equipment (PPE) such as safety glasses, gloves, and a laboratory coat must be worn in designated areas and while handling samples and chemical materials to protect against physical contact with samples that contain potentially hazardous chemicals and exposure to chemical materials used in the procedure.
- Concentrated corrosives present additional hazards and are damaging to skin and mucus membranes. For procedures that require use of acids, use acids in a fume hood whenever possible with PPE designed for handing these materials. If eye or skin contact occurs, flush with large volumes of water. When working with acids, always add acid to water to prevent violent reactions. For procedures that that emit large volumes of solvents (evaporation/concentration processes), these activities must be performed in a fume hood or apparatus that reduces exposure.

6.0 SAMPLE COLLECTION, PRESERVATION, HOLDING TIME, AND STORAGE

The laboratory provides containers for the collection of samples upon client request. Refer to laboratory SOP ENV-SOP-LENE-0107 for procedures related to preparation of bottle kits for the test method(s) associated with this SOP.

The laboratory performs samples collection for samples to be analyzed by this SOP in accordance with laboratory SOP ENV-SOP-LENE-0025. Refer to this SOP for these instructions.

General Requirements

Matrix	Routine Container	Minimum Sample Amount[1]	Preservation	Holding Time
Aqueous	Plastic or glass (250 or 500-mL)	10 mL	Thermal: ≤6°C Chemical: 1 mL 1N zinc acetate solution and 0.5 mL 50% NaOH.	Collection to Prep: 7 days Prep to Analysis: Immediate
Aqueous Dissolved*	Plastic or glass (250 or 500-mL)	10 mL	Thermal: ≤6°C Chemical: If containing Suspended Matter: Treat with AlCl3 in a 100 ml glass bottle add 0.2 ml of 6 N NaOH. Add 0.2 ml AlCl3. Stopper, mix and allow to flocculate. Let Settle and draw clear supernatant off. Preserve supernatant as above for Aqueous	Collection to Prep: 7 days Prep to Analysis: Immediate

[1]*Minimum amount needed for each discrete analysis.*

**Must be treated in the field.*

Thermal preservation is checked and recorded on receipt in accordance with laboratory SOP ENV-SOP-LENE-0021. Chemical preservation is checked and recorded at time of receipt or prior to sample preparation.

After receipt, samples are stored at ≤6°C until sample preparation. Prepared samples (extracts, digestates, distillates, other) are stored at ≤6C until sample analysis.

After analysis, samples are retained as stated in the Pace® standard terms and conditions, unless otherwise specified in the analytical services contract. Samples are then disposed of in accordance with Federal, State, and Local regulations.

7.0 EQUIPMENT AND SUPPLIES

7.1 Equipment

Equipment	Vendor	Model/Version	Description
UV-Visible spectrophotometer	Shimadzu	UV-1800	capable of reading absorbance at 664 nm
Centrifuge	International Equipment	0644319	or equivalent
Adjustable Pipettor	Eppendorf	various	or equivalent
Volumetric Flasks	10, 50,100-mL class A	Fisher	
Graduated Cylinder	10-mL, TD	Fisher / 08-553B/ Class A	
Magnetic Stirrer	N/A	Fisher / 14-259-265	or equivalent

7.2 Supplies

Item	Description	Vendor / Item # / Description
Stirbars	6 x 25mm, PTFE-coated	Fisher / 14-513-94
Centrifuge tubes	50-mL, graduated	Fisher / 06-443-19

8.0 REAGENTS AND STANDARDS

8.1 Reagents

Table 8.1

Reagent	Concentration/ Description	Requirements/ Vendor/ Item #
Reagent water	ASTM Type II	SOP ENV-SOP-LENE-0131 (latest revision)
6N NaOH	6N / 4L RICCA	Fisher / 7466-1

8.2 Standards

Table 8.2

Reagent	Concentration/ Description	Requirements/ Vendor/ Item #
Sulfide Reagent Set	Contains Sulfide Reagents #1 & #2	Hach / 2244500
Sulfide Standard Primary	Ampule 1000 mg/L	Absolute Standards / 54139
Sulfide Standard Secondary	Crystalline Reagent / Strem Chem.	Fisher / 50-901-13904

All reagents are stored in manufacturer recommended conditions. Hach Sulfide reagents used are USEPA approved for reporting wastewater analysis, equivalent to Standard Method 4500-S2-D.

8.3 Intermediate Sulfide Standards (Calibration)

Add 0.5 mL of Sulfide Standard to a 50-mL volumetric flask containing reagent water, dilute to the mark, and invert three times to mix. These standards are unstable and made daily.

8.4 Intermediate Sulfide Standards (Secondary Verification, Daily Linearity, Continuing Calibration)

Create a 1.25N NaOH solution by adding 10.41 mL 6N NaOH to 25 mL DI water in a 50mL volumetric flask and filling to the mark with DI. Dissolve 3.5g Sulfide Crystals in the NaOH solution. Transfer this solution to a 500 mL flask containing ~100 mL DI water. Fill to the mark and invert several times. This will yield a 10 ppm intermediate standard. Store in 2 mL amber vials with no headspace. Standard expires after 6 months or when daily linearity checks fail.

8.5 Working Sulfide Standards

Add varied aliquots of the intermediate calibration Sulfide Standard (see Table 10.2 below) to 10-mL volumetric flasks containing reagent water, dilute to the mark, invert three times to mix and transfer to individual centrifuge tubes. Working standards are made daily.

Table 8.3 – Working Calibration Standard Preparation

Standard	Intermediate Standard Amount (mL)	Final Solvent	Final Volume (mL)	Final Concentration (mg/L)
CAL0 / ICB / CCB	0	Water	10	0
CAL1	0.05	Water	10	0.05
CAL2	0.2	Water	10	0.2

Standard	Intermediate Standard Amount (mL)	Final Solvent	Final Volume (mL)	Final Concentration (mg/L)
CAL3 CCVB / CCV / LCS	0.5	Water	10	0.5
CAL4	.75	Water	10	0.8
CAL5 / CCVA	1.0	Water	10	1.0
ICV	0.5	Water	10	0.5

Add 0.5 mL of Sulfide Reagent #1 to each working standard, swirl to mix.

Add 0.5 mL of Sulfide Reagent #2 to each working standard. Cap the centrifuge tube and immediately invert to mix. The solution will turn pink initially and then turn blue if sulfide is present.

Wait five minutes and proceed to calibrate the instrument.

8.6 Second Source Verification (SSV/ICV/CCVA/CCVB/CCV) Standard

Add 0.5 mL of the working ICV sulfide standard to a 10-mL volumetric flask containing reagent water, dilute to the mark, invert three times to mix, and transfer to a centrifuge tube.

Add 0.5 mL of Sulfide Reagent #1 and swirl to mix.

Add 0.5 mL of Sulfide Reagent #2. Cap the centrifuge tube and immediately invert to mix. The solution will turn pink initially and then turn blue if sulfide is present.

Wait five minutes and proceed to verify the initial calibration.

9.0 PROCEDURE

9.1 Equipment Preparation

9.1.1 Support Equipment

Refer to Pace Analytical Services – Kansas SOP ENV-SOP-LENE-0030, Support Equipment, or equivalent replacement, for additional information on calibration requirements for support equipment that may be used in this procedure.

Balances are checked prior to use on each working day with NIST traceable references in the expected range of use, and the results are recorded in the logbook assigned to the balance.

9.1.2 Instrument

9.1.2.1 Routine Instrument Operating Conditions

Turn on the spectrophotometer. The spectrophotometer should be on at least one hour before analyzing standards or samples.

Open the Sulfide method on the UV-Visible spectrophotometer. Ensure the wavelength is set to 664 nm.

9.2 Initial Calibration

The calibration curve is prepared at approximate six month intervals or as needed. The curve is verified immediately by an ICV and ICB. Daily confirmation is provided by the analysis of a CCVA, CCVB, CCV's and CCB's.

Pour the 0 mg/L standard into two cuvettes, place them into the reference and sample cells and zero the baseline.

Individually read the remaining calibration standards in the sample cell, leaving the 0 mg/L standard in the reference cell, to establish the curve plotting absorbance versus concentration.

The correlation coefficient must be >0.995. Read back of the calibration standards is required. Using the curve parameters, enter the absorbance for each standard, calculate the observed concentration and record on the raw data.

Save the method as Sulfide mmddyy.

9.2.1 Calibration Sequence

Order	Sample ID	Concentration mg/L
1	CAL0	0.000
2	CAL1	0.050
3	CAL2	0.200
4	CAL3	0.500
5	CAL4	0.750
6	CAL5	1.000
7	ICV	0.500
8	ICB	0.00

9.2.2 ICAL Evaluation

9.2.2.1 Curve Fit

Calibration Curve Fit – The calibration curve is a representation of the relationship of the instrument response and analyte concentration. The curve is used to quantitate the concentration of an unknown based on its response and this known relationship.

Linear Regression – The linear regression calibration curve is derived from a least squares regression analysis of the calibration points. A calibration curve based on this technique will have the format of y = ax + b where "a" is the slope of the line and "b" is the y-intercept. Linear regression is not forced through the origin; therefore, there is a possibility that very low levels of contaminants below the response of the lowest calibration point may generate erroneous reportable results. A calculation of the correlation coefficient "r" is used to determine the acceptability of a linear regressed curve.

9.2.2.2 Relative Standard Error (RSE)

Initial calibrations using linear regression must be evaluated for their relative error using the following equation:

$$\% \text{ Relative Error} = \frac{\text{Calculated Value} - \text{True Value}}{\text{True Value}} \times 100$$

Back calculate the concentration of each calibration point in the calibration curve. The back-calculated and true concentrations should agree within ±10%. At the lower limit of the operational range, acceptance criteria are ±50%.

9.2.2.3 Initial Calibration Verification

In addition to meeting the linearity criteria, any new calibration curve must be assessed for accuracy in the values generated. This verification process is known as *Second Source Verification and it is performed using the standard referred to as the LCS*. Accuracy is a function of both the "fit" of the curve to the points used and the accuracy of the standards used to generate the calibration points. By meeting the fit criteria, the accuracy relative to the goodness of fit is addressed. However, because all calibration points are from the same source, it is possible that the calibration points may meet linearity criteria but not be accurately made in terms of their true value.

Prepare and analyze the ICV as specified in Section 8 immediately after the initial calibration.

To assess the accuracy relative to the purity of the standards, a single standard from a secondary source must be analyzed and the results obtained must be assessed relative to the known true value. This secondary source must be from an alternative vendor or, in the event an alternative vendor is not available, from a different lot from the same vendor. The accuracy of the standard is assessed as a percent difference from the true value according to the following equation:

$$\%\text{Difference} = \frac{(\text{Result}_{ICV} - \text{True Value}_{ICV})}{\text{True Value}_{ICV}}$$

9.2.3 Continuing Calibration Verification

As part of the analytical process, the instrumentation must be checked periodically to determine if the response has changed significantly since the initial calibration was established. This verification process is known as Continuing Calibration Verification (CCV). The validity of the initial calibration is checked after every ten samples and at the end of the analytical sequence by analyzing a midpoint calibration standard. The accuracy of the standard is assessed as percent drift from the true value according to the following equation:

$$\%\text{Drift} = \frac{(\text{Result}_{CCV} - \text{True Value}_{CCV})}{\text{True Value}_{CCV}}$$

9.2.4 High (CCVA) and Low (CCVB) Check Standards

If an ICAL is not analyzed the day of analysis, then the validity of the initial calibration should be checked by the analysis of both a high check standard and a low check standard.

The accuracy of the standard is assessed as percent drift from the true value according to the following equation:

$$\%\text{Drift} = \frac{(\text{Result}_{CHK} - \text{True Value}_{CHK})}{\text{True Value}_{CHK}}$$

9.3 Sample Preparation

9.3.1 Homogenization and Subsampling

Refer to SOP ENV-SOP-LENE-0135, Sample Homogenization and Sub-sampling as needed for complex samples.

9.4 Analysis

9.4.1 Example Analytical Sequence

Sample	Cup No.
CCVA	1
CCVB	2
CCB	3
MB (Method Blank)	4
LCS (Laboratory Control Sample)	5
MS	6
DUP (Sample Duplicate)	7
Client Sample ID	8
Client Sample ID	9
Client Sample ID	10
Client Sample ID	11
Client Sample ID	12
Client Sample ID	13
CCV	14
CCB	15
Client Sample ID	16
CCV1	17
CCB1	18
Repeat Sequence as needed with CCV/CCB every 10 samples	

9.5 Procedure

Ensure that the proper method is loaded in the spectrophotometer software.

Method Blank (MB) – Measure 10.0 mL of reagent water into a 50-mL centrifuge tube.

Laboratory Control Sample (LCS) - Measure 9.5 mL of reagent water into a 50-mL centrifuge tube and spike with 0.5 mL of the IntermediateSulfide Standard. This will yield a 0.5 mg/L concentration.

Matrix Spike (MS) - Randomly select a sample from the analytical batch for matrix spiking. Measure 10.0 mL of the selected sample into a 50-mL centrifuge tube and spike with 0.5 mL of the Stock Sulfide Standard. This will yield a 0.5 mg/L spike concentration.

Client Samples - Measure 10.0 mL of sample into a 50-mL centrifuge tube. The sample aliquot may be diluted first if the expected sulfide content is high. If the sample is high in sediment, do a dilution to prove the sample is not overloaded with sulfide.

Add 0.5 mL of Sulfide Reagent #1 to each QC and client sample, swirl to mix.

Add 0.5 mL of Sulfide Reagent #2 to each QC and client sample. Cap the centrifuge tube and immediately invert to mix. The solution will turn pink initially and then turn blue if sulfide is present.

Wait five minutes and proceed to analyze.

Dissolved sample procedure

Pour 20 mls of sample into a 50 ml centrifuge tube and centrifuge for 30 minutes.

Decant and volumetrically place 10 mls of sample into a centrifuge tube.

9.6 Data handling

Transfer the data file to S:WETCHEM/WETDATA/SULFIDE. Open Limslink and select the UV VIS SPEC method. After reviewing the data, post the data to EPIC PRO.

10.0 Data Analysis And Calculations

10.1 Quantitative Identification

This is a direct colorimetric procedure. See the Interferences section.

10.2 Calculations

See the Laboratory Quality Assurance Manual for equations for common calculations.

11.0 Quality Control and Method Performance

11.1 Quality Control

The following QC samples are prepared and analyzed with each batch of samples. Refer to Appendix B for acceptance criteria and required corrective action.

QC Item	Acronym	Frequency
Method Blank	MB	1 per batch of 20 or fewer samples. If batch exceeds, 20 samples, every 20.
Laboratory Control Sample	LCS	1 per batch of 20 or fewer samples. If batch exceeds, 20 samples, every 20.
Laboratory Control Sample Duplicate	LCSD	as requested by client
Matrix Spike	MS	1 per batch of 20 or fewer sample. If batch exceeds 20 samples, every 20
Sample Duplicate	SD	1 per batch of up to 20 samples

11.2 Instrument QC

The following Instrument QC checks are performed. Refer to Appendix B for acceptance criteria and required corrective action.

QC Item	Acronym	Frequency
Initial Calibration	ICAL	Approximately every 6 months or as needed
Initial Calibration Verification (Second Source)	ICV	Immediately after each initial calibration
Initial Calibration Blank	ICB	After each ICV, Low check or CCV
Continuing Calibration Verification	CCV	Every 10 samples and at the end of the sequence
Continuing Calibration Blank	CCB	Every 10 samples and at the end of the sequence
High Cal Check	CCVA	Daily prior to sample sunless initial calibration is run that day
Low Cal Check	CCVB	Daily prior to samples unless initial calibration is run that day

11.3 Method Performance

11.3.1 Method Validation

Refer to corporate SOP ENV-SOP-CORQ-0011 for general requirements and procedures for method validation.

Establish detection limits (DL) and limits of quantitation (LOQ) at initial method set up and verify the DL and LOQ on an on-going basis thereafter. Refer to corporate policy and/or SOP for DL and LOQ requirements and procedures.

12.0 Data Review And Corrective Action

12.1 Data Review

The data review process of Pace® Analytical Services includes a series of checks performed at different stages of the process by different people to ensure that SOPs were followed, the analytical record is complete, and properly documented, QC criteria were met, proper corrective actions were taken for QC failure and other nonconformance(s), and test results are reported with proper qualification, when necessary.

The review and checks that are performed by the employee performing the task is called primary review.

All data and test results are also peer reviewed.

This process, known as secondary review is performed to verify SOPs were followed, that calibration, instrument performance, and QC criteria were met and/or proper corrective actions were taken, qualitative ID and quantitative measurement is accurate, all manual integrations are justified and documented, and approved in accordance with the Pace® Analytical Services SOP for manual integration, calculations are correct, the analytical record is complete and traceable, and that results are properly qualified.

Lastly, a third-level review, called a completeness check, is performed by reporting or project management staff to verify the test report is complete.

Refer to laboratory SOP ENV-SOP-LENE-0088 for specific instructions and requirements for each step of the data review process.

12.2 Corrective Action

Corrective action is required when QC or sample results are not within acceptance criteria.

Refer to Appendix B for a complete summary of QC, acceptance criteria, and recommended corrective actions for QC associated with this test method.

If corrective action is not taken or was not successful, the decision/outcome must be documented in the analytical record. The primary analyst has primary responsibility for taking corrective action when QA/QC criteria are not met. Secondary data reviewers must verify that appropriate action was taken and/or that results reported with QC failure are properly qualified.

Corrective action is also required when carryover is suspected and when results are over range.

Samples analyzed after a high concentration sample must be checked for carryover and reanalyzed if carryover is suspected. Carryover is usually indicated by low concentration detects of the analyte in successive samples analyzed after the high concentration sample.

Sample results at concentrations above the upper limit of quantitation must be diluted and reanalyzed. The result in the diluted samples should be within the upper half of the calibration range. Results less than the mid-range of the calibration indicate the sample was over diluted and analysis should be repeated with a lower level of dilution. If dilution is not performed, any result reported above the upper range is considered a qualitative measurement and must be qualified as an estimated value.

13.0 Pollution Prevention And Waste Management

Pace® proactively seeks ways to minimize waste generated during work processes. Some examples of pollution prevention include but are not limited to reduced solvent extraction, solvent capture, use of reusable cycletainers for solvent management, and real-time purchasing.

The EPA requires that laboratory waste management practices comply with all applicable federal and state laws and regulations. Excess reagents, samples, and method process wastes are characterized and disposed of in an acceptable manner in accordance with the Pace® Chemical Hygiene Plan / Safety Manual. Refer to this manual for these procedures.

14.0 MODIFICATIONS

The procedures in this SOP have been modified from the reference test method as follows:

Modification	Test Method Procedure	Justification for Modification
The dissolved procedure in Section 9.14 above is a modified procedure used only when the client wants Dissolved Sulfide and does not flocculate in the field.		

When applicable, comparability and/or equivalency studies necessary to validate the modification as required per corporate SOP ENV-SOP-CORQ-0011 are retained by local quality personnel for historical reference.

15.0 RESPONSIBILITIES

- All PAS employees that perform any part this procedure in their work activities must have a signed Read and Acknowledgement Statement (R&A) in their training file.
- PAS supervisors and managers are responsible for training employees on the procedures in this SOP, implementing the SOP in the work area, and monitoring on-going adherence to the SOP the work area(s) they oversee.
- Local quality personnel are responsible for tracking the currency of the R&A on this SOP for employees at the locations they are assigned to and for notifying the department leaders of overdue assignments.
- All employees of PAS are responsible for following the procedures in this SOP. Unauthorized deviations or departures from this SOP are not allowed except with documented approval from the local Quality Manager and only when those deviations do not violate the Pace® Code of Ethics or Professional Conduct (COR-POL-0004) or associated policy and procedure(s). Hand-edits or manual change to the SOP are not permitted. If a change is desired or necessary, employees must follow the procedures for document revision specified in corporate SOPs ENV-SOP-CORQ-0015, *Document Managemen*t and ENV-SOP-CORQ-0016, *SOP for Creation of SOP and SWI*.
- Local quality personnel are responsible for monitoring conformity to this SOP during routine internal audits of work areas that utilize this SOP and for communicating gaps and deviations found during monitoring to the work area supervisor, who is responsible for correction of the situation.

16.0 ATTACHMENTS

- Appendix B: QC Summary & Corrective Action Table

17.0 REFERENCES

- ENV-SOP-CORQ-0006, *Manual Integration*, current version.
- ENV-SOP-CORQ-0011, *Method Validation*, current version.

- ENV-SOP-CORQ-0015, *Document Management*, current version.
- ENV-SOP-CORQ-0016, *SOP for SOP and SWI,* current version.
- ENV-TMP-CORQ-0007, *Quality Manual Template*, current version.
- COR-POL-0004, *Code of Ethics and Professional Conduct*, current version.
- COR-MAN-001, *Pace® Safety Manua*l, current version.
- Standard Methods for the Examination of Water and Wastewater, Method 4500-S^{2-} D (2000).
- Methylene Blue Method 8131, Edition 5, February 2008, DOC316.53.01136, Hach Company.

18.0 REVISION HISTORY

Authorship

Primary Author[1]	Job Title	Date Complete
Lenzie Boring	Inorganic Manager	10/18/2022

[1]The primary author is the individual / role responsible for the content of this SOP. Send questions or suggestions for content to the primary author. See the Quality Manager for questions or concerns related to implementation of this SOP.

Revisions Made from Prior Version

Section	Description of Change
Various	Updated to new SOP template language
8.2	Updated standard to be ISO 17034

Document Succession: This version replaces the following documents:

Document Number & Version	Document Title	Effective Date:
ENV-SOP-LENE-0109, v01	Sulfide by Methylene Blue	12/26/2019

Appendix B: QC Summary

QC Item	Frequency	Acceptance Criteria	Corrective Action	Qualification
ICAL	At instrument set up, after CCV failure	Must meet one of curve fit options presented in Section 9.0. Curve must also pass RSE test at the low and midpoint calibration standard. ± 10% of the true value. (%R). Low curve point must be within ± 50% of the true value. (%R)	Identify and correct source of problem, repeat	None. Do not proceed with analysis
ICV	After Each ICAL	All analytes must be within ± 10% of the true value. (%R)	Identify source of problem, re-analyze. If repeat failure, repeat ICAL. Analysis may proceed if it can be demonstrated that the ICV exceedance has no impact on analytical measurements. For example, the ICV %R is high, CCV is within criteria, and the analyte is not detected in sample(s).	Qualify analytes with ICV out of criteria if results are not affected (high bias ICV and ND results)
CCV	Daily, before sample analysis, after every 10, and at end of analytical window.	Opening CCV: All analytes within ± 10 %D Ending CCV: ± 10 D	If the requirements for continuing calibration are not met, corrective actions must be taken prior to reanalysis of standards. Only two analyses of the same standard are permitted back to back.	Qualify analytes with CCV out of of criteria.
Method Blank	Reagent water, 1 per batch of up to 20 samples	≤ RL	1) Re-analyze blank to confirm failure. 2) Qualify results and / or re-analyze associated samples. ***Exceptions:*** If sample ND, report sample without qualification	Qualify results and / or re-analyze associated samples
LCS	Reagent water spiked with sulfide standard, 1 per batch of up to 20 samples	80-120% Recovery	1) Reanalyze the LCS to verify failure 2) If problem persists, check spike solution ***Exceptions:*** 1) If LCS rec > QC limits and these compounds are non-detect in the associated samples, the sample data may be reported with appropriate data qualifiers.	If LCS rec > QC limits and these compounds are non-detect in the associated samples, the sample data may be reported with appropriate data qualifiers.

QC Item	Frequency	Acceptance Criteria	Corrective Action	Qualification
MS/MSD	1 per batch of up to 20 samples	75-125% Recovery	Report with Qualifier on the sample failing	As required
Sample Duplicate	1 per batch of up to 20 samples	20% RPD	Report with Qualifier on the sample failing	As required
Equipment Blank	Used if treated in the field	< RL	Report with Qualifier on the sample failing	As required
Low CCV, High CCV	Daily prior to samples unless initial calibration is run that day	90-110%	If not met, remake standard and recalibrate as needed	None
ICB	After each ICV	< RL	1) Re-analyze blank to confirm failure. 2) Qualify results and / or re-analyze associated samples. ***Exceptions:*** If sample ND, report sample without qualification	Qualify results and / or re-analyze associated samples
CCB	After each Low/High check or CCV	<RL	3) Re-analyze blank to confirm failure. 4) Qualify results and / or re-analyze associated samples. ***Exceptions:*** If sample ND, report sample without qualification	Qualify results and / or re-analyze associated samples

Document Information

Document Number: ENV-SOP-LENE-0016 **Revision:** 02

Document Title: Ammonia, Nitrogen by 350.1

Department(s): Wet Chemistry

Date Information

Effective Date: 10 Nov 2021

Notes

Document Notes:

All Dates and Times are listed in: Central Time Zone

Signature Manifest

Document Number: ENV-SOP-LENE-0016 **Revision:** 02

Title: Ammonia, Nitrogen by 350.1

All dates and times are in Central Time Zone.

ENV-SOP-LENE-0016 (Ammonia by 350.1)

QM Approval

Name/Signature	Title	Date	Meaning/Reason
Kenneth Busch (991414)	Manager - Quality	21 Oct 2021, 03:47:46 PM	Approved

Management Approval

Name/Signature	Title	Date	Meaning/Reason
Kenneth Busch (991414)	Manager - Quality	21 Oct 2021, 03:48:01 PM	Approved
Charles Girgin (002243)	General Manager 2	22 Oct 2021, 10:07:51 AM	Approved
Joshua Cunningham (003261)	Manager	10 Nov 2021, 02:11:11 PM	Approved

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TEST METHOD STANDARD OPERATING PROCEDURE
TITLE: Determination of Ammonia Nitrogen in Liquids and Solids
TEST METHOD EPA 350.1
ISSUER: Pace ENV – Lenexa Quality – LENE

1.0 SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the laboratory procedure for the determination of Ammonia by flow injection analysis.

1.1 Target Analyte List and Limits of Quantitation (LOQ)

Table 1: Routine Analyte List and Limits of Quantitation (LOQ)[1]

Analyte	Water (mg/L)	Soil (mg/kg)
Ammonia	0.1	20

[1] Values in place as of effective date of this SOP. LOQ are subject to change. For the most up to date LOQ, refer to the LIMS or contact the laboratory.

LOQ are established in accordance with Pace policy and SOPs for method validation and for the determination of detection limits (DL) and quantitation limits (LOQ). DL and LOQ are routinely verified and updated when needed. The current LOQ for each target analyte that can be determined by this SOP as of the effective date of this SOP is provided in Table 1.

The reporting limit (RL) is the value to which analytes are reported as detected or not detected in the final report. When the RL is less than the lower limit of quantitation (LLOQ), all detects and non-detects at the RL are qualitative. The LLOQ is the lowest point of the calibration curve used for each target analyte.

DL, LOQ, and RL are always adjusted to account for actual amounts used and for dilution.

2.0 SUMMARY OF METHOD

Ammonia reacts with alkaline phenol and hypochlorite to form a blue dye. Sodium nitroferricyanide is added to intensify the color. The intensity of the color, measured at 630 nm, is proportional to the ammonia concentration. The method is performed using the Lachat QuickChem 8500 Automated Flow Injection Analyzer.

Ammonium is separated from the sample matrix by gas diffusion. The sample is mixed with an alkaline solution and ammonia diffuses across a hydrophobic semi-permeable membrane into an acceptor solution. The acceptor solution is heated with salicylate hypochlorite in an alkaline phosphate buffer producing an emerald, green color which is directly proportional to the ammonia concentration in the sample. Absorbance is measured at 660nm.

3.0 INTERFERENCES

3.1 Calcium and magnesium may precipitate. Add EDTA to prevent this.

3.2 Turbidity is an interference. Samples must be aqueous and free of suspended matter. Ammonia is very soluble; samples may be pre-treated by centrifuging or filtering to remove solids prior to analysis.

3.3 Color may interfere. Correct for color by running the sample through the manifold without color formation.

3.4 Cyanate will hydrolyze to some extent even at pH 9.5. Distill the sample.

3.5 Residual chlorine can produce a negative interference by limiting reduction efficiency. Before analysis, check samples for chlorine and, if required, treat with sodium thiosulfate. This is not applicable to surface water, ground water or influent samples.

3.6 The system can be easily contaminated by ambient Ammonia. Blank water must be freshly prepared, and all glassware must be freshly rinsed.

3.7 Cover carrier, acceptor, and wash solutions with laboratory film to prevent contamination by ambient ammonia.

3.8 Placing an uncovered, stirred beaker containing a dilute solution of H_2SO_4 in the vicinity of the auto-sampler can aid in reducing contamination by ambient ammonia as well, by acting as an ammonia sink.

3.9 Lauryl sulfate and detergents can cause low ammonia recoveries by wetting the gas diffusion membrane.

3.10 Oil and grease will cause low ammonia recoveries by wetting the gas diffusion membrane.

4.0 DEFINITIONS

Refer to the Laboratory Quality Manual for a glossary of common lab terms and definitions.

5.0 HEALTH AND SAFETY

The toxicity or carcinogenicity of each chemical material used in the laboratory has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable.

The laboratory maintains documentation of hazard assessments and OSHA regulations regarding the safe handling of the chemicals specified in each method. Safety data sheets for all hazardous chemicals are available to all personnel. Employees must abide by the health, safety and environmental (HSE) policies and procedures specified in this SOP and in the Pace Chemical Hygiene / Safety Manual.

Personal protective equipment (PPE) such as safety glasses, gloves, and a laboratory coat must be worn in designated areas and while handling samples and chemical materials to protect against physical contact with samples that contain potentially hazardous chemicals and exposure to chemical materials used in the procedure.

Concentrated corrosives present additional hazards and are damaging to skin and mucus membranes. Use these acids in a fume hood whenever possible with additional PPE designed for handing these materials. If eye or skin contact occurs, flush with large volumes of water. When working with acids, always add acid to water to prevent violent reactions. Any processes that emit large volumes of solvents (evaporation/concentration processes) must be in a hood or apparatus that prevents employee exposure.

Contact your supervisor or local HSE coordinator with questions or concerns regarding safety protocol or safe handling procedures for this procedure.

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6.0 SAMPLE COLLECTION, PRESERVATION, HOLDING TIME, AND STORAGE

Samples should be collected in accordance with a sampling plan and procedures appropriate to achieve the regulatory, scientific, and data quality objectives for the project.

The laboratory does not perform sample collection or field measurements for this test method. To assure sample collection and field checks and treatment are performed in accordance with applicable regulations Pace project managers will inform the client of these requirements at the time of request for analytical services when the request for testing is received prior to sample collection. If samples were already collected, the laboratory will record any nonconformance to these requirements in the laboratory's sample receipt record when sufficient information about sample collection is provided with the samples.

The laboratory will provide containers for the collection of samples upon client request for analytical services. Bottle kits are prepared in accordance with laboratory SOP ENV-SOP-LENE-0025, *Assembly of Sample Container Kits*. For this test method, immediately after sample collection, samples should be checked for X and X and field treated. The bottle kits provided by the laboratory should include field test kits and treatment reagent.

Requirements for container type, preservation, and field quality control (QC) for the common list of test methods offered by Pace are included in the laboratory's quality manual.

General Requirements

Matrix	Routine Container	Minimum Sample Amount[1]	Preservation	Holding Time
Aqueous	Plastic 250mL	150 mL	Thermal: ≤6°C Chemical: H2SO4; pH <2	Collection to Analysis: 28 days
Solid	4-oz glass jar	15g	Thermal: ≤6°C Chemical: None	Collection to Analysis: 28 days

[1]*Minimum amount needed for each discrete analysis.*

Field / Matrix QC

Trip Blank	Equipment Blank	MS/MSD	Field Duplicate
N/A	N/A	N/A	N/A

Thermal preservation is checked and recorded on receipt in the laboratory in accordance with laboratory SOP ENV-SOP-LENE-0021, *Sample Management*. Chemical preservation is checked and recorded at time of receipt or prior to sample preparation.

After receipt, samples are stored at ≤6°C until sample preparation. Prepared samples (extracts, digestates, distillates, other) are stored at ≤6°C until sample analysis.

After analysis, unless otherwise specified in the analytical services contract, samples are retained for 30 days from date of final report and then disposed of in accordance with Federal, State, and Local regulations.

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7.0 EQUIPMENT AND SUPPLIES

7.1 Gas Diffusion

7.1.1 Equipment

Equipment	Description	Vendor/ Item # / Description
Flow Injection Analyzer	Lachat QuickChem 8500 Automated Flow Injection Analyzer	Lachat QuickChem 8500 Automated Flow Injection Analyzer
Autosampler		Lachat or equivalent
Horizon	Data reporting software	See master list of current version

7.1.2 Supplies

Supply	Description	Vendor/ Item # / Description
Interference Filter	660 nm	Lachat or equivalent
Sample Loop	80 cm, used with manually prepared, individual calibration curve standards	Lachat or equivalent
Data System Parameters	Attachment VI	
Manifold Diagram	Attachment VII	
Two-Stop PVC pump tubing	Red/Red carrier (ID 1.143mm)	Hach Part No. 53410 or equivalent
Two-Stop PVC pump tubing	Red/Red Alkaline Donor (ID 1.143mm)	Hach Part No. 53410 or equivalent
Two-Stop PVC pump tubing	Grey/Grey Ammonia Acceptor (ID 1.295mm)	Hach Part No. 53411 or equivalent
Two-Stop PVC pump tubing	Black/Black Buffer (ID 0.762mm)	Hach Part No. 53407or equivalent
Two-Stop PVC pump tubing	White/White Salicylate (ID 1.016mm)	Hach Part No. 53409 or equivalent
Two-Stop PVC pump tubing	Orange/Orange DCIC (ID 0.889mm)	Hach Part No. 53408 or equivalent
Two-Stop PVC pump tubing	Green/Green (ID 1.85mm)	Hach Part No. 53414 or equivalent
Two-Stop PVC pump tubing	Purple/Purple (ID 2.057mm)	Hach Part No. 53415 or equivalent
Environmental Express	Syringe Filter 0.45um	SF045E

7.1.3 Miscellaneous Supplies

Supply	Vendor	Model / Version	Comments
Analytical balance	Mettler-Toledo	AE240	Or equivalent
Volumetric flasks	Fisher	Class A	1-L, 500- and 100-mL
Centrifuge tubes	Fisher	06-443-19	50-mL
Hach gas diffusion board	Hach	10-107-06-5-J	
10 mL Eppendorf Pipette	Fisher	05-403-116	1mL-10mL pipette/ or equivalent
1 mL Eppendorf Pipette	Fisher	13-690-032	0.1mL-1mL pipette/ or equivalent

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8.0 REAGENTS AND STANDARDS

8.1 Reagents and Standards

8.1.1 Reagents

Reagent	Concentration/ Description	Requirements/ Vendor/ Item #	Expiration Date
Dechlorinating reagent, Sodium Thiosulfate	Dissolve 3.5g $Na_2S_2O_3 \cdot 5H_2O$ in reagent water and dilute to 1L. One mL of this solution will remove 1 mg/L of residual chlorine in 500mL of sample.	Alfa Aesar 10102-17-7*	Remake daily
Dilution Water, Type I Water From Cation/Anion System	Use fresh water from the Cation/Anion system.	Barnstead Nanopure II	NA
Reagent 1: Alkaline Donor	To a 1 L volumetric flask, add ~800 mL DI water and 30.0 g Na_2EDTA. Mix with a magnetic stirrer and add 12.4 g Boric Acid, 40 g NaOH while mixing. Dilute to 1 L with DI water.	EDTA-Fisher S311-500* Boric Acid-Fisher A74-500* NaOH-Acros 44728-0050*	1 month
Reagent 2: Buffer	In a 2 L volumetric flask containing 1 L of DIW, dissolve 30.0 g NaOH, 25.0 g Na_2-EDTA, 67 g sodium phosphate dibasicheptahydrate ($Na_2HPO_4.7H_20$). Dilute to 2L with DI, invert 3 times	NaOH-Acros 44728-0050* $Na_2HPO_4.7H_20$-Fisher S373-500*	1 month
Reagent 3: Salicylate-Nitroprusside Color	In a 1 L volumetric flask, dissolve 350g sodium salicylate and3.5g sodium nitroprusside. Dilute to 1 L with DI water.	Sodium Salicylate-Fisher S395-500* Sodium Nitroprusside-Acros 424361000*	1 week , or if solution turns blue
Reagent 4: DCIC (Hypochlorite generator)	In a 500 mL volumetric flask, dissolve 2.5 g NaOH and 2.5g Sodium Dichloroisocyanurate Dihydrate CAS#51580-86-0. Dilute to 500mL.	NaOH-Fisher S318-5* Sodium Dichloroisocyanurate Dihydrate-Acros 436452500*	Remake daily
Reagent 5: Carrier and Diluent for Preserved Samples	In a 2 L volumetric flask containing 1 L of DI water, dilute 4 mL concentrated H_2SO_4 to the mark with DI water.	Fisher A300-212*	1 month

*= or equivalent

8.1.2 Standards

Standard	Concentration/ Description	Requirements/ Vendor/ Item #
Stock Ammonia Calibration Standard, 1000 mg/L	NIST/ISO 17035 certified standard, 1000 mg/L	Absolute Standards/ 54113 or equivalent
Stock Ammonia ICV/Second Source Standard, 1000 mg/L	NIST/ISO 17035 certified standard, 1000 mg/L	Spex / AS-NH3N9-2Y or equivalent
Intermediate Ammonia ICAL Standard, 100 mg/L	5 mL of Stock ICAL standard into 50 mL final volume using NH3 Carrier Reagent	Used for Calibration Standards
Intermediate Ammonia ICV Standard, 250 mg/L	12.5 mL of Stock ICV standard into 50 mL final volume using NH3 Carrier Reagent	Used for ICV/LCS/MS

8.1.3 Calibration Standards for Gas Diffusion

Standard	Volume of Intermediate CalibrationStandard, able 8.1.2	Volume of Solvent Reagent 5 (NH3 Carrier)Table 8.1.1	Final Total Volume	Final Concentration
Cal 0/ICB/CCB	0.00 mL	50mL	50 mL	0.00 mg/L
Cal 1	0.05 mL	49.95 mL	50mL	0.10 mg/L
Cal 2	0.125 mL	49.875 mL	50mL	0.25 mg/L
Cal 3	0.25 mL	49.75 mL	50 mL	0.50 mg/L
Cal 4	0.50 mL	49.50mL	50 mL	1.00 mg/L
Cal 5	1.25 mL	48.75 mL	50 mL	2.50 mg/L
Cal 6	2.50 mL	47.50 mL	50 mL	5.00 mg/L
Cal 7 / CCV	5.00 mL	45.00 mL	50 mL	10.00 mg/L
Cal 8	10.00 mL	40 mL	50 mL	20.00 mg/L
LCS	1mL ICV intermediate	49.00 mL	50 mL	5.00 mg/L

9.0 PROCEDURE

9.1 Equipment Preparation

9.1.1 Support Equipment:

9.1.1.1 Balance: Verify balance each day of use.

9.1.2 Instrument

9.1.2.1 Routine Instrument Operating Conditions: Prior to analysis, allow at least 20 minutes for the instrument heating block to warm up to 60°C. Place all reagent and sample feed lines in DI H_2O, raise tension levers on peristaltic pump cassettes, and allow DI H_2O to flow through the system. Check for leaks and clogged lines prior to analysis.

9.1.3 Maintenance

Please refer to the instrument manuals for maintenance procedures performed by the lab.

All maintenance activities are listed daily in maintenance logs that are assigned to each separate instrument.

9.2 Initial Calibration

9.2.1 Calibration Design

Linear - Weighted Linear Regression (1st Order)

A weighting factor applied as compensation to a linear curve fit reduces the potential bias at lower calibration levels. Weighting the sum of the squares of the differences (weighted linear) may significantly improve the ability of the least squares regression to fit the model to the data, especially at the low end of the calibration curve.

9.2.2 Calibration Sequence

9.2.2.1 Gas Diffusion

Sequence	Standard	Concentration, mg/L
1	Cal 0	0
2	Cal 1	0.10
3	Cal 2	0.25
4	Cal 3	0.50
5	Cal 4	1.00
6	Cal 5	2.50
7	Cal 6	5.00
8	Cal 7	10.00
9	Cal 8	20.00
10	ICV	5.00
12	ICB	0
14	CCV	10.00
16	CCB	0

9.2.3 ICAL Evaluation

9.2.3.1 Curve Fit: r = 0.995.

9.2.3.2 **%Relative Error (%RE):** At the end of each calibration, the instrument calculates the actual concentration of Nitrogen, Ammonia, in mg/L, of each calibration standard. The results are summarized in table form (see example below, Det. Conc, mg/L column). The instrument will also display the correlation coefficient (r) after the calibration is complete. Assess the %RE for the lowest calibration level and the midpoint of the curve. For a calibration curve to be acceptable, both the low-level and mid-level %RE measures must meet acceptance criteria. The acceptance criteria for the %RE of the lowest calibration standard is 60% to 140% of the true value. The acceptance criteria for the %RE for the midpoint of the curve is 90% to 110% of the true value. Document the %RE assessment of each calibration curve on the data review checklist.

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Table : 1 (Ammonia)

	Known Conc. (mg N/L as NH3)	Rep.	Peak Area (V.s)	Peak Height (V)	% RSD	% Residual	Det. Conc (mg N/L as NH3)	Detection Date	Detection Time
1	20.0000	1	131.0345	4.6751	0.0	3.3	19.2948	8/2/2021	11:22:56 AM
2	10.0000	1	68.5358	2.5081	0.0	-1.0	10.0775	8/2/2021	11:21:17 AM
3	5.0000	1	36.3340	1.3442	0.0	-6.7	5.3284	8/2/2021	11:19:39 AM
4	2.5000	1	18.5162	0.6865	0.0	-8.1	2.7007	8/2/2021	11:18:00 AM
5	1.0000	1	7.3964	0.2804	0.0	-6.0	1.0607	8/2/2021	11:16:21 AM
6	0.5000	1	3.5743	0.1355	0.0	0.5	0.4971	8/2/2021	11:14:43 AM
7	0.2500	1	1.7292	0.0636	0.0	9.0	0.2249	8/2/2021	11:13:05 AM
8	0.1000	1	0.8558	0.0312	0.0	3.2	0.0961	8/2/2021	11:11:27 AM
9	0.0000	1	0.1807	0.0061			-0.0034	8/2/2021	11:09:50 AM

9.2.3.3 For a standard curve to be acceptable, the correlation coefficient criteria must be met, and both the low-level and mid-level %RE measures must meet acceptance criteria.

9.2.3.4 **Initial Calibration Verification:** Must be within 90 to 110% of the True Value.

9.2.3.5 **Continuing Calibration Verification:** Must be within 90 to 110% of the True Value**.**

9.2.4 Calibration or Linearity Problems

9.2.4.1 The lowest and/or highest level calibration standards may be removed from the calibration as long as the remaining number of concentration levels meets the minimum established by the method and standard operating procedure. For multi-parameter methods, this may be done on an individual analyte basis. The reporting limit must be adjusted to the lowest concentration remaining in the calibration curve and the upper limit of quantitation must be adjusted to the highest concentration remaining in the calibration curve.

9.3 Continuing Verification Problems

9.3.1 Reanalyze the original CCV standard to determine instrument consistency.

9.3.2 Prepare and analyze a new CCV standard to determine preparation consistency / standard integrity.

9.3.3 Document instrument maintenance

9.3.4 Reanalyze CCV standard to determine if maintenance was effective in restoring performance.

9.3.5 Complete recalibration of instrument.

9.3.6 If samples were analyzed in spite of verification failures, note the exceptions for addressing those results. Deviations from this requirement must be noted on the injection log with a thorough explanation for the deviation from policy.

9.4 Sample Preparation

9.4.1 Homogenization and Subsampling

9.4.1.1 **Liquids:** Invert samples gently to homogenize prior to poring a sample aliquot.

9.4.1.1.1 The water MB is Carrier/Diluent solution.

9.4.1.1.2 Use an aliquot of ICV solution as the LCS. The true value of the LCS is 5.0 mg NH_3-N/L.

9.4.1.1.3 Randomly select a sample from the analytical batch for matrix spiking. In a 50 mL volumetric, add 1 mL of the second source intermediate and bring to volume. Invert several times to mix. The true value of the spike added is 5.0 mg NH_3-N/L.

9.4.1.2 **Soils:** Homogenize sample prior to taking a sample aliquot. Do not selectively choose small or fine particles; the aliquot must be representative of the sample received. Transfer to a larger beaker or clean container to allow for adequate particle size reduction. See ENV-SOP-LENE-0042 (or equivalent replacement) for details.

9.4.1.2.1 Prepare the MB by measuring 5 g of glass beads plus 50 mL of the Carrier/Diluent and place into a 50-mL centrifuge tube.

9.4.1.2.2 Prepare the LCS by measuring 5 g of glass beads into a 50mL centrifuge tube. Spike with 1 mL of second source intermediate and add 49 mL Carrier/Diluent. This will yield a spike concentration of 50 mg NH_3-N/kg.

9.4.1.2.3 Weigh 5 g of the sample into a 50-mL centrifuge tube and add 50 mL of Carrier/Diluent solution. Less sample size may be used if the expected ammonia concentration is higher than the calibration curve.

9.4.1.2.4 Randomly select a sample from the analytical batch for matrix spiking. Weigh 5 g of the selected sample into a 50-mL centrifuge tube, spike with 1.0 mL of the second source intermediate solution and add 49 mL of Carrier/Diluent solution. The true value of the spike added is 50 mg NH_3-N/kg.

9.4.1.2.5 Place the centrifuge tubes on a shaker and shake for 20 minutes.

9.4.1.2.6 Remove from shaker and centrifuge for 10 minutes.

9.4.1.2.7 The supernatant liquid is now ready for analysis.

9.4.2 Gas Diffusion

9.4.2.1 Prepare reagents (Table 8.1.1) and standards (Table 8.1.2).

9.4.2.2 Check samples for chlorine. If necessary, dechlorinate with Sodium Thiosulfate.

9.4.2.3 Check for cloudy or dirty samples. Filter if necessary.

9.4.2.4 Prepare the calibration and QC as defined in 8.1.3, 8.1.4, 8.1.5.

9.4.2.5 Verify the calibration with an ICVA, ICVB, ICB, and CRDL.

9.4.2.6 Proceed with sample analysis on the Lachat Omnion software as per section 9.4.3.

9.5 Analysis **Lachat Operation Analysis**

9.5.1 For Gas Diffusion, refer to Attachments VI and VII to set up system parameters, manifold, and pump tubing.

9.5.2 Turn on power and select the ammonia method.

9.5.3 Answer "Yes" to the question "Do you want to change the set points or relevant heaters?" This will turn the heater on. The heater needs to reach 60ºC before the run can start.

9.5.4 Place all reagents, feed lines in DIW, raise tension levers on pump cassettes, and turn pump on.

9.5.5 Observe system for leaks and make adjustments as necessary.

9.5.6 Pump DIW through lines for ~5 minutes.

9.5.7 Populate your run sheet with samples and necessary QC.

9.5.8 Transfer the buffer feed line to the buffer and pump through the system for ~1 min.

9.5.9 Fill tubes with appropriate standards, samples, QC samples and place in specific positions as per the run sheet. After analyzing all samples, remove feed tubes from reagent bottles in the reverse numerical order and rinse with DIW. Let the buffer run for 5 minutes before putting in DI water to prevent clogs.

9.5.10 Pump DI water through the system for ≥5 minutes.

9.5.11 Remove the feed tubes from DI water and pump air through the system for ~5 minutes.

9.5.12 Release the tension levers on all pump cassettes.

9.5.13 Example Analytical Sequence

Sequence	Sample ID
1	CCV
2	CCB
3	LCS
4	MB
5	Sample 1
6	Sample 1 MS
7	Sample 1 MSD
8	Sample 2
9	Sample 3
10	Sample 4
11	Sample 5
12	Sample 6
13	CCV
14	CCB

10.0 DATA ANALYSIS AND CALCULATIONS

10.1 Calculations

See the Laboratory Quality Assurance Manual for equations for common calculations.

11.0 QUALITY CONTROL AND METHOD PERFORMANCE

11.1 Quality Control

The following QC samples are prepared and analyzed with each batch of samples. Refer to Appendix A for acceptance criteria and required corrective action.

QC Item	Frequency
Method Blank (MB)	1 per batch of 20 or fewer samples. If batch exceeds 20 samples, every 20.
Laboratory Control Sample (LCS)	1 per batch of 20 or fewer samples. If batch exceeds 20 samples, every 20.
Laboratory Control Sample Duplicate (LCSD)	As needed
Matrix Spike (MS)	1 per 10 samples
Matrix Spike Duplicate (MSD)	1 per 10 samples

11.1 Instrument QC

The following Instrument QC checks are performed. Refer to Appendix A for acceptance criteria and required corrective action.

QC Item	Frequency
Initial Calibration	Daily
Initial Calibration Verification	Once per calibration
Initial Calibration Blank	Once per calibration, after ICV
Continuing Calibration Verification	After initial calibration, after every 10 samples, and at the end of every analytical sequence.
Continuing Calibration Blank	After initial calibration, after every CCV.

11.2 Method Performance

11.2.1 Method Validation

11.2.1.1 Detection Limits

Detection limits (DL) and limits of quantitation (LOQ) are established at initial method setup and verified on an on-going basis thereafter. Refer to Pace ENV corporate SOP ENV-SOP-CORQ-0011 Method Validation and Instrument Verification.

11.3 Analyst Qualifications and Training

Employees that perform any step of this procedure must have a completed Read and Acknowledgment Statement for this version of the SOP in their training record. In addition, prior to unsupervised (independent) work on any client sample, analysts that prepare or analyze

samples must have successful initial demonstration of capability (IDOC) and must successfully demonstrate on-going proficiency on an annual basis. Successful means the initial and on-going DOC met criteria, documentation of the DOC is complete, and the DOC record is in the employee's training file. Refer to laboratory SOP ENV-SOP-LENE-0110, *Training Procedures*, for more information.

12.0 DATA REVIEW AND CORRECTIVE ACTION

12.1 Data Review

Pace's data review process includes a series of checks performed at different stages of the analytical process by different people to ensure that SOPs were followed, the analytical record is complete and properly documented, proper corrective actions were taken for QC failure and other nonconformance(s), and that test results are reported with proper qualification.

The review steps and checks that occur as employee's complete tasks and review their own work is called primary review.

All data and results are also reviewed by an experienced peer or supervisor. Secondary review is performed to verify SOPs were followed, that calibration, instrument performance, and QC criteria were met and/or proper corrective actions were taken, qualitative ID and quantitative measurement is accurate, all manual integrations are justified and documented in accordance with the Pace ENV's SOP for manual integration, calculations are correct, the analytical record is complete and traceable, and that results are properly qualified.

A third-level review, called a completeness check, is performed by reporting or project management staff to verify the data report is not missing information and project specifications were met.

Refer to laboratory SOP ENV-SOP-LENE-088, *Data Reduction, Review and Reporting*, for specific instructions and requirements for each step of the data review process.

12.2 Corrective Action

Corrective action is expected any time QC or sample results are not within acceptance criteria. If corrective action is not taken or was not successful, the decision/outcome must be documented in the analytical record. The primary analyst has primary responsibility for taking corrective action when QA/QC criteria are not met. Secondary data reviewers must verify that appropriate action was taken and/or that results reported with QC failure are properly qualified.

Corrective action is also required when carryover is suspected and when results are over range.

Samples analyzed after a high concentration sample must be checked for carryover and reanalyzed if carryover is suspected. Carryover is usually indicated by low concentration detects of the analyte in successive samples analyzed after the high concentration sample.

Sample results at concentrations above the upper limit of quantitation must be diluted and reanalyzed. The result in the diluted samples should be within the upper half of the calibration range. Results less than the mid-range of the calibration indicate the sample was over diluted and analysis should be repeated with a lower level of dilution. If dilution is not performed, any result

reported above the upper range is considered a qualitative measurement and must be qualified as an estimated value.

Refer to Appendix A for a complete summary of QC, acceptance criteria, and recommended corrective actions for QC associated with this test method.

13.0 POLLUTION PREVENTION AND WASTE MANAGEMENT

Pace proactively seeks ways to minimize waste generated during our work processes. Some examples of pollution prevention include but are not limited to: reduced solvent extraction, solvent capture, use of reusable cycletainers for solvent management, and real-time purchasing.

The EPA requires that laboratory waste management practice to be conducted consistent with all applicable federal and state laws and regulations. Excess reagents, samples and method process wastes must be characterized and disposed of in an acceptable manner in accordance with Pace's Chemical Hygiene Plan / Safety Manual.

14.0 MODIFICATIONS

A modification is a change to a reference test method made by the laboratory. For example, changes in stoichiometry, technology, quantitation ions, reagent or solvent volumes, reducing digestion or extraction times, instrument runtimes, etc. are all examples of modifications. Refer to Pace ENV corporate SOP ENV-SOP-CORQ-0011 *Method Validation and Instrument Verification* for the conditions under which the procedures in test method SOPs may be modified and for the procedure and document requirements.

14.1 The soil analysis procedure is a modification of EPA 350.1. Documentation supporting this modification is stored by the QA office.

14.2 The analysis of NH_3 by gas diffusion by Lachat QuikChem Method 10-107-06-5-J 2015 is a modification of EPA 350.1. This modification is supported by 40 CFR 136.6. Documentation supporting this modification is stored by the QA office.

15.0 RESPONSIBILITIES

Pace ENV employees that perform any part this procedure in their work activities must have a signed Read and Acknowledgement Statement in their training file for this version of the SOP. The employee is responsible for following the procedures in this SOP and handling temporary departures from this SOP in accordance with Pace's policy for temporary departure.

Pace supervisors/managers are responsible for training employees on the procedures in this SOP and monitoring the implementation of this SOP in their work area.

16.0 ATTACHMENTS

Appendix A: QC Summary

Attachment VI: System Parameters: Gas Diffusion

Attachment VII: Ammonia Manifold Diagram: Gas Diffusion

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17.0 REFERENCES

Pace Quality Assurance Manual- most current version.

TNI Standard, Management and Technical Requirements for Laboratories Performing Environmental Analyses, EL-V1-2009.

TNI Standard, Management and Technical Requirements for Laboratories Performing Environmental Analyses, EL-V1-2016-Rev.2.1.

U.S. Environmental Protection Agency, Methods for Determination of Inorganic Substances in Environmental Samples, EPA-600/R-93-100, August 1993, Method 350.1, Revision 2.

APHA Standard Methods for the Examination of Water and Wastes, Method 4500-NH3 H-97 online.

Lachat QuikChem Method 10-107-06-5-J "Determination of Ammonia by Flow Injection Analysis Gas Diffusion Separation Method Salicylate Method" Revision Date 16 January 2015.

18.0 REVISION HISTORY

This Version: ENV-SOP-LENE-0016; Rev 02

Section	Description of Change	Date
All	Converted to new template.	Aug 10, '21

This document supersedes the following document(s):

Document Number	Reason for Change	Date
KS-I-2302-E	Grammatical/Removal of outdated information.	May 9, 2001
KS-I-2302-F	Grammatical/Removal of outdated information.	July 9, 2003
KS-I-003-rev.6	Grammatical/Removal of outdated information.	September 14, 2005

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Document Number	Reason for Change	Date
S-KS-I-003-rev.7	Sec. 9.3: Changed volumetric pipettes to calibrated Eppendorf pippeters. Sec. 9.7: Removed degassing with Helium. Sec. 10: Reagents and Standards section – updated vendor and catalog number information. Sec. 10.8: Added calibration spiking soln. Preparation instructions and changed original 10.8 to 10.9. Sec. 10.10: Added instructions on preparation of ICB/CCB soln. Sec. 11.1: Removed Sec. 11.2: Changed wording from working stock solution to calibration spiking soln. Sec. 11.4: Changed wording on printing cal. Graph and procedure if cal. Curve fails. Sec. 11.5: added the word "half" to the phrase CCB must be less than half the PRL. Sec. 11.6: Added instructions on procedure if CCV/CCB set fail. Sec. 12.2.2: Changed wording from Calibration Working soln. To ICV Spiking soln. Sec. 12.4.1: Added SM reference to distillation section. Sec. 13.1-31: Revised QC content to be more specific.	November 8, 2007
S-KS-I-003-rev.8	SOP – Updated to corporate template format. Section 10 – Revised phenolate reagent. Section 11 – Revised for new instrument. Changed calibration point. Section 12 – Removed distillation. Changed spike volume for soil LCS. Section 13 – Added DOC procedure. Added second MS. Section 16 - Revised references	August 26, 2010
S-KS-I-003-rev.9	SOP - Updated to latest prescribed format. Section 14 – Revised water equation. Section 12 – Replaced reagent water with Carrier/Diluent, where appropriate. Section 18 – Inserted MDL procedure. Section 23 - Revised references. Attachment 1 – Inserted client-specific criteria.	February 5, 2013

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Document Number	Reason for Change	Date
S-KS-I-003-rev.10	Table 11.1 – Reworded some comments for clarity Section 18.2 – Revised MDL frequency to once every six months Section 19.2 – Added LCR verification by evaluation of co-relation coefficient	August 8, 2013
S-KS-I-003-rev.11	SOP - Updated to latest prescribed format. Added sections for Instrument/Equipment Maintenance and Troubleshooting. Table 10.2 – Revised for standards sourcing. Table 11.1 – Revised for corrective actions. Section 12.6 – Added LIMSLINK posting instructions. Table 13.1 – Revised for corrective actions. Section 18.2 – Changed MDL frequency to every 6 months. Section 19.2 – Added this section.	November 20, 2014
S-KS-I-003-rev.12	Section 1 – Added gaseous diffusion Section 2 – Added gaseous diffusion Section 6.4 – Added Section 7 – Revised to Solids Extraction/Analysis in 28 days Table 9.1 – Added gaseous diffusion board Table 10.2 – Added reagents Section 10 – Modified reagent recipes, modified calibration curve Section 11.2 – Allow linear weighted curve, added second order calibration Sections 12.2 to 12.4 – Modified recipes Section 25 – Added a reference to 40 CFR Part 136, Table 1B, Footnote 6	March 30, 2016
S-KS-I-003-rev.13	Section 10.7 – Error correction for secondary standard makeup (new final conc.). Section 10.8 – Correction to use 2.0 mL ICV intermediate instead of 5 mL Section 12.3.1 – Revised wording	May 13,2016
S-KS-I-003-rev.14	SOP – Revised cover page	May 30, 2018

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Document Number	Reason for Change	Date
ENV-SOP-LENE-0016-01	SOP – Removed cover page, TOC and headers Sections 10.3 – 10.6 – Added preparation frequency/expirations Sections 10.7 and 10.8 – Changed preparation formulas Section 12.6 – Revised Epic posting information Section 18.0 – Revised SOP references Section 23.0 – Revised SOP reference	July 18, 2019

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Appendix A: QC Summary

QC Item	Frequency	Acceptance Criteria	Corrective Action	Qualification
ICAL	At instrument set up, after CCV failure	Must meet the curve fit option presented in Section 9.0. r ≥ 0.995 (linear curve, Distilled) r ≥ 0.995 (second order curve, Gas Diffusion) The curve must also pass %RE criteria at the low and midpoint calibration standard.	Identify and correct source of problem, repeat	None. Do not proceed with analysis
ICV	Immediately after Each ICAL	Target analytes must be within ± 10% of the true value. (%Recovery 90 to 110%)	Identify source of problem, re-analyze. If repeat failure, repeat ICAL.	None. Do not proceed with analysis
ICB	After the ICV	The absolute value of target analytes must be less than the reporting limit. If results are reported to the MDL, target analytes in the blank should be non-detect. Per QAPP or client specific criteria, alternate criteria such as 1/2/RL evaluation may apply.	Identify source of problem, re-analyze. If repeat failure, repeat ICAL.	None. Do not proceed with analysis
CRDL	After the ICB and if specified by QAAP	Target analytes must be within 60 to 140% of True Value.	If not met, stop analysis. Review for preparation or calculation errors. Re-analyze one time. If CRDL passes, proceed with analysis. If CRDL still fails, terminate the analysis, correct the problem and recalibrate the instrument.	None. Do not proceed with analysis
CCV (Distilled), or CCVA, CCVB (Gas Diffusion)	Daily, before sample analysis, after every 10 samples, and at end of analytical window.	Target analytes must be within ± 10% of the true value. (%Recovery 90 to 110%)	If not met, stop analysis. Review for preparation or calculation errors. Re-analyze one time. If CCV passes, proceed with analysis. If CCV still fails, stop analysis and recalibrate instrument. Reanalyze all samples since the last passing CCV.	None. Do not proceed with analysis
CCB	analytical sequence, after every 10 samples and at the end of the analytical sequence (after every CCV)	The absolute value of target analytes must be less than the reporting limit. If results are reported to the MDL, target	Identify source of problem, re-analyze. If repeat failure, repeat ICAL.	None. Do not proceed with analysis

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QC Item	Frequency	Acceptance Criteria	Corrective Action	Qualification
		analytes in the blank should be non-detect. Per QAPP or client specific criteria, alternate criteria such as 1/2/RL evaluation may apply.		
Method Blank	One per batch of twenty samples	The absolute value of target analytes must be less than half the reporting limit. If results are reported to the MDL, target analytes in the blank should be non-detect. Per QAPP or client specific criteria, alternate criteria such as 1/2/RL evaluation may apply.	Reanalyze associated samples. ***Exceptions:*** If samples are ND, report samples without qualification; If sample result >10x MB detects, report the data as it is not impacted by the blank detections; If sample results are reported to the MDL and the method blank result >MDL but <RL, the data is qualified with appropriate qualifier unless individual tech specs differ. If sample result <10x MB detects and cannot be re-prepared or reanalyzed, report sample with appropriate qualifier to indicate an estimated value. Client must be alerted and authorize this condition.	B flag – Analyte detected in the associated Method Blank
LCS	One per batch of twenty samples	Liquids: Target analytes must be within ± 10% of the true value. (%Recovery 90 to 110%) Soils: Target analytes must be within ± 20% of the true value. (%Recovery 80 to 120%)	If LCS fails, investigate instrument performance, verify preparation and concentration. Analyze LCS one additional time. If LCS passes, proceed with analysis. If LCS still fails, stop analysis, perform instrument maintenance if needed, recalibrate instrument prior to proceeding with sample analysis.	None
MS/MSD	One per batch of ten samples	Percent Recovery: Liquids 90-110% R Soils 80-120% R Percent RPD: Liquids and Soils ≤ 10%	If outside the acceptance criteria, reanalyze. If problem persists, and MB and LCS are acceptable, MS may be reported with appropriate footnote indicating matrix interference (M1). If the added spike is greater than or equal to one-fourth of the sample result, the MS/MSD and associated parent sample must be reported with appropriate footnote (P6). For MN Admin contract clients – all MS/MSD failures require reanalysis of the MS/MSD and the original sample. If it is still out of control, investigate and	M1 – Matrix spike recovery exceeded QC limits. Batch accepted based on laboratory control sample (LCS) recovery. P6 – Matrix spike recovery was outside laboratory control limits due to a parent sample concentration notably higher

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QC Item	Frequency	Acceptance Criteria	Corrective Action	Qualification
			document the cause in the associated narrative as well as qualifying appropriately.	than the spike level.

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Attachment VI System Parameters: Gas Diffusion

DATA SYSTEM PARAMETERS FOR THE QUIKCHEM 8000/8500 FOR AMMONIA

The timing values listed below are approximate and will need to be optimized using graphical events programming.

Sample Throughput (high)	32 samples per hour, 110s/sample
Pump Speed:	35
Cycle Period High:	110s

Analyte Data:

Concentration Units:	mg N/L or µg N/L
Chemistry **High Range**:	Direct/Bipolar
Peak Base Width:	76.7s
Inject to Peak Start:	73.8s
Calibration Rep Handling:	Average
Calibration Fit Type:	2nd order Polynomial
Weighting Method:	1/x
Force through zero:	No

Sampler Timing:

Min. Probe in Wash Period:	6.5s
Probe in Sample Period:	34.5s

Valve Timing:

Time to Valve:	32.0s
Load Period	35.0s
Inject Period	75.0s

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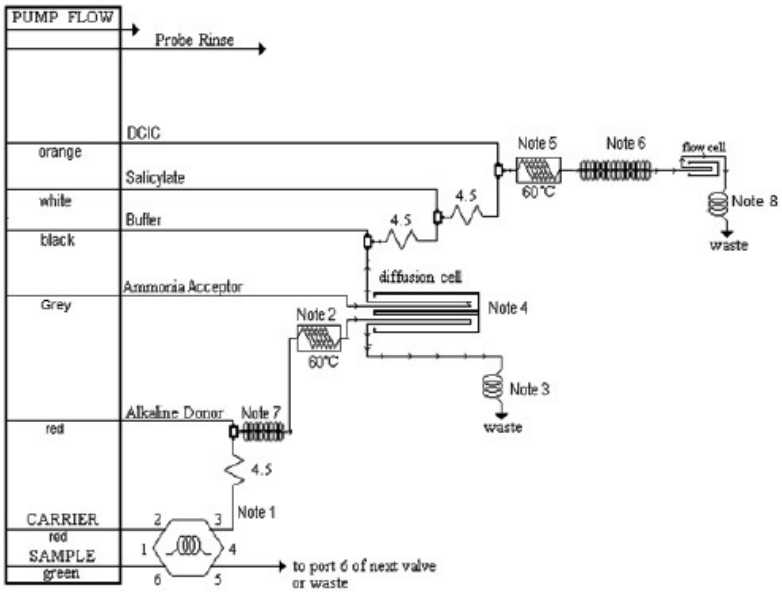
Attachment VII: Ammonia Manifold Diagram: Gas Diffusion

17.4. AMMONIA MANIFOLD DIAGRAM (REV. 2.0)



Carrier: **DI water for ammonia or Reagent 5 for TKN**
Acceptor: **DI water**
Manifold Tubing: **0.8 mm (0.032 in) i.d.** This is **5.2 µL/cm**.
8000/8500 Sample Loop: 350 cm Low Range Ammonia
80 cm High Range Ammonia and TKN
Interference Filter: 660 nm

Apparatus: An injection valve, a 10 mm path length flow cell, and a colorimetric detector module is required. The ⌇⌇⌇ shows 175 or 650 cm of tubing wrapped around the heater block at the specified temperature.

4.5: **70** cm of tubing on a 4.5 cm coil support
⌇⌇⌇ tubing wrapped in a figure 8 around 2, 7 or 22 cm coil supports (see below)

PVC PUMP TUBES MUST BE USED WITH THIS METHOD.

Note 1: 30 cm of manifold tubing is used to connect Port 3 to the first tee.
Note 2: 175 cm of tubing on the heater
Note 3 400 cm of 0.022" i.d. tubing backpressure loop, then to waste. **Waste container for the diffusion block should be on the bench with the instrument.** Placing this on the floor can lead to poor precision due to cavitation/vapor lock.
Note 4: Diffusion block with membrane PN 5033101-10 (Pack of 10 3.5 x 8.6 mm). Flow is **concurrent.** Be sure to place a membrane in the block before beginning. **Run**

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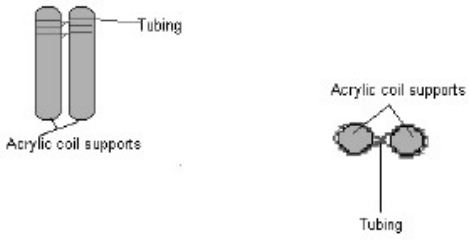
water in place of all reagents to be sure there are no leaks.

Note 5: 650 cm of tubing on the heater

Note 6: **510** cm of tubing wrapped in a figure 8 around 2, 22 cm coil supports

Note 7: **200** cm of tubing wrapped in a figure 8 around 2, 7 cm coil supports



Note 8: 50 cm of 0.022" i.d. tubing backpressure loop, then to waste

17.5 MANIFOLD ASSEMBLY - DIFFUSION CELL ASSEMBLY

From	To	Length
Carrier/Alkaline donor solution tee outlet from 175 cm section on heater	Inlet of the bottom half of the diffusion cell	10cm x 0.8 mm id
Outlet of the bottom half of the diffusion cell	Directly to the 400 cm backpressure loop, then to waste line	400 cm x 0.5 mm id
Ammonia Acceptor Reagent	Inlet of the top half of the diffusion cell	70 cm x 0.8 mm id
Outlet of the top half of the diffusion cell	Tee with buffer line	20 cm x 0.8 mm id

ISOTECH
a Stratum Reservoir brand
1308 Parkland Court
Champaign, IL 61821
P 217-398-3490
isotechlabs.com

δD (Hydrogen Isotope Analysis) and $\delta^{18}O$ (Oxygen Isotope Analysis) of H_2O

Equipment

3mL syringes
0.2 micron syringe filters
2mL glass vials with septum caps
Picarro CRDS (cavity ringdown spectrometer) model L1102-i fitted with a Leap autosampler

Method/Procedure Water samples are individually filtered into 2mL vials with 0.2 micron syringe filters. If samples are high salinity brines, they should be vacuum distilled prior to loading. The vials are then loaded onto trays which are installed on the autosampler. Samples are analyzed by the CRDS in replicate in accordance with the manufacturer's recommendation.

$\delta^{13}C$ (Carbon Isotope Analysis) of Dissolved Inorganic Carbon (DIC)

Equipment and Supplies

Thermo GasBench II
Thermo Delta V Plus
12mL Exetainer® with septum cap
Micro spin bar
1mL syringe
23G needle
85% Phosphoric acid
0.1N HCl

Method/Procedure The $\delta^{13}C$ of DIC is determined by injecting up to 1 ml of sample water into a helium flushed 12mL Exetainer® containing 0.1mL of 85% phosphoric acid and a magnetic spin bar. Sample size is determined based on alkalinity, which is measured by titration with 0.1N HCl.

The sample is stirred for a minimum of one hour and then allowed to equilibrate for 24 hours. At time of analysis the sample vials are placed in the GasBench tray. The CO_2 generated is flushed out of the vial via a two port needle. Water is removed by two nafion traps, and pure CO_2 is separated using a GC column. The CO_2/helium mixture then enters the mass spectrometer and is compared against a reference standard a total of six times.