Appendix C
Updated Standard Operating Procedures

The standard operating procedures (SOPs) included in this attachment are updates of those provided in Appendix E of the Pre-Design Investigation (PDI) quality assurance project plan (QAPP) (Windward and Anchor QEA 2022). Therefore, original numbering and lettering from that appendix have been retained to allow for direct comparison.

E7 (REVISED)	SOP for SVOC Analysis (ALS)
E10 (REVISED)	SOP for the Analysis of Dioxins/Furans (Cape Fear)
E12 (REVISED)	SOP for the Analysis of PAH-PCP Analysis (ALS)
E14 (REVISED)	SOP for the Analysis of Chlorinated Pesticides (ALS)
E27 (REVISED)	SOP for Sediment Thickness over Armored Banks: Hand Probe
E29 (NEW)	SOP for Diver Sediment Sampling and Precipitate Layer Coring (Gravity SOP SW-65)
E30 (NEW)	SOP for Understructure Vibracoring (Gravity SOP SW-34)
E31 (NEW)	SOP for Sediment-Water Shake Test
E32 (NEW)	SOP for Acute Fish Toxicity Testing (Spheros)
E33 (NEW)	SOP for TCLP testing (ARL)
E34 (NEW)	SOP for Isotherm Study (EGL)
E35 (NEW)	SOP for Laboratory XRF (EGL)
E36 (NEW)	SOP for Sequential Extraction of Arsenic in Sediment (EGL)
E37 (NEW)	SOP for Porewater Collection
E38 (NEW)	SOP for Seepage Measurements
E39 (NEW)	SOP for Conductivity (ARL)
E40 (NEW)	SOP for pH (ARL)
E41 (NEW)	SOP for Sulfide (ARL)
E42 (NEW)	SOP for Extraction of Sediment Porewater by Centrifugation (EGL)
E43 (NEW)	SOP for Synthetic Sediment Porewater Extraction (EGL)

Table C-1 presents an overview of the SOPs that have been included in the previous PDI QAPP or QAPP Addenda. Only SOPs that have revised from Phase I or Phase II, or those that are new for this QAPP Addendum, are included in this appendix. Most SOPs that are included in this appendix have been added to support Phase III engineering PDI elements, including the following:

- Section 5.2 – Field SOPs for sediment thickness probing (SOP E27 and E29)
- Section 5.6 – Laboratory SOPs for acute fish toxicity and TCLP testing of sediment to support waste profiling (SOP E32 and E33)
- Section 5.7 – Field and laboratory SOPs to support cap design (SOPs E34, E35, E36, E37, E38, E39, E40, E41, E42, and E43)
- Section 5.9 – Field SOP for sediment sheen testing (SOP E31)

Table C-1. Summary of SOPs from the PDI QAPP And QAPP Addenda

SOP No.	Title	PDI QAPP (Phase I)	QAPP Addendum No. 1 (Phase II)	QAPP Addendum No. 2 (Phase II)	QAPP Addendum No. 3 (Phase III)
E1	Wet-Sieve Grain Size Determination	Included	--	--	--
E2	Amphipod Toxicity Test (EcoAnalysts SOP)	Included	Revised	--	--
E3	Larval Toxicity Test (EcoAnalysts SOP)	Included	--	--	--
E4	Polychaete Toxicity Test (EcoAnalysts SOP)	Included	Revised	--	--
E5	Mercury Cold Vapor Analysis (ARL SOP)	Included	--	--	--
E6	Metals Analysis (ARL SOP)	Included	--	--	--
E7	SVOC Analysis (ARL SOP)	Included	--	--	Revised (ALS SOP)
E8	PCB (Aroclor) Analysis (ARL SOP)	Included	--	--	--
E9	Ammonia Analysis (ARL SOP)	Included	--	--	--
E10	Analysis of Dioxins/Furans (ARL SOP)	Included	--	--	Revised (Cape Fear SOP)
E11	Sulfide by Iodometric Titration (ARL SOP)	Included	--	--	--
E12	PAH-PCP Analysis (ARL SOP)	Included	--	--	Revised (ALS SOP)
E13	Total Organic Carbon Analysis of Soil and Sediment (ARL SOP)	Included	--	--	--
E14	Chlorinated Pesticides Analysis (ARL SOP)	Included	--	--	Revised (ALS SOP)
E15	Total Solids Analysis (ARL SOP)	Included	--	--	--
E16	Data Validation Process (LDC SOP)	Included	Revised (EcoChem SOP)	--	--
E17	Under Structure Sample Collection	Included	--	--	--

SOP No.	Title	PDI QAPP (Phase I)	QAPP Addendum No. 1 (Phase II)	QAPP Addendum No. 2 (Phase II)	QAPP Addendum No. 3 (Phase III)
E18	Surface Sediment Collection	Included	--	--	--
E19	Subsurface Sediment Collection	Included	Revised		--
E20	Hand Auger Sampling	Included	--	--	--
E21	SPT and Split Spoon Sampling	Included	--	--	--
E22	Thin Wall Sampling	Included	--	--	--
E23	Cone Penetrometer Testing	Included	--	--	--
E24	Push Probe Sampling	Included	--	--	--
E25	Vane Shear Test	Included	--	--	--
E26	Dynamic Cone Penetrometer Testing	Included	--	--	--
E27	Sediment Thickness over Armored Banks: Hand Probe	Included	--	--	Revised
E28	Sediment Thickness Over Armored Bank: Jet Probe	Included	--	--	--
E29	Diver Sediment Sampling and Precipitate Layer Coring (Gravity SOP)	--	--	--	New
E30	Understructure Vibracoring	--	--	--	New
E31	Sediment-Water Shake Test	--	--	--	New
E32	Acute Fish Toxicity Testing (Spheros SOP)	--	--	--	New
E33	TCLP testing (ARL SOP)	--	--	--	New
E34	Isotherm Study (EGL SOP)	--	--	--	New
E35	Laboratory XRF (EGL SOP)	--	--	--	New
E36	Sequential Extraction of Arsenic in Sediment (EGL SOP)	--	--	--	New
E37	Porewater Collection	--	--	--	New
E38	Seepage Measurements	--	--	--	New
E39	SOP for Conductivity (ARL SOP)	--	--	--	New
E40	SOP for pH (ARL SOP)	--	--	--	New
E41	SOP for Sulfide (ARL SOP)	--	--	--	New
E42	SOP for Extraction of Sediment Porewater by Centrifugation (EGL SOP)	--	--	--	New
E43	SOP for Synthetic Sediment Porewater Extraction (EGL SOP)	--	--	--	New

Notes:
ALS: ALS Environmental – Kelso Laboratory
ARI: Analytical Resources Inc.
ARL: Analytical Resources, LLC
EGL: Environmental Geochemistry Laboratory
LDC: Laboratory Data Consultants
PAH: polycyclic aromatic hydrocarbon
PCB: polychlorinated biphenyl
SOP: standard operating procedures

SVOC: semivolatile organic compound
TCLP: Toxicity Characteristic Leaching Procedure
XRF: X-ray fluorescence

1) Scope & Applicability

1.1. This procedure is used to determine low level concentrations of Semi-Volatile Organic Compounds in water and soil using EPA Method 8270D. This procedure may also be applicable to various miscellaneous waste samples. Table 1 indicates compounds that may be determined by this method and lists their method reporting limits (MRLs) in water and soil. Equivalent nomenclature for MRL includes Estimated Quantitation Limit (EQL) or Low Level of Quantitation (LLOQ). The reported MRL may be adjusted if required for specific project requirements; however, the capability of achieving other reported MRLs must be demonstrated. The laboratory DQO Table lists Method Detection Limits (MDLs) that have been achieved. MDLs may change as studies are updated or new studies performed, and will vary depending on the preparation method.

1.2. This procedure can be used to quantitate most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted without derivatization as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone phase. Such compounds 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, including nitrophenols. Other compounds than those listed in Tables 4 and 6 may be analyzed. Refer to Section 1 of method 8270D.

1.3. In cases where there is a project-specific quality assurance plan (QAPP), the project manager identifies and communicates the QAPP-specific requirements to the laboratory. In general, project specific QAPP's supersede method specified requirements. An example of this are projects falling under DoD ELAP. QC requirements defined in the SOP *Department of Defense Projects – Laboratory Practices and Project Management – QSM 5.X* (ADM-DOD5) may supersede the requirements defined in this SOP.

2) Summary of Procedure

2.1 This method provides Gas Chromatography/Mass Spectrometry (GC/MS) conditions for the detection of Semi-volatile Organic Compounds. Prior to the use of this method, an appropriate sample preparation method must be used to recover the analytes of interest. An aliquot of the extract is injected into the gas chromatograph (GC) using a Agilent Multi-Mode Injector (MMI). The compounds are separated on a fused silica capillary column. Compounds of interest are detected by a mass selective detector. Identification of the analytes of interest is performed by comparing the retention times of the analytes with the respective retention times of an authentic standard, and by comparing mass spectra of analytes with mass spectra of reference materials. Quantitative analysis is performed by using the authentic standard to produce a response factor and calibration curve, and using the calibration data to determine the concentration of an analyte in the extract. The concentration in the sample is calculated using the sample weight or volume and the extract volume.

2.2 The following compounds may require special treatment when being determined by this method. Hexachlorocyclopentadiene is subject to decomposition in the injection port of the gas chromatograph, to a chemical reaction in acetone, and can undergo photochemical decomposition. N-Nitroso-dimethylamine is difficult to separate from the solvent under the chromatographic conditions described. N-Nitroso-diphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine. Benzoic acid, pentachlorophenol, 2,4-dinitrophenol, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

3) Definitions

3.1 For laboratory definitions applicable to most analyses, refer to the SOP for *Sample Batches.*

4) Responsibilities

4.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. This demonstration is in accordance with the training program of the laboratory. Final review and sign-off of the data is performed by the department supervisor/manager or designee.

4.2 It is the responsibility of the department supervisor/manager to document analyst training .and method proficiency, as described in: *Employee Training and Orientation* (ADM-TRAIN).

5) Interferences

5.1 Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation of the samples. Corrective action should be taken to eliminate the interferences.

5.2 Accurate determination of phthalate esters can pose difficulties when using this methodology. 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 may occur when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Interferences from phthalates can best be minimized by avoiding contact with any plastic materials. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination.

5.3 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of a solvent blank to check for cross contamination.

6) Safety

6.1 Chemicals, reagents and standards must be handled as described in the ALS safety policies, approved methods and in SDSs where available. Refer to the ALS Environmental, Health and Safety Manual and the appropriate SDS prior to beginning this method.

6.2 This method uses Dichloromethane, a known human carcinogen. Refer to the methylene chloride policy document, ENV-HSE-NA-TR-021-EN for proper handling.

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7) Sample Collection, Containers, Preservation, and Storage

7.1 Certified clean containers should be purchased for sample collection. The sample containers should be of glass or Teflon and have screw-top covers with Teflon liners.

Plastic containers or lids may not be used for the storage of samples due to the possibility of sample contamination from the phthalate esters and other hydrocarbons within the plastic.

7.2 Water and soil samples should be iced or refrigerated at <6°C from time of collection until extraction.

7.3 Water samples must be extracted within 7 days and the extracts analyzed within 40 days following extraction. Soil samples must be extracted within 14 days and the extract analyzed within 40 days following extraction. Extracts are stored at ≤10ºC.

8) Standards, Reagents, and Consumable Materials

8.1 Solvents: Acetone, methylene chloride, methanol, and other appropriate solvents.

8.2 Stock Standard Solutions (See Table 2)

8.2.1 Commercially prepared stock standards are typically used when available at a concentration of 1000µg/mL or more. They must be obtained from an A2LA or ISO9000 certified vendor. Standard concentrations can be verified by comparison versus an independently prepared standard. Alternatively, prepare stock standard solutions at a concentration of 1000µg/ml by dissolving 0.0100g of reference material in methylene chloride or other suitable solvent and diluting to volume in a 10mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Store according to vendors recommendations.

8.2.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at ≤10ºC and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

8.2.3 Stock standard solutions must be replaced after one year, or sooner, if comparison with check standards or samples indicates a problem.

8.3 Internal Standard Solutions (See Table 4) – The internal standards are 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12} (See Table 4 for corresponding compounds). The nominal concentration of the standard is 100ng/µL. Each 1mL of sample extract undergoing analysis should be spiked with 10µL of the internal standard solution, resulting in a concentration of 1.0ng/µL of each internal standard. Store at -10ºC or less when not being used. When using premixed certified solutions, store according to the vendors recommendations.

8.4 GC/MS Tuning Standard – Use a methylene chloride solution containing 50ng/µL of decafluorotriphenylphosphine (DFTPP). This will result in 50ng on column injection of DFTPP. The standard should also contain 2.5ng/µL of benzidine, DDT, and pentachlorophenol, to verify injection port inertness and GC column performance. Store at -10ºC or less when not being used, or store according to the manufacturer's recommendations. A less concentrated solution is acceptable as long as all acceptance criteria are met.

8.5 Calibration Standards (See Table 2)

8.5.1 A minimum of five initial calibration standards should be prepared from stock solutions. One of the calibration standards should be at a concentration at or below the method reporting limit; the others should correspond to the range of concentrations found in real samples, but should not exceed the working range

of the GC/MS system. At least one calibration standard must be at a concentration corresponding to a sample concentration meeting project-specific data quality objectives. Each standard should contain each analyte for detection by this method. Each 1 ml aliquot of calibration standards should be spiked with 10µL of the internal standard solution prior to analysis. All calibration standards should be stored at -10ºC or less and should be freshly prepared once a year, or sooner if check standards indicate a problem.

8.5.2 The daily calibration standard (CCV) is prepared from stock solutions at a concentration at the midpoint of the calibration curve (typically 2-4ng/µL). The CCV is prepared weekly and can be stored at 4±2ºC, or as recommended by the manufacturer. The DFTPP standard may be combined with this standard (maintaining a 1-50ng on column injection) providing tuning verification and calibration verification can be done without interferences.

8.6 QC Standards (See Table 3)

8.6.1 Surrogates: Prepare a working solution in methanol containing 2-fluorophenol, phenol-d_6, and 2,4,6-tribromophenol at 150ng/µL and nitrobenzene-d_5, 2-fluorobiphenyl, and terphenyl-d_{14} at 100ng/µL. Aliquots of the solution are spiked into all extracted samples, blanks, and QC samples according to the extraction SOP used.

8.6.2 Matrix Spike Standards: Prepare a working solution in methanol containing all analytes of interest (full list spike) at 100ng/µL (Pyridine is at 200ng/µL). Aliquots of the solution are spiked into the selected QC aliquots according to the extraction SOP used.

NOTE: The spiking level of surrogate and spike may need to be adjusted according to project requirements, if dilutions are expected due to high levels of extracted components, or if a lower calibration range is used

9) Apparatus and Equipment

9.1 Gas Chromatograph/Mass Spectrometer System

9.1.1 Gas Chromatograph – HP 5890, Agilent 6890, or Agilent 7890 -An analytical system complete with a temperature-programmable gas chromatograph suitable for large volume injection with cryogenic cooling, or for small volume injection without cryogenic cooling.

9.1.1.1 Atas Optic 2 or 3 large volume injector units – This allows for injection of up to 100µL of solvent for each analysis. After injection into the cold injector, the solvent is vented while the analytes are retained within a specially packed liner. The injector is then flash heated and the analytes are transferred into the GC. The unit also controls gas flow rates.

9.1.1.2 Agilent Split/Splitless Injector – The injector is held at a constant temperature allowing for the direct transfer of analytes onto the analytical column. The unit also controls the gas flow rates.

9.1.1.3 Agilent MMI injector – This allows for injection of up to 1000µL of extract. The injector can be temperature programmed and is equipped with cryogenic cooling. The unit also controls gas flow rates.

9.1.1.4 Autosampler – HP 7673, Agilent 7683, Agilent 7693, or equivalent with programmable operation.

9.1.1.5 All other required accessories, syringes, analytical columns, and gases. The capillary column should be directly coupled to the source.

9.1.2 Column – ZB semivolatiles, 30mx0.25mm ID x0.25µm film thickness silicone-coated fused-silica capillary column with 10 m guard column (or equivalent).

9.1.3 Mass Spectrometer – HP 5972, Agilent 5973, or Agilent 5975 – Capable of scanning from 35 to 500amu every 1 second or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets all of the criteria in Table 1A or 1B when a 10-50 ng tune standard is injected onto the GC

9.1.4 GC/MS Interface – Any GC-to-MS interface that gives acceptable calibration points for each compound of interest and achieves acceptable tuning performance criteria may be used.

9.1.5 Data System – A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. NIST98 Mass Spectral Library is used for spectral comparisons.

9.2 Appropriate analytical balance (0.0001g), volumetric flasks, syringes, vials, and bottles for standards preparation.

10) Preventative Maintenance

10.1 All maintenance activities are recorded in a maintenance logbook kept for each instrument. Pertinent information (serial numbers, instrument I.D., etc.) must be in the logbook. Maintenance entries should include date, symptom of problem, corrective actions, and description of maintenance, date, and name. The log should contain a reference to return to analytical control.

10.2 Carrier gas – Inline purifiers or scrubbers should be in place for all sources of carrier gas. These are selected to remove water, oxygen, and hydrocarbons. Purifiers should be changed as recommended by the supplier.

10.3 Gas Chromatograph

10.3.1 Whenever GC maintenance is performed, care should be taken to minimize the introduction of air or oxygen into the column. Injection port maintenance includes changing the injection port liner, seal, washer, O-ring, septum, column ferrule, and autosampler syringe as needed. Liners and seals should be changed when recent sample analyses predict a problem with chromatographic performance. In some cases liners and seals may be cleaned and re-used.

10.3.2 Clipping off a small portion of the head of the column often improves chromatographic performance. When cutting off any portion of the column, make sure the cut is straight and “clean” (uniform, without fragmentation) by using the proper column cutting tool. The column head pressure must be adjusted to maintain proper flow rates.

10.3.3 Over time, the column will exhibit poorer overall performance, as indicated by poor peak shape and reduced responses. The length of time for this to occur will depend on the samples analyzed. When a noticeable decrease in performance is evident, more thorough maintenance is necessary. Some steps are to solvent rinse the split vent and septum lines with a mix of 20% methanol in DCM. When these and other maintenance options do not result in improvement, the column should be replaced. This is especially true when evident in conjunction with calibration difficulties.

10.4 Mass Spectrometer

10.4.1 For units under service contract, certain maintenance is performed by instrument service staff, including pump oil changed, vacuuming boards, etc., as recommended by the manufacturer.

10.4.2 MS source cleaning should be performed as needed, depending on the performance of the unit. This may be done by the analyst or by instrument service staff.

10.4.3 Tune the MS as needed to result in consistent and acceptable performance while meeting the required ion abundance criteria.

11) Procedure

11.1 Sample Preparation

11.1.1 Water samples

11.1.1.1 Water samples are prepared using continuous liquid-liquid extraction and EPA method 3520C. Refer to EXT-3520 or samples may be prepared using separatory funnel procedures (EPA 3510C). Refer to EXT-3510.

11.1.1.2 Perform the extraction on a 1000mL or less aliquot of sample.

11.1.2 Soil, sediment, and solid samples are prepared using automated soxhlet extraction EXT-3541. The nominal sample size is 20g. Sample amounts may be decreased in the case of high-concentration waste samples. GPC cleanup may be used (SOP SOC-3640A).

11.1.3 Extracts should be screened by GC/FID (SOC-SCR).

11.1.4 Following sample preparation, sample extracts are then transferred to the extract cold storage unit. Extracts must be analyzed within 40 days of extraction.

11.2 The recommended GC/MS operating conditions are listed below. The GC conditions may be modified to accommodate specific instrument models and configurations.

Mass range:	35-500amu
Scan Time:	1sec/scan
Injector temp/program:	5:1 split electronic pressure control with pulse.
Carrier Gas:	Helium at 32cm/sec constant pressure.

11.3 Initial Calibration

NOTE: The calibration procedure(s) and options chosen must follow the ALS protocols. Any exceptions to the calibration procedures detailed in SOC-CAL, *Calibration of Instruments for Organics Chromatographic Analyses* are described as follows:

11.3.1 Prior to calibration, analyze the GC/MS tuning standard using instrument conditions used for calibration. Obtain the spectrum for evaluation using one of the following options:

- Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the DFTPP peak or part of any other closely eluting peak.
- Use one scan at the apex of the peak. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the DFTPP peak or part of any other closely eluting peak.
- Use one scan either directly preceding or following the apex of the peak. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the DFTPP peak or part of any other closely eluting peak.
- Use the average across the entire peak up to a total of 5 scans. If the peak is wider than 5 scans, the tune will consist of the peak apex scan and the two scans immediately preceding and following the apex. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the DFTPP peak or part of any other closely eluting peak.

11.3.2 Evaluate the spectrum obtained for DFTPP against the tuning criteria. Criteria are given in Tables 1and 1A. The GC/MS must meet the DFTPP ion abundance criteria prior to further analyses. To assess column performance and injection port inertness, pentachlorophenol and benzidine should be present at an acceptable level and peak tailing should not exceed a tailing factor of 2. DDT degradation should not exceed 20%. If excessive tailing, poor chromatography, or degradation of >20% is noted, the injection port may require cleaning. It may also be necessary to remove the first 15-30 cm of the GC column. If hardware tuning criteria cannot be met, the source may need cleaning, filaments replaced or other maintenance.

11.3.3 The internal standards should permit most of the components of interest in the chromatogram to have retention times of 0.80-1.20 relative to one of the internal standards. Refer to Table 4 for internal standards and corresponding analytes assigned for quantitation. Use the base peak ion from the specific internal standard as the primary ion for quantitation (see Table 1 in EPA method 8270D). If interferences are noted, use the next most intense ion as the quantitation ion (i.e. for 1,4-dichlorobenzene-d_4, use 152m/z for quantitation).

11.3.4 Analyze 2µL of each calibration standard (containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each compound (see Table 1 in EPA method 8270D). Calculate response factors (RFs) for each compound relative to one of the internal standards as follows:

$$RF = (A_x C_{is})/(A_{is} C_x)$$

Where: A_x = Area of the characteristic ion for compound being measured.
A_{is} = Area of the characteristic ion for specific internal standard.
C_{is} = Concentration of the specific internal standard (ng/µL).
C_x = Concentration of the compound being measured (ng/µL).

11.3.5 The percent relative standard deviation (%RSD) should be less than or equal to 20% for each compound. It is also recommended that a minimum response factor for the most common target analytes, as noted in Table 5, be demonstrated as a means to ensure that these compounds are performing as expected.

$$\%RSD = \frac{SD}{\overline{RF}} \; x \; 100$$

Where: RSD = relative standard deviation.
$\overline{RF}$ = mean of initial RFs for a compound.
SD = standard deviation of average RFs for a compound.

$$SD = \sqrt{\sum_{i=1}^{N} \frac{(RF_i - RF)^2}{N - 1}}$$

Where: RF_i = RF for each of the calibration levels
N = Number of RF values (e.g., 6)

11.3.6 The relative retention times (RRT) of each compound in each calibration run should agree within 0.06 relative retention time units.

$$RRT = \frac{\text{Retention time of the analyte}}{\text{Retention time of the internal standard}}$$

11.3.7 Linearity – If the % RSD of any compound is 20% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation.

11.3.8 If the %RSD for a compound is >20%, then alternative calibration models should be used. Refer to SOC-CAL, Calibration of Instruments for Organics Chromatographic Analysis for alternative fit guidance.

11.3.9 If more than 10% of the compounds included with the initial calibration exceed the 20% RSD limit and do not meet the minimum correlation coefficient (0.99) for alternate curve fits, then the chromatographic system is considered too reactive for analysis to begin. Clean or replace the injector liner and/or capillary column, then repeat the calibration procedure.

11.3.10 When calculating the calibration curves using the alternative curve fits, a minimum quantitation check on the viability of the lowest calibration point should be performed by re-fitting the response from the low concentration calibration standard back into the curve (see Method 8000C for additional details). It is not necessary to re-analyze a low concentration standard; rather the data system can recalculate the concentrations as if it were an unknown sample. The recalculated concentration of the low calibration point should be within ±30% of the standard's true concentration.

11.3.11 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times.

Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 50% of the average of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. The resolution should be verified on the mid-point concentration of the initial calibration as well as the laboratory designated continuing calibration verification level if closely eluting isomers are to be reported

11.4 Independent Calibration Verification

11.4.1 Following initial calibration, analyze an ICV standard. The ICV solution must contain all analytes in the calibration standards at a concentration in the middle of the range of the initial calibration. Calculate the concentration using the typical procedure used for quantitation. Calculate the percent difference (%D) from the ICV true value. The maximum allowed % Difference or % Drift is ±30%.

11.4.2 If a second source standard is not available or is cost prohibitive (such as certain non-routine analytes), then a second lot number may be used as the ICV and must meet the criteria above.

11.4.3 After the multi-point calibration has passed all of the above criteria, and the Independent Calibration Verification has been performed, samples can be analyzed. The calibration curve mid-point standard may serve as the CCV for the opening set of samples within the same 12-hour window as the initial calibration.

11.5 Continuing Calibration

11.5.1 A calibration standard, or standards, at mid-concentration (See Table 2) containing all semivolatile analytes, DFTPP, and all required surrogates, must be analyzed every 12 hours during analysis. The DFTPP must result in a mass spectrum which meets the criteria given in Tables1A or 1B. These criteria must be demonstrated during each 12 hour shift. Obtain the DFTPP spectrum as described.

11.5.2 The internal standard responses and retention times in the calibration check standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from that in the midpoint standard of the most recent initial calibration sequence, the chromatographic system must be inspected for malfunctions and corrective action identified, as required. If the EICP area for any of the internal standards changes by a factor of two (50% to 200%) from that in the midpoint standard of the most recent initial calibration sequence, the chromatographic system must be inspected for malfunctions and corrective action identified, as appropriate. When corrective action is taken, reanalysis of samples analyzed while the system was malfunctioning is required. Update the reference spectra and retention times in the quantitation database for the instrument method or ID file. The initial calibration average RF or calibration curve is then used in the quantitation of subsequent analyses.

11.5.3 If the percent difference or percent drift for each compound is less than or equal to 20%, the initial calibration is assumed to be valid and the analysis of samples may begin. Calculate the percent drift using:

$$\%\,Drift = \frac{C_I - C_c}{C_I} \times 100$$

Where: C_I = Compound standard concentration.
C_c = Measured concentration using selected quantitation method.

11.5.4 Due to the large number of compounds that may be analyzed by this method, some compounds may fail to meet the ≤20% criteria. If no more than 20% of the compounds, included in the initial calibration, differ from their true concentration by 40%, the initial calibration is valid and no corrective action is necessary.

11.5.5 In cases where compounds fail, they may still be reported as non-detects if it can be demonstrated that there was adequate sensitivity to detect the compound at the applicable quantitation limit. This is done by analyzing a MRL check standard for the failing compounds, where the resulting peaks for the failing compounds must pass 3:1 signal to noise.

11.5.6 Non-detected analytes can be reported from analyses when a CCV exhibit a positive bias (i.e., outside the upper control limit), no further documentation is required.

11.5.7 For situations when the CCV fails to meet the criterion in section 11.5.4, and a confirmed detection exceeds the MRL, the sample must be reanalyzed to ensure accurate quantification. If it is not possible to reanalyze the sample, the result must be reported as an estimated value.

11.5.8 A blank (method blank, GPC blank, or solvent blank) should be analyzed after the CCV, or at any other time during the analytical shift, to prove the system is free of contaminants. If contaminants are found in a method blank or GPC blank, then a solvent blank should be analyzed to help isolate the source of contamination.

11.5.9 Each of the most common target analytes in the calibration verification standard should meet the minimum response factors noted in Table 5.

11.5.10 If the minimum response factors are not met, the system should be evaluated, and corrective action should be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination of the front end of the analytical column, and active sites in the column or chromatographic system.

11.6 GCMS Analysis

11.6.1 Evaluate FID screen and make proper dilution (See FID screening SOP).

11.6.2 Spike the 1mL extract obtained from sample preparation with 10µL of the internal standard solution just prior to analysis. Use the same operating conditions as were used for initial calibration.

11.6.3 If the response for any quantitation ion exceeds the initial calibration curve range of the GC/MS system, extract dilution must take place. Additional internal standard must be added to the diluted extract to maintain the required 1.0ng/µL of each internal standard in the extracted volume. The diluted extract must be reanalyzed.

11.6.4 Store the extracts at -10ºC or less, protected from light in vials equipped with unpierced Teflon lined septa. Archive the extract in freezer for 3 months after analysis in the instrument/date specific storage boxes.

12) QA/QC Requirements

12.1 In addition to instrument criteria for calibration, the ability of each analyst/instrument to generate acceptable accuracy and precision must be documented prior to sample analysis (IPR study). This must be validated before analysis of samples begins, or

whenever significant changes to the procedures have been made. To do this, four tap water samples are spiked with each target analyte, extracted, and analyzed.

12.2 Method Detection Limits

12.2.1 A method detection limit (MDL) study, or verification of an existing LOD from an equivalent instrument must be completed prior to analysis of samples. To establish detection limits that are precise and accurate, the analyst must perform the following procedure. Spike a minimum of seven blank replicates with a MDL spiking solution (at a level below the MRL) for each target analyte, extract, and analyze. The MDL studies should be done for each matrix, prep method, and instrument. Refer to the SOP Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantification.

12.2.2 Calculate the average concentration found (x) in the sample concentration, and the standard deviation of the concentrations for each analyte. Calculate the MDL for each analyte using the correct T value for the number of replicates. The MDL study must be verified annually.

12.3 Limits of Quantification (LOQ)

12.3.1 The laboratory establishes a LOQ for each analyte as the lowest reliable laboratory reporting concentration or in most cases the lowest point in the calibration curve which is less than or equal to the desired regulatory action levels, based on the stated project requirements. Analysis of a standard or extract prepared at the lowest point calibration standard provides confirmation of the established sensitivity of the method. The LOQ recoveries should be within the laboratories LCS acceptance limits to verify the data reporting limit. Refer to the SOP Performing and Documenting Method Detection Limit Studies and Establishing Limits of Detection and Quantification (CE-QA011/ADM-MDL).

12.4 The Method Reporting Limits (MRLs) used at ALS are the routinely reported lower limits of quantitation which take into account day-to-day fluctuations in instrument sensitivity as well as other factors. These MRLs are the levels to which ALS routinely reports results in order to minimize false positive or false negative results. The MRL is normally two to ten times the method detection limit.

12.5 Ongoing QC Samples required are described in the ALS-Kelso Quality Assurance Manual and in the SOP for Sample Batches. Additional QC Samples may be required in project specific quality assurance plans (QAPP). General QA requirements for DoD QSM are defined in the laboratory SOP, Department *of Defense Projects – Laboratory Practices and Project Management (ADM-DOD5).* General QC Samples are:

12.5.1 Method blank - A method blank is extracted and analyzed with every batch of 20 or fewer samples to demonstrate that there are no method interferences. The method blank must demonstrate that interferences from the analytical and preparation steps are minimized. No target analytes should be detected above the MRL in the method blank. For some project specific needs, exceptions may be noted and method blank results above the MRL may be reported for common lab contaminants (phthalate esters, etc.).

12.5.2 A lab control sample (LCS) must be extracted and analyzed with every batch of 20 or fewer samples. The LCS is prepared by spiking a blank with the matrix spike solution, and going through the entire extraction and analysis. Calculate percent recovery (%R) as follows:

$$\%R = X/TV \times 100$$

Where: X = Concentration of the analyte recovered
TV = True value of amount spiked

12.5.2.1 Acceptance criteria for lab control samples can be found in the laboratory Data Quality Objectives (DQO) tables. The accuracy of the analysis is controlled on a subset of target analytes. If the project analyte list is fewer than 20 analytes, all are considered control analytes. Analytes which are used for control analytes are listed in Table 6. For DoD projects all project target analytes are considered control analytes. If the LCS recovery for any control analyte fails acceptance limits, the cause is evaluated and corrective action taken as necessary. If instrument corrective action is not applicable or ineffective, re-extraction of the associated samples may be required. If any other analyte fails the advisory acceptance limits, the analyst must evaluate the impact on data quality and take any necessary corrective action, which may include re-extraction of the associated samples. Project-specific requirements may require all compounds to be treated as control analytes, or dictate use of project acceptance criteria.

12.5.3 A matrix spike/duplicate matrix spike (MS/DMS) must be extracted and analyzed with every batch of 20 or fewer samples. The MS is prepared by spiking a sample aliquot with the matrix spike solution, and going through the entire extraction and analysis. Calculate percent recovery (%R) as follows:

$$\%R = \frac{X - X1}{TV} \times 100$$

Where: X = Concentration of the analyte recovered
X1 = Concentration of unspiked analyte
TV = True value of amount spiked

Calculate Relative Percent Difference (RPD) as:

$$\%RPD = \frac{R1 - R2}{(R1 + R2)/2} \times 100$$

Where: R1= %recovery of the MS
R2= %recovery of the DMS

12.5.3.1 The acceptance limits for the MS/DMS recovery can be found in the laboratory Data Quality Objectives (DQO) tables. If the MS/DMS recovery is out of acceptance limits for reasons other than matrix effects, corrective action must be taken. (See Quality Assurance Manual section 11) The RPD acceptance limits are 30% for water and 40% for soils, sediments, and solids. Project-specific requirements may dictate the use of project acceptance criteria.

12.5.4 The acceptance limits for the surrogates can be found in the laboratory Data Quality Objectives (DQO) tables. If any surrogate recovery is outside acceptance criteria, the sample data must be closely evaluated for possible matrix interferences. If none are present, then corrective action must be taken. The sample should be re-analyzed if instrument factors (calibration, injection port) are suspected. If not, re-extraction and re-analysis is required, except in cases of high recovery and no positive hits in the sample for the analyte class represented by the particular surrogate.

12.5.5 The acceptance criteria listed in the laboratory Data Quality Objective (DQO) Tables are current criteria, but are subject to change as control limits are updated.

12.6 Additional QA/QC measures include control charting of QC sample results

13) Data Reduction and Reporting

13.1 Qualitative Analysis – The qualitative identification of compounds determined by this procedure is based on retention time, and comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the instrument and conditions used for the sample analysis. The characteristic ions from the reference mass spectrum are defined to be 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 should be identified as present when the criteria below are met.

13.1.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

13.1.2 The RRT of the sample component is within ±0.06 RRT units of the RRT of the standard component.

13.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum.

13.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is <25% of the sum of the 2 peak heights. Otherwise, structural isomers are identified as isomeric pairs.

13.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks appear to represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important. Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification. When analytes coelute, the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

13.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. Refer to method 8270D for guidance on tentatively identified compound (TIC) identification and quantification.

13.3 Quantitation and Calculations

13.3.1 The GC/MS data stations, in current use, all use the H-P RTE Integrator to generate the raw data used to calculate the standards $\overline{RF_x}$ values, the sample amounts, and the spike values. The software does three passes through each data file. The first two identify and integrate each internal standard and

surrogate. The third pass uses the time-drift information from the first two passes to search for all method analytes in the proper retention times and with the proper characteristic quantitation ions

When $\overline{RF_x}$ is used, calculate the extract concentration as follows:

$$C_{ex} = \frac{(Resp_x)(Amt_{ISTD})}{(Resp_{ISTD})(\overline{RF_x})}$$

Where: C_{ex} = the concentration in the sample extract (ppb);
$Resp_x$ = the peak area of the analytes of interest;
$Resp_{ISTD}$ = the peak area of the associated internal standard;
Amt_{ISTD} = the amount, in ppb, of internal standard added
$\overline{RF_x}$ = the average response from the initial calibration.

13.3.2 The concentration of analytes in the original sample is computed using the following equations:

Aqueous Samples: $$Concentration\ (\mu g / L) = \frac{(Cex)\ (Vf)\ (D)}{(Vs)}$$

Where: Cex = Concentration in extract in ng/mL
Vf = Final volume of extract in mL
D = Dilution factor
Vs = Volume of sample extracted, liters

Non-aqueous Samples: $$Concentration\ (ug/Kg) = \frac{(Cex)(Vf)(D)}{(W)}$$

Where: Cex = Concentration in extract in ng/mL
Vf = Final volume of extract in mL
D = Dilution factor
W = Weight of sample extracted in grams

13.4 Data Review and Assessment

13.4.1 Following primary data interpretation and calculations, all data is reviewed by a secondary analyst. Following generation of the report, the report is also reviewed. Refer to the SOP *Laboratory Data Review Process (ADM-DREV)* for details. The person responsible for final review of the data report and/or data package should assess the overall validity and quality of the results and provide any appropriate comments and information to the Project Chemist to inclusion in the report narrative

13.5 Reporting

13.5.1 Refer to the SOP for Data Reporting and Report Generation for reporting guidelines.

13.5.2 Reports are generated in the ALS LIMS by compiling the SMO login, sample prep database, instrument, date, and client-specified report requirements (when specified). This compilation is then transferred to a file which the Stealth reporting system uses to generate a report. The forms generated may be ALS standard reports, DOD, or client-specific reports. The compiled data from LIMS is also used to create EDDs.

14) Contingencies for Handling Out-of-Control or Unacceptable Data

14.1 Refer to the SOP for *Nonconformance and Corrective Action Procedures* (ADM-NCAR) for procedures for corrective action. Personnel at all levels and positions in the laboratory are to be alert to identifying problems and nonconformities when errors, deficiencies, or out-of-control situations are detected.

15) Method Performance

15.1 This method was validated through single laboratory studies of accuracy and precision. Refer to the reference method for additional method performance data available.

15.2 The method detection limit (MDL) is and related method reporting limit(s) were established using the procedure described in SOP *Performing and Documenting Method Detection Limit Studies and Establishing Limits of Detection and Quantification* (Ce-QA011/ADM-MDL). Method Reporting Limits are established for this method based on MDL studies and as specified in the ALS Quality Assurance Manual.

16) Pollution Prevention and Waste Management

16.1 The laboratory will comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the ALS Lab Waste Management Plan.

16.2 This method uses Methylene Chloride and any waste generated from this solvent must be placed in the collection cans in the lab. The solvent will then be added to the hazardous waste storage area and recycled off site.

16.3 This method uses non-halogenated solvents and any waste generated from this solvent must be placed in the collection cans in the lab. The solvent will then be added to the hazardous waste storage area and disposed of in accordance with Federal and State regulations.

17) Training

17.1 Training is documented following ADM-TRAIN, ALS-Kelso Training Procedure.

18) Method Modifications

18.1 Section 11.5.4 - No limit defined in reference method, so lab assigned a limit of 40% based on CLP protocols.

18.2 Lower reporting levels are achieved in this procedure through injection of larger volumes and a lower calibration range. Lower limits of quantitation for soils are >10µg/Kg for soils and >0.2µg/L for waters.

18.3 Minimum Response factors listed in Table 5 were determined from representative initial calibrations performed after system maintenance. Recommended minimum response factors listed in Table 4 of EPA 8270D are not applicable due the differences in quantitation levels from the reference method.

19) References

19.1 *Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry*, Method 8270D, EPA Test Methods for Evaluating Solid Waste, SW-846, Final Update IV, February 2007.

19.2 *Determinative Chromatographic Separations*, Method 8000C, EPA Test Methods for Evaluating Solid Waste, SW-846, On-Line March 2003.

19.3 DoD Quality Systems Manual for Environmental Laboratories current version.

19.4 TNI Standard, Volume 1- 2009, 2016.

19.5 ISO/IEC 17025: 2017

20) Changes Since the Last Revision

Summary of Revision Changes			
Rev. #	Effective Date	Document Editor	Description of Changes
11.0	12/2/2020	K Clarkson	Section 6.1: updated chemical handling and storage references. Sections 7.1 & 7.2: updated container and sample storage requirements. Section 11.1.1.1 & 11.1.1.2: Updated applicable water extraction methods and volume requirements Section 11.1.2: updated applicable soil extraction methods and mass requirements. Section 17.1: updated training documentation
12.0	2/17/2022	E. Davelaar	Updated SOP Signatories. Section 2.1: Removed "1uL" aliquot specification. Section 8.4: Removed "20uL injection" specification and changed concentration of DFTPP to 50 ng/uL. Changed last sentence to state that a less concentrated solution is acceptable. Section 9.1.2: Changed column to ZB semivolatiles and changed guard column to 10 m. Removed P/N. Section 11.2: Updated GC/MS recommended operating conditions. Section 11.3.4: Changed volume to 2uL.
12.0	Reviewed: 5/17/2023	E. Davelaar	Updated SOP Signatories. No technical changes needed at this time.
	Reviewed: 2/24/2025	K. Brown	Updated SOP Signatories. No technical changes needed at this time.

21) Attachments, Tables, and Appendices

21.1 Table 1A - DFTPP Key Ions and Ion Abundance Criteria.

21.2 Table 1B - DFTPP Key Ions and Ion Abundance Criteria for 5973 and newer GC/MS Systems.

21.3 Table 2 - 8270 LL Standards.

21.4 Table 3 - QC Standards.

21.5 Table 4 - Semivolatile Internal Standards With Corresponding Analytes Assigned for Quantitation.

21.6 Table 5 - Recommended Minimum Response Factors.

21.7 Table 6 - Control Analyties for Non- DoD Projects.

21.8 Table 7 - Summary of Corrective Actions.

Table 1A
DFTPP Key Ions and Ion Abundance Criteria

Method 8270D Ion Abundance Criteria		CLP OLM04.2 Ion Abundance Criteria	
Mass	Ion Abundance Criteria	Mass	Ion Abundance Criteria
51	30-60% of mass 198	51	30-80% of mass 198
68	< 2% of mass 69	68	<2% of mass 69
70	< 2% of mass 69	69	Present
127	40-60% of mass 198	70	<2% of mass 69
197	< 1% of mass 198	127	25-75% of mass 198
198	Base peak,100% relative abundance	197	<1% of mass 198
199	5-9% of mass 198	198	Base peak,100% relative abundance
275	10-30% of mass 198	199	5-9% of mass 198
365	> 1% of mass 198	275	10-30% of mass 198
441	Present but less than mass 443	365	>0.75% of mass 198
442	> 40% of mass 198	441	Present, but less than mass 443
443	17-23% of mass 442	442	40-110% of mass 198
		443	15-24% of mass 442

Table 1B
DFTPP Key Ions and Ion Abundance Criteria
FOR **5973** and newer GC/MS SYSTEMS

Mass	Ion Abundance Criteria
51	10-80% of mass 198
68	0-2% of mass 69
70	0-2% of mass 69
127	10-80% of 198
197	0-2% of 198
198	30-100% of 442 (alternate base)
199	5-9% of 198
275	10-60% of 198
365	1-50% of 442
441	0.01-100% of 443
442	30-100% of 198 (alternate base)
443	15-24% of 442

Alternate tuning criteria (from Method 525.2 or CLP OLM04.2) may be used provided that method performance is not adversely affected and that method performance criterion is met. The criteria used must be the same for **all** ion abundance criteria checks associated with a given analysis. For example, initial calibration, continuing calibration(s), QC, and sample analyses for a given sample must all use the same criteria.

Table 2
8270-LL Standards

CALIBRATION

The calibration curve is prepared from the following Supelco stock standards (or equivalent from other vendors*):8270 CLP Mix, Equity 8270 Mix 4, Equity Benzidines Mix, Equity N-Nitrosodiphenylamine, 1-Methylnaphthalene, Acetophenone and 8270 Surrogates Mix.

The mix of standards to prepare the ICAL intermediate may be changed to meet project requirements.

Calibration curve is prepared from a 100ppm intermediate solution and ranges from 50 – 10000ppb depending upon project requirements. Add internal standard when curve is prepared.

Place in amber autosampler vial, cap.

Store at -10°C. Expiration is 1 year from date prepared or expiration of parent standard(s), whichever is earlier.

ICV

Recommended: AccuStandard catalog # (or equivalent from other vendors*):

CLP-HC-BN-R	2000ppm BN mix
CLP-HC-A-PAK	2000 ppm Acid composite mix
Z-014E-R3	2000ppm Composite 3 mix
M-8270-SS-PAK	4000ppm Surrogates mix
Z-014J	4000ppm Internal standards mix
M-625C	25000ppm DFTPP
Z-014F	2000ppm Benzidines mix

Add 10µL internal standard for each 1 ml of ICV prepared.

Place in autosampler vial, analyze, recap, and refrigerate.

Expiration is one year after ICV was prepared or the expiration date from the manufacturer, which ever is earlier.

CCV & TUNE

Prepare 1mL 8270_LL CCV standard that falls near the mid point of the calibration curve. DFTPP is added to the CCV to give a final concentration of 2.5µg/mL. The CCV is stored in an amber autosampler vial and is good for one week.

RECAP AND STORE IMMEDIATELY AFTER INJECTING

* Vendor must be A2LA and/or ISO9000 certified.

Table 3
QC Standards

Surrogate Spiking Solution					
Parent	Initial Concentration	Aliquot	Final Volume	Final Concentration	Solvent
8-61377*	5000µg/mL	20mL	1000mL **	100 µg/mL	Methanol
8-61376*	10000µg/mL	15mL		150µg/mL	
S-8522*	5000µg/mL	20mL		100µg/mL	
Expiration – Unopened = 6 months from prep date					
* 8-61377 – Supelco BN Surrogate Standard (custom mix) – reorder 4 at a time					
* 8-61376 – Supelco Acids Surrogate Standard (custom mix) – reorder 3 at a time					
* S-8522 – Accustandard custom – reorder 4 at a time.					
** Split into 4 – 250 mL bottles.					
LCS/MS Spiking Solution					
Parent	Initial Concentration (ppm)	Aliquot (mL)	Final Volume	Final Concentration	Solvent
50608	1000	10	100mL	100ppm	MeOH
4-8467	2000	5			
46702-u	5000	2			
86-1148	2000	5			
79131	1000	10			
48462	2000	5			
App9186-20x	2000	5			
Expiration –6 months from prep date.					

TABLE 4
Semivolatile Internal Standards with corresponding Analytes Assigned for Quantitation

1,4-Dichlorobenzene-d4 Internal Standard		
N-Nitrosodimethylamine	2-Chlorophenol	N-Nitrosodi-n-propylamine
Aniline	Benzyl Alcohol	Hexachloroethane
2-Fluorophenol (surrogate)	Pyridine	2-Methylphenol
Bis(2-chloroethyl) Ether	1,2-Dichlorobenzene	3- and 4-Methylphenol (coeluting cpds)
Phenol-d_6 (surrogate)	1,3-Dichlorobenzene	Bis(2-chloroisopropyl) Ether
Phenol	1,4-Dichlorobenzene	Nitrobenzene
Nitrobenzene-d5 (surrogate)		
Naphthalene-d8 Internal Standard		
Naphthalene	2,4-Dimethylphenol	4-Chloroaniline
Benzoic Acid	Isophorone	Hexachlorobutadiene
2,4-Dichlorophenol	Bis(2-chloroethoxy)methane	2-Methylnaphthalene
1-Methylnaphthalene	4-Chloro-3-methylphenol	1,2,4-Trichlorobenzene
2-Nitrophenol		
Acenaphthene-d10 Internal Standard		
2-Fluorobiphenyl (surrogate)	Acenaphthylene	Fluorene
Hexachlorocyclopentadiene	Acenaphthene	4-Nitrophenol
2-Chloronaphthalene	Dibenzofuran	2,4,6-Trichlorophenol
2-Nitroaniline	2,4-Dinitrotoluene	2,4,5-Trichlorophenol
3-Nitroaniline	2,6-Dinitrotoluene	2,4-Dinitrophenol
4-Nitroaniline	Diethyl Phthalate	Azobenzene
Dimethyl Phthalate	4-Chlorophenyl Phenyl Ether	2,2,4,6-Tetrachlorophenol
2-Methyl-4,6-dinitrophenol		

Table 4 (continued)

Phenanthrene-d10 Internal Standard		
Phenanthrene	Anthracene	Pentachlorophenol
4-Bromophenyl Phenyl Ether	Di-n-butyl Phthalate	Carbazole
Hexachlorobenzene	Fluoranthene	
Chrysene-d12 Internal Standard		
Pyrene	Benz(a)anthracene	Terphenyl-d14 (surrogate)
Butylbenzyl Phthalate	Bis(2-ethylhexyl) Phthalate	
3,3'-Dichlorobenzidine	Chrysene	
Perylene-d12 Internal Standard		
Di-n-octyl Phthalate	Benzo(a)pyrene	Benzo(g,h,i)perylene
Benzo(b)fluoranthene	Indeno(1,2,3-c,d)pyrene	
Benzo(k)fluoranthene	Dibenz(a,h)anthracene	

Table 5
Recommended Minimum Response Factors

Compound	Minimum Response Factor (RF)
Benzaldehyde	0.010
Phenol	0.800
Bis(2-chloroethyl) Ether	0.700
2-Chlorophenol	0.800
2-Methylphenol	0.500
2,2'-Oxybis-(1-chloropropane)	0.010
Acetophenone	0.010
4-Methylphenol	0.600
N-Nitrosodi-n-propylamine	0.500
Hexachloroethane	0.300
Isophorone	0.300
Nitrobenzene	0.200
2-Nitrophenol	0.100
2,4-Dimethylphenol	0.100
Bis(2-chloroethoxy)methane	0.200
2,4-Dichlorophenol	0.100
Naphthalene	0.700
4-Chloroaniline	0.010
Hexachlorobutadiene	0.010
Caprolactam	0.010
2-Methylnaphthalene	0.300
Hexachlorocyclopentadiene	0.050
2,4,6-Trichlorophenol	0.200
2,4,5-Trichlorophenol	0.200
1,1'-Biphenyl	0.010
2-Chloronaphthalene	0.700
2,-Nitroaniline	0.010
Dimethyl Phthalate	0.010

Table 5 (continued)

Compound	Minimum Response Factor (RF)
2,6-Dinitrotoluene	0.100
Acenaphthylene	0.900
3-Nitroaniline	0.010
Acenaphthene	0.700
2,4-Dinitrophenol	0.010
4-Nitrophenol	0.010
Dibenzofuran	0.800
2,4-Dinitrotoluene	0.200
Diethyl phthalate	0.010
1,2,4,5-Tetrachlorobenzene	0.010
4-Chlorophenyl-phenyl ether	0.400
Fluorene	0.800
4-Nitroaniline	0.010
4,6-Dinitro-2-methylphenol	0.010
4-Bromophenyl-phenyl ether	0.100
N-Nitrosodiphenylamine	0.010
Hexachlorobenzene	0.100
Atrazine	0.010
Pentachlorophenol	0.050
Phenanthrene	0.600
Anthracene	0.600
Carbazole	0.010
Di-n-butyl phthalate	0.010
Fluoranthene	0.600
Pyrene	0.600
Butyl benzyl phthalate	0.010
3,3'-Dichlorobenzidine	0.010
Benzo(a)anthracene	0.600

Table 5 (continued)

Compound	Minimum Response Factor (RF)
Chrysene	0.600
Bis-(2-ethylhexyl)phthalate	0.010
Di-n-octyl phthalate	0.010
Benzo(b)fluoranthene	0.600
Benzo(k)fluoranthene	0.600
Benzo(a)pyrene	0.600
Indeno(1,2,3-cd)pyrene	0.500
Dibenz(a,h)anthracene	0.400
Benzo(g,h,i)perylene	0.500
2,3,4,6-Tetrachlorophenol	0.010

Table 6
Control Analytes for Non-DoD Projects

1,2,4-Trichlorobenzene
1,4-Dichlorobenzene
2,4-Dinitrotoluene
2-Chloronaphthalene
2-Chlorophenol
4-Bromophenyl Phenyl Ether
4-Chloro-3-methylphenol
4-Nitrophenol
Acenaphthene
Benzo(a)pyrene
Diethyl Phthalate
Hexachloroethane
N-Nitrosodi-n-propylamine
Pentachlorophenol
Phenol
Pyrene

Table 7

Summary of Corrective Actions

Method Reference	Control	Specification and Frequency	Acceptance Criteria	Corrective Action
EPA 8000C, EPA 8270D	ICAL	Prior to sample analysis	%RSD ≤20 COD ≥0.990	Correct problem then repeat ICAL
EPA 8000C,	ICV	After ICAL	±30% Diff	Correct problem and verify second source standard; rerun second source verification. If fails, correct problem and repeat initial calibration.
EPA 8270D	CCV	Prior to sample analysis	±20% Diff	Correct problem then repeat CCV or repeat ICAL
EPA 8000C,	Method Blank	Include with each analysis batch (up to 20 samples)	<MRL	If target exceeds MRL, reanalyze to determine if instrument was cause. If still noncompliant then: Re-extract or reanalyze samples containing contaminate, unless samples contain >20x amount in blank.
EPA 8270D	Laboratory Control Sample	Include with each analysis batch (up to 20 samples)	See DQO Tables	If exceeds limits, re-extract and re-analyze
EPA 8000C,	Matrix Spike	Include with each analysis batch (up to 20 samples)	See DQO Tables	Evaluate data to determine if the there is a matrix effect or analytical error
EPA 8270D	Sample Duplicates	Include with each analysis batch (up to 20 samples)	W: RPD ≤30 S: RPD ≤40	Re-homogenize and re-analyze if result is >5X the MRL

STANDARD OPERATING PROCEDURE

FOR

THE ANALYSIS OF POLYCHLORINATED DIBENZO-p-DIOXINS

AND POLYCHLORINATED DIBENZOFURANS (PCDDs/PCDFs)

BY

HIGH-RESOLUTION GAS CHROMATOGRAPHY/HIGH-

RESOLUTION MASS SPECTROMETRY (HRGC/HRMS)

CF-OA-E-002

APPLICABLE TO METHODS:
EPA SW-846 Method 8290A, EPA Method 1613B, EPA SW-846 Method 0023A, EPA Method TO-9a

CFA's Document Control Officer certifies this document to be a true copy of the fully executed original.

Date: 26-Sep-2025

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1.0 STANDARD OPERATING PROCEDURE FOR THE ANALYSIS OF POLYCHLORINATED DIBENZO-P-DIOXINS AND POLYCHLORINATED DIBENZOFURANS (PCDD/PCDF) BY HIGH-RESOLUTION GAS CHROMATOGRAPHY/HIGH-RESOLUTION MASS SPECTROMETRY (HRGC/HRMS)

2.0 METHOD OBJECTIVE, PURPOSE, CODE, AND SUMMARY

This standard operating procedure (SOP) covers the analytical determination of PCDD/PCDFs according to the following methods:

2.1 SW-846 Method 8290A

2.2 EPA Method 1613B

2.3 SW-846 Method 0023A

2.4 EPA Method TO-9a (Jan 99)

3.0 APPLICABLE MATRICES

Applicable matrices for methods 8290A and 1613B include groundwater, wastewater, surface water, leachate, soil, sediment, sludge, oil, and tissue. The applicable matrix for method 0023A is an air sampling train, which may contain XAD resin (a hydrophobic crosslinked polystyrene copolymer resin, supplied as 20-60 mesh size white insoluble beads), filters, impinger water and solvent rinses. TO-9a is an ambient air sampling train which may contain polyurethane foam (PUF, a polyurethane foam, supplied as 1-3 inch cylinders approximately 3 inches long), XAD resin, filters, and solvent rinses.

4.0 METHOD SCOPE, APPLICABILITY, AND DETECTION LIMIT

4.1 Methods 8290A, 1613B and 0023A may be used to quantify PCDD/PCDFs that are soluble in methylene chloride and/or toluene. The compounds are separated using a gas chromatograph (GC) and detected using a high-resolution double focusing mass spectrometer (HRMS). Appendix 1 lists the analytes currently analyzed using these methods and their practical quantitation limits.

4.2 The practical quantitation limit (PQL) is the lowest level in the calibration curve. The PQL is the lowest level at which compounds may be accurately quantitated and is compound dependent. The calibration curve typically ranges from 1.0 ng/mL to 1000 ng/mL for methods 8290A, 0023A, and TO-9a, and from 0.5 ng/mL to 2000 ng/mL for method 1613B. These ranges reflect instrument readings, which are in ng/mL (ppb). It should be noted that the calibration range may vary between calibrations and instruments.

4.3 Method detection limit studies (MDLs) are performed and/or verified on an annual basis. MDLs are done for aqueous, solid, tissue and XAD matrices. For more information regarding MDLs, refer to The Determination of Method Detection Limits, CF-LB-E-001.

4.4 Qualified analysts must demonstrate proficiency initially and annually thereafter with an IDOC, CDOC, or PT study. Acceptability criteria may be found in the applicable analytical method.

4.4.1 To establish the ability to generate acceptable accuracy and precision, the analyst should perform an "analyst validation study" or Initial Demonstration of Capability. Four LCS standards are extracted and analyzed. Calculate the average recovery and the standard deviation of the recovery for each analyte of interest using the four results. Then compare the average and the standard deviation with the corresponding criteria found in Table 6 of method 1613B,

or with the determined limits for methods 8290A and 0023A. If the average and the standard deviation for all analytes of interest meet the acceptance criteria, then the analyst may begin work on actual samples. If the validation study fails for one or more of the compounds, then the study must be repeated for those compounds which failed.

5.0 METHOD VARIATIONS

5.1 Cape Fear Analytical analyzes a calibration point at 0.25 ng/mL, which is below the method required low point.

5.2 Standards and sample extracts are stored at room temperature to avoid analyte loss. Many of the target analytes in these methods form a strong cohesive bond with solids such as glass in cold temperatures; this type of analyte loss is not addressed in the method. (This is a variance from the following method recommendations: ≤6° per method 8290A; < -10°C per 1613B; -10° to -20° C per DoD QSM.)

5.3 Cape Fear Analytical utilizes the DB-5ms GC column (and may use the ultra inert version), which is capable of better resolution of the TCDF isomers. This column exhibits a different elution pattern than the DB-5 column referenced in the analytical methods. Relative retention time limits have been determined for this column for use with method 1613B, and are listed in Table 9.

5.4 Method 1613B does not address the reporting of EDL and EMPC. These values are reported for this method only when requested by the client.

5.5 See document CF-UD-F-133 for a list of personnel performing this SOP with the preceding method 1613B modifications.

6.0 DEFINITIONS

6.1 Accuracy: The degree of agreement between an observed value and an accepted reference value.

6.2 AlphaLIMS: The Laboratory Information Management System used at CFA, LLC.

6.3 Blank: An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and standard additions that are used with other samples. The LMB (Lab Method Blank) is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus. Contamination may be derived during sampling, transportation, storage or analysis. The blank may be used to establish a background value.

6.4 Calibration Standard (CAL): An aliquot of a primary standard solution or stock standard solution. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

6.5 Calibration Verification Standard (CVS, CCAL, CS3WT): A solution of target analytes with a concentration near the mid-point of the calibration range. It should be obtained from a second source vendor and is used to verify the initial calibration on a basis described in the determinative method. This solution may also contain the window defining analytes and the column performance mix.

6.6 Cleanup Standards: Isotopes added prior to cleanup that are used to measure the efficiency of the fractionation step alone. Method 1613B uses one compound (37Cl4-2378-TCDD) as the Cleanup Standard. Method 8290A does not address the use of cleanup standards.

6.7 Duplicate Analysis: The analysis or measurement of the variable of interest performed identically on two field subsamples of the same sample. The results from duplicate analyses are used to evaluate analytical or measurement precision of sample, preservation, or storage internal to the laboratory.

6.8 Estimated Detection Limit (EDL): A calculation of the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background signal level. The EDL is calculated for each 2378-substituted congener that is not identified.

6.9 Estimated Maximum Possible Concentration (EMPC): A calculation for a peak characterized by a response with a signal-to-noise ratio of at least 2.5 for both the quantitation ions, and meeting all identification criteria except ion ratio. EMPC is a worst-case estimate of the concentration.

6.10 Extraction Standards: Isotopes added prior to extraction that serve as internal standards for many 2,3,7,8 substituted congeners. In addition, to measure the overall extraction and fractionation efficiencies. Method 8290A names them Internal Standards while Method 1613B uses the Labeled Compounds terminology.

6.11 Injection Standards: Isotopes added prior to injection to determine the recoveries of the Extraction and Cleanup Standards. Method 8290A names them Recovery Standards while Method 1613B calls them Internal Standards.

6.12 Internal Standard (ISTD): A known amount of standard added to a test portion of a sample as a reference for evaluating the retention time and concentration of dependent analytes and controlling the precision and bias of the applied analytical method.

6.13 Laboratory Control Standard (LCS): An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

6.14 Laboratory Duplicate (DUP): Aliquots of a sample taken from the same container and processed in the same manner under identical laboratory conditions. The aliquot is analyzed independently from the parent sample and the results are compared to measure precision and accuracy.

6.15 Matrix Spike and Matrix Spike Duplicate (MS and MSD): Two separate aliquots of an environmental sample to which known quantities of the method analytes are added in the laboratory. The MS and MSD are analyzed exactly like a sample, and their purpose is to determine whether the sample matrix contributes bias to the analytical results. The concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS/MSD adjusted. Percent recovery is calculated for both aliquots, and RPD is calculated between the two.

6.16 Method Detection Limit (MDL): The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

6.17 Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves, a data quality

indicator. Precision is usually expressed as standard deviation, variance or range in either absolute or relative terms.

6.18 Quantitation Limits (also PQL, RL): The value at which an instrument can accurately measure an analyte at a specific concentration (i.e., a specific numeric concentration can be quantified). These points are established by the upper and lower limits of the linear calibration range.

6.19 Sampling Standards: Isotopes added prior to field sampling for Method 0023A and Method TO-9a that are used to measure the efficiency of the sampling step alone.

7.0 INTERFERENCES/LIMITATIONS

7.1 Contaminants found in extraction glassware, solvents, and other sample processing hardware may jeopardize the integrity of this method.

7.2 Glassware must be scrupulously cleaned as soon as possible after extraction.

7.3 Contamination may also occur in the GC/MS system. High boiling materials tend to build up in the injection port and the front end of the column. The analyst should maintain a thorough working knowledge of keeping the injection port free of contamination, including changing out the septum, injection port liner, O-ring, ferrule, and gold seal.

7.4 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between samples. If carryover is suspected, potentially impacted samples must be re-analyzed after any needed maintenance, solvent replacement, and/or cleaning has been done.

7.5 Upon review of a completed sequence, if one is required to perform a 200x or greater dilution, or if peaks are saturated, regardless of dilution, because of a sample's target concentrations, that the rinse vials on the instrument that determined this dilution need must have it's solvent replaced. This action should be documented in the maintenance log.

8.0 SAFETY PRECAUTIONS AND WARNINGS

METHYLENE CHLORIDE IS A SUSPECTED CARCINOGEN AND A KNOWN SKIN IRRITANT.

NO OCCUPATIONAL EXPOSURE LIMIT FOR DIOXIN HAS BEEN ESTABLISHED. IT IS A KNOWN AND PROBABLE HUMAN CARCINOGEN.

CONTACT WITH OXIDIZERS MAY GENERATE EXPLOSIVE MIXTURES.

PREVENT SKIN AND EYE CONTACT BY USING SPECIFIED PERSONAL PROTECTIVE EQUIPMENT WHEN MAKING STOCK REAGENTS.

WORK UNDER A HOOD TO PREVENT INHALATION WHEN USING METHYLENE CHLORIDE.

8.1 Eye protection should be worn when handling samples, reagents, or standards.
NOTE: Contact lenses pose a special problem; soft lenses may absorb irritants and all lenses concentrate them. DO NOT wear contact lenses in the laboratory.

8.2 Treat all chemicals and samples as potential health hazards and reduce exposure to these chemicals to the lowest level possible. CFA maintains a current reference file of Material Safety Data Sheets (MSDS). These documents and individual sample MSDS provided by clients are maintained in the laboratory.

8.3 Personal Protective Equipment (PPE)

8.3.1 Gloves and eye protection should be worn when handling reagents, solvents, standards and samples.

8.3.2 Analysts should prepare samples and standards under the hood.

8.4 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

8.5 Never leave gas cylinders unchained or untied.

8.6 In the event of an accident or medical emergency, call for help immediately. When time and safety permit, management should be notified of all accidents.

8.7 Fire escape routes are posted in the lab, and all personnel should be familiar with them. In addition, fire safety equipment such as fire extinguishers and fire blankets are located in the lab. Training is available on the proper operation of this equipment.

8.8 The analyst must use care when assembling and operating instrumentation. Check to see that the gas chromatograph equipment is properly assembled and hooked up to the proper gas cylinder and power, referencing the appropriate manual. Analytical equipment must only be operated by qualified personnel.

8.9 For further safety instructions, consult the Safety Manual, CF-LB-N-001.

9.0 APPARATUS, EQUIPMENT AND INSTRUMENTATION

9.1 Equipment associated with this method includes:

9.1.1 Gas tight syringes

9.1.2 2 mL high recovery (conical) autosampler vials and storage racks

9.1.3 Teflon crimp tops

9.1.4 Crimper/De-crimper

9.1.5 GC Columns

9.1.5.1 Agilent DB5-MS or equivalent (i.e. ui); 60 m, 0.25 mm, 0.25 um

9.1.5.2 Agilent DB-225 or equivalent; 30 m, 0.25 mm, 0.25 um

9.1.6 Quartz/Glass injection port liners

9.1.7 Injection port liner O-ring seals

9.1.8 Gold seals

9.1.9 Ferrules

9.1.10 Column cleaving tool

9.1.11 Septa (thermogreen)

9.1.12 10-100 uL adjustable air displacement pipette with disposable tips

9.2 Instrumentation

9.2.1 Waters Autospec Premier high resolution mass spectrometer

9.2.1.1 The MassLynx workstation software is used for instrument control and data acquisition of the AutoSpec-NT SIOS hardware embedded PC based system running the industry standard VxWorks real-time. The workstation operating system used is Windows XP SP2 or SP3 to support Masslynx v4.1.

9.2.1.2 The TargetLynx Application Manager is used for post-acquisition processing and general data manipulation. The workstation operating system used is Windows XP SP2 or SP3 to support Targetlynx v4.1. Post-acquisition processing and

general data manipulation can be carried out by an additional computer workstation and software installation.

9.2.2 Agilent 7890 Gas Chromatograph

9.2.2.1 A suggested temperature program for primary analysis follows:

Initial Temp.	140° C
Hold Time	1.0 min.
Rate 1	20° C/min.
Temperature 2	180° C
Time 2	2°/min
Temperature 3	235° C
Rate 3	30° C/min.
Final Temp.	290° C
Hold Time	13 min.
Run Time:	45 minutes (may vary due to column length or flow rate)
Solvent Delay:	18.0 min.
Splitless Valve Time:	1.5 min.
Flow:	1.8 mL/min.
Mass Range:	See descriptor definitions (Table 2)

NOTE: These instrument conditions and rates are guidelines which may change.

9.2.3 LEAP Technologies GC PAL Autosampler

9.2.3.1 Suggested parameters:

Sample volume – 1 µL
Air volume – 0.5 µL
Solvent push volume – 1 µL
Number of sample washes - 0
Solvent washes - 30
Sample viscosity wait – 1 second
Number of sample pumps - 0
Injection mode - Fast

10.0 REAGENTS AND STANDARDS

10.1 Reagents and standards

10.1.1 Nonane

10.1.2 Source Standards: Source Standards are purchased directly from vendors and may be diluted to make stock, intermediate, or working standards. These may include extraction standard, matrix spiking standard, cleanup standard, injection standard, as well as others. Source standards expire per the vendor expiration date or after five years from the date opened, whichever is shorter. Please reference CF-LB-E-007 and CF-OA-E-002 for further information regarding standards and their preparation.

10.1.3 Initial Calibration (ICAL) Standards: Certified calibration standards are purchased from commercial vendors at a minimum of five concentration levels. One of the calibration standards is at a concentration near, but above, the method detection limit; the others should correspond to the expected range of compounds found in samples. Calibration standards expire after a maximum of five years and should be monitored frequently for signs of degradation.

10.1.4 Calibration Verification Standards (CVS, CCAL, CS3WT): A certified CVS is purchased from a second source commercial vendor at a concentration that is near to the midpoint of the calibration curve.

10.1.5 Window Defining Mix and Column Performance Mix (WDM and CPM): A standard containing the first and last eluters for each homolog group, as well as the dioxin and furan isomers used to demonstrate isomer specificity on the GC column in use. These may be contained in the same standard as the calibration verification (known as CS3WT).

11.0 SAMPLE HANDLING AND PRESERVATION

11.1 Sample extracts have no maximum recommended holding time from the date of extraction by method 8290A, and a 365 day holding time from the date of extraction by 1613B. Sample extracts have a 45-day holding time from the date of extraction by 0023A. TO-9a cartridges are considered clean for 30 days from preparation; samples must be extracted 7 days from collection and analyzed 40 days from extraction. See Table 13.

11.2 Sample extracts are delivered from the prep lab to the instrument lab and are stored in a darkened hood at room temperature. The extracts are usually grouped according to preparation batches and are accompanied by the batch pull sheet and other pertinent paperwork.

11.3 Custody of samples is monitored using the AlphaLIMS sample tracking system. Each analyst should scan the samples planned to run into their custody prior to analysis.

11.4 All sample extracts should be treated with caution as potential health hazards. Refer to Section 8.0 on safety.

12.0 SAMPLE PREPARATION

12.1 Before extracts can be analyzed on the instrument, they must first be evaporated to dryness under nitrogen and then spiked with injection standard to set the final volume nominally at 20 µL. A determination must also be made as to whether the extract should be diluted. The decision to dilute a sample extract is based on several factors: sample screening, historical data about the sample or sample site, the appearance of the extract (color, viscosity, incidental odor, turbidity, etc.), or regulatory considerations. The experience of the analyst is invaluable in making this determination.

NOTE: Sample extracts may contain multiple layers or sediment. Samples that contain sediment are returned to cleanup. Multiple layers are treated on a case-by-case basis. If the extract can be homogenized, then a uniform sample is achieved. If the extract remains bi-phasic, the PM and client are contacted for further guidance.

12.2 Witness: Check the vial labeling, standards, and pipet settings. When witnessing is complete, please initial the injection prep logbook with LIMS.

12.3 If a sample is to be analyzed without dilution ('neat'), 2 nanograms of injection standard solution is added to the extract using a pipette (20 µL of a 0.1 ng/µL = 100 pg/µL extract concentration). A cap is then placed on the vial and secured by crimping before vortexing the sample to ensure complete mixing and vial wall washing.

12.4 If samples require dilution, the dilution is made using nonane or appropriate solvent. If not previously added, 2 nanograms of JS is added to the autosampler vial. Dilution prep may involve the addition of supplemental extraction standard (ES) and is documented in the injection prep logbook.

12.5 Once samples are prepped, they are ready to be injected onto the instrument. An autosampler is used to inject standards and sample extracts on the instrument.

12.6 The need for dilution may also be determined after analysis is performed, and may still be performed as above. Under normal circumstances, a sample would be diluted if any chromatographic peaks saturate the detector.

13.0 QUALITY CONTROL REQUIREMENTS

Typically a blank (LMB), laboratory control sample (LCS) and laboratory control sample duplicate (LCSD) are extracted and analyzed with each prep batch. Other client requirements may include a matrix spike (MS) and matrix spike duplicate (MSD) or sample duplicate (DUP).

13.1 Blanks

13.1.1 A blank is extracted with each batch of 20 or fewer samples to demonstrate that interferences from glassware, reagents and the analytical system are under control. Blanks are carried through all stages of sample preparation and analysis.

13.1.1.1 For Method 1613B, an acceptable blank must be below the minimum levels listed in Table 2 of the method for all analytes.

13.1.1.2 For Methods 8290A, 0023A, and TO-9a, all analytes must be below the Lower Method Calibration Limits.

13.1.1.3 For DOD work, an acceptable blank must have no analytes detected > 1/2 the laboratory's LOQ or > 1/10th the amount measured in any sample or 1/10th the regulatory limit, whichever is greater. (see QSM v5.3 table B-6)

13.1.2 The percent recovery of each labeled standard (extraction and cleanup) is calculated as shown in Sec. 17.4.5. Recoveries must be within the limits in Table 7 for method 1613B. For methods 8290A and 0023A, extraction standard recoveries must be within 40-135%. Sampling standards for Method 0023A must be within 70-130%. For method TO-9a, extraction standards must be within 50-120% for tetra- through hexa- and within 40-120% for hepta- and OCDD. Sampling standards for Method TO-9a must be within 50-120%.

13.2 Laboratory Control Samples and Matrix Spikes

13.2.1 The spiking standard for LCS/LCSDs and MS/MSDs contains all analytes listed in Table 5. For each LCS, LCSD, MS and MSD, the concentration of each analyte and its percent recovery are calculated as shown in Sec.17.4.1 and 17.4.5. For methods 8290A and 0023A, percent recoveries should be within 70-130%. For method 1613B, recovered concentrations should be within the limits in Table 6.

13.2.2 If recovery is not within these limits, the data may need to be re-checked for errors, or the samples and QC may need to be re-analyzed. In addition, the instrumentation may need to be checked for performance problems. If the LCS fails to meet acceptance criteria due to low recovery, the associated samples may have to be re-extracted and re-analyzed when possible. If one or more recoveries are high in the LCS and these analytes are not detected in the samples, the event should be documented and data may be reported. If the MS and MSD both fail due to matrix interference and/or dilution, data may be reported provided the associated LCS passes acceptance criteria.

NOTE: Many clients have contract specific criteria that must be considered when evaluating recovery of the Quality Control samples.

13.2.3 The percent recovery of each labeled standard (extraction and cleanup) is calculated as shown in Sec. 17.4.5. Recoveries must be within the limits in Table 6 for method 1613B. For methods 8290A and 0023A, extraction standard recoveries must be within 40-135%. Sampling standards for Method 0023A must be within 70-130%. For method TO-9a, extraction standards must be within 50-120% for tetra- through hexa- and within 40-120% for hepta- and OCDD. Sampling standards for Method TO-9a must be within 50-120%.

13.3 Samples

13.3.1 The percent recovery of each labeled standard (as listed in SOP CF-OA-E-001) is calculated as shown in Sec. 17.4.5. Recoveries must be within the limits in Table 7 for method 1613B or 40-135% for method 8290A. For method TO-9a, extraction standards must be within 50-120% for tetra- through hexa- and within 40-120% for hepta- and OCDD. Sampling standards for Method TO-9a must be within 50-120%.

13.3.2 Calculated EDLs should be below the PQLs in Table 1. Any reported EDLs above the PQLs should be noted in the case narrative.

14.0 INSTRUMENT CALIBRATION, STANDARDIZATION, AND PERFORMANCE

14.1 Mass spectrometer performance

14.1.1 The mass spectrometer is operated in electron ionization mode. A static resolving power of at least 10,000 (10 percent valley definition) must be demonstrated at appropriate masses before any analysis is performed. Static resolving power checks must be performed at the beginning and at the end of each 12-hr period of operation. Corrective action must be implemented whenever the resolving power does not meet the requirement.

14.1.1.1 Chromatography time for PCDDs and PCDFs exceeds the long term mass stability of the mass spectrometer. Because the instrument is operated in the high-resolution mode, mass drifts of a few ppm (e.g., 5 ppm in mass) can have serious adverse effects on instrument performance. Therefore, a mass drift correction is mandatory. A lock-mass ion from the reference compound PFK is used for tuning the mass spectrometer. The selection of the lock-mass ion is dependent on the masses of the ions monitored within each descriptor. Lock mass ions may be found in the descriptor table, Table 2. The level of the reference compound (PFK) metered into the ion chamber during HRGC/HRMS analyses should be

adjusted so that the amplitude of the most intense selected lock-mass ion signal (regardless of the descriptor number) does not exceed 10 percent of the full scale deflection for a given set of detector parameters. Under these conditions, sensitivity changes that might occur during the analysis can be more effectively monitored. NOTE: Excessive PFK (or any other reference substance) may cause noise problems and contamination of the ion source resulting in an increase in downtime for source cleaning.

14.1.2 Documentation of the instrument resolving power must be accomplished by recording the peak profile of the high-mass reference signal (m/z 380.9760) obtained during the above peak matching experiment by using the low mass PFK ion at m/z 304.9824 as a reference. The minimum resolving power of 10,000 must be demonstrated on the high-mass ion while it is transmitted at a lower accelerating voltage than the low-mass reference ion, which is transmitted at full sensitivity. The format of the peak profile representation (Figure 2) must allow manual determination of the resolution, i.e., the horizontal axis must be a calibrated mass scale (amu or ppm per division). The result of the peak width measurement (performed at 5 percent of the maximum, which corresponds to the 10 percent valley definition) must appear on the hard copy and cannot exceed 100 ppm at m/z 380.9760 (or 0.038 amu at that particular mass).

14.2 System Performance

System performance criteria are presented below. The laboratory may use the recommended GC column described in Sec. 9.1. The laboratory must document that all applicable system performance criteria are met before sample analysis begins. Sec. 9.2.2 provides recommended GC conditions that may be used to satisfy the required criteria. Mass spectrometer resolving power checks must be performed at the beginning and the end of each 12-hr period of operation. A GC column performance check is required at the beginning of each 12-hr period during which samples are analyzed. For Method 1613B, a continuing calibration must be performed at the beginning of the sequence, while for Methods 0023A and 8290A, continuing calibrations must be performed at both the beginning and the end of a sequence. An ending continuing calibration may also serve as the beginning check for the next sequence.

14.2.1 GC Column performance check

14.2.1.1 Inject 1 µL of an aliquot of the column performance check solution (Sec. 10.1.5) and acquire selected ion monitoring (SIM) data within a total cycle time of $\leq$ 1 second. The chromatographic separation between 2,3,7,8-TCDD and the peaks representing any other unlabeled TCDD isomers must be resolved with a valley of $\leq$ 25 percent (Figure 1), where:

Valley percent = (x/y) × 100

x = measured as in Figure 1 from the 2,3,7,8-closest TCDD eluting isomer

y = the peak height of 2,3,7,8-TCDD

For 2378-TCDF confirmatory analysis, the chromatographic separation between 2378-TCDF and its closest eluters must be resolved with a valley of $\leq$ 25 percent.

14.2.1.2 It is the responsibility of the laboratory to verify the conditions suitable for the appropriate resolution of 2,3,7,8-TCDD from all other TCDD isomers. The GC column performance check solution also contains the known first and last PCDD/PCDF eluters under the conditions described in this SOP. Their retention times are used to determine the five homologue retention time windows that are used for qualitative (Sec. 15.3.1.1) and quantitative purposes. All peaks (including 13C12-2,3,7,8-TCDD) should be labeled and identified on the chromatograms. All first eluters of a homologous series should be labeled with the letter "F," and all last eluters of a homologous series should be labeled with the letter "L". Any individual selected ion current profile (SICP) or the reconstructed homologue ion current constitutes an acceptable form of data presentation. A SICP for the labeled compounds is also required.

14.2.1.3 Particular caution should be exercised for the switching time between the last tetra-chlorinated congener (1,2,8,9-TCDF) and the first penta-chlorinated congener (1,3,4,6,8-PeCDF), as these two compounds elute within 15 sec of each other on the 60m DB-5 column, and overlap on the 60m DB-5ms column. Both congeners must be acquired within one analysis.

14.2.1.4 The absolute retention time of $^{13}C_{12}$-1,2,3,4-TCDD must exceed 25.0 minutes on the primary GC column in use, and 15.0 minutes on the confirmatory GC column.

14.3 Initial Calibration

14.3.1 Prior to running a multi-level calibration, take precautions to ensure that the instrument meets system performance criteria. The analyst must document that all system performance criteria are met before analyzing an initial calibration.

14.3.2 Initial calibration is required before any samples are analyzed for PCDDs and PCDFs and must meet the acceptance criteria listed below. Initial calibration is also required if any routine calibration does not meet the required criteria listed in Sec. 15.2, and at a minimum, annually.

14.3.3 At a minimum, all five high-resolution concentration calibration solutions listed in Table 5 must be used for the initial calibration.

14.3.4 Tune the instrument with PFK to meet the above-specified system performance criteria.

14.3.5 Inject the GC column performance check solution and acquire SIM mass spectral data. The total cycle time for each descriptor must be < 1 second. The laboratory must not perform any further analysis until it is demonstrated and documented that the criteria listed in Sec. 15.1.1.1 are met.

14.3.6 By using the same conditions (GC and MS) that produced acceptable results with the column performance check solution, analyze each of the five concentration calibration solutions. Each injection must meet the following ion ratio and signal-to-noise (S/N) requirements:

14.3.6.1 The ratio of the areas of the integrated ion current for the ions appearing in Table 2 (homologous series quantitation ions) must be

within the indicated control limits (set for each homologous series) in Table 3. These ion ratio requirements must be within the specified control limits simultaneously in one run. It is the analyst's responsibility to take corrective action if the ion abundance ratios are outside the limits.

14.3.6.2 For each selected ion current profile (SICP) and for each GC signal corresponding to the elution of a target analyte and of its labeled standards, the S/N ratio must be better than or equal to 10. Manual measurement of S/N is required for any GC peak that has an apparent S/N of less than 15:1. The result of the calculation must appear on the SICP above the GC peak in question.

14.3.7 Calculate the 17 relative response factors (RF) for unlabeled target analytes relative to their appropriate internal standards (see Table 10). Also calculate the RFs for the ESs and CSs relative to the appropriate injection standards according to the following formula:

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

Where:

Ax = Sum of the Areas of the two characteristic ions for the compound being measured.

Ais = Sum of the Areas of the two characteristic ions for the specific internal standard.

Cis = Concentration of the specific internal standard.

Cx = Concentration of the compound being measured.

The RF is a dimensionless quantity; the units used to express Cis and Cx must be the same.

14.3.8 The RF for other isomers within a homolog group shall be determined from the average RF of the 2,3,7,8-substituted isomers. For example, the RF for non-2,3,7,8-substituted HxCDD isomers (totals peaks) is the average of the three 2,3,7,8-substituted isomers. NOTE: If only one 2,3,7,8-substituted isomer is present in the calibration then use that isomer's RF for all isomers within its homolog group.

14.3.9 Because more than five calibration levels may be analyzed, the analyst may choose to deactivate one or more levels. The low standard representing the PQL cannot be deactivated. CFA only includes calibration points below the PQL at the request of the client (drinking water states, TMDL, etc.). If warranted, a mid-level standard is deactivated for all analytes (globally) in that calibration mixture. An upper level(s) standard may be deactivated to meet method criteria for single compounds. This practice results in a narrower calibration range. The analyst must get supervisory approval before deactivating any calibration levels within the method calibration range. Following approval, management will document the situation, including reasonable cause for calibration level removal. Calibrations with rejected mid-level points are not used for DOE clients or NC Drinking Water clients.

Please note that this practice does not represent "cherry picking," which is acknowledged as an unacceptable laboratory practice.

14.3.10 The average RF must be calculated for each compound as follows:

$$RF_{avg} = \frac{\sum_{i=1}^{n} X}{n}$$

Where:

N = number of calibration levels
X_i; i=1 to n, are the compounds RF values for each calibration point

14.3.11 Criteria for acceptable initial calibration

The criteria listed below for acceptable calibration must be met before sample analyses are performed.

14.3.11.1 Per method 8290A, the percent relative standard deviations for the mean response factors from the 17 unlabeled standards must not exceed ± 20 percent, and those for the nine labeled reference compounds must not exceed ± 20 percent. These limits also apply to Method 0023A. Per method 1613B, the percent relative standard deviations for the mean response factors from the 17 unlabeled standards must not exceed ± 20 percent, and those for the fifteen labeled reference compounds must not exceed ± 35 percent. See Table 12 for method TO-9a minimum requirements.

$$\%RSD = \frac{SD}{\bar{x}} \times 100$$

Where:

RSD = relative standard deviation
$\bar{x}$ = mean of 5 or more initial RFs for a compound
SD = standard deviation of average RFs for a compound

$$SD = \sqrt[2]{\frac{\sum_{i=1}^{n}(X - A)}{n-1}}$$

where:

n = number of calibration levels
X_i; i=1 to n, are the compounds RF values for each calibration point
A = average of the RFs from above

15.0 PROCEDURE FOR ANALYSIS AND INSTRUMENT OPERATION

15.1 Resolution check

15.1.1 At the beginning and end of each 12-hour window, mass resolution must be tuned and/or verified. A static resolving power of at least 10,000 must be demonstrated at appropriate masses before analysis is performed.

15.1.2 Using a PFK molecular leak, tune the instrument to the minimum required resolving power of 10,000 at m/z 330.9792 (for day to day operations, the

instrument may be tuned to approximately 11,000). Verify that the exact mass of m/z 380.9760 is within 5 ppm of the required value.

15.2 Column Performance/Window Defining/Continuing Calibration Check (CS3WT)

15.2.1 Inject 1 uL of the CS3WT or CPM. This standard is obtained from a different manufacturer or is a different lot from the same manufacturer than the initial calibration standard. Note that for NC drinking waters a different manufacture must be used. Verify that all column performance and window defining criteria in Section 14.2.1 have been met.

15.2.2 The CS3WT also contains the analytes for continuing calibration. The initial calibration curve for each compound of interest must be verified once every 12 hours.

Calculate the percent difference using:

$$\% \text{ Difference} = \frac{\left|\overline{RF}_i - RF_c\right|}{\overline{RF}_i} \times 100$$

Where:

$\overline{RF}_i$ = average response factor from initial calibration

RF_C = response factor from current CS3WT

Calculate analyte concentrations using:

$$\left[PCDD/PCDF\right] = \frac{\left(A_{unk}^{ion1} + A_{unk}^{ion2}\right)}{\left(A_{ES}^{ion1} + A_{ES}^{ion2}\right)} \times \frac{Q_{ES}}{\overline{RF}}$$

Where:

A_{unk} and A_{ES} = the integrated area for each ion monitored.
Q_{ES} = the amount of extraction standard in pg/uL
RF = Average RF from the ICAL for the compound

15.2.2.1 For methods 0023A and 8290A, if the percent difference for each native analyte in the CS3WT is $\leq$ 20%, and for each labeled analyte is $\leq$ 30%, the initial calibration is assumed to be valid. For method 1613B, analyte concentrations must fall within the limits in Table 8. If the criteria are not met, corrective action should be taken. If no source of the problem can be determined after corrective action has been taken, a new calibration may need to be generated. For Method TO-9a See Table 12 for minimum requirements.

15.2.2.2 All ion ratios must be within the limits in Table 3.

15.2.2.3 For methods 0023A and 8290A, if no more than two unrelated compounds in the continuing calibration check performed at the end of a 12-hour period fail by no more than $\pm$25% for the 17 unlabeled compounds and $\pm$35% for the 9 labeled compounds, the average RF values from the beginning and ending continuing calibration checks should be used to compute the analyte concentrations, instead of the RF values obtained from the initial calibration. No further sample analyses should be performed until an acceptable calibration is achieved.

15.3 Sample Analysis

15.3.1 Data Interpretation

15.3.1.1 Qualitative Determination

For a peak to be identified as a PCDD or PCDF, it must meet all of the criteria listed below.

15.3.1.1.1 The signals for the two m/z's being monitored must be present and maximize within ±2 seconds of each other.

15.3.1.1.2 The signal-to-noise ratio between the two m/z's must be $\geq$ 2.5 for native compounds and $\geq$ 10 for labeled compounds.

15.3.1.1.3 Ion ratios must be within the limits in Table 3.

15.3.1.1.4 Relative Retention Times

15.3.1.1.4.1 For Methods 0023A and 8290A, congeners which have an isotopically labeled compound must fall within -1 to +3 seconds of the labeled compound. Congeners with no labeled compound must be within 0.005 retention time units of the RRT measured in the continuing calibration. (See Table 11.) For method TO-9a, congeners which have an isotopically labeled compound must fall within -3 to +3 seconds of the labeled compound. Congeners with no labeled compound must be within 0.005 retention time units of the RRT measured in the continuing calibration.

15.3.1.1.4.2 For Method 1613B, relative retention times must be within the RRT limits found in Table 9.

15.3.1.1.4.3 For non-2378 peaks, retention times must be within the retention time windows established by the analysis of the window defining mixture (Sec. 14.2.1.2).

15.3.1.1.5 For PCDFs, no peak may be present in the associated PCDPE channel at the same retention time. If a PCDPE peak is present, the PCDF peak should be reported with a flag denoting the interference.

15.3.1.1.6 Any sample in which 2378-TCDF has been identified at or above the method reporting limit must be confirmed on a second column (DB-225 or equivalent).

15.3.1.2 Calibration Limit Exceedance

15.3.1.2.1 If a compound in a sample exceeds the upper calibration limit, all subsequent samples must be checked for carryover contamination.

15.3.1.2.2 When a subsequent sample is non-detect for the compound in question, the sequence is again considered acceptable for reporting.

15.3.1.2.3 All affected samples between the exceeding sample and the non-detect sample must be re-analyzed.

16.0 EQUIPMENT AND INSTRUMENT MAINTENANCE

16.1 Preventive maintenance on a HRGC/HRMS system involves the following basic areas:

16.1.1 Vane type vacuum pumps for the inlets, source, and analyzer need a change of oil and scroll type pumps may need tip seals changed about every year or when system performance indicates it is needed.

16.1.2 The GC injection port is cleaned as needed, approximately once a week. It is recommended that the septum and injection port liner be replaced at the time of cleaning. Additionally, the gold plated seal should be cleaned or replaced.

16.1.3 Ion source maintenance is usage dependent. The type and quantity of samples that have been injected determine the frequency of ion source cleaning and filament replacement.

16.1.4 Autosampler maintenance is primarily that of cleanliness. Most autosamplers need their moving parts to be clean and lightly lubricated. The most frequent corrective maintenance is that of changing the syringe, usually about once per month.

16.1.5 Instrument maintenance logs are kept with each instrument and serve as a record of all the maintenance that has been done on the instrument.

16.2 Non-Routine Maintenance Procedures (Special, Operational or Failure Mode Maintenance)

16.2.1 Service is provided to the instrument via the analyst, the in-house instrument service engineer, or a technical support specialist from the manufacturer. When instrument failure occurs, different parts of the instrument are isolated to determine the root cause. For example, the injection port may be capped off if a leak is suspected to prove the leak is/is not coming from that source. Instrument maintenance logbooks are kept for each instrument detailing the type of maintenance performed on the instrument and when it was performed. Preventive maintenance visits are scheduled annually for the mass spectrometers.

16.2.2 Analytical GC columns are clipped or replaced when the existing column shows signs of excessive degradation or the inability to properly resolve chromatographic peaks. Excessive peak tailing, poor responses, and baseline disturbances may also indicate that the column needs to be replaced.

17.0 DATA RECORDING, CALCULATION AND REDUCTION METHODS

17.1 Data are evaluated qualitatively and quantitatively using a software program such as Waters MassLynx, or equivalent data system.

17.2 Data are reviewed, and a hard copy is generated. If manual integrations are made, a hard copy of the manual integration is printed and initialed by the analyst and included with the raw data.

17.3 Additional supporting documentation, such as totals pages generated by the software may be included with the data.

17.4 Quantitative Analysis

17.4.1 The concentration (ng/L for aqueous, ng/g for solids) of each identified compound in the sample is calculated as follows:

$$\left[PCDD/PCDF\right] = \frac{\left(A_{unk}^{ion1} + A_{unk}^{ion2}\right)}{\left(A_{ES}^{ion1} + A_{ES}^{ion2}\right)} \times \frac{Q_{ES}}{W_{unk} \times D \times \overline{RF}}$$

Where:

A_{unk} and A_{ES} = the integrated area for each ion monitored.
Q_{ES} = the amount of extraction standard added to the sample in nanograms
W_{unk} = the initial sample aliquot size, in liters for waters and in grams for solids.
D = (% moisture in sample)/100, or 1 for waters
$\overline{RF}$ = Average RF from the ICAL for the compound

17.4.2 The estimated detection limit (EDL) is calculated as follows:

$$\left[EDL_{ppt}\right] = 2.5 \times \frac{\left(H_{unk}^{ion1} + H_{unk}^{ion2}\right)}{\left(H_{ES}^{ion1} + H_{ES}^{ion2}\right)} \times \frac{Q_{ES}}{W_{unk} \times \overline{RF}}$$

Where:

H_{unk} = the height of the noise present in each ion monitored.
H_{ES} = the height of the extraction standard peak in each ion monitored.
2.5 = signal-to-noise factor for minimum height of peak.

17.4.3 The estimated maximum possible concentration (EMPC) is calculated in the same manner as a concentration (Section 17.4.1).

17.4.4 The concentration of each extraction and cleanup standard is calculated as follows:

$$\left[ES_{ng}\right] = \frac{\left(A_{ES}^{ion1} + A_{ES}^{ion2}\right)}{\left(A_{JS}^{ion1} + A_{JS}^{ion2}\right)} \times \frac{Q_{JS}}{\overline{RF}}$$

Where:

A_{ES} and A_{JS} = the integrated area for each ion monitored.
Q_{JS} = the amount of injection standard added to the sample in nanograms
$\overline{RF}$ = Average RF from the ICAL for the compound

The cleanup standard concentration is calculated as above, substituting the area of the individual cleanup standard ions for the extraction standard ions.

17.4.5 Percent recovery is calculated as follows:

$$\%R = \frac{R_{ng}}{S_{ng}} \times 100$$

Where:

R_{ng} = the amount of standard recovered in nanograms.
S_{ng} = the amount of standard spiked in nanograms.

18.0 POLLUTION/CONTAMINATION

18.1 Work area should be maintained free of dust and dirt accumulations.

18.2 Fume hoods are utilized to remove fumes and reduce the risk of airborne contaminants to ensure personnel safety. Hoods are monitored in accordance with CF-FC-E-003 for Fume Hood Face Velocity Performance Checks.

18.3 The laboratory area is restricted to authorized personnel.

19.0 DATA REVIEW, APPROVAL AND TRANSMITTAL

19.1 A review process is used to insure the quality of the data. Raw data are reviewed first by the analyst, then by a second (peer) analyst or a data validator. When the analyst is satisfied that the data have been correctly processed and uploaded to the LIMS, a data report is generated from AlphaLIMS. The AlphaLIMS report along with the raw data and supporting documentation, such as a run log and case narrative, are submitted for review to the data validator or another experienced analyst. The reviewer goes through the raw data as if he/she was working it up for the first time and verifies that they are correct. In addition, he/she must make sure that the data have been correctly entered into AlphaLIMS. AlphaLIMS reports may be self-reviewed. If errors are discovered in either the raw data or the AlphaLIMS report, then the two analysts should discuss the differences and how best to resolve them. In some cases, the peer review process may uncover errors that lead to a sample being re-extracted or re-run. In cases such as these, a nonconformance report (NCR) should be completed and submitted to the Quality department. It is recommended that a copy of the NCR be given to the prep analyst if it involves a re-extraction and that a copy be kept with the original data.

19.2 Once the data review has been completed by the reviewer, the batch is returned to the analyst for corrections (if applicable) and the status is updated from REVW to DONE in AlphaLIMS.

19.3 Data may be transmitted automatically to AlphaLIMS. This automatic "upload" procedure may be activated prior to data review or after data review is complete. In either case, the data recorded in AlphaLIMS are checked by the analyst for accuracy and completeness.

20.0 CORRECTIVE ACTION FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

Corrective action for out-of-control data may require instrument maintenance, re-analysis, re-extraction, or a more complex set of actions. When troubleshooting measures fail to bring an analytical process or data into control, a nonconformance report and/or corrective action should be initiated in accordance with CF-QS-E-004 for the Documentation of Nonconformance Reporting and Dispositioning and Control of Nonconforming Items, and CF-QS-E-002 for Conducting Corrective Action.

21.0 CONTINGENCIES FOR HANDLING THESE SITUATIONS

Troubleshooting is used to determine the appropriate action to take when an initial or continuing calibration, blank and/or laboratory control sample fails to meet the acceptance criteria defined for the method. Troubleshooting may involve one or more of the following actions:

21.1 If analytes in a multi-point calibration fail to meet specified criteria, additional standards for the failing compounds may need to be reanalyzed. If they still do not meet specifications, instrument maintenance or new standards may be required before work is continued.

21.2 If a continuing calibration fails to meet specified criteria, instrument tuning or inlet maintenance may be required. If routine maintenance procedures fail to produce a second consecutive calibration verification within acceptance criteria, then the laboratory must demonstrate acceptable performance after further corrective action with two consecutive calibration verifications, or a new initial calibration must be analyzed.

21.3 If a method blank fails to meet defined criteria, the source of contamination should be found and eliminated before proceeding with analysis.

21.4 If normal equipment and software operating procedures do not resolve trouble-shooting efforts, the manuals for software, hardware and other equipment discussed in this SOP are available for consultation and resolution. On-line support may be available from software and instrument manufacturers, as well. Any revisions, repairs or corrective actions required must be documented in accordance with the laboratory's Quality System as described in CF-QS-B-001.

22.0 RECORDS MANAGEMENT

22.1 Run logs are generated for each instrument each day that the instrument is run. These run logs serve as records of what is run on the instrument, including samples, QC, calibrations, tunes, etc. Additional information is provided in the run log, including the analyst's initials, run date and time, and file name.

22.2 Raw data are stored in the lab in filing cabinets and/or boxes as long as there is space available. When space runs out, the data are boxed and sent to storage.

22.3 All records generated as a result of this procedure are maintained as quality documents in accordance with CF-QS-E-008 for Quality Records Management and Disposition.

23.0 LABORATORY WASTE HANDLING AND DISPOSAL

Sample extracts that have been run are temporarily stored in case they have to be reanalyzed. Once space is no longer available to keep them in the lab, they are moved to Waste Disposal where they are handled and disposed in accordance with the Laboratory Waste Management Plan, CF-LB-G-001.

24.0 REFERENCES

24.1 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/ Chemical Methods, Volume 1B, SW-846, 3rd Edition, Feb. 2007. Method 8290A, "Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High Resolution Gas Chromatorgraphy/ High Resolution Mass Spectrometry (HRGC/HRMS)," Rev. 1, Feb. 2007. USEPA, Office of Solid Waste and Emergency Response, Washington, DC 20460.

24.2 Method 1613, "Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS," Rev. B, Oct. 1994. USEPA, Office of Water, Engineering and Analysis Division, 401 M Street SW, Washington, D.C. 20460.

24.3 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/ Chemical Methods, Volume 1B, SW-846, 3rd Edition, Feb. 2007. Method 0023A, "Sampling Method for Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofuran Emissions From Stationary Sources," Rev. 1, Dec. 1996. USEPA, Office of Solid Waste and Emergency Response, Washington, DC 20460.

24.4 Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition. "Compendium Method TO-9A, Determination of Polychlorinated, Polybrominated and Brominated/Chlorinated Dibenzo-p-Dioxins

and Dibenzofurans in Ambient Air." January 1999. Center for Environmental Research Information, Office of Research and Development, USEPA, Cincinatti, OH 45268.

24.5 The NELAC Institute, (TNI) 2009 Standard, EL-V1-2009.

25.0 HISTORY

Revision 1: Section 15.3.1.2 added.

Revision 2: Absolute RT information added in 14.2.1.4; Calibration limit exceedance information added in section 15.3.1.2; Table 8 footnote describing RRT window adjustment to column used.

Revision 3: Method 0023A requirements added.

Revision 4: 2378-TCDF confirmation procedure and requirements added.

Revision 5: Injection standard changed from Tridecane to nonane. Discussion of equipment use and operation instructions was added, per DoD ELAP gray box 22.

Revision 6: Added TO-9a support and additional Tables for Method 8290.

Revision 7: Removed references to 8290 cleanup standard. Added TO-9a reference.

Revision 8: RRT limits for 1613 adjusted to method limits, except for three which have methods widths but db-5ms centers.

Revision 9: Added air matrix descriptions.

Revision 10: Table 9 updated. Maintenance rule for highly contaminated samples. TNI reference updated.

Revision 11: Changed EDL signal to noise value to 2.5. Updated Table references.

Revision 12: Added Table 13, Method Holding Times.

Revision 13: Added a NC requirement that a 1613 DW CCAL standard must only be obtained from a different manufacturer.

Revision 14: Adjusted TO-9a SS limits, added DB-5ms ui column use.

Revision 15: Added a document reference for Method 1613.

Revision 16: Updated section 9 to include hardware and software requirements.

Revision 17: Updated 8290 holding times.

Revision 18: Added DoD MB acceptance limits.

Revision 19: Updated 14.3.9 to clarify calibration level deactivation protocol.

Revision 20: Improved 14.3.9.

Revision 21: Added JS witnessing.

Revision 22: Added language to 7.5 related to action taken with saturated peaks. Included exception for NC Drinking Water clients in 14.3.9.

TABLE 1: METHOD ANALYTES AND PQLs

Analyte	Solid/Tissues (pg/g)	Aqueous (pg/L)	Air (pg)	CAS Number*
2378-TCDD	1	10	10	1746-01-6
12378-PeCDD	5	50	50	40321-76-4
123478-HxCDD	5	50	50	39227-28-6
123678-HxCDD	5	50	50	57653-85-7
123789-HxCDD	5	50	50	19408-74-3
1234678-HpCDD	5	50	50	35822-39-4
OCDD	10	100	100	3268-87-9
2378-TCDF	1	10	10	51207-31-9
12378-PeCDF	5	50	50	57117-41-6
23478-PeCDF	5	50	50	57117-31-4
123478-HxCDF	5	50	50	70648-26-9
123678-HxCDF	5	50	50	57117-44-9
234678-HxCDF	5	50	50	60851-34-5
123789-HxCDF	5	50	50	72918-21-9
1234678-HpCDF	5	50	50	67562-39-4
1234789-HpCDF	5	50	50	55673-89-7
OCDF	10	100	100	39001-02-0

* Chemical Abstract Services number

TABLE 2: MASS DESCRIPTORS

Function (#)	Channel (#)	Mass (amu)	Dwell Time (ms)	I.C. Delay (ms)
1	1	303.9016	50	10
1	2	305.8987	50	10
1	3	315.9419	50	10
1	4	304.9824	50	10
1	5	304.9824	(Lock)	10
1	6	317.9389	50	10
1	7	319.8965	50	10
1	8	321.8936	50	10
1	9	327.8847	50	10
1	10	331.9368	50	10
1	11	333.9339	50	10
1	12	339.8597	50	10
1	13	341.8568	50	10
1	14	375.8364	50	10
2	1	339.8597	50	10
2	2	341.8568	50	10
2	3	351.9	50	10
2	4	353.897	50	10
2	5	355.8546	50	10
2	6	357.8517	50	10
2	7	366.9792	50	10
2	8	366.9792	(Lock)	10
2	9	367.8949	50	10
2	10	369.8919	50	10
2	11	409.7974	50	10
3	1	373.8207	50	10
3	2	375.8178	50	10
3	3	380.976	50	10
3	4	380.976	(Lock)	10
3	5	383.8639	50	10
3	6	385.861	50	10
3	7	389.8156	50	10
3	8	391.8127	50	10
3	9	401.8559	50	10
3	10	403.853	50	10
3	11	445.7555	50	10
4	1	407.7818	50	10
4	2	409.7788	50	10
4	3	417.8253	50	10
4	4	419.822	50	10
4	5	423.7767	50	10
4	6	425.7737	50	10
4	7	430.9728	50	10
4	8	430.9728	(Lock)	10
4	9	435.8169	50	10
4	10	437.814	50	10
4	11	479.7165	50	10
5	1	441.7427	50	10
5	2	443.7398	50	10
5	3	454.9728	50	10
5	4	454.9728	(Lock)	10
5	5	457.7377	50	10
5	6	459.7348	50	10
5	7	469.778	50	10
5	8	471.775	50	10
5	9	513.6775	50	10

TABLE 3: THEORETICAL ION RATIOS AND CONTROL LIMITS

Level of Chlorination	Theoretical Ratio	Control Limits	
		Lower	Upper
4	0.77	0.65	0.89
5	1.55	1.32	1.78
6	1.24	1.05	1.43
6[a]	0.51	0.43	0.59
7	1.05	0.88	1.20
7[b]	0.44	0.37	0.51
8	0.89	0.76	1.02

[a] Used only for ^{13}C-HxCDF
[b] Used only for ^{13}C-HpCDF

TABLE 4: 1613B LIMITS FOR TETRA ONLY TESTS

Compound Name	Test Conc. (pg/µL)	CCAL Limits (pg/µL)	OPR Limits (pg/µL)	Sample Limits (pg/µL)
2,3,7,8-TCDD	10	8.2 - 12.3	7.3 - 14.6	-
2,3,7,8-TCDF	10	8.6 - 11.6	8.0 - 14.7	-
$^{13}C_{12}$-2,3,7,8-TCDD	100	85 - 117	25 - 141	31 - 137
$^{13}C_{12}$-2,3,7,8-TCDF	100	76 - 131	26 - 126	29 - 140
$^{37}Cl_4$-2,3,7,8-TCDD	10	8.3 - 12.1	3.7 - 15.8	4.2 - 16.4

TABLE 5: INITIAL CALIBRATION CONCENTRATIONS

Analyte	Concentration (pg/uL) CS-0.5	CS-2	CS-3	CS-4	CS-5
2378-TCDD	0.25	2	10	40	200
2378-TCDF	0.25	2	10	40	200
12378-PeCDD	1.25	10	50	200	1000
12378-PeCDF	1.25	10	50	200	1000
23478-PeCDF	1.25	10	50	200	1000
123478-HxCDD	1.25	10	50	200	1000
123678-HxCDD	1.25	10	50	200	1000
123789-HxCDD	1.25	10	50	200	1000
123478-HxCDF	1.25	10	50	200	1000
123678-HxCDF	1.25	10	50	200	1000
123789-HxCDF	1.25	10	50	200	1000
234678-HxCDF	1.25	10	50	200	1000
1234678-HpCDD	1.25	10	50	200	1000
1234678-HpCDF	1.25	10	50	200	1000
1234789-HpCDF	1.25	10	50	200	1000
OCDD	2.5	20	100	400	2000
OCDF	2.5	20	100	400	2000
Extraction Standards					
^{13}C-2378-TCDD	100	100	100	100	100
^{13}C-2378-TCDF	100	100	100	100	100
^{13}C-12378-PeCDD	100	100	100	100	100
^{13}C-12378-PeCDF	100	100	100	100	100
^{13}C-23478-PeCDF	100	100	100	100	100
^{13}C-123678-HxCDD	100	100	100	100	100
^{13}C-123478-HxCDD	100	100	100	100	100
^{13}C-123478-HxCDF	100	100	100	100	100
^{13}C-123678-HxCDF	100	100	100	100	100
^{13}C-123789-HxCDF	100	100	100	100	100
^{13}C-234678-HxCDF	100	100	100	100	100
^{13}C-1234678-HpCDD	100	100	100	100	100
^{13}C-1234678-HpCDF	100	100	100	100	100
^{13}C-1234789-HpCDF	100	100	100	100	100
^{13}C-OCDD	200	200	200	200	200
Cleanup Standards					
^{37}Cl-2378-TCDD	0.25	2	10	40	200
Injection Standards					
^{13}C-1234-TCDD	100	100	100	100	100
^{13}C-123789-HxCDD	100	100	100	100	100

TABLE 6: METHOD 1613B LCS LIMITS

LCS Recovery Limits		
Analyte	**Amount Spiked**	**Limit**
	(pg/uL)	**(pg/uL)**
2378-TCDD	10	6.7-15.8
12378-PeCDD	50	35-71
123478-HxCDD	50	35-82
123678-HxCDD	50	38-67
123789-HxCDD	50	32-81
1234678-HpCDD	50	35-70
OCDD	100	78-144
2378-TCDF	10	7.5-15.8
12378-PeCDF	50	40-67
23478-PeCDF	50	34-80
123478-HxCDF	50	36-67
123678-HxCDF	50	42-65
123789-HxCDF	50	39-65
234678-HxCDF	50	35-78
1234678-HpCDF	50	41-61
1234789-HpCDF	50	39-69
OCDF	100	63-170
^{13}C-2378-TCDD	100	20-175
^{13}C-12378-PeCDD	100	21-227
^{13}C-123478-HxCDD	100	21-193
^{13}C-123678-HxCDD	100	25-163
^{13}C-1234678-HpCDD	100	26-166
^{13}C-OCDD	200	26-397
^{13}C-2378-TCDF	100	22-152
^{13}C-12378-PeCDF	100	21-192
^{13}C-23478-PeCDF	100	13-328
^{13}C-123478-HxCDF	100	19-202
^{13}C-123678-HxCDF	100	21-159
^{13}C-123789-HxCDF	100	17-205
^{13}C-234678-HxCDF	100	22-176
^{13}C-1234678-HpCDF	100	21-158
^{13}C-1234789-HpCDF	100	20-186
^{37}Cl-2378-TCDD	10	3.1-19.1

TABLE 7: METHOD 1613B ES (SAMPLES & LMB) RECOVERY LIMITS

Compound Name	Amount Spiked (pg/µL)	Limits %
$^{13}C_{12}$-2,3,7,8-TCDD	100	25 - 164
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	25 - 181
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	32 - 141
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	28 - 130
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	23 - 140
$^{13}C_{12}$-OCDD	200	17 - 157
$^{13}C_{12}$-2,3,7,8-TCDF	100	24 - 169
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	24 - 185
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	21 - 178
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	26 - 152
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	26 - 123
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	28 - 136
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	29 - 147
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	28 - 143
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	26 - 138
$^{37}Cl_4$-2,3,7,8-TCDD	10	35 - 197

TABLE 8: METHOD 1613B CONTINUING CALIBRATION LIMITS

Compound Name	CCAL (pg/µL)	Limits (pg/µL)	Compound Name	CCAL (pg/µL)	Limits (pg/µL)
2,3,7,8-TCDD	10	7.8 - 12.9	$^{13}C_{12}$-2,3,7,8-TCDD	100	82 - 121
1,2,3,7,8-PeCDD	50	39 - 65	$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	62 - 160
1,2,3,4,7,8-HxCDD	50	39 - 64	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	85 - 117
1,2,3,6,7,8-HxCDD	50	39 - 64	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	85 - 118
1,2,3,7,8,9-HxCDD	50	41 - 61	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	72 - 138
1,2,3,4,6,7,8-HpCDD	50	43 - 58	$^{13}C_{12}$-OCDD	200	96 - 415
OCDD	100	79 - 126	$^{13}C_{12}$-2,3,7,8-TCDF	100	71 - 140
2,3,7,8-TCDF	10	8.4 - 12	$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	76 - 130
1,2,3,7,8-PeCDF	50	41 - 60	$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	77 - 130
2,3,4,7,8-PeCDF	50	41 - 61	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	76 - 131
1,2,3,4,7,8-HxCDF	50	45 - 56	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	70 - 143
1,2,3,6,7,8-HxCDF	50	44 - 57	$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	73 - 137
2,3,4,6,7,8-HxCDF	50	44 - 57	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	74 - 135
1,2,3,7,8,9-HxCDF	50	45 - 56	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	78 - 129
1,2,3,4,6,7,8-HpCDF	50	45 - 55	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	77 - 129
1,2,3,4,7,8,9-HpCDF	50	43 - 58	$^{37}Cl_4$-2,3,7,8-TCDD	10	7.9 - 12.7
OCDF	100	63 - 159			

TABLE 9: METHOD 1613B RELATIVE RETENTION TIME LIMITS

Compound	RRT Reference	RRT Limits
2,3,7,8-TCDD	13C -2,3,7,8-TCDD	0.999 - 1.002
1,2,3,7,8-PeCDD	13C -1,2,3,7,8-PeCDD	0.999 - 1.002
1,2,3,4,7,8-HxCDD	13C -1,2,3,4,7,8-HxCDD	0.999 - 1.001
1,2,3,6,7,8-HxCDD	13C -1,2,3,6,7,8,-HxCDD	0.997 - 1.003
1,2,3,7,8,9-HxCDD	13C -1,2,3,6,7,8,-HxCDD	0.997 - 1.016
1,2,3,4,6,7,8-HpCDD	13C -1,2,3,4,6,7,8-HpCDD	0.999 - 1.001
OCDD	13C –OCDD	0.999 - 1.001
2,3,7,8-TCDF	13C -2,3,7,8-TCDF	0.999 - 1.003
1,2,3,7,8-PeCDF	13C -1,2,3,7,8-PeCDF	0.999 - 1.002
2,3,4,7,8-PeCDF	13C -2,3,4,7,8-PeCDF	0.999 - 1.002
1,2,3,4,7,8-HxCDF	13C -1,2,3,4,7,8-HxCDF	0.999 - 1.001
1,2,3,6,7,8-HxCDF	13C -1,2,3,6,7,8-HxCDF	0.996 - 1.004
2,3,4,6,7,8-HxCDF	13C -2,3,4,6,7,8,-HxCDF	0.999 - 1.001
1,2,3,7,8,9-HxCDF	13C -1,2,3,7,8,9-HxCDF	0.999 - 1.001
1,2,3,4,6,7,8-HpCDF	13C -1,2,3,4,6,7,8-HpCDF	0.999 - 1.001
1,2,3,4,7,8,9-HpCDF	13C -1,2,3,4,7,8,9-HpCDF	0.999 - 1.001
OCDF	13C –OCDD	1.002 - 1.011
13C -2,3,7,8-TCDD	13C -1,2,3,4-TCDD	0.986 - 1.053
13C -1,2,3,7,8-PeCDD	13C -1,2,3,4-TCDD	0.849 - 1.416
13C -1,2,3,4,7,8-HxCDD	13C -1,2,3,7,8,9-HxCDD	0.980 - 1.003
13C -1,2,3,6,7,8-HxCDD	13C -1,2,3,7,8,9-HxCDD	0.983 - 1.005
13C -1,2,3,4,6,7,8-HpCDD	13C -1,2,3,7,8,9-HxCDD	1.068 - 1.092
13C –OCDD	13C -1,2,3,7,8,9-HxCDD	1.050 - 1.329
13C -2,3,7,8-TCDF	13C -1,2,3,4-TCDD	0.904 - 1.084
13C -1,2,3,7,8-PeCDF	13C -1,2,3,4-TCDD	0.893 - 1.318
13C -2,3,4,7,8-PeCDF	13C -1,2,3,4-TCDD	0.869 - 1.384
13C -1,2,3,4,7,8-HxCDF	13C -1,2,3,7,8,9-HxCDD	0.960 - 0.986
13C -1,2,3,6,7,8-HxCDF	13C -1,2,3,7,8,9-HxCDD	0.962 - 0.988
13C -2,3,4,6,7,8,-HxCDF	13C -1,2,3,7,8,9-HxCDD	0.957 - 1.019
13C -1,2,3,7,8,9-HxCDF	13C -1,2,3,7,8,9-HxCDD	0.973 - 1.043
13C -1,2,3,4,6,7,8-HpCDF	13C -1,2,3,7,8,9-HxCDD	1.026 - 1.068
13C -1,2,3,4,7,8,9-HpCDF	13C -1,2,3,7,8,9-HxCDD	1.050 - 1.144
37Cl -2,3,7,8-TCDD	13C -1,2,3,4-TCDD	0.988 - 1.051

Due to the use of the DB-5ms column, some compounds exhibit slightly different elution times, resulting in RRT limits which vary from the method. The widths of the limits are the same as the method, only the center of the window has been adjusted to the DB-5ms's elution times.

TABLE 10: Method 8290 IS assignments

Internal Standard References
Method 8290

Analytes	Internal Standards
2378-TCDD	^{13}C-2378-TCDD
12378-PeCDD	^{13}C-12378-PeCDD
123478-HxCDD	^{13}C-123678-HxCDD
123678-HxCDD	^{13}C-123678-HxCDD
123789-HxCDD	^{13}C-123678-HxCDD
1234678-HpCDD	^{13}C-1234678-HpCDD
OCDD	^{13}C-OCDD
2378-TCDF	^{13}C-2378-TCDF
12378-PeCDF	^{13}C-12378-PeCDF
23478-PeCDF	^{13}C-12378-PeCDF
123478-HxCDF	^{13}C-123678-HxCDF
123678-HxCDF	^{13}C-123678-HxCDF
123789-HxCDF	^{13}C-123678-HxCDF
234678-HxCDF	^{13}C-123678-HxCDF
1234678-HpCDF	^{13}C-1234678-HpCDF
1234789-HpCDF	^{13}C-1234678-HpCDF
OCDF	^{13}C-OCDD
Extraction Standards	**Injection Standards**
^{13}C-2378-TCDD	^{13}C-1234-TCDD
^{13}C-12378-PeCDD	^{13}C-1234-TCDD
^{13}C-123678-HxCDD	^{13}C-123789-HxCDD
^{13}C-1234678-HpCDD	^{13}C-123789-HxCDD
^{13}C-OCDD	^{13}C-123789-HxCDD
^{13}C-2378-TCDF	^{13}C-1234-TCDD
^{13}C-12378-PeCDF	^{13}C-1234-TCDD
^{13}C-123678-HxCDF	^{13}C-123789-HxCDD
^{13}C-1234678-HpCDF	^{13}C-123789-HxCDD
Injection Standards	
^{13}C-1234-TCDD	NA
^{13}C-123789-HxCDD	NA

TABLE 11: 8290 Retention time limits

Retention Time Limits
Method 8290

Analytes	Description	Limits
2378-TCDD	2,3,7,8-substituted congeners, which have an isotopically-labeled standard present in the sample extract	must be within -1 to +3 seconds of the isotopically-labeled standard
12378-PeCDD		
123678-HxCDD		
123789-HxCDD		
1234678-HpCDD		
OCDD		
2378-TCDF		
12378-PeCDF		
123678-HxCDF		
123789-HxCDF		
1234678-HpCDF		
123478-HxCDD	2,3,7,8-substituted compounds that do not have an isotopically-labeled standard present in the sample extract	must fall within 0.005 retention time units of the relative retention time as determined from the daily routine calibration
23478-PeCDF		
123478-HxCDF		
234678-HxCDF		
1234789-HpCDF		
OCDF		
Total TCDDs	Non-2,3,7,8-substituted target compounds	must be within the corresponding homologous retention time windows established by analyzing the column performance check solution, relative to an isotopically-labeled standard in the sample
Total PeCDDs		
Total HxCDDs		
Total HpCDDs		
Total TCDFs		
Total PeCDFs		
Total HxCDFs		
Total HpCDFs		
^{13}C-2378-TCDD	Isotopically-labeled standards	No method limits: allowed to shift as long as the predicted RT of the native window defining isomers established by analyzing the column performance check solution remain within the descriptor switching time
^{13}C-12378-PeCDD		
^{13}C-123678-HxCDD		
^{13}C-1234678-HpCDD		
^{13}C-OCDD		
^{13}C-2378-TCDF		
^{13}C-12378-PeCDF		
^{13}C-123678-HxCDF		
^{13}C-1234678-HpCDF		
^{13}C-1234-TCDD		
^{13}C-123789-HxCDD		

TABLE 12: METHOD TO-9A MINIMUM REQUIREMENTS FOR INITIAL AND DAILY CALIBRATION

Unlabeled Analytes	ICAL (RSD)	CVS (%D)
2,3,7,8-TCDD	25	25
2,3,7,8-TCDF	25	25
1,2,3,7,8-PeCDD	25	25
1,2,3,7,8-PeCDF	25	25
2,3,4,7,8-PeCDF	25	25
1,2,4,5,7,8-HxCDD	25	25
1,2,3,6,7,8-HxCDD	25	25
1,2,3,7,8,9-HxCDD	25	25
1,2,3,4,7,8-HxCDF	25	25
1,2,3,6,7,8-HxCDF	25	25
1,2,3,7,8,9-HxCDF	25	25
2,3,4,6,7,8-HxCDF	25	25
1,2,3,4,6,7,8-HpCDD	25	25
1,2,3,4,6,7,8-HpCDF	25	25
OCDD	25	25
OCDF	30	30
Internal Standards		
13C-2,3,7,8-TCDD	25	25
13C-1,2,3,7,8-PeCDD	30	30
13C-1,2,3,6,7,8-HxCDD	25	25
13C-1,2,3,4,6,7,8-HpCDD	30	30
13C-OCDD	30	30
13C-2,3,7,8-TCDF	30	30
13C-1,2,3,7,8-PeCDF	30	30
13C-1,2,3,4,7,8-HxCDF	30	30
13C-1,2,3,4,6,7,8-HpCDF	30	30
Surrogate Sampling Standards		
37Cl-2,3,7,8-TCDD	25	25
13C-2,3,4,7,8-PeCDF	25	25
13C-1,2,3,4,7,8-HxCDD	25	25
13C-1,2,3,4,7,8-HxCDF	25	25
13C-1,2,3,4,7,8,9-HpCDF	25	25

TABLE 13: METHOD HOLDING TIMES

Method	Collection to Extraction	Extraction to Analysis
8290A	None	
1613B	365 days	365 days
DLM02.2	365 days	365 days
M23	30 days	45 days
TO-9a	7 days	40 days
CBC01.2	35 days collect to analysis	
1668A/C	365 days	365 days

FIGURE 1: 2378-TCDD CHROMATOGRAPHIC SEPARATION

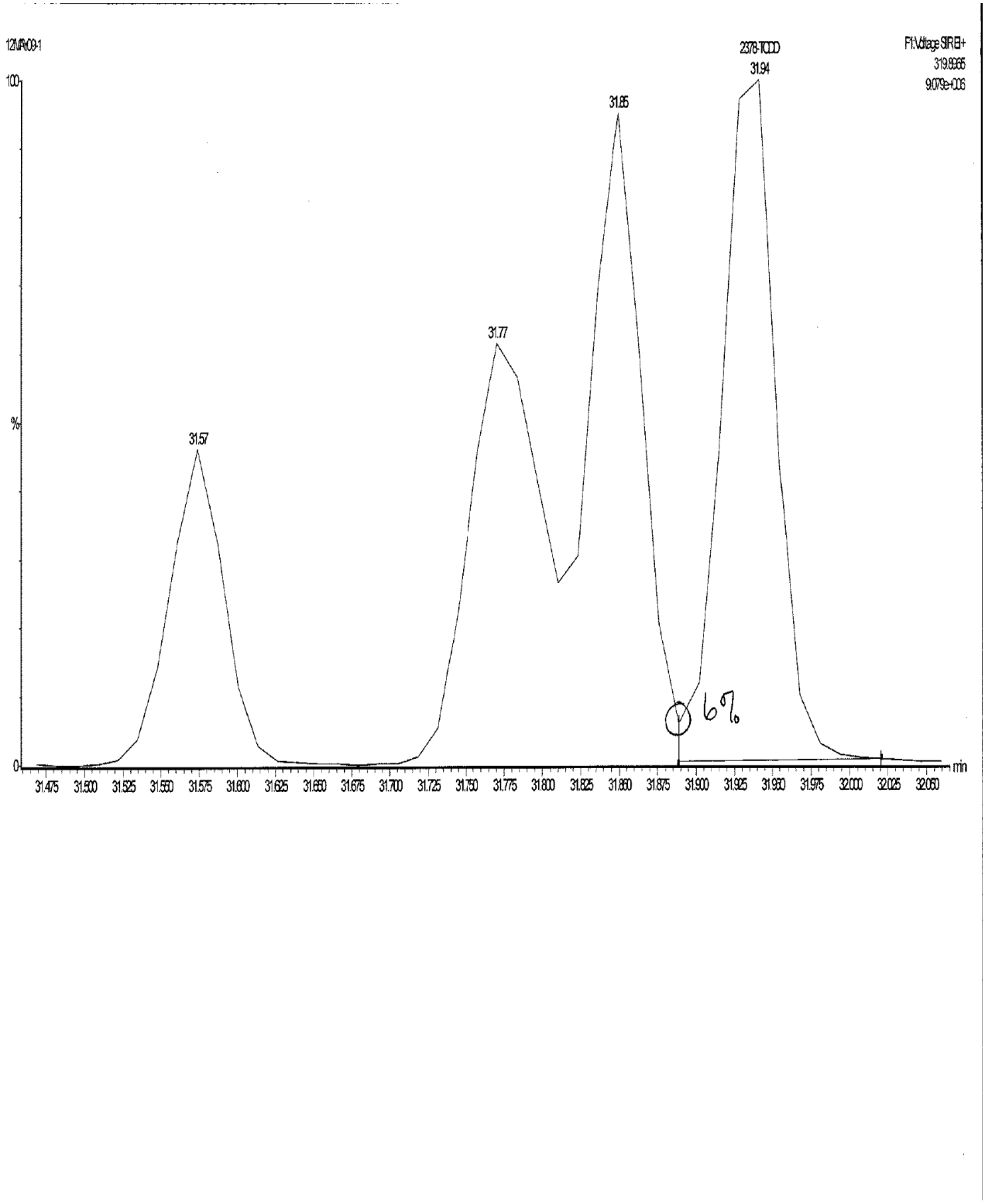

FIGURE 2: INSTRUMENT RESOLVING POWER (EXAMPLE)

Experiment Calibration Report **MassLynx 4.1** Page 1 of 1

File: Experiment: dioxin_db5ms.exp Reference: pfk.ref Function: 1 @ 200 (ppm)

Printed: Saturday, June 09, 2012 10:43:58 Eastern Standard Time

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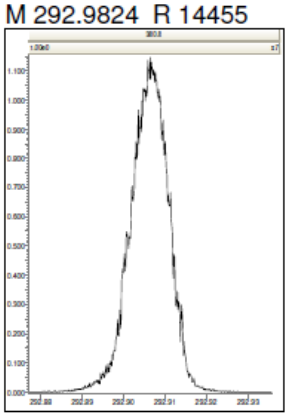

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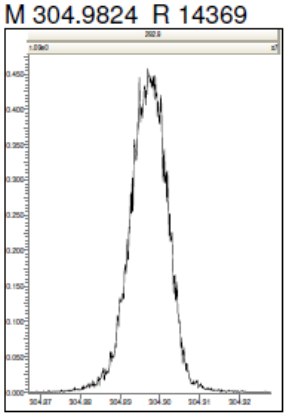

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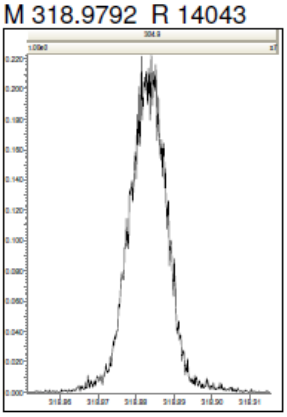

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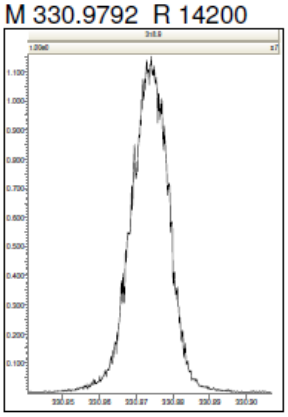

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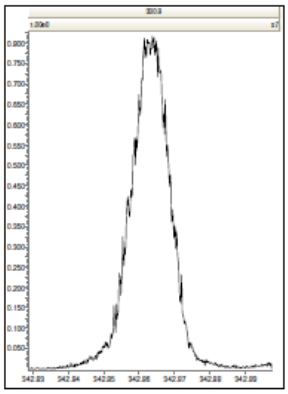

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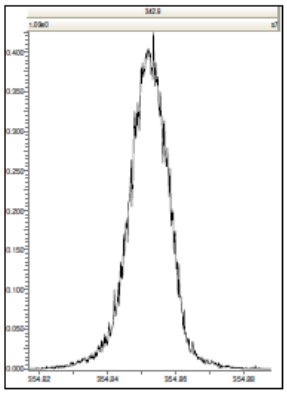

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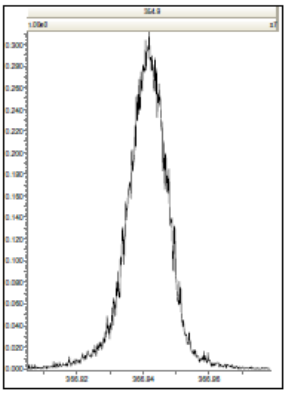

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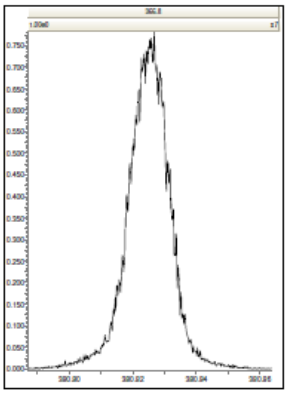

1) Scope & Applicability

1.1. This procedure is used to determine the concentrations of Semi-Volatile Organic This procedure is used to determine the concentrations of Semi-Volatile Organic Compounds in water, soil, and tissue matrices using EPA Method 8270D SIM. This procedure may also be applicable to various miscellaneous waste samples. Table 1A lists compounds that may be determined by this method and the standard method reporting limits (MRLs) in water, soil, and tissue. Table 1B lists additional low-level MRLs in soil. Alkylated PAHs listed in Table 1C may also be determined using this procedure. The MDLs that have been achieved are listed in the DQO tables and are subject to change as MDL studies are repeated.

1.2. The procedure is intended for samples containing trace-level amounts of target compounds. Samples containing high concentrations of target analyte will not be analyzed undiluted. All MRLs will be adjusted in accordance with this dilution. Therefore, samples containing high levels of PAHs will not be analyzed to achieve the optimum MRLs for the analysis.

1.3. This procedure can be used to quantitate most neutral organic compounds that are soluble in methylene chloride and capable of being eluted without derivatization as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone phase. This procedure is optimized for the analysis of polynuclear aromatic hydrocarbons.

1.4. Compounds other than those listed in Tables 1 and 1A may be analyzed. However, analytes not summarized in Table 1 have not been validated with a method detection limit study. Therefore, the lab will not use this procedure to analyze for non-routine analytes unless a similar analyte has been validated with a MDL study. As a general rule, the MRL for these compounds will equal the MRL of a similar compound in the routine analyte list. Results will not be reported below this estimated MRL.

1.5. In cases where there is a project-specific quality assurance plan (QAPP), the project manager identifies and communicates the QAPP-specific requirements to the laboratory. In general, project specific QAPP's supersede method specified requirements. An example of this are projects falling under DoD ELAP. QC requirements defined in the SOP *Department of Defense Projects – Laboratory Practices and Project Management (*ADM-DOD) may supersede the requirements defined in this SOP.

2) Summary of Procedure

2.1 This method provides Gas Chromatography/Mass Spectrometry (GC/MS) conditions for the detection of Semi-volatile Organic Compounds. Prior to the use of this method, water samples are extracted using EPA Method 3511 (EXT-3511), 3520 (EXT-3520) or 3535 (EXT-3535) and soil/solid samples are extracted using EPA Method 3541 (EXT-3541) or 3546 (EXT-3546).

2.2 All soil, tissue, and colored water extracts will be cleaned using EPA Method 3630 (SOC-3630) prior to analysis. In cases where project-specified analytes are not amenable to silica gel cleanup, gel permeation chromatography (SOC-3640) will be used for cleanup prior to analysis.

2.3 An aliquot of the extract is injected into the gas chromatograph (GC). The compounds are separated on a fused silica capillary column. Compounds of interest are detected by a mass selective detector in the selective ion mode. Identification of the analytes of interest is performed by comparing the retention times of the analytes with the respective retention times of an authentic standard, and by comparing mass spectra of

analytes with mass spectra of reference materials. Quantitative analysis is performed by using the authentic standard to produce a response factor and calibration curve, and using the calibration data to determine the concentration of an analyte in the extract. The concentration in the sample is calculated using the sample weight or volume and ct volume.

3) Definitions

3.1 For laboratory definitions applicable to most analyses, refer to the SOP for *Sample Batches*.

4) Responsibilities

4.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. This demonstration is in accordance with the training program of the laboratory. Final review and sign-off of the data is performed by the department supervisor/manager or designee.

4.2 It is the responsibility of the department supervisor/manager to document analyst training .and method proficiency, as described in: *Employee Training and Orientation* (ADM-TRAIN).

5) Interferences

5.1 Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation of the samples. Corrective action should be taken to eliminate the interferences.

5.2 Contamination can occur from trace levels of target compounds remaining on any glassware or equipment used on samples containing high levels of analytes. Glassware is cleaned according to the SOP *Organic Extractions Glassware Cleaning* (EXT-GC) and rinsed with the extraction solvent prior to use.

5.3 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. When carryover is detected in the instrument blanks, changing the autosampler rinse vials, cleaning the injection port and baking out the instrument has been shown to eliminate or reduce the contamination. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of an instrument blank to check for carryover.

6) Safety

6.1 Chemicals, reagents and standards must be handled as described in the ALS safety policies, approved methods and in SDS where available. Refer to the ALS Chemical Hygiene Plan and the appropriate SDS prior to beginning this method.

6.2 This method uses Dichloromethane, a known human carcinogen. Refer to the methylene chloride policy document, ENV-HSE-NA-EX-006-EN for proper handling.

G:\SAFETY\TRAINING\Methylene Chloride\Methylene Chlor ide - NA 031419.pdf.

7) Sample Collection, Containers, Preservation, and Storage

7.1 Containers used to collect samples should be purchased pre-cleaned containers. Alternatively, containers used to collect samples for the determination of semivolatile organic compounds may be soap and water washed followed by methanol (or isopropanol) rinsing. The sample containers should be of glass or Teflon and have screw-top covers with Teflon liners. In situations where Teflon is not available, solvent-rinsed aluminum foil may be used as a liner. Highly acidic or basic samples may react with the aluminum foil, causing eventual contamination of the sample. Plastic containers or lids may not be used for the storage of samples due to the possibility of sample contamination from the phthalate esters and other hydrocarbons within the plastic.

7.2 Water and soil samples should be iced or refrigerated at 0-6ºC from time of collection until extraction. Tissue samples are stored frozen until extraction.

7.3 Water samples must be extracted within 7 days. Soil samples must be extracted within 14 days. Holding times for tissues are typically defined by project specifications, otherwise tissue samples may be held frozen up to one year before extraction. Extracts are stored at -10ºC and must be analyzed within 40 days following extraction.

8) Standards, Reagents, and Consumable Materials

8.1 Reagent grade chemicals shall be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lowering the accuracy of the determination. The preparation for all laboratory prepared reagents and solutions must be documented in a laboratory logbook. Refer to the SOP *Reagent/Standards Login and Tracking,* for the complete procedure and documentation requirements.

8.2 Solvents: Acetone, methylene chloride, methanol, and other appropriate solvents.

8.3 Stock Standard Solutions

8.3.1 Commercially prepared stock standards are typically used when available at a concentration of 100 µg/ml or more. They must be A2LA or ISO9000 certified by the manufacturer. Standard concentrations can be verified by comparison versus an independently prepared standard. Alternatively, prepare stock standard solutions at a concentration of 1000 µg/ml by dissolving 0.0100 g of reference material in methylene chloride or other suitable solvent and diluting to volume in a 10mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard.

8.3.2 Transfer stock standard solutions into amber Teflon™ sealed crimp top autosampler vials. Store at -10ºC and protect from light, or store as recommended by the manufacturer. Standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

8.3.3 Unopened stock standards and neat materials have an expiration date equal to the manufacturer's recommendation. Neat material that does not have a manufacturer's recommended expiration date should be replaced after five years. Stock standard solutions received in sealed ampoules with manufacture expiration dates in excess of 1 year have an expiration date of 1 year from the date of opening the sealed ampoule.

8.3.4 For the alkylated PAH option, a crude oil SRM 1582 is used. This SRM is a petroleum crude oil which has been cleaned up using GPC and silica gel cleanup procedures. All of the homologs are present in the SRM.

8.4 Internal Standard Solutions - The internal standards are naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12} (See Table 3 for corresponding compounds). The nominal concentration of the standard is 20 ng/µL. See Table 5 for standard preparation instructions. Each 1 ml of sample extract undergoing analysis should be spiked with 10 µL of the internal standard solution, resulting in a concentration of 0.2 ng/µL of each internal standard. Store at -10ºC or less when not being used. When using premixed certified solutions, store according to the manufacturer's recommendations.

8.5 GC/MS Tuning Standard - A methylene chloride solution containing 3 ng/mL of decafluorotriphenylphosphine (DFTPP). The standard also contains 3 ng/mL of pentachlorophenol to verify injection port inertness and GC column performance. This injection is acquired in full scan mode and evaluated in accordance with the method specified criteria. Store at -10ºC or less when not being used, or store according to the manufacturer's recommendations.

8.6 Calibration Standards

8.6.1 Prepare an intermediate surrogate standard by diluting 50 µl of the 4000 ppm stock (M-8270-SS) and 40 µl of a 5000 ppm stock (S-64011), both from AccuStandard to 2.0 mL in DCM, resulting in 100 µg/mL solution. An intermediate standard is prepared by combining a PAH mix obtained from Absolute at 100 ppm with the surrogate intermediate standard. See Table 5 for preparation instructions.

8.6.2 A minimum of six initial calibration standards should be prepared from the intermediate standard (note that a seven point calibration is recommended). One of the calibration standards should be at a concentration at or below the method reporting limit. The others should correspond to the range of concentrations found in samples, but should not exceed the working range of the GC/MS system. Each 1 mL aliquot of calibration standards should be spiked with 10 µL of the internal standard solution prior to analysis.

8.6.3 All calibration standards should be stored at -10ºC or less and should be freshly prepared from stocks every 365 days, or sooner if check standards indicate a problem.

8.6.4 The following calibration standards are recommended: 0.002 ng/µl, 0.004 ng/µl, 0.008 ng/µl, 0.02 ng/µl, 0.1 ng/µl, 0.2 ng/µl, 0.4 ng/µl, 1.0 ng/µl, 1.6 ng/µl and 2.0 ng/µl. See Table 5 for preparation instructions.

8.6.5 The independent calibration verification (ICV) standard is prepared at a nominal 0.4 ng/µL concentration from stock solutions (see Table 5). The ICV is prepared at the time of initial calibration and is stored at 4 ± 2ºC.

8.6.6 The daily calibration standard (CCV) is prepared at a nominal 0.4 ng/µL concentration from stock solutions (see Table 5). The CCV is prepared weekly and is stored at 0-6ºC.

8.7 QC Standards

8.7.1 Surrogates: Prepare a working spiking solution in methanol containing Fluorene-d_{10}, Fluoranthene-d_10, and Terphenyl-d_{14} at 100 ng/µL. This solution may be combined with the surrogate solution used to monitor analyses for

8270 full list. Aliquots of the solution are spiked into all extracted samples, blanks, and QC samples according to the extraction SOP used.

8.7.2 Matrix Spike Standards: Prepare a working spiking solution in methanol containing all analytes of interest ("full list spike"). All analytes are prepared at 25 ng/µl. Aliquots of the solution are spiked into the selected QC aliquots according to the extraction SOP used.

9) Apparatus and Equipment

9.1 Gas Chromatograph/Mass Spectrometer System

9.1.1 Gas Chromatograph - Each GC/MS system is equipped with an Agilent GC oven/column that is cooled to ambient temperatures. The injector is capable of split/splitless or large volume and attached directly to the GC. The column is directly interfaced with the MSD. Each system is controlled by the Agilent-MSDOS ChemStation software.

9.1.2 Column: 5% Diphenyl, 95% Dimethyl Polysiloxane - 30 m x 0.25 mm ID x 0.25 µm film thickness silicone-coated fused-silica capillary column or equivalent. Recommended: Phenomenex with Integra-guard, catalog #7HG-G010-11-GGC.

9.1.3 Mass Spectrometer - Capable of scanning from 35 to 500 amu every 1 second or less, using 70 volts (nominal) electron energy in the electron impact ionization mode, and capable of operating in the SIM mode.

9.1.4 GC/MS Interface - Any GC-to-MS interface that gives acceptable calibration points for each compound of interest and achieves acceptable tuning performance criteria may be used.

9.1.5 Data System - A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits.

9.1.6 Instrumental systems are identified as follows:

Instrument I.D.	Analytical System	Injector
MS14	6890/5973	Optic 2
MS20	6890N/5973	7683
MS25	7890A/5975C	7693

9.2 Appropriate analytical balance (0.0001 g), volumetric flasks, syringes, vials, and bottles for standards preparation.

10) Preventative Maintenance

10.1 All maintenance activities are recorded in a maintenance logbook kept for each instrument. Pertinent information (serial numbers, instrument I.D., etc.) must be in the logbook. Maintenance entries should include date, symptom of problem, corrective actions, and description of maintenance, date, and name. The log should contain a reference to return to analytical control.

10.2 Carrier gas - Inline purifiers or scrubbers should be in place for all sources of carrier gas. These are selected to remove water, oxygen, and hydrocarbons. Purifiers should be changed as recommended by the supplier.

10.3 Gas Chromatograph

10.3.1 Whenever GC maintenance is performed, care should be taken to minimize the introduction of air or oxygen into the column. Injection port maintenance includes changing the injection port liner, seal, washer, O-ring, septum, column ferrule, and autosampler syringe as needed. Liners and seals should be changed when recent sample analyses predict a problem with chromatographic performance. In some cases liners and seals may be cleaned and re-used.

10.3.2 Clipping off a small portion of the head of the column often improves chromatographic performance. When cutting off any portion of the column, make sure the cut is straight and “clean” (uniform, without fragmentation) by using the proper column cutting tool.

10.3.3 Over time, the column will exhibit poorer overall performance, as contaminated sample matrices are analyzed. The length of time for this to occur will depend on the samples analyzed. When a noticeable decrease in column performance is evident and other maintenance options do not result in improvement, the column should be replaced. This is especially true when evident in conjunction with calibration difficulties.

10.4 Mass Spectrometer

10.4.1 For units under service contract, certain maintenance is performed by instrument service staff, including pump oil changed, vacuuming boards, etc., as recommended by the manufacturer.

10.4.2 MS source cleaning should be performed as needed, depending on the performance of the unit. This may be done by the analyst or by instrument service staff.

10.4.3 Tune the MS as needed to result in consistent and acceptable performance while meeting the required ion abundance criteria.

11) Procedure

11.1 Sample Preparation

11.1.1 Water, soil, tissue and waste samples are prepared using the appropriate extraction and cleanup methods (refer to SOPs) and may be screened by GC/FID (see SOP SOC-SCR).

11.1.2 An appropriate cleanup procedure may be performed depending on the sample matrix and target analytes. Perform cleanups on all soil, tissue, and colored water extracts using method 3630 (silica gel cleanup, SOP EXT-3630) prior to

analysis. In cases where project-specified analytes are not amenable to silica gel cleanup, perform method 3640 GPC cleanup (SOP EXT-3640) prior to analysis.

11.1.3 Following sample preparation, sample extracts are then transferred to the extract cold storage unit. Extracts must be analyzed within 40 days of extraction.

11.2 The recommended GC/MS operating conditions:

Ion dwell time:	10 – 50 msec per ion
Initial temperature:	40ºC, hold for 1 minute
Temperature program:	40-140ºC at 30ºC /min hold for 0 minutes
Temperature program:	140-270ºC at 10ºC /min hold for 4 minutes
Final temperature:	270-320ºC at 20º /min, hold for 1.10 minutes
Injector temperature:	320ºC
Detector interface temp:	300ºC
Injector:	splitless, electronic pressure control with pulse
Sample volume:	1 - 5.0 µL (will vary by instrument)
Carrier gas:	helium at 1.2ml/min (constant flow)

11.3 Selected Ion Acquisition

11.3.1 Determine the ions to be monitored for the compounds of interest. Refer to Table 2 for characteristic ions. At a minimum, 2 ions should be monitored for each compound, and 3 monitored for compounds with more complex fragmentation patterns. Set the SIM windows in order to monitor the correct ions at the correct time, based on chromatographic elution of the compounds. This can be setup by analyzing a standard using a full scan analysis and using the GC conditions of the SIM analysis. This analysis will give retention time and spectral information for determining the location of start times for the SIM groups or windows. This is often referred to as a "locator" analysis.

11.3.2 Select the dwell times to be used for each group of ions to be monitored. Dwell times should be selected in order to provide a sufficient number of measurements across the chromatographic peak to accurately define the peak shape. Too few measurements across the peak will result in poor definition of the peak and subsequently result in poor accuracy and precision of results. Too many measurements across the peak may result in inconsistent detector behavior over the calibration range. Significant differences in dwell times may also affect sensitivity.

11.4 Initial Calibration

NOTE: The calibration procedure(s) and options chosen must follow the ALS protocols. Any exceptions to the calibration procedures detailed in the ALS SOP for *Calibration of Instruments for Organics Chromatographic Analyses* (SOC-CAL) are described as follows:

11.4.1 Prior to calibration, analyze the GC/MS tuning standard using instrument conditions used for calibration. Obtain the spectrum for evaluation using one of the following options:

- Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to elution of DFTPP. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the tune peak or part of any other peak eluting close to the tune peak.

- Use one scan at the apex of the peak. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the tune peak or part of any other peak eluting close to the tune peak.
- Use one scan either directly preceding or following the apex of the peak. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the tune peak or part of any other peak eluting close to the tune peak.
- Use the average across the entire peak up to a total of 5 scans. Peak integration must be consistent with standard operating procedure. If the peak is wider than 5 scans, the tune will consist of the peak apex scan and the two scans immediately preceding and following the apex. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the tune peak or part of any other peak eluting close to the tune peak.

11.4.2 Evaluate the spectrum obtained for DFTPP against the tuning criteria in Table 4 or 4A (dependent upon instrumentation). The GC/MS must meet the DFTPP ion abundance criteria prior to further analyses. Pentachlorophenol must be present at the normal response, with no visible peak tailing, as demonstrated by the peak tailing factors.

11.4.3 The acceptance criteria for the peak tailing factor for pentachlorophenol is <5.0. If excessive tailing or poor chromatography is noted, the injection port may require cleaning. It may also be necessary to remove the first 15-30 cm of the GC column. If hardware tuning criteria cannot be met, the source may need cleaning, filaments replaced or other maintenance.

11.4.4 The internal standards should permit most of the components of interest in the chromatogram to have retention times of 0.80-1.20 relative to one of the internal standards. Refer to Table 3 for internal standards and corresponding analytes assigned for quantitation. Use the base peak ion from the specific internal standard as the primary ion for quantitation (See Table 2). If interferences are noted, use the next most intense ion as the quantitation ion (i.e. for acenaphthene-d_{10}, use 162 m/z for quantitation).

11.4.5 Analyze each calibration standard (containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each compound (as indicated in Table 2). Calculate response factors (RFs) for each compound relative to one of the internal standards as follows:

$$RF = (A_x C_{is})/(A_{is} C_x)$$

Where:
A_x = Area of the characteristic ion for compound being measured.
A_{is} = Area of the characteristic ion for specific internal standard.
C_{is} = Concentration of the specific internal standard (ng/µL).
C_x = Concentration of the compound being measured (ng/µL).

11.4.6 Evaluate the response factor for the low calibration standard. The minimum acceptable average RF for these compounds is given in Table 2. If they are not acceptable, perform GC maintenance.

11.4.7 The percent relative standard deviation (%RSD) should be less than 20% for each compound. The relative retention times of each compound in each calibration run should agree within 0.06 relative retention time units.

$$\%RSD = \frac{SD}{\overline{RF}} \; x \; 100$$

Where:

RSD = relative standard deviation.
RF = mean of 5 initial RFs for a compound.
SD = standard deviation of average RFs for a compound.

$$SD = \sqrt{\sum_{i=1}^{N} \frac{(RF_i - RF)^2}{N - 1}}$$

Where:

RF_i = RF for each of the 5 calibration levels
N = Number of RF values (i.e., 5)

11.4.8 If the %RSD for a compound is >20%, then alternative calibration models should be used. See the SOP *Calibration of Instruments for Organics Chromatographic Analysis* (SOC-CAL) for further guidance.

11.4.9 When analysis for alkylated PAHs is to be performed, follow the calibration procedure given in Appendix A.

11.5 Review of calibration curve

11.5.1 The calibration curve must be reviewed to ensure it represents the calibration data. This is done by re-fitting each calibration level against the true concentration of each calibration standard. See the SOP *Calibration of Instruments for Organics Chromatographic Analysis* (SOC-CAL) for further guidance.

11.5.2 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 50% of the average of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. The resolution should be verified on the mid-point concentration of the initial calibration as well as the laboratory designated continuing calibration verification level if closely eluting isomers are to be reported

11.6 Independent Calibration Verification

11.6.1 Following initial calibration, analyze an ICV standard. The ICV solution must contain all analytes in the calibration standards. Calculate the concentration using the typical procedure used for quantitation. Calculate the percent difference (%D) from the ICV true value. For each compound of interest, the calculated value must be ± 30% of the true value for the initial calibration to be valid.

11.7 Continuing Calibration

11.7.1 Following an acceptable tune, a calibration standard, or standards, at mid-concentration containing all PAH analytes, and all required surrogates, must be analyzed every 12 hours during analysis.

11.7.2 For each compound in the daily calibration standard, a minimum response factor given in Table 2 should be met. If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. 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.

11.7.3 If the percent drift for each compound of interest is less than or equal to 20%, the initial calibration is assumed to be valid. If the criterion is not met (> 20% drift) for any one compound, corrective action must be taken. If no source of the problem can be determined after corrective action has been taken, a new initial calibration must be generated. This criterion must be met before sample analysis begins.

Calculate the percent drift using:

$$\%\,Drift = \frac{C_I - C_c}{C_I} \times 100$$

Where:

C_I = Compound standard concentration.
C_c = Measured concentration using selected quantitation method.

11.7.4 When analysis for alkylated PAHs is to be performed, follow the calibration procedure given in Appendix A.

11.7.5 The internal standard responses and retention times in the calibration check standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from that in the midpoint standard of the most recent initial calibration sequence, the chromatographic system must be inspected for malfunctions and corrective action identified, as required. If the EICP area for any of the internal standards changes by a factor of two (50% to 200%) from that in the midpoint standard of the most recent initial calibration sequence, the chromatographic system must be inspected for malfunctions and corrective action identified, as appropriate.

11.7.6 When corrective action is taken, reanalysis of samples analyzed while the system was malfunctioning is required. Update the reference spectra and retention times in the quantitation database for the instrument method or ID file. The initial calibration average RF or calibration curve is then used in the quantitation of subsequent analyses.

11.7.7 A blank (method blank, GPC blank, or solvent blank) should be analyzed after the CCV to prove the system is free of contaminants. If contaminants are found in a method blank or GPC blank, then a solvent blank should be ran to help isolate the source of contamination.

11.8 GC/MS Analysis

11.8.1 Spike the 1 ml extract obtained from sample preparation with 10 µL of the internal standard solution just prior to analysis. Use the same operating conditions as were used for initial calibration.

11.8.2 If the response for any quantitation ion exceeds the initial calibration curve range of the GC/MS system, extract dilution must take place. Additional internal standard must be added to the diluted extract to maintain the required 0.2 ng/µL of each internal standard in the extracted volume. The diluted extract must be reanalyzed.

11.8.3 Store the extracts at -10ºC or less, protected from light in vials equipped with unpierced Teflon lined septa. Archive extract in freezer for 3 months, or longer if required by client, after analysis in the instrument/date specific storage boxes.

12) QA/QC Requirements

12.1 Initial Precision and Recovery Validation

12.1.1 The accuracy and precision of the procedure must be validated before analyses of samples begin, or whenever significant changes to the procedures have been made. To do this, four water samples are spiked with the LCS spike solution, then prepared and analyzed.

12.2 Method Detection Limits and Method Reporting Limits

12.2.1 A method detection limit (MDL) study must be undertaken before analysis of samples can begin. To establish detection limits that are precise and accurate, the analyst must perform the following procedure. Spike a minimum of seven blank replicates with a MDL spiking solution (at a level below the MRL) for each target analyte, extract, and analyze.

12.2.2 Calculate the average concentration found (x) in µg/mL, and the standard deviation of the concentrations (s) in µg/mL for each analyte. Calculate the MDL for each analyte. Refer to SOP *Performing and Documenting Method Detection Limit Studies and Establishing Limits of detection and Quantification* (CE-QA011/ADM-MDL). The MDL study must be verified annually.

12.3 Limits of Quantification (LOQ)

12.3.1 The laboratory establishes a LOQ for each analyte as the lowest reliable laboratory reporting concentration or in most cases the lowest point in the calibration curve which is less than or equal to the desired regulatory action levels, based on the stated project requirements. Analysis of a standard or extract prepared at the lowest point calibration standard provides confirmation of the established sensitivity of the method. The LOQ recoveries should be within the LCS acceptance limits to verify the data reporting limit. Refer to CE-QA011/ADM-MDL.

12.4 The Method Reporting Limits (MRLs) used at ALS are the routinely reported lower limits of quantitation which take into account day-to-day fluctuations in instrument sensitivity as well as other factors. These MRLs are the levels to which ALS routinely reports results in order to minimize false positive or false negative results. The MRL is normally two to ten times the method detection limit. Current MDLs and LODs can be found in the laboratory Data Quality Objectives.

12.5 Ongoing QC Samples required are described in the ALS-Kelso Quality Assurance Manual and in the SOP for *Sample Batches* (ADM-BATCH). In general, these include:

12.5.1 Method blank - A method blank is extracted and analyzed with every batch of 20 or fewer samples to demonstrate that there are no method interferences. The method blank must demonstrate that interferences from the analytical and

preparation steps minimized. No target analytes should be detected above the MRL in the method blank. For some project specific needs, exceptions may be noted and method blank results above the MRL may be reported for common lab contaminants (phthalate esters, etc.).

Note: DoD requires no analytes detected at > ½ the RL or 1/10 the regulatory limit, whichever is greater. For common laboratory contaminates there should be no detection > the RL.

12.5.2 A lab control sample (LCS) must be extracted and analyzed with every batch of 20 or fewer samples. The LCS will routinely contain the entire target analyte list. The LCS is prepared by spiking a blank with the matrix spike solution, and going through the entire extraction and analysis. Calculate percent recovery (%R) as follows:

$$\%R = X/TV \times 100$$

Where: X = Concentration of the analyte recovered
TV = True value of amount spiked

Compare the %R to LCS acceptance criteria, located in the current ALS-Kelso DQO tables. If the lab control sample (LCS) fails acceptance limits for any of the compounds, the analyst must evaluate the system and calibration. Corrective action must be taken.

12.5.3 A matrix spike/duplicate matrix spike (MS/DMS) must be extracted and analyzed with every batch of 20 or fewer samples. The MS is prepared by spiking a sample aliquot with the matrix spike solution, and going through the entire extraction and analysis. Calculate percent recovery (%R) as follows:

$$\%R = \frac{X - X1}{TV} \times 100$$

Where: X = Concentration of the analyte recovered
X1 = Concentration of unspiked analyte
TV = True value of amount spiked

Calculate Relative Percent Difference (RPD) as:

$$\%RPD = \frac{R1 - R2}{(R1 + R2)/2} \times 100$$

Where: R1 = recovered concentration in the higher result
R2 = recovered concentration in the lower result

Compare the %R and RPD to MS/DMS acceptance criteria, located in the current ALS-Kelso DQO tables. If the MS/DMS recovery is out of acceptance limits for reasons other than matrix effects, corrective action must be taken.

12.5.4 The acceptance limits for the surrogates are given in the current ALS-Kelso DQO tables. If any surrogate recovery is outside acceptance criteria, the sample data must be closely evaluated for possible matrix interferences. If none are present, then corrective action must be taken. The sample should be re-analyzed if instrument factors (calibration, injection port) are suspected. If not, re-extraction and re-analysis is required, except in cases of high recovery and no positive hits in the sample for the analyte class represented by the particular surrogate.

12.6 Corrective action – When a data quality objective is not met, the initial corrective action will include a review of the raw data for potential calculation and/or integration errors. If

this review does not correct the problem, the following corrective actions will be performed.

12.6.1 Method Blank – No target analyte should be detected in a method blank at or above the method reporting limit (1/2 the MRL for DoD projects). If target analytes are detected in the method blank, the sample data must be reviewed for possible laboratory contribution. Detections of target analytes greater than the MRL require a Nonconformity and Corrective Action Report (NCAR). A decision to re-extract the associated samples will depend on the level of the contamination, data quality implications, and the intended use of the data. At a minimum, all positive detections in the associated samples that are not more than 20X the concentration in the blank will be qualified with a "B". Also, as part of the corrective action, the problem will be discussed with the appropriate sample prep personnel in an effort to identify the contamination source.

12.6.2 Laboratory Control Sample – The analysis should include a full list LCS spike. All target analytes will be evaluated. The following cases require corrective action:

- If any analytes do not meet acceptance criteria, the analytical batch should be considered out of control for that analyte. Corrective action may include reinjection to verify the result. If the result is confirmed, a NCAR will be filed and the problem investigated to determine that cause. A decision to re-extract the associated samples will depend on the data quality implications and the intended use of the data, and should involve the Project Chemist and client. If re-extraction is not feasible, all reported results for that analyte will be qualified and the implications will be discussed in the case narrative.
- In cases where a result is outside the upper control criterion, corrective action is only required if that analyte was also detected in field samples. The associated samples with positive results should be re-extracted. In cases where a result is outside the lower control criterion, the associated samples should be re-extracted. If re-extraction is not feasible, all reported results for that analyte will be qualified and the data quality implications will be discussed in the case narrative. However, investigation into the cause of the failure should still be performed.

12.6.3 Matrix Spike and Duplicate Matrix Spike Samples – If a recovery is outside of control criteria, review the consistency between the two analyses. If the result is supported between the two analyses, the outlier can be attributed to matrix interference. Do not reanalyze the extract. If the results do not support each other, reanalyze the extracts to verify the results. If the results confirm, review the LCS recovery and take corrective action accordingly. If the LCS recovery is acceptable, flag the matrix spike data and discuss potential data quality implications in the case narrative.

12.6.4 Relative Percent Difference – For MS/DMS or LCS/DLCS, no corrective action is required based on RPD data alone. However, the data should be reviewed for information that will help determine if the RPD problem is the result of a sample specific issue (e.g., the DMS was concentrated to dryness), or if the problem is representative of the entire analytical batch. When the problem is apparently universal to the batch, a NCAR will be filed and the batch will be re-extracted. If results of the re-extraction confirm the original analyses of the field samples, the original data is reported and the RPD problems are discussed in the case narrative. If results of the re-extraction confirm a problem in the original data, only the re-extracted data is reported.

12.6.5 Surrogates – Corrective action includes reinjection to verify the result. If the result is confirmed, a NCAR will be filed and the sample will be re-extracted. If the re-extraction confirms the original results are biased due to matrix interferences, report the original data. If re-extraction is not feasible, the surrogate will be qualified and the data quality implications will be discussed in the case narrative.

12.7 Additional QA/QC measures include control charting of QC sample results

13) Data Reduction and Reporting

13.1 Qualitative Analysis - The qualitative identification of compounds determined by this procedure is based on retention time, and comparison of the sample mass spectrum with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the instrument and conditions used for the sample analysis. The characteristic ions from the reference mass spectrum are defined to be the ions monitored in the SIM mode and typically are the two or three ions of greatest relative intensity. Compounds are identified as present when the criteria below are met.

13.1.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

13.1.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

13.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum.

13.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is <50% of the average of the 2 peak heights. Otherwise, structural isomers are identified as isomeric pairs.

13.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When the gas chromatographic peaks appear to represent more than one component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important. Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification. When analytes coelute, the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

13.1.6 Evaluate internal standard areas in each sample. If the area in the sample is less than 50% or greater than 200% the area of in the CCV, corrective action must be taken. Depending on the analysis, this corrective action may include reinjection or dilution of the extract followed by reinjection.

13.2 Tentatively identified compounds (TICs) cannot be reported using this method.

13.3 Quantitation and Calculations

13.3.1 The GC/MS data stations, in current use, all run EnviroQuant and use the H-P RTE Integrator to generate the raw data used to calculate the standards $\overline{RF_x}$ values, the sample amounts, and the spike values. The software does three passes through each data file. The first two identify and integrate each internal standard and surrogate. The third pass uses the time-drift information from the first two passes to search for all method analytes in the proper retention times and with the proper characteristic quantitation ions. When $\overline{RF_x}$ is used, calculate the extract concentration as follows:

$$C_{ex} = \frac{(Resp_x)(Amt_{ISTD})}{(Resp_{ISTD})(\overline{RF_x})}$$

Where:
C_{ex} = the concentration in the sample extract (ppm);
$Resp_x$ = the peak area of the analytes of interest;
$Resp_{ISTD}$ = the peak area of the associated internal standard;
Amt_{ISTD} = the amount, in ppm, of internal standard added
$\overline{RF_x}$ = the average response from the initial calibration.

13.3.2 The concentration of analytes in the original sample is computed using the following equations:

Aqueous Samples: $Concentration\ (\mu g / L) = \frac{(Cex)\ (Vf)\ (D)}{(Vs)}$

Non-aqueous Samples: $Concentration\ (ug/Kg) = \frac{(Cex)(Vf)(D)}{(W)}$

Where:
Cex = Concentration in extract in ng/mL
Vf = Final volume of extract in mL
D = Dilution factor
Vs = Volume of sample extracted, liters
W = Weight of sample extracted in grams.

13.4 Data Review

13.4.1 Following primary data interpretation and calculations, all data is reviewed by a secondary analyst. Following generation of the report, the report is also reviewed. Refer to the SOP Laboratory Data Review Process (ADM-DREV) for details.

13.5 Reporting

13.5.1 Reports are generated in the ALS LIMS by compiling the SMO login, sample prep database, instrument, date, and client-specified report requirements (when specified). This compilation is then transferred to a file which the Stealth reporting system uses to generate a report. The forms generated may be ALS standard reports, DoD, or client-specific reports. The compiled data from LIMS is also used to create EDDs.

14) Contingencies for Handling Out-of-Control or Unacceptable Data

14.1 Refer to the SOP for *Nonconformance and Corrective Action Procedures* (ADM-NCAR) for procedures for corrective action.

14.2 Personnel at all levels and positions in the laboratory are to be alert to identifying problems and nonconformities when errors, deficiencies, or out-of-control situations are detected.

15) Method Performance

15.1 This method was validated through single laboratory studies of accuracy and precision. Refer to the reference method for additional method performance data available.

15.2 The method detection limit (MDL) is and related method reporting limit(s) were established using the procedure described in SOP *Performing and Documenting Method Detection Limit Studies and Establishing Limits of Detection and Quantification*. Method Reporting Limits are established for this method based on MDL studies and as specified in the ALS Quality Assurance Manual.

16) Pollution Prevention and Waste Management

16.1 The laboratory will comply with all Federal, State and local regulations governing waste restrictions as specified in the ALS Lab Waste Management Plan.

16.2 This method uses Methylene Chloride and any waste generated from this solvent must be placed in the collection cans in the lab. The solvent will then be added to the hazardous waste storage area and recycled off site.

17) Training

17.1 All analysts performing this analysis are required to read and understand this SOP.

17.2 Training is documented following the *Employee Training and New Employee Orientation* (ADM-TRAIN).

17.3 It is required that an initial demonstration of capability and periodic analysis of laboratory reagent blanks, laboratory fortified blanks, and other QC solutions as a continuing check on performance.

18) Method Modifications

18.1 This SOP applies to a subset of target analytes that are commonly found in sites contaminated with petroleum based products. The breakdown of DDT to assess column inertness, as described in 8270D, is not performed in this SOP. The analytes determined in the procedure, PAH, are not impacted in the same way as DDT when assessing column performance.

19) References

19.1 *Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry*, Method 8270D Revision 4, EPA Test Methods for Evaluating Solid Waste, SW-846, Update IV, February 2007.

19.2 Exon Valdez Spill Assessment Procedure EV89-2, Revision 2.0, June 1989.

19.3 Standard Methods Manual for Environmental Sampling and Analysis in San Francisco Bay, US Army Corps of Engineers, November 1992 Draft, Volume 2 of 3.

19.4 Quantifying and Reporting Alkylated Homologs of Polycyclic Aromatic Hydrocarbons for

Gulf Oil Spill Analyses, ALS-Kelso SOP SVM-8270PQAH, draft revision 0.

19.5 DoD Quality Systems Manual for Environmental Laboratories, current version.

19.6 TNI Standard, Volume 1, 2009 & 2016.

19.7 ISO/17025:2017 American National Standard, General Requirements for the Competence of Testing and Calibration Laboratories.

20) Changes Since the Last Revision

Summary of Revision Changes			
Revision Number	SOP Review	Document Editor	Description of Changes
11.0		T .Caron	Admin Changes only not affecting technical content. Documented date of annual SOP Review, updated SOP signatories; boiler plate standard paragraphs have been updated to reflect current practices.
11.0	J.James 2.8.2021		Reviewed and approved; no technical changes at this time.
		E. Davelaar	Updated SOP signatories. Minor grammatical and formatting changes not affecting content. No technical changes needed.
11.0	Reviewed: 2/14/2024	K. Brown	Updated SOP Signatories. No technical changes needed at this time.
	Reviewed: 2/24/2025	K. Brown	No technical changes needed at this time.

21) Attachments, Tables, and Appendices

21.1 Table 1A – Routine Target Analytes - Soil.

21.2 Table 1B – Routine Target Analytes – Water

21.3 Table 1C – Routine Target Analytes - Tissue

21.4 Table 1D – Target Analytes – Soil Low level.

21.5 Table 1E - Alkylated Homologs.

21.6 Table 2 – Target Compounds, Primary, Secondary Ions and Minimum RF.

21.7 Table 3 - Semi-Volatile Internal Standards with Corresponding analytes Assigned for Quantitation.

21.8 Table 4A - DFTPP Key Ions and Ion Abundance Criteria for **5973** and **5975** GC/MS systems.

21.9 Table 4B - DFTPP Key Ions and Ion Abundance Criteria for **5972** GC/MS systems.

21.10 Table 5 - Standards Preparation.

21.11 Appendix A - Procedure for quantifying alkylated homologs of polynuclear aromatic hydrocarbons.

TABLE 1A
Routine Target Analytes - Soil

ANALYTE	CAS No.	MATRIX	MRL	UNITS
1-Methylnaphthalene	90-12-0	Soil	5	µg/Kg
1-Methylphenanthrene	832-69-9	Soil	5	µg/Kg
2,3,5-Trimethylnaphthalene	2245-38-7	Soil	5	µg/Kg
2,6-Dimethylnaphthalene	581-42-0	Soil	5	µg/Kg
2-Methylnaphthalene	91-57-6	Soil	5	µg/Kg
Acenaphthene	83-32-9	Soil	5	µg/Kg
Acenaphthylene	208-96-8	Soil	5	µg/Kg
Anthracene	120-12-7	Soil	5	µg/Kg
Benz(a)anthracene	56-55-3	Soil	5	µg/Kg
Benzo(a)pyrene	50-32-8	Soil	5	µg/Kg
Benzo(b)fluoranthene	205-99-2	Soil	5	µg/Kg
Benzo(b)thiophene	95-15-8	Soil	5	µg/Kg
Benzo(e)pyrene	192-97-2	Soil	5	µg/Kg
Benzo(g,h,i)perylene	191-24-2	Soil	5	µg/Kg
Benzo(k)fluoranthene	207-08-9	Soil	5	µg/Kg
Biphenyl	92-52-4	Soil	5	µg/Kg
Carbazole	86-74-8	Soil	5	µg/Kg
Chrysene	218-01-9	Soil	5	µg/Kg
Dibenz(a,h)anthracene	53-70-3	Soil	5	µg/Kg
Dibenzofuran	132-64-9	Soil	5	µg/Kg
Dibenzothiophene	132-65-0	Soil	5	µg/Kg
Fluoranthene	206-44-0	Soil	5	µg/Kg
Fluorene	86-73-7	Soil	5	µg/Kg
Indeno(1,2,3-cd)pyrene	193-39-5	Soil	5	µg/Kg
Naphthalene	91-20-3	Soil	5	µg/Kg
Naphthobenzothiophene	239-35-0	Soil	5	µg/Kg
Perylene	198-55-0	Soil	5	µg/Kg
Phenanthrene	85-01-8	Soil	5	µg/Kg
Pyrene	129-00-0	Soil	5	µg/Kg
Fluoranthene-d10 (Surr.)	93951-69-0	Soil	NA	%
Fluorene-d10 (Surr.)	81103-79-9	Soil	NA	%
Terphenyl-d14 (Surr.)	1718-51-0	Soil	NA	%

Table 1B
Routine Target Analytes – Water

ANALYTE	CAS No.	MATRIX	MRL	UNITS
1-Methylnaphthalene	90-12-0	Water	0.02	µg/L
1-Methylphenanthrene	832-69-9	Water	0.02	µg/L
2,3,5-Trimethylnaphthalene	2245-38-7	Water	0.02	µg/L
2,6-Dimethylnaphthalene	581-42-0	Water	0.02	µg/L
2-Methylnaphthalene	91-57-6	Water	0.02	µg/L
Acenaphthene	83-32-9	Water	0.02	µg/L
Acenaphthylene	208-96-8	Water	0.02	µg/L
Anthracene	120-12-7	Water	0.02	µg/L
Benz(a)anthracene	56-55-3	Water	0.02	µg/L
Benzo(a)pyrene	50-32-8	Water	0.02	µg/L
Benzo(b)fluoranthene	205-99-2	Water	0.02	µg/L
Benzo(b)thiophene	95-15-8	Water	0.02	µg/L
Benzo(e)pyrene	192-97-2	Water	0.02	µg/L
Benzo(g,h,i)perylene	191-24-2	Water	0.02	µg/L
Benzo(k)fluoranthene	207-08-9	Water	0.02	µg/L
Biphenyl	92-52-4	Water	0.02	µg/L
Carbazole	86-74-8	Water	0.02	µg/L
Chrysene	218-01-9	Water	0.02	µg/L
Dibenz(a,h)anthracene	53-70-3	Water	0.02	µg/L
Dibenzofuran	132-64-9	Water	0.02	µg/L
Dibenzothiophene	132-65-0	Water	0.02	µg/L
Fluoranthene	206-44-0	Water	0.02	µg/L
Fluorene	86-73-7	Water	0.02	µg/L
Indeno(1,2,3-cd)pyrene	193-39-5	Water	0.02	µg/L
Naphthalene	91-20-3	Water	0.02	µg/L
Naphthobenzothiophene	239-35-0	Water	0.02	µg/L
Perylene	198-55-0	Water	0.02	µg/L
Phenanthrene	85-01-8	Water	0.02	µg/L
Pyrene	129-00-0	Water	0.02	µg/L
Fluoranthene-d10 (Surr.)	93951-69-0	Water	NA	%
Fluorene-d10 (Surr.)	81103-79-9	Water	NA	%
Terphenyl-d14 (Surr.)	1718-51-0	Water	NA	%

Table 1C
Routine Target Analytes - Tissue

ANALYTE	CAS No.	MATRIX	MRL	UNITS
1-Methylnaphthalene	90-12-0	Tissue	0.5	µg/Kg
1-Methylphenanthrene	832-69-9	Tissue	0.5	µg/Kg
2,3,5-Trimethylnaphthalene	2245-38-7	Tissue	0.5	µg/Kg
2,6-Dimethylnaphthalene	581-42-0	Tissue	0.5	µg/Kg
2-Methylnaphthalene	91-57-6	Tissue	1.0	µg/Kg
Acenaphthene	83-32-9	Tissue	0.5	µg/Kg
Acenaphthylene	208-96-8	Tissue	0.5	µg/Kg
Anthracene	120-12-7	Tissue	0.5	µg/Kg
Benz(a)anthracene	56-55-3	Tissue	0.5	µg/Kg
Benzo(a)pyrene	50-32-8	Tissue	0.5	µg/Kg
Benzo(b)fluoranthene	205-99-2	Tissue	0.5	µg/Kg
Benzo(e)pyrene	192-97-2	Tissue	0.5	µg/Kg
Benzo(g,h,i)perylene	191-24-2	Tissue	0.5	µg/Kg
Benzo(k)fluoranthene	207-08-9	Tissue	0.5	µg/Kg
Biphenyl	92-52-4	Tissue	0.5	µg/Kg
Carbazole	86-74-8	Tissue	0.5	µg/Kg
Chrysene	218-01-9	Tissue	0.5	µg/Kg
Dibenz(a,h)anthracene	53-70-3	Tissue	0.5	µg/Kg
Dibenzofuran	132-64-9	Tissue	0.5	µg/Kg
Dibenzothiophene	132-65-0	Tissue	0.5	µg/Kg
Fluoranthene	206-44-0	Tissue	0.5	µg/Kg
Fluorene	86-73-7	Tissue	0.5	µg/Kg
Indeno(1,2,3-cd)pyrene	193-39-5	Tissue	0.5	µg/Kg
Naphthalene	91-20-3	Tissue	1.0	µg/Kg
Perylene	198-55-0	Tissue	0.5	µg/Kg
Phenanthrene	85-01-8	Tissue	0.5	µg/Kg
Pyrene	129-00-0	Tissue	0.5	µg/Kg
Fluoranthene-d10 (Surr.)	93951-69-0	Tissue	NA	%
Fluorene-d10 (Surr.)	81103-79-9	Tissue	NA	%
Terphenyl-d14 (Surr.)	1718-51-0	Tissue	NA	%

Table 1D
Target Analytes - Soil Low Level

ANALYTE	CAS No.	MATRIX	MRL	UNITS
2-Methylnaphthalene	91-57-6	Soil-Low	1.0	µg/Kg
Acenaphthene	83-32-9	Soil-Low	0.5	µg/Kg
Acenaphthylene	208-96-8	Soil-Low	0.5	µg/Kg
Anthracene	120-12-7	Soil-Low	0.5	µg/Kg
Benz(a)anthracene	56-55-3	Soil-Low	0.5	µg/Kg
Benzo(a)pyrene	50-32-8	Soil-Low	0.5	µg/Kg
Benzo(b)fluoranthene	205-99-2	Soil-Low	0.5	µg/Kg
Benzo(g,h,i)perylene	191-24-2	Soil-Low	0.5	µg/Kg
Benzo(k)fluoranthene	207-08-9	Soil-Low	0.5	µg/Kg
Chrysene	218-01-9	Soil-Low	0.5	µg/Kg
Dibenz(a,h)anthracene	53-70-3	Soil-Low	0.5	µg/Kg
Dibenzofuran	132-64-9	Soil-Low	0.5	µg/Kg
Fluoranthene	206-44-0	Soil-Low	0.5	µg/Kg
Fluorene	86-73-7	Soil-Low	0.5	µg/Kg
Indeno(1,2,3-cd)pyrene	193-39-5	Soil-Low	0.5	µg/Kg
Naphthalene	91-20-3	Soil-Low	1.0	µg/Kg
Phenanthrene	85-01-8	Soil-Low	0.5	µg/Kg
Pyrene	129-00-0	Soil-Low	0.5	µg/Kg
Fluoranthene-d10 (Surr.)	93951-69-0	Soil	NA	%
Fluorene-d10 (Surr.)	81103-79-9	Soil	NA	%
Terphenyl-d14 (Surr.)	1718-51-0	Soil	NA	%

Table 1E
Alkylated Homologs

ANALYTE	CAS No.	MATRIX	MDL	MRL	UNITS
C1, C2, C3, C4-Chrysenes	NA	Soil	-	5	µg/Kg
C1, C2, C3-Dibenzothiophenes	NA	Soil	-	5	µg/Kg
C1, C2, C3 -Fluoranthenes/Pyrenes	NA	Soil	-	5	µg/Kg
C1, C2, C3-Fluorenes	NA	Soil	-	5	µg/Kg
C1, C2, C3, C4-Phenanthrenes/Anthracenes	NA	Soil	-	5	µg/Kg
C2, C3, C4-Naphthalenes	NA	Soil	-	5	µg/Kg
C1, C2, C3, C4-Chrysenes	NA	Water	-	0.02	µg/L
C1, C2, C3-Dibenzothiophenes	NA	Water	-	0.02	µg/L
C1, C2, C3 -Fluoranthenes/Pyrenes	NA	Water	-	0.02	µg/L
C1, C2, C3-Fluorenes	NA	Water	-	0.02	µg/L
C1, C2, C3, C4-Phenanthrenes/Anthracenes	NA	Water	-	0.02	µg/L
C2, C3, C4-Naphthalenes	NA	Water	-	0.02	µg/L
Fluoranthene-d10 (Surr.)	93951-69-0	Water	NA	NA	%
Fluorene-d10 (Surr.)	81103-79-9	Water	NA	NA	%
Terphenyl-d14 (Surr.)	1718-51-0	Water	NA	NA	%

Table 2
Target Compounds Primary, Secondary Ions and Minimum RF

Compound	Primary Ion	Secondary Ion	Minimum Response Factor (RF)
Naphthalene-d 8 (I.S.)	136	68	
Naphthalene	128	127	0.700
2-Methylnaphthalene	141	142	0.400
1-Methylnaphthalene	141	142	0.500
Biphenyl	154	153	0.100
2,6-Dimethylnaphthalene	156	155	0.500
Acenaphthene-d 10 (I.S.)	164	162	-
Acenaphthylene	152	153	0.900
Acenaphthene	154	153	0.900
Dibenzofuran	168	139	0.800
2,3,5-Trimethylnaphthalene	170	155	0.500
Fluorene	166	165	0.900
Phenanthrene-d 10 (I.S.)	188	94	-
Dibenzothiophene	184	152	0.500
Phenanthrene	178	179	0.700
Anthracene	178	176	0.700
1-Methylphenanthrene	192	150	0.500
Fluoranthene	202	203	0.500
Chrysene-d 12 (I.S.)	240	236	-
Pyrene	202	203	0.600
Benzo(a)anthracene	228	226	0.800
Chrysene	228	226	0.700
Perylene-d 12 (I.S.)	264	260	-
Benzo(b)fluoranthene	252	126	0.700
Benzo(k)fluoranthene	252	126	0.700
Benzo(e)pyrene	252	126	0.500
Benzo(a)pyrene	252	126	0.700
Perylene	252	126	0.500
Indeno (1,2,3-cd)pyrene	276	277	0.500
Dibenz(a,h)anthracene	278	276	0.400
Benzo(g,h,i)perylene	276	277	0.500
Carbazole			0.05
Fluorene-d10 (surr.)	176	175	-
Fluoranthene-d10 (surr.)	212	213	-
Terphenyl-d 14 (surr.)	244	122	-

Table 3
Semivolatile Internal Standards with Corresponding Analytes Assigned for Quantitation

Naphthalene-d8	**Acenaphthene-d10**	**Phenanthrene-d10**
Naphthalene	Acenaphthene	Dibenzothiophene
2-Methylnaphthalene	Acenaphthylene	Phenanthrene
1-Methylnaphthalene	Dibenzofuran	Anthracene
Biphenyl	2,3,5-Trimethylnaphthalene	1-Methylphenanthrene
2,6-Dimethylnaphthalene	Fluorene	Fluoranthene
	Fluorene-d_{10} (surr.)	Carbazole
		Fluoranthene-d_{10} (surr.)

Chrysene-d12	**Perylene-d12**
Pyrene	Benzo(b)fluoranthene
Benzo(a) anthracene	Benzo(k)fluoranthene
Chrysene	Benzo(e)pyrene
Terphenyl-d_{14} (surr.)	Benzo(a)pyrene
	Perylene
	Indeno (1,2,3-ccd)pyrene
	Dibenz(a,h)anthracene
	Benzo(g,h,i)perylene

Table 4A
DFTPP Key Ions and Ion Abundance Criteria
For **5973** and **5975** GC/MS systems

Mass	Ion Abundance Criteria
51	10-80% of mass 198
68	0-2% of mass 69
70	0-2% of mass 69
127	10-80% of 198
197	0-2% of 198
198	30-100% of 442 (alternate base)
199	5-9% of 198
275	10-60% of 198
365	1-50% of 442
441	0.01-100% of 443
442	30-100% of 198 (alternate base)
443	15-24% of 442

Table 4B
DFTPP Key Ions and Ion Abundance Criteria
For **5972** GC/MS systems

Mass	Ion Abundance Criteria
51	30-80% of mass 198
68	0-2% of mass 69
69	Present
70	0-2% of mass 69
127	25-75% of 198
197	0-1% of 198
198	100% Relative abundance, Base Peak
199	5-9% of 198
275	>0.75% of 198
365	1-50% of 442
441	0.01-99.99% of 443
442	40-110% of 198
443	15-24% of 442

Table 5
Standard Preparation

Internal Standard Working Standard

Parent Solution	Initial Concentration	Aliquot	Final Volume	Final Concentration	Solvent
AccuStandard Z-014J	4000 µg/mL	50 µl	10 mL	20 µg/mL	DCM

Initial Calibration Intermediate Standard

Parent Solution	Initial Concentration	Aliquot	Final Volume	Final Concentration	Solvent
Absolute PAH Mix	100 µg/mL	80 µl	2 mL	4 µg/mL	DCM
PAH Surr. Intermediate	100 µg/mL	80 µl	↓	4 µg/mL	↓

Initial Calibration Standards

Initial Cal. Intermediate Std. 4 µg/mL	Internal Std Working Std 20 µg/mL	Final Volume	Solvent	Final Concentration PAH	Final Concentration Int Std
5 µl	100 µl	10 mL	DCM	0.002 µg/mL	0.2 µg/Ml
5 µl	50 µl	5 mL		0.004 µg/mL	
4 µl	20 µl	2 mL		0.008 µg/mL	
5 µl	10 µl	1 mL		0.02 µg/mL	
25 µl				0.1 µg/mL	
50 µl				0.2 µg/mL	
100 µl				0.4 µg/mL	
250 µl				1.0 µg/mL	
400 µl				1.6 µg/mL	
500µl				2.0 µg/mL	
	↓	↓	↓		↓

Independent Calibration Verification (ICV) Standard

Parent Solution	Initial Concentration	Aliquot	Final Volume	Final Concentration	Solvent
Cerilliant PAH Mix CSQ-4049	100 µg/mL	20 µl	5 mL	0.4 µg/mL	DCM
PAH Surr. Intermediate	100 µg/mL	20 µl	↓	0.4 µg/mL	↓
Int. Std Working Std	20 µg/mL	50 µl	↓	0.2 µg/mL	↓

Appendix A
Procedure for quantifying alkylated homologs of polynuclear aromatic hydrocarbons

1. Analyze a PAH ICAL using the A_PAHK method. These acquisition parameters will acquire data for the parent PAHs as well as the homologs. Process the data and update the calibration table. Go into EDIT COMPOUNDS which is under the INITCAL menu. Enter the peak areas from the parent compounds into the corresponding levels in the associated homologs calibration table as listed below.

PARENT	HOMOLOG
Naphthalene	C2-Naphthalenes
	C3-Naphthalenes
	C4-Naphthalenes
Fluorene	C1-Fluorenes
	C2-Fluorenes
	C3-Fluorenes
Dibenzothiophene	C1-Dibenzothiophenes
	C2-Dibenzothiophenes
	C3-Dibenzothiophenes
Phenanthrene	C1-Phenanthrenes/Anthracenes
	C2-Phenanthrenes/Anthracenes
	C3-Phenanthrenes/Anthracenes
	C4-Phenanthrenes/Anthracenes
Pyrene	C1-Fluoranthenes/Pyrenes
	C2-Fluoranthenes/Pyrenes
	C3-Fluoranthenes/Pyrenes
Chrysene	C1-Chrysenes
	C2-Chrysenes
	C3-Chrysenes
	C4-Chrysenes

   Use the same Curve Fit for the Homolog as is used for the Parent compound. Use the average RF if the %RSD is less than 20%. Use a quadratic curve if the %RSD exceeds 20%.

2. Analyze the PAH-ALKH SRM. This SRM is a petroleum crude oil which has been cleaned up using GPC and silica gel cleanup procedures. All of the homologs are present in the SRM.

3. Process the SRM data against the ICAL. Review the SRM data in QEDIT and manually integrate the homologs using the example in the SOP book as a guide. Print a graphics report for each homolog.

4. Update the calibration table using the PAH CCV. Enter the average retention time for each of the homologs into the processing method.

5. Analyze the sample extracts and process the data against the ICAL. Using the SRM data as a guide, manually integrate the homologs. Print graphics reports for e.

Organochlorine Pesticides by Gas Chromatography

DOCUMENT ID: SOC-8081, REV 26.0

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1) Scope & Applicability

1.1 This Standard Operating Procedure (SOP) describes the procedure used to determine the concentrations of Organochlorine Pesticides in liquid and solid matrices using EPA Method 8081B.

1.2 Table 1 indicates compounds that are routinely determined by this procedure and lists the method reporting limits (MRLs) in water and a low-level water option. Table 2 lists the MRLs in soil/sediment/tissues. Additional analytes may also be determined as required by specific projects. The reported MRL may be adjusted if required for specific project requirements; however, the capability of achieving other reported MRLs must be demonstrated. Method Detection Limits (MDLs) that have been achieved are listed in the ALS-Kelso DQO tables. The MDL/LODs may change as repeat studies are conducted.

1.3 In cases where there is a project-specific quality assurance plan (QAPP), the project manager identifies and communicates the QAPP-specific requirements to the laboratory. In general, project specific QAPPs supersede method specified requirements. An example of this are projects falling under DoD ELAP. QC requirements defined in the SOP *Department of Defense Projects – Laboratory Practices and Project Management (ADM-DOD)* may supersede the requirements defined in this SOP.

2) Summary of Procedure

2.1 This procedure provides gas chromatographic conditions for the detection of low concentration (typically parts-per-billion level organochlorine pesticides) pesticides. Target analytes are extracted from the sample and isolated via extract cleanup if needed. Liquid samples are extracted using shaker table microextraction (Method 3511, SOP EXT-3511). TCLP leachates are extracted using separatory funnel (Method 3510, SOP EXT-3510). In general, solid samples are extracted using automated microwave extraction (Method 3546, SOP EXT-3546). Tissue and paperboard samples are extracted using automated Soxhlet extraction (Method 3541, SOP EXT-3541).

2.2 A portion of the extract is analyzed using a gas chromatograph (GC) equipped with dual column fused silica capillary columns and dual electron capture detectors (ECD). Identification is based on comparison of sample retention times to the retention times of known target compounds. Quantitative analysis is performed by using certified standards to produce a calibration curve response factor. Analyte concentration can then be calculated using the response factor of the calibration curve. Sample concentration is calculated using the extract concentration and the extracted sample weights, volumes and dilution factors.

3) Definitions

3.1 For general definitions applicable to most analyses refer to the SOP for *Sample Batches*, ADM-BATCH.

4) Responsibilities

4.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. This demonstration is in

accordance with the training program of the laboratory. Final review and sign-off of the data is performed by the department supervisor/manager or designee.

4.2 It is the responsibility of the department supervisor/manager to document analyst training. Documenting method proficiency, as described in the *SOP Employee Training and Orientation*.

5) Interferences

5.1 Solvents, reagents, glassware, gases, and sample processing hardware may yield discrete artifacts and/or elevated baselines, causing misinterpretation of the chromatograms. All of these materials must be demonstrated to be free from interferences, under the conditions of the analysis, by running method blanks.

5.2 Interferences from phthalate esters introduced during sample handling can pose a problem with pesticide determinations. Analysts should take precautions not to introduce phthalates during the analysis and sample preparation process. Much interference can be removed using Florisil cleanup (SOP EXT-FLOR). Florisil cleanup is typically used to reduce matrix interferences caused by polar compounds. The presence of elemental sulfur will result in peaks interfering with early eluting pesticides. Cleanup via method 3660 (SOP SOC-3660) may be used for the removal of sulfur if GPC cleanup is inadequate. Other co-extractables such as lipids, waxes, etc., are removed via GPC cleanup. A cleanup procedure using carbon cartridges (SOP EXT-CARCU) that eliminates non-polar compounds that interfere with gas chromatographic analyses may also be utilized.

6) Safety

6.1 Chemicals, reagents and standards must be handled as described in the ALS safety policies, approved methods and in SDSs where available. Refer to the ALS Kelso Chemical Hygiene Plan and the appropriate SDSs prior to beginning this method.

7) Sample Collection, Containers, Preservation, and Storage

7.1 Containers used to collect samples should be purchased pre-cleaned containers. Alternatively, containers used to collect samples for the determination of semivolatile organic compounds may be soap and water washed followed by methanol (or isopropanol) rinsing. The sample containers should be of glass or Teflon and have screw-top covers with Teflon liners. In situations where Teflon is not available, solvent-rinsed aluminum foil may be used as a liner. Highly acidic or basic samples may react with the aluminum foil, causing eventual contamination of the sample. Plastic containers or lids may <u>not</u> be used for the storage of samples due to the possibility of sample contamination from the phthalate esters and other hydrocarbons within the plastic. Sampling should be performed according to SW-846 guidelines or project-specific procedures.

7.2 Water and soil samples must be iced or refrigerated at ≤6°C from time of collection until extraction. Water samples must be extracted within 7 days of collection and soil/sediment samples must be extracted within 14 days of collection.

7.3 Sample extracts are stored at 4ºC in the dark and must be analyzed within 40 days

8) Standards, Reagents, and Consumable Materials

8.1 Standards

8.1.1 The following commercially prepared stock standards and ICV stock standards are purchased from various vendors and must be certified by the manufacturer. The ICV stock standards are obtained from a different source from the initial calibration. The expiration date for unopened ampules is the manufacturer's assigned expiration date. If the manufacturer does not assign a date, an expiration date of 1 year from receipt is assigned. Stock standards are stored at the recommended temperature from the vendor. The intermediate stock standards prepared by the analysts are stored in freezer.

Standard	Concentration	Use
8081	1000µg/mL	ICAL
8081 Surrogate[a]	200µg/mL	ICAL
Isodrin	100µg/mL	ICAL
Hexachlorobenzene	100µg/mL	ICAL
8081 Misc. compounds*	250µg/mL	ICAL
Chlordane	100µg/mL	ICAL
Toxaphene	1000µg/mL	ICAL
8081	1000µg/mL	ICV
Isodrin	100µg/mL	ICV
Hexachlorobenzene	100µg/mL	ICV
8081 Misc. compounds	250µg/mL	ICV
Chlordane	1000µg/mL	ICV
Toxaphene	1000µg/mL	ICV
8081 Internal Standard[b]	5000µg/mL	Internal standard

Surrogates are Decachlorobiphenyl (DCB) and 2,4,5,6-Tetrachlorometaxylene (TCMX).

Internal standard is 1-Bromo-2-nitrobenzene.

8.1.2 Intermediate standard solutions and ICV solutions are made in hexane by diluting stock standards to intermediate concentrations listed below. The ICV intermediates are prepared from the ICV stock standards obtained from a different source from the initial calibration stocks.

ICAL Intermediate	Concentration	Preparation
Combined 8081, isodrin, hexachlorobenzene, and surrogate.	2.0µg/mL	1:500 dilution of 8081 stock, 1:50 dilution of isodrin & hexachlorobenzene stocks, 1:100 dilution of surr. stock.
8081 2,4' DDX compound	2.0µg/mL	1:125 dilution of stock
8081 Misc. compounds*	1.0µg/mL	1:250 dilution of stock
Perthane compound	5.0µg/mL	1:20 dilution of stock
Chlordane	1.0µg/mL	1:1000 dilution of stock
Toxaphene	2.0µg/mL	1:500 dilution of stock

Intermediate ICV Standard	Concentration	Preparation
8081 2.4' DDX compound	1.0µg/mL	1:250 dilution of stock
8081 Misc. compounds	1.0µg/mL	1:250 dilution of stock
Perthane	1.0µg/mL	1:350 dilution of stock
8081 Internal Standard	1.0µg/mL	1:500 dilution of stock
Chlordane	1.0µg/mL	1:1000 dilution of stock
Toxaphene	2.0µg/mL	1:500 dilution of stock

8.1.3 Working Standard Solutions

8.1.3.1 Calibration standards are prepared containing surrogates and analytes in hexane. Calibration standards are stored at 4ºC for up to six months. A series of standards are prepared from a common intermediate representing the MRL (or lower) to a value near the high end of the linear range. See Table 4 for preparation and concentrations, including standards designated as CCVs.

8.1.3.2 The independent calibration verification (ICV) standards are prepared from stock solutions from a different source from the initial calibration as listed below. Expiration periods are the same as for equivalent stock and calibration standards.

ICV Standard	Concentration	Preparation
Combined 8081, isodrin, and hexachlorobenzene	2.0µg/L	1:500 dilution of combined 8081 ICV intermediate.
8081 Misc. compounds	2.0µg/L	1:500 dilution of 8081 misc. compounds intermediate.
Chlordane	50µg/L	1:20 dilution of Chlordane ICV stock.
Toxaphene	200µg/L	1:10 dilution of Toxaphene ICV stock.

8.1.3.3 A surrogate spiking solution is prepared at 0.5µg/mL for water and 0.8µg/mL for solids. The surrogate solution is stored at 4ºC or up to six months.

8.1.3.4 An internal standard solution is prepared at 10µg/ml (1µg/ml for low-level) by diluting the internal stock standard in hexane. 10.0µL of internal standard is added to each 1mL of standard, blank and sample prior to analysis for a final concentration of 100ng/mL.

8.1.3.5 All matrix spike solutions are prepared by diluting the stock solution in methanol. This solution is stored at 4ºC. The 8081-Isodrin-HCB spike is good for 4 weeks, while the others are good for 6 months. The matrix spike solution is added to all matrix spikes and lab control samples as outlined in section 12.

Spiking Solution	Concentration	Preparation
8081, isodrin, and hexachlorobenzene.	0.5µg/mL	1:2000 dilution of 8081, isodrin & hexachlorobenzene stocks.
8081 Misc. compounds*	0.5µg/mL	1:500 dilution of stock
Chlordane**	10µg/mL	1:100 dilution of stock
Toxaphene	20µg/mL	1:50 dilution of stock

*Prepare only as needed for projects requiring non-routine additional compounds.

**Prepare only as needed for project requirements.

8.1.4 Solvents: Hexane, acetone, methylene chloride, isooctane, and methanol. Pesticide grade or equivalent.

9) Apparatus and Equipment

9.1 GC Instrumentation - Dual Column

9.1.1 The dual column approach involves a single injection split between two columns mounted in a single gas chromatograph (Hewlett Packard 6890, 7890 or equivalent) equipped with split/splitless, temperature programmable, or multi-mode injection system; with dual ECDs. See Table 3 for typical chromatographic conditions. Hydrogen is used as the carrier gas. Nitrogen is used as the detector make-up gas. Current instrumental systems are identified as follows:

Instrument I.D.	Analytical System	Routine Matrix
GC23	Agilent 6890	Water/Solid
GC34	Agilent 7890A	Water/Solid
GC37	Agilent 7890A	Water/Solid

9.1.2 Columns, J&W columns typically are used;

Column 1: DB-XLB 30mx0.32mm ID, 0.50µm df or equivalent*
Column 2: DB-35MS 30mx0.32mm ID, 0.25µm df or equivalent*

NOTE: Column diameter and film thickness may vary depending on instrument. Refer to the instrument maintenance logbook for the columns used for a specific instrument configuration.

9.1.3 Autosampler, capable of reproducible injections, Hewlett Packard/Agilent 7673 or equivalent.

9.2 Data System – A computer data system must be interfaced to the GC/ECD. The system must allow the continuous acquisition and storage on machine-readable media of all chromatographic data obtained throughout the duration of the chromatographic program. The computer must have software that includes automated calibration,

identification, and quantitation routines. The software must also be capable of integrating the chromatographic peaks abundances.

10) Preventative Maintenance

10.1 All maintenance activities are recorded in a maintenance logbook kept for each instrument. Pertinent information (serial numbers, instrument I.D., etc.) must be in the logbook. This includes the routine maintenance described herein. The entry in the log must include: date of event, the initials of who performed the work, and a reference to analytical control.

10.2 Carrier gas – Inline purifiers or scrubbers should be in place for all sources of carrier gas. These are selected to remove water, oxygen, and hydrocarbons. Purifiers should be changed as recommended by the supplier.

10.3 Gas Chromatograph

10.3.1 Whenever GC maintenance is performed, care should be taken to minimize the introduction of air or oxygen into the column. Injection port maintenance includes changing the injection port liner, seal, washer, o-ring, septum, column ferrule, and autosampler syringe as needed. Liners and seals should be changed when recent sample analyses predict a problem with chromatographic performance. In some cases liners and seals may be cleaned and re-used.

10.3.2 Clipping off a small portion of the head of the column often improves chromatographic performance. When cutting off any portion of the column, make sure the cut is straight and “clean” (uniform, without fragmentation) by using the proper column cutting tool.

10.3.3 Over time, the column will exhibit poorer overall performance, as contaminated sample matrices are analyzed. The length of time for this to occur will depend on the samples analyzed. When a noticeable decrease in column performance is evident and other maintenance options do not result in improvement, the column should be replaced. This is especially true when evident in conjunction with calibration difficulties.

11) Procedure

11.1 Sample Preparation

11.1.1 Water samples, (100mL for LL, 200mL for ULL) are extracted via shaker table microextraction (SOP EXT-3511). TCLP leachates are extracted using separatory funnel (SOP EXT-3510). Refer to the applicable extraction SOP for the applicable procedure. For extraction by 3535, acidification of the sample prior to extraction may be allowable if project objectives and performance requirements of methods 3535 and 8081 are met.

NOTE: For projects originating from Alaska and South Carolina use the 3535 extraction method only.

11.1.2 Soil/sediment samples are extracted using EPA Method 3546 (SOP EXT-3546). Refer to the applicable extraction SOP.

11.1.3 Tissue and paperboard samples are extracted using EPA Method 3541 (SOP EXT-3541). Refer to the applicable extraction SOP.

11.1.4 Additional sample cleanup procedures may be used as appropriate for the samples. See Section 5.2 and refer to the applicable cleanup SOP.

11.2 Calibration

11.2.1 Refer to the SOP *Sample Batches* (ADM-BATCH) for guidance on analytical calibration and sample batches. Refer to the SOP *Calibration of Instruments for Organics Chromatographic Analyses (*ADM-CAL*)*, where calibration procedures and policies are described. The calibration procedure(s) and options chosen must follow the SOP ADM-CAL.

11.2.2 Check for degradation of 4,4'-DDT and Endrin by injecting a standard containing only 4,4'-DDT at 10ppb and Endrin at 5 ppb.

$$\%\ Breakdown = \frac{Total\ DDT\ degradation\ peak\ area\ (DDE + DDD)}{Total\ DDT\ \ peak\ area\ (DDT + DDE + DDD)}\ x\ 100$$

$$\%\ Breakdown = \frac{\begin{array}{c}Total\ endrin\ degradation\ peak\ area\\ endrin\ aldehyde + endrin\ ketone\end{array}}{\begin{array}{c}Total\ endrin\ \ peak\ area\\ endrin + endrin\ aldehyde + endrin\ ketone\end{array}}\ x100$$

If degradation of either DDT or Endrin exceeds 15%, perform any necessary maintenance before proceeding with calibration. The breakdown of DDT and Endrin must be measured before samples are analyzed and at the beginning of each analytical sequence.

11.2.3 After determining that degradation is within acceptance, calibrate the system immediately prior to conducting any analyses. Analyze each calibration standard (containing internal standards) and tabulate the area against concentration for each compound. For multi-component analytes, only those specified in the project plan or work specification are used for calibration. Calculate response factors (RFs) for each compound relative to the internal standard as follows:

RF = (AxCis)/(AisCx)

Where: Ax = Area of the compound being measured.
Ais = Area of the specific internal standard.
Cis = Concentration of the specific internal standard (ng/µL).
Cx = Concentration of the compound being measured (ng/µL).

NOTE: For Chlordane, a minimum of 3 peaks must be chosen and for Toxaphene a minimum of 4 peaks must be chosen. The peaks must be characteristic of the compound of interest.

11.2.3.1 Calculate the mean response factor $(\overline{RF_x})$ for each analyte and surrogate from the calibration levels. Calculate standard deviation (SD) and the percent relative standard deviations (%RSD) for each analyte from the mean with:

11.2.3.2 The %RSD should be less than 20% for each compound.

11.2.3.3 If the %RSD for a given compound is 20% or less, linearity can be assumed over the calibration range, and the relative response

factor for each analyte and surrogate is used to quantitate sample analytes.

11.2.3.4 If the %RSD exceeds 20%, then a linear curve or a quadratic calibration with a coefficient of determination (COD, R^2) of 0.990 or greater may be used.

11.2.4 Following initial calibration, analyze an ICV standard. The ICV solution must contain all analytes in the calibration standards. Calculate the concentration using the typical procedure used for quantitation. Calculate the percent difference (%D) from the ICV true value. Evaluate the ICV as described in the ADM-CAL SOP. The acceptance criterion is ± 20% from the analytes assigned value.

11.2.5 Continuing Calibration Verification

11.2.5.1 The working calibration curve or calibration response factors must be verified on each analytical sequence by the analysis of one or more mid-range calibration standards (CCV). A CCV must be injected at the start of each 12 hour shift or every 20 samples, whichever is first. The 12 hour window starts with the injection time of the first CCV. The use of internal standard calibration technique does not require that all sample results be bracketed with calibration verification standards.

NOTE: DoD projects require a CCV analysis every 10 field samples. Work under QSM versions 5x of the QSM require a closing CCV for single-component analytes.

11.2.5.2 The acceptance criteria for all analytes in the CCV analysis are a response (RF or concentration) within ±20 %D of the expected value, as compared to the initial calibration. Refer to the SOP ADM-CAL.

NOTE: For samples originating in Arizona and results reported for compliance purposes, the CCV criteria is ±15 %D, per Method 8081A. However, response factor averaging is not allowed for analysis of Arizona samples.

11.2.5.3 The measured area of the internal standard must be no more than -50% to +200% difference from the average area calculated during initial calibration.

11.2.5.4 The retention time of the internal standard must also be evaluated. A retention time shift of >30 seconds necessitates system maintenance and reanalysis of CCV.

11.2.6 Retention Time Windows

11.2.6.1 Establish retention time windows with the GC system in acceptable operating conditions. Make three injections of all analytes throughout the course of a 72-hour period. Serial injections over less than a 72-hour period may result in retention time windows that are too tight. Using retention times from these analyses, calculate retention time windows. Refer to EPA Method 8000 for detailed instructions.

11.2.6.2 The retention time window is defined as ±3x the standard deviation of the absolute retention times for each standard;

however, the experience of the analyst should weigh heavily in the interpretation of chromatograms. In those cases where the standard deviation for a particular standard is zero, the laboratory may use a default window of ±0.03 minutes. If the peak width is >0.06 minutes, use a default window of 0.1 minutes.

11.2.6.3 Calculate retention time windows for each standard on each GC column and whenever a new GC column is installed. Retain this data in the method file.

11.3 Sample Analysis

11.3.1 Table 3 indicates the typical operating conditions for the GC. Setup the analysis sequence of sample and QC samples. Also, refer to the SOP *Sample Batches* (ADM-BATCH) for guidance.

11.3.2 Calibrate the system as described in Section 11.2. Evaluate the CCVs as discussed in Section 11.2.5. If any standard falls outside of their daily retention time window, evaluate the chromatogram for possible causes such as carryover from a highly contaminated sample. If a problem related to GC system has been determined to be the cause of retention time shift, perform whatever maintenance is necessary before re-injecting a CCV or recalibrating and proceeding with sample analysis.

11.3.3 Spike 10µl of the internal standard 1-Bromo-2-nitrobenzene at 10 ppm into each 1ml of sample extract to give a final concentration of 100 ng/ml. The measured area of the internal standard must be -50% to +200% as measured from the average of the most recent calibration. Any samples falling outside of this criterion require reanalysis.

11.3.4 The retention time of the internal standard must also be evaluated. A retention time shift of >30 seconds requires reanalysis of all affected samples.

11.4 Identification of Analytes

11.4.1 Tentative identification of an analyte occurs when a peak from a sample extract falls within the daily retention time window and the s/n ratio of the peak is >3. A tentatively identified compound is confirmed when the retention time for the compound on the confirmatory detector is within the retention time window on that system.

11.4.2 Confirmation of all tentative hits should be made. Confirmation is made by injecting the sample extract on two columns with dissimilar phases simultaneously. If the retention time matches on both columns, then the hit for the analyte is considered a confirmed hit. Refer to the SOP *Confirmation of Organic Analytes* (SOC-CONF).

11.4.3 For Chlordane, a minimum of 3 peaks must be chosen and, for Toxaphene, a minimum of 4 peaks must be chosen for identification purposes. Refer to Section 13.2 for quantitation procedures for multi-response analytes.

11.5 Perform all necessary calculations as described in Sections 12 and 13.

12) QA/QC Requirements

12.1 Initial Precision and Recovery Validation

12.1.1 The precision of the extraction procedure and the GC procedure must be validated before analysis of samples begins, or whenever significant changes to the procedures have been made. To do this, four reagent water samples are spiked at a level near the midpoint of the calibration range (typically the LCS level), then extracting and proceeding with Section 11. The spiking solution may be prepared from pure standard materials, or purchased as certified solutions. If prepared by the laboratory, stock standards prepared independently from those used for calibration should be used. The concentration of the analytes to be spiked is 20x the MRL.

12.2 Method Detection Limits and Method Reporting Limits

12.2.1 A method detection limit (MDL) study must be undertaken before analysis of samples can begin. To establish detection limits that are precise and accurate, the analyst must perform the following procedure. Spike seven blank matrix (water or soil) samples with MDL spiking solution at a level below the MRL. Follow the analysis procedures in Section 11 to analyze the samples.

12.2.2 Calculate the average concentration found (x) in µg/mL, and the standard deviation of the concentrations (s) in µg/mL for each analyte. Calculate the MDL for each analyte. Refer to the SOP *Performing and Documenting Method Detection Limit Studies and Establishing Limits of Detection and Limits of Quantitation.* The MDL/LOD must be verified annually.

12.2.3 Limits of Quantification (LOQ)

12.2.3.1 The laboratory establishes a MRL/LOQ for each analyte as the lowest reliable laboratory reporting concentration or in most cases the lowest point in the calibration curve which is less than or equal to the desired regulatory action levels, based on the stated project requirements. Analysis of a standard or extract prepared at the lowest point calibration standard provides confirmation of the established sensitivity of the method. The LOQ recoveries should be within 50-150% of the true values to verify the data reporting limit. Refer to the SOP *Performing and Documenting Method Detection Limit Studies and Establishing Limits of Detection and Limits of Quantitation.*

12.2.4 The Method Reporting Limits (MRLs) used at ALS Kelso are the routinely reported lower limits of quantitation which take into account day-to-day fluctuations in instrument sensitivity as well as other factors. These MRLs are the levels to which ALS Kelso routinely reports results in order to minimize false positive or false negative results. The MRL is normally two to ten times the method detection limit.

12.3 Ongoing QC Samples required are described in the ALS-Kelso Quality Assurance Manual and in the SOP for Sample Batches. Additional QC Samples may be required in project specific quality assurance plans (QAPP). General QA requirements for DoD QSM are defined in the laboratory SOP *Department of Defense Projects – Laboratory*

Practices and Project Management (ADM-DOD) or *Department of Defense Projects – Laboratory Practices and Project Management.* General QC Samples are:

12.3.1 Method Blank

12.3.1.1 A method blank is extracted and analyzed with every batch of 20 (or fewer) samples to demonstrate that there are no method interferences. If the method blank shows any hits above the reporting limit, corrective action must be taken. Corrective action includes recalculation, reanalysis, system cleaning, or re-extraction and reanalysis. For some project specific needs, exceptions may be noted and method blank results above the MRL may be reported for common lab contaminants (phthalate esters, etc.).

NOTE: DoD projects require that no analyte be detected >½ the RL or 1/10 the regulatory limit, whichever is greater.

12.3.2 Lab Control Sample (LCS) must be extracted and analyzed with every batch of 20 samples. The LCS is spiked as follows:

3511 LL: 50µL of 8081 Pest, 8081 Misc., 24-DDX, Toxaphene and Chlordane to 100mL of reagent water.

3511 ULL: 10µL of 8081 Pest, 8081 Misc., 24-DDX, Toxaphene and Chlordane to 200mL of reagent water.

3546: 100µL of 8081 Pest, 8081 Misc., 24-DDX, Toxaphene and 50µL Chlordane to 2g.

For project-specific low-level extractions, spiking amounts can be adjusted accordingly.

12.3.2.1 Calculate the LCS recovery as follows:

$$\%R = X/TV \times 100$$

Where: X = Concentration of the analyte recovered
TV = True value of amount spiked

12.3.2.2 Current ALS QC acceptance criteria for lab control samples are listed in the current ALS-Kelso DQO tables. Project-specific or program-specific acceptance criteria may supersede ALS criteria. For example, for samples requiring South Carolina DHEC certification the acceptance criteria are 70-130 % recovery. If the lab control sample (LCS) fails acceptance limits for any of the compounds, corrective action must be taken. Corrective action includes recalculation, reanalysis, or re-extraction and reanalysis. Refer to the ALS-Kelso Quality Assurance Manual for guidance in evaluating recoveries that exceed LCS limits.

12.3.3 Matrix Spike

12.3.3.1 A matrix spike (MS) and duplicate matrix spike (DMS) must be prepared and analyzed with every batch of 20 (or fewer) samples. The MS/DMS is prepared by adding the same volume of the matrix spike solution to the sample as listed for the LCS, then proceeding with Section 11. Calculate percent recovery (%R) as:

$$\%R = \frac{X - X1}{TV} \times 100$$

Where: X = Concentration of the analyte recovered
X1 = Concentration of unspiked analyte
TV = True value of amount spiked

12.3.3.2 Calculate Relative Percent Difference (RPD) as:

$$RPD = \frac{|R1 - R2|}{(R1 + R2)/2} \times 100$$

Where: R1= Higher Result
R2= Lower Result

12.3.3.3 Current QC acceptance criteria for MS/DMS are listed in the current ALS-Kelso DQO tables. Project-specific acceptance criteria may supersede lab criteria. If the MS/DMS recovery is out of acceptance limits for reasons other than matrix effects, corrective action must be taken. Corrective action includes recalculation, reanalysis, or re-extraction and reanalysis.

12.3.3.4 Following analysis of the MS the percent recovery is calculated and compared to acceptance limits. If the recovery is within control limits the results may be reported. If not, and the LCS is within control limits, this indicates that the matrix potentially biases analyte recovery. It is verified that the spike level is at least five times the background level. If not, the results are reported with a qualifier that the background level is too high for accurate recovery determination. If matrix interferences are present or results indicate a potential problem with sample preparation, steps may be taken to improve results; such as performing any additional cleanups, dilution and reanalysis, or re-preparation and reanalysis. Results that do not meet acceptance limits are reported with an appropriate qualifier.

12.3.4 Surrogate

12.3.4.1 Surrogate spike is added to every sample, blank and spike prior to extraction. Two surrogate standards (Tetrachloro-m-xylene and Decachlorobiphenyl) are added to each sample. The surrogate spike amounts are:

3511 LL:	50µL of 0.5ppm to 100mL
3511 ULL:	10µL of 0.5ppm to 200mL
3546:	50µL of 0.8ppm to 2g

12.3.4.2 Calculate surrogate percent recovery (%R) as:

%R = S/V x 100

Where S = Amount of surrogate recovered
V = Amount spiked

12.3.4.3 Current QC acceptance criteria for surrogates are listed in the current ALS-Kelso DQO tables. Project-specific acceptance criteria may supersede lab criteria. Both surrogate recoveries must be

within the acceptance limits. If either (or both) surrogate is outside of acceptance limits for reasons other than matrix interferences, corrective action must be taken. Corrective actions include recalculation, reanalysis, or re-extraction and reanalysis. The acceptance criteria listed are current criteria, but are subject to change as control limits are updated.

12.3.5 Control charts for QC results should be reviewed periodically for trends in results. Control limits for QC analyses may be determined using the control charts or similar mechanism on an annual basis.

13) Data Reduction and Reporting

13.1 Both detectors are used as primary and/or confirmatory systems when not interfered with by the sample matrix.

13.2 Calculations

13.2.1 Quantitation of analytes in sample extracts is performed by comparing total area of residue peaks to total area or peaks from the appropriate reference materials.

13.2.2 Quantitation of multi-response analytes:

13.2.2.1 The quantitation of Chlordane, Toxaphene, and other multi-response analytes is accomplished by comparison of the sample chromatogram to that of the authentic standard. All calibration acceptance criteria as described in section 11 must be met before reporting any results. Sample results should then be reported according to the SOP *Confirmation of Organic Analytes* (SOC-CONF). Results may be reported from either of the columns as long as all calibration acceptance criteria are met.

13.2.2.2 Once the analyte pattern has been identified, compare the responses of the major peaks in the calibration standard with the peaks observed in the sample extract. The amount of analyte is calculated using the individual calibration factor for each peak and the calibration model selected in section 11. The concentration is determined using the characteristic peaks and then the concentrations are averaged to determine the concentration. If there are interfering peaks that cause the average to be falsely overstated, then that interference peak is Q-Q-deleted using the data system, provided 3 peaks remain for Chlordane and 4 peaks

for Toxaphene. The average is then recalculated so that the average more truly represents the concentration in the sample.

13.2.3 The concentration of each analyte in the sample extract (C_{ex}) is computed. When $\overline{RF_x}$ is used, calculate the extract concentration as follows:

$$C_{ex} = \frac{(Resp_x)(Amt_{ISTD})}{(Resp_{ISTD})(\overline{RF_x})}$$

Where: C_{ex} = the concentration in the sample extract (ppb);
$Resp_x$ = the peak area of the analytes of interest;
$Resp_{ISTD}$ = the peak area of the associated internal standard;
Amt_{ISTD} = the amount, in ppb, of internal standard added
$\overline{RF_x}$ = the average response from the initial calibration.

13.2.4 The concentration of analytes in the original sample is computed using the following equations:

Aqueous Samples: $Concentration\ (\mu g / L) = \frac{(Cex)\ (Vf)\ (D)}{(Vs)}$

Where: *Cex* = Concentration in extract in µg/mL
Vf = Final volume of extract in mL
D = Dilution factor
Vs = Volume of sample extracted, liters

Non aqueous Samples: $Concentration\ (mg / Kg) = \frac{(Cex)\ (Vf)\ (D)}{(W)}$

Where: *Cex* = Concentration in extract in µg/mL
Vf = Final volume of extract in mL
D = Dilution factor
W = Weight of sample extracted in grams.

13.3 Data Review

13.3.1 Following primary data interpretation and calculations, all data is reviewed by a secondary analyst. Following generation of the report, the report is also reviewed. Refer to the SOP *Laboratory Data Review Process* (ADM-DREV) for details. The person responsible for final review of the data report and/or data package should assess the overall validity and quality of the results and provide any appropriate comments and information to the Project Chemist to inclusion in the report narrative.

13.4 Reporting

13.4.1 Reports are generated using the Data Reporting System which compiles the SMO login information. The compiled data from LIMS is also used to create EDDs.

13.4.2 Sample concentrations are reported when all QC criteria for the analysis have been met or the results are qualified with an appropriate footnote. For Arizona projects the appropriate Arizona qualifier must be used.

14) Contingencies for Handling Out-of-Control or Unacceptable Data

14.1 Refer to the SOP for *Non Conformance and Corrective Action* for corrective action.

14.2 Personnel at all levels and positions in the laboratory are to be alert to identifying problems and nonconformities when errors, deficiencies, or out-of-control situations are detected.

15) Method Performance

15.1 This method was validated through single laboratory studies of accuracy and precision. Refer to the reference method for additional method performance data available. In addition, this procedure was validated through single laboratory studies of accuracy and precision as specified in Section 12.1.

15.2 The method detection limit (MDL) is established using the procedure described in the SOP *Performing and Documenting Method Detection Limit Studies and Establishing Limits of Detection and Quantification.* Method Reporting Limits are established for this method based on the low calibration point and the MDL study results.

16) Pollution Prevention and Waste Management

16.1 The laboratory will comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the ALS Lab Waste Management Plan.

17) Training

17.1 All analysts performing this analysis are required to read and understand this SOP.

17.2 Training is documented following the SOP for *Employee Training and New Employee Orientation*.

18) Method Modifications

18.1 This method includes modifications to include additional analyte determinations, outside what is listed for EPA 8081B. These include 2,4'-DDD, 2,4'-DDE, 2,4'-DDT, Chlorpyrifos, and cis-Nonachlor.

19) References

19.1 EPA SW-846, Test Methods for Evaluating Solid Waste, Third Edition, Update IV, February 2007, Method 8081B, Revision 2.

19.2 EPA SW-846, Test Methods for Evaluating Solid Waste, Third Edition, Update III, December 1996, Method 8081A, Revision 1.

19.3 EPA SW-846, Determinative Chromatographic Separations, Update III, December 1996, Method 8000B, Revision 2.

19.4 EPA SW-846, Determinative Chromatographic Separations, On-Line, March 2003, Method 8000C, Revision 3.

19.5 DoD Quality Systems Manual for Environmental Laboratories, current version.

19.6 8000C Method criteria, Arizona DHS, 2/13/2007. Available online at https://www.azdhs.gov/documents/preparedness/state-laboratory/lab-licensure-certification/technical-resources/additional-resources/method-criteria-8000.pdf

19.7 TNI Standard, Volume 1, -2009.

19.8 ISO/IEC 17005:2017 American National Standard, General requirements for the competence of testing and calibration laboratories.

20) Changes Since the Last Revision

Revision Number	Effective Date	Document Editor	Description of Changes
22.0	2/15/2021	T. Caron	Updated SOP signatories. Standard paragraph edits. Reference Section has been edited to include ISO 17025. Section 8.1.3.4: 10ul of internal standard is added to each 1ml of standard, blank and sample prior to analysis for a final concentration of 100ng/ml has been added. Section 9.1.1: Added GC37. Sections 11 and 12: Edited to reference 3511 LL. Section 11/1/1: Water samples (100mL for LL, 200mL for ULL). Procedural change form submitted by UA 2.27.20. Procedural Change form submitted 2/15/2021 by R. Enzor.
23.0	2/14/2022	E. Davelaar	Updated SOP Signatories. Section 1.2: Updated Table 2 to reference MRLs of soil, sediments, and tissues. Section 5.2: Removed GPC reference for interference removal. Section 8.1.2: Edited ICAL Indeterminate and Intermediate ICV Standard tables. Section 11.1.1: Removed solid phase extraction. Section 12.3.2 and 12.3.4.1: Removed 3535A. Section 13.4.1: Removed mention of STEALTH.
24.0	10/19/2022	E. Davelaar	Updated SOP Signatories. Section 2.1 and 11.1.3: Included extraction of tissue and paperboard samples by EXT-3541. Section 18: Updated to include additional analytes.
25.0	12/8/2023	Reviewed by: J. Dunfield Edited by: B. Davis	Updated SOP Signatories.
26.0 26.0	1/03/2024 Reviewed: 2/24/2025	K. Brown K. Brown	Section 11.2.5.3: Change from "-50% to +100% " difference, to "-50% to +200% difference." Section 11.3.3: Change from "-50% to +100% difference" to "-50% to +200% difference." No technical changes needed at this time.

21) Attachments, Tables, and Appendices

21.1 Table 1 – Target Analytes and Method Reporting Limits* - Water.

21.2 Table 2 – Target Analytes and Method Reporting Limits* - Soil/Sediment/Tissue.

21.3 Table 3 – Gas Chromatograph Operating Conditions*.

21.4 Table 4 – Calibration Standard Preparation.

21.5 Table 5 – Summary of Corrective Actions.

TABLE 1
TARGET ANALYTES and METHOD REPORTING LIMITS* - WATER

Analyte	Standard MRL (µg/L)	Low-Level MRL (ng/L)
2,4'-DDD	0.01	1.0
2,4'-DDE	0.01	1.0
2,4'-DDT	0.01	1.0
4,4'-DDD	0.01	1.0
4,4'-DDE	0.01	1.0
4,4'-DDT	0.01	1.0
Aldrin	0.01	1.0
alpha-BHC	0.01	1.0
alpha-Chlordane	0.01	1.0
beta-BHC	0.01	1.0
Chlordane	0.2	20
Chlorpyrifos	0.01	1
cis-Nonachlor	0.01	1.0
delta-BHC	0.01	1.0
Dieldrin	0.01	1.0
Endosulfan I	0.01	1.0
Endosulfan II	0.01	1.0
Endosulfan Sulfate	0.01	1.0
Endrin	0.01	1.0
Endrin Aldehyde	0.01	1.0
Endrin Ketone	0.01	1.0
gamma-BHC (Lindane)	0.01	1.0
gamma-Chlordane	0.01	1.0
Heptachlor	0.01	1.0
Heptachlor Epoxide	0.01	1.0
Hexachlorobenzene	0.01	1.0
Hexachlorobutadiene	0.01	1.0
Hexachloroethane	0.01	1.0
Isodrin	0.01	1.0
Methoxychlor	0.01	1.0
Mirex	0.01	1.0
Oxychlordane	0.01	1.0
Toxaphene	1.0	50
trans-Nonachlor	0.01	1.0

*For some analytes, LOQs may vary slightly from MRLs due to program/project requirements.

TABLE 2
TARGET ANALYTES and METHOD REPORTING LIMITS* - SOIL/SEDIMENT/TISSUE

Analyte	MRL (µg/kg)
2,4'-DDD	1.0
2,4'-DDE	1.0
2,4'-DDT	1.0
4,4'-DDD	1.0
4,4'-DDE	1.0
4,4'-DDT	1.0
Aldrin	1.0
alpha-BHC	1.0
alpha-Chlordane	1.0
beta-BHC	1.0
Chlordane	10
Chlorpyrifos	1.0
cis-Nonachlor	1.0
delta-BHC	1.0
Dieldrin	1.0
Endosulfan I	1.0
Endosulfan II	1.0
Endosulfan Sulfate	1.0
Endrin	1.0
Endrin Aldehyde	1.0
Endrin Ketone	1.0
gamma-BHC (Lindane)	1.0
gamma-Chlordane	1.0
Heptachlor	1.0
Heptachlor Epoxide	1.0
Hexachlorobenzene	1.0
Hexachlorobutadiene	1.0
Hexachloroethane	1.0
Isodrin	1.0
Methoxychlor	1.0
Mirex	1.0
Oxychlordane	1.0
Toxaphene	100
trans-Nonachlor	1.0

*For some analytes, LOQs may vary slightly from MRLs due to program/project requirements.

TABLE 3
GAS CHROMATOGRAPH OPERATING CONDITIONS*

Gas Chromatograph: Agilent 6890	Agilent 6890
Injection Port Temperature: 40˚C, 40-250˚C at 250˚C/min., hold for 15 min.,	250-325˚C at 250˚C/min., hold for 5min.
Oven Temperature Program:	50˚C hold for 0.5min., 50-150˚C at 40˚C/min.; Ramp 13˚C/min. to 320˚C, hold for 3.92min.
Detector Temperature:	325˚C
Injection Volume:	1µL (2µL for ultra-low level analysis)
Column 1:	30m, 0.32mm ID, DB-XLB, 0.50µm film thickness or equivalent
Column 2:	30m, 0.32mm ID, DB-35MS, 0.25µm film thickness or equivalent.
Carrier Gas:	Hydrogen
Auxiliary Gas:	Nitrogen
Data System:	HP EnviroQuant

*The above instrument temperatures may be modified when determining additional single response or multi-response pesticides.

TABLE 4
CALIBRATION STANDARD PREPARATION

Initial Calibration Standards*

8081 Intermediate Std.	Initial Concentration	Final Volume	Solvent	Final Concentration	
1.0µL	2.0µg/mL	10mL	Hexane	0.2µg/L	
2.5µL				0.5µg/L	
5.0µL				1.0µg/L	
10µL				2.0µg/L	CCV Standard
25µL				5.0µg/L	
50µL				10µg/L	

Chlordane Intermediate Std.	Initial Concentration	Final Volume	Solvent	Final Concentration	
10µL	2.0mg/L	10mL	Hexane	2.0µg/L	
25µL				5.0µg/L	
50µL				10µg/L	
100µL				20µg/L	CCV Standard
250µL				50µg/L	
500µL				100µg/L	
1.0mL				200µg/L	

Toxaphene Intermediate Std.	Initial Concentration	Final Volume	Solvent	Final Concentration	
10µL	10mg/L	10mL	Hexane	10µg/L	
20µL				20µg/L	
50µL				50µg/L	
100µL				100µg/L	CCV Standard
200µL				200µg/L	
500µL				500µg/L	

*As needed for projects requiring non-routine additional compounds, similar dilutions are prepared to obtain calibration standards for these compounds.

TABLE 5

SUMMARY OF CORRECTIVE ACTIONS

Method Reference	Control	Specification and Frequency	Acceptance Criteria	Corrective Action
EPA 8000C EPA 8081B	ICAL	Prior to sample analysis	% RSD ≤ 20 COD ≥ 0.990	Correct problem then repeat ICAL
EPA 8000C EPA 8081B	ICV	After ICAL	± 20% Diff	Correct problem and verify second source standard; rerun second source verification. If fails, correct problem and repeat initial calibration.
EPA 8000C EPA 8081B	CCV	Prior to sample analysis	± 20% Diff	Correct problem then repeat CCV or repeat ICAL
EPA 8000C EPA 8081B	Method Blank	Include with each analysis batch (up to 20 samples)	<MRL	If target exceeds MRL, reanalyze to determine if instrument was cause. If still noncompliant then: Re-extract or reanalyze samples containing contaminate, unless samples contain > 20x amount in blank.
EPA 8000C EPA 8081B	Laboratory Control Sample	Include with each analysis batch (up to 20 samples)	See DQO	If exceeds limits, re-extract and re-analyze
EPA 8000C EPA 8081B	Matrix Spike	Include with each analysis batch (up to 20 samples)	See DQO	Evaluate data to determine if the there is a matrix effect or analytical error
EPA 8000C EPA 8081B	Matrix Spike Duplicates	Include with each analysis batch (up to 20 samples)	See DQO	Evaluate data to determine if the there is a matrix effect or analytical error

STANDARD OPERATING PROCEDURE E27, REV. 1
SEDIMENT THICKNESS OVER ARMORED BANKS: HAND PROBE

A Introduction

The following standard operating procedure (SOP) details the steps involved to survey sediment thickness by land or by diver using a hand-operated sediment probe device. This SOP has been updated to focus on remedial action areas and data needs arising from the Preliminary (30%) Remedial Design (RD).

B Station Location and Positioning

Sediment hand probing will be performed at targeted locations identified in the middle reach pre-design investigation Quality Assurance Project Plan Addendum No. 3 (for Phase III) to which this document is an appendix. Positioning will be determined using a handheld differential global positioning system receiver or traditional surveying methods by the topographic surveyor (if field activities align). Horizontal coordinates will be recorded in either latitude and longitude (WGS 1984, decimal degrees) or x and y in WGS 1984 UTM (meters). The investigation will be performed by shore-based personnel if the mudline is visible above water at low tide. If the mudline is underwater at low tide, work will be performed by a diver during an appropriate tide. Once a starting point has been determined based on preliminary probing parallel and perpendicular to the slope to identify the toe of the slope, coordinates will be recorded every 5 to 15 feet to delineate the toe of the armored slope.

Property access agreements must be in place before entering survey areas located on private property.

C Equipment and Supplies Required

The following equipment is necessary for sediment hand probing:

- Steel rod or equivalent, sharpened at one end and calibrated in 2-in. intervals (note: a specific probe will be selected during field preparation activities)
- Measuring tape
- Handheld differential global positioning system receiver
- Field notebook/log sheets

D Procedures

Sediment hand probing should be conducted within two hours of low tide. Probing will occur as follows:

1. Start at the apparent lateral edge of armoring or 20 feet beyond the remedial action area boundary for areas of continuous armoring. Walk down the bank at low tide, using visual and

probing methods to identify toe of armoring. Once toe of armoring has been identified, record starting position.

2. If toe of armoring is buried by sediment, advance the probe into the sediment and note depth of penetration and type of resistance met by the probe (if discernable). Additionally, record the location of the armor-sediment interface upslope (i.e., point where the armor is not buried). If no sediment is on the surface, note 0 feet as sediment thickness. Note additional observations regarding armoring, such as visible armoring, if the armoring is continuous; armoring type (concrete rubble, riprap, etc.); or other debris or structures in the area, as appropriate.

3. Record information in field notebook/log sheets.

4. Move laterally along the toe of armoring and record location between every 5 to 15 feet (depending on uniformity of the toe and field conditions). Repeat step 2 at each location, as applicable.

5. Record the location of the observed/assumed edge of downslope armoring in the field notebook/log sheets.

Note: For sediment thickness probing conducted by a diver (in areas where toe of armoring is below the water line at low tide), the same procedures will generally apply. Instead of starting from the top of bank and working waterward, the diver will deploy from a vessel and work from bottom of slope upward to identify the toe of armoring. The vessel will have a GPS (submeter) GNSS system along with an Ultra Shortline Baseline (USBL) transmitter and receiver for positioning of divers. The USBL system will be connected to HYPACK navigation software and provide real-time tracking of the divers, who will carry a USBL pinger. Starting point coordinates will be recorded in either latitude and longitude (WGS 1984, decimal degrees) or x and y in WGS 1984 UTM (meters). Subsequent locations will be recorded in field notebook/log sheets with direction and distance from the starting point.

For limited visibility, probe penetration into the sediment to armoring refusal may be done by feel/palpation (e.g., by placing groves or markers on the probe that can be counted by the diver by hand and reported to the surface to be recorded).

STANDARD OPERATING PROCEDURE (SOP) SW-65

Diver Sediment Sampling – LDW Precipitate Layer Coring

1) Purpose

Collect a representative sediment sample beneath a precipitate layer (consisting of cemented material) on the bottom of a water body using diver operations supported from a boat. The method covers locating the sample point, coring through asphalt, and collecting underlying sediment while preventing cross-contamination and sample loss.

2) Personnel and Roles

- **Field Lead / Scientist:** Defines sample locations, depth intervals, containers, preservation, and labeling; maintains chain-of-custody.
- **Dive Supervisor:** Controls dive plan, safety, communications, and abort criteria.
- **Diver(s):** Perform coring, precipitate layer plug removal, and sediment collection.
- **Boat Operator / Deck Crew:** Maintain station, assist line handling, sample receipt, and equipment decontamination.

3) Equipment and Materials

Positioning / Marking

- The Gravity vessel will have a GPS (submeter) GNSS system along with an Ultra Shortline Baseline (USBL) transmitter and receiver for positioning of divers. The USBL system will be connected to HYPACK navigation software and provide real-time tracking of the divers, who will carry a USBL pinger. In addition, a weighted marker (that is connected to the vessel) will mark the start point for the diver to progress to each target.

Cemented Layer Coring

- Underwater-capable **core drill** (hydraulic or pneumatic preferred) with:
    - **Diamond core bit** sized to project needs (4 in ID).
    - **Core barrel**, retaining springs/catcher if needed
- Backup: chisel/pry bar, small sledge/hammer (use only if allowed and safe).

Sediment Sampling Under Cemented Layer:

- **Hand core tube** (clear polycarbonate 3-inch OD) with core catcher and caps, or
- **Mini-piston/slide-hammer corer** if higher resistance sediment is expected.

Sample Handling

- Pre-cleaned jars (wide mouth, appropriate for analytes), labels, custody seals.
- Zip bags, absorbent, cooler with ice, temperature blank (if required).
- Rinse water (DI) and detergent (as required), brushes, aluminum foil, nitrile gloves.

Containment / Turbidity Control (recommended)

- Small **silt curtain skirt** / localized turbidity shroud, or
- Weighted "donut" tarp around work area, plus low-flow vacuum/filter system if permitted.

4) Pre-Dive Planning (Boat-Supported)

1. **Confirm objectives:** depth below cemented layer, sample volume, number of replicates, and analytes (drives jar type, preservation, and decontamination rigor).
2. **Hazard review:** boat traffic, entanglement risks, poor visibility, overhead hazards, contamination concerns, drill hazards, and decompression limits.
3. **Station-keeping plan:** anchor or hold position (spot-lock) so the boat remains directly over or up-current of the site.
4. **Communications:** diver-to-surface comms preferred; otherwise, line-pull signals with a dedicated tender.
5. **Contamination control:** define "clean" and "dirty" areas on deck; keep sample containers sealed until use.

5) Site Setup

1. Navigate to sample coordinates. Deploy a **weighted marker/shot line** at the target point.
2. Record: time, GPS, water depth, conditions, and any deviations.
3. If turbidity control is required, deploy a **localized shroud** or skirt around the marker area before drilling (as feasible).

6) Diver Procedure — Core Through Cemented Layer

1. **Locate the point** at the base of the shot line; confirm composition of cemented layer and note thickness if visible at edges/cracks.
2. **Prepare the drill:**

- Confirm bit integrity, barrel tightness, and that no lubricants/oils will contact the sample area.
- Verify drill power hose/air line management to avoid entanglement.

3. **Seat the core bit** perpendicular to the cemented layer surface. Apply steady pressure and begin drilling.
4. **Core advancement:**
   - Maintain a controlled feed rate to avoid bit wandering and excessive turbidity.
   - Periodically pause to clear cuttings; keep the work area contained as much as possible.
5. **Penetration criteria:** drill fully through the cemented layer and slightly into underlying material (typically 10–30 mm) to ensure complete breach.
6. **Retrieve cemented layer core plug:**
   - If the plug remains in the barrel, carefully withdraw the corer and retain the plug (if required as a sample/record).
   - If the plug remains seated, use a thin pry tool to lift it without disturbing underlying sediment.
7. **Minimize disturbance:** avoid sweeping fin kicks; hold position neutrally buoyant.

Quality note: If cemented layer thickness is critical, measure the recovered plug length and document (photo/notes).

7) Diver Procedure — Collect Underlying Sediment

After the hole is open, proceed with one of the following (prefer coring when stratigraphy matters):

Option A: Core Tube (recommended for representative profile)

1. Remove any loose cemented layer crumbs from the rim of the hole (do not push debris downward).
2. Insert the **hand core tube** through the cored opening into sediment.
3. Advance the tube to the target depth using steady downward pressure (or gentle twist).
4. Seal the top (cap or hand) and extract the core slowly to maintain suction.
5. Cap both ends underwater if possible; keep upright.

Option B: Grab Sample (when only bulk sediment is needed)

1. Using a pre-cleaned scoop/trowel, collect sediment from just below the cemented layer interface and (if required) deeper increments.

2. Fill jars carefully to avoid headspace if required for volatile analyses (follow the project's container/preservation requirements).

3. Keep the jar mouth away from disturbed edges; avoid including cemented layer fragments unless specified.

Option C: Mini-Piston / Slide-Hammer Corer (for dense sediment)

1. Align the corer through the hole; drive to depth with controlled hammer strokes.

2. Engage core catcher; extract and cap.

8) Sample Transfer to Boat

1. Diver places sealed samples into a **hand-up bag** or passes to tender at the line.

2. On deck, the sampler/Field Lead:

    - Confirms label (site ID, depth interval, date/time, diver initials).
    - Applies custody seals if required.
    - Places in cooler immediately.

9) Decontamination Between Locations

1. Decon drill bit/core barrel exterior and sediment tools per project QA/QC:

    - Detergent wash → tap rinse → DI rinse (as required).

2. Keep drill power unit and hoses in "dirty" area; prevent rinse water from contacting sample containers.

10) QA/QC and Documentation

- Field log: GPS, water depth, cemented layer thickness (if measured), hole diameter, sediment type, core depth, turbidity observations, and any deviations.
- Photo/video (underwater) if available to document cemented layer breach and sampling.
- Collect field duplicates and blanks per the sampling plan.

11) Acceptance Criteria

- Cemented layer fully penetrated with minimal spalling into the hole.
- Sediment sample collected from the specified depth interval(s) beneath the cemented layer.
- Samples sealed, labeled, preserved, and cooled within required time.
- Chain-of-custody complete.

12) Abort / Stop-Work Triggers (examples)

- Loss of station-keeping that risks diver safety or sample integrity.
- Excessive turbidity preventing safe tool use.
- Drill malfunction (uncontrolled rotation, hose issues, overheating).
- Evidence of contaminant sheen, unexpected utilities/structures, or unstable pavement.

STANDARD OPERATING PROCEDURE (SOP) SW-34

VIBRACORE STANDARD OPERATING PROCEDURES FOR UNDER-DOCK

SCOPE AND APPLICATION

This SOP describes the protocol for collecting sediment core samples from under-dock locations using a vibracorer, custom float frame, and a Research Vessel.

Station Access

Prior to entering select areas such as private beaches, embayments, or proximity to docks, it may be necessary to acquire permission from the landowner to access the property. Access permission must be acquired in advance of the sampling program and may require a written agreement.

Station Location

Samples will be collected at specific transects identified in project HV QAPP.

Positioning & Coordinates

Horizontal positioning will be determined by the onboard differential global positioning system (DGPS) based on target coordinates. Measured station positions will be converted to latitude and longitude (North American Datum [NAD] 83) to the nearest 0.1 second. The accuracy of measured and recorded horizontal coordinates will be within 2 meters. Vertical elevation of each boring station will be measured using a fathometer or lead line and converted to the applicable local elevation datum. If no GPS is available under-dock a tape line will be measured back to the main vessel and a position will be estimated.

Safety and Hazardous Materials Management

General Lab Safety- All general laboratory safety practices should be complied with, including wearing a lab coat, safety glasses, and gloves. Samples should be treated with regard to possible toxicity and microbiological potential.

Analysis - From a Vessel - Sampling personnel will follow standard safety procedures while on board the sampling vessel. The vessel skipper has ultimate responsibility for safety while the vessel is underway. During deployment of equipment, the operator and the skipper must communicate with one another to avoid potential loss of the instrument due to propeller interface with the underwater field cable.

Analysis – Streams/Rivers – Sampling personnel will always enter streams/rivers cautiously and follow standard safety procedures when entering these flowing bodies of water. There are many hazards associated with streams and rivers sampling. Some of these hazards include traffic, fast moving or deep water, steep slopes to sampling sites, and hostile dogs or people. Use extreme caution when exiting sampling vehicles, walking along busy highways or sampling on bridges. Fast moving water can cause the sampling personnel to lose balance and fall into the water. This can result in injury or drowning. Many of the

sampling sites require personnel to walk over riprap or other extremely rough and slippery terrain. Again, extreme caution combined with slow movements can minimize potential injury. Be aware of your surroundings and potential presence of other people, especially under bridges or in culverts.

SUMMARY OF METHOD

Gravity's RIC 5500 vibracore operates at 1800 vibrations per minute with an impact force of 5000 ft/lbs of force. The frequency of the unit can be adjusted in the field to minimize disturbance of the sediment substrates for optimum collection of representative layers. The vibracorer will use polycarbonate tubes that are 4 inches in diameter. The tubes have an internal lexan finger system to retain substrate at the tip as well as a custom check-valve inside the tube designed help retain core and minimize loss.

The custom float frame has a remote outboard motor, small a-frame and coring cable pulley. The float frame is towed by the larger research vessel into place at which point the vibracorer is mounted to the float frame and deployed under the dock. The float frame is connected to the main vessel by a winch and is moved into place with either the remote controlled outboard or by an operator on-board. Once the frame is in position it is anchored or tied to surrounding pilings and the winch safety is disengaged.

EQUIPMENT

The following procedure will be used to decontaminate sample tubes prior to use:

- Rinse and pre-clean with potable water
- Wash and scrub the tubes in a solution of laboratory grade, non-phosphate-based soap and potable water
- Rinse with potable water
- Seal both ends of each core tube with aluminum foil

PROCEDURES

Sample Collection

The vibracorer is lowered to the bottom, where the unit is energized and allowed to penetrate. The core will be driven to its maximum length or to refusal. Acceptance criteria for a sediment core sample are as follows:

- The core penetrated to, and retained material to, project depth or refusal
- Recovery was at least 75 percent of the length of core penetration
- Cored material did not extend out the top of the core tube or contact any part of the sampling apparatus at the top of the core tube
- There are no obstructions in the cored material that might have blocked the subsequent entry of sediment into the core tube and resulted in incomplete core collection

If core rejections require the core station to be relocated, two additional attempts will be made within a radius of 25 feet of the target. If penetration or retention continue to be an issue consistently across the site Gravity provides the following options

- For recovery, an internal piston or vacuum system can be used to remove backpressure and actively pull material into the tube
- For recovery, a lexan tip with a flexible nitrile liner can help keep soft muds retained
- For penetration, a waterjet can be used to penetrate areas unsuccessful by other methods and a sample collected below problem areas
- For penetration, a smaller diameter tube can be used to drive deeper

The core tube caps will be removed immediately prior to placement into the coring device. Care will be taken during sampling to avoid contact of the sample tube with potentially contaminated surfaces. Extra sample tubes will be available during sampling operations for uninterrupted sampling in the event of a potential core tube breakage or contamination. Core tubes suspected to have been accidentally contaminated will not be used. Logs and field notes of all core samples will be maintained as samples are collected and correlated to the sampling location map.

Sample Handling

Sediment processing will be conducted aboard the sampling vessel. Filled sample containers will be stored in coolers containing ice to maintain the samples at 4°± 2°C until delivery or shipping to the analytical laboratories.

All working surfaces and instruments will be thoroughly cleaned, decontaminated, and covered with aluminum foil to minimize outside contamination between sampling events. Disposable gloves will be discarded after processing each station and replaced prior to handling decontaminated instruments or work surfaces.

Sample containers will be kept in packaging as received from the analytical lab until use; a sample container will be withdrawn only when a sample is to be collected.
The steps for processing the samples are provided below.

1. Extrude sample material from sample core tube onto a stainless steel tray using a vibrating core-extruder. Alternatively, the core may be cut longitudinally using a circular saw, taking care not to penetrate the sediment while cutting.
2. Fill container with sample as full as possible to eliminate air space in sample jar (it may be necessary to slightly overfill jar to reach a convex meniscus and slide the the cap liner, with PTFE side down, expelling the additional sample).
3. Screw cap on the container and tighten.
4. Repeat steps 2 through 4 for the second 2-ounce glass container.
5. Record the description of the core sample on the core log form for the following parameters as appropriate and present:
   - Sample recovery (depth in feet of penetration and sample compaction)

- Physical soil description in accordance with the Unified Soil Classification System (includes soil type, density/consistency of soil, and color)
- Odor (e.g., hydrogen sulfide, petroleum, etc.)
- Vegetation
- Debris
- Biological activity (e.g., detritus, shells, tubes, bioturbation, and live or dead organisms)
- Presence and depth (in feet) of the redox potential discontinuity layer
- Presence of oil sheen
- Any other distinguishing characteristics or features

6. Using a clean spoon, place sample material from the core into a cleaned stainless steel bowl or HDPE bucket, homogenize using a stainless steel paddle and variable speed drill,
7. Collect and process grain size analysis with Field Sieve Kit using the PSDDA volumeteric method.
8. Collect and process Shear Stress using a Humboldt Mini Torvane test kit (H4212 MH)
9. Thoroughly check all sample containers for proper identification, analysis type, and lid tightness.
10. Pack each container carefully to prevent breakage and place upright inside a cooler with ice for storage at the proper temperature (4°± 2°C for all samples).

RECORDING

The following information will be included in this log:

- Elevation of each station sampled as measured from MLLW
- Location of each station as determined by DGPS
- Date and time of collection of each sediment core sample
- Names of field supervisor and person(s) collecting and handling the sample
- Observations made during sample collection including: weather conditions, complications, ship traffic, and other details associated with the sampling effort
- The sample station identification
- Length and depth intervals of each core and estimated recovery for each sediment sample as measured from MLLW
- Qualitative notation of apparent resistance of sediment column to coring
- Any deviation from the approved SAP

Environmental Monitoring of vibracoring activities

Gravity has extensive experience operating vibracorers in sensitive habitat areas and has conducted a significant amount of field monitoring to assure minimal impact of the vibracore system. Below are some key monitoring considerations

Suspended sediments – the vibracorer produces minimal impact to surface waters. Vibration typically settles particles and because most the energy from the coring is located at the subsurface driving tip, surface sediments are often not disturbed. In-water turbidity

monitoring has been conducted during coring at a variety of sites with different sediment substrates. Project NTU has not been observed above 2 NTU over background.

Noise – the vibracorer does not cause mechanical impact, but centrifugal impact and therefore is not comparative to typical pile driving operations. Gravity has monitored with hydrophones near vibracoring sites and we have not observed decibel readings of 20.

STANDARD OPERATING PROCEDURE E31
SEDIMENT-WATER SHAKE TEST

A Introduction

The following standard operating procedure details the equipment, field procedures, materials, and documentation procedures necessary to perform sediment-water shake testing.

B Equipment and Supplies Required

The following is a list of equipment that may be necessary to carry out the activities in this SOP. Additional equipment may be required, depending on field conditions.

- Field notebook/logs
- Photoionization detector (PID)
- Disposable, 4-ounce, clear plastic containers with covers
- Light source (such as an LED flashlight or work lights)
- Distilled water (≥40ºF)
- Tape measure demarcated with centimeters (cm) and millimeters
- Camera
- Whiteboard and pens/markers
- Paper towels
- Stainless-steel spoon

C Procedures

The procedure for conducting shake tests for sediment cores collected in the field will follow Steps 1 through 10. The procedure for conducting shake tests for frozen, archived samples will follow Steps 5 through 10 after the sample is thawed in a laboratory.

Step 1: Cut and process sediment cores for visual observations (consistent with procedures used for processing of subsurface sediment cores for sediment chemistry [SOP E19]).

Step 2: As part of conducting visual observations, categorize the core as follows:

1) Visual observations of potential nonaqueous phase liquid (NAPL; blebs, coated, or saturated, as defined in the Physical Description of Subsurface Sediment and Native Material Key [Attachment E31-1])

2) Visual observations of sheen (as defined in the Physical Description of Subsurface Sediment and Native Material Key [Attachment E31-1])

3) No visual observations of potential NAPL or sheen

Step 3: Collect PID readings at 1-foot intervals during core processing and record the readings in the field notebook or sediment core log.

Step 4: Select one interval from the core for conducting the shake test within the elevations identified for dredging. The field crew will consider the following when selecting the interval:

- Visual evidence of the presence of sheen or NAPL
- Elevated PID readings (i.e., relative to other intervals in the core)
- Presence of petroleum odor

If none of the above criteria are useful in identifying an interval for the shake test, the field crew will randomly select one interval (within the range or dredge elevations) for conducting the test.

Step 5: Perform the shake test as follows:

a. Label the 4-oz container with the station ID, depth interval, date, and time of shake test, and mark a sediment fill line at 1 cm from the bottom of the jar and a water fill line at 3 cm from the bottom of the jar.
b. Add sediment up to the sediment fill line on the jar.
c. Add distilled water up to the water fill line on the jar.
d. Cap the jar and shake gently by inverting the jar repeatedly for 10 seconds to suspend sediment.
e. Allow the sample to sit and sediments to settle for a minimum of 10 minutes but no longer than 1 hour.[1]

Step 6: Record observations regarding color and transparency of the sample in the Sediment-Water Shake Test Field Log provided in Attachment E31-1. Illuminate the shake test container and water surface with a light source (e.g., LED flashlight or work light) when observing the shake test results and record observations of NAPL presence/absence and/or sheen, as detailed in step 7.

Step 7: Observations following completion of the sediment-water shake test recorded in the Sediment-Water Shake Test Field Log (Attachment E31-1) will be determined as follows:

a. If observable NAPL is present in the sample, blebs or a layer of a separate phase material will be apparent on the side of the jar, in the water, or on the surface of the water in the jar. Record in the field log that NAPL is present, and describe the NAPL color, relative amount, and distribution (frequency and size of blebs or thickness of layer) in accordance with the Physical Description of Sediment-Water Shake Test Results Key (Attachment E31-1).

[1] This time range is designed to allow separation to occur so an observation of NAPL can be made.

b. If there is **no** observable NAPL, record in the field log that there is no observed NAPL.[2]

c. If a sheen (a silvery or rainbow film on the surface of water) is observed, record in the field log the sheen color in accordance with the Physical Description of Sediment-Water Shake Test Results Key (Attachment E31-1).

Step 8: Take horizontal and vertical color photographs of the shake test container without the lid to document the shake test results. Include the station ID, depth interval, date, and time of the shake test in the photograph.

Step 9: All working surfaces and instruments will be thoroughly cleaned and decontaminated in accordance with project requirements.

Step 10: Disposable PPE and shake test jars will be discarded after processing at each station, in accordance with project requirements and replaced prior to conducting shake tests on the subsequent core (in the field) or sample (in the laboratory).

D Attachment

Attachment E31-1 Required Field Logs

- Sediment-Water Shake Test Field Log
- Soil/Sediment Classification Field Guide
- Physical Description of Sediment-Water Shake Test Results Key

[2] Note that it is possible for NAPL material (e.g., ash, miscellaneous flocculent, or bio-slime) to float on the water surface or adhere to the sidewalls of the shake test container. Such observations will be noted in the Sediment-Water Shake Test Field Log (Attachment E31-1).

DRAFT

Attachment E31-1
Required Field Logs

Sediment-Water Shake Test Field Log

Project: LDW- Middle Reach Station ID: ____________
Project No.: 210075-01.03 Date: ____________
Staff: ____________

Depth Interval/ Soil-Water Mixing Time	Shake Test Results			
	Time of Observation	Water Color/ Transparency	Visual Observation of NAPL or Sheen[1] *Check result and provide additional notes as needed*	
				NAPL Blebs Observed *Color and degree of accumulation:*
				NAPL Layer Observed *Color and thickness of layer:*
				Sheen Observed *Sheen color:*
				No Observed NAPL or Sheen
				NAPL Blebs Observed *Color and degree of accumulation:*
				NAPL Layer Observed *Color and thickness of layer:*
				Sheen Observed *Sheen color:*
				No Observed NAPL or Sheen
				NAPL Blebs Observed *Color and degree of accumulation:*
				NAPL Layer Observed *Color and thickness of layer:*
				Sheen Observed *Sheen color:*
				No Observed NAPL or Sheen
				NAPL Blebs Observed *Color and degree of accumulation:*
				NAPL Layer Observed *Color and thickness of layer:*
				Sheen Observed *Sheen color:*
				No Observed NAPL or Sheen

Notes:
1 = Visual observation of sheen or NAPL described in accordance with SOP 2.16 Attachment 3 – Physical Description of Soil-Water Shake Test Results Key
NAPL = nonaqueous phase liquid

SOIL/SEDIMENT CLASSIFICATION FIELD GUIDE

ANCHOR QEA

SOIL/SEDIMENT DESCRIPTION COMPONENTS: USCS name (USCS symbol): density/consistency, moisture, color, list gravel/silt/sand by %; additional remarks

Density of Coarse-grained (Cohesionless) Soils	
Density	***Standard Penetration (N; blows/foot)***
Very Loose	0 to 4
Loose	4 to 10
Medium Dense	10 to 30
Dense	30 to 50
Very Dense	More than 50

Consistency of Fine-grained (Cohesive) Soils			
Consistency	***Standard Penetration (N; blows/foot)***	***Unconfined Compressive Strength (tsf)***	***Manual Penetration Test***
Very Soft	0 to 2	<0.25	Thumb will penetrate soil more than 1 inch
Soft	2 to 4	0.25 to 0.5	Thumb will penetrate soil about 1 inch
Medium Stiff	4 to 8	0.5 to 1	Molded by moderate to firm finger pressure
Stiff	8 to 15	1 to 2	Readily indented by thumb, difficult to penetrate
Very Stiff	15 to 30	2 to 4	Readily indented by thumbnail
Hard	More than 30	>4	Indented with difficulty by thumbnail

Gray

Gray-brown

Olive-brown

Olive

Olive-gray

Dark brown

Red-gray

Red-brown

Brown

Red

Light brown

Tan

Yellow-brown

Red-yellow

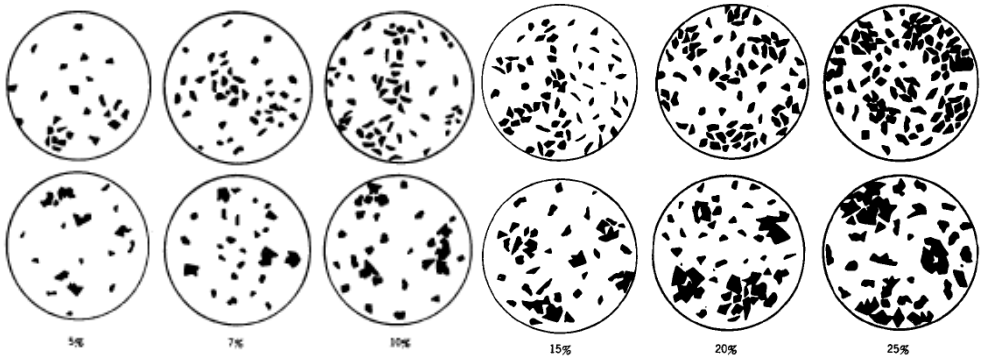
Yellow

Moisture Content	
Dry	Absence of moisture, dusty, dry to the touch
Moist	Damp, but no visible water
Wet	Visible, free water

Particle Shape/Angularity	
Description	***Criteria***
Rounded	Near-spherical or oval
Sub-rounded	Primarily rounded corners and edges
Sub-angular	Slightly rounded corners and edges
Angular	Sharp corners and edges

Grain Size				
Soil Component		***Anthropogenic Component***	***Size Range (U.S. Standard Sieve)***	***Approximate Size***
Boulders		Blocks	>12 inches	larger than basketball
Cobbles		Pieces	3 to 12 inches	fist to basketball
Gravel	Coarse	Fragments	3/4 to 3 inches	thumb to fist
	Fine		#4 to 3/4 inches	pea to thumb
Sand	Coarse	Particles	#10 to #4	rock salt to pea
	Medium		#40 to #10	sugar to rock salt
	Fine		#200 to #40	flour to sugar
Fine Grained	Silt	Specks	Pass #200	finer than flour
	Clay			

Charts for Estimating Percentages (After Compton, 1962)



Index of Plasticity	
Description	***Criteria***
Non-plastic	A 1/8 inch (3 mm) thread cannot be rolled at any water content. Has definite structure but can easily be separated or crumbled. Is readily rinsed off sampling equipment. Breaks easily when pieces are dried.
Low Plasticity	A thread can barely be rolled.
Medium Plasticity	A thread is easily rolled. Stays together relatively well when molded (i.e., behaves like Play-Doh). Can be washed off sampling equipment easily. Requires some effort to break when pieces are dried.
High Plasticity	A threat is easily rolled, and can be rerolled several times. Can be easily molded and stays together very well, but takes effort to rinse off of sampling equipment. Difficult to break when pieces are dried.

Criteria for Describing Soil Structure	
Decomposed	Visible signs of breakdown, applicable to organic matter and rock.
Homogeneous	Same color and appearance throughout.
Interbedded	Alternating soil layers of different composition.
Lens	A very thin cohesive layer, less than .5-inch thick.
Layer	A general term for material lying essentially parallel to the surfaces against which it was formed (.5-inch to 12-inch thick).
Varved	A cyclic sedimentary couplet consisting of a coarser and a finer layer, representing variation in depositional energy.
Washed	Material missing in core tube due to loss through the bottom of sampler due to improper closing.

1. Visual Impacts	
1a. Sheen (no sheen observed unless noted) (Modified from ASTM F2534-06)	
If a sheen is observed (a silvery or rainbow film on the surface of the shake test water), **record the sheen color.**	
Silvery	Metallic, silver/gray colored
Rainbow	Multicolored
Dark Rainbow	Multicolored with some dark metallic or brown/black coloring
Dark	Dark metallic or brown/black colored
Distinguishing hydrocarbon sheen from biological sheen: If disturbed, a hydrocarbon sheen will typically coalesce, whereas an inorganic sheen will break apart and has a blocky appearance.	
1b. NAPL **(no NAPL observed unless noted)**	
If NAPL is observed, **record the NAPL color and whether it is present as blebs or a layer** on the sides of the shake test jar, in the water, or on the surface of the water.	
Blebs	Blebs are discrete sphericals of NAPL present on the side of the shake test jar, in the water, or on the surface of the water in the jar. The degree of accumulation should be described.
Layer	NAPL appears as a distinct layer within the shake test jar. If possible, the thickness of the NAPL layer will be measured.

Note:

NAPL = nonaqueous phase liquid

1.0 SCOPE

To determine the percent mortality of *Oncorhynchus mykiss* exposed to 10 mg/L (extremely hazardous waste [EHW] designation threshold) and/or 100 mg/L (dangerous waste [DW] designation threshold) for 96 hours. The test sample fails the bioassay by exhibiting a median lethal concentration (LC_{50}) less than or equal to (i.e., toxicity greater than or equal to) the regulatory threshold (i.e., 100 mg/L for DW or 10 mg/L for EHW) The standard protocol that will be followed is the **Washington State DOE 80-12.**

Title	Citation
Biological Testing Methods 80-12 for the Designation of Dangerous Waste: Static Acute Fish Toxicity Test. Publication no. 80-12. Revised September 2020	WDOE 2020

2.0 SUMMARY OF TEST

2.1 Approach

Number of replicates per concentration	3
Number of concentrations per sample	1 (10 mg/L for EHW and 100 mg/L for DW)
Volume of test chamber	7500 mL (minimum)
Volume of test samples and controls	6000 mL (minimum), minimum depth 15 cm
Biological loading	< 0.8 g/L
Number of test organisms per chamber	10
Test substance renewals	None
Type of biological observations	Survival, weight (wet weight, used to determine loading) and standard length
Definition of death for this test	Lack of movement after a pulse of water has been applied from a disposable pipette
Times of biological observations	Survival - daily; wet weight and standard length at end of test (10 control fish)
Types of water quality analyses	DO, temperature, conductivity, and pH in all tanks at test initiation. DO and pH in one replicate per concentration, daily thereafter. Temperature measured continuously in one tank. Hardness and alkalinity in control and test concentrations at test initiation
Sample Holding Time	45 days from collection

2.2 Physical Requirements

DO	90% (9.7 mg/L) at test initiation. DO should not drop below 60% (6.4 mg/L) and must not drop below 50% (5.4 mg/L) over the remainder of the test. Aerate if DO is in danger of dropping below 6.4 mg/L.
Temperature	12 ± 2.0°C
pH	7.4 – 8.3 (dilution water requirements [USEPA 2002]), 6.0-9.0 (sample / organism tolerance). pH of samples is not adjusted if out of range.
Hardness	40 - 100 (mg/L as $CaCO_3$)
Lighting	16 hours light, 8 hours dark at approximately 50-100 foot-candles (550-1050 lux)

2.3 Biological Requirements

Feeding	Test organisms will not be fed up to 48 hours before testing or during the test
Life stage	Juvenile, 30-90 (preferred) day old fish from swim-up date (± 5-day age range required), < 3.0 grams (required)
Dilution water	40-100 (mg/L $CaCO_3$) hardness water; dechlorinated tap water (preferred) or reconstituted moderately hard water

3.0 TEST ORGANISM

The rainbow trout, *Oncorhynchus mykiss*, will be the test organism. This organism is widely used in toxicity testing.

3.1 Test Organism Specifications

Species:	*Oncorhynchus mykiss*
Source:	Troutlodge, Inc. Sumner, WA; Thomas Fish Company, Anderson, CA; or suitable supplier
Age:	Juvenile rainbow trout 30-90 days old from swim-up (preferred), < 3.0 grams (required), as uniform in size as possible. All fish must be from the same batch and not vary in age by more than 4 to 5 days (required).
Identification:	Before exposure to test substances, individuals will be positively identified as *Oncorhynchus mykiss* using Moyle (1976)

3.2 Test Organism Care

Records of the stock shipments will be kept, including the original source, feeding regime, and culture water characteristics. All efforts will be made to obtain fish that are disease-free, as from a hatchery that will certify the fish are disease-free.

Test organisms should ideally be held for 14 days before testing, however if fish are obtained from a commercial hatchery and meet the performance standards below an acclimation period of 48 hours is acceptable. If greater than 10% of the organisms are unhealthy upon receipt or during acclimation, contact the lab manager. If more than 10% of the fish die during the acclimation period, discard the entire batch. If < 5% die, then the batch is acceptable for testing. If 5-10% die, extend the acclimation period to 7 days. If ≥ 5% die between 24 hours after arrival and the end of the extended 7-day acclimation period, discard the entire batch.

Test organisms should be held at 12 ± 2°C in the same water type that will be used in testing. Water quality will be monitored during acclimation. The test organisms should be the same age and from the same source. *Oncorhynchus mykiss* will be fed *ad libitum* fine texture trout chow through the holding period up to 48 hours prior to testing. Fish will not be fed 48 hours before testing or during the test. Food identification, source, preparation, and quality will be tracked.

4.0 TEST SUBSTANCE

The test substance will be labeled, properly stored, and tracked by internal chain-of-custody procedures throughout its tenure at the Port Gamble Laboratory. The test substance will not be heated, filtered, distilled, frozen, or otherwise altered without prior written consent by the Client. The test substance is stored at 4°C in a secure and distinct storage area. Before opening the sample container, a wrist-action shaker may be used to make certain it is as homogenous as possible. A rotary mixer may be used to mix samples with dilution water for 18 hours. The water should pass through a 9.5-mm sieve, but if particles do not, they can be crushed or ground to a smaller size.

5.0 EQUIPMENT

5.1 Instrumentation

500-mL wide mouth glass jars with Teflon-lined lids
7.5-L plastic containers
Virgin square-bottomed plastic bags of food-grade quality
Plastic covers with air input and exhausts ports
Automatic temperature logger
Rotary agitation apparatus capable of 30 ± 2 rpm

Light meter
Orion Star Model A329 pH/ISE/Conductivity/DO mulitmeter and probes
Colorimetric titration kits for water hardness and alkalinity

5.2 Apparatus

5.2.1 Test Area

The test area consists of a water bath, temperature controlled room, or incubator capable of maintaining constant temperature and appropriate illumination. The facility will be well ventilated and free of fumes.

5.2.2 Lighting

Overhead lighting will be at 50-100 foot-candles (550-1050 Lux), with a photoperiod of 16 hours light and 8 hours dark (± 15 min.).

5.2.3 Test Chambers

7.5-L plastic container, lined with virgin square-bottomed plastic bags of food-grade quality.
Plastic cover, with air input and exhausts ports.

6.0 PROCEDURE

Dangerous or Extremely Hazardous Materials testing will be conducted as defined in WDOE 80-12 (revised 2020). Material submitted for such testing will be extracted by use of rotary agitation apparatus capable of 30 ± 2 rpm.

Prior to conducting the extraction, determine the need for reducing the sample particle size. Particle reduction is required for solid samples unless the surface area per gram of material is equal to or greater than 3.1 cm^2, or is smaller than 1 cm in its narrowest dimension (i.e., is capable of passing through a 9.5 mm [0.375 inch] standard sieve). If the surface area is smaller or the particle size larger than described above, prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to an acceptable surface area or particle-size. Note: Surface area criteria are meant for filamentous (e.g., paper, cloth, and similar) waste material. Actual measurement of surface area is not required, nor recommended.

The appropriate weight of sample (either solids or fluids) will be added to a measured volume of dilution water (approximately 200 mL) in a 500-mL wide-mouth glass jar and secured with a closure containing a Teflon cap. One jar is prepared for each treatment replicate and blank jars containing no sample are prepared for use in the test controls. These jars are then agitated for

18 ± 2 hours at 23 ± 2°C. Use a temperature logger to record extraction temperature. Rinse the outside of the extraction jars with deionized water, remove the cap then add the slurry to dilution water in the test chamber, such that the total volume is 6 L and the target concentrations of sample are achieved. After rinsing the interior of the jar with test chamber water, the glass jar will be placed on its side in the test chamber along with the Teflon cap liner. Blank jars and liners will be placed in the controls.

The Excel spreadsheet (Figure 1) below may be used for determining sample and diluent volumes for achieving the desired concentrations.

Once temperature has been equilibrated, water quality parameters are recorded for each treatment being analyzed. Once water quality has been confirmed to be within test range, the test is initiated via the methods described below.

Note: pH adjustment is not allowed.

Figure 1.

Rainbow Trout 80-12 Dangerous Waste

Concentration (mg/L)	100	10	TS Balance/Pipette ID	
Total Volume (TV) (mL)	6000	6000	Shake DW Balance ID	
Grams of Substance	0.6	0.06	Chamber DW Balance ID	
Date/Time Shake Start		Date/Time Shake End	Temperature °C	

Rep 1

Conc. (ppm)	Target TS Weight (g)	Actual TS Weight (g)	Target Shake DW Volume (g)	Actual Shake DW (g)	Target Chamber DW (g) (TV - E&C)	Actual Chamber DW (g)	Final Conc. (ppm) (C*1000) / ((E+G)/1000)	Initials
A	B	C	D	E	F	G	H	
0	0.00		200.00					
10	0.06		199.94					
100	0.60		199.40					

Rep 2

Conc. (ppm)	Target TS Weight (g)	Actual TS Weight (g)	Target Shake DW Volume (g)	Actual Shake DW (g)	Target Chamber DW (g) (TV - E&C)	Actual Chamber DW (g)	Final Conc. (ppm) (C*1000) / ((E+G)/1000)	Initials
A	B	C	D	E	F	G	H	
0	0.00		200.00					
10	0.06		199.94					
100	0.60		199.40					

Rep 3

Conc. (ppm)	Target TS Weight (g)	Actual TS Weight (g)	Target Shake DW Volume (g)	Actual Shake DW (g)	Target Chamber DW (g) (TV - E&C)	Actual Chamber DW (g)	Final Conc. (ppm) (C*1000) / ((E+G)/1000)	Initials
A	B	C	D	E	F	G	H	
0	0.00		200.00					
10	0.06		199.94					
100	0.60		199.40					

TS = Test Sample; DW = Dilution Water

6.1 Preparation

6.1.1 Labware Preparation

Labware is described as any plastic or glass material used in the laboratory that will come into contact with any of the test substances or organisms in this evaluation. Labware must be cleaned prior to use following the procedures outlined in SOP ***LAB019***.

6.1.2 Dilution Water Preparation

The dilution water will be a freshwater source deemed appropriate by the laboratory and may include reconstituted water (prepared from deionized water and reagent grade salts, SOP ***LAB020***), or carbon filtered municipal water. Carbon filtered municipal water is preferred. The dilution water is recommended to be of a moderate hardness (80 -100 mg/L $CaCO_3$) and should be no less than 40 mg/L mg/L $CaCO_3$.

6.1.3 Test Organism Acclimation

Stock cultures will be acclimated in the same dilution water and at the same temperature as in the test procedures. If organisms are transferred to new conditions, then temperature changes will not exceed 3°C within a 24-hour period. Do not feed for 48-hours prior to testing.

Test organisms should ideally be held for 14 days before testing, however if fish are obtained from a commercial hatchery and meet the performance standards below an acclimation period of 48 hours is acceptable. If greater than 10% of the organisms are unhealthy upon receipt or during acclimation, contact the lab manager. If more than 10% of the fish die during the acclimation period, discard the entire batch. If < 5% die, then the batch is acceptable for testing. If 5-10% die, extend the acclimation period to 7 days. If ≥ 5% die between 24 hours after arrival and the end of the extended 7-day acclimation period, discard the entire batch.

6.2 Primary Task

6.2.1 Test Dilution Preparation

Test substance dilutions will be prepared according to section 6.0 using labware cleaned according to Section 6.1.1 or using pre-cleaned materials of a disposable nature. The final test substance dilutions will be 10 mg/L for EHW and 100 mg/L for DW. Dilution water will be the only water used in making up all stock and final dilutions and should have a dissolved oxygen saturation of 90-100% (≥ 9.7 mg/L at 12°C). There will be enough test dilution water made for requisite chemical analysis (if needed). Each test chamber will be labeled with a coded test chamber number, representing the specific test, the concentration, and the replicate number.

6.2.2 Reference Substance Test

A reference toxicant test will be conducted on each batch of test organisms either concurrently with project samples or monthly, depending upon QA requirements. The reference toxicant test will consist of a 96-hour exposure to at least five concentrations of a reference substance (sodium dodecyl sulfate) used to assess the health and sensitivity of the test organisms. Dilutions will be selected to bracket laboratory historical 96-hour LC_{50}. The LC_{50} results will be compared with historical data from definitive bioassays with the reference substance. The results of the 96-hour mortality, determined during this study, will be reported and used in combination with control mortality to characterize the health of the test organisms.

6.2.3 Test Organism Addition

O. mykiss will be captured using a small aquarium net (fine, soft mesh) and carefully transferred to the holding tanks or test chambers beneath the water. The volume in the holding chamber will be reduced, and the fish will be captured, one at a time, and placed into test chambers. Test organisms will be transferred to test chambers in a manner to avoid systematic bias. Test chambers will be arranged randomly in the water bath.

6.2.4 Test Initiation

The test is initiated when the first test organism enters a test chamber.

6.2.5 Test Measurements

Data are recorded on data sheets.

Water Quality. All probes will be cleaned thoroughly before initial use. Follow measurement procedures outlined in SOPs ***EQP060***, ***EQP061***, ***EQP062***, ***LAB021*** and ***LAB022***. Data collection will start in the controls and proceed from the lowest test dilution to the highest. The probes will be rinsed with dilution water between each holding flask. Readings will be taken the first time interval where all animals are found to be dead in all replicates of a test dilution, but no subsequent readings will be taken from this test dilution.
Measurements to be taken are:

- Dissolved oxygen (all chambers at test initiation and 1 replicate per concentration daily thereafter)
- Temperature (all chambers at test initiation and continuous with temperature logger in one chamber)
- pH (all chambers at test initiation and 1 replicate per concentration daily thereafter)
- Hardness (test initiation only, one measurement for each concentration)

- Conductivity (all chambers at test initiation)
- Alkalinity (test initiation only, one measurement for each concentration)

Chemistry. No chemical analyses other than hardness and alkalinity are specifically required for this fish toxicity test; however, chemistry samples may be collected depending upon specific project needs. Refer to project specific documents for further details.

Biological. Observations will be made daily

Measurements to be taken are:

- Number of test organisms alive (required)
- Abnormal behavior (recommended)
- At test termination ten control fish will be weighed (to 0.01 g) and measured (standard length to caudal penduncle).
- Dead test organisms will be removed and placed in appropriate containers, and at termination these organisms and those surviving will be disposed of in accordance with state laws.

Disposal.

Surviving fish are euthanized by immersing in a 100% ethanol solution or freezing, bagged, and placed in the municipal waste dumpster. If the test findings indicated that the samples analyzed were not dangerous or extremely dangerous waste, the remaining test solutions may be disposed of down the municipal sewer line. In the event of DW or EHW finding test solutions will be retained for additional testing or hazardous waste disposal.

6.3 Post-task

6.3.1 Calculations

Results Needed:

- Percent mortality at reference toxicant dilutions and an LC_{50} (if applicable).
- Cumulative deaths in each test chamber at 96 hours
- Total number of deaths out of 30 animals at each concentration
- Tables showing biological, chemical, and physical data
- Statistical evaluation (if needed) following 80-12 procedures

6.3.2 Method

Use the methods as described in WDOE 2020 in the Calculation of Results section beginning on page 16. Within a 90 percent confidence limit, the test sample fails the bioassay by exhibiting a median lethal concentration (LC_{50}) less than or equal to (i.e., toxicity greater than or equal to) the

regulatory threshold (i.e., 100 for DW or 10 mg/L for EHW) when the calculated t statistic is greater than a critical t value.

7.0 HEALTH AND SAFETY CONSIDERATIONS

Proper laboratory protection, including lab hood or ventilation system, lab coat, closed-toe shoes, gloves and safety glasses, is required when working with chemicals and unprocessed samples.

Refer to the Port Gamble Laboratory's Health and Safety Plan at S:\Health and Safety for procedures to ensure safe operation in the laboratory and for contingency plans in the event of an accident or emergency.

For specific chemical health and safety information, refer to the Safety Data Sheet log.

8.0 PERSONNEL

Any technician trained in these procedures may perform them.

9.0 QUALITY ASSURANCE REQUIREMENTS

Test acceptability criteria are:

- > 90% survival in control.
- Test loading rate should not exceed 0.8 g wet fish tissue per Liter of exposure volume as determined from fish weights taken at test termination. This is not a strict criterion per se, but would be used to determine if fish mortality may have been caused by overcrowding.

10.0 REFERENCE DOCUMENTS

10.1 Internal Documents

EQP060 - Calibration/Operation/Maintenance of Orion Star Model A329 pH/ISE/Conductivity/ DO Meter (pH)
EQP061 - Calibration/Operation/Maintenance of Orion Star Model A329 pH/ISE/Conductivity/DO Meter (DO)
EQP062 - Calibration/Operation/Maintenance of Orion Star Model A329 pH/ISE/Conductivity/DO Meter (Conductivity and Temperature)
LAB019 - Labware Washing Procedure

LAB020 - Preparation of Reconstituted Moderately Hard Water
LAB021 - Determination of Alkalinity
LAB022 - Determination of Water Hardness

10.2 Method Guidance Documents

Moyle, P.B. 1976. Inland Fishes of California. Univ. of Calif. Press, Berkeley and Los Angeles, CA.

USEPA. 2002. Methods for measuring the acute toxicity of effluents and receiving waters to freshwater and marine organisms. 5th ed. EPA-821-R-02-012 Environmental Monitoring Systems Laboratory, Office of Research and Development, EPA, Cincinnati, OH.

Washington Department of Ecology. 2020. Biological Testing Methods 80-12 for the Designation of Dangerous Waste: Static Acute Fish Toxicity Test. Publication No. 80-12.

11.0 APPENDIX OF CHANGE

8/20/15 Changed test organism acclimation section to reflect a 10% mortality threshold in assessing the organism's health

06/13/16 Added "uncontrolled" statement to SOP footer and updated Health and Safety section

3/28/17 Updated health and safety information, removed branding, added review documentation section. Updated information on animal health upon receipt.

1/5/21 Test temperature changed from 12 ± 1.0 to 12 ± 2.0°C. Added minimum depth. Dissolve oxygen requirements changed to 90% (9.7 mg/L) at test initiation. DO should not drop below 60% (6.4 mg/L) and must not drop below 50% (5.4 mg/L) over the remainder of the test. Aerate if DO is in danger of dropping below 6.4 mg/L. Specified in section 6.2.1 that dilution water should have 90-100% (≥9.7 mg/L) saturation prior to solution preparation. Aerate if necessary. Clarified hardness limits and that hardness and alkalinity must be measured in all test concentrations at test initiation. In section 2.3 and 3.1 trout age specified as juvenile, < 3.0 grams, variation in age not more than 4 to 5 days, all fish should be from same batch of animals (age range from swim-up retained). Extended fish acclimation period to a preferred 14 days. Added the following verbiage to section 3.2 and 6.1.3: Test organisms should ideally be held for 14 days before testing, however if fish are obtained from a commercial hatchery and meet the performance standards below an acclimation period of 48 hours is acceptable. If

greater than 10% of the organisms are unhealthy upon receipt or during acclimation, contact the lab manager. If more than 10% of the fish die during the acclimation period, discard the entire batch. If < 5% die, then the batch is acceptable for testing. If 5-10% die, extend the acclimation period to 7 days. If ≥ 5% die between 24 hours after arrival and the end of the extended 7-day acclimation period, discard the entire batch. Specified that tumbler should be capable of 30 ± 2 rpm. Added pH adjustment statement and following verbiage to section 6.0: Prior to conducting the extraction, determine the need for reducing the sample particle size. Particle reduction is required for solid samples unless the surface area per gram of material is equal to or greater than 3.1 cm^2 or is smaller than 1 cm in its narrowest dimension (i.e., is capable of passing through a 9.5 mm [0.375 inch] standard sieve). If the surface area is smaller or the particle size larger than described above, prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to an acceptable surface area or particle-size. Note: Surface area criteria are meant for filamentous (e.g., paper, cloth, and similar) waste material. Actual measurement of surface area is not required, nor recommended. Added use of temperature logger during extraction. Clarified cleaning of outside of test jar post-extraction before adding the solution to the test chamber. Updated timing of water quality and use of temperature logger in section 2.1 and 6.2.5. Specified use of sodium dodecyl sulfate as reference toxicant in section 6.2.2. Added passing criteria for samples in sections 1.0 and 6.3.2. Updated references.

5/11/23 Updated pH range for dilution water to match ranges allowed in USEPA 2002 (per page 26 of the 80-12 guidance document); previous range was only for reconstituted water, and lab primarily uses dechlorinated tap water. Removed use of diluted mineral water in section 6.1.2. Updated Figure 1. Added verbiage to section 2.2 that pH of samples is not adjusted if out of range.

12.0 DOCUMENT REVIEW

SOP Approval

Name	Signature	Title	Date
		Quality Systems Director	
		Laboratory Manager	

Acknowledgement below indicates that the individuals have read and understood the concepts summarized in this document.

Name	Signature	Date

Analytical Resources, LLC
Analytical Chemists and Consultants

Standard Operating Procedure

TCLP Extraction for Nonvolatile Organic & Inorganic Parameters
SW-846 Method 1311 TCLP
ARLLC Prep Code: LEN/LEM

SOP 531S
Revision 010.2

Revision Date: 12/02/25
Effective Date: 2/23/17

Prepared By:

Jay Kuhn

Approvals:

Laboratory Manager

David R Mitchell

Quality Assurance

Annual Review

SOP Number:

Title: TCLP Extraction for Nonvolatile Organic & Inorganic Parameters SW-846 Method 1311 ARLLC Prep Code: LEN/LEM

The ARLLC employee named below certifies that this SOP is accurate, complete and requires no revisions

Name	Reviewer's Signature	Date

1. Scope and Application

1.1. This is the Toxicity Characteristic Leaching Procedure (TCLP) extraction procedure designed to determine the mobility of both nonvolatile organic and inorganic contaminants present in liquid, solid, or multiphase wastes. Samples prepared by this method will be labeled with preparation code “LEN” or, in the case of Mercury, “LEM.”

2. Summary of the Procedure

2.1. For liquids, wastes containing less than 0.5% dry solids, the liquid after filtration through a 0.6 to 0.8 µm glass fiber filter is defined as the TCLP extract.

2.2. For wastes containing greater than or equal to 0.5% solids, the liquid, if any, is separated from the solid phase and stored for later analysis, and if necessary the particle size of the solid is reduced. The solid phase is extracted with a volume of predetermined extraction fluid equal to 20 times the weight of the solid phase of the waste. Following extraction, the liquid extract is filtered through a 0.6 to 0.8 µm glass fiber filter. If compatible the initial liquid phase is added to the filtered extract and analyzed. If the liquids are not compatible they are analyzed separately and the results are mathematically combined to give a volume-weighted average concentration.

3. Definitions

3.1. TCLP - Toxicity Characteristic Leaching Procedure

3.2. RPM - Revolutions per minute. The number of revolutions an extractor makes over a period of one minute.

4. Interferences

4.1. Potential interferences that may be encountered during analysis are described in the appropriate analytical SOPs.

5. Safety

5.1. The toxicity or carcinogenicity of each reagent used in this SOP is not precisely defined. Treat each chemical compound as a potential health hazard. Reduce exposure to all chemicals to the lowest possible level by whatever means available.

5.2. Always wear appropriate PPE (personal protective equipment) when working in the Laboratory. Gloves, safety glasses, ear protection, lab coats, respirators, face shields, etc. are provided for your protection.

5.3. DO NOT attempt to cleanup acid spills in the laboratory. Immediately evacuate the area and contact a member of the Emergency Response Team (ERT).

5.4. Material Safety Data Sheets (MSDS) that outline hazards, exposure treatments and regulatory guidelines are available for all chemicals used in this procedure and should be consulted as the need may arise. The MSDS file is located in the central project management area. MSDS are also available online, at http//hazard.com/MSDS/.

5.5. Environmental Samples may contain hazardous waste; treat them as potential health hazards.

5.6. Dispose of all unwanted, broken glassware into a broken glassware disposal box. Inspect every piece of glassware. Do not use glassware that is chipped, cracked, etched, or scratched. Glassware with minor damage should be set aside for repair.

6. Equipment and Supplies

6.1. Equipment

6.1.1. Personal protective equipment (PPE)

6.1.2. Gloves

6.1.3. Laboratory coat

6.1.4. Safety Glasses or Goggles

6.2. Extraction vessels, 2000 mL borosilicate glass and 1000 mL acid-rinsed HDPE.

6.3. Teflon film.

6.4. Beakers, 500 mL.

6.5. Watch glasses, 90 mm flat.

6.6. Magnetic stir bars, Teflon coated.

6.7. pH Meter, accurate to ±0.05 units at 25° C, calibrated daily and checked against a reference buffer.

6.8. End-over-end rotator.

6.9. Stopwatch or timer.

6.10. Filter holder.

6.11. Filter flask.

6.12. Filter, borosilicate glass microfiber, 42.5 mm and 110 mm diameter, 0.6 - 0.8 um pore size, acid-rinsed with 5% Nitric Acid followed by deionized water.

6.13. Polyethylene 100 and 50 mL HotBlock tubes.

6.14. Amber glass sample bottles, 250 mL, 500 mL, and 1000 mL.

6.15. Carboy, 20 L, Nalgene.

6.16. Standard sieves, 1 mm and 9.5 mm (.375”).

6.17. Laboratory balance, accurate to within ± 0.1g, calibrated regularly and tracked by QA officer and/or supervisor.

6.18. Thermometer, NIST traceable.

6.19. Hydrochloric Acid (1N), HCl: use trace metal grade HCl that has been lot QC checked.

6.20. Nitric Acid, HNO3: use trace metal grade HNO3 that has been lot QC checked.

6.21. Glacial Acetic Acid (1N), HOAc (low metals).

6.22. Sodium Hydroxide (1N), NaOH: dissolve 40 grams of NaOH pellets in 1000 mL of deionized water. Mark reagent bottle with the date, reagent number, and initial.

6.23. Hotplate.

7. Reagents and Standards

7.1. Extraction Fluids

7.1.1. Fluid #1: Add 5.7 mL glacial acetic acid to 500 mL deionized water. Add 64.3 mL of 1.0N NaOH and dilute to 1000 mL. Measure pH, it should be (4.93, ±0.05). If the pH is not within the above specification, the fluid should be discarded and fresh extraction fluid prepared. This reagent is usually prepared in a 20 liter carboy using 114 mL of glacial acetic acid and 1286 mL of 1.0N NaOH with 20 L deionized water. Label the carboy with the date, reagent batch number and initial.

7.1.2. Fluid #2: Add 11.4 mL of glacial acetic acid to 2000 mL deionized water. Measure pH, it should be (2.88, ±0.05). If the pH is not within the above specification, the fluid should be discarded and fresh extraction fluid prepared. Any amount of excess extraction fluid that is to be saved for later use should be labeled as described in step 6.22.

7.1.3. NOTE: These extraction fluids should be monitored frequently for impurities. The pH should be checked and if the pH is not within the above specifications or if impurities are found, the fluid should be discarded and fresh extraction fluid prepared.

8. Sample Collection, Preservation, Shipment and Storage

8.1. Preservatives shall not be added to samples before extraction.

8.2. Samples may be refrigerated unless refrigeration results in irreversible physical change to the waste.

8.3. TCLP extracts should be prepared for analysis and analyzed as soon as possible following extraction. Extracts for metals determination must be acidified with nitric acid to a pH <2.

8.4. Occasionally ARLLC will receive multiphase heterogeneous samples. Do not process multiphase samples without specific, documented instructions from ARLLC's Project Manager or Client. Note: When conducting an environmental investigation, the investigator generally has some specific purpose in mind. He/she then designs and executes a sampling program oriented toward providing information relative to that specific purpose. One goal of environmental sampling is that the sample be representative of either the environment from which it was taken or some specific characteristic of interest. Any unbiased environmental sample has the potential to contain materials (rocks, biological material, multiple phases etc.) that are non-representative of either the matrix or the characteristic. Such materials will often be excluded or separated from the sample when they are judged to be irrelevant to the specific purpose of the investigation or the characteristic of interest. A fundamental principle of environmental sampling is that only the designer of the sampling program makes decisions concerning the representativeness of materials contained within a sample. That person makes the decision to exclude materials from the sample. When a sample arrives at the laboratory, ARLLC can only assume that it represents the specific purpose and desires of the investigator. Decisions as to the exclusion of materials or separation of phases have already been made by the investigator and sampling personnel. It is not the role of ARLLC personnel to exclude materials or phases from a sample for analysis unless it is done with the knowledge and under the specific

direction of ARLLC's client.

8.5. Holding times are as follows:

SAMPLE MAXIMUM HOLDING TIMES (DAYS)				
	From: Field collection To: TCLP extraction	From: TCLP extraction To: Preparative extraction	From: Preparative extraction To: Analysis	Total elapsed time
Semi-volatiles	14	7	40	61
Mercury	28	NA	28	56
Metals, except Hg	180	NA	180	360

8.6. Some samples are shared with the organics and or conventionals laboratories. These samples are placed in a share bin in Refrigerator 5. SOP 1019S includes procedures for handling shared samples.

9. Quality Control

9.1. The extraction fluids are monitored for purity by the analysis of method blank samples. Each extraction batch includes at least one method blank sample for each extraction fluid used in the preparation of the batch.

9.2. Extraction fluids are tested for pH prior to use. (See section 7.0)

9.3. The balances and pH meter are calibrated according to the appropriate SOPs.

9.4. Matrix spike and duplicate samples are prepared after the extraction by splitting the extract into two or more aliquots after extraction. Appropriate sample volumes need to be filtered to ensure enough extract will be available. For samples being analyzed without digestion spiking solutions are added at the instrument. For samples to be digested follow the appropriate preparation SOP. A spike and duplicate need to be analyzed with each job and/or batch, not greater than 20 samples. The sample to be used for QC purposes is specified in the batch in Element. For each extraction fluid used, a method blank is extracted along with the rest of the job and/or batch, not greater than 20 samples.

10. Calibration and Standardization

10.1. All calibrations for the ICP, ICP-MS and CVA instruments are covered in the appropriate analytical SOPs.

10.2. The pH Meter must be calibrated before each use.

10.2.1. Calibrate the pH meter according to manufacturer's instructions using at least a 2-point calibration (pH 4 and 7).

11. Procedure

11.1. Perform Preliminary Determinations:

11.1.1. Determine percent solids is performed by vacuum filtration.

11.1.1.1. Homogenize the sample. If the sample does not appear to be moist and obviously contains no filterable liquid, then the sample is assumed to be dry and consist of 100% solids. In this case, the sample is classified as a Solid Waste. Proceed to step 11.1.2. Otherwise, follow steps B1 through B11 on the bench sheet to determine the percent solids of the sample. First weigh the filter flask, enter the value in section B1 then weigh the funnel and filter paper and record in B2 and B3. Assemble the filter apparatus and weigh a weighing boat, record the weight in B4. Next weigh up to 100 grams of sample into the weigh boat, do not zero the balance, and record the weight of the boat plus the sample in section B5. Transfer sample to the weighed filtering apparatus. At this point zero the balance and reweigh the boat with any sample residue remaining and record this weight in section B6. Calculate the weight of the sample filtered, B7 on the bench sheet. NOTE: ARLLC routinely uses 40 grams of sample for extraction. If the client requests strict adherence to Method 1311, a minimum of 100 grams and pressure filtration must be used.

11.1.1.2. Filter the weighed sample, using only one acid-rinsed filter. Gradually apply vacuum or gentle pressure of 1-10 psi to the filter until air/liquid starts moving through it. When no liquid has passed through the filter for a period of about 2 minutes increase the vacuum or pressure at 10 psi increments again until air/liquid starts to again move through the filter. Again, wait until no liquid has passed through the filter for 2 minutes and repeat by continuing to increase vacuum or pressure to a maximum of 50 psi until no liquid will pass for the given period of time (2 minutes). NOTE: Application of instantaneous vacuum or pressure may cause the filter to plug, care should be taken. Do not under any circumstances replace the original filter with a fresh filter. Centrifugation may be used as an aid to filtration. If the TCLP extract of the sample will not be analyzed for metals, the filter does not need to be acid rinsed. If no liquid passes through the filter, then the sample is 100% solids and is classified as a Solid Waste. Proceed to step 11.1.2.

11.1.1.3. Determine the weight of the flask plus the filtrate and record the value in B8. Calculate the weight of the filtrate, B9, by subtracting the weight of the flask, B1, from the weight of the flask and the filtrate contained inside, B8. The (wet) percent solids, B10, is 100 times the solid weight, B7 minus B9, divided by the sample weight B7. If the same subsample used for percent solids determination will also be used for the extraction, include the filter with the solid phase during the extraction process. Record the (wet) percent solids B10 in the logbook. If the percent solids is less than 0.5%, then the sample is classified as a Liquid Waste. Proceed to step 11.2.1 (Method 1).

11.1.1.4. NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying vacuum and/or pressure filtration, this material may not filter. If this is the case, the material within the filtration device is defined as a solid. Before proceeding with these types of samples, the project manager and/or the division manager

should be consulted so the client can be informed as to the potential problems.

11.1.1.5. Calculate the weight ratio of solid to liquid, B11, by dividing the weight of subsample filtered, B7 minus B9, by the weight of initial filtrate B9. Record this ratio.

11.1.2. Determine extraction fluid:

11.1.2.1. If necessary, crush, cut, or grind 5 or more grams of sample so that it has a particle size of 1 mm or less, a 1mm standard sieve can be used, if required, to ensure proper particle size.

11.1.2.2. Weigh 5.0 grams of solid into a 100 mL Hot Block tube and add a magnetic stir-bar and 96.5 mL of deionized water. Stir vigorously for 5 minutes. Measure and record pH, C1 on the bench sheet. If pH is <5.0 then use Extraction Fluid #1 and proceed to step 11.2.2.

11.1.2.3. If the pH is >5.0 then add 3.5 mL 1N HCl, mix, cover, heat to 50°C and hold for 10 minutes then cool for 30 minutes or to room temperature. Measure the pH, record C2 on the bench sheet. If it is <5.0, use Extraction Fluid#1. If pH is >5.0, use Extraction Fluid #2.

11.2. TCLP Extraction of Liquid, Solid and Multiphase Wastes.

11.2.1. Method I: Liquid Wastes

11.2.1.1. Filter enough sample for all analyses. The waste after filtration through an acid rinsed 0.6 - 0.8 µm glass fiber filter is defined as the TCLP extract.

11.2.1.2. Extracts for non-volatile organic analysis are stored in amber glass sample bottles obtained from Sample Receiving and labeled with the sample identification, date and prep (TCLP). The Organics Extraction Lab will notify the Metals Lab regarding the amount of extract desired.

11.2.1.3. Extracts for metals analysis are stored in 50 mL digest tubes and are preserved with 0.5% Nitric Acid. Label the extract with the sample identification, date and “LEN” for ICP analysis and/or “LEM” for the portion to be used for mercury determination. Transfer custody of the extracts to the lab(s), which will perform the analyses.

11.2.1.4. Metals samples at this point require digestion. Digestion method is TWC (SOP #510S) prep for ICP analysis. Reduced volume digestions (25 mL) can be done to expedite the procedure. Hg is always digested using TWM (SOP #533S) prep. QC samples should be prepared as specified in the digestion SOP.

11.2.1.5. NOTE: Extracts or portions of extracts for organic contaminants must not be acidified. They should be refrigerated and the organic extraction supervisor should be notified that the extracts are ready for organic preparation procedures.

11.2.2. Method II: Solid Wastes

11.2.2.1. If particle size reduction is needed, crush, cut, or grind the sample to pass through a 9.5 mm (.375”) sieve. For paper, cloth, and similar waste materials, such size reduction will not be necessary so long as the solid has a surface area per gram of 3.1 sq. cm or greater or is smaller than 1 cm in its narrowest dimension. Surface area per gram measurements are to be made by visual inspection unless the material is particularly dense. To measure surface area per gram on dense materials, cut

a rectangular piece of sample approximately 5 cm by 5 cm. Measure two adjacent sides of the rectangle with a centimeter stick (ruler) and multiply the lengths together. This product is the surface area. Weigh the rectangular piece on the balance (in grams) and divide the surface area by this mass. The result is the surface area per gram. For example, a 5 cm by 5 cm piece weighing 8 grams would have a surface area per gram of 3.125 sq. cm per gram and would not need particle size reduction.

11.2.2.2. Weigh 100 grams of solids into a 2 Liter glass extraction vessel. Record weight. If the client has approved the modification, weigh 40.0 grams of solids into in a 1 liter HDPE extraction bottle. If extraction is for nonvolatile organics, make certain the extraction is performed in a glass bottle with a Teflon-lined cap.

11.2.2.3. Add a volume of extraction fluid equal to (20 x weight of sample). Record volume.

11.2.2.4. Quarterly, verify the tumbler rotating speed of 30 rpm ±2 (SOP 1000S).

11.2.2.5. Place samples in tumbler and rotate at 30 rpm (± 2) for 18 hours (± 2). Record the start time and temperature of the extraction. Ambient temperature must be maintained at 23 ± 2 °C. Tumbling outside of this temperature window is a method deviation that requires client approval, supervisor notification, and make a notation in the TCLP logbook. .

11.2.2.6. Filter through special acid-rinsed glass fiber filters.

11.2.2.7. Calibrate the pH meter (Section 10.2), measure and record the pH of an aliquot of the TCLP extract. Discard the aliquot used for pH determination.

11.2.2.8. Place the filtrate in a properly labeled poly digest tube and preserve with HNO_3. Do not preserve extracts to be used for organic analyses. Samples are now ready for digestion and/or analysis (See 11.2.1.4.) Transfer custody of the extracts the lab(s), which will perform the analyses.

11.2.3. Method III: Multiphase Wastes

11.2.3.1. If the same sample aliquot from preliminary determination (11.1.1.1) will be used for the extraction, skip to step 11.2.2. Use the same flask as was used for the preliminary determinations, but replace the rest of the filtering apparatus with clean components. Tare an acid-rinsed filter and place it in the filtering apparatus.

11.2.3.2. Tare a clean weigh boat and weigh out a 100-gram subsample, if available, to 0.1 grams. (See 11.1.1.1.) More may need to be filtered to ensure an adequate amount of extract will be obtained. Record the weight of the subsample.

11.2.3.3. Pass the liquid fraction through the filter.

11.2.3.4. Refrigerate the liquid fraction (filtrate) at 4°C.

11.2.3.5. Weigh the remaining solids and the filter to 0.1 grams. Record the weight in the logbook, E11 on the bench sheet.

11.2.3.6. If particle size reduction is needed, grind the solids to pass through a 9.5 mm sieve. (See step 11.2.2.1.)

11.2.3.7. Place the sample in an extraction bottle, and add a volume of extraction fluid equal to (20 x weight of the solid) mL. Use the extraction fluid to rinse any solids clinging to funnels, etc.

11.2.3.8. Rotate the extraction bottle for 18 hours (±2). (See 11.2.2.7.)

11.2.3.9. Filter enough sample for all analyses. (See 11.2.2.8.) Before adding the initial filtrate to the filtered extract, test for miscibility. The miscibility test should be performed in a small plastic cup with a milliliter or less of each filtrate. Stir the mixture and look for suspensions, precipitates, layering or any other sign of poor miscibility. Discard the liquid used for this test. If the initial filtrate (liquid fraction) and the filtrate (filtered extract) are immiscible, store the liquids separately and indicate on the sample bottles that they are two phases of the same extract. If the liquids are miscible, add the initial filtrate to the filtered extract and mix. If the weight of solids extracted was less than the weight of solids remaining after filtration, the amount of initial filtrate to add back should be adjusted proportionally using the weight ratio of solid to liquid calculated in the preliminary determinations. To make this adjustment, measure the volume of the filtered extract, record in section G2 of the bench sheet, in a graduated cylinder. To calculate the amount of solids this represents, divide the volume by twenty (20). Divide the resulting quotient by the ratio of solid to liquid obtained earlier to find the weight of initial filtrate to add to the filtered extract G3 on the bench sheet. This mixture becomes the TCLP extract.

11.2.3.10. Calibrate the pH meter, measure and record the pH of an aliquot of the TCLP extract. Discard the aliquot used for pH determination.

11.2.3.11. Place the filtrate in a properly labeled poly digest tube and preserve with HNO_3. Do not preserve extracts to be used for organic analyses. Samples are now ready for digestion. (See 11.2.1.2 and 11.2.1.3.) Transfer custody of the digested extracts the Metals Instrument Laboratory, which will perform the analyses.

12. Data Analysis and Calculations

12.1. Logbooks are periodically reviewed by the QA officer and/or supervisor.

12.2. Data are reviewed according to the Metals Data Review SOP Method Performance

12.2.1. QA maintains control charts for the recovery of surrogate standards and spiked compounds.

12.2.2. Management periodically reviews the charts to detect and correct any negative trends in analyte recovery.

13. Pollution Prevention

13.1. Disposed expired standards into the designated barrel in the hazardous waste room.

13.2. Samples that are designated as hazardous waste by the LIMS “Hazardous Report” must be placed in the designated drum in the Hazardous Waste Storage Area when they are disposed. This process is described in SOP 1003S.

14. Data Assessment and Acceptance Criteria for Quality Control Measures

14.1. All quality control acceptance criteria are covered in the appropriate analytical SOPs.

15. Corrective Actions for Out of Control Events

15.1. Quality control corrective actions are covered in the appropriate analytical SOPs.

15.2. If a method blank is out of control indicating a contaminated extraction solution, any remaining extraction fluid from the batch used for the extraction is properly disposed and the container is cleaned. All samples associated with the method blank will be re-extracted.

15.3. If the pH of an extraction fluid is out of range, the extraction fluid is properly disposed and the container is cleaned.

15.4. When a recorded temperature is not within method criteria (23 ± 2°C), a corrective action must be documented.

15.5. Any unusual sample or problem that arises must be noted both in the logbook and on an Analyst Notes Form. Also bring the problem to the attention of the supervisor/manager.

16. Contingencies for Handling Out-of-Control or Unacceptable Data

16.1. Unacceptable quality control data noted during analysis may result in a request for re-extraction. A complete description of the out of control event and its resolution should be explained on a corrective action form.

17. Waste Management

17.1. ARLLC properly profiles and disposes all hazardous waste using an EPA registered TSD (Treatment, Storage and Disposal) facility.

17.2. Place samples and remaining extracts that are determined to be hazardous using the LIMS “Hazardous Report” in the designated drum in the Hazardous Waste Storage Area. SOP 1003S describes the process for disposal of samples.

17.3. All acid waste should be neutralized before sink disposal.

17.4. Dispose of expired standards in the designated barrel in the hazardous waste room.

17.5. ARLLC’s Laboratory Chemical Hygiene Plan (CHP) describes internal hazardous waste handling procedures. All analysts must be familiar with these requirements.

17.6. ARLLC properly profiles and disposes all hazardous waste using an EPA registered TSD (Treatment, Storage and Disposal) facility.

18. Method References

18.1. USEPA Test Methods for Evaluating Solid Waste, SW-846, Volume IC, Method 1311, July 1992.

Standard Operating Procedure E34 – Adsorption Isotherm Test for 1,4-Dichlorobenzene Using Granular Activated Carbon

Scope and Application

This Environmental Geochemistry Laboratory (EGL) standard operating procedure (SOP) is applicable to conducting adsorption isotherm studies for 1,4- dichlorobenzene (DCB) using granular activated carbon (GAC). This procedure is based on the methods described by U.S. Army Corps of Engineers. (2001), Randtke and Snoeyink (1983), and Crittenden et al., (1987). Procedures outlined in this SOP will be followed, and any deviations must be noted in your laboratory notebook.

Health and Safety

All laboratory work will be performed in accordance with the EGL *Chemical Hygiene Plan* (CHP) by staff approved by the laboratory manager and chemical hygiene officer. Approval to work in the EGL requires orientation to laboratory safety procedures and potential hazards under the guidance of the laboratory manager, as specified in the CHP.

Hazards and controls associated with this SOP are listed in the following sections and explicitly linked in **Table A**. Hazards associated with project-specific samples are addressed in the Project Safety Analysis (PSA) document. Occupational exposure limits (OELs) for chemicals used in this SOP are attached as **Table B**.

Chemical Safety Data Sheets

The following Safety Data Sheets (SDSs) must be reviewed prior to beginning the procedure:

- 1,4-DCB, >99.0% American Chemical Society (ACS)-grade (or similar)
- CT2050C Virgin GAC (or similar)

Hazards Associated with this Standard Operating Procedure

- Breakage of glassware
- Inhalation, ingestion, and skin or eye contact with contaminants or small particles
- Handling 1,4-DCB
- Skin contact with the heated surface of oven
- Operating the shaker table

Engineering Controls

- Perform work in an operational fume hood.

Administrative Controls

- Carry glassware with two hands.
- The indicator light on the outside of the oven shows when the oven is on.
- Ensure lids are secure on sample containers.
- Place samples securely in secondary containment.
- Ensure the shaker table has normal sound prior to leaving the area.

Personal Protective Equipment

- Laboratory coat
- Safety glasses
- Ansell® TouchNTuff® 92-600
- Ansell Microflex 93-260 (when using methanol or solvent)

Inspection Requirements

- Inspect personal protective equipment (PPE) prior to use.
- Inspect glassware prior to use.
- Confirm fume hood face velocity prior to use.

Equipment and Supplies

The following is a list of equipment and supplies necessary to carry out the procedures contained in this SOP:

- Analytical balance with a precision of ± 0.1 milligram (mg)
- Standard balance with a precision of ± 10 mg
- 1-liter (L) glass beaker
- 100-milliliter (mL) glass beaker
- 100-mL volumetric flask
- Ceramic dish
- Aluminum foil
- Weigh boats or paper
- Drying oven
- Stainless-steel spatula
- Disposable pipettes
- Laboratory oven
- Desiccator with desiccant
- 4-ounce (oz)/125-mL amber septa Boston round bottles (Level 1) (Reaction vessel)
- 4-L cleaned narrow-mouth amber glass jug with Teflon-lined cap
- 1,4-DCB, >99.0& ACS grade from Sigma Aldrich (or similar)

- Methanol (high-performance liquid chromatography [HPLC] grade)
- CT2050C Virgin GAC (manufactured from coconut shell, U.S mesh size: 20 ×50, Iodine number: >900 milligrams per gram [mg/g])
- Micropipette (10- to 1,000-microliters [µL])
- Micropipette tips
- Stirring plate
- Magnetic stir bar
- pH probe
- Specific conductivity probe
- 0.45-micron (µm) pore size polytetrafluoroethylene (PTFE) syringe filter
- 100-mL gas-tight glass syringe
- Luer-lock syringe needle
- 40-mL pre-preserved (hydrochloric acid [HCl]) volatile organic analysis (VOA) vials
- Rotary shaker
- Deionized (DI) water

Procedure

Task 1: Prepare Dissolved Organic Matter-loaded Granular Activated Carbon

1. Transfer a few grams of GAC (sufficient for the test) into a 1-L glass beaker using a stainless-steel spatula.
2. Wash the GAC with DI water several times to remove fine particles.
3. Decant the supernatant containing fine particles.
4. Repeat Step 3 until the floating fine particles are completely removed.
5. Transfer the washed GAC into a ceramic dish and dry in an oven at 110°C to a constant weight.
6. Cool the GAC in a desiccator.
7. Transfer the dried GAC into the porewater sample prepared following the procedures in EGL SOP #318: Synthetic Sediment Porewater Extraction, at 100 milligrams per liter (mg/L) for 1 week to preload dissolved organic matter (DOM) onto the GAC.
8. After DOM preloading, decant the supernatant and recover DOM-loaded GAC into a ceramic dish and dry in an oven at 60°C to a constant weight.
9. Cool the GAC in a desiccator and store until further use.

Task 2: Prepare 1,4-DCB Stock Solution

1. Determine the concentration of 1,4-DCB in the stock solution (e.g., 1.0 gram per liter [g/L]).
2. Accurately weigh the required mass of 1,4-DCB using an analytical balance and record the mass.
3. Transfer the solid into a 100-mL volumetric flask.

4. Add HPLC-grade methanol to about 70% to 80% of the final volume and swirl or gently mix until the solid is completely dissolved.
5. Bring the solution to the final volume with methanol.
6. Mix thoroughly by inverting or swirling several times.
7. Transfer the solution to a 125-mL amber glass Boston bottle, tightly seal the bottle for storage, and label the bottle appropriately.

Task 3: Prepare Test Solution (Synthetic Porewater)

1. Follow the procedures in EGL SOP #317: Direct Water Extraction, to prepare sediment porewater.
2. Transfer the porewater prepared in Step 1 into a 4-L amber glass bottle, minimizing headspace to prevent volatilization loss of 1,4-DCB in the following steps.
3. Add the 1,4-DCB stock solution prepared in Task 2 using a micropipette to achieve a target concentration.
4. Seal the bottle tightly with a Teflon-lined screw cap.
5. Stir the solution overnight (>12 hours) using a stirring plate and a magnetic stir bar.
6. Collect a sample of the porewater using a 100-mL gas-tight glass syringe with Luer-lock syringe needle and filtered through 0.45-µm pore size PTFE syringe filters to remove any suspended solids.

Task 4: Set Up Batch Bottles for Preliminary Kinetic Test

To evaluate the uptake kinetics of 1,4-DCB on GAC and estimate its uptake capacity, several batch bottles will be prepared with a fixed GAC dose and porewater spiked with 1,4-DCB at a reasonable concentration. The bottles will be agitated on a shaker table for up to 7 days, and individual bottles will be periodically sacrificed to measure 1,4-DCB concentrations (e.g., at 0, 1, 3, and 7 days). The effluent 1,4-DCB concentrations will be plotted as a function of reaction time to estimate the time required for 1,4-DCB to reach equilibrium with GAC. The preliminary batch bottles will be prepared, agitated, and sampled in the same manner as described in Task 5 below.

Task 5: Set Up Batch Bottles for Isotherm Test

1. Review literature to estimate the uptake capacity of GAC for the target compound or similar chemicals and determine the GAC dose for each test bottle (see Table 1 for an example). The GAC doses should cover a wide range of aqueous equilibrium concentrations. Note that DOM loading may significantly impact the uptake capacity of GAC; therefore, the selected doses should account for this effect.
2. Label 125-mL amber glass Boston bottles, pre-weigh them using a standard balance, and record their masses.
3. Weigh the GAC using an analytical balance and record the mass. Transfer the GAC into 125-mL amber glass Boston bottles.

4. Collect water sample in the 4-L container into 40-mL HCl-preserved glass vials provided by an analytical laboratory using a 50-mL gas-tight glass syringe with Luer-lock syringe needle, and filter the sample through 0.45-µm pore size PTFE syringe filters to remove any suspended solids.
5. Add the synthetic porewater to each bottle using a 100-mL glass syringe, minimizing headspace to prevent volatilization loss of the target compound. Immediately seal the glass bottles tightly.
6. Weigh the 125-mL amber glass Boston bottles and record the mass of porewater added to each bottle.
7. Place the 125-mL amber glass Boston bottles on a rotary shaker and agitate at 60 revolution per minute for duration determined from the preliminary kinetic test.
8. After the equilibration period, collect water samples in the glass bottles into 40-mL HCl-preserved glass vials into using a 50-mL gas tight glass syringe with Luer-lock syringe needle, and filter the samples through 0.45-µm pore size PTFE syringe filters to remove any suspended solids. Submit for analysis via U.S. Environmental Protection Agency (EPA) Method 8260.

Table 1: GAC Doses (example)

Bottle No.	Mass (grams)
1	10.0
2	8.0
3	6.0
4	5.0
5	4.0
6	3.0
7	2.0
8	1.0
9	0.8
10	0.6
11	0.50
12	0.40
13	0.20
14	0.10
15	0.08
16	0.06
17	0.05
18	0.04
19	0.02
20	0.01
21 (control)	0.00

Task 6: Data Analysis

The Freundlich isotherm model is a commonly used empirical model for describing adsorption on heterogeneous surfaces, such as the adsorption of organic compounds onto GAC. The Freundlich isotherm model is applied to the adsorption of a target chemical onto GAC, and the corresponding Freundlich parameters (i.e., K_F and 1/n) are calculated. The initial and equilibrium concentrations of 1,4-DCB (i.e., C_0 and C_e) will be measured at an analytical laboratory, and the volume of solution and mass of GAC added in each bottle (i.e., V and m) will be recorded. The Freundlich parameters can be determined by plotting the logarithms of q_e and C_e and fitting a straight line using linear regression.

Equation 1: Freundlich Isotherm

$$\frac{x}{m} = \frac{(C_0 - C_e) \times V}{m} = q_e = K_F C_e^{(\frac{1}{n})}$$

where:

x	=	mass of 1,4-DCB adsorbed to GAC at equilibrium (microgram [µg])
m	=	mass of GAC added in a glass bottle (gram [g])
C_0	=	initial concentration of 1,4-DCB in an aqueous solution (microgram per liter [µg/L])
C_e	=	concentration of 1,4-DCB in an aqueous solution at equilibrium (µg/L)
V	=	solution volume (L)
q_e	=	concentration of 1,4-DCB in GAC at equilibrium (microgram per gram [µg/g])
K_F	=	Freundlich capacity constant ([µg/g]/[µg/L]$^{1/n}$)
n	=	Freundlich exponent (-)

Quality Assurance/Quality Control

Quality assurance/quality control (QA/QC) samples are collected during the procedure. The QA/QC samples are described as follows:

- **Replicate samples:** Duplicate or replicate samples should be prepared and analyzed at a project-appropriate rate, with at least one duplicate to calculate the reproducibility.
- **Method blank:** A method blank will be prepared.
- **Temperature blank:** A temperature blank will be prepared to ensure that samples are maintained at an appropriate temperature (i.e., approximately 4°C) during shipping to the analytical laboratory.

If relative percent differences (RPDs) exceed 30%, notify the EGL task lead and discuss the RPD results within the scope of the project. In cases where RPDs exceed 30%, the data may still be of good quality. High RPDs may result from sample heterogeneity or other factors.

Closeout

The unused reagent solutions can be disposed of as described in Table 2.

Table 2
Disposal of Unused Reagent Solutions

Unused Reagent Solution	Disposal Considerations	Disposal Procedure
Synthetic Porewater	1,4-DCB carries the waste code D027 with a regulatory level of 7.5 mg/L and a toxicity characteristic leaching procedure screening value of 150 milligrams per kilogram. Materials with concentrations above these levels must be managed and disposed of as hazardous waste. 1,4-DCB is an EPA Priority Pollutant.	If hazardous, collect material in a hazardous waste accumulation container. Ensure that all constituents are clearly listed on the label. Coordinate with laboratory management for hazardous waste disposal by a licensed waste contractor.
GAC		

References

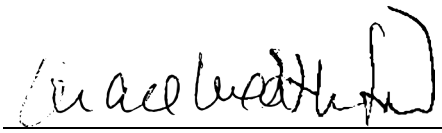
Crittenden, J.C., D.W. Hand, H. Arora, and B.W. Lykins Jr., 1987. "Design Considerations for GAC Treatment of Organic Chemicals." *Journal American Water Works Association* 79(1):74.

Randtke, S.J., and V.L. Snoeyink, 1983. "Evaluating GAC Adsorptive Capacity." *Journal American Water Works Association* 75(8):406–413.

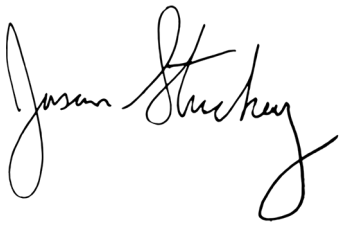
U.S. Army Corps of Engineers, 2001. *Adsorption Design Guide*. Engineer Design Guide DG 1110-1-2. Washington, DC.

Standard Operating Procedure Approval Page

This standard operating procedure, Adsorption Isotherm Test for 1,4-Dichlorobenzene Using Granular Activated Carbon, has been reviewed and is approved for use in the Environmental Geochemistry Laboratory.

Signature:  Date: 05/04/2026

Grace Weatherford, Chemical Hygiene Officer

Signature:  Date: 05/04/2026

Jason Stuckey, Laboratory Manager

Table A
Hazards

Table A
Hazards

Potential Hazard(s)	Engineering Controls	Administrative Controls (Includes Work Practices)	PPE	Inspection Requirements
Inhalation, ingestion, and skin or eye contact with contaminants or small particles	Perform work in an operational fume hood.	--	- Safety glasses - Laboratory coat - Nitrile gloves (Ansell® TouchNTuff® 92-600)	- Inspect PPE prior to use. - Confirm fume hood face velocity prior to use.
Handling flammable chemicals (methanol, hexane)	Perform work in an operational fume hood.	--	- Safety glasses - Flame resistant laboratory coat - Nitrile gloves (Microflex 93-260)	- Inspect PPE prior to use. - Confirm fume hood face velocity prior to use.
Handling limited quantities of corrosive chemicals for pH adjustment (sodium hydroxide)	Perform work in an operational fume hood.	--	- Safety glasses - Laboratory coat - Nitrile gloves (Microflex 93-260)	- Inspect PPE prior to use. - Confirm fume hood face velocity prior to use.
Handling irritant chemicals (aluminum sulfate)	Perform work in an operational fume hood.	--	- Safety glasses - Laboratory coat - Nitrile gloves (Microflex 93-260)	- Inspect PPE prior to use. - Confirm fume hood face velocity prior to use.
Operating the shaker table	--	- Ensure lids are secure on sample containers - Place samples securely in secondary containment - Ensure shaker table has normal sound prior to leaving the area	- Safety glasses - Laboratory coat - Nitrile gloves (Ansell® TouchNTuff® 92-600)	- Inspect PPE prior to use. - Inspect shaker table prior to use.

Table A
Hazards

Potential Hazard(s)	Engineering Controls	Administrative Controls (Includes Work Practices)	PPE	Inspection Requirements
Breakage of glassware	--	Carry glassware with two hands.	- Safety glasses - Laboratory coat - Nitrile gloves (Ansell® TouchNTuff® 92-600)	- Inspect PPE prior to use. - Inspect glassware prior to use.

Notes:

--: not applicable

PPE: personal protective equipment

Table B
Occupational Exposure Limits

Table B
Occupational Exposure Limits

SOP No.	Title	Chemicals Used	CAS Number	Exposure Routes	Symptoms	Target Organs	OEL (ppm)	NIOSH/ OSHA/ ACGIH Values	Vapor Pressure (mmHg)	Ionization Potential (eV)	First Aid
317	Direct Water Extraction	Methanol	67-56-1	Inhalation, skin absorption, ingestion, skin and/or eye contact	Irritation of eyes, skin, upper respiratory system; headache, drowsiness, dizziness, nausea, vomiting; visual disturbance, optic nerve damage (blindness); dermatitis	Eyes, skin, respiratory system, central nervous system, gastrointestinal tract	200	NIOSH REL TWA: 200 ppm (260 mg/m^3) ST 250 ppm (325 mg/m^3) [skin] OSHA PEL TWA: 200 ppm (260 mg/m^3)	96 mmHg	10.84 eV	Eye: Irrigate immediately Skin: Water flush promptly Breathing: Respiratory support Swallow: Medical attention immediately
317	Direct Water Extraction	Hexane	110-54-3	Inhalation, ingestion, skin and/or eye contact	Irritation eyes, nose; nausea, headache; peripheral neuropathy: numb extremities, muscle weak; dermatitis; dizziness; chemical pneumonitis (aspiration liquid)	Eyes, skin, respiratory system, central nervous system, peripheral nervous system	50	NIOSH REL TWA: 50 ppm (180 mg/m^3) OSHA PEL TWA: 500 ppm (1800 mg/m^3) ACGIH TLV TWA: 50 ppm (176 mg/m^3)	124 mmHg	10.18 eV	Eye: Irrigate immediately Skin: Soap wash immediately Breathing: Respiratory support Swallow: Medical attention immediately
317	Direct Water Extraction	Aluminum Sulfate ($[Al_2(SO_4)_3]$ Alum)	7784-24-9	Inhalation, ingestion, skin and/or eye contact	May cause slight irritation to skin and/or eyes	--	--	--	--	--	Eye: Irrigate with water for 15 minutes Skin: Irrigate with water for 15 minutes Breathing: Give oxygen, artificial respiration if necessary Swallow: Do not induce vomiting, call physician immediately

Notes:
--: not applicable
ACGIH: American Conference of Governmental Industrial Hygienists
CAS: Chemical Abstracts Service
eV: electronvolt
mg/m^3: milligram per cubic meter
mmHg: millimeter of mercury
NIOSH: National Institute for Occupational Safety and Health
OEL: occupational exposure limit
OSHA: Occupational Safety and Health Administration or Act
PEL: permissible exposure limit
ppm: part per million
REL: recommended exposure limit
SOP: Standard Operating Procedure
ST: short term
TLV: threshold limit value
TLV: threshold limit value

Standard Operating Procedure E35 – X-Ray Fluorescence Spectroscopy (SciAps X-550)

Scope and Application

This Environmental Geochemistry Laboratory (EGL) standard operating procedure (SOP) is applicable to the use of a SciAps X-550 X-ray fluorescence (XRF) analyzer. XRF is a non-destructive analytical technique used to determine the elemental composition of materials. XRF analyzers measure the fluorescent (or secondary) X-rays emitted from a sample when excited by a primary X-ray source. Each of the elements present in a sample produces a set of characteristic X-rays or "fingerprints." XRF is an appropriate tool to use for qualitative and quantitative measurements only for elements heavier than sodium. The procedures outlined in this SOP will be followed, and any deviations must be noted in your laboratory notebook.

Health and Safety

All laboratory work will be performed in accordance with the *EGL Chemical Hygiene Plan* (CHP) by approved staff. Approval to work in the EGL requires orientation to laboratory safety procedures and potential hazards under the guidance of the laboratory manager, as specified in the CHP. XRF operators must be current in radiation safety training per the Radiation Safety Program.

Hazards and controls associated with this SOP are listed in the following sections and explicitly linked in **Table A**. Three primary factors minimize radiation exposure: time, distance, and shielding. Hazards associated with project-specific samples are addressed in the Project Safety Analysis (PSA) document. The SciAps X-500 XRF Flyer is included as Attachment 1.

Hazards Associated with this Standard Operating Procedure

- Inhalation, ingestion, and skin or eye contact with contaminants or small particles
- Radiation exposure from XRF

Engineering Controls

- Perform work in an operational fume hood when handling small particles.
- The XRF should only be used with the stand (never use the manual trigger) and with the lid closed.

Administrative Controls

- The device should never be aimed at yourself or others, especially when the primary beam (X-ray) lights are illuminated.
- The user can verify when the XRF is actively emitting X-rays by observing the lights on the XRF stand. The light is green when the device is powered on but not actively emitting X-rays, red

when the X-ray pulse is charging in the chamber, and blinks red when actively emitting X-rays. The user must **never** open the XRF stand when the indicator light is blinking red.
- The user should post signage in the laboratory when the XRF is in use.
- To comply with the State, monitoring of the radiation exposure for all laboratory personnel (trained on the XRF) began in 2023 and is continuing to be monitored quarterly, using personal dosimeters procured from CHP dosimetry. The XRF user must wear the dosimeter during use and when working in the laboratory. The recommendation is to clip the dosimeter to one's laboratory coat.

Personal Protective Equipment

The following personal protective equipment (PPE) will be worn at all times while handling samples:

- Laboratory coat
- TouchNTuff 92-600 Nitrile gloves
- Safety glasses

Inspection Requirements

- Inspect PPE prior to use.
- Confirm fume hood face velocity prior to use.
- Check the warning light prior to opening the stand lid.

Equipment and Supplies

The following is a list of equipment that may be necessary to carry out the procedures contained in this SOP; additional equipment may be required:

- SciAps X-550 Handheld XRF Analyzer with shielded support stand
- Micro-USB cable to connect analyzer to PC
- Clean, known, 316 steel sample for unit calibration
- Dried and ground sample(s)
- Sample cups, rings, and caps suitable for XRF[1] analysis
- Polypropylene thin film[2]
- The user's personal dosimeter, which must always be worn when working in the laboratory

Procedure

Sample Cup Assembly

1. Place thin film over the ring (A in Figure 1).

[1] Purchase link here: https://www.premierlabsupply.com/product/double-open-ended-cupringcap-suitable-for-niton-sc-4331/.
[2] Purchase link here: https://www.premierlabsupply.com/product/polypropylene-film-4-0/.

2. Insert the sample cup (B in Figure 1) into the ring (A in Figure 1) to cover the sample cup on one end. Apply sufficient pressure so that the sample cup and closed ring cap are securely attached to each other, separated by the thin film. This will form the face of the sample that is exposed to the X-ray beam from the XRF.
3. Keeping the film facing downward onto a soft Kimwipe/paper towel, fill the sample container to 100% capacity with dry and ground sample. Keep tapping gently to ensure the container is packed well and filled to its limit.
    a. Note: Packing is critical with an XRF because it uses diffraction principles to provide sample information. Loose packing can cause deflections of the beam, which could result in lost information from the samples.
    b. The sample may be ground using a mortar and pestle or a planetary ball mill (see EGL SOP #402: Ball Mill Processing for information on this procedure).
4. Place a thin film over this packed sample cup (B in Figure 1).
5. Stretch the thin film so that it is tight and place the cap (C in Figure 1) over the film. Firmly push the cap onto the sample cup (B in Figure 1) until a click is heard. Inspect the sample container to make sure that all components are flush with each other. Figure 2 illustrates the final assembly. The open end of the sample cup will be exposed to the XRF for analysis.
    a. Note: When handling thin film, try to touch only the edge of the film and not the center.
6. Inspect the sample. Check to make sure the packing is tight (no loose material inside the cup) and that there are no rips on the films, because that would alter the packing and the XRF data.
7. Label sample cup assembly with Sample ID.
8. Repeat steps 1 through 5 for each sample that needs to be analyzed.[3]

[3] Note that cups, rings, and caps can be reused, but thin films should not be reused. It is recommended to completely clean sample cup components if reuse is desired. To open the sample cup, use a flathead screwdriver to pry the top and bottom off of the barrel in the seam where they are joined. This procedure might also be necessary if a thin film accidentally rips during the assembly process.

Figure 1
Sample Cup Components

Figure 2
Sample Cup Assembly

Procedure

Analysis with XRF

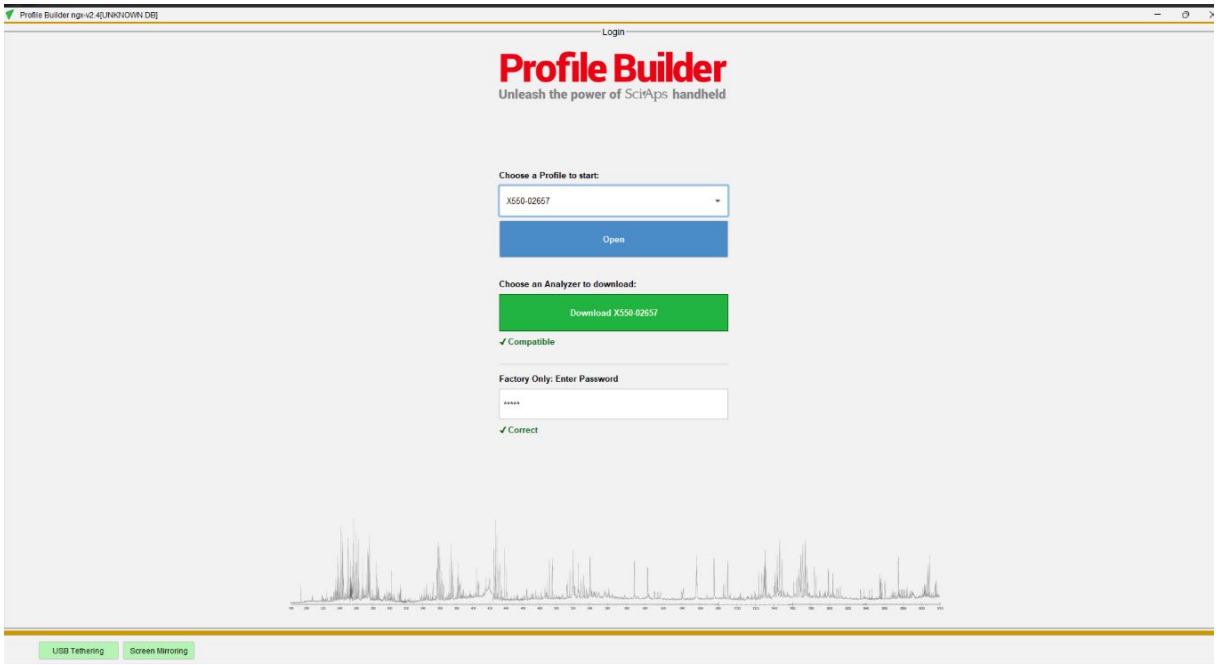
1. If a battery is not already inserted in the XRF gun, insert the battery into the handle until the connectors click into place. The battery is housed in the handle and forms the bottom of the handle.
    a. Note that the battery is directional and keyed to only go in one way. Do not force it.

2. Ensure that XRF gun is properly housed in the test stand.
3. Turn the instrument on (power button on the top of the unit). Hold the power button down for a couple of seconds.
4. Log into the XRF.
    a. Note that the screen is difficult to access when the gun is in the test stand. The stand can be tilted if needed.
5. The X-ray warning screen will appear. Press "OK".

Profile Builder Mode

1. If using the Profile Builder mode, power the desktop computer on by pressing the circular button on the back of the computer. Log in using the pin number (96321).
2. Open the Profile Builder app on the desktop and log in: all information should be filled out by default as in Figure 3.

Figure 3
Profile Builder Login



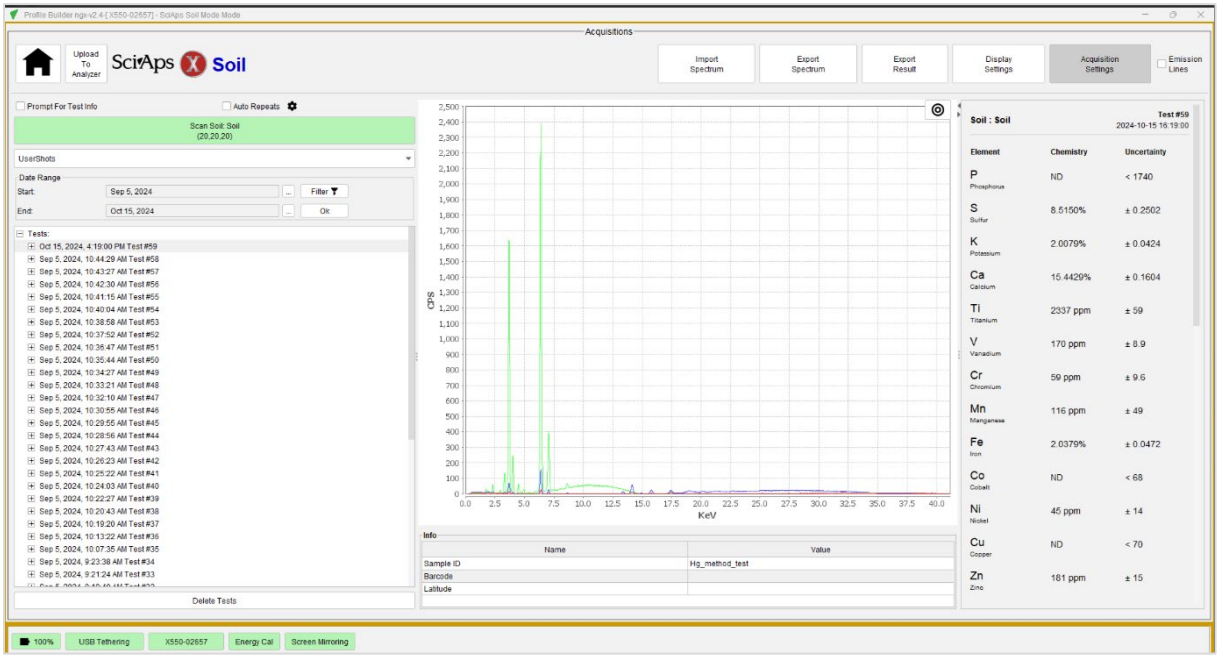
3. Verify that the USB Tethering is on (indicated by a green button on the lower lefthand of the screen [Figure 3]).
4. If USB Tethering is not on, swipe to the left on the XRF screen to access the right-hand menu. Tap "remote services", navigate to the settings, and select/check "auto tether".
5. Once tethered, the XRF can be operated from the desktop computer using the Profile Builder app.

6. Perform the Energy Calibration through Profile Builder.
    a. Place the known standard coupon on the nose. A 316 coupon should come with the unit, but a clean, known 316 steel sample can also be used. Ensure the coupon completely covers the analysis window, as shown in Figure 4.
    b. Click the "Energy Cal" button on Profile Builder. The Energy Calibration should take several seconds, then the "Energy Cal" button will turn green.

Figure 4
Handheld XRF Calibration Set Up

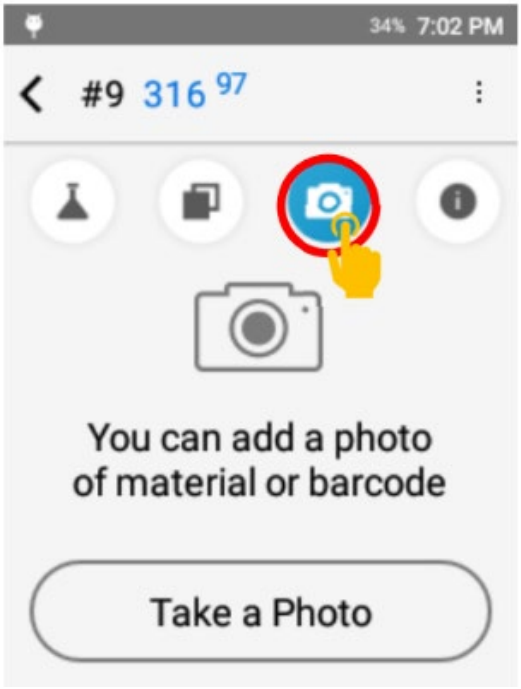
7. From the Profile Builder home screen, select the desired method (i.e., "Soils"), then navigate to Testing and Results (Figure 5).

Figure 5
Profile Builder Analysis Screen



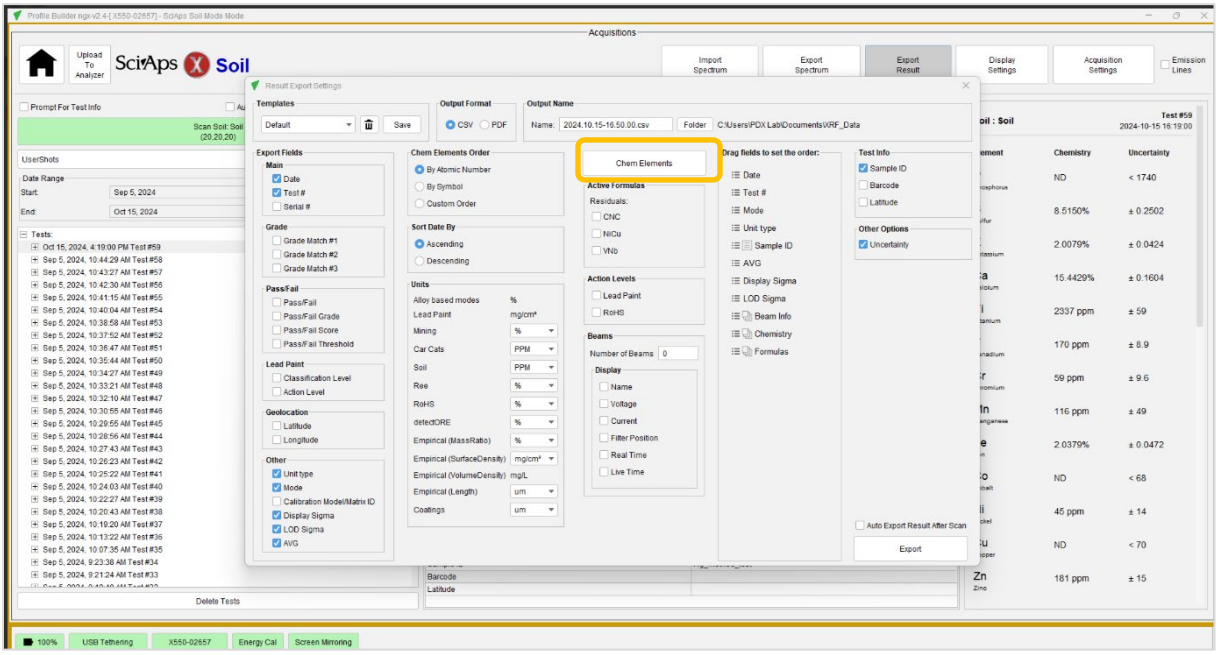
8. Select the "Prompt For Test Info" box in the top left corner. This will prompt the user for a Sample ID prior to running each sample.
9. Check the "Acquisition Settings" and modify the "Test Times" as needed (i.e., if lower detection limits are desired, the test times can be increased).
10. Gently wipe off the sample cup's exposed thin film with a Kimwipe.
11. Ensure that the lights on the stand are green; this indicates that the instrument is in Standby Mode and is not generating X-rays.
12. Open the XRF lid and place the sample cup face down over the device aperture. The exposed-film side should be down and facing the XRF instrument. Make sure that the sample inside of the sample cup covers the entire exposed surface area of the thin film. A couple gentle taps on the counter or XRF stand plate can aid with compaction.
13. Note: If there is dust on the surface of the XRF aperture, it can be gently cleaned with a Kimwipe. The camera view will show any dust that needs to be cleaned. To view the camera image, click on the ">>" icon on the right-hand side of the screen until the third page, and click on the camera icon that pops up (Figure 6). Choose video size under "Video".

Figure 6
Turn On Instrument Camera



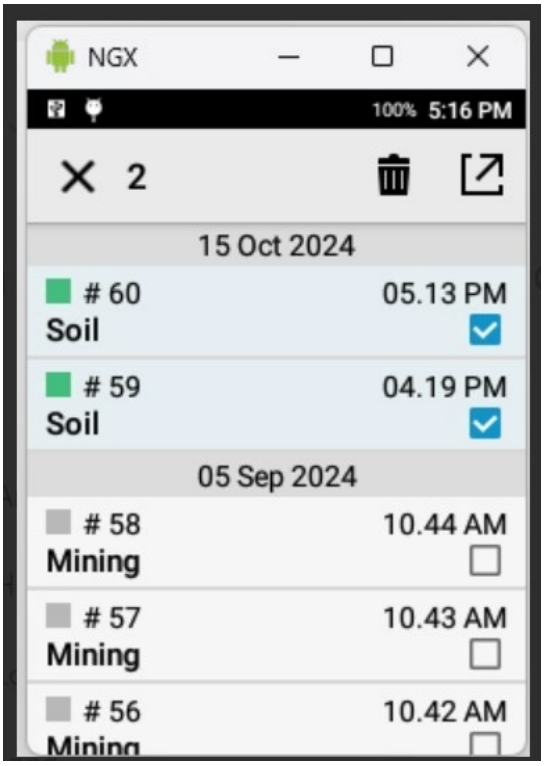
14. Close the lid.
15. Click on the "Scan" button (Figure 5; green, top left).
    a. The screen will prompt the user for Sample ID, which can be typed into the Value Field.
    b. Once the user clicks "Save" on the Sample ID, the XRF will begin running. This is indicated by blinking red lights on the test stand.
16. Run the subsequent samples, quality control (QC) samples, and calibration samples as appropriate.
17. When the runs are complete, check the "Export Result Settings -> Chem Elements" to ensure all desired elements are selected (Figure 7).
    a. Check to ensure that the "default" template is selected in the top lefthand corner.
    b. Note that if a sample does not have a factory calibration, it will be blank in the exported results.
    c. The "Export Result Settings" can also be edited for other parameters as needed.

Figure 7
Profile Builder Export Screen with Chem Elements Selection



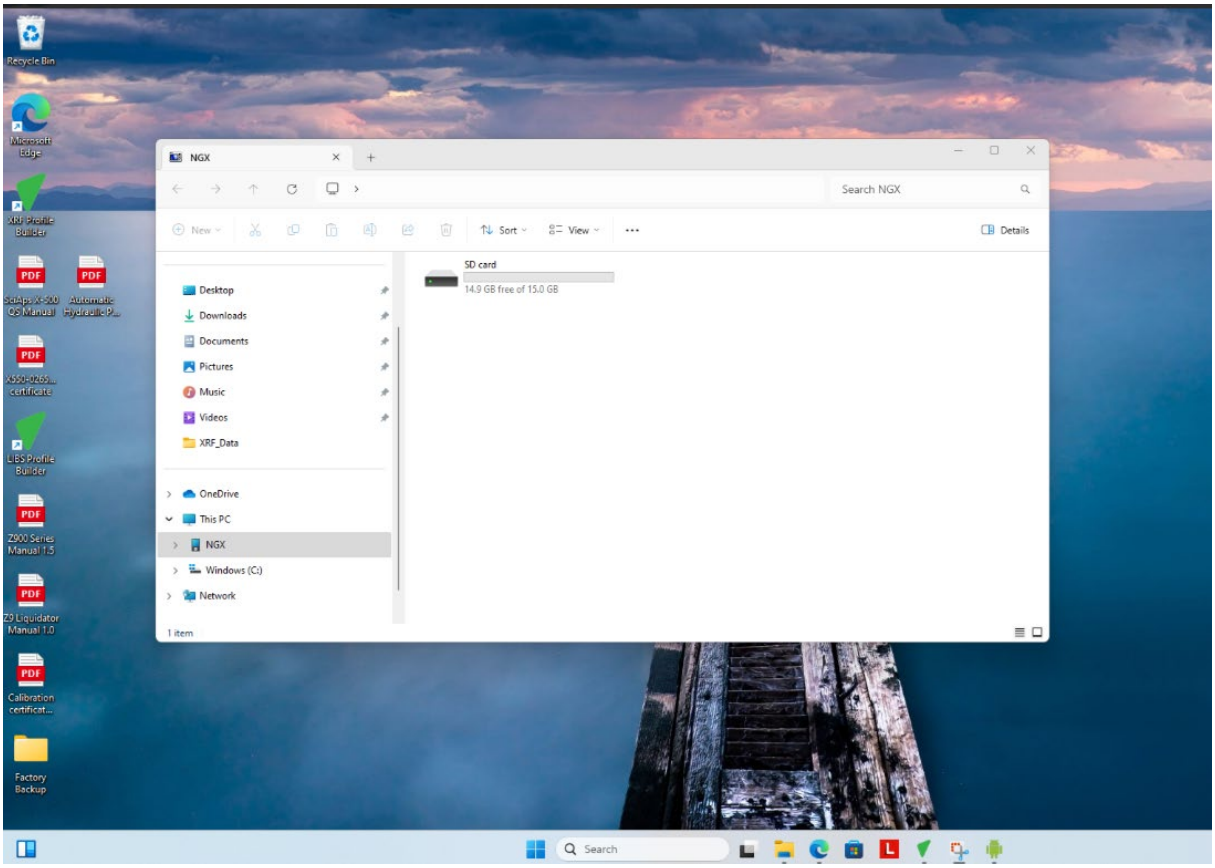
18. Press “Upload to Analyzer”. A warning screen will appear: “This will override the analyzer database, continue?” Press “Yes”.
19. Navigate to the mirrored XRF gun screen.
20. Exit out of Remote/USB-Tethered mode and navigate to the XRF gun home screen with the circle-shaped menu.
21. Click on “Results”.
22. Note that lighter elements, such as magnesium, may not be detected unless concentrations exceed approximately 1 weight percent.
23. The settings menu can be accessed to change the export template here (as well as in Profile Builder). The Soil/Mining template should reflect the format selected from the Export Result Settings in Profile Builder.
24. The default screen will list all the tests taken on the instrument (Figure 8). Select the “Menu” button to open additional export options, including “Filter by Date” to quickly export a batch of results.
25. Tap the check box to export multiple results (Figure 8).
26. When ready to finalize the export, tap the “Export Result” button and select “Excel” as the desired export format.
27. Tap the filename to change the export location and file name or tap the template name (“Default” or “Soil/Mining”) to finish the export.

Figure 8
SciAps Gun Results Export Screen



28. Click “Export to SD Card”. Modify the file name as needed. The screen will give a message when complete.
29. To access the SD card data, plug the tethering USB cable in and out of the computer. This will automatically open the SD card file location (Figure 9). Navigate to the export location selected at time of export (default location is the “Export” folder within the NGX/SD card).

Figure 9
SD Card Export Screen

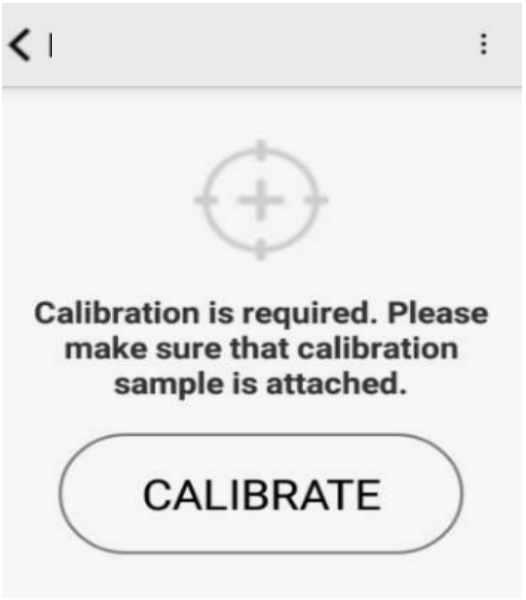


30. To turn off the XRF, press and hold the “on/off” button at the top of the X-ray gun for 2 seconds. A “Power Off” screen should appear on the XRF gun. Tap “Power Off” to shut down the device.

Handheld Mode

1. After the XRF is powered on through the “on/off” button, the “Analyze” screen will appear. Tap “Analyze” to start your first analysis of a sample.
2. This will take the screen to a list of the applications installed on the unit. Tap the mode for the type of analysis you intend to do (for example, “Alloy” mode).
3. The first time that the unit is being used, the unit will need to be calibrated. If required, the unit will automatically bring up the calibration window (Figure 10). If settings such as precision, uncertainty, and non-detection results need to be modified before calibration, tap “…” in the upper right corner to display the settings.

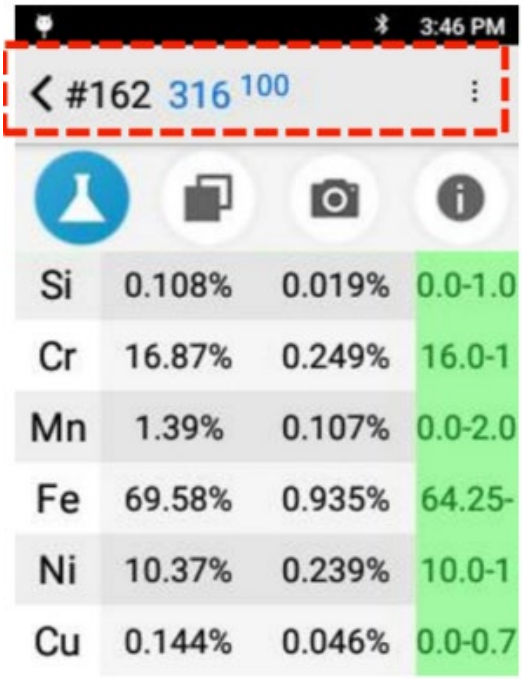
Figure 10
XRF Calibration Screen



4. Place the known standard coupon on the nose. A 316 coupon should come with the unit, but a clean, known 316 steel sample can also be used. Ensure the coupon completely covers the analysis window, as shown in Figure 4.
5. Tap "Calibrate" to begin the process. Calibration should take 15 seconds.
6. If calibration fails, an error message will be displayed. Confirm the piece of 316 coupon is correctly positioned in front of the window and retry the calibration.
7. When calibration is successful, the "Start" screen will appear. Remove the 316 coupon from the front of the aperture.
8. The instrument is now ready to analyze samples and QC/duplicates as appropriate. Sample processing should follow the steps outlined in the "Sample Assembly" section of the procedure.
9. To commence the run, navigate to the start screen.
10. Document the Sample ID under "Data Entry". Record the blank or standard ID within the sample name by clicking on the keyboard icon.
11. Gently wipe off the sample cup's exposed thin film with a Kimwipe.
12. Open the XRF lid and place the sample cup face down over the device aperture. The exposed-film side should be down and facing the XRF instrument. Make sure that the sample inside of the sample cup covers the entire exposed surface area of the thin film. A couple gentle taps on the counter or XRF stand plate can aid with compaction.

13. Note: If there is dust on the surface of the XRF aperture, it can be gently cleaned with a Kimwipe. The camera view will show any dust that needs to be cleaned. To view the camera image, click on the ">>" icon on the right-hand side of the screen until the third page, and click on the camera icon that pops up (Figure 6). Choose video size under "Video."
14. Close the lid.
15. Press "Start" to begin the run. Red flashing lights indicate that the run is in progress. Wait for the XRF lights to turn green to indicate the run is completed. Press the back button on the device to get return to the main menu.
16. Run the subsequent samples, QC samples, and calibration samples as appropriate.
17. When completed, navigate to "Home > Results" to explore results from this run and any subsequent runs (the instrument stores it in memory). The default screen will list all the tests taken on the instrument (see Figure 11).
18. Once all samples have been processed, navigate to the "Results" screen. Here you can look at results and compare tests. The top portion of the screen lists test number and top grade match (if in "Alloy" mode).

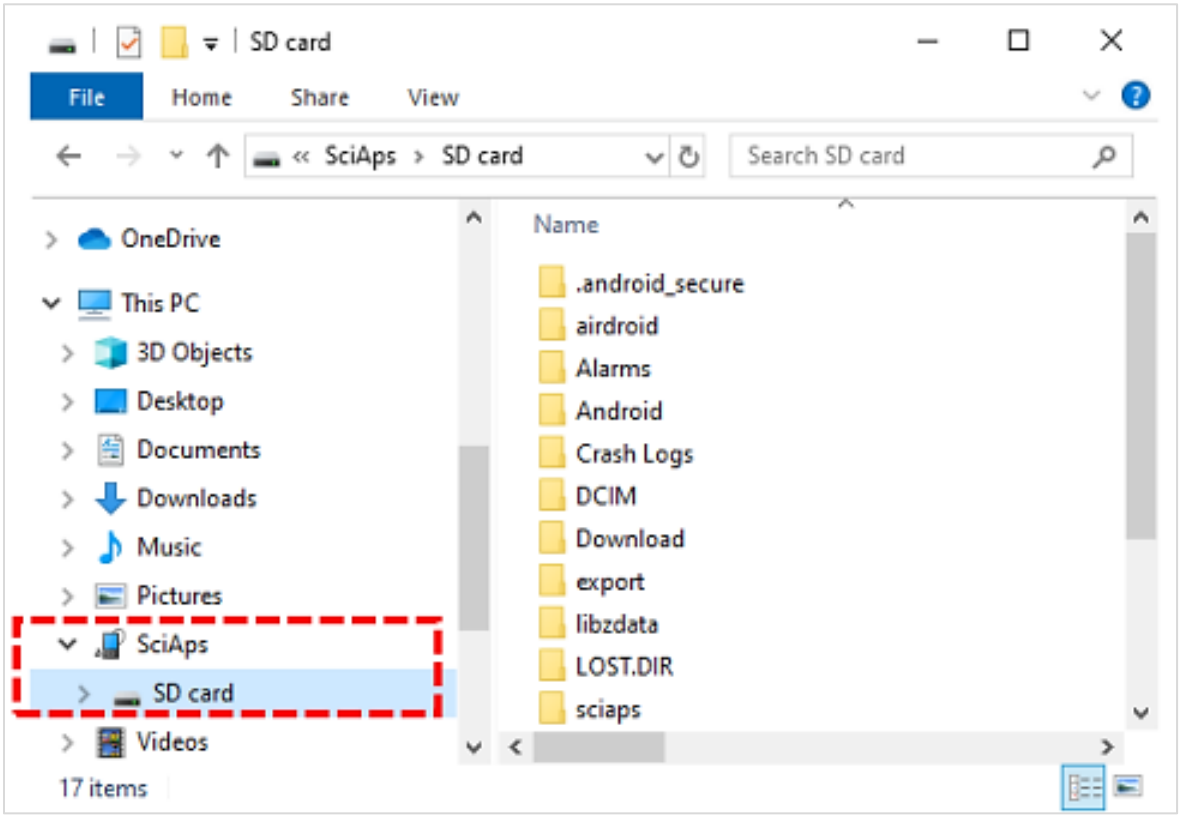
Figure 11
Example Results for Steel 316



19. The default screen will list all the tests taken on the instrument. Tap the "Menu" button to open additional export options, including "Filter by Date" to quickly export a batch of results.
20. Tap the check box to export multiple results.

21. When ready to finalize the export, tap the "Export Result" button and select "CSV" as the desired export format.
22. Tap the filename to change the export location and file name or tap the template name ("Default") to finish the export.
23. Connect the analyzer to a computer using the micro-USB cable. Once connected, the analyzer's SD card will show as a new drive from the computer's file explorer, as seen in Figure 12.

Figure 12
Export Data



24. Navigate to the export location selected at time of export (default location is NGX/SD card/export).
25. Drag the exported files over from the SD card to the desktop to save copies locally on the computer.
26. Open the Excel sheet. If desired, sort columns alphabetically in the Excel sheet (in the "Sort" dialog box, click "Options," and then select the "Sort Left to Right" radio button).
    a. If date/time samples appear as "#####", drag the column to expand it, and the data should appear.
27. To turn off the unit, press and hold the on/off button for 2 seconds. The "Power Off" screen will appear, where you can select "Power Off".

Quality Assurance/Quality Control

A duplicate sample should be processed with every 10 samples. If there is not enough sample mass to produce two separate sample cups for the duplicate sample, simply conduct two independent runs with the same sample vial. A blank and one of the standards (preferably the Resources Conservation and Recovery Act [RCRA] standard) should be processed at the end of the run or every 20 samples, whichever comes first. This will ensure that there was no drift in the instrument during the session.

The reproducibility is determined for duplicate samples as shown in Equation 1.

Equation 1

$$RPD = \frac{(X_1 - X_2) \times 100}{(X_1 + X_2) \div 2}$$

where:

RPD	=	relative percent difference
X_1	=	larger result value
X_2	=	smaller result value

If relative percent differences (RPDs) exceed 30%, notify the EGL task lead and discuss the RPD results within the scope of the project. In cases where RPDs exceed 30%, the data may still be of good quality. High RPDs may result from sample heterogeneity or other factors.

Closeout

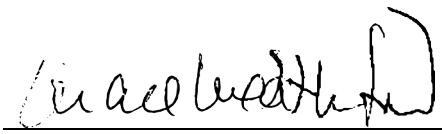
The remaining media from this experiment can be disposed of as described in Table 1. Project-specific media disposal is outlined in the Project Closeout Plan (PCP). If other unforeseen media is generated from this procedure, laboratory personnel and project managers will coordinate to characterize and dispose of those materials in accordance with federal, state, and local regulations.

Table 1
Disposal of Remaining Media

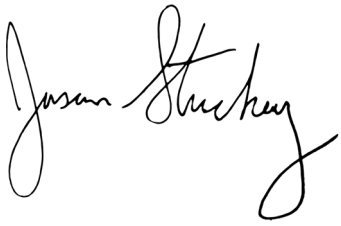
Remaining Media	Disposal Considerations	Disposal Procedure
Dried soil or sediment	Refer to the PCP for potentially regulated constituents.	Refer to the PCP for project-specific disposal methods.

Standard Operating Procedure Approval Page

This standard operating procedure, X-Ray Fluorescence Spectroscopy (SciAps X-550), has been reviewed and is approved for use in the Environmental Geochemistry Laboratory.

Signature:  Date: 05/04/2026

Grace Weatherford, Chemical Hygiene Officer

Signature:  Date: 05/04/2026

Jason Stuckey, Laboratory Manager

Table A
Hazards

Table A
Hazards

Potential Hazard(s)	Engineering Controls	Administrative Controls (Includes Work Practices)	PPE	Inspection Requirements
Inhalation, ingestion, and skin or eye contact with contaminants or small particles	Perform work in an operational fume hood.	--	- Safety glasses - Laboratory coat - Nitrile gloves (Ansell® TouchNTuff® 92-600)	- Inspect PPE prior to use. - Confirm fume hood face velocity prior to use.
Radiation exposure from XRF	The XRF should only be used with the stand (never use the manual trigger) and with the lid closed.	- The device should never be aimed at yourself or others, especially when the primary beam (X-ray) lights are illuminated. - The user can verify when the XRF is actively emitting X-rays by observing the lights on the XRF stand. The light is green when the device is powered on but not actively emitting X-rays, red when the X-ray pulse is charging in the chamber, and blinks red when actively emitting X-rays. The user must never open the XRF stand when the XRF is in use. - The user should post signage in the laboratory when the XRF is in use. - The XRF user must wear the dosimeter during use and when working in the laboratory. The recommendation is to clip the dosimeter to one's laboratory coat.	- Safety glasses - Laboratory coat - Nitrile gloves (Ansell® TouchNTuff® 92-600)	- Inspect PPE prior to use. - Check the warning light prior to opening the stand lid.

Notes:

--: not applicable

PPE: personal protective equipment

XRF: X-ray fluorescence

Attachment 1
SciAps X-500 XRF Flyer

Thermo Scientific™ Niton™ XRF Analyzers

CERTIFICATE OF ANALYSIS

Type P/N Element	RM 180-706 USGS SdAR-M2	CRM 180-649 NIST 2709a	Blank 180-647 SiO2 99.995%	QC Material 180-661 RCRA1
Ba Barium 56	990	979	<10	1000
Cs Cesium 55	12		<10	
Te Tellurium 52	<10		<10	
Sb Antimony 51	107	<30	<10	
Sn Tin 50	<10		<10	
Cd Cadmium 48	<10	<10	<10	500
Ag Silver 47	15		<10	500
Pd Palladium 46			<10	
Mo Molybdenum 42	13.3		<10	
Zr Zirconium 40	259	195	<10	
Sr Strontium 38	144	239	<10	
U Uranium 92	<10	<10	<10	
Rb Rubidium 37	149	99	<10	
Th Thorium 90	14.2	10.9	<10	
Pb Lead 82	808	17.3	<10	500

Type P/N Element	RM 180-706 USGS SdAR-M2	CRM 180-649 NIST 2709a	Blank 180-647 SiO2 99.995%	QC Material 180-661 RCRA1
Au Gold 79	<10		<10	
Se Selenium 34	<10		<10	500
As Arsenic 33	76	10.5	<10	500
Hg Mercury 80	<10	0.9	<10	
Zn Zinc 30	760	103	<10	
W Tungsten 74	<10		<10	
Cu Copper 29	236	33.9	<10	
Ni Nickel 28	48.8	85	<10	
Co Cobalt 27	<50	<50	<10	
Fe Iron 26	18395	33600	<10	
Mn Manganese 25	1038	529	<10	
Cr Chromium 24	49.6	130	<10	500
V Vanadium 23	25.2	110	<10	
Ti Titanium 22	1798	3360	<10	
Sc Scandium 21	<10	11.1	<10	

Part Number: 143-00131, Rev. D.
1-218 03/2016

—continued next page

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Thermo Scientific Niton XRF Analyzers

CERTIFICATE OF ANALYSIS — PAGE 2

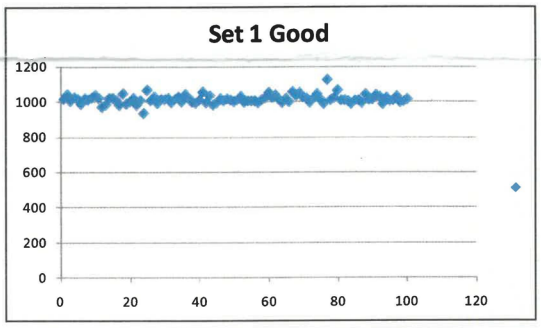
Use of reference materials

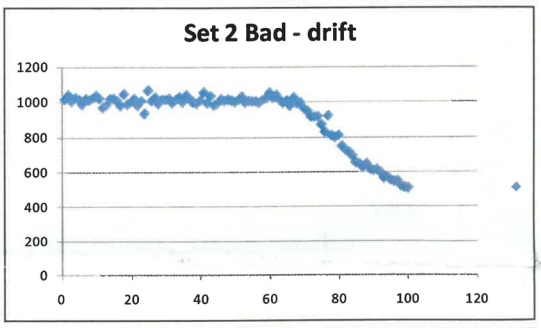
The reference materials provided with your analyzer are to help ensure the ongoing performance of your analyzer. These standards should be analyzed on a daily basis and the values obtained checked against this certificate of analysis. For quality assurance purposes you may wish to keep a running chart of the values obtained and monitor them for consistency.

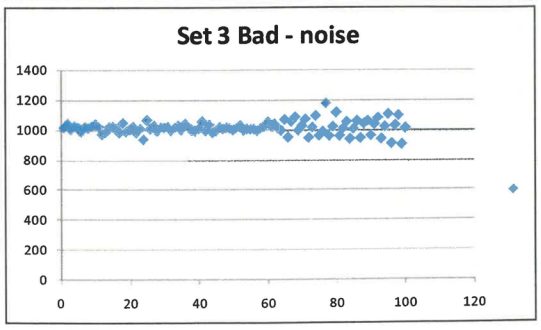
If one or more of the elements begins to change in terms of reported concentration outside of the normal expected variability, the sample may have become damaged or contaminated. This may occur for a number of reasons. For example, oils and salts may transfer from hand contact onto the surface, dust or lint from the surroundings may be deposited onto the sample, or the thin film on the front of the cup may have pinholes or have been torn. If the cup film has torn or has been damaged in any other way, it should be replaced immediately; this will prevent loss of the material and prevent contamination of the instrument and other samples.

If the film has been torn and the sample exposed for a period of time, then it may be best to assume the sample is contaminated. Dispose of it following your local regulations, and then replace it as soon as possible. Also check the front window of the instrument and clean or replace it if necessary.

Examples of daily quality assurance charts are shown below; learn to understand normal variance and recognize drift and noise. Results from your instrument may be as much as +/-20% of the listed values, depending on the model you have. However, by using the same integration time every time, your results should be consistent with themselves. If you have more questions, please refer to the Statistical Aspects of Spectrometry section of the manual under Reference Documents, or call our Customer Support group.







Type P/N Element	RM 180-706 USGS SdAR-M2	CRM 180-649 NIST 2709a	Blank 180-647 SiO2 99.995%	QC Material 180-661 RCRA1
Ca Calcium 20	6003	19100	<10	
K Potassium 19	41507	21100	<10	
Cl Chlorine 17				
S Sulfur 16	970		<10	
P Phosphorus 15	345	688	<10	
Si Silicon 14	343331	303000	467400	
Al Aluminum 13	65997	73700	<10	
Mg Magnesium 12	2955	14600	<10	

Requires GOLDD technology for mining & minerals mode

Notes:

- All results are listed in ppm (mg/kg).
- To convert to %, divide by 10,000; e.g., 33,600ppm Fe (NIST 2709) is 3.36%.
- Original certificates of analysis (if available) are on the Virtual Center of Excellence (vCoE) and can be requested from customer support.
- While every effort is made to ensure the high quality of these reference samples and their data, the use of the materials and interpretation of the results is the sole responsibility of the user.

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Standard Operating Procedure E36 – Sequential Extraction of Arsenic in Soil and Sediment

Scope and Application

This Environmental Geochemistry Laboratory (EGL) standard operating procedure (SOP) is applicable to sequential extraction of geologic (soil, sediment, or rock) samples to characterize the distribution of arsenic. The extraction procedure is designed to fractionate metals in a sample according to their reactivity by subjecting the sample to a sequence of progressively aggressive chemical treatments that target specific chemical forms (Keon et al. 2001; Tessier et al. 1979; Zimmerman and Weindorf 2010). Procedures outlined in this SOP will be followed, and any deviations must be noted in your laboratory notebook.

Health and Safety

All laboratory work will be performed in accordance with the *EGL Chemical Hygiene Plan* (CHP) by staff approved by the laboratory manager and chemical hygiene officer. Approval to work in the EGL requires orientation to laboratory safety procedures and potential hazards under the guidance of the laboratory manager, as specified in the CHP.

Hazards and controls associated with this SOP are listed in the following sections and explicitly linked in **Table A**. Hazards associated with project-specific samples are addressed in the Project Safety Analysis (PSA) document. Occupational exposure limits (OELs) for chemicals used in this SOP are attached as **Table B**.

Chemical Safety Data Sheets

The following Safety Data Sheets (SDSs) must be reviewed prior to beginning the procedure:

- Magnesium chloride
- Monosodium phosphate
- Hydroxylamine hydrochloride
- Nitric acid
- Hydrochloric acid (used for pH adjustment)
- Sodium hydroxide (used for pH adjustment)
- Iron oxide materials such as granular ferric hydroxide (GFH) and Bayoxide E33 (used for unused reagent solution disposal)
- Baking soda or soda ash (used for unused reagent solution disposal)
- pH buffer standards (4.01, 7.00, 10.01)
- pH electrode storage solution

Hazards Associated with this Standard Operating Procedure

- Inhalation, ingestion, and skin or eye contact with contaminants or small particles
- Handling limited quantities of corrosive chemicals for pH adjustment (hydrochloric acid, nitric acid, sodium hydroxide)
- Handling hydroxylamine hydrochloride (extraction fluid 3)
- Handling concentrated (16 molar [M]) nitric acid (extraction fluid 4)
- Operating the centrifuge
- Operating the shaker table
- Skin contact with heated surface of oven
- Breakage of glassware

Engineering Controls

- Perform work in an operational fume hood.
- The centrifuge will not operate if the lid is not secure (Thermo Scientific only).

Administrative Controls

- Ensure lids are secure on sample containers.
- Ensure the centrifuge lid is closed prior to operating.
- Verify the centrifuge has normal operational sound prior to leaving the area.
- Place samples securely in secondary containment (prior to operating the shaker table).
- The indicator light on the outside of the oven shows when the oven is on.
- Carry glassware with two hands.

Personal Protective Equipment

- Safety glasses
- Laboratory coat
- Microflex 93-260 nitrile gloves (when handling corrosive chemicals)
- Ansell® TouchNTuff® 92-600 nitrile gloves (when not handling corrosive chemicals)
- Face shield (when handling hydroxylamine hydrochloride or concentrated [16 M] nitric acid)
- Tychem2000 sleeves over a laboratory coat (when handling concentrated [16 M] nitric acid)

Inspection Requirements

- Inspect PPE prior to use.
- Confirm fume hood face velocity prior to use.
- Inspect shaker table prior to use.
- Inspect centrifuge prior to use.
- Inspect glassware prior to use.

Equipment and Supplies

The following is a list of equipment that may be necessary to carry out the procedures contained in this SOP; additional equipment may be required:

- Glove bag or other controlled-atmosphere chamber with nitrogen gas source
- Plastic bowls and spoons for sample processing
- No. 10 mesh sieve (2-millimeter [mm])
- Plastic spatulas
- Weighing dishes and weighing papers
- Analytical balance with a precision of 0.1 mg
- Volumetric flasks
- Parafilm
- High-density polyethylene (HDPE) bottles to store the extraction fluids 1–3
- U.S. Environmental Protection Agency (EPA) pre-cleaned glass jar to store the extraction 4 (i.e., 16 N nitric acid)
- 2-ounce (oz) EPA pre-cleaned glass jar to store the extracted solution samples (fraction 1–4 or F1–F4)
- 4-oz EPA pre-cleaned glass jar to store the extracted solution samples (F1–F4)
- 1- or 2-oz EPA pre-cleaned glass jar to store the fraction 5 (F5) residual solid samples
- Magnetic stir bars
- pH meter
- pH buffer standards for calibration (pH 4, 7, and 10)
- Hydrochloric acid (American Chemical Society [ACS] grade)
- 10 N sodium hydroxide solution (ACS grade)
- Disposable transfer pipette
- Centrifuge
- 50-milliliter (mL) centrifuge tubes
- Deionized (DI) water
- Magnesium chloride hexahydrate (ACS grade)
- Monosodium phosphate monohydrate (ACS grade)
- Higher grade (BioXtra, for molecular biology, ≥99.5%, Sigma Aldrich) for lithium analysis
- Hydroxylamine hydrochloride (OmniTrace grade)
- Nitric acid (OmniTrace grade)
- Plastic graduated cylinders (10- and 50-mL)
- Micropipette and pipette tips (approximately 10-mL)
- Sample shaker/tumbler
- Nitric acid-preserved sample bottles
- Disposable syringes (30- and 60-mL)

- Polyethersulfone (PES) syringe filters (0.45-micrometer [µm] pore size)
- Hydrophilic polytetrafluoroethylene (PTFE) syringe filters (0.45-µm pore size)
- Baking soda (sodium bicarbonate) or soda ash (sodium carbonate) for unused reagent solution disposal
- Iron oxide materials for unused reagent solution disposal
- Litmus pH test strips

Procedure

Sample Preparation

Please refer to the Sample Intake Form and check with the EGL Project Lead to confirm whether samples need to be processed under a nitrogen atmosphere or for other sample preparation considerations.

If redox sensitive samples are tested, sample processing and extraction procedures will be conducted under a nitrogen atmosphere in a disposable glove bag or anaerobic chamber until the F3 process is completed. After tightly sealing the sample tubes, agitation and centrifugation of sample tubes will be conducted outside the glove bag or anaerobic chamber for all of the fraction steps.

Rock samples will be crushed and homogenized prior to analysis according to project needs. Soil or sediment samples will be passed through a 2-mm sieve to remove larger rock fragments and other debris and homogenized prior to processing. When samples are wet, determine the moisture content (wet-basis) according to the EGL SOP #201: Moisture Content and use the samples without drying. Approximately 1 gram (g) (dry-mass basis) of homogenized sample will be weighed into a centrifuge tube and extracted according to the procedure detailed in Table 1.

Before preparing extraction fluids, determine volume needed for each extraction fluid based on the number of samples including method blank and duplicate(s). Note the extraction fluid volume is higher for F3 and F4 than for F1 and F2.

Table 1
Sequential Extraction Procedure

Target Fraction	Extraction Fluid	Procedure
F1: Soluble	1 M magnesium chloride, pH 8.0±0.1 (adjust pH using sodium hydroxide or hydrochloric acid if necessary)	1. Weigh and record an empty centrifuge tube with cap on. 2. Add 1 g solid sample (dry-mass basis) to centrifuge tube. 3. Add 8 mL fluid to centrifuge tube and agitate vigorously using Vortex to suspend the sample. 4. Agitate on shaker/tumbler for 1 hour at room temperature at 120 RPM. 5. Centrifuge for 25 minutes at 3,000 RPM to settle suspended solids. 6. Gently decant fluid to an EPA pre-cleaned glass jar, avoiding loss of solids from the centrifuge tube. 7. Repeat steps 3 to 6 with new extraction fluid. 8. Repeat steps 3, 5, and 6 with DI water. 9. Filter the combined extraction fluid using disposable syringe and 0.45-µm PES syringe filter into pre-weighed (with cap) nitric acid-preserved bottle to maintain pH <2 and record the mass of the extraction fluid recovered. 10. Submit the sample to analyze for arsenic by EPA Method 6020B or 200.8, depending on sample nature and project needs.
F2: Exchangeable	1 M monosodium phosphate, pH 5.0±0.1 (adjust pH using sodium hydroxide or hydrochloric acid if necessary)	1. Add 8 mL of fluid to the same centrifuge tube from F1 and agitate vigorously using the Vortex to resuspend the sample. 2. Agitate on shaker/tumbler for 5 hours at room temperature at 120 RPM. 3. Centrifuge for 25 minutes at 3,000 RPM to settle suspended solids. 4. Gently decant fluid to an EPA pre-cleaned glass jar, avoiding loss of solids from the centrifuge tube. 5. Repeat steps 1 to 4 with new extraction fluid with agitation for 24 hours. 6. Repeat steps 1, 3, and 4 with DI water. 7. Filter the combined extraction fluid using disposable syringe and 0.45-µm PES syringe filter into pre-weighed (with cap) nitric acid-preserved bottle to maintain pH <2 and record the mass of the extraction fluid recovered. 8. Submit the sample to analyze for arsenic by EPA Method 6020B or 200.8, depending on sample nature and project needs.

Target Fraction	Extraction Fluid	Procedure
F3: Reducible (Iron and/or Manganese Oxide Bound)	0.1 M hydroxylamine hydrochloride acidify to pH 2.0±0.1 with nitric acid (OmniTrace grade)	1. Add 20 mL of fluid to the same centrifuge tube from F2 and agitate vigorously using the Vortex to resuspend the sample. 2. Agitate on agitator/tumbler for 2 hours at room temperature at 120 RPM. 3. Centrifuge for 25 minutes at 3,000 RPM to settle suspended solids. 4. Gently decant fluid to an EPA pre-cleaned glass jar, avoiding loss of solids from the centrifuge tube. 5. Repeat steps 1 to 4 with new extraction fluid. 6. Repeat steps 1, 3, and 4 with DI water. 7. Filter the combined extraction fluid using disposable syringe and 0.45-µm PES syringe filter into pre-weighed (with cap) nitric acid-preserved bottle to maintain pH <2 and record the mass of the extraction fluid recovered. 8. Submit the sample to analyze for arsenic by EPA Method 6020B or 200.8, depending on sample nature and project needs.
F4: Oxidizable (Sulfide and/or Organic Bound)	16 N nitric acid (OmniTrace grade)	1. Add 20 mL of fluid to the same centrifuge from F3. Begin by adding 2 to 3 drops of fluid to observe the extent of effervescence (bubbling). Then add the remainder of the 20 mL of fluid, ensuring the sample suspension does not overflow. 2. Keep the centrifuge tubes uncapped in the fume hood for 5 minutes to confirm the effervescent reaction between the solid sample and fluid has stabilized. 3. Cap the centrifuge tube tightly and agitate vigorously using the Vortex to resuspend the sample. 4. Place centrifuge tubes in two layers of plastic bags and clearly label the area. Agitate on shaker/tumbler for 2 hours at room temperature at 120 RPM. 5. Centrifuge for 25 minutes at 3,000 RPM to settle suspended solids. 6. Gently decant fluid to an EPA pre-cleaned glass jar, avoiding loss of solids from the centrifuge tube. 7. Repeat steps 1 to 6 with new extraction fluid. 8. Repeat steps 1, 3, 5, and 6 with DI water. 9. Filter the combined extraction fluid using disposable syringe and 0.45-µm PTFE syringe filter into pre-weighed (with cap) nitric acid-preserved bottle to maintain pH <2 and record the mass of the extraction fluid recovered. 10. Submit the sample to analyze for arsenic by EPA Method 6020B or 200.8, depending on sample nature and project needs.

Target Fraction	Extraction Fluid	Procedure
F5: Residual	EPA Method 3050B	1. Dry the solid residue sample in the centrifuge tube from F4 in operational fume hood overnight. 2. Weigh the centrifuge tube with the cap on and subtract the empty centrifuge tube weight to determine the residual sample mass. 3. Transfer the residual sample to EPA pre-cleaned glass jar. 4. Submit the sample to an analytical laboratory for preparation by EPA Method 3050B for acid digestion and analysis for arsenic by EPA Method 6020B or 200.8, depending on sample nature and project needs.

Notes:
N: normal
RPM: revolution per minute

Calculation of the Extractable Arsenic by Fraction

The extractable arsenic and other metals in each fraction are reported as milligram of metal per kilogram of solid. This value is calculated from the reported concentration in the extraction solution, the total volume of extraction solution collected (as calculated from the measured extraction solution mass and density), and the mass of soil or sediment extracted (Equation 1).

Equation 1

$$C_s = \frac{C_l \times (M \div D)}{S}$$

where:

C_s = metal concentration in a fraction in sediment (milligram per kilogram [mg/kg])
C_l = metal concentration in extraction solution (milligram per liter [mg/L])
M = mass of diluted extraction solution (kilogram [kg])
D = density of solution (kg/L). Density of final diluted F1 solution = 1.02 kg/L, F2 solution = 1.03 kg/L, F3 solution = 0.989 kg/L, and F4 solution = 1.25 kg/L.
S = mass of soil or sediment extracted, dry-mass basis (kg)

This calculation is performed for each fraction and each metal of interest.

Quality Assurance/Quality Control

Quality assurance/quality control (QA/QC) samples are collected during the procedure. The QA/QC samples are described as follows:

- **Duplicate samples:** Duplicate or replicate samples should be analyzed at a project appropriate rate, with at least one duplicate to calculate the reproducibility. The reproducibility is determined for duplicate samples as shown in **Equation 2**.
- **Method blank:** A method blank will be prepared for each extraction step by using a centrifuge tube without a sample to assess if any analytical background contaminants are introduced during the procedure.
- **Temperature blank:** A temperature blank will be prepared to ensure that samples are maintained at an appropriate temperature (i.e., approximately 4°C) during shipping to the analytical laboratory.

Equation 2

$$RPD = \frac{(X_1 - X_2) \times 100}{(X_1 + X_2) \div 2}$$

where:

RPD	=	relative percent difference
X_1	=	larger result value
X_2	=	smaller result value

If relative percent differences (RPDs) exceed 30%, notify the EGL task lead and discuss the RPD results within the scope of the project. In cases where RPDs exceed 30%, the data may still be of good quality. High RPDs may result from sample heterogeneity or other factors.

Closeout

The remaining media from this experiment can be disposed of as described in Table 2. Project-specific media disposal is outlined in the Project Closeout Plan (PCP). If other unforeseen media is generated from this procedure, laboratory personnel and project managers will coordinate to characterize and dispose of those materials in accordance with federal, state, and local regulations.

Table 2
Disposal of Unused Remaining Media

Remaining Media	Disposal Considerations	Disposal Procedure
1 M magnesium chloride (pH 8±0.1)	Magnesium chloride is not a regulated waste material.	Dispose down the drain with an excess of running tap water.
1 M monosodium phosphate (pH 5±0.1)	Sodium phosphate is not a regulated waste material.	Dispose down the drain with an excess of running tap water.
0.1 M hydroxylamine hydrochloride acidified to pH 2 with nitric acid	Aqueous solutions with a pH <2 or >12.5 carry the federal waste code of Corrosivity (EPA 2024). Additionally, the municipal discharge guideline requires a pH of 5.0 to 11.5 for drain disposal (City of Portland 2019). Hydroxylamine hydrochloride is not a regulated waste material but is toxic to aquatic life.	1. Gently add iron oxide materials such as GFH and Bayoxide E33 to the reagent solution to oxidize hydroxylammonium chloride (Half reaction: $NH_3OH^+ = 1/2N_2 + 2H^+ + H_2O + e^-$). 2. Neutralize pH to 5.0 to 11.5 using baking soda (sodium bicarbonate) or soda ash (sodium carbonate). Check the final pH using litmus pH test strips. 3. Dispose down the drain with an excess of running tap water. 4. Allow solids to dry, then bag and place in the trash.
16 N nitric acid	Aqueous solutions with a pH <2 or >12.5 carry the federal waste code of Corrosivity (EPA 2024). Additionally, the municipal discharge guideline requires a pH of 5.0 to 11.5 for drain disposal (City of Portland 2019).	1. Add large volume of tap water to a plastic beaker. 2. Dilute the reagent solution by adding it to the tap water. **Always Add Acid ("AAA") to water.** 3. Neutralize pH to 5.0 to 11.5 using baking soda or soda ash. Check the final pH using litmus pH test strips. 4. Dispose down the drain with an excess of running tap water.

References

City of Portland, 2019. Sanitary Discharge and Pretreatment Program Administrative Rules: ENB – 4.03. Accessed June 2, 2023. Available at: https://www.portland.gov/sites/default/files/2020-06/enb-4-03-sanitary-discharge-and-pretreatment-program-7-19-465822.pdf.

EPA (U.S. Environmental Protection Agency), 2024. Defining Hazardous Waste: Listed, Characteristic and Mixed Radiological Wastes. Accessed November 11, 2024. Available at: https://www.epa.gov/hw/defining-hazardous-waste-listed-characteristic-and-mixed-radiological-wastes.

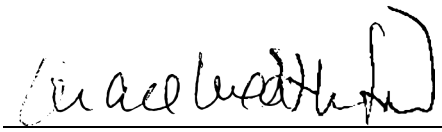
Keon, N.E., C.H. Swartz, D.J. Brabander, C. Harvey, and H.F. Hemond, 2001. "Validation of an Arsenic Sequential Extraction Method for Evaluating Mobility in Sediments." *Environmental Science & Technology* 35(13): 2778–2784.

Tessier, A., P.G.C. Campbell, and M. Bisson, 1979. "Sequential Extraction Procedure for the Speciation of Particulate Trace Metals." *Analytical Chemistry* 51(7):844–851.

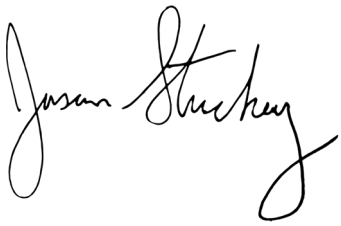
Zimmerman, A.J., and D.C. Weindorf, 2010. "Heavy Metal and Trace Metal Analysis in Soil by Sequential Extraction: A Review of Procedures." *International Journal of Analytical Chemistry* 2010 (dx.doi.org/10.1155/2010/387803).

Standard Operating Procedure Approval Page

This standard operating procedure, Sequential Extraction of Arsenic in Soil and Sediment, has been reviewed and is approved for use in the Environmental Geochemistry Laboratory.

Signature:  Date: 05/04/2026

Grace Weatherford, Chemical Hygiene Officer

Signature:  Date: 05/04/2026

Jason Stuckey, Laboratory Manager

Table A
Hazards

Table A
Hazards

Potential Hazard(s)	Engineering Controls	Administrative Controls (Includes Work Practices)	PPE	Inspection Requirements
Inhalation, ingestion, and skin or eye contact with contaminants or small particles	Perform work in an operational fume hood.	--	- Safety glasses - Laboratory coat - Nitrile gloves (Ansell® TouchNTuff® 92-600)	- Inspect PPE prior to use. - Confirm fume hood face velocity prior to use.
Handling corrosive chemicals (hydrochloric acid, nitric acid, sodium hydroxide)	Perform work in an operational fume hood.	--	- Safety glasses - Laboratory coat - Nitrile gloves (Microflex 93-259)	- Inspect PPE prior to use. - Confirm fume hood face velocity prior to use.
Handling hydroxylamine hydrochloride	Perform work in an operational fume hood.	--	- Safety glasses - Laboratory coat - Nitrile gloves (Microflex 93-259) - Face shield	- Inspect PPE prior to use. - Confirm fume hood face velocity prior to use.
Handling concentrated (16 M) nitric acid	Perform work in an operational fume hood.	--	- Safety glasses - Laboratory coat - Nitrile gloves (Microflex 93-259) - Face shield - Tychem2000 sleeves over laboratory coat	- Inspect PPE prior to use. - Confirm fume hood face velocity prior to use.
Operating the centrifuge	- Thermo Scientific: Centrifuge will not operate if the lid is not secure. - Old: --	- Ensure lids are secure on sample containers. - Ensure centrifuge lid is closed prior to operating. - Verify centrifuge has normal operational sound prior to leaving the area.	- Safety glasses - Laboratory coat - Nitrile gloves (Ansell® TouchNTuff® 92-600)	- Inspect PPE prior to use. - Inspect centrifuge prior to use.

Table A
Hazards

Potential Hazard(s)	Engineering Controls	Administrative Controls (Includes Work Practices)	PPE	Inspection Requirements
Operating the shaker table	--	- Ensure lids are secure on sample containers. - Place samples securely in secondary containment. - Ensure shaker table has normal sound prior to leaving the area.	- Safety glasses - Laboratory coat - Nitrile gloves (Ansell® TouchNTuff® 92-600)	- Inspect PPE prior to use. - Inspect shaker table prior to use.
Skin contact with heated surface of oven	Perform work in an operational fume hood.	The indicator light on the outside of the oven shows when the oven is on.	- Safety glasses - Laboratory coat - Nitrile gloves (Ansell® TouchNTuff® 92-600) - Oven mitts	- Inspect PPE prior to use. - Confirm fume hood face velocity prior to use.
Breakage of glassware	--	Carry glassware with two hands.	- Safety glasses - Laboratory coat - Nitrile gloves (Ansell® TouchNTuff® 92-600)	- Inspect PPE prior to use. - Inspect glassware prior to use.

Notes:

--: not applicable

PPE: personal protective equipment

Table B
Occupational Exposure Limits

Table B
Occupational Exposure Limits

SOP No.	Title	Chemicals Used	CAS Number	Exposure Routes	Symptoms	Target Organs	OEL	NIOSH/ OSHA/ ACGIH Values	Vapor Pressure (mmHg)	Ionization Potential (eV)	First Aid
308	Sequential Extraction Arsenic	Magnesium Chloride	7786-30-3	Inhalation, ingestion, skin and/or eye contact	Skin irritation, eye irritation, nausea, headache, shortness of breath	Eyes, skin, respiratory system	15 mg/m^3	OSHA PEL TWA: (Total Dust) 15 mg/m^3 (50 mppcf)	--	--	Inhalation: Remove victim to fresh air and keep at rest in position comfortable for breathing Skin: Soap wash for 15 to 20 minutes Eye: Protect unexposed eye. Flush for 15 to 20 minutes. Remove contact lenses if able. Ingestion: Rinse mouth thoroughly. Do not induce vomiting.
308	Sequential Extraction Arsenic	Monosodium Phosphate	10049-21-5	Inhalation, ingestion, skin and/or eye contact	None reasonably foreseeable	Eyes, skin, respiratory system	--	--	--	--	Eye: Rinse for 15 minutes. Get medical attention Skin: Wash off immediately and rinse for 15 minutes. Seek medical attention if symptoms occur. Inhalation: Remove to fresh air. Seek medical attention if symptoms occur. Ingestion: Clean mouth with water and drink afterwards plenty of water. Seek medical attention if symptoms occur.
308	Sequential Extraction Arsenic	Hydroxylamine Hydrochloride	5470-11-1	Inhalation, ingestion, skin and/or eye contact	May cause allergic skin reaction: rash, itching, swelling, trouble breathing, tingling of hands and feet, dizziness, lightheadedness, chest pain, muscle pain or flushing	Eyes, skin, respiratory system	--	--	Negligible	--	Eye: Rinse irrigate immediately for at least 15 minutes. Immediate medical attention is required. Skin: Flush immediately for at least 15 minutes. Immediate medical attention is required. Inhalation: Remove to fresh air. If breathing is difficult, give oxygen. Do not use mouth-to-mouth if victim ingested or inhaled. Immediate medical attention. Ingestion: Do NOT induce vomiting. Call Poison Control immediately.
308	Sequential Extraction Arsenic	Nitric Acid	7697-37-2	Inhalation, ingestion, skin and/or eye contact	Irritation of eyes, skin, mucous membrane; delayed pulmonary edema, pneumonitis, bronchitis; dental erosion	Eyes, skin, respiratory system, teeth	2 ppm	NIOSH REL and OSHA PEL TWA 2 ppm	48 mmHg	11.95	Eye: Irrigate immediately Skin: Water flush immediately Breathing: Respiratory support Swallow: Medical attention immediately

Table B
Occupational Exposure Limits

SOP No.	Title	Chemicals Used	CAS Number	Exposure Routes	Symptoms	Target Organs	OEL	NIOSH/ OSHA/ ACGIH Values	Vapor Pressure (mmHg)	Ionization Potential (eV)	First Aid
308	Sequential Extraction Arsenic	Hydrochloric Acid	7647-01-0	Inhalation, ingestion (solution), skin and/or eye contact	Irritation of nose, throat, larynx; cough, choking; dermatitis; solution: eye, skin burns; liquid: frostbite; in animals: laryngeal spasm; pulmonary edema	Eyes, skin, respiratory system	2 ppm	NIOSH REL: C 5 ppm (7 mg/m^3) OSHA PEL: C 5 ppm (7 mg/m^3) ACGIH TLV-C: 2 ppm	40.5 atm	12.74	Eye: Irrigate immediately (solution)/Frostbite Skin: Water flush immediately (solution)/Frostbite Breathing: Respiratory support Swallow: Medical attention immediately (solution)
308	Sequential Extraction Arsenic	Sodium Hydroxide	1310-73-2	Inhalation, ingestion, skin and/or eye contact	Irritation of eyes, skin, mucous membrane; pneumonitis; eye, skin burns; temporary loss of hair	Eyes, skin, respiratory system	2 mg/m^3	NIOSH REL and OSHA PEL 2 mg/m^3	0 mmHg	--	Eye: Irrigate immediately Skin: Water flush immediately Breathing: Respiratory support Swallow: Medical attention immediately
308	Sequential Extraction Arsenic	Ferric Oxide	1317-61-9	Inhalation, ingestion, skin and/or eye contact	None reasonably foreseeable	Eyes, skin, respiratory system	--	--	--	--	Eye: Irrigate immediately. Remove contact lenses. Skin: Remove contaminated clothing and rinse with water/shower. Breathing: Remove to fresh air. Swallow: Drink plenty of water. Consult doctor if feeling unwell.
308	Sequential Extraction Arsenic	Baking Soda	144-55-8	Inhalation, ingestion, skin and/or eye contact	Shortness of breath, irritation, nausea, headache, may cause adverse liver effects, alkalosis, diarrhea, hypertension	Eyes, skin, respiratory system	--	--	--	--	Eye: Irrigate immediately. Seek medical advice. Skin: Wash immediately. Breathing: Remove victim to fresh air and keep at rest Swallow: Do not induce vomiting. Seek medical attention immediately.

Notes:
--: not applicable
ACGIH: American Conference of Governmental Industrial Hygienists
atm: atmosphere
CAS: Chemical Abstracts Service
eV: electron volt
mg/m^3: milligram per cubic meter
mmHg: millimeter of mercury
mppcf: millions of particles per cubic foot
NIOSH: National Institute for Occupation Safety and Health
OEL: Occupational Safety and Health Administration Act
OSHA: Occupational Safety and Health Administration or Act
PEL: permissible exposure limit
ppm: part per million
REL: recommended exposure limit
SOP: Standard Operating Procedure
TLV: threshold limit value
TWA: time-weighted average

Standard Operating Procedure E37 – Porewater Sample Collection

Standard Operating Procedure Acknowledgement Form

Project Number: 210075-01.03 Project Name: Middle Reach of the Lower Duwamish Waterway

My signature below certifies that I have read and understand the procedures specified in this Standard Operating Procedure.

Date	Name (print)	Signature	Company

Purpose

The purpose of this Standard Operating Procedure (SOP) is to establish uniform procedures for the collection of porewater. Porewater samples will be analyzed for sulfide, dissolved iron, dissolved arsenic, dissolved manganese, and arsenic speciation. To minimize the risk of sample oxidation (and associated arsenic species conversion in samples collected for analysis of arsenic speciation) these samples will be collected and handled in a manner that minimizes exposure to the atmosphere.

This SOP describes the equipment, field procedures, materials, and documentation procedures necessary to perform the activities described in the previous paragraph. The details within this SOP should be used in conjunction with the *Quality Assurance Project Plan Addendum No. 3* (QAPP; Anchor QEA 2022), and other project-specific SOPs.

Scope and Application

This SOP is applicable to the collection of porewater. Porewater will be collected via one of the following methods:

- Option A: Micro-push-point Sampler
- Option B: Direct-Push Drill Rig and Screen Point Sampling System

Procedures outlined in this SOP are expected to be followed. Substantive deviations from these procedures will be recorded in the Daily Activity Log or field log book and on a Field Deviation Form and will be reported to the project manager before implementation in the field.

Health and Safety Warnings

Health and safety issues for work associated with this SOP, including physical and chemical hazards, are addressed in the project Health and Safety Plan (HASP).

Staff Qualifications

Field staff executing these procedures will have read, be familiar with, and comply with the requirements of this SOP, and all associated project planning documents, such as the QAPP, and other project-specific SOPs. Additionally, field staff will be under the direct supervision of qualified professionals who are experienced in performing the tasks required for sample collection.

Equipment and Supplies

The following equipment may be necessary to carry out the procedures contained in this SOP. Additional equipment may be required depending on field conditions:

- Approved project-specific documents, including the Work Plan, QAPP, HASP, and other project SOPs

- Appropriate personal protective equipment and clothing, as defined in the HASP
- Field laptop or tablet and/or paper field forms, as necessary
- Spill kit and absorbent boom
- Standardized field log forms (field forms)
- Black ballpoint pen
- Sharpie permanent marker (or equivalent)
- Engineer's ruler or tape (at least 6 feet long)
- Tubing
- 0.45-micrometer (µm) inline filter
- Syringes
- Needles
- Sharps container
- Mylar bags
- Oxygen adsorbers
- Tape

Sample Container Size and Type

Table 1 contains details for sample handling and storage, including sample container sizes and type, preservation method and holding times.

Field Equipment Decontamination

Dedicated, disposable tubing, syringes, screens, and filters will be used to eliminate cross-contamination during sampling. Re-usable equipment will be used when practicable (e.g., micro-push-point samplers). To prevent sample cross contamination, sampling and processing equipment in contact with the environmental media will undergo the following decontamination procedures prior to and between collection activities in accordance with U.S. Environmental Protection Agency (EPA) protocols (EPA 2001). Between sample locations, all sampling equipment will be decontaminated prior to use by the following procedures:

- Rinse with river water and wash with a scrub brush or pressure washer until free of sediment.
- Wash with phosphate-free detergent (e.g., Alconox).
- Visually inspect the sampler and repeat the rinse-and-scrub step, if necessary. If scrubbing and rinsing with Alconox is insufficient to remove visually observable tar- or oil-related contamination on sampling equipment, the equipment will be scrubbed and rinsed using acetone (or similar type solution) until all visual signs of contamination are absent.
- Rinse with deionized water three times.

Option A: Micro-push-point Sampler

Porewater samples will be collected in situ with a micro-push-point sampler, or similar, using a peristaltic pump.

Samples will be collected using the following procedure:

1. Measure and mark the length of the micro-push-point sampler needed to reach the target depth. Drive the micro-push-point sampler to the target depth.
2. Attach tubing to the sampler port.
3. Prior to activating the pump, collect a co-located near-bottom surface water quality reading and porewater below the target interval water quality reading using a miniature flow-through cell and a calibrated multiparameter water quality meter. Readings will be used to assess whether a sufficient seal has been achieved to prevent surface water influences in the porewater sample. The following parameters will be recorded: temperature, specific conductance, oxidation reduction potential (ORP), turbidity, and pH.
    a. Surface water field parameters will be measured at a depth of approximately 12 inches above mudline if the water is more than 2 feet deep or the midpoint of the water column if the water is less than 2 feet deep.
    b. Porewater below the target interval field parameters will be measured at a depth of approximately 1 foot below the sample target depth.
    c. Surface water and porewater collected below target depth are expected to exhibit different parameter values.
    d. Surface water and deeper porewater water quality readings will be recorded periodically (approximately every 15 minutes). Continue collecting surface water and deeper porewater measurements until the readings stabilize (e.g., three consecutive readings), then compare the results to determine the distinct parameters.
4. When a sufficient seal has been confirmed, the sampling pump will be activated at a low initial rate (less than 500 milliliters [mL] per minute).
5. Water quality readings will be collected using a using a miniature flow-through cell and a calibrated multiparameter water quality meter. The following parameters will be recorded: temperature, specific conductance, ORP, turbidity, and pH.
6. Continue measuring the surface water and deeper porewater water quality parameters to ensure a sufficient seal remains during sampling.
7. Samples for arsenic speciation will be collected directly from the micro-push-point sampler using analytical laboratory-provided syringes and Vacuette tubes and will contain ethylenediaminetetraacetic acid (EDTA) preservative (see Table 1). The procedure for transfer from the micro-push-point sampler to the laboratory-provided Vacuette tubes is as follows:
    a. Connect the syringe to the tubing and fill the syringe with the sample.

b. Attach the 0.45-µm inline filter (influent) to the end of the syringe. Attach the Luer-lock needle to the other end (effluent) of the filter.
c. Remove the sheath from the needle, then expel and discard a small amount (approximately 2 to 3 mL) of sample from the syringe apparatus prior to filling the sample bottle.
d. Carefully insert the tip of the needle through the septum in the Vacuette's cap. Gently depress the plunger to fill the container. Leaving a small amount of headspace (approximately 1 mL) in the vial is acceptable.
e. Remove the needle from Vacuette, then gently invert the container several times to fully solubilize the EDTA preservative within the Vacuette.
f. Label the Vacuette with the sample identification number, then place the container into the mylar bags with oxygen absorbers. Partially seal the bag, leaving a small hole for air to escape, roll down the top, slowly pushing as much air out of the bag as possible prior to sealing the bag. Place tape over the closed seal.
g. Log each sample on the supplied chain-of-custody (COC) form.
h. Dispose of each used needle into an appropriate sharps disposal container.

8. Collect samples for other analyses directly into the sample bottles specified in Table 1.
   a. Filter samples for sulfide and dissolved metals analyses using a 0.45-µm inline filter.
   b. Cap bottles immediately to minimize exposure to the atmosphere.
   c. Label sample bottles and place in mylar bags with oxygen absorbers. Partially seal the bag, leaving a small hole for air to escape, roll down the top, slowly pushing as much air out of the bag as possible prior to sealing the bag. Place tape over the closed seal.
9. Place packaged samples inside of a cooler with ice for storage at the proper temperature (4°C to ± 2°C for all samples) and ship to the appropriate laboratory. Pack each container carefully to prevent breakage.

Option B: Direct-Push Drill Rig and Screen Point Sampling System

In situ porewater sampling will be conducted using a direct-push drill rig and screen point sampling system. To achieve the target depths, porewater samplers must be deployed using a direct-push drill rig. Once the tip of the porewater sampler has been advanced to the target depth (36 inches or as specified by the field lead) the porewater sample will be collected using standard groundwater sampling pumps (e.g., peristaltic) deployed within the screen point of the drill rods in the same manner that a standard groundwater sampling pump would be deployed within the screen point of a conventional technology such as a Trident probe.

Samples will be collected in the following manner:

1. The vessel will be maneuvered to the proposed location.
2. The drilling equipment will be decontaminated.

3. The depth to mudline will be measured using a lead line and recorded, along with the time, on the field collection form.
4. A decontaminated screen point will be fixed to the leading end of the drill rods.
5. The screen point will be lowered to mudline.
6. The screen point will be advanced to the depth where the approximately 1-foot screen will be centered at the target depth. The total depth will be recorded on the sample collection form, along with the water depth.
7. Once the screen point is properly installed at the target depth, porewater samples will be collected using the following procedures:
    a. A length of pump tubing will be prepared that is long enough to reach the bottom of the screen point.
    b. The pump tubing will be lowered to the target sampling depth at the vertical midpoint of the screen point.
    c. The top of the tubing will be connected to the sample pump (e.g., peristaltic pump).
    d. Prior to activating the pump, a colocated near-bottom surface water quality reading and a deeper porewater water quality reading will be collected and used to assess whether a sufficient seal has been achieved to prevent surface water influences in the porewater sample, using the same methods stated above for the micro-push-point sampler.
    e. When a sufficient seal has been confirmed, the sampling pump will be activated at a low initial rate (less than 500 mL per minute).
        i. Samples for arsenic speciation will be collected directly from the sampling pump using the same methods stated above for the micro-push-point sampler.
        ii. Samples for other analyses will be collected directly into the sample bottles and capped immediately to minimize exposure to the atmosphere.
8. Label sample bottles and place in mylar bags with oxygen absorbers. Partially seal each bag, leaving a small hole for air to escape, roll down the top, slowly pushing as much air out of the bag as possible prior to sealing the bag. Place tape over the closed seal.
9. Place packaged samples inside of a cooler with ice for storage at the proper temperature (4°C to ± 2°C for all samples) and ship to the appropriate laboratory. Pack each container carefully to prevent breakage.

Quality Assurance/Quality Control

Entries in the field forms or field books will be double-checked by the field team staff to verify that the information is correct. Programming of transducers will be checked by one other field staff to ensure properly programmed. It is the responsibility of the field team leader to periodically check to ensure that the procedures are in conformance with those stated in this SOP.

As stated in Section 4.10.1 of the QAPP (Anchor QEA 2022), QA/QC samples, such as field duplicate samples, are generally used to evaluate the variability attributable to sample handling and processing. For porewater samples, a minimum of 1 duplicate sample for every 20 samples will be collected. Field duplicate samples will be analyzed for the same analytes as the parent sample. Field blank samples will be collected at a frequency of one per sampling event per media. Field blank samples will be analyzed for the entire analytical suite for the specified media type.

References

Anchor QEA, 2022. *Pre-Design Investigation Quality Assurance Project Plan for the Lower Duwamish Waterway Middle Reach*. October 2022.

Anchor QEA, 2025. *Quality Assurance Project Plan Addendum No. 3 For the Lower Duwamish Waterway Middle Reach – Phase III Sampling*. January 2026.

EPA (U.S. Environmental Protection Agency), 2001. *Methods for Collection, Storage and Manipulation of Sediments for Chemical and Toxicological Analyses: Technical Manual*. Office of Water (4305). EPA-823-B-01-002. October 2001.

List of Tables

List of Attachments

Table 1
Sample Handling and Storage

Table 1
Sample Handling and Storage

Parameter	Method	Reference	Laboratory	Container	Preservative	Sample Holding Time
Porewater Samples						
Conductivity	Resistor	EPA 120.1	Analytical Resources, LLC	YSI-brand	Cool <6°C	--[2]
pH	Resistor	EPA 150.1			Cool <6°C	--[3]
Sulfide	Colorimetric	SM 4500 S^{-2} D		125-mL HDPE	$ZnAc_2$ + NaOH, Cool <6°C	7 days
Metals (As, Fe, Mn)	ICP-MS	EPA 6020		250-mL HDPE	HNO_3, Cool <6°C	180 days
Arsenic speciation	ICP-MS	BAL 4100[1]	Brooks Applied Labs	50-mL glass vacutainer	Field filtered, 0.45-µm PES; EDTA; Cool to ≤6°C	28 days

Notes:

1. BAL provided the following summary of BAL 4100: An aliquot of the preserved sample is injected onto an anion-exchange column, which separates the target arsenic species. The column eluent is injected into a collision/reaction cell-equipped ICP-MS, where individual arsenic species are detected and quantified. QA/QC parameters are included in Table 1 of Phase III QAPP Appendix A.

2. If analysis is not completed within 24 hours of sample collection, sample should be filtered through a 0.45-µm filter and stored at 4°C. Filter and apparatus must be washed with high quality distilled water and pre-rinsed with sample before use.

3. The method does not state specific holding time but specifies analyte will be tested for as soon as practicable. Sample containers should be filled completely and kept sealed prior to analysis.

--: not applicable
µm: micrometer
As: arsenic
BAL: Brooks Applied Laboratory
EDTA: ethylenediaminetetraacetic acid
EPA: U.S. Environmental Protection Agency
Fe: iron
GC: gas chromatography
HDPE: high-density polyethylene
HNO_3: nitric acid
ICP-MS: inductively coupled plasma mass spectrometry
mL: milliliter
Mn: manganese
MS-SIM: mass
N/A: not applicable
NaOH: sodium hydroxide
PES: polyethersulfone
SM: Standard Method
$ZnAc_2$: zinc acetate

Attachment 1
Porewater Field Data Sheet

Porewater Retrieval Form

Project: _____

Field Program: _____

Staff: _____

Date: _____

Station ID	Coordinates		Retrieval Time	Sample Depth (cm)	Water Quality			Sampling Notes
	Easting	Northing			Temp. (°C)	pH (pH)	Conductivity (µS/cm)	

Standard Operating Procedure E38 – Seepage Measurement

Standard Operating Procedure Acknowledgement Form

Project Number: 210075-01.03 Project Name: Middle Reach of the Lower Duwamish Waterway

My signature below certifies that I have read and understand the procedures specified in this Standard Operating Procedure.

Date	Name (print)	Signature	Company

Purpose

The purpose of this Standard Operating Procedure (SOP) is to establish uniform procedures for the collection of vertical hydraulic gradient (VHG) and vertical hydraulic conductivity data.

This SOP describes the equipment, field procedures, materials, and documentation procedures necessary to perform the activities described in the previous paragraph. The details within this SOP should be used in conjunction with the *Quality Assurance Project Plan Addendum No. 3* (Anchor QEA 2025; QAPP) and other project-specific SOPs.

Scope and Application

This SOP is applicable to the collection of VHG and vertical hydraulic conductivity data. VHG data will be collected via installation of piezometers within the sediment bed. Piezometers will be equipped with pressure transducers and dataloggers and will be installed below the sediment surface. Vertical hydraulic conductivity data will be measured empirically using sediment cores collected within the study area as well.

Procedures outlined in this SOP are expected to be followed. Substantive deviations from the procedures detailed in this SOP will be recorded in the Daily Activity Log or field log book and on a Field Deviation Form, as well as reported to the project manager before implementation in the field.

Health and Safety Warnings

Health and safety issues for work associated with this SOP, including physical and chemical hazards, are addressed in the project Health and Safety Plan (HASP).

Staff Qualifications

Field staff executing these procedures will have read, be familiar with, and comply with the requirements of this SOP and all associated project planning documents, such as the QAPP, and other project-specific SOPs. Additionally, field staff will be under the direct supervision of qualified professionals who are experienced in performing the tasks required for sample collection.

Equipment and Supplies

The following equipment and documents may be necessary to carry out the procedures contained in this SOP. Additional equipment may be required, pending field conditions.

Vertical Hydraulic Conductivity and Vertical Hydraulic Gradient

- Approved project-specific documents, including the QAPP, HASP, and other project SOPs
- Appropriate personal protective equipment (PPE) and clothing as defined in the HASP
- Field laptop or tablet and/or paper field forms (as necessary)

- Decontamination equipment
- Spill kit and absorbent boom
- Standardized field log forms (field forms) printed on Rite in the Rain® paper
- Black ballpoint pen
- Sharpie permanent marker (or equivalent)
- Engineer's ruler or tape (at least 5 feet long)
- Duct tape
- Perforated core-tube caps
- Filter material (e.g., steel wool, glass wool, permeable geotextile, coffee-filter material, or the equivalent)
- Multiple measuring cups or containers with openings larger than 3 inches
- Plastic graduated cylinders with capacities ranging from approximately 10 to 50 milliliters (mL)
- Sampling vessel equipped with necessary GPS navigation and communication equipment
- Nominal 1- to 2-inch-diameter stainless steel well screen with water-tight couplings and 2-foot-long, 0.010-inch-slotted screen sections (the piezometer diameter will be selected based on the diameter of the transducers selected for the project)
- Preassembled VHG piezometer
- Pressure transducers
- Small-diameter wire with wire rope clips
- Underwater camera
- Vibracore head adaptor (rented from Gravity Marine)
- Submersible buoys
- Small air compressor capable of 100 pounds per square inch (psi) or greater

Seepage Direct Measurement with Seepage Rings

- Approved project-specific documents, including the QAPP, HASP, and other project SOPs
- Seepage rings
- Sled or similar clean, hard work surface for transporting and working with equipment in intertidal zone
- Standardized field log forms (field forms) printed on Rite in the Rain® paper
- Black or blue Rite in the Rain® pens, or similar
- Peristaltic pump
- Bulb baster or similar equipment
- Graduated cylinders from approximately 10 to 500 mL
- Transfer beakers
- Dedicated bottle for seepage collection, one per seepage ring

Vertical Hydraulic Conductivity Data Collection

Vertical hydraulic conductivity will be measured empirically using sediment cores collected from locations identified in the QAPP. The following procedures will be followed to collect sediment cores for empirical measurement of vertical hydraulic conductivity during the installation of the deeper VHG device at each VHG monitoring location:

1. Cores will be collected in 5-foot-long increments as outlined in SOP E19 – Subsurface Sediment Collection. For vertical hydraulic conductivity measurements, cores will be collected in Lexan tubes, and the upper 5 feet of the sediment bed will be collected as outlined in the QAPP. Cores will be collected continuously from the sediment surface to the final depth.
2. To minimize the influence of consolidation on the measured vertical hydraulic conductivity (Kv) values, no less than 80% recovery is required for Kv cores. Recovery rates for Kv cores will be documented and used to calculate an adjustment factor.
3. Once each core is collected and recovered, it will be capped and returned to a vertical position as quickly as possible.
4. Once capped and secured, each 5-foot-long core will be transferred in a vertical position to the processing area and maintained in a vertical position.
5. With the core secured in a vertical position, the vertical hydraulic conductivity will be measured empirically by collecting measured volumes of porewater that drain from the inside of the tube in a sequence of time increments, as described below. The core will be maintained in a vertical position throughout the measurement process.
6. The outside of the core tube will be wiped dry with a disposable towel so that the outside of the core is dry enough to clearly mark with an indelible pen.
7. The total length of the core tube will be measured and recorded to the nearest 0.01 foot.
8. Approximately 1-inch-long, horizontal lines will be marked on the tube using the indelible pen to indicate the sediment level (labeled "S") and the initial water level (labeled "W"), as viewed through the transparent Lexan tube.
    a. If no overlying water is observed, contact project team for direction on core re-saturation.
9. The recovered sediment length and the total height of water above the bottom of the tube (or the distance of the water level down from the top of the tube) will be measured to the nearest 0.01 foot and recorded, along with the core sample designation, on the Vertical Hydraulic Conductivity Field Test Data Sheet form (Attachment 1). If the water level is not visible (within the sediment), that will be noted as "water level not visible."
10. Remove the bottom cap on the core tube and quickly replace it with a tight-fitting, perforated cap lined with a fine filter material (e.g., geotextile, steel wool, glass wool, coffee-filter material, or similar). The bottom cap will be the punctured to produce 10 holes approximately 1/8-inch in diameter using a 1/8-inch punch or a Phillips head screwdriver. If any sediment comes out of the bottom of the tube with the removed initial bottom cap, that sediment will be transferred into

the perforated cap above the filter material before placing the perforated bottom cap on the tube. The perforated cap will then be secured with one or more pieces of duct tape, which will not interfere with the perforations in the cap.

11. The top cap will then be removed from the tube or punctured, allowing the core sample to drain freely under the force of gravity. The tube will be watched until water is visibly flowing or dripping out of the perforated bottom cap.
12. After draining water is observed, an empty measuring cup or other suitable container will be placed beneath the bottom of the dripping core tube to collect the water that drains from the inside of the core, and the clock time will immediately be noted and recorded to the nearest second (HH:MM:SS) on the Vertical Hydraulic Conductivity Field Test Data Sheet form (Attachment 1)—on the same row in the "Notes" column, the words "Start Test" will be written.
13. After approximately 1 minute, the container will be replaced with another empty container to continue collecting the water that drips from the core, and the clock time will immediately be noted and recorded to the nearest second (HH:MM:SS) on the next row of the data sheet. In replacing one container with the next, care will be taken to collect all of the water that drips from the core, to the extent practicable. The water collected in the newly removed container will be carefully transferred into a graduated cylinder, and the collected volume of water will be measured to the nearest 0.1 mL; this volume will be recorded on the same line of the data sheet as the clock time when that volume increment stopped being collected from the draining vertical core. The measured volume of water will then be poured into a final, sealable container that will be used to verify the cumulative volume of water drained during the test.
14. Repeat Step 12, approximately every 2 minutes up to a total of 10 minutes, then every 5 minutes for an hour to collect and measure the volume and timing of multiple discrete increments of porewater that drain from the core. Continue collecting and recording volume increments and times until a cumulative volume of at least 20 mL of water has been measured. After measuring and recording the volume of each increment, the water will then be poured into the same final container that will be used to verify the cumulative volume of water drained during the test. If a total of 100 mL of water has been collected before 1 hour of testing, the test can be considered complete.
15. During testing, a small quantity of porewater will be allowed to freely drain from the core by gravity, through a perforated bottom cap. The actual total drainage volume and associated test duration will depend on the vertical hydraulic conductivity of the core.
16. The duct tape and perforated bottom cap will be removed and replaced with a standard tube cap, and the clock time will immediately be noted and recorded to the nearest second (HH:MM:SS) on the next row of the data sheet. The water collected in the final container will be carefully transferred into a graduated cylinder, and the collected volume of water will be measured to the nearest 0.1 mL; this final volume increment will be recorded on the data sheet.

The measured final increment of water will then be poured into the same final container for the test, which will be used to verify the cumulative volume of water drained during the test.

17. The top cap will be replaced. Both caps will be secured with duct tape.
18. An approximately 1-inch-long, horizontal line will be marked on the tube using the indelible pen to indicate the final water level (labeled "WF"), as viewed through the transparent Lexan tube. The final height of water above the bottom of the tube (or the distance of the water level down from the top of the tube) will be measured to the nearest 0.01 foot and recorded.
19. The tube will be photographed in a vertical position clearly showing the marked and labeled horizontal lines and an engineer's ruler or tape held or affixed to the outside of the tube.
20. The total cumulative volume of water will be transferred into a graduated cylinder, measured to the nearest 0.1 mL, and recorded near the bottom of the data sheet with the words "Final Total Volume."
21. After the test is completed, the data sheet will be photographed and retained in the project records; the core will then be processed for other purposes, as outlined in SOP E19 – Subsurface Sediment Collection.

Vertical Hydraulic Gradient Device Installation and Retrieval

VHG devices will be deployed for 6 weeks to capture water levels that will be used to calculate seepage rates over a range of tidal conditions. The VHG devices will consist of a piezometer constructed of stainless steel pipe and equipped with sealed pressure transducers (e.g., Solinst Levelogger or similar). To install each VHG device, the following procedures will be followed.

Horizontal Positioning Procedures

1. Coordinates for each sampling location will be entered as a waypoint into the GPS unit.
2. The GPS antennae will be maintained in a safe location that accurately represents the actual sample or measurement collection point (e.g., mounted to the top of the vibracore), or handheld units will be placed above or near the vessel sampling moon hole.
3. Using navigational data from the GPS, the vessel operator will navigate to and approach the actual sampling/measurement location.
4. For sediment sampling, the vessel will be secured within 15 feet of the sampling location by lowering spud poles or securely anchoring.
5. Once the vessel is on location (and secured for sediment sampling), the coordinates from the GPS unit will be noted and stored electronically in the GPS unit.
6. For repeated attempts at a sampling location, the vessel will be moved within the radius of 15 or fewer feet from the target coordinates. The new position for each attempt (as necessary) will be recorded on the appropriate field form and stored electronically.

7. For the VHG piezometer, use an underwater camera to photograph the location and verify that limited debris is in the proposed location. Move VHG locations as necessary to avoid debris; the GPS coordinates will be re-collected and stored.

Vertical Elevation Measurement Procedures

1. At each sampling location, the water depth (from the top of the water level surface to the top of the sediment surface) will be determined using a calibrated weighted line, tape measure, or an electronic depth measurement device/sounder.
2. The date and time of the measurement will be recorded on the appropriate field form.
3. Water depth and tidal elevation (i.e., raw data), as well as the calculated mudline elevation of each location relative to mean lower low water, will be recorded on the appropriate field form.

Prior to installing the VHG device, complete the necessary sediment sampling activities as outlined in the QAPP.

Vertical Hydraulic Gradient Piezometer Installation Procedures

The VHG piezometers will be installed using the following procedures:

1. Safety checks will be made, including arranging all winch cables and checking for kinks or burrs, checking the sampling vessel for fluid leaks, and checking that all "kill" switches are operational.
2. Install sealed pressure transducers in the preassembled VHG piezometer provided by Gravity Marine (see Figure 1):
    a. Sealed pressure transducers with a pressure rating of 30 to 50 PSI and sufficient internal memory and battery power to record/store data for the collection duration (6 to 8 months) will be deployed. The transducers will be pre-programmed (following manufacturer's guidelines) to collect data every 5 minutes at appropriate calendar dates and clock times and synchronized so that both transducers record readings simultaneously. The start of data collection will be noted.
    b. Install the transducers using wiring attached from the top of the piezometer so they fall within the screened portions of the set-up, ensuring the correct transducers are installed at the top and the bottom.
    c. Measure and record the distance of each of the pressure transducers from the top of the piezometer.
    d. Check and verify VHG piezometer components are tightly secured.
3. Attach the rope to the VHG piezometer for future retrieval.
    a. Option A:
        i. The length of rope should be determined and cut based on submerging the buoy about 4 feet below the water surface, based on a low tide.

ii. The rope should be of sufficient strength to pull the piezometer from the sediments.
iii. Tie the rope to the buoy.
iv. Tie a loop of coated cable under the buoy at the same knot as the connection to the buoy to allow for future hook-up with the gaffer hook/rake.
v. Tie the rope to the VHG piezometer using the attachment point provided by Gravity Marine.
vi. Tie a small fishing bobber on fishing line to the top of the buoy to ease future retrieval.

b. Option B:
i. An anchor will be placed near, and attached to, the VHG Piezometer.
ii. The length of rope should be determined and cut based on attaching it to an anchor or a time release buoy system.

c. Option C:
i. For deployments near an overwater structure, or the shoreline, a tagline can be attached to a nearby piling or other structure to help locate the VHG Piezometer during retrieval.
ii. The length of rope should be determined and cut based on attaching to a nearby structure or shoreline.

4. Attach the prefabricated VHG piezometer to the vibracore head using the vibracore head adaptor provided by Gravity Marine and the pneumatic attachment.
5. Lower the VHG piezometer, rope, and buoy at the proposed location through the water column to a set water depth of about 5 feet from the mudline.
6. Allow the unit to rest at about 5 feet above the mudline and collect data for a period of at least 60 minutes. The data collected during this period will represent "zero-gradient" data, which will later be used to calculate the head difference associated with the VHG, as discussed in the Data Usability section below.
7. Following 60 minutes of zero-gradient data collection, note the date and time.
8. Lower the apparatus through the water column to the sediment surface.
9. Advance the piezometer through the sediment until the piezometer's flange is flush with the sediment surface. Total penetration should be about 5 feet below the sediment surface. Advance the piezometer using vibration sparingly and the weight of the unit as much as practicable.
10. Use an underwater camera to photograph and document VHG installation and final penetration.
11. Detach the VHG piezometer from the vibracore head using the pneumatic release.
12. Lift the vibracore head up through the water column, leaving the VHG piezometer deployed.

Vertical Hydraulic Gradient Retrieval

The following procedures will be used to perform another zero-gradient data collection and retrieve the VHG device. To retrieve the VHG device, the following procedures will be followed:

1. Maneuver a support vessel into position based on GPS coordinates of the VHG device and securely anchor.
2. Use a rake or hook to connect to the submerged buoy, anchor, anchor line, or tag line.
3. The support vessel will lift the VHG piezometer out of the sediment using a winch about 5 feet from the mudline. Once the VHG piezometer is lifted, the VHG piezometer borehole will be considered abandoned because it will likely collapse.
4. Allow the VHG device to hang in place and collect data for a period of at least 60 minutes. The data collected during this period will represent "zero-gradient" data, which will later be used to calculate the head difference associated with the VHG.
5. Each pressure transducer will be connected to a computer or tablet, and the data will be downloaded, stored, and checked to ensure the transducer is functioning properly.
   After collection, the VHG devices will be decontaminated for reuse and removed from the site.

Seepage Direct Measurement with Seepage Ring

Given the various challenges associated with seepage meter operation in the intertidal zone, an empirical seepage measurement is proposed (i.e., "seepage ring"). Seepage data will be collected at the top of the exposed sediment utilizing a seepage collection ring, similar to a standard seepage meter (55-gallon drum) but with no top, partially inserted into the top of sediment. Water discharging upward across the sediment surface within the ring will be contained and collected to provide an empirical measurement of the seepage at relatively low tide conditions, when the intertidal zone is subaerial.

The volume of porewater discharging upward at the mudline is expected to change with tidal fluctuations, with the highest discharge rate occurring around low tide due to the higher VHG between groundwater and the surface water. Thus, measurements during low tide should provide upper bound discharge rates in the study area. The empirical seepage measurement method will be conducted starting during the falling stage of the tidal cycle and will continue through low tide to the early portion of the rising stage of the tidal cycle.

Seepage Measurement Procedures

Seepage rings will be fashioned from 55-gallon drums by cutting off the bottom of the drum and segmenting into thirds. Seepage ring dimensions will be documented on field forms prior to data collection. A flat-bottomed sled for transporting equipment and data collection in the intertidal zone during seepage measurements. Similarly, field personnel deploying and monitoring the seepage rings will avoid disturbing the area near the rings by minimizing activity near the rings, stepping

gently when moving around the seepage rings, and when feasible, working from a piece of plywood[1], to distribute and minimize the impact of their weight on the sediment.

Prior to empirical seepage measurement, the intertidal zone of the offshore area will be observed at low tide for signs of visible porewater discharge. If water is observed to be discharging from the sediment, then a designated seepage measurement point may be adjusted by up to 30 feet in the field to coincide with this location. GPS coordination for the final locations will be recorded on the field. Seepage rings will not be installed in standing water or in places where the seepage ring intersects a puddle. If no visibly active discharge is observed, the seepage measurement rings will be installed at the approximate locations shown on the project-specific QAPP.

1. As the tide falls, equipment will be prepared. Each seepage ring will be monitored continuously by field personnel during data collection.
2. Each seepage ring will be installed a minimum of 2 hours before low tide and data will be collected for at least 4 hours. The rings will be inserted until the bottom edge of the ring is a few inches below the sediment surface to ensure that the ring stays in place and stable during data collection. Any standing water that accumulates within the seepage ring during installation will be evacuated prior to the beginning of seepage data collection. The installation location will be documented on the field form.
3. Once the standing water has been evacuated, seepage data collection will begin and the start time will be noted. The water level within the seepage ring will be monitored frequently (approximately every 5 minutes). Any visible accumulation of water within the ring will be removed approximately every 15 minutes using a peristaltic pump. For areas with suspected low seepage rates, a bulb baster or similar equipment may be used in place of a peristaltic pump. For areas with higher observed seepage rates, more frequent sampling may be required to prevent accumulation of water greater than 2 inches in height. If more than 2 inches of water accumulates in the ring it will be documented on field forms and data collected during that time will be potentially excluded from the net seepage calculation after consideration of conditions.
4. The pumped volume of water will be measured using a graduated cylinder, and the volume will be recorded in the field notebook, along with the time of collection.
5. The pumped water will be decanted into a dedicated, labeled bottle (one per seepage ring location). This mode of seepage collection will continue for at least 4 hours, encompassing the low point of the tide.
6. At the completion of data collection, the seepage measurement ring will be removed, and the total volume of water collected at each seepage ring location will be measured using a graduated cylinder and recorded. (The total volume measured at the end of sampling will equal the sum of the water measured at each interval during sampling.)

[1] The plywood will be modified to include non-slip surface strips and will be secured to prevent horizontal movement using steel corner-edging stakes.

7. The successive volume measurements will be used to calculate the temporally variable seepage rate, and the final measurement will be used to calculate the average seepage rate for each seepage ring location.
8. At termination of the test, collect an approximate 0-6-inch sediment sample for geotechnical properties testing (i.e., grain size with hydrometer, Atterberg limits, moisture content and specific gravity) from each seepage ring area. Refer to Middle Reach Phase I PDI QAPP Table 5-1 for analytical methods and sample handling requirements.

Throughout the period of seepage measurements, continuous water level data will be collected using pressure transducers at an approximately co-located piezometer (i.e., the VHG). This will allow the discharge rate measured by the seepage ring to be compared with VHG data. Tidal elevation data will also be recorded on 10-minute intervals from a tide gauge located in the middle reach.

Data Usability

Vertical Hydraulic Conductivity

Using the data collected during each vertical hydraulic conductivity (K_v) test, the K_v of the tested sediment interval will be calculated as follows using a form of Darcy's Law:

Equation 1

$$K_v = Q/(A\ i_v)$$

where:

Kv	=	vertical hydraulic conductivity of test sample
Q	=	average flow rate during period of approximately constant flow
A	=	circular area of the bottom of the cylindrical core sample
i_v	=	VHG through the test sample

Recovery rates for Kv cores are be documented during collection and will be used to calculate an adjustment factor. For example, assuming an average sediment void ratio of 1.7 (porosity of 0.63) and a recovery of 90%, the multiplier would be 2.0. This means if a sample has 90% recovery, with 10% volume reduction of the whole core sample, we can multiply the measured Kv value by 2.0 to estimate what the K value would have been if the sample had undergone no consolidation at all (i.e., if the recovery had been 100%). Given that hydraulic conductivity values range by multiple orders of magnitude, that is a very small adjustment.

The VHG during the test will be calculated as follows:

Equation 2

$i_v = dH/dL$

where:

dH = head change between the top and the bottom of the saturated sediment sample

dL = vertical length of the saturated sediment sample

dH is equal to the height of the water level within the liner, measured from the bottom of the sediment sample. If the water level is within the sediment sample (i.e., not visible above the sample), dH and dL are equal and, therefore, i_v equals 1.

Vertical Hydraulic Gradient

The hydraulic head recorded in the transducers will be used to calculate a continuous record of the VHG (i_v) for each VHG location as follows:

Equation 3

$i_v = (dH - dH_c)/dZ$

where:

iv = vertical hydraulic gradient (calculated every five minutes) [L/L]

dH = head difference measured between deep and shallow transducer [L]

dHc = calibrated zero-gradient head difference [L]

dZ = vertical separation between the midpoints of the two screens if the upper screen is within the sediment, or the distance from the mudline to the midpoint of the deep screen

dH_c is the head difference measured between the piezometer and the lake, with the piezometer cap loosened so that both measurements are directly hydraulically connected to the lake.

Quality Assurance/Quality Control

Entries in the field forms or field books will be double-checked by the field team staff to verify that the information is correct. Programming of transducers will be checked by one other field staff to ensure they are properly programmed. It is the responsibility of the field team leader to periodically check to ensure that the procedures are in conformance with those stated in this SOP.

Reference

Anchor QEA, 2025. *Quality Assurance Project Plan Addendum No. 3 For the Lower Duwamish Waterway Middle Reach – Phase III Sampling*. January 2026.

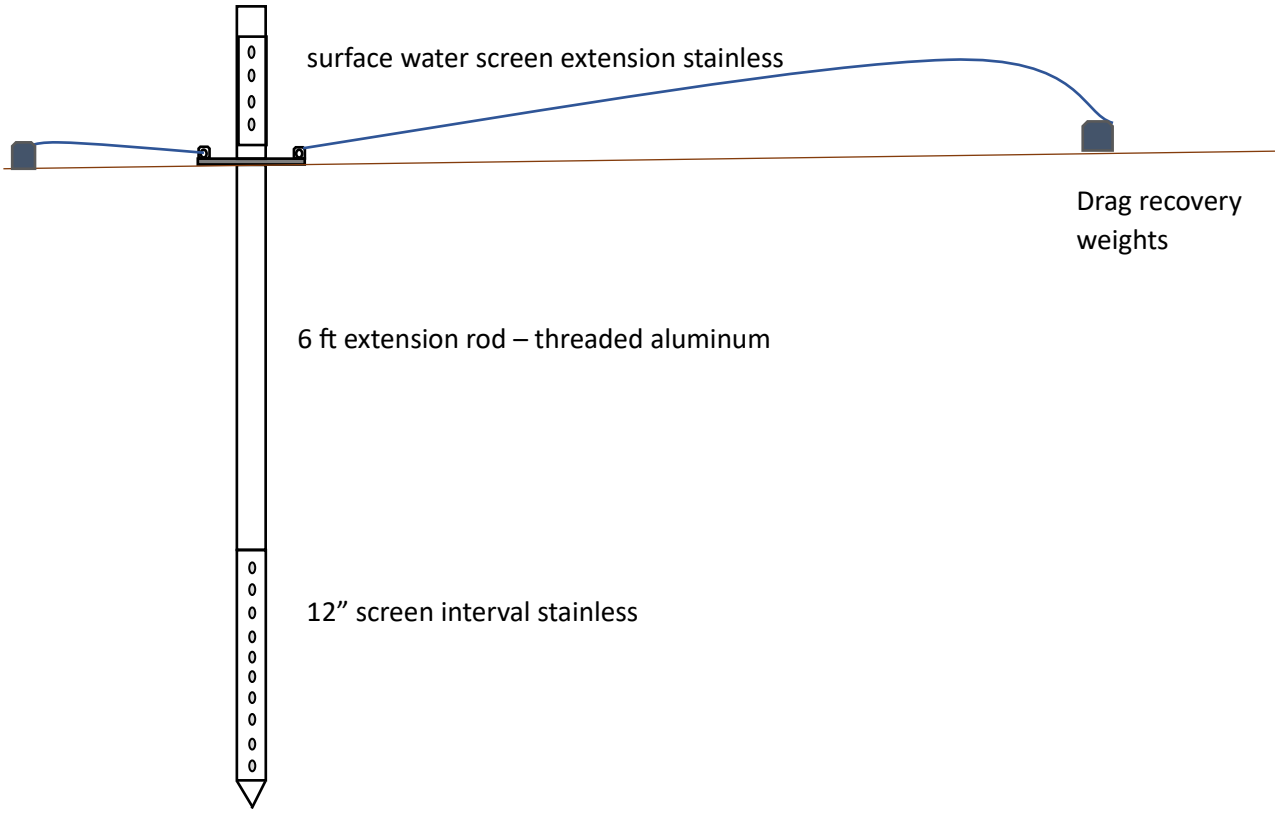
List of Figures

List of Attachments

Figure 1
Gravity Marine VHG Piezometer

Gravity Marine Piezometer

Vibracorer for driving points



Attachment 1
Vertical Hydraulic Conductivity Field Test Data Sheet

Vertical Hydraulic Conductivity Field Test
Data Sheet

Core ID = _____
Sample Depth Interval (feet) = _____ (to nearest 0.1 foot)
Pre-Test Sediment Sample Length (feet) = _____ (to nearest 0.1 foot)
Post-Test Sediment Sample Length (feet) = _____ (to nearest 0.1 inch or 0.01 foot)
Total Core Liner Length = _____ (to nearest 0.1 inch or 0.01 foot)
Core Diameter = _____ (to nearest 0.1 inch or 0.01 foot)
Water-Level Reference Point = _____ ("Top of Liner" or "Bottom of Liner")

Date	Cumulative Time (HH:MM:SS)	Water Level (feet)*	Pore Water Collected (ml)**		Notes
			Discrete	Cumulative	

Attachment 2
Seepage Ring Deployment Form

Seepage Ring Deployment Form

Project: _____

Field Program: _____

Staff: _____

Date: _____

Ring Diameter: _____

Station ID	Coordinates		Deployment Time	Water Depth (m)	Deployment Depth (cm)	Sampling Notes
	Easting	Northing				

Attachment 3
Seepage Measurement Form

Seepage Measurement Form

Project: _____ Station ID: _____

Field Program: _____ Tube Diameter: _____

Staff: _____ Purge Start Time: _____

Date: _____ Water Measurement Method _____

Easting: _____ Northing: _____

Measurement No.	Time	Water-Level Measurement (cm)	Estimated Water Volume (mL)	Tide Flow (flood, slack, or ebb)	Notes
1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
11					
12					
13					
14					
15					
16					
17					
18					
19					
20					
21					
22					
23					
24					
25					

Analytical Resources, LLC
Analytical Chemists and Consultants

Standard Operating Procedure

Conductivity
(Specific Conductance at 25 ºC)

SOP 611S
Version 6.1

Revision Date: 12/22/2025
Effective Date: 8/21/24

Prepared by:

Mike Perkins

Approvals:

Casey English, Laboratory Supervisor

Eric Larson, Inorganics Division Manager

Annual Review

SOP Number: 611S

Title: Conductivity (Specific Conductance at 25 ºC)

The ARLLC employee named below certifies that this SOP is accurate, complete and requires no revisions

Name	Reviewer's Signature	Date

Standard Operating Procedure
Conductivity (Specific Conductance at 25 ºC)

1. Scope and Application

1.1. This method is applicable for the determination of conductivity in drinking, surface and saline waters, domestic and industrial wastes. The procedure presented here is based upon those given in EPA 120.1, SW-846 9050A and Standard Methods 2510 B-11 as they relate to the specifics of the meter and conductivity probe being used.

1.2. Conductivity is an expression of the ability of water to conduct an electric current. This ability is dependant upon the concentration of inorganic ions (salts or electrolytes) in solution and hence conductivity is also an estimate of the concentration of total dissolved solids (TDS) or salinity.

1.3. The method can also be applied to soils by extraction with DI water and measuring the conductivity of the extract. This forms a basis for defining soil salinity. Salinity is usually defined for the analysis of a “saturation paste” extract but other soil: water extraction ratios (e.g. 1:1, 1:5) are easier to perform and can also provide useful information (Methods of Soil Analysis).

2. Summary of the Procedure

2.1. Conductivity is determined by inserting a calibrated conductivity probe into an aqueous solution or extract, applying a voltage (V) and measuring the resulting electrical current (I) between fixed electrodes on the probe. Resistance (R in Ohms) is determined from Ohms Law describing the relationship between voltage, current and resistance (R = I / V). Conductance is the reciprocal of resistance.

2.2. Conductivity is the conductance times a determined “cell constant” for the electrode configuration used and is reported in units of “mhos” or Siemens per centimeter. Due to scale, units are usually expressed as either micromhos (µmhos) or microSiemens (µS) per centimeter. Siemens is the accepted international unit and will be used in this SOP with the understanding that mhos and Siemens are equivalent.

2.3. Conductivity is strongly dependent upon temperature and results must be reported equivalent to a standardized temperature of 25 ºC. Measurement should be made at a temperature close to 25 ºC (77 ºF) or room temperature. Conductivity and temperature are read directly with a conductivity probe (Orion 011510) and meter (Orion 115) that yields units automatically compensated and normalized to a temperature of 25 ºC.

2.4. Standardization of the meter is done by measurement of a standard potassium chloride solution (0.0100 N) that has a theoretical conductivity of 1413 µS/cm at 25 ºC.

3. Detection Limit

3.1. The Orion 115 meter can read conductivity to tenths of a µS but the reporting limit is set at 1.0

µS/cm. The recommended application range for the probe (Orion model 011510) is 10 µS/cm to 200 mS/cm. However, measurements using this probe are fairly precise at low levels (< 15 µS/cm) with an MDL of 0.25 µS/cm and a relative standard deviation (RSD) of 0.8%.

4. Definitions

4.1. Conductance - The reciprocal of resistance (in ohms) between opposing faces of a 1 cm cube of water at a specified temperature (typically 25 ºC). Since conductance is the reciprocal of resistance, the traditional units of conductance were the reciprocal of ohms or "mhos". The standard unit is now Siemens (S).

4.2. Cell constant (K) - Conductance depends upon electrode geometry (area and distance between plates) and for fixed electrodes, these define the cell constant (K = distance / Area = cm-1). Conductivity is the product of the conductance (S) times the cell constant (cm-1) which yields the unit of S/cm. The cell constant can vary relative to features such as polarization and/or fouling of the electrode surfaces and must be determined for each set of measurements. Determining the cell constant represents the process of calibration.

4.3. International System of Units (SI) - The unit of conductance in the international system is the Siemen. Conductivity then is reported as millisiemens / meter (mS/m) where 1mS / m = 10 µS/cm = 10µmho/cm. More generally, 1µS/cm = 1 µmho/cm. To report in SI units, divide µmho / cm or µS / cm by 10.

4.4. Calibration - Two modes of calibration are possible on the Orion 115, "DirectCal" and "Cell Constant Adjustment". Both have to do with setting the cell constant (K) relative to a standard of known conductivity (0.01 N KCl = 1413 µS/cm @ 25 ºC) at the temperature of measurement. The difference between the two approaches is that under DirectCal the temperature corrected conductivity value is entered and the meter determines the cell constant while under "Cell Constant Adjustment", the cell constant is manually adjusted to read the correct conductivity value for the temperature of measurement. Orion indicates that there is no difference in the final result, the determination of K, using either approach. DirectCal requires fewer instrument operations, is easier to conduct and is the procedure of choice.

4.5. An analytical batch will consist of a maximum of 20 client samples. Each batch will have an independent initial calibration followed by initial and continuing calibration verification standards and blanks. Dependant upon client request, each batch will have at least one client sample run in duplicate.

4.6. Analysis of TDS by conductivity is only a rough approximation since conductivity measures only ionized constituents. Non-ionized constituents (e.g. non-polar organics, colloidal particulates, microbes) are not detected but can contribute to the TDS load. Conductivity in µS/cm is multiplied

by a conversion factor which may range from 0.55 - 0.80 with a routine standard factor of approximately 0.66.

4.7. Salt concentration (mg/L) in a soil extract is roughly related to conductivity by multiplying the measured conductivity (µS / cm X 0.001 = mS / cm or dS / m) by 640. Other useful relationships are shown in the table below (derived from U.S. Soil Salinity Laboratory Staff, 1954, U.S. Dept Agriculture Handbook No. 956).

Conductivity of Saturation extract (mS/cm)	Total Salt Content (%)	Classification
< 2	< 0.1	Nonsaline
2 - 4	0.1 - 0.15	slightly saline
4 - 8	0.15 - 0.35	moderately saline
8 - 16	0.35 - 0.70	very saline
> 16	> 0.70	extremely saline

5. Interferences

5.1. Temperature variation is the largest source of error (1-3% per degree centigrade) in the determination. The Orion probe and meter provide temperature compensation and correction to a selected temperature of either 20 or 25 ºC.

5.2. Highly saline solutions (greater than 100 mS) can result in underestimation of conductivity due to impedance of ion movement and fouling of electrode surfaces. Conductivity probes with a 4 cell electrode configuration and larger cell constants can be used for determination in highly saline solutions.

5.3. Deposits can form on the surface of the electrodes and lead to underestimation of conductivity. Samples should be gently shaken during measurement to avoid localized deposition and the electrodes should be rinsed with DI water between measurements. Minor electrode fouling is compensated for during calibration.

5.4. Very low conductivity solutions (<15 µS/cm) can be influenced by absorption of atmospheric carbon dioxide leading to over estimation of conductivity. Avoid extended measurement time for low conductivity solutions.

5.5. Measurement container edges can contribute to “fringe field effects” and influence conductivity values. During measurement, place the probe into the center of the container as far as possible from the edges.

6. Safety

6.1. NOTE: ALWAYS WEAR PROPER EYE PROTECTION IN THE LABORATORY!

6.2. Gloves and lab coats should be worn when handling samples, spike solutions, acids, bases and other reagents.

6.3. All the non-hazardous wastewater can be dumped into sink if its pH range is 10 - 5. If it is not, the wastewater has to be neutralized before dumping. Review the Laboratory Safety Manual and the Contingency Plans and Emergency Procedures for a Hazardous Waste Generator.

6.4. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available.

6.5. A reference file of material data handling sheets is kept in the office area, across from the entrance to the tech room (room A316J). Refer to this file for any material you handle. Update this file upon receiving new chemicals or reagents. The MSDS for many chemicals can also be viewed online, at http://hazard.com/MSDS/

6.6. Dispose of all unwanted, broken glassware into a broken glassware disposal box. Inspect every piece of glassware. Do not use any that are chipped, cracked, etched, or scratched. Glassware with minor damage should be stored for repair.

7. Equipment and Supplies

7.1. Orion Model 115 Conductivity meter (temperature compensating).

7.2. Orion Model 011510 Conductivity probe, 2 cell epoxy graphite electrode with built in temperature sensor and a cell constant K = 1.0 cm-1, application range of 10 µS to 200 mS is recommended.

7.3. Glass or plastic measurement container (e.g. 100 mL beaker) to fit conductivity probe, allow sample circulation and full immersion of the electrodes and temperature sensor. Avoid using tightly constraining containers that could contribute edge effects to the conductivity determination.

8. Reagents and Standards

8.1. De-ionized Water - Type I water is defined as a water having a specific conductance <0.1 µmho/cm (or a resistivity >10 megohm, Standard Methods 1080, Page 1-32) which should be satisfied by proper maintenance of our deionized water system. In practice, our DI water quality varies between Type I and Type II. Most laboratory waters run from 0.5 to 3 µS/cm. Conductivity will increase upon storage of the water (air contact and dissolution of materials from the container wall) hence, use only freshly delivered water for preparation of conductivity standards and calibration blank analysis.

8.2. Potassium Chloride Calibration Standard (0.0100 N KCl) - Dissolve 745.6 mg anhydrous KCl (dried at 105 ºC) in fresh DI water and dilute to 1,000 mL. This solution has a conductivity of 1413

µS/cm at 25 ºC and should be used for primary calibration of the conductivity meter. Store the standard in a tightly closed container to avoid evaporation. Prepare fresh standard every 6 months. An NIST traceable 1413 µS Calibration Standard is also available from Fisher Scientific (09-328-11).

8.3. Calibration Verification Standard (CVS) - This standard should be derived from a solution other than that used for primary calibration. The standard should be an NIST Traceable Conductivity Standard (e.g. Fisher No.09-328-3 or VWR No 23226-625) certified at a temperature of 25 ºC. The CVS is usually composed of KCl and again would have a shelf life of 6 months.

9. Sample Collection, Preservation, Shipment and Storage

9.1. Samples can be collected in either polyethylene or glass containers.

9.2. No preservative is required but samples should be kept cold (4 ºC) during shipment and storage.

9.3. EPA Method 120.1 specifies that analysis should be completed within 24 hours. If not completed within 24 hours, the sample should be filtered (0.45 µm) and conductivity determined within 28 days of collection. Neither Standard Methods Manual nor SW-846 Method 9050A include this stipulation. According to EPA (James O'Dell , Office of Drinking Water) this requirement no longer applies and has been superseded by requirements promulgated in 40 CFR 136.6, i.e. analysis within 28 days without filtration.

10. Quality Control

10.1. Initial calibration will be verified by the analysis of an Initial Calibration Blank (ICB) and a second source Initial Calibration Verification (ICV) standard. The ICB will be fresh DI water. The ICV standard will be a commercially prepared solution certified for conductivity at 25 ºC.

10.2. Continuing calibration verification standards (CCV's) and blanks (CCB's) will be run after every ten samples analyzed. The CCV will be the same standard as the ICV.

10.3. Every batch of 20 or less samples will have at least one client sample run in duplicate. The frequency of duplication will depend upon client request.

10.4. For instrument ID's, equipment manufacturers, model numbers, venders and brands used, refer to QAPP available in the QA office.

11. Calibration and Standardization

11.1. Two modes of calibration are possible on the Orion 115, "DirectCal" and "Cell Constant Adjustment". Use the DirectCal approach for routine calibration and the "Cell Constant Adjustment" approach only if difficulties are encountered with the DirectCal approach.

11.2. Open the conductivity benchsheet (ARLLC 6019 CONDrev.xlt) and enter the date and time.

11.3. Calibration will be conducted using the 1413 Conductivity Standard (prepared 0.01 N KCl or a

commercially prepared 1413 standard). The standard should be at or near the reference temperature of 25 ºC but room temperature is fine.

11.4. DirectCal Standardization

11.4.1. Press the **CAL** key twice. The "**CALIBRATE**" indicator, "**199.9 µS**" and "**Temp**" should appear in the display.

11.4.2. Select the appropriate calibration range for the 1413 standard by repeatedly pressing the **CAL** key until the range displays "**1999 µS**" (this is the range for the 1413 standard).

11.4.3. Insert the probe into the standard and gently agitate to remove any air bubbles. The "**READY**" indicator will be displayed when a stable reading is attained. Note the temperature of measurement and record it in the Cal Temp (ºC) cell of the benchsheet.

11.4.4. Using the recorded temperature, the corrected conductivity value (µS) for the 1413 standard will be selected from the list of values on the benchsheet. The benchsheet covers a temperature range of 13 to 27 ºC (If the temperature is outside this range, determine the value from the Table on page 8 of the operating manual).

11.4.5. Enter the temperature corrected value into the Orion meter by scrolling with **UP** or **DOWN** arrows for each digit. When the correct value for each digit is displayed, accept it by pressing the **YES** key.

11.4.6. After the last digit has been accepted, the word "**CALIBRATE**" should flash and the display should go blank while the meter calibrates.

11.4.7. The display will briefly show the new constant and then return to the measurement mode. Record the new cell constant when it appears.

11.4.8. Remove the probe from the 1413 standard, rinse thoroughly with de-ionized water and then proceed with calibration verification

11.5. Cell Constant Adjustment

11.5.1. Use this procedure only if problems are encountered with the DirectCal approach.

11.5.2. Temperature compensation must be turned off in order to use the cell constant adjustment procedure. Remember to turn temperature compensation back on before resuming routine measurement. To turn off temperature compensation:

11.5.2.1. Press the **SETUP** button once on the meter Keypad.

11.5.2.2. The display should read "**S-1**" with "**2.1% /ºC**" at the bottom.

11.5.2.3. Use the **DOWN** arrow key to change the percent value to "**0.0% /ºC**".

11.5.2.4. Accept the change to 0% by pressing the **YES** key

11.5.2.5. Return to measurement mode by pressing the **MODE** key

11.5.3. Press the **CAL** key once to begin calibration. The "**CALIBRATE**" indicator and the value of the last cell constant should appear in the display. Record the last cell constant into the

"Current Value" cell of the benchsheet

11.5.4. Insert the probe into the standard and gently agitate to remove any air bubbles. Accept the current value for the cell constant by pressing the **YES** key until the meter automatically returns to the measurement mode (repeated pressing of the **YES** key cycles through decimal placement and digit scrolling).

11.5.5. The "**READY**" indicator will be displayed when a stable reading is attained. Note the temperature of measurement and record it on the benchsheet in the "Cal Temp (ºC)" cell of the benchsheet. The temperature corrected value for the 1413 standard will be selected from the list of conductivity values and automatically entered into the "Expected" cell of the benchsheet. If the temperature is outside the range of 13 to 27 ºC, determine the value from the Table on page 8 of the operating manual and then manually enter the "Expected" value.

11.5.6. Enter the displayed value into the "Displayed" cell of the benchsheet.

11.5.7. The benchsheet will automatically calculate the percent error associated with the displayed conductivity value and an adjusted value for the cell constant (the value appearing in the "Adjust to" cell of the benchsheet). If the error is less than 1%, the "Adjust to" cell will read "OK as is". Restore temperature compensation and proceed with calibration verification.

11.5.8. If the error is greater than 1%, enter the "Adjust to" value for the new cell constant as follows:

11.5.8.1. Press the **CAL** key once to display the current cell constant.

11.5.8.2. Scroll through the digits using the **YES** key.

11.5.8.3. Change each digit to match the "adjust to" value using the **UP** and **DOWN** arrows.

11.5.8.4. Accept each digit by pressing the **YES** key. The meter will return to the measurement mode after the last digit has been accepted.

11.5.9. Restore the temperature compensation to 2.1% / ºC by pressing the **SETUP** key once to get to the "**S-1**" display and adjusting the % value to 2.1 with the **up** arrow key. Press **YES** to accept the change and **MODE** to return to measurement. Proceed with calibration verification.

11.6. Calibration Verification

11.6.1. Remove the probe from the 1413 standard and rinse thoroughly with de-ionized water.

11.6.2. Verify that the meter is in the measurement mode for conductivity.

11.6.3. Determine conductivity values for the de-ionized water blank and the Calibration Verification Standard.

11.6.4. Record values onto the benchsheet and verify a blank < 1 µS and verification standard recovery within 10% of the known value.

12. Procedure

12.1. Remove samples from refrigerator and allow them to warm to room temperature (preferably 25 ºC).

12.2. Proceed with Instrument calibration using the 1413 µS/cm calibration standard and the DirectCal approach. Proceed with samples only if verification is successful.

12.3. Pour a 50 to 100 mL aliquot of sample into a suitable measuring container that will allow free circulation of the sample and complete immersion of the electrode plates and temperature sensor. A 100 mL beaker would be ideal as it would allow for sample circulation and avoidance of edge effects.

12.4. Rinse the probe with fresh deionized water. Blot dry to remove excess water (to avoid static buildup do not wipe or rub the probe).

12.5. Place the probe into the sample making sure to fully immerse the electrodes and temperature sensor. Mix to circulate the sample and wait for a steady reading ("**READY**" indicator on the display).

12.6. The meter will read either milliSiemens (mS) or microSiemens (µS) dependant upon ion concentration. If displayed units are in mS, enter the value in the mS/cm column and calculate the µS equivalent (µS = 1000 X mS) entering it in the µS/cm column (note: the meter displays only the Siemens part of the units because it bases on a cell constant of 1 cm-1 for which conductivity = conductance, the true cell constant is included in the displayed value so that the units are actually for conductivity in µS/cm). Record the temperature of measurement only as a point of reference.

12.7. The conductivity probe has a stated operating range up to 200 mS. However, to avoid potential electrode interference due to fouling and impedance dilute samples having greater than 100 mS conductivity with deionized water. Enter the dilution factor as the ratio of the final volume divided the sample volume.

12.8. Perform duplicate analysis for at least one sample within the analytical batch of twenty and for any specific client requested sample.

13. Review

13.1. The analyst will review all data for accuracy and completeness and enter the data into the LIMS system (initial creation of worklist files).

13.2. The Conventionals Supervisor or Lead will review all benchsheets and LIMS worklists and submit the package for QC review.

13.3. QC review will again verify data entry for all batch and sample matrix QC and distribute the worklist files if data entry are sufficient.

14. Data Analysis and Calculations

14.1. The measurement is a direct read as conductivity temperature compensated to 25 ºC. The only

calculations that are required are the conversion of mS values to µS (mS X 1000) for reporting and the inclusion of a dilution factor for high level samples (> 100 mS).

14.2. The Relative Percent Difference (RPD) is calculated as:

RPD (%) = ABS[original – duplicate] / average X 100

14.3. The Relative Standard Deviation (RSD) is calculated as:

RSD (%) = Standard Deviation / average X 100

15. Method Performance

15.1. The Orion 115 meter can read conductivity to tenths of a µS but the reporting limit is set at 1.0 µS/cm. The recommended application range for the probe (Orion model 011510) is 10 µS / cm to 200 mS / cm. However, measurements using this probe are fairly precise at low levels (< 15 µS/cm) with an MDL of 0.25 µS / cm and a relative standard deviation (RSD) of 0.8%.

16. Pollution Prevention

16.1. There are no polluting chemicals associated with this analysis.

17. Data Assessment and Acceptance Criteria for Quality Control Measures

17.1. Calibration is verified by the analysis of a second source, NIST traceable Conductivity Standard. The result of this analysis must be a value within 10% of the certified value for the standard.

17.2. A method blank will be run after initial calibration and again with each continuing calibration verification standard. The blank should return a reading less than the reporting limit (1 µS/cm) or less than 1/10th the lowest sample value within the analytical batch. Blanks that are greater than 10 µS / cm indicate potential electrode problems.

17.3. Duplicate analysis for any sample within the analytical batch should return an RPD less than 20%.

18. Corrective Actions for Out of Control Events

18.1. If the ICV standard is out of control, the probe will be rinsed and the ICV standard re-measured. If still out of control, the calibration will be repeated using the DirectCal approach and the ICV re-measured. If the ICV again fails, the probe will be re-calibrated using “cell constant adjustment” protocol and the ICV reanalyzed. If ICV again fails, the supervisor will be consulted for evaluation of possible probe failure, miss-entry of the cell constant or other error in analytical technique. Analysis of client samples will not proceed without a passing ICV.

18.2. Calibration verification will be repeated after every ten samples analyzed. If a continuing verification standard fails, the standard will be immediately re-analyzed. If the second analysis fails, the probe will be re-calibrated and verified. All samples analyzed between the last passing

standard and the failed standard will be re-analyzed.

18.3. Conductivity blank failures have less meaning with respect to samples and are hard to define due to the difficulty associated with obtaining completely ion free water (atmospheric absorption of carbon dioxide). To the extent that there are no chemicals involved in sample analysis, contamination should not be an issue and we will generally not control on blanks values less than 10 µS/cm.

18.4. Blanks >10 µS/cm could indicate possible electrode fouling, particularly after a very high level sample had been analyzed. The probe should be thoroughly rinsed and the blank analysis repeated. If the blank again fails, there may be probe problems and this would be verified by analysis of the following CCV. If the blank and CCV both fail analysis should stop and the supervisor consulted.

18.5. If the RPD for any duplicate analysis returns a value greater than 20%, the analysis for that sample will be repeated. If any of the three values is a statistical outlier (using Grubb's Test or some other equivalent statistical test), it will be rejected and the RPD recalculated. If there are no obvious outliers, the RSD will be calculated and reported to the client along with a qualifier indicating possible heterogeneity.

19. Contingencies for Handling Out-of-Control or Unacceptable Data

19.1. Not Applicable

20. Waste Management

20.1. The only chemical solution generated is the KCl standard and this is sink disposable.

21. Method References

21.1. Method 2510 Conductivity, Standard Methods for the Examination of Water and Wastewater, 22nd edition, 2012

21.2. Method 120.1 Conductance (Specific Conductance, µmhos at 25 ºC). Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020 (Rev March 1983).

21.3. Method 9050A Specific Conductance, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, EPA SW-846

21.4. Methods of Soil Analysis, Agronomy Part 2 No. 9, 2nd ed. Chapter 10, Soluble Salts (10-2.3.2, 0-3.3)

21.5. Models 105 and 115 Conductivity Meters, Instruction Manual, Orion 1996

22. Appendices

22.1. Conductivity – TDS Benchsheet

Appendix 22.1

Conductivity - TDS Benchsheet

CONDUCTIVITY - TDS BENCHSHEET — Date / Time: 3/16/06 0:00

Temperature compensated to 25C — Analyst: map

INSTRUMENT: Orion Model 115 — *ELECTRODE: Orion #011510* — K= 1 cm-1

Direct Calibration		Cell Constant Adjustment		
1413 Calibration Standard	0.01 N KCl	1413 Calibration Standard		0.01N KCl
ARI #	0057-7		ARI #	0057-7
µS/cm =	1,413	Current value	Cal Temp (°C)	20.7
Cal Temp (°C) =	20.7	1.010	Expected	#N/A
Input µS =	#N/A	Adjust to	Displayed	1310
Cell constant =	1.010	#N/A	%	#N/A

Calibration Verification Standard — *Record Certified Values*

Source: Traceable Conductivity Standards — µS / cm = 1000

Lot Number: 3401 (ARI I2409) — TDS (mg/l) =

Sample Data

(NOTE: Record both conductivity and TDS values from probe, mS values will convert automatically to µS)

ARI Number	Sample Dilution	Temp (C)	CONDUCTIVITY @ 25C (mS/cm)	CONDUCTIVITY @ 25C (µS/cm)	TDS (mg/L)	Notes & Flags
ICB				0.9		OK!
ICV				1029		102.90%
MDL 1				12.0		
MDL 2				11.9		
MDL 4				11.9		
MDL 5				11.9		
MDL 6				12.0		
MDL 7				12.1		
MDL 8				12.1		
MDL 9				12.1		
mean				12.0	RSD =	0.72%
stdev				0.087	MDL =	0.25
CCB				0.8		OK!
CCV				1026		102.60%
CCB						
CCV						

Analytical Resources, LLC
Analytical Chemists and Consultants

Standard Operating Procedure

pH (Electrometric)

SOP 618S

Revision 9.4

Revision Date: 12/31/25

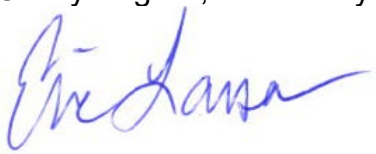
Effective Date: 2/19/16

Prepared by:

Mike Perkins

Approval:

Casey English, Laboratory Supervisor



Eric Larson, Inorganics Division Manager

Annual Review

SOP Number: 618S

Title: pH (Electrometric)

The ARLLC employee named below certifies that this SOP is accurate, complete and requires no revisions

Name	Reviewer's Signature	Date

1. Scope and Application

1.1. This SOP is for the electrometric determination of pH in drinking water, surface water, saline water, domestic wastewater, industrial wastewater, and acid rain. The method described is applicable to most aqueous solutions in which the water content is at least 20%. This SOP is based upon the requirements of Methods: EPA 150.1, SW-846 9040C and Standard Methods (20th ed) 4500-H^+.

1.2. Analysis of soil and sediment samples follows the requirements of SW-846 9045D. Samples or wastes may be solids, sludges or non-aqueous liquids. If water is present, it must constitute less than 20% of the total sample volume.

2. Summary of Method

2.1. pH is determined electrometrically using a pH electrode, reference electrode and a pH meter. The electrodes immersed in a solution generate a voltage (millivolt potential) proportional to the hydrogen ion (H^+) concentration of the solution. The pH meter is a voltmeter capable of measuring the voltage differences between the pH electrode and a reference electrode and expressing it as a pH value. The resulting readings are dependent upon temperature, condition of the electrodes, and ionic strength of the solution being measured.

2.2. pH electrodes generally consist of a tube filled with an electrolyte solution having a fixed pH and ionic strength and having a pH sensitive glass tip or bulb. The electrode contains a silver wire that establishes contact between the solution and the meter and measures the voltage between the solution and the inside wall of the glass tip. Changes in the hydrogen ion concentration on the outside wall of the glass tip (the sample) result in voltage changes on the inside wall and electrolyte solution.

2.3. The reference electrode typically consists of the electrode (silver wire), a filling solution (concentrated potassium chloride) and reference junction through which the filling solution can flow and establish electrical contact with the test solution. The filling solution must flow freely through the junction to allow proper operation of the electrode. We use a combination electrode that incorporates both pH and reference electrodes into a single unit.

2.4. The electrode and meter system must be calibrated against NIST traceable pH buffers that bracket the expected pH of the samples to be measured. The buffers should have pH values that differ by three or more pH units.

2.5. The calibrated electrode is introduced into an aliquot of sample and allowed to equilibrate by gently stirring to achieve a stable value. The measurement is repeated until successive readings differ by less than 0.1 pH unit.

2.6. Soil or solid waste are extracted in de-ionized water at a sample to water ratio of 1:1.

3. Definitions

3.1. pH: A measure of the degree of acidity or alkalinity of an aqueous solution. It is based upon the effective activity of Hydrogen (H^+) ion in solution (approximately equivalent to its molar concentration in dilute solutions) and is defined by the following equation:

$$pH = - \text{Log } [H^+] = \text{Log } (1/[H^+])$$

pH ranges in scale from 0 to 14 units based upon the dissociation constant for water (Kw),

$$HOH \leftrightarrow H^+ + OH^-$$

with the hydrogen ion concentration of pure water at 25 ºC being 1 X 10^{-7} moles/liter and balanced by equal concentration of hydroxyl ions (OH^-) such that

$$Kw = [H^+] \text{ X } [(OH^-] = [1x10^{-7}] \text{ X } [1x10^{-7}] = 1x10^{-14}$$

3.2. Since the H^+ concentration of pure water is $1X10^{-7}$ the pH of pure water is 7. Because it is electrically balanced by OH^-, pH 7 is considered to be neutral. Values less than 7 represent solutions having H^+ in excess of OH^- and are considered to be acidic. Solutions having pH values greater than 7 represent solutions having OH^- in excess of H^+ and are termed alkaline or basic.

3.3. Precision: pH values represent H^+ activity on a logarithmic scale. Precision for pH analysis is expressed relative to the allowed variation in pH units (± 0.05 units for recovery and ± 0.10 for absolute difference). Statistical evaluation of precision is based upon variation in hydrogen ion activity (the antilog of pH) over the allowed range. Precision is calculated as the coefficient of variation or relative percent difference (standard deviation / mean) for hydrogen ion activity expressed as a percentage. Values are transformed back to pH units to allow expression on the pH scale such that a difference of 0.05 pH units would represent a precision of approximately 11% for hydrogen ion activity while a difference of 0.1 pH unit would represent a precision of approximately 22% in hydrogen ion activity.

3.4. Analytical Batch: An analytical batch will consist of no more than 20 samples including one distillation blank, one Laboratory Control Standard, two distilled Curve Standards and matrix spikes and duplicates.

4. Interferences

4.1. Temperature. Temperature influences both the mechanical operation of the electrode-meter system and the chemical equilibrium of the sample.

4.2. Most modern pH meters have built in “automatic temperature compensation” that accounts for electrode variation and corrects for the temperature of measurement. In order to minimize the effect of temperature upon the electrode, it is best to have sample temperatures as close as possible to the temperature of the buffers used to calibrate the electrode. This procedure requires samples to be within ±2 C° of the calibration buffers.

4.3. Temperature effects upon chemical equilibrium are sample dependent and measurements reflect the "true" pH of the solution at that temperature. These effects are not an error and should not be compensated (this is the reason why pH Buffers have specified temperatures). For this reason, both pH and temperature should be recorded at the time of analysis.

4.4. Sodium. Development of voltages on the glass electrode is related to the exchange of sodium and hydrogen on the glass surface. As solutions become more alkaline, there is a possible sodium error as high as 0.5 pH units. The error can be compensated for using low sodium glass in the pH electrode and Fisher electrodes employ this feature.

4.5. Coatings of oily films or particulate matter can impair electrode response. The electrode should always be rinsed between readings to remove any coatings or films. If films cannot be removed, the electrode can be gently washed with detergent to remove coatings, rinsed with 0.1N HCl and then thoroughly rinsed with DI water. Be very careful not to touch the bulb during this operation.

5. Safety

5.1. Some samples submitted for analysis may qualify as RCRA Corrosive wastes (pH <2 or pH >12.5) and should be handled with caution. Wear gloves and eye protection when handling all samples.

6. Equipment and Supplies

6.1. pH meter, temperature compensating (Fisher Accumet AR 60 or equivalent)

6.2. Fisher accuFlow combination electrode (13-620-111) or equivalent.

6.3. The electrode has a built-in temperature sensor and is permanently gel filled, thus requiring little to no maintenance.

6.4. Between measurements, the electrode should be rinsed with DI water and stored in storage solution.

6.5. Cleaning. Sluggish behavior of the electrode may be due to contamination of the glass bulb or clogging of the reference junction. Clean the glass bulb by alternating 15 second treatments with 0.1 N HCl and 0.1 N KOH. Rinse with DI water between each treatment and repeat the cycle several times, finishing with the acid treatment. Rinse the electrode with DI water and place into pH 7 buffer for storage. Clean the reference junction by soaking the electrode in warm water for 5-10 minutes followed by a warm, saturated KCl solution. Allow electrode and KCl solution to cool to room temperature.

6.6. Record the date of any cleaning operation in the maintenance logbook and initial.

6.7. Beakers (polyethylene or glass), 100 mL

6.8. Magnetic stirrer and TFE stir bar.

7. Deviations from Referenced Methods

7.1. ARLLC replaces standard buffers when they reach the manufacturer's expiration date. EPA Methods 9040C and 9045D recommend replacing buffers monthly and SM 4500-H+ B-11 recommends 4 weeks. ARLLC discards all aliquots of buffer daily once they are removed from the original container.

8. Reagents and Standards

8.1. Calibration Standard Buffers. (pH 2, 4, 7, 10, 12) These must be certified NIST traceable buffer solutions. Buffers should be stored at room temperature. Examples would be:

8.1.1. pH 2 (Ricca 1493-32).
8.1.2. pH 4 (Fisher SB98-500).
8.1.3. pH 7 (Ricca 1551-32).
8.1.4. pH 10 (Fisher SB116-500).
8.1.5. pH 12 (Ricca 1615-32).

8.2. Calibration Verification Buffer. Use an NIST traceable pH 7 buffer derived from a source other than that used for calibration (Fisher SB108-500 or equivalent).
8.3. 4M KCl. 18.625 g potassium chloride to 250 mL DI.
8.4. Storage Solution. 1:1 mixture of 4M KCl and pH 4 buffer.

9. Sample Collection, Preservation, Shipment and Storage

9.1. Preferably, pH measurements for environmental samples are conducted in the field at the time of collection. If samples are transported to the laboratory they should be completely filled (no head space) and tightly sealed to prevent contact with the atmosphere.
9.2. There is no preservation for pH other than to minimize atmospheric contact. The pH should be determined as soon as possible after receipt in the lab. However, if samples are cold, they should be allowed to warm to room temperature in order to minimize the effect of temperature differences between the sample and calibration buffers.

10. Quality Control

10.1. Each batch of 10 or fewer samples must be bracketed by the measurement of a second source pH 7 calibration verification buffer. The recorded readings must be within 0.05 pH unit (6.95 - 7.05) of the known value (precision of approximately 11.5%).
10.2. Each sample aliquot is measured twice to ensure electrode stability. These readings must agree within 0.05 pH units.
10.3. Each batch of 10 or fewer samples requires one sample to be read in duplicate. Measurement of these duplicate sample aliquots must agree within ± 0.1 pH unit (precision of approximately 22.9%).

10.4. The date opened and analyst's initials will be documented on the label of a buffer solution container when it is initially opened.

11. Calibration and Standardization

11.1. Initial Calibration. pH Meters should be calibrated daily (recommended 8-hour interval) and verified prior to and immediately after each batch of samples analyzed. A new aliquot of each buffer must be used for each calibration. Pour fresh buffer for each calibration and discard it when calibration is complete. Enter the calibration data into the "pH Logbook" each time a meter is calibrated.

11.2. The Accumet pH meter is setup to automatically recognize 5 buffers (pH 2, 4, 7, 10, and 12) when calibrating. Calibrate over the entire 5 buffer range to cover all possible sample contingencies.

11.3. Calibrate the pH meter according to manufacturer's instructions using 5-point calibration (pH of 2, 4, 7, 10 and 12). Make sure the auto-temperature compensating (ATC) probe is attached. Proceed as follows:

11.4. Touch "std" on the screen to access standardization.

11.5. Touch "clear" to delete the previous standardization.

11.6. Touch "std." Place electrode into the pH 2 buffer solution and gently stir until the pH stabilizes. Touch "std" again to confirm the pH 2 point. The meter will automatically recognize the buffer as pH 2, the point will be saved, and an icon of a beaker with "2" will appear on the meter's display.

11.7. Repeat the process in section 10.1.2.3 for the four remaining standards.

11.8. Use the second source pH 7 buffer for calibration verification. Repeat the verification after every 10 samples analyzed and then again at the end of the batch. The verification standard should return a pH value within the range of 6.95 to 7.05 (± 0.05 pH unit).

12. Procedure

12.1. 12.1. Aqueous Solutions

12.1.1. Check the time of last calibration on the pH meter. If more than 8 hours have elapsed, repeat the five-point calibration. Otherwise, proceed with the pH 7 calibration verification buffer using fresh buffer. If the calibration verification fails (pH <6.95 or >7.05) the entire five-point calibration must be performed and verified before proceeding with client samples.

12.1.2. Transfer an aliquot of sample into a sample cup sufficient enough to cover the sensing elements of the electrode (approximately 20 mL) and allow clearance for the stirring bar. Place sample cup on magnetic stirrer and mix gently in order to achieve equilibrium between the electrode and sample solution. Avoid excessive stirring to minimize atmospheric CO2 exchange. This is particularly important for poorly buffered samples having pH values <7.

12.1.3. Temperature of the sample must be within ±2 ºC of the buffers.

12.1.4. Insert the electrode into the solution. Wait until meter signals a stable pH reading and the pH value stabilizes. Record the reading and temperature of the sample in the logbook.

12.1.5. Re-read the sample to verify electrode stability and record all successive readings until the stable values differ by less than 0.05 pH units.

12.1.6. Report the first reading of the stable pair in LIMS.

12.1.7. Make sure to thoroughly rinse with deionized water and shake off excess water after each rinse.

12.2. Soil and Sediment. There is space on the "Soils Conductivity-pH" benchsheet for this entry. Open the computer and print a copy of the benchsheet. In addition to the pH logbook, use this for all raw handwritten data entry. Make sure to record both the temperature of the extract and the temperature of the pH buffers used to calibrate the electrode at the time of measurement. Temperature of the extract must be within 2 ºC of the buffers.

12.3. DI water extraction

12.3.1. Add 20 grams of solid sample to a 50 mL centrifuge tube. Add 20 mL of DI water solution and shake for 15 minutes. Additional dilutions are allowed for very hygroscopic soils and other problem matrices (e.g. those that completely absorb the added water).

12.3.2. Allow 30 to 60 minutes for settling of particulates and suspended clay. The sample may be filtered or centrifuged for particulate removal. Decant the supernatant solution to a 50 mL beaker (or other appropriate container) for determination of pH or measure the pH of the clarified extract directly in the extraction vessel. Prepare a duplicate extraction for every 20 client samples of equivalent matrix.

12.3.3. Replicate readings are also required for soil or solid material extracts. These are only to verify that a stable reading has been obtained and are not reported as a measure of precision.

12.3.4. Record the actual weight of soil used, the volume of extract and the temperature and pH value on the benchsheet.

13. Data Analysis and Calculations

13.1. Analyst verifies workorder and conducts the analysis. All data, including successive pH readings and temperature will be manually recorded in the pH logbook. A scan of the pH logbook page will be made, and the data will be entered into LIMS. The completed LIMS data will be reviewed for completion and errors.

14. Method Performance

14.1. Method performance is tracked with a second source pH 7 verification buffer run immediately after initial calibration and repeated after every 10 samples analyzed.

14.2. Samples having pH values outside the range of pH 4 to 10 will be verified by the measurement of the closest standard to the sample result; either a pH 2 or pH 4 buffer for acidic samples, or pH 10 or pH 12 buffer for basic samples immediately following the sample or samples in question. This is to establish the accuracy of the extremes of the calibration at the time of analysis and any bias to the sample result.

14.3. Each sample aliquot is measured twice to ensure electrode stability. These readings must agree within 0.05 pH units.

14.4. Each batch of samples requires one sample to be read in duplicate. Measurement of these duplicate sample aliquots must agree within ± 0.1 pH unit (precision of approximately 22.9%).

15. Pollution Prevention

15.1. Samples that would qualify as RCRA Corrosive wastes (pH <2 or pH >12.5) will be collected and neutralized prior to sink disposal.

16. Data Assessment and Acceptance Criteria for Quality Control Measures

16.1. Calibration verification pH buffers (pH 7, 2 and 12) must return values within 0.05 pH unit of the identified standard at the temperature of measurement.

16.2. Replicate determinations on successive sample aliquots must return values within 0.1 pH unit. Duplicate preparations for soil samples should be evaluated relative to an absolute difference of 0.1 pH unit.

16.3. Any sample showing extremes of pH (i.e. <4 or >10), is suspect and should be brought to the attention of your supervisor. Very extreme pH values may indicate a possible mix-up in sample containers (a preserved sample may have been miss-labeled) hence the identity of such samples should be confirmed prior to conducting any further analysis on any of the samples which may be associated with that suspect sample.

17. Corrective Actions for Out-of-Control Events

17.1. If any verification standard does not return a value within 0.05 pH unit of its known value, first repeat the measurement to verify the "out-of-control" reading and then proceed as follows:

17.1.1. pH 7 buffer. If verified and sample readings are greater than 4 but less than 10, conduct a three-point calibration using pH 4, 7 and 10 buffers and repeat the verification process. Re-run all samples between the last in-control reading and the out-of-control reading. All samples must be bracketed by in-control verification buffers.

17.1.2. pH 2 or pH 12 buffers. Calibrate the pH meter using two-point calibration for either the pH 2 and 4 buffer (acidic samples) or the pH 7 and 12 buffers (basic samples, calibration buffers must be separated by at least 3 pH units). Verify the calibration and repeat the readings for all samples affected by the out-of-control condition.

17.2. If a sample pH reading is less than 2 or greater than 12, narrate the sample as being unsupported by acceptable pH verification and possibility RCRA Corrosive materials.

18. Contingencies for Handling Out-of-Control or Unacceptable Data

18.1. The analyst will narrate through a Corrective Action Sheet or Analysts Narrative Green Sheet any analytical result derived from an out-of-control condition that could not be corrected. This would include all samples having a pH reading less than 2 or greater than 12.

19. Waste Management

19.1. Samples that would qualify as RCRA Corrosive waste (pH less than 2 or pH greater than 12.5) will be collected and neutralized prior to sink disposal.

20. Method References

20.1. pH Value, Electrometric Method. Standard Methods for the Examination of Water and Wastewater. 2011. Method Number 4500-H^+ B

20.2. pH (Electrometric). Methods for Chemical Analysis of Water and Wastes. EPA 600/4-79-020 (Rev March 1983). Method 150.1

20.3. pH Electrometric Measurement. Test Methods for Evaluating Solid Waste. SW-846. 2002. Method 9040 C.

20.4. Soil and Waste pH. Test Methods for Evaluating Solid Waste. SW-846. 2002. Method 9045 D.

20.5. AR60, User Manual. Fisher Scientific

Analytical Resources, LLC
Analytical Chemists and Consultants

Standard Operating Procedure

Sulfide Preservation and Distillation

SOP 640S
Version 6.1

Revision Date: 12/22/2025
Effective Date: 11/30/16

Prepared by:

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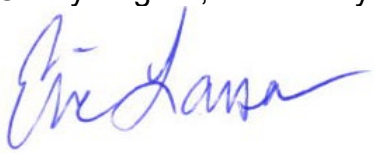


Eric Larson, Inorganics Division Manager

Annual Review

SOP Number: 640S

Title: Sulfide Preservation and Distillation

The ARLLC employee named below certifies that this SOP is accurate, complete and requires no revisions

Name	Reviewer's Signature	Date

1. Scope and Application

1.1. Sulfide in environmental samples may exists in a variety of states dependent upon pH and redox potential of the sample matrix. Primary forms include H_2S, HS^-, S^{-2}, and various metal sulfide complexes that vary widely in their degree of solubility.

1.2. This SOP describes the procedures used by ARLLC to preserve sulfide contained in environmental samples and to release the combined sulfides into a form (H_2S) that is measurable by routine finish analyses. The finish analyses, iodometric titration and methylene blue colorimetry, are covered under separate SOPs, ARLLC 650S and 653S, respectively.

1.3. This SOP is written to conform with the requirements of: Standard Methods 4500-S^{2-} Sulfide; Plumb, 1981; USEPA and Puget Sound Water Quality Authority PSEP) 1986; SW-846 Method 9030B (Acid Soluble only); and, Allen, et al. 1991 (Acid Volatile Sulfides and Simultaneously Extractable Metals).

2. Summary of Procedure

2.1. There are multiple procedures available. The client, and Project Manager must select the appropriate procedure for their needs prior to sampling and receipt of samples by the laboratory.

2.2. Aqueous samples can be analyzed for:

2.2.1. Dissolved sulfide if the sample is:

2.2.1.1. Unpreserved and contains no particulates.

2.2.1.2. Unpreserved and contains particulates that are removed by flocculation prior to finish analysis.

2.2.2. "Total sulfide"

2.2.2.1. Without distillation if the sample has been preserved with zinc acetate and is sufficiently clear (without significant turbidity) to allow either titrimetric or colorimetric analysis; or

2.2.2.2. With distillation if the sample has been preserved, is turbid, and cannot be read directly (*note: SW-846 Method 9030B is the only distillation procedure that covers aqueous samples*)

2.3. Sediment / soil or highly turbid aqueous samples are acidified under anoxic conditions to release sulfide from the matrix as H_2S. The released H_2S gas is then trapped in zinc acetate solution to precipitate sulfide (as zinc sulfide). Finish analysis is conducted on the trapping solution. **Three distillation procedures are available: SW-846 Method 9030B (Acid Soluble), PSEP 1986, and Acid Volatile Sulfide (AVS).** These vary primarily in the pH and temperature conditions under which the distillation is conducted and do not necessarily release equivalent amounts of sulfide as noted in Sections 3.7 and 3.8 below.

2.4. Sulfide can form highly insoluble complexes with a number of metals that might not be released for analytical determination by the procedures employed here. In this sense, "Total sulfide" actually represents that amount of sulfide that is released under the conditions of the distillation and not, necessarily, the total amount of sulfide that is present in the sample matrix.

3. Definitions

3.1. Sulfide: Sulfide exists in a variety of states dependent upon pH and redox potential of the sample matrix. Forms include hydrogen sulfide (H_2S), bisulfide ion (HS^{-1}), sulfide ion (S^{-2}), and metal sulfide complexes which vary widely in their degree of solubility (generally pH dependent dissociation to bisulfide and metal ions). Dissolved hydrogen sulfide (H_2S) and bisulfide ion (HS^{-1}) exist in equilibrium dependent upon pH and ionic strength with gaseous H_2S predominating at low pH. Sulfide ion (S^{-2}) is usually negligible due to the high dissociation constant for bisulfide to sulfide.

3.2. Hydrogen Sulfide. Combines with metals to form slightly soluble metal precipitates. Normally, these will respond to the acidic conditions used in the finish analyses to release the "acid soluble" sulfide into a measurable form (H_2S). Some metal complexes are virtually insoluble (copper and silver sulfides), will not respond to the test conditions and thus are not included in the definition of either Total or Dissolved Sulfide.

3.3. Hydrogen Sulfide Gas. Toxic to humans, creates nuisance odors, and can lead to serious corrosion problems. Dissolved hydrogen sulfide is toxic to aquatic organisms and partitioning into H_2S and HS^{-1} is sometimes required to more closely define possible toxicity.

3.4. Acid Volatile Sulfide. The presence of various iron sulfides (mackinawite, Fe(II) monosulfide, greigite, Fe_3S_4 and some pyrite, FeS_2) and the development of slightly soluble metal sulfide precipitates in anoxic sediments and sludge's leads to the formation of a class of sulfides referred to as Acid Volatile Sulfides (AVS). These are operationally defined by the conditions of extractive distillation. Our AVS procedure follows Allen, et al. (1991). AVS are significant since they are thought to influence the bioavailability of toxic metals in sediments. Simultaneously Extracted Metals (SEM) in the digest solution are often determined to address the relationship between metals and sulfide in the sample being tested. Acid Volatile Sulfide (AVS) is defined as solid phase sediment sulfide which is released by extraction in hydrochloric acid (1 to 1.2 N HCl) at room temperature for 60 minutes. Evolved H_2S is trapped in Zinc Acetate solution. The procedure described here for the extraction of AVS follows Allen, et al. 1991 (EPA Draft Method 1991).

3.5. Dissolved (Soluble) Sulfide. Includes aqueous phase sulfide which remains in solution after suspended solids have been removed by flocculation and settling with aluminum chloride and sodium hydroxide. Dissolved sulfide can only be determined on samples which have not been preserved with zinc acetate.

3.6. "Total sulfide." Includes dissolved soluble sulfides as well as most metal complexed sulfides with the exception of some highly insoluble forms (e.g. CuS, AgS, SnS_2). The analysis of total sulfide in solid phase samples (soils or sediments) is operationally defined by the procedure used to extract the sulfide from the sample matrix. Extraction is conducted by acid distillation from the sample matrix, the main difference between the distillation procedures is the acid used for extraction, the pH of the extracting medium and temperature. Different conditions of distillation can lead to significant variations in the amount of sulfide released when different procedures are used on the same sample. PSEP is the least aggressive of the distillation protocol (pH 3 to 4) and should be expected to release the least amount of sulfide from

the matrix. Method 9030B is more rigorous (pH <1) and should provide a better estimate of the total acid soluble sulfide. AVS uses a 1 to 1.2 N HCl extracting solution with a theoretical pH of 0 and should be the most acidic and aggressive of the distillation procedures.

3.7. Puget Sound Water Quality Authority 1986 (PSEP) "Total Sulfide". This is the acidification of a sediment sample with pre-treated, concentrated hydrochloric acid to methyl orange pH (3.5 - 4.5) with heated distillation (90ºC). Our procedure is a modification of the original PSEP method using a bromophenol blue indicator (pH 3.0 - 4.6) and temperatures below the boiling point to avoid carry over of water into the zinc acetate trapping solution. There is no specified time period for extraction, but 60 minutes would be consistent with other extraction procedures.

3.8. EPA SW-846 Acid Method 9030B (Acid Soluble Sulfide). This procedure estimates total acid soluble sulfide as that sulfide released by sulfuric acid extraction at 70 ºC and a pH <1 for 90 minutes. It does not include the highly insoluble metal complexes. Trapping is conducted in zinc acetate with formaldehyde added to prevent interference associated with other reduced forms of sulfur. Iodometric titration is the prescribed finish analysis. The ARLLC procedure is modified to use a colorimetric finish analysis hence removing the requirement for using formaldehyde in the trapping solution.

3.9. Preparation and Analytical batches. Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents.

3.9.1. Preparation batch: Involves a sulfide distillation and is composed of one to twenty environmental samples of the same quality systems matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. The twenty environmental samples do not include method blanks, LCS, matrix spikes or matrix duplicates. At a minimum, each batch must include a Method Blank, a Laboratory Control Standard, and a Detection and Quantitation Limit (DQL) standard prepared at a concentration equal to the low curve point (0.05 mg/L) for colorimetric finish and/or the reporting limit (1 mg/L) for titrimetric analysis.

3.9.2. Analytical batch: (i.e. just the colorimetric analysis or the titrimetric analysis) is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various quality system matrices and can exceed 20 samples (NELAC 2016. Quality Systems: General Requirements. The NELAC Institute.

4. Interferences

4.1. Sulfide is highly volatile and subject to rapid oxidation to elemental sulfur and sulfate. Exercise care in the handling of samples to minimize atmospheric contact during all phases of the sub-sampling and distillation procedures.

4.2. Aqueous samples preserved with zinc acetate/sodium hydroxide will have the sulfide bound in a zinc sulfide precipitate. This precipitate must be uniformly distributed throughout the sample bottle by gentle mixing prior to withdrawing the aliquot for analysis.

4.3. Volatilization (even under anoxic conditions) can be particularly problematic for solid phase samples where sulfide is typically not uniformly distributed within the sample matrix and sample jar. Try to mix the sample rapidly and within the original sample jar. Highly variable replicate results and matrix spike recoveries can result. Note any unusual characteristics in the appearance or smell of the sample (layers of different color, particularly black or red). Loss of volatile sulfide will be immediately evident by the characteristic “rotten egg” smell and should be noted as a potential negative bias in the observed result.

4.4. Highly calcareous sediments or soils (e.g. marine sediments containing shell fragments) will tend to neutralize the acid over the course of the distillation. This is particularly a problem for AVS determination where there is no control or compensation for potential acid neutralization. PSEP distillation uses a pH color indicator to adjust acid addition and 9030B requires pre-determination of the required acid volume. AVS calls only for the addition of a set amount of 6N hydrochloric acid to achieve the final normality of 1.0 to1.2 (pH 0). 20 mL acid is added to 100 -120 mL of sediment-water matrix (including the water content of the sediment).

5. Safety

5.1. The toxicity or carcinogenicity of each reagent used in this SOP has not been precisely defined. Treat each chemical compound as a potential health hazard. Reduce exposure to all chemicals to the lowest possible level by whatever means available.

5.2. Hydrogen sulfide gas is toxic to humans and creates nuisance odors. Sediment extraction must be conducted in a fume hood.

5.3. Always wear appropriate PPE (personal protective equipment) when working in the Laboratory. Gloves, safety glasses, ear protection, lab coats, respirators, face shields, and other safety items are provided for your protection.

5.4. Environmental Samples may contain hazardous waste; treat them as potential health hazards.

5.5. All sample waste must be disposed following the ARLLC Chemical Hygiene Plan.

5.6. Dispose of all unwanted, broken glassware into a broken glassware disposal box. Inspect every piece of glassware. Do not use any that are chipped, cracked, etched, or scratched. Glassware with minor damage should be stored for repair.

6. Equipment and Supplies

6.1. Gas Evolution Apparatus (see Figure below).

6.1.1. 250 mL, 3 neck distillation flasks, 24/40 ground glass joints (Kontes 606020-0624)

6.1.2. Nitrogen gas inlet adaptor, 24/40 taper (Kontes 179700-0824)

6.1.3. Outlet adaptor, 24/40 taper (Kontes 183000-2440)

6.1.4. Acid addition funnel, 125 mL, 24/40 taper (Kontes 634580-0125)

6.1.5. 125 mL gas washing bottles with straight glass frit (Wilmad LG-3761-100)

6.1.6. Teflon sleeves for 24/40 ground glass joints (Fisher 14-320 F)

6.1.7. Optional: Keck clips for 24/40 joints (Fisher CG14505) of each distillation unit.

6.2. 6-place stirring / heating manifold for 250 mL flasks (Electrothermal, EME Series Electromantle). The control knob set points on each mantle giving temperatures of 70 and 90 °C in the reaction flask should be determined and marked for use in future distillations.

6.3. Nitrogen gas cylinder with nitrogen regulator (10 psi maximum pressure).

6.4. Oxygen trap for nitrogen supply (Altech Oxy-Trap AT4001 coupled with Indicating Oxy-Trap AT4004).

6.5. pH meter and electrode

6.6. Top loading balance (accurate to 0.001 gram)

6.7. Environmental Express Vessels, 100 ml plastic graduated tubes with white screw cap.

6.8. Weighing Paper, 3" x 3". Fisherbrand Cat. No. 09-898-12A.

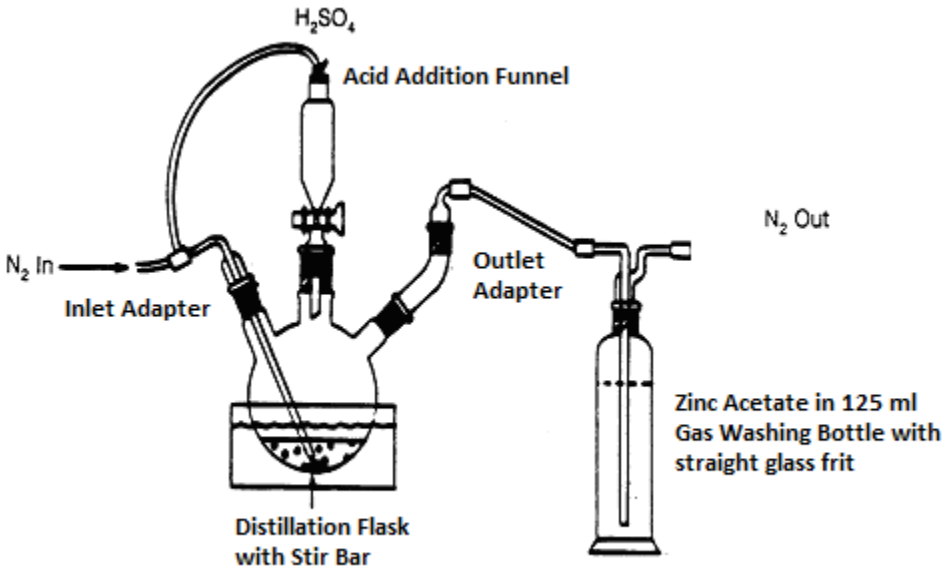


Figure. General setup for a Sulfide Distillation.

7. Reagents

7.1. Deoxygenated Reagent Water. Some reagents and all sample dilutions should be made with deoxygenated / deionized water (DDIW). A sufficient volume (enough to last for the days use) should be prepared daily by purging with an inert gas (e.g. helium or nitrogen) for at least 20 minutes. Keep the container tightly closed and open only when needed. This nitrogen purged water will also be used as a dispersing medium for distillation, as required.

7.2. Zinc acetate for preservation (2N = 1M): Dissolve 220 g Zinc acetate ($Zn(C_2H_3O_2)_2 \cdot 2H_2O$, FW = 219.49) in 800 mL DI and dilute to final volume of 1000 mL with DI. Store in polyethylene or glass bottle.

7.3. Zinc acetate trapping solution (0.2N = 0.1M): Add 5 ml of 6N NaOH and 20 ml of Acetic Acid to 200 ml of 2N Zinc Acetate solution and dilute to 2 liters.

7.4. Sodium Hydroxide (1 M = 1N): Dissolve 40 grams NaOH in DI water and dilute to 1 liter. Store in a polyethylene bottle.

7.5. PSEP Distillation Reagents.

7.5.1. Hydrochloric acid (HCl, treated): In a fume hood, carefully place one or two strips of aluminum foil in a beaker containing 250 mL concentrated HCL (vigorous reaction). After reaction, decant HCL to a separate bottle for use with PSEP distillations.

7.5.2. Zinc acetate trapping solution (Section 7.4)

7.6. 9030B Reagents

7.6.1. Sulfuric acid (H_2SO_4 concentrated): Use for adjusting distillation to pH ≤ 1 in 9030B distillation.

7.6.2. Zinc acetate trapping Solution (Section 7.4). Formaldehyde called for in the method is omitted because ARI use a colorimetric finish rather than the iodometic titration called for in the method.

7.7. AVS Reagents

7.7.1. Hydrochloric acid (6M): Carefully, and with mixing, add 500 mL conc. HCl to 400 mL DI then bring to a final volume of 1000 mL. Purge with nitrogen for 1 hour prior to use. <u>If used for AVS/SEM extraction, use ultrapure HCl. If only AVS, use our standard HCl.</u>

7.8. Aluminum chloride ($AlCl_3$•$6H_2O$, Fisher S75023): Aluminum chloride hexahydrate will rapidly accumulate water and become caked. Purchase in 100 gram bottles (Fisher S75023) and use the complete 100 grams each time a solution is prepared. Dissolve the contents of the bottle in 144 mL of reagent water.

7.9. Sodium hydroxide (NaOH, 6M): Dissolve 120 grams NaOH in 300 mL reagent water. CAUTION: NaOH solution will get hot! Cool and dilute to 500 mL. Store in a plastic bottle.

7.10. Sodium sulfide Standards: Sodium sulfide standards are required for batch and matrix quality control during distillation (LCS and matrix spikes). Sulfide standards cannot be accurately weighed. Prepared solutions must be standardized by iodometric titration before use. Instructions for doing this are contained in the Sulfide, Iodometric Titration SOP.

8. Sample Collection, Preservation, Shipment and Storage

8.1. Samples for “Total Sulfide” must be preserved at the time of collection. Unless the requested analysis is for soluble or dissolved sulfide, preservation of aqueous samples is accomplished in the field by the addition of zinc acetate resulting in the formation of slightly soluble zinc sulfide (a white colored precipitate). The pH of the sample must also be adjusted to greater than 9 with sodium hydroxide. Sample bottles sent out to clients will contain the required volume of 2N zinc acetate (2 mL of 2N /500 mL sample volume). To avoid the transport and usage of caustic chemicals by field personnel, sodium hydroxide is added once the samples are returned to the laboratory. Upon receipt in the laboratory, the samples are adjusted to pH >9 using 6N sodium hydroxide. The lab must verify that the sample bottle is labeled “zinc acetate” and that the pH is greater than 9. Laboratory personnel will add zinc acetate and sodium hydroxide as necessary.

8.2. Analysis should proceed as soon as possible after collection. The regulatory holding time for analysis is 7 days from the date of collection (EPA 2012, 40 CFR Part 136.3, Identification of Test Procedures, Table II). Standard Methods (SM1060 Table 1) allows a 28 day holding time for preserved samples while recognizing the regulatory holding time of 7 days.

8.3. Analysis for "Dissolved Sulfide" can only be conducted on samples which have not been preserved and should be run within 24 hours of collection.

8.4. Sediment samples can be collected in either glass or plastic jars. These can be preserved by addition of 2N zinc acetate over the surface (2 mL / 2 oz jar) but the efficiency of this treatment is unknown (Plumb, 1981). Sediment and waste samples should be transported to the lab on ice and stored at 4 ºC. Plumb, 1981 does not specify a holding time other than "as soon as possible". Standard Methods (4500-S2- A.3, Sampling and Storage) states that analysis should be conducted within 14 days. ARLLC standard procedure is to analyze within 7 days.

8.5. AVS samples should be filled with minimal head space and stored at 4 ºC. The maximum holding time for AVS sulfide is 14 days.

8.6. Solid samples require homogenization prior to sub-sampling the aliquot for analysis. Sulfide can rapidly volatilize during mixing hence the mixing should be done quickly and within the original sample container just prior to withdrawing the aliquot for analysis. Note any unusual characteristic or occurrence that could bias the sample result (e.g. if a sulfide odor is noted during the homogenization indicating that sulfide is being volatilized and the result will have a low bias). If possible, samples for Total Solids analysis should be taken after the aliquot for sulfide determination has been withdrawn.

8.7. All samples within a sulfide job should be analyzed the same way, either as preserved or unpreserved for each matrix set to not compromise data.

9. Quality Control *(Essential QC components following 40 CFR Part 136.7, May 18, 2012, EPA 2012 Method Update Rule).*

9.1. Demonstration of Capability. Each analyst performing this procedure must complete an initial "Demonstration of Capability" by preparing and analyzing 4 replicates of a QC Check Solution through distillation procedure. The recovery (Accuracy) must be within the range of ±10% with a relative standard deviation (Precision) less than 1%.

9.2. Method Detection Limit. The detection and quantitation limits for the methods are determined following the procedures described in ARLLC SOP 1018S

9.3. Laboratory Reagent Blank (Method Blank). Used as a Negative Control to verify the absence of contamination. Negative control is provided by a preparatory Method Blank. The preparatory Method Blank consists of DI water that has been processed along with and under the same conditions as associated samples. One Method Blank is processed along with each analytical batch of 20 samples. Ottawa sand should be used in conjunction with DI water for the solid phase method blank.

9.4. Laboratory Fortified Blank (Blank Spike or Laboratory Control Sample). Used as a Positive Control for the recovery of known additions. Positive control is provided by the analysis of a Laboratory Control Standard (LCS) which is equivalent to a laboratory fortified blank. The Laboratory Control Standards are processed exactly the same as the samples in the associated analytical batch. The LCS is spiked with sulfide solution which has been standardized by iodometric titration. This standard is used to verify recovery through all steps of the batch analysis.

9.5. Matrix Spike (MS) and Matrix Spike Duplicate (MSD). Matrix spikes will be run for each of 1 in 20 client samples (5% spiking) or as requested by the client. These spikes will be used to evaluate the accuracy (% Recovery) of the analysis relative to the sample matrix. Spiking will be at a level in the range of 1 to 10 times the sample background or at a minimum of 0.5 mg/L (10 times the low curve point). MSD's for the evaluation of the precision of the analysis (Relative Standard Deviation, RSD) will be run upon request of the client. Otherwise, precision of the analysis will be evaluated by the duplicate analyses.

9.6. Matrix Duplicates and Matrix Triplicates: Matrix duplicates will be run for each of 1 in 20 client samples (5%) or as requested by the client. Triplicates may be run at client request. These samples will be used to evaluate the variability of the sampling and analysis for a given sample matrix.

9.7. Internal Standards and Surrogate Standards are not applicable to colorimetric sulfide analysis.

9.8. Control charts for trend analysis. Control charts for the analysis of the Method Blank and LCS will be constructed and updated monitor method performance.

9.9. QC samples will be run with each batch of samples as defined above.

10. Calibration and Standardization

10.1. Analytical balances are verified each day using routine ARLLC balance verification procedures specified in ARLLC SOP 1003S Balance Monitoring, and recorded in a logbook.

10.2. Volumetric devices are verified using routine ARLLC procedures for verification of volumetric equipment, see SOP 1015S, Pipette Verification.

10.3. Class A volumetric glassware is used and volumetric vessel tubes are certified by the manufacturer for volume accuracy.

10.4. Sulfide standards used for the preparation of Laboratory Control Standards and matrix spiking are standardized using iodometric titration as described in SOP 650S, Sulfide Titration.

11. Procedure

11.1. **Total Aqueous Sulfide**. This procedure is for the measurement of total sulfide in turbid or highly colored aqueous samples. If the sample is not highly colored, excessively turbid or does not contain reducing substances which might interfere with the analysis (e.g. thiosulfate, sulfite) proceed directly to either the iodometric titration (SOP 650S) or the methylene blue colorimetric technique (SOP 653S). The described method will measure dissolved and most complexed sulfides with the exception of some highly insoluble metal sulfides (notably copper, tin and silver complexes).

11.1.1. In general, if the sample is turbid, highly colored or known to contain thiosulfate or sulfite, pre-treatment to remove interferences will be necessary. Pre-treatment could be either further precipitation of sulfide or distillation and trapping in zinc acetate. *Note: ARLLC typically distills as the preferred pre-treatment for these types of samples.*

11.1.2. The sample should have been preserved with zinc acetate at the time of collection resulting in the formation of a white zinc sulfide precipitate. If an ARLLC bottle was used for collection, the bottle should be labeled as "Total Sulfide preserved with ZnOAc". If the sample has not been preserved (e.g. samples collected for soluble sulfide), add 2N zinc acetate (2 mL per 500 mL of sample) and adjust to pH >9 using 1M NaOH. Preserved samples must be analyzed within 7 days of sampling.

11.1.3. Precipitation to remove color and or turbidity.

11.1.3.1. This procedure can be used as an alternative to ARLLC's preferred pre-treatment by distillation.

11.1.3.2. If the sample is highly colored or turbid, precipitate the sulfide with additional zinc acetate and adjust to pH >9.

11.1.3.3. Mark the sample bottle to indicate the "original sample volume" and add an additional 3-4 drops of 2N zinc acetate.

11.1.3.4. Adjust to pH >9 by dropwise addition of 1M NaOH and allow precipitate to settle for 30 minutes.

11.1.3.5. Decant or siphon as much of the supernatant solution as possible without losing any of the precipitate and refill to the "original volume" mark with deoxygenated water.

11.1.3.6. If the sample is still colored or turbid, adjust the pH as necessary and repeat the precipitation. Again decant or siphon the supernatant and refill to the "original volume" mark.

11.1.3.7. If the solution is now clarified, proceed to either the titrimetric or colorimetric analysis on the treated sample. If the level of the precipitate cannot be clearly distinguished or if the sample does not clarify after two repeated precipitations, proceed to the 9030B distillation procedure for releasing the sulfide and trapping it in zinc acetate.

11.1.3.8. Precipitation to concentrate the sulfide. This same procedure can be used to concentrate the sulfide in a low level sample by bring the volume back to a level less than that of the original sample.

11.2. **Soluble (dissolved) Aqueous Sulfide.**

11.2.1. This procedure is for dissolved or soluble sulfide in <u>unpreserved</u> aqueous samples. Samples for dissolved sulfide must be prepared on the day of sample collection or preserved in lab with zinc acetate for preparation the next day. The described procedure will measure dissolved sulfides which remain in solution after precipitation of particulate materials and complexed metal sulfides with aluminum chloride and sodium hydroxide. If the sample is free of turbidity and particulate materials, there is generally no need to run the precipitation and dissolved sulfide will equal total sulfide as determined by either colorimetric or titrimetric procedures. If the sample is turbid or contains particulate materials or precipitates (potential source of complexed sulfides), these must be removed by flocculation-

precipitation with aluminum chloride at an alkaline pH (pH 6-9). Precipitation is carried out in a 300 mL BOD bottle. Use care in transferring solutions to minimize aeration of the sample.

11.2.2. Add 0.6 mL 6M NaOH solution to a 300 mL BOD bottle. Carefully fill the bottle with sample using minimum agitation and entrapping no air bubbles.

11.2.3. Add 0.6 mL $AlCl_3$ solution, place stopper in bottle (**NO AIR BUBBLES !!**) and mix by repeatedly inverting the bottle for 1 minute. Additional reagent may be added if absolutely necessary to effect flocculation and precipitation. Solution pH must be maintained between 6 and 9.

11.2.4. Allow precipitate to settle for 5-15 minutes or until a clear supernatant can be drawn off for analysis. Remove the clarified supernatant as soon as is practically possible. Do not allow extended settling times !!

11.2.5. Proceed immediately with the analysis of sulfide using either iodometric titration (for high levels) or the colorimetric procedure.

11.2.6. The analyst must clearly identify that aluminum chloride precipitation has been used. Indicate this on an "Analyst Notes Sheet" along with an additional comment on the actual benchsheet used for finish analysis.

11.3. **Distillation Procedures.** Distillation / extraction is required for all solid phase samples and for those aqueous samples which are highly colored or turbid. Three different procedures for the distillation of sulfide in aqueous and/or solid phase samples are available. The characteristics of the three distillations are shown in Table 1.

11.3.1. For practical application, the procedures have been modified for the use of equivalent glassware in all three methods while retaining the basic chemical and timing conditions required for each. The procedures have been scaled for the use of a 250 mL reaction flask in line with a 125 mL fritted gas washing bottle. Notable differences in the procedure are:

11.3.1.1. The 9030B acid soluble distillation requires a pre-determination of the acid addition necessary to achieve the specified pH conditions (pH <1).

11.3.1.2. The AVS distillation requires knowledge of the water content of the field moist sediment so that the normality of the acid in the dispersing medium will be equivalent for all samples.

11.3.1.3. The PSEP procedure does not discuss the need for dispersing the sample aliquot in the reaction flask.

11.3.2. The need for dispersing the sample aliquot in the reaction flask is discussed in 9030B and is generally applicable to all three procedures. 9030B states, "For an efficient distillation, the mixture in the distillation flask must be of such a consistency that the motion of the stirring bar is sufficient to keep the solids from settling. The mixture must be free of solids that could disrupt the stirring bar."

11.3.3. The determination of dry weight is required for all solid samples. In general, this should be conducted after the sample aliquot has been taking for distillation (avoiding loss due to volatilization). First, gently homogenize the sample and examine for the presence of coarse elements that are not

representative of the overall nature of the sample. Such elements can interfere with the stirring of the sample during the distillation and should not be included in the aliquot taken for distillation. Consult with the PM and remove such elements from the sample jar to achieve a more homogeneous matrix. Document such removal on the "Analysts Notes Sheet".

Table 1. Characteristics for sulfide distillation methods

	AVS	9030 B	PSEP	*ARLLC*
Reaction Flask (mL)	250	500	1000	***250***
Gas trap	2 X 100-250 mL impingers with non-fritted outlets	125 mL gas washing bottle, fritted outlet	100 mL Nessler tubes	***125 mL gas washing bottle, fritted***
Absorbent	0.2 N (0.1M) zinc acetate	0.2 N (0.1M) zinc acetate	0.2 N (0.1M) zinc acetate	**0.2 N (0.1M) zinc acetate**
Absorbent Volume	2 x 80 mL	115 mL	20 mL	***50 mL***
Dispersing water	100 mL including sediment water content	200 mL	Not defined	***100 mL***
Nitrogen purge (1)	10 min @ 100 ccm	Not defined	10 min	
Sample wt	2 – 10 grams	0.2 to 50 mg sulfide but < 25 grams total weight	Aliquot containing < 50 µg sulfide	***0.5 to 10 grams dependent upon sample***
Nitrogen purge (2)	10 min @ 40ccm	15 min @ 25 ccm	Not defined	***10 min***
Extraction acid	6M HCl, de-aerated	H_2SO_4 conc	Aluminum treated HCL conc	***as per method***
Acid volume	20 mL	Pre-determined + 10 mL	To methyl orange pH (3.1 – 4.4)	***as per method except use of bromphenol blue in PSEP and 10 ml for 9030B.***
Acid concentration	1M or pH < 1	pH ≤ 1	pH < 3.1	***as per method***
Temperature	Ambient	70 °C	90 °C	***as per method except PSEP is 90*** °C
Time	1 hour @ 20 ccm	90 min @ 25ccm	Time to 20 mL distillate (60 min)	***as per method except PSEP is 60 min***

11.3.4. Distillation Log Book. Documentation of the distillation conducted for each sample in a batch is provided by manual entry of the appropriate data to the Sulfide Distillation Log book (ARLLC 6171F). This form must be completed for each distillation batch at the time the sample processing is being conducted. A distillation batch should not include more than one distillation method. Distillation pre-treatment is required for 9030B to determine acid addition required to attain target pH. A pre-treatment bench sheet is available for printing as needed.

11.3.4.1. Sediment and soil samples may vary in their ability to react with and neutralize the acid added during the distillation. The 9030B acid soluble distillation requires a pre-determination of the acid addition necessary to achieve the specified pH conditions (pH <1) for individual samples such that all samples will be reacted under equivalent pH conditions.

11.3.4.2. PSEP calls for the use of a color indicator to determine a pH <3 in the reaction flask.

11.3.4.3. Pre-treatment: For 9030 B, volume required must be pre-determined by taking an aliquot of the sample equivalent to that which will be used for the extraction, placing it in a beaker and adding DI water to a total volume of 100 mL. Stir and measure the pH. Add concentrated H2SO4 to achieve a pH <1. Note the volume of acid required. Add this pre-determined volume of acid plus an additional 5 mL to the addition funnel. The same procedure is used for turbid aqueous samples.

11.3.5. General Set-up. Assemble the 6 place heating/stirring mantle, glassware (three neck, 250 mL reaction flask, nitrogen inlet adapter, outlet adapter, acid addition funnel) and nitrogen gas train. Close nitrogen valves to the individual reactors and verify the following conditions.

11.3.5.1. The nitrogen tank pressure is less than or equal to 10 psi.

11.3.5.2. The Oxytrap and indicating column are installed in the gas line and are in good condition. The indicator color should be a beige-green; a dark brown color indicates an exhausted column and the column should be replaced.

11.3.5.3. All 24/40 ground glass joints should have Teflon® sleeves installed. The sleeves should be clean and in good condition.

11.3.5.4. Rinse each reaction flask with DI water to remove any acid residue and place a magnetic stir bar in each flask.

11.3.5.5. The nitrogen gas inlet tube extends close to the bottom of the reaction flask (sufficient to extend below the surface of the liquid which will be added to the flask) but not so as to interfere with the movement of the stir bar.

11.3.5.6. Sulfide Gas Traps. Obtain the required number of gas washing bottles and thoroughly rinse each three times with DI water. Clean the frit by forcing pressurized DI water directly from the faucet through the frit tubing. If you detect a sulfide odor during the rinsing process, repeat the rinse (using 0.1N HCl if necessary) until no such odor is observed. The final rinse must be with DI water to remove any acid residuals.

11.3.5.7. If a samples appears to have a high level of sulfide (black, smelly sediment), it is advisable to place two sulfide traps in sequence in order to avoid loss of sulfide due to saturation in the first trap. Carry over of sulfide to the second trap would be evident by the appearance of zinc sulfide cloudiness in the second trap. The contents of the two traps would be combined for the finish analysis.

11.3.5.8. Extraction Acid. Before connecting distillation flask or acid trap add about 60 mL of the required acid to each addition funnel and purge with Nitrogen gas for 10 minutes.

11.3.5.8.1. **PSEP**. Aluminum foil treated HCl (reagent 7.4.1). Add 60 mL of extracting acid to each acid addition funnel. Addition volumes will be based upon changes in the Bromphenol Blue color indicator during the course of the extraction. The change will be from a dark blue to yellow at pH < 3. 20 mL of concentrated acid should be sufficient for most samples.

11.3.5.8.2. **9030 B**. Concentrated H_2SO_4.

11.3.5.8.3. **AVS**. 6N HCl (reagent 7.6.1). Add 20 mL of extracting acid to each acid addition funnel.

11.3.5.9. Add enough 0.2N zinc acetate (reagent 7.4.2) to completely cover the frit of each gas washing bottle. Verify that the glass frit is below the surface of the absorbent.

11.3.5.10. Add 2 drops of bromophenol blue indicator (the color should be dark blue) If the color is green or yellow, acid is present in the flask. In this case, add a few drops of 1N NaOH, disassemble and rinse the apparatus to remove all traces of acid.

11.3.5.11. Connect all system components (nitrogen inlet, acid addition funnel and outlet to gas traps) after the dispersing water has been added to the reaction flask. Turn on the nitrogen supply to the individual reaction flasks by unclamping the acid funnels and clamping the frits with the acid funnel side arms turned open. The acid chamber should be bubbling and adjust nitrogen to equalize the gas bubbling rate within each gas trapping bottle (approximately 5 bubbles /sec). Check each ground glass joint of acid funnel with "Snoop" solution to verify the absence of leaks. Purge at least 10 minutes. Close off the nitrogen supply to the addition funnel by switching the pinch clamp from the frit and replacing it on top of the acid funnel with the side arm closed, then allow the system to purge through the reaction flask for at least 10 minutes.

11.3.5.12. Withdraw the Sample for Analysis. While the system is purging, open the sample jar and gently homogenize to obtain a uniform consistency and incorporation of any overlying liquid. In consultation with the PM, remove any coarse elements that are not representative of the sample. Document such removal on the ‘Analysts Notes Sheet’ so that it will be plainly evident to ARLLC< Project Manager.

11.3.5.13. Using the top loading balance, weigh out an aliquot of the homogenized sample onto a piece of tared dissolvable weighing paper (2 to 10 grams, 5 would be most appropriate but do not use less than 2 unless you are certain that sulfide levels are very high). Record the sample weight to 0.001 grams on the Sulfide Distillation Log.

11.3.5.14. Fold and quickly transfer the weigh paper and contained sample to the reaction flask using the outlet port. Insure that all sample gets transferred and that no grit, sand or mud adheres to any portion of the ground glass joint or Teflon sleeve. It is important that no grit particles are lodged within the joint as this will result in gas leaks and low recoveries

11.3.5.15. Dispersing water. Add 100 mL de-oxygenated water to each reaction flask to wash the sample completely into the flask, out of the weight paper, and to ensure glass joint is free of grit.

11.3.5.16. Close the system by inserting the frit back into the reaction flask and keeping the side arm of the acid addition funnel closed to allow the system to purge through the reaction flask for an additional 10 minutes. During this time, verify that the nitrogen inlet tube is below the surface of the liquid in the reaction flask. Adjust the flow of nitrogen to achieve a comparable bubbling rate in all gas washing bottles. Again, you should check all ground glass joints with "Snoop" solution to verify the absence of leaks.

11.3.5.17. Timing and Temperature. While the system is equilibrating prior to acid addition, turn on the magnetic stirrers and heating units as required. Use the pre-determined set points (70 and 90 °C) for temperature control. All distillations should be constantly stirred at a rate that does not create an excessive vortex in the reaction flask, but sufficient enough to keep material suspended. Temperature regimes and timing will vary as shown in the table below

11.3.5.18. **Table 2. Temperature and Timing Conditions.**

Distillation	Temperature (ºC)	Time (minutes)
PSEP	90	60
9030 B	70	90
AVS	ambient	60

11.3.5.19. Once the system has equilibrated to the proper temperature and you have confirmed the absence of leaks, open the acid addition funnel to slowly release the acid into the reaction flask. Begin timing the extraction according to the table above.

11.3.5.20. At the end of the extraction period, quantitatively transfer the zinc acetate trapping solution to a 100 mL Environmental Express vessel, rinsing all trapping solution out with 0.2N zinc acetate, then bring to 100 ml volume. If two traps were used, combine the contents of each and make up to a known volume (150 – 200 mL). Make sure you have entered the final trap volume on the distillation log. The sample is now ready for analysis using either the colorimetric or titrimetric finish procedure.

12. Review

12.1. Not applicable

13. Data Analysis and Calculations

13.1. Not applicable

14. Method Performance

14.1. Not applicable

15. Pollution Prevention

15.1. The procedures discussed in this SOP generate wastes which are hazardous for the characteristic of Corrosivity (RCRA Code D002). These wastes will be collected in a satellite accumulation container and neutralized prior to sink discharge.

15.2. These procedures may also result in the generation and identification of aqueous wastes having sulfide concentrations in excess of 10 mg/L. These will be collected and treated to oxidize contained sulfide prior to sink discharge.

16. Data Assessment and Acceptance Criteria for QC Measure

16.1. Not applicable

17. Corrective Actions for Out of Control Events

17.1. A sample should be re setup for distillations for any of the following problems:

17.1.1. If a leak is detected in the glass joints (not tight fit, or lack of bubbles in reaction flask) then the sample should be re setup and the leaking sample should be discarded.

17.1.2. If it is noticed that the reaction flask lacks a stir bar, or the heat is not turned on then the sample should be re setup.

17.1.3. If the trapping solution is knocked over after distillation than the sample must be reset for distillation.

17.1.3.1. If the sample is prepped the same day then another method blank or LCS is not required for the distillation setup.

17.1.4. If the trapping solution is brought up to a volume over 100 mls, than the excess volume is taken out using a pipette to determine the exact final volume.

17.2. If the samples will not be analyzed the same day than the environmental express vessels containing transferred sample and the standard may be kept in the refrigerator overnight. All must be removed in the morning and brought to room temperature before continuing with analysis.

17.3. Record any corrective actions taken on the Yellow Corrective Action form.

18. Contingencies for Handling Out-of-Control or Unacceptable Data

18.1. Not applicable

19. Waste Management

19.1. Reaction flask solutions are acidic wastes (pH <2) and should be collected for neutralization and sink discharge.

19.2. Trapping solutions are caustic (pH >12) and should be collected and neutralized for sink discharge.

19.3. Samples and distillates having sulfide concentrations in excess of 10 mg/L (ppm) should be collected and treated with bleach to oxidize container sulfide prior to sink discharge.

20. Method References

20.1. Standard Method for the Examination of Water and Wastewater On-Line, 2001. 4500-S^{2-} Sulfide.

20.2. EPA 2012. 40 CFR Part 136. “Guidelines Establishing Test Procedures for the Analysis of Pollutants…”. Federal Register Friday, March 18, 2012.

20.3. EPA SW-846. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods. Method 9030B. Acid Soluble and Acid Insoluble Sulfides: Distillation.

20.4. Allen, et al.,1991. Determination of Acid Volatile Sulfide and Selected Simultaneously Extractable Metals in Sediment. EPA 821-R-91-100. Draft Analytical Method for Determination of Acid Volatile Sulfide in Sediment.

20.5. Plumb, R. 1981. PROCEDURES FOR HANDLING AND CHEMICAL ANALYSIS OF SEDIMENT AND WATER SAMPLES. Technical Committee on Criteria for Dredged and Fill Material. Environmental laboratory, US Army Engineers Waterways Experiment Station. USEPA/USACOE AD/A103 788.

20.6. PSEP 1986. Conventional Sediment Variables. Total Sulfides. Recommended Protocols for Measuring Conventional Sediment Variables in Puget Sound. USEPA and Puget Sound Water Quality Authority. Modified 2003.

20.7. 40 CFR Part 136, Guidelines Establishing Test Procedures for the Analysis of Pollutants, Appendix B. Definition and Procedures for Determining the Method Detection Limit.

20.8. TNI Standard. 2016. The NELAC Institute.

20.9. FACDQ10-13. 2007. DQFAC Single Laboratory DL-QL Procedure (version 2.4). 8/30/2007

21. Appendices

21.1. N/A

Standard Operating Procedure E42 – Extraction of Sediment Porewater by Centrifugation

Scope and Application

This Environmental Geochemistry Laboratory (EGL) Standard Operating Procedure (SOP) is applicable to the extraction of porewater from sediment samples using centrifugation for geochemical analyses. This method provides sufficient porewater recovery for a wide range of analytes while maintaining sample integrity when properly conducted. This procedure is based on the methods described by Environment Canada (1994), U.S. Environmental Protection Agency (2001), ASTM International (2013). Procedures outlined in this SOP will be followed, and any deviations must be noted in your laboratory notebook.

Health and Safety

All laboratory work will be performed in accordance with the EGL *Chemical Hygiene Plan* (CHP) by staff approved by the laboratory manager and chemical hygiene officer. Approval to work in the EGL requires orientation to laboratory safety procedures and potential hazards under the guidance of the laboratory manager, as specified in the CHP.

Hazards and controls associated with this SOP are listed below and explicitly linked in **Table A**. Hazards associated with project-specific media are addressed in the Project Safety Analysis (PSA) document. Occupational exposure limits (OELs) for chemicals used in this SOP are attached as **Table B**.

Chemical Safety Data Sheets

The following Safety Data Sheets (SDSs) must be reviewed prior to beginning the procedure:

- Mix gas (5% hydrogen/95% nitrogen)
- Nitrogen gas

Hazards Associated with this Standard Operating Procedure

- Inhalation, ingestion, and skin or eye contact with contaminants or small particles
- Operating the centrifuge
- Breakage of glassware

Engineering Controls

- The centrifuge will not operate if lid is not secure.

Administrative Controls

- Ensure lids are secure on sample containers.
- Ensure the centrifuge lid is closed prior to operating.
- Verify the centrifuge has normal operational sound prior to leaving the area.

Personal Protective Equipment

- Laboratory coat
- Safety glasses
- Nitrile gloves (Ansell® TouchNTuff® 92-600)

Inspection Requirements

- Inspect personal protective equipment (PPE) prior to use.
- Confirm fume hood face velocity prior to use.
- Inspect the centrifuge prior to use.
- Inspect glassware prior to use.

Equipment and Supplies

The following is a list of equipment and supplies necessary to carry out the procedures contained in this SOP:

- Stainless-steel bowl and spatula
- Disposable glove bag for anoxic processing
- Ultra high purity grade nitrogen gas cylinder
- Anaerobic chamber
- Laboratory centrifuge (capable of a g-force [g] of 3,000)
- Centrifuge bottles (polypropylene or Teflon, high-strength)
- Centrifuge bottle caps
- Micropipettes and tips or graduated dropper glass liquid pipettes with rubber caps
- Pre-cleaned glass jars (appropriate size)
- Balance for centrifuge bottle balancing (±0.1 gram or per manufacturer guidance)

Procedure

Task 1: Sediment Homogenization

1. Thoroughly mix sediment samples using a stainless-steel bowl and spatula. Perform this task in a disposable glove bag filled with nitrogen gas for anoxic processing to minimize exposure to air if redox-sensitive analytes will be measured in sediment porewater. Otherwise, this step may be performed on the benchtop under ambient conditions.

2. Transfer sediment into appropriately sized centrifuge bottles made of suitable material, filling no more than 80% of capacity. Tightly close the lids if redox-sensitive analytes are being analyzed.
3. Gently tap the bottom of the centrifuge bottles to remove air bubbles where possible.
4. Collect remaining sediment samples in appropriate size pre-cleaned glass jars and store them in a refrigerator at 4°C.

Task 2: Centrifugation for Sediment Porewater Collection

1. Balance the centrifuge bottles within acceptable tolerance (±0.1 gram or per manufacturer guidance).
2. Place tubes symmetrically in centrifuge rotor.
3. Centrifuge at 3,000 g for 30 minutes at 4°C.
4. Allow the centrifuge to come to a complete stop before opening.
5. Carefully remove the centrifuge bottles without resuspending sediments.
6. Carefully transfer the centrifuge bottles into an anaerobic chamber if redox-sensitive analytes are being analyzed.
7. Gently collect supernatant into a sample bottle using a micropipette or glass pipette.

Project Closeout

Please refer to project closeout plan for project-specific disposal methods for extracted sediments.

References

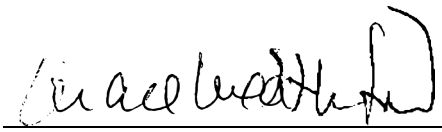
ASTM International, 2013. ASTM D3974-09(2013): Standard Practices for Extraction of Trace Elements from Sediments. West Conshohocken, PA: ASTM International.

Environment Canada, 1994. *Guidance Document on Collection and Preparation of Sediments for Physicochemical Characterization and Biological Testing*. Environmental Protection Series. Report EPS 1/RM/29. December 1994.

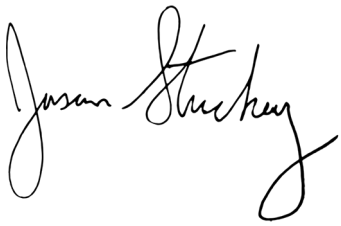
U.S. Environmental Protection Agency, 2001. *Methods for Collection, Storage and Manipulation of Sediments for Chemical and Toxicological Analyses: Technical Manual*. EPA-823-B-01-002. Office of Water. Washington, DC.

Standard Operating Procedure Approval Page

This standard operating procedure, Extraction of Sediment Porewater by Centrifugation, has been reviewed and is approved for use in the Environmental Geochemistry Laboratory.

Signature:  Date: 05/04/2026

Grace Weatherford, Chemical Hygiene Officer

Signature:  Date: 05/04/2026

Jason Stuckey, Laboratory Manager

Table A
Hazards

Table A
Hazards

Potential Hazard(s)	Engineering Controls	Administrative Controls (Includes Work Practices)	PPE	Inspection Requirements
Inhalation, ingestion, and skin or eye contact with contaminants or small particles	Perform work in an operational fume hood.	--	- Safety glasses - Laboratory coat - Nitrile gloves (Ansell® TouchNTuff® 92-600)	- Inspect PPE prior to use. - Confirm fume hood face velocity prior to use.
Operating the centrifuge	- Thermoscientific: Centrifuge will not operate if lid is not secure	- Ensure lids are secure on sample containers. - Ensure centrifuge lid is closed prior to operating. - Verify centrifuge has normal operational sound prior to leaving area.	- Safety glasses - Laboratory coat - Nitrile gloves (Ansell® TouchNTuff® 92-600)	- Inspect PPE prior to use. - Inspect centrifuge prior to use.
Breakage of glassware	--	Carry glassware with two hands.	- Safety glasses - Laboratory coat - Nitrile gloves (Ansell® TouchNTuff® 92-600)	- Inspect PPE prior to use. - Inspect glassware prior to use.

Notes:

--: not applicable

PPE: personal protective equipment

Table B
Occupational Exposure Limits

Table B
Occupational Exposure Limits

SOP No.	Title	Chemicals Used	CAS Number	Exposure Routes	Symptoms	Target Organs	OEL (ppm)	NIOSH/OSHA/ACGIH Values	Vapor Pressure (mmHg)	Ionization Potential (eV)	First Aid
319	Extraction of Sediment Porewater by Centrifugation	Gas Mixture: Hydrogen 0.1% to 5.5%/ Nitrogen 94.5% to 99.9%	Nitrogen 7727-37-9 Hydrogen 1333-74-0	Inhalation, skin and/or eye contact	Contact with rapidly expanding gas may cause burns or frostbite	Eyes, skin, respiratory system	--	ACGIH TLV (United States, 1/2021). Oxygen Depletion (Asphyxiant). Explosive potential.	--	--	Eyes: Irrigate immediately for 10 minutes. Remove contact lenses. Skin: Water flush immediately. Remove contaminates clothing. Wash clothing and shoes before reuse. Breathing: Remove victim to fresh air and keep at rest in a position comfortable for breathing. If not breathing, if breathing is irregular, or if respiratory arrest occurs, provide artificial respiration or oxygen by trained personnel. It may be dangerous to the person providing aid to give mouth-to-mouth resuscitation. Get medical attention if adverse health effects persist or are severe. If unconscious, place in recovery position and get medical attention immediately. Maintain an open airway. Loosen tight clothing such as a collar, tie, belt or waistband. In case of inhalation of decomposition products in a fire, symptoms may be delayed. The exposed person may need to be kept under medical surveillance for 48 hours. Swallow: Refer to inhalation section.
319	Extraction of Sediment Porewater by Centrifugation	Nitrogen Gas	7727-37-9	Inhalation, skin and/or eye contact	Contact with rapidly expanding gas may cause burns or frostbite. At very high concentrations, it can displace the normal air and cause suffocation from lack of oxygen.	Eyes, skin, respiratory system	--	ACGIH TLV (United States, 1/2021). Oxygen Depletion (Asphyxiant)	--	--	See First Aid for Gas Mixture: Hydrogen 0.1% to 5.5%/ Nitrogen 94.5% to 99.9% (above)

Notes:
ACGIH: American Conference of Governmental Industrial Hygienists
CAS: Chemical Abstracts Service
eV: electronvolt
mmHg: millimeter of mercury
NIOSH: National Institute for Occupational Safety and Health
OEL: occupational exposure limit
OSHA: Occupational Safety and Health Administration or Act
ppm: part per million
SOP: Standard Operating Procedure
TLV: threshold limit value

Standard Operating Procedure E43 – Synthetic Sediment Porewater Extraction

Scope and Application

This Environmental Geochemistry Laboratory (EGL) Standard Operating Procedure (SOP) is applicable to preparing synthetic sediment porewater. In this procedure, project-appropriate water is contacted with sediment for a sufficient duration to prepare sediment porewater. Note that water used in this procedure may be deionized (DI) water, site water, or other, depending on the goals of the project. After the equilibration period, suspended solids in the water sample are settled down. The supernatant is then carefully filtered to remove suspended solids while avoiding resuspending the solids. This procedure is based on the methods described by ASTM International (ASTM) D3987–85 (ASTM 1985), McDonough et al. (2008), and Yan et al. (2022). Procedures outlined in this SOP will be followed, and any deviations must be noted in your laboratory notebook.

Health and Safety

All laboratory work will be performed in accordance with the EGL *Chemical Hygiene Plan* (CHP) by staff approved by the laboratory manager and chemical hygiene officer. Approval to work in the EGL requires orientation to laboratory safety procedures and potential hazards under the guidance of the laboratory manager, as specified in the CHP.

Hazards associated with this SOP are listed in the following sections and explicitly linked in **Table A**. Hazards associated with project-specific media are addressed in the Project Safety Analysis (PSA) document. Occupational exposure limits (OELs) for chemicals used in this SOP are attached as **Table B**.

Chemical Safety Data Sheets

The following Safety Data Sheets (SDSs) must be reviewed prior to beginning the procedure:

- Hexane
- Methanol

Hazards Associated with this Standard Operating Procedure

- Inhalation, ingestion, and skin or eye contact with contaminants or small particles
- Handling flammable chemicals (hexane, methanol)
- Operating the shaker table
- Breakage of glassware

Engineering Controls

- Perform work in an operational fume hood.

Administrative Controls

- Ensure lids are secure on sample containers.
- Place samples in secondary containment (prior to operating the shaker table).
- Ensure the shaker table has normal sound prior to leaving the area.
- Carry glassware with two hands.

Personal Protective Equipment

- Safety glasses
- Laboratory coat
- Flame resistant laboratory coat (when handling flammable chemicals)
- Microflex 93-260 nitrile gloves (when handling flammable chemicals)
- Ansell® TouchNTuff® 92-600 nitrile gloves (when not handling flammable chemicals)

Inspection Requirements

- Inspect personal protective equipment (PPE) prior to use.
- Confirm fume hood face velocity prior to use.
- Inspect the shaker table prior to use.
- Inspect glassware prior to use.

Equipment and Supplies

The following is a list of equipment and supplies necessary to carry out the procedures contained in this SOP:

- Laboratory balance of appropriate precision (±0.1 gram)
- Stainless-steel bowl
- Stainless-steel scoop
- Methanol (high-performance liquid chromatography [HPLC]-grade)
- Hexane (HPLC-grade)
- Aluminum foil
- 1-liter (L) graduated cylinder
- 64-ounce wide-mouth glass jar with Teflon-lined cap
- Water (project-appropriate)
- Electrical tape
- Laboratory orbital shaker
- Peristaltic pump and pump tubing
- Polytetrafluoroethylene (PTFE) tubing and appropriate fittings
- 0.45-micron (µm) polyethersulfone (PES) in-line capsule filter

Procedure

The following procedure should be used to prepare each soil/sediment slurry:

1. Rinse a stainless-steel spatula and stainless-steel bowl using HPLC-grade hexane and methanol.
2. Homogenize a sediment sample thoroughly using a stainless-steel spatula and stainless-steel bowl.
3. Transfer 300 grams of wet sediment into a 64-ounce U.S. Environmental Protection Agency (EPA) pre-cleaned glass jar using a stainless-steel spatula.
4. Add 800 milliliters of water (project-appropriate) to provide sufficient water volume for analytical measurements or other uses (multiple replicates may be needed).
5. Place the sediment slurry jar on a laboratory orbital shaker and agitate at 120 revolutions per minute for 28 days to achieve sediment-water equilibrium at room temperature.
6. After 28 days, remove the jar from the shaker table and allow contents to settle for 24 hours.
7. Gently remove the water without disturbing the settled sediment with tubing and a peristaltic pump.
8. If multiple jars were used, composite the recovered porewater in a clean glass container.
9. Filter porewater using a peristaltic pump equipped with PTFE tubing and a 0.45-µm PES in-line capsule filter, and transfer it to a 64-ounce pre-cleaned glass jar.
10. Store the porewater sample jars at 4°C in a refrigerator.

Closeout

The remaining media from this experiment can be disposed of as described in Table 1. Project-specific media disposal is outlined in the Project Closeout Plan (PCP). If other unforeseen media is generated from this procedure, laboratory personnel and project managers will coordinate to characterize and dispose of those materials in accordance with federal, state, and local regulations.

Table 1
Disposal of Remaining Media

Remaining Media	Disposal Considerations	Disposal Procedure
Rinse HPLC-grade water	Water is not a regulated waste material.	Pour down the drain.
Organic solvent rinse waste (hexane, methanol)	Methanol and hexane carry the federal waste code of Ignitibility. Methanol also carries the waste code for spent solvents (EPA 2024).	Collect solution in a hazardous waste accumulation container. Ensure that all constituents are clearly listed on the label. Coordinate with laboratory management for hazardous waste disposal by a licensed waste contractor.
Residual sediment slurry	Refer to the PCP for potentially regulated constituents.	Refer to the PCP for project-specific disposal methods.

References

ASTM (ASTM International), 1985. ASTM D3987-85: Standard Test Method for Shake Extraction of Solid Waste with Water. ASTM International.

City of Portland, 2019. Sanitary Discharge and Pretreatment Program Administrative Rules: ENB – 4.03. Accessed June 2023. https://www.portland.gov/sites/default/files/2020-06/enb-4-03-sanitary-discharge-and-pretreatment-program-7-19-465822.pdf.

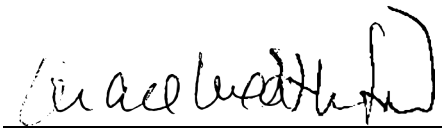
EPA (U.S. Environmental Protection Agency), 2024. Defining Hazardous Waste: Listed, Characteristic and Mixed Radiological Wastes. Accessed November 2024. https://www.epa.gov/hw/defining-hazardous-waste-listed-characteristic-and-mixed-radiological-wastes.

McDonough, K.M., J.L. Fairey, and G.V. Lowry, 2008. "Adsorption of Polychlorinated Biphenyls to Activated Carbon: Equilibrium Isotherms and a Preliminary Assessment of the Effect of Dissolved Organic Matter and Biofilm Loadings." *Water Research* 42:575–584.

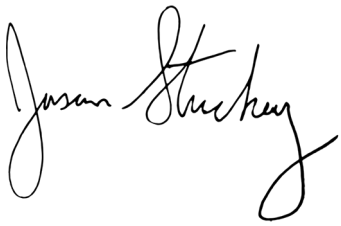
Yan, S., M. Bokare, and U. Ghosh, 2022. "Equilibration Porewater Measurement of PCBs and PAHs Using Direct Water Extraction and Comparison with Passive Sampling." *Environmental Science & Technology* 56(14):10020–10029.

Standard Operating Procedure Approval Page

This standard operating procedure, Synthetic Sediment Porewater Extraction, has been reviewed and is approved for use in the Environmental Geochemistry Laboratory.

Signature:  Date: 05/04/2026

Grace Weatherford, Chemical Hygiene Officer

Signature:  Date: 05/04/2026

Jason Stuckey, Laboratory Manager

Table A
Hazards

Table A
Hazards

Potential Hazard(s)	Engineering Controls	Administrative Controls (Includes Work Practices)	PPE	Inspection Requirements
Inhalation, ingestion, and skin or eye contact with contaminants or small particles	Perform work in an operational fume hood.	--	- Safety glasses - Laboratory coat - Nitrile gloves (Ansell® TouchNTuff® 92-600)	- Inspect PPE prior to use. - Confirm fume hood face velocity prior to use.
Handling flammable chemicals (methanol, hexane)	Perform work in an operational fume hood.	--	- Safety glasses - Flame resistant laboratory coat - Nitrile gloves (Microflex 93-260)	- Inspect PPE prior to use. - Confirm fume hood face velocity prior to use.
Operating the shaker table	--	- Ensure lids are secure on sample containers. - Place samples securely in secondary containment. - Ensure shaker table has normal sound prior to leaving the area.	- Safety glasses - Laboratory coat - Nitrile gloves (Ansell® TouchNTuff® 92-600)	- Inspect PPE prior to use. - Inspect shaker table prior to use.
Breakage of glassware	--	Carry glassware with two hands.	- Safety glasses - Laboratory coat - Nitrile gloves (Ansell® TouchNTuff® 92-600)	- Inspect PPE prior to use. - Inspect glassware prior to use.

Notes:

--: not applicable

PPE: personal protective equipment

Table B
Occupational Exposure Limits

Table B
Occupational Exposure Limits

SOP No.	Title	Chemicals Used	CAS Number	Exposure Routes	Symptoms	Target Organs	OEL (ppm)	NIOSH/ OSHA/ ACGIH Values	Vapor Pressure (mmHg)	Ionization Potential (eV)	First Aid
318	Synthetic Sediment Porewater Extraction	Methanol	67-56-1	Inhalation, skin absorption, ingestion, skin and/or eye contact	Irritation of eyes, skin, upper respiratory system; headache, drowsiness, dizziness, nausea, vomiting; visual disturbance, optic nerve damage (blindness); dermatitis	Eyes, skin, respiratory system, central nervous system, gastrointestinal tract	200	NIOSH REL TWA: 200 ppm (260 mg/m^3) ST 250 ppm (325 mg/m^3) [skin] OSHA PEL TWA: 200 ppm (260 mg/m^3)	96 mmHg	10.84 eV	Eye: Irrigate immediately Skin: Water flush promptly Breathing: Respiratory support Swallow: Medical attention immediately
318	Synthetic Sediment Porewater Extraction	Hexane	110-54-3	Inhalation, ingestion, skin and/or eye contact	Irritation eyes, nose; nausea, headache; peripheral neuropathy: numb extremities, muscle weak; dermatitis; dizziness; chemical pneumonitis (aspiration liquid)	Eyes, skin, respiratory system, central nervous system, peripheral nervous system	50	NIOSH REL TWA: 50 ppm (180 mg/m^3) OSHA PEL TWA: 500 ppm (1800 mg/m^3) ACGIH TLV TWA: 50 ppm (176 mg/m^3)	124 mmHg	10.18 eV	Eye: Irrigate immediately Skin: Soap wash immediately Breathing: Respiratory support Swallow: Medical attention immediately

Notes:
--: not applicable
ACGIH: American Conference of Governmental Industrial Hygienists
CAS: Chemical Abstracts Service
eV: electronvolt
mg/m^3: milligram per cubic meter
mmHg: millimeter of mercury
NIOSH: National Institute for Occupational Safety and Health
OEL: occupational exposure limit
OSHA: Occupational Safety and Health Administration or Act
PEL: permissible exposure limit
ppm: part per million
REL: recommended exposure limit
SOP: Standard Operating Procedure
ST: short term
TLV: threshold limit value
TWA: time-weighted average