

EXHIBIT D

INTRODUCTION TO ANALYTICAL METHODS

THIS PAGE INTENTIONALLY LEFT BLANK

Exhibit D - Introduction to Analytical Methods

Table of Contents

<u>Section</u>	<u>Page</u>
1.0 INTRODUCTION.....	5
2.0 METHODS FLOW CHARTS.....	5
3.0 GLASSWARE CLEANING.....	7
4.0 STANDARD STOCK SOLUTIONS.....	7
5.0 VERIFICATION OF SAMPLE CONDITION AND PRESERVATION.....	8
6.0 SAMPLE CHARACTERIZATION.....	9
7.0 SAMPLE DILUTIONS.....	10
8.0 DISSOLVED METALS.....	10
9.0 REPLICATE INTEGRATIONS/EXPOSURES.....	10
10.0 RAW DATA REQUIREMENTS.....	11
11.0 ANALYTICAL STANDARDS REQUIREMENTS.....	11
12.0 SAFETY.....	12
13.0 POLLUTION PREVENTION.....	13
14.0 WASTE MANAGEMENT.....	13

THIS PAGE INTENTIONALLY LEFT BLANK

1.0 INTRODUCTION

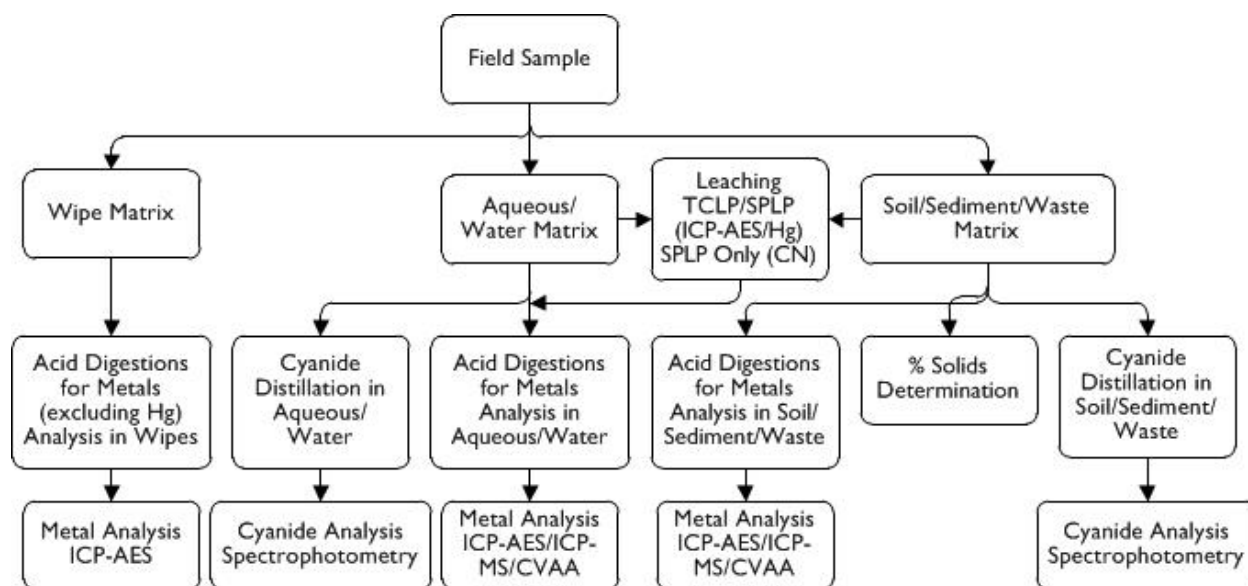
This analytical service provides a contractual framework for laboratories. The framework applies the U.S. Environmental Protection Agency (EPA) Contract Laboratory Program (CLP) analytical methods for the isolation, detection, and quantitative measurement of: low/medium volatiles, semivolatiles, pesticides, Aroclors, metals (including mercury), and cyanide in aqueous/water, soil/sediment, and waste samples; Total Organic Carbon (TOC) and anions in aqueous/water and soil/sediment samples; hexavalent chromium and trace volatiles in aqueous/water samples; low/medium volatiles, semivolatiles, pesticides, metals (including mercury), and cyanide in leachates from Toxicity Characteristic Leaching Procedure (TCLP) or Synthetic Precipitation Leaching Procedure (SPLP) extraction; and pesticides, Aroclors, and metals (excluding mercury) in wipe samples.

The analytical methods that follow are designed to analyze aqueous/water, TCLP/SPLP leachate, soil/sediment, waste, and wipe samples from hazardous waste sites for the presence of the analytes contained in the Target Analyte List and Contract Required Quantitation Limits (see Exhibit C - Target Analyte List and Contract Required Quantitation Limits). The methods describe multiple preparation procedures, alternative analysis procedures for some analytes, and Quality Control (QC) requirements. Analytical techniques include: Gas Chromatography/Mass Spectrometry (GC/MS), Gas Chromatography/Electron Capture Detector (GC/ECD), Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES), Inductively Coupled Plasma - Mass Spectrometry (ICP-MS), Cold Vapor Atomic Absorption Spectroscopy (CVAA), Spectrophotometry, Ion Chromatography (IC), and TOC by infrared (IR) or conductimetry.

2.0 METHODS FLOW CHARTS

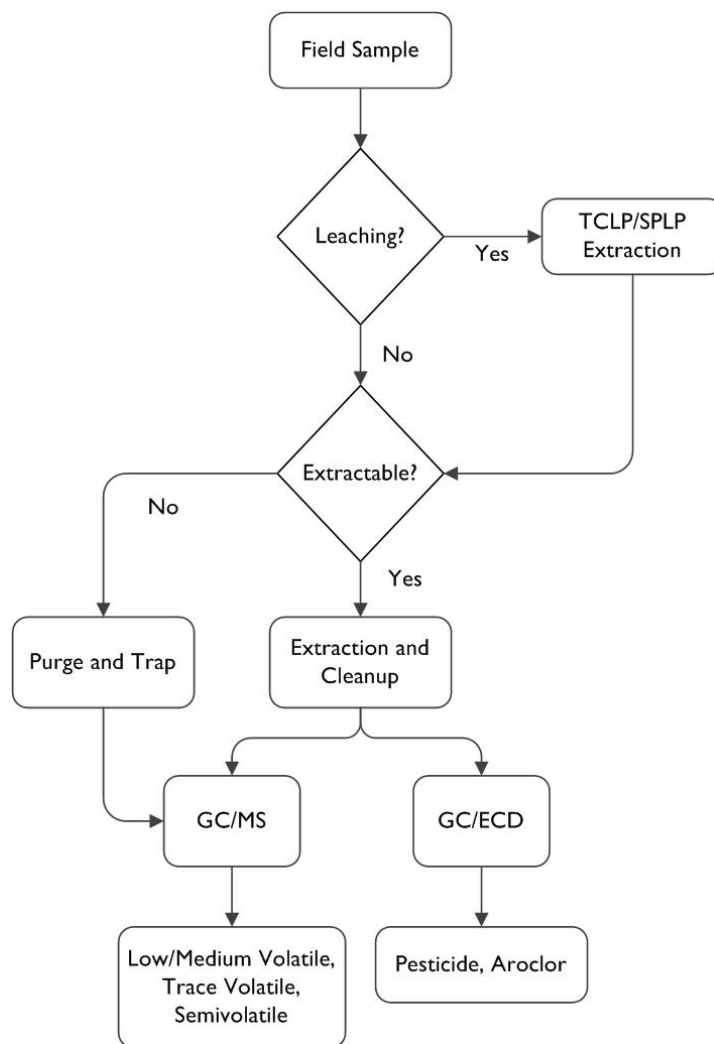
- 2.1 Figure 1 outlines the general analytical scheme the Contractor shall follow in performing standard trace metals and cyanide analyses under this contract.

Figure 1 - Inorganic Methods Flow Chart



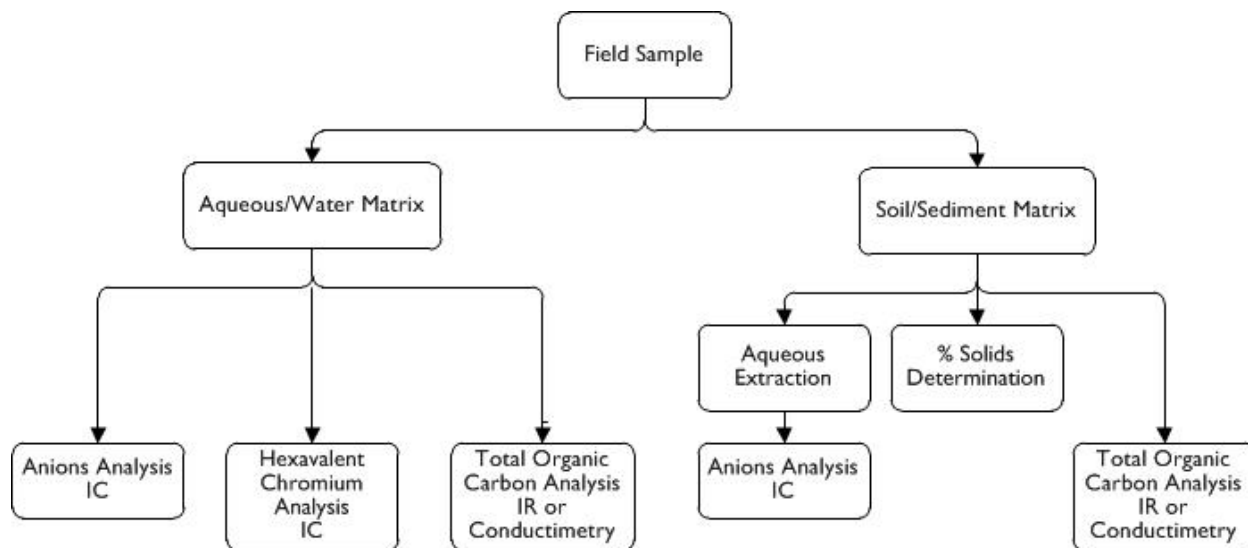
2.2 Figure 2 outlines the general analytical scheme the Contractor shall follow in performing standard organics analyses under this contract.

Figure 2 - Organic Methods Flow Chart



- 2.3 Figure 3 outlines the general analytical scheme the Contractor shall follow in performing standard anions, hexavalent chromium, and TOC analyses under this contract.

Figure 3 - Anions, Hexavalent Chromium, and Total Organic Carbon Methods Flow Chart



3.0 GLASSWARE CLEANING

- 3.1 Laboratory glassware to be used for metals and cyanide analyses shall be acid cleaned according to the EPA's manual, Methods for Chemical Analysis of Water and Wastes (EPA/600/4-79-020) or an equivalent procedure. An electronic version of this manual can be found via the EPA's National Service Center for Environmental Publications (NSCEP) website at <https://www.epa.gov/nscep> (search on EPA Manual 600479020).

- 3.2 Laboratory glassware to be used for organic analyses shall be scrupulously cleaned according to EPA SW-846 Chapter 4, Organic Analytes, Section 4.1.6, Revision 5, July 2014, or an equivalent procedure. An electronic version of this manual can be found at <https://www.epa.gov/hw-sw846/chapter-four-sw-846-compendium-organic-analytes>.

- 3.3 Equivalent procedures are those which meet the Preparation Blank requirements in the Statement of Work (SOW).

4.0 STANDARD STOCK SOLUTIONS

Stock solutions to be used for preparing instrument or method standards may be purchased or prepared as described in the individual methods in Exhibit D. Stock solutions that are past the manufacturer's expiration date shall not be used to prepare analytical standards.

5.0 VERIFICATION OF SAMPLE CONDITION AND PRESERVATION

- 5.1 At the time of sample receipt, the Contractor shall check the condition of each sample container and its contents, and note the condition in a sample receipt log if the condition is not acceptable. The Contractor shall determine if sufficient sample volume has been provided for all tests scheduled and listed on the Traffic Report/Chain of Custody (TR/COC) Record. Containers of aqueous/water samples for volatile organic analysis should be completely filled without air bubbles. Preservation of samples, if required, should be noted on the sample label and TR/COC Record. The Contractor shall determine the pH of aqueous/water samples designated for metals, cyanide, hexavalent chromium, or TOC analysis and note in a sample receipt log if the pH is ≤ 2 for metals or TOC samples, > 8 for hexavalent chromium samples, or ≥ 10 for cyanide samples.
- 5.1.1 If a sample for metals analysis has not been properly preserved, the Contractor shall adjust the pH of the sample (according to the procedures in Exhibit D) and note this in the Sample Delivery Group (SDG) Narrative. If the pH is > 9 at the time of receipt, the Contractor should consider the possibility that the labels for the metals and cyanide samples were switched in the field. Do not add acid to samples designated for metals analysis and with a pH > 9 unless the pH of the samples designated for cyanide analysis has been checked and is acceptable for cyanide analysis.
- 5.1.2 The Contractor shall not adjust the pH of a sample for cyanide analysis. If the pH of a cyanide sample is < 10 , contact the Sample Management Office (SMO) for further instructions before proceeding with the preparation and analysis.
- 5.1.3 The Contractor shall not adjust the pH of a sample for hexavalent chromium analysis. If the pH of a hexavalent chromium sample is ≤ 8 , contact SMO for further instructions before proceeding with the analysis.
- 5.1.4 The Contractor shall not adjust the pH of a sample for TOC analysis. If the pH of a TOC sample is > 2 , contact SMO for further instructions before proceeding with the preparation and analysis.
- 5.1.5 The Contractor shall not adjust the pH of samples scheduled for TCLP or SPLP extraction.
- 5.1.6 The Contractor shall not adjust the pH of a sample for volatiles analysis.

6.0 SAMPLE CHARACTERIZATION

6.1 If multiphase samples (e.g., two-phase liquid sample, oily sludge/sandy soil/sediment sample) are received by the Contractor, the Contractor shall contact SMO to notify them of the type of sample received. SMO will contact the EPA Region.

6.1.1 If all phases of the sample are amenable to analysis, the EPA Region may require the Contractor to do any of the following:

- Mix the sample and analyze an aliquot from the homogenized sample.
- Separate the phases of the sample and analyze one or more of the phases, separately. SMO will provide the EPA Sample Numbers for the additional phases, if required.
- Not analyze the sample.

6.1.2 If one or more of the phases are not amenable to analysis (i.e., outside scope), the EPA Region may require the Contractor to do any of the following:

- Separate the phases and analyze the phase(s) that is (are) amenable to analysis. SMO will provide the EPA Sample Numbers for the additional phases, if required.
- Not analyze the sample.

6.1.3 The Contractor shall document the EPA Region's decision in the SDG Narrative.

6.2 Unless instructed otherwise by the EPA Regional CLP Contracting Officer's Representative (COR), all samples shall be mixed thoroughly prior to aliquoting for extraction, digestion, or distillation. Sediment samples for organic analyses shall be decanted and the water layer discarded. There are no specific procedures provided herein for the homogenization of soil and sediment samples; however, an effort shall be made to obtain a representative sample. Coarse stones, twigs, or debris that are not representative of the soil or sediment sample shall be excluded from the aliquot.

7.0 SAMPLE DILUTIONS

- 7.1 The Contractor shall follow the requirements for sample dilutions as described in the individual methods in Exhibit D. The Contractor shall use the least dilution necessary to bring the analyte concentration(s) within the calibration range. Unless the Contractor can submit proof (e.g., screening results data, photographic evidence of opaque or turbid samples, or viscometry measurements) that dilution was required to obtain valid results, or to avoid damage to instruments or detectors, both diluted and undiluted sample measurements shall be present in the raw data. All samples for multi-analyte metals analysis shall be analyzed undiluted, unless the adjusted detection limits for all analytes are below the Contract Required Quantitation Limits (CRQLs).
- 7.2 Samples may be analyzed at an initial dilution if the results of a screening analysis indicate that this is necessary.
- 7.3 When an analyte concentration exceeds the calibrated range, appropriate dilution (but not below the CRQL) and reanalysis is required. For ICP-AES, ICP-MS, and anions analyses, the Contractor shall use the least dilution necessary to bring the analyte(s) instrument reading within the upper 75% of the calibrated range. For trace volatile [including Selected Ion Monitoring (SIM)], low/medium volatile, semivolatile (including SIM), pesticide, and Aroclors analyses, the Contractor shall use the least dilution necessary to bring the analyte(s) instrument reading within the upper half of the calibrated range. In all cases, report the highest valid value for each analyte as measured from the undiluted and diluted analyses.
- 7.4 For single analyte analysis (i.e., mercury, cyanide, hexavalent chromium, and TOC), a diluted sample analysis may be the only sample analysis performed if the analyte's instrument result is in the upper 75% of the calibrated range. An undiluted sample analysis does not have to be performed in this case. The sample and its associated matrix spike and laboratory duplicate shall initially be analyzed at the same dilution.
- 7.5 All sample dilutions shall be made using the same solvent or with reagent water mixed with the appropriate acid(s) or base(s) (cyanide or hexavalent chromium) to be consistent with the acid or base concentration in the sample, extract, digestate, or distillate.

8.0 DISSOLVED METALS

If dissolved mercury or metals by ICP-AES or ICP-MS analysis is requested by the EPA Region, the Contractor shall digest the field-filtered samples according to the procedures in Exhibit D of the analytical method and report the results as dissolved metals.

9.0 REPLICATE INTEGRATIONS/EXPOSURES

If the Contractor analyzes samples using multiple integrations/exposures, the Contractor shall use the data obtained from all integrations/exposures to calculate the final sample result even if more than the minimum number of integrations/exposures are taken.

10.0 RAW DATA REQUIREMENTS

The Contractor is reminded and cautioned that the collection and reporting of raw data may or may not be referred to within the individual methods of Exhibit D or the Quality Assurance (QA) protocol of Exhibit F - Programmatic Quality Assurance/Quality Control Elements. The raw data collected and provided in association with the performance of analyses under this contract shall conform and be delivered as specified in Exhibit B - Reporting and Deliverables Requirements.

If the Contractor analyzes samples or standards by chromatography using manual integrations, the Contractor shall clearly label the manual integrations used to calculate the final sample result and provide the raw data, as specified in Exhibit B - Reporting and Deliverables Requirements.

11.0 ANALYTICAL STANDARDS REQUIREMENTS

The EPA will not supply analytical reference standards for either direct analytical measurements or the purpose of traceability. All Contractors shall be required to prepare, from materials or purchase from private chemical supply companies, those standards necessary to successfully and accurately perform the analyses required in this protocol.

11.1 Preparation of Chemical Standards from Neat High Purity Bulk Materials

- 11.1.1 If the Contractor cannot obtain analytical reference standards, the Contractor shall prepare its own chemical standards. The Contractor shall obtain the highest purity possible when purchasing chemical standards. Standards purchased at less than 97% purity shall be documented as to why a higher purity could not be obtained.
- 11.1.2 The chemical standards shall be kept at manufacturer-recommended conditions when not being used in the preparation of standard solutions. Proper storage of chemical compounds is essential to safeguard them from decomposition.
- 11.1.3 The Contractor is responsible for having analytical documentation demonstrating that the purity of each compound is correctly stated. The Contractor shall use appropriate techniques when performing purity confirmation. Use of two or more independent methods is recommended. The correction factor for impurity when weighing neat materials in the preparation of solution standards is determined using Equation 36 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.
- 11.1.4 Logbooks are to be kept for all weighing and dilutions of standards and reagents. All subsequent dilutions from the primary standard and the calculations for determining their concentrations are to be reviewed and verified by a second person.
- 11.1.5 All solution standards are to be refrigerated, if required, when not in use.
- 11.1.6 All solution standards are to be clearly labeled to include the identity of the analyte(s), concentration, standard ID number of the solution, date prepared, solvent, solvent lot number, expiration date of the solution, special storage requirements (if any), and initials of the preparer.

Exhibit D - Sections 11-12

11.2 Purchase of Chemical Standards Already in Solution

Solutions of analytical reference standards can be purchased by Contractors provided they meet the following criteria.

- 11.2.1 Contractors shall maintain documentation of the purity confirmation of the material to verify the integrity of the standard solutions they purchase.
- 11.2.2 The quality of the reference standards purchased shall be demonstrated statistically and analytically by a method of the supplier's choice.

11.3 Documentation of the Verification and Preparation of Chemical Standards

It is the responsibility of the Contractor to maintain the necessary documentation to show that the chemical standards used in the performance of the CLP analysis conform to the requirements previously listed.

- 11.3.1 In those cases where the documentation is supportive of the analytical results of data packages sent to the Government, such documentation is to be kept on-file by the Contractor for a period of one year.
- 11.3.2 Upon request by the EPA Regional CLP COR, the Contractor shall submit their most recent previous year's documentation (12 months) for the verification and preparation of chemical standards within 14 days of receipt of the request to the designated recipients.

12.0 SAFETY

- 12.1 The Contractor is advised that the samples received under this contract are usually from known or suspected hazardous waste sites. The samples may contain high levels of organic and inorganic materials of a potentially hazardous nature and of unknown structure and concentration, and should be handled throughout the analysis with appropriate caution. It is the Contractor's responsibility to take all necessary measures to ensure laboratory safety and to prepare samples as described in the respective Exhibit D - Analytical Methods for the requested analysis type.
- 12.2 The Contractor is also advised that the toxicity or carcinogenicity of each reagent used in this SOW has not been precisely defined; however, each chemical compound shall 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. The Contractor is responsible for maintaining a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of chemicals specified in these methods. A reference file of Safety Data Sheets (SDS) shall be made available to all personnel involved in the chemical analysis.
- 12.3 The laboratory facility shall be provided with basic safety equipment, including but not limited to: Personal Protective Equipment (PPE); chemical safety showers; eyewash stations; fire extinguishers; spill mitigation kits; ventilation hoods; chemical resistant work surfaces; and bulk chemical containment.

13.0 POLLUTION PREVENTION

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the EPA recommends recycling as the next best option.

14.0 WASTE MANAGEMENT

The EPA requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The EPA urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with applicable environmental rules and regulations. Solvent reclamation during extract concentration is recommended.

THIS PAGE INTENTIONALLY LEFT BLANK

EXHIBIT D
GENERAL ANALYSIS

THIS PAGE INTENTIONALLY LEFT BLANK

Exhibit D – General Analysis

Table of Contents

<u>Section</u>	<u>Page</u>
1.0 SCOPE AND APPLICATION.....	5
2.0 SUMMARY OF METHOD.....	5
3.0 DEFINITIONS.....	5
4.0 INTERFERENCES.....	5
4.1 pH Determination.....	5
5.0 SAFETY.....	5
6.0 EQUIPMENT AND SUPPLIES.....	6
6.1 Percent Solids Determination.....	6
6.2 pH Determinations.....	6
6.3 TCLP and SPLP Leaching.....	7
7.0 REAGENTS AND STANDARDS.....	8
7.1 Reagents.....	8
8.0 SAMPLE COLLECTION, PRESERVATION, STORAGE, AND HOLDING TIMES.....	9
8.1 Sample Collection and Preservation.....	9
8.2 Sample Storage.....	9
8.3 Contract Required Holding Times.....	10
9.0 CALIBRATION AND STANDARDIZATION.....	10
9.1 pH Meter Calibration.....	10
10.0 PROCEDURE.....	11
10.1 Sample Characterization.....	11
10.2 TCLP and SPLP Extraction Procedures.....	13
11.0 DATA ANALYSIS AND CALCULATIONS.....	21
12.0 QUALITY CONTROL.....	21
12.1 Leachate Extraction Blank.....	21
12.2 Summary of Quality Control Operations.....	21
13.0 METHOD PERFORMANCE.....	21
14.0 POLLUTION PREVENTION.....	21
15.0 WASTE MANAGEMENT.....	22
16.0 REFERENCES.....	22
17.0 TABLES/DIAGRAMS/FLOWCHARTS.....	22

THIS PAGE INTENTIONALLY LEFT BLANK

1.0 SCOPE AND APPLICATION

This Exhibit provides procedures for the use of General Analysis to determine the percent solids of soil/sediment samples, pH, and the leaching of samples by Toxicity Characteristic Leaching Procedure (TCLP) (EPA Method 1311) or Synthetic Precipitation Leaching Procedure (SPLP) (EPA Method 1312).

2.0 SUMMARY OF METHOD

These methods describe the determination of sample characteristics by gravimetry, electrometry, or the leaching of samples for subsequent analysis by the other analytical methods in this Statement of Work (SOW).

3.0 DEFINITIONS

See Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations for a complete list of definitions.

4.0 INTERFERENCES

4.1 pH Determination

- 4.1.1 Samples with very low or very high pH may give incorrect readings on the meter. For samples with a true pH >10, the measured pH may be incorrectly low. This error can be minimized by using a low-sodium-error electrode. Strong acid solutions or samples with a pH <1 may give incorrectly high pH measurements.
- 4.1.2 Coatings of oily material or particulate matter can impair electrode response. These coatings can generally be removed by gentle wiping or detergent washing followed by rinsing with reagent water. Treatment with 10% HCl may be necessary to remove some films.
- 4.1.3 Temperature changes can affect measurements. This can be minimized by use of instruments with temperature compensation. The temperature of the sample can change the sample pH. The temperature at which pH measurements are carried out shall be noted in the pH measurement log.

5.0 SAFETY

See Section 12.0 in Exhibit D - Introduction to Analytical Methods.

6.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here; however, a demonstration of equivalent performance meeting the requirements of this SOW is the responsibility of the Contractor. The Contractor shall document any use of alternate equipment or supplies in the Sample Delivery Group (SDG) Narrative.

All instruments, balances, heating, and measuring equipment and devices shall be uniquely identified and labeled to allow traceability to any corresponding records of use.

6.1 Percent Solids Determination

6.1.1 Disposable weigh boats with covers.

6.1.2 Oven capable of maintaining a temperature of 105°C ($\pm 5^\circ\text{C}$). The oven shall be in a well-ventilated area and shall vent to exhaust outside the facility.

6.1.3 Balance - Top-loader, 300 grams (g) capacity, and a minimum sensitivity of ± 1.0 milligrams (mg).

The balance calibration shall be checked with known masses once per each day of use. This verification shall consist of a check with two weights covering the range expected (approximately $\pm 50\%$ of the expected measured mass) for each balance and be accurate to ± 1.0 mg. The masses that are used to check the balances daily shall be checked on a monthly basis using National Institute of Standards and Technology (NIST)-traceable known reference masses (Class '1' or '2') as defined by ASTM E617-13 or equivalent (e.g., earlier Class 'S' defined masses). All balances shall be checked at least annually by a certified technician. The reference masses used by the Contractor shall be recertified every five years or sooner if there is reason to believe damage (corrosion, nicks) has occurred. The Contractor shall maintain documentation that demonstrates that these criteria have been met.

6.2 pH Determinations

6.2.1 pH meter with reference electrode accurate to at least ± 0.05 pH units. The pH meter/probe shall be equipped with a means of temperature compensation, either manual or automatic.

6.2.2 pH paper, wide-range or narrow-range pH paper strip.

6.2.3 Magnetic stirrer with fluoropolymer-coated stir bar.

6.2.4 Beakers - Preferably glass or polyethylene.

6.2.5 Various volumetric flasks (Class A) and calibrated pipettes. Manufacturer's instructions should be followed for the calibration and maintenance of adjustable pipettes.

6.2.6 Thermometer that covers a range of the sample temperature with a minimum accuracy of $\pm 1^\circ\text{C}$.

6.2.7 Centrifuge - Optional.

6.2.8 Whatman No. 42 filter paper (or equivalent).

6.3 TCLP and SPLP Leaching

- 6.3.1 Agitation Apparatus - Capable of rotating the extraction vessel(s) in an end-over-end fashion at 30 ± 2 revolutions per minute (rpm).
- 6.3.2 Extraction Vessels - Jar with sufficient capacity to hold sample and extraction fluid. Vessels shall be constructed of polytetrafluoroethylene (PTFE), high-density polyethylene, polypropylene, polyvinyl chloride, stainless steel, borosilicate glass, or other suitable inert material.
- 6.3.3 It is recommended that borosilicate glass bottles be used instead of other types of glass for the analysis of inorganic constituents. Stainless steel vessels must not be used when extracts will be analyzed for metals.
- 6.3.4 PTFE, borosilicate glass, or stainless steel are the only materials suitable when TCLP extracts will be analyzed for organic constituents.
- 6.3.5 Filters - Borosilicate glass with no binder material with an effective pore size of 0.6-0.8 micrometers (μm). Acid wash with 1 N nitric acid prior to use, followed by three consecutive rinses with reagent water [a minimum of 1 Liter (L) per rinse is recommended]. Glass fiber filters are fragile and should be handled with care.
- 6.3.6 Filtration Device - Capable of exerting pressures up to 50 pounds per square inch (psi). Use of units having an internal volume of 1.5 L and capable of accommodating a 142 millimeter (mm) filter is recommended.
- 6.3.7 Beaker - 500 milliliters (mL).
- 6.3.8 Balance - Any laboratory balance accurate to within ± 0.01 g may be used (all weight measurements are to be within ± 0.1 g). All requirements in Section 6.1.3 shall be met.
- 6.3.9 Zero-Headspace Extraction (ZHE) Vessel - For volatile analytes, it allows for initial liquid/solid separation, extraction, and final extract filtration without opening the vessel while effectively excluding headspace. The vessel must be made of inert type 316 stainless steel which will not leach or adsorb sample components. The vessel must have an internal volume of 500-600 mL and be equipped to accommodate a 90-110 mm diameter, 0.6-0.8 μm glass fiber filter. The device contains VITON® O-rings which shall be replaced as needed.
- 6.3.10 An in-line glass fiber filter may be used to filter the material within the ZHE vessel when it is suspected that the glass fiber filter has been ruptured.
- NOTE: The ZHE vessel shall be free of contaminants and cleaned between TCLP samples. Manufacturer-recommended testing procedures shall be performed to ensure that the apparatus is functioning properly before proceeding with the extraction.
- 6.3.11 ZHE Extract Collection Devices - TEDLAR® bags or glass, stainless steel, or PTFE gas-tight syringes to collect the initial liquid phase and the final TCLP extract from the ZHE device.
- 6.3.12 ZHE Extraction Fluid Transfer Devices - Capable of transferring the extraction fluid into the ZHE vessel without changing the nature of the extraction fluid (e.g., a positive displacement or peristaltic pump, a gas-tight syringe).

Exhibit D - Sections 6-7

6.3.13 pH meter with reference electrode accurate to at least ± 0.05 units at 25°C. The pH meter/probe shall be equipped with a means of temperature compensation, either manual or automatic.

6.3.14 Magnetic stirrer with a fluoropolymer-coated stir bar.

6.3.15 Centrifuge - Optional.

6.3.16 PTFE thread sealing tape.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

7.1.1 Reagent water - The purity of this water must be equivalent to ASTM Type II water (ASTM D1193-06). Use this water for all reagents, standards, and dilutions. For the preparation of the pH buffer solutions, it may be necessary to boil and cool the water prior to use.

7.1.2 Hydrochloric acid, (1 N) - Add 83.5 mL of concentrated hydrochloric acid, 32-38% (specific gravity 1.19), to 400 mL of reagent water and dilute to 1 L.

7.1.3 Nitric acid, (1 N) - Add 62 mL of concentrated nitric acid, 67-70% (specific gravity 1.41), to 400 mL of reagent water and dilute to 1 L.

7.1.4 Sodium hydroxide, (1 N) - Add 40 g of reagent grade NaOH to 400 mL of reagent water and dilute to 1 L.

7.1.5 Glacial acetic acid - Reagent grade.

7.1.6 Sulfuric acid/Nitric acid, (60/40 weight percent mixture) - Cautiously mix 60 g (approximately 33 mL) of concentrated sulfuric acid, 95-98% (specific gravity 1.84), with 40 g (approximately 28 mL) of concentrated nitric acid. The Contractor may prepare a more diluted version of this reagent for ease in adjusting extraction fluid pH.

7.1.7 Extraction Fluids

Extraction fluids shall be monitored for impurities and the pH checked prior to use. If impurities are found or the pH is not within specifications, the fluid shall be discarded and fresh extraction fluid prepared. Solutions are unbuffered and exact pH may not be attained.

7.1.7.1 TCLP Extraction Fluid #1 - Add 5.7 mL of glacial acetic acid to 500 mL of reagent water, add 64.3 mL of 1 N NaOH solution, and dilute to 1 L. The pH of this solution must be 4.93 ± 0.05 . For ZHE, use TCLP Fluid #1.

7.1.7.2 TCLP Extraction Fluid #2 (do not use Fluid #2 for ZHE) - Dilute 5.7 mL of glacial acetic acid with reagent water to a final volume of 1 L. The pH of this solution must be 2.88 ± 0.05 .

7.1.7.3 SPLP Extraction Fluid #1 - Use this solution with samples from east of the Mississippi River. Add sufficient 60/40 Sulfuric/Nitric acid solution to reagent water until the pH is 4.20 ± 0.05 .

7.1.7.4 SPLP Extraction Fluid #2 - Use this solution with samples from west of the Mississippi River. Add sufficient 60/40 sulfuric/nitric acid solution to reagent water until the pH is 5.00 ± 0.05 .

- 7.1.7.5 SPLP Extraction Fluid #3 - This fluid is reagent water and is used to determine volatiles and cyanide leachability.
- 7.1.8 Standard Buffers for pH meter calibration. At a minimum, two standard buffer solutions are required to bracket the expected pH of the samples. The solutions must be separated by at least three pH units.

8.0 SAMPLE COLLECTION, PRESERVATION, STORAGE, AND HOLDING TIMES

8.1 Sample Collection and Preservation

Aqueous/water samples for TCLP or SPLP extraction and all soil/sediment/waste samples for metals analysis should be collected in glass or polyethylene containers. Aqueous/water samples for TCLP or SPLP extraction for semivolatiles and pesticides analyses and all soil/sediment/waste samples should be collected in glass containers only. ZHE samples should be collected in PTFE-lined septum-capped glass vials. All aqueous/water samples for TCLP or SPLP extraction and all soil/sediment/waste samples should be iced or refrigerated at a temperature of $\leq 6^{\circ}\text{C}$, but not frozen, from the time of collection until receipt at the laboratory.

8.2 Sample Storage

All aqueous/water samples for TCLP or SPLP extractions and all soil/sediment/waste samples shall be stored at $\leq 6^{\circ}\text{C}$, but not frozen, from the time of sample receipt until preparation. ZHE samples shall be opened just prior to extraction to minimize the loss of volatiles and/or contamination with organic vapors in the laboratory environment. All samples (except volatile soil/sediment/waste samples) shall be stored in an upright position.

8.2.1 Unused Sample Storage

Following preparation for percent solids determination or sample characterization, the remaining unused portion of aqueous/water and soil/sediment/waste samples shall be returned to storage at a temperature of $\leq 6^{\circ}\text{C}$, but not frozen, and protected from light. After all applicable leaching procedures, extractions, digestions, and/or distillations have been completed, the remaining unused portion of the aqueous/water and soil/sediment/waste samples shall be stored within the laboratory until 60 days after delivery of a complete, reconciled data package to the U.S. Environmental Protection Agency (EPA). The Contractor may store these samples at room temperature. After 60 days, the samples may be disposed of in a manner that complies with all applicable regulations.

8.2.2 Leachate Sample Storage

The remaining unused portion of the preserved TCLP or SPLP leachates shall be stored within the laboratory until 180 days after delivery of a complete, reconciled data package to the EPA. The Contractor may store these samples at room temperature.

8.2.3 Container Storage

The Contractor shall retain the empty sample containers for 60 days after delivery of a complete, reconciled data package to the EPA. The sample container may be photographed in lieu of retention.

8.2.4 Temperature Records

- 8.2.4.1 The temperature of all sample and sample extract storage refrigerators and freezers shall be recorded daily.

Exhibit D - Sections 8-9

- 8.2.4.2 Temperature excursions shall be noted and appropriate corrective actions shall be taken to correct problems, when required.
- 8.2.4.3 Corrective action Standard Operating Procedures (SOPs) shall be posted on the refrigerators and freezers.

8.3 Contract Required Holding Times

- 8.3.1 The holding time for ZHE extraction of volatile soil/sediment/waste samples containing $\geq 0.5\%$ solids is 10 days from the Validated Time of Sample Receipt (VTSR). The holding time for TCLP or SPLP extraction of non-volatile organic soil/sediment/waste samples containing $\geq 0.5\%$ solids is 10 days from VTSR.
- 8.3.2 The holding time for TCLP or SPLP filtration of volatile and non-volatile aqueous/water samples is 5 days from VTSR.
- 8.3.3 The holding time for TCLP or SPLP extraction of metals samples (all matrices) is 180 days from VTSR. The holding time for TCLP or SPLP extraction of mercury samples (all matrices) is 26 days from VTSR. The holding time for SPLP extraction of cyanide samples (all matrices) is 12 days from VTSR.

9.0 CALIBRATION AND STANDARDIZATION

9.1 pH Meter Calibration

Because of the differences between various makes and models of satisfactory instruments, no detailed operating instructions can be provided. Instead, the analyst should follow the instructions provided by the manufacturer of the particular instrument. Each instrument and electrode shall be calibrated at a minimum of two points that bracket the expected pH of the samples. The calibration points must be separated by at least three pH units.

Adjust the meter until the readings are within ± 0.05 pH units of the buffer solution value. Verify and document that pH meter calibration is acceptable by measuring the pH of a certified buffer between the calibrated buffer pH values and achieves a measured pH within ± 0.05 pH units of the certified pH.

10.0 PROCEDURE

10.1 Sample Characterization

10.1.1 Percent Solids Determination

Percent Solids determination is based on Standard Method (SM) 2540G. This procedure is required for soil/sediment samples only.

- 10.1.1.1 Transfer 5-10 g of sample to an individually tared weighing boat and record the total weight to the nearest 0.01 g. Sample handling and drying shall be conducted in a well-ventilated area.
- 10.1.1.2 Dry the sample in an oven maintained at 105°C (±5°C) for at least 12 hours, but no more than 24 hours. At the start of drying and at the end of drying, record the oven temperature and date/time.
- 10.1.1.3 Remove the sample from the oven and allow it to cool in a desiccator.
- 10.1.1.4 Weigh the sample to the nearest 0.01 g and calculate the percent solids using Equation 29 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations. This value will be used for calculating the analytical concentrations on a dry weight basis.
- 10.1.1.5 For 14 and 21-day turnaround samples without Preliminary Results, the Contractor is required to perform the percent solids determination prior to sample preparation and analysis. This requirement does not apply to 7-day turnaround or Preliminary Results samples.
- 10.1.1.6 For samples scheduled for semivolatile, pesticide, or Aroclor analysis, if the sample contains ≤30% solids, the Contractor shall notify the Sample Management Office (SMO) immediately of the samples affected. SMO will contact the EPA Region for instructions. The EPA Region may require the Contractor to do any of the following:
 - Use a higher mass of soil/sediment sample (up to 50 g).
 - Separate the phases by centrifugation or settling and analyze one or more of the phases separately. SMO will provide EPA Sample Numbers for the additional phases, if required.
 - Not analyze the sample.
- 10.1.1.7 For samples scheduled for Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES), Inductively Coupled Plasma - Mass Spectrometry (ICP-MS), mercury, cyanide, anions, and Total Organic Carbon (TOC) analysis, if the samples contain ≤30% solids, the Contractor shall prepare the samples at higher sample weights for all analytical methods to yield a dry weight equivalent to the weight range specified in the analytical preparation method.
 - 10.1.1.7.1 Calculate the required sample weight by dividing the minimal method weight specified in the method by the percent solids expressed as a decimal using Equation 30 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.
- 10.1.1.8 For samples containing >30% solids and <50% solids, the Contractor shall proceed with sample analysis and document the issue in the SDG Narrative.
- 10.1.1.9 For samples containing ≥50% solids, proceed with sample analysis.

Exhibit D - Section 10

10.1.1.10 Duplicate analyses are not required for percent solids determination.

10.1.2 pH Determinations

10.1.2.1 Aqueous/Water pH Determination

The determination of pH is required for all aqueous/water samples at the time of the receipt at the laboratory or after sample aliquots have been taken. To verify the preservation of aqueous/water volatile organic, metals, mercury, cyanide, hexavalent chromium, or TOC samples, the use of pH paper is sufficient. The Contractor shall follow the procedures for pH measurement based on EPA Method 9041A or EPA Method 9040C [electrometric method (i.e., pH meter and electronic hand-held pen)].

- For samples scheduled for ICP-AES, ICP-MS, or mercury analysis, if the pH is >2 , the Contractor shall add sufficient nitric acid to the sample to reduce the pH to ≤ 2 , return the sample to storage for a minimum of 16 hours before proceeding with the preparation of the sample, and document the pH adjustment in the SDG Narrative.
- For samples scheduled for cyanide analysis, if the pH is <10 , the Contractor shall immediately notify SMO of the affected sample(s) and pH value(s). SMO will contact the EPA Region. The EPA Region may require the Contractor to either proceed with the analysis or to not analyze the sample(s). The EPA resolution shall be documented in the SDG Narrative.
- For samples scheduled for hexavalent chromium analysis, if the pH is ≤ 8 , the Contractor shall immediately notify SMO of the affected sample(s) and pH value(s). SMO will contact the EPA Region. The EPA Region may require the Contractor to either proceed with the analysis or to not analyze the sample. The EPA resolution shall be documented in the SDG Narrative.
- For samples scheduled for TOC analysis, if the pH is >2 , the Contractor shall immediately notify SMO of the affected sample(s) and pH value(s). SMO will contact the EPA Region. The EPA Region may require the Contractor to either proceed with the analysis or to not analyze the sample(s). The EPA resolution shall be documented in the SDG Narrative.
- For aqueous samples scheduled for volatile organic analysis, sample pH is not measured until after an aliquot of the sample is removed.

10.1.2.1.1 pH Measurement by pH Paper

Place one or two drops of sample on the pH paper and record the pH for the sample.

10.1.2.1.2 pH Measurement by Electrometric Method

10.1.2.1.2.1 Transfer a sufficient volume of sample to a beaker to cover the sensing elements of the electrode(s) and to give adequate clearance for the magnetic stirring bar. The sample shall not be diluted.

10.1.2.1.2.2 If the sample temperature differs by more than 2°C from the temperature of the buffer solutions used to standardize the meter, the measured pH values shall be corrected.

- 10.1.2.1.2.3 After rinsing and gently wiping the electrode(s) if necessary, immerse the electrode(s) in the sample beaker and stir at a constant rate to provide homogeneity and suspension of solids. The rate of stirring shall minimize the air transfer rate at the air/water interface. Record the sample pH and the temperature. Repeat measurements on successive volumes of sample until values differ by less than 0.1 pH units.

10.1.2.2 Soil/Sediment pH Determination

The determination of pH for soil/sediment samples is not required as a routine procedure to be completed at the laboratory.

However, if requested at the time of scheduling, the Contractor shall follow the procedures based on the EPA Method 9045D to determine the pH by electrometric method (i.e., pH meter or electronic hand-held pen).

- 10.1.2.2.1 Transfer 20 g of well-mixed sample to a 50 mL beaker, add 20 mL of reagent water, cover, and continuously stir the suspension for 1 hour. Additional water may be added if the soils are hygroscopic or contain large amounts of salts.
- 10.1.2.2.2 Let the soil suspension stand for at least 1 hour to allow most of the suspended clays to settle. Difficult samples may be filtered or centrifuged to separate the aqueous layer for pH determination. If the supernatant is biphasic, decant the oily phase and measure the pH of the aqueous phase.
- 10.1.2.2.3 Measure and record the pH for the sample.
- 10.1.2.2.4 Measure and record the temperature for the sample. If the sample temperature differs by more than 2°C from the temperature of the buffer solutions used to standardize the meter, the measured pH values shall be corrected.

10.2 TCLP and SPLP Extraction Procedures

The extraction methods are based on EPA Method 1311, Toxicity Characteristic Leaching Procedure (TCLP) or EPA Method 1312, Synthetic Precipitation Leaching Procedure (SPLP).

TCLP vessels and devices shall be free of contaminants and cleaned between TCLP samples. Testing procedures shall be performed to ensure the apparatus is functioning properly before proceeding with the extraction.

10.2.1 Preliminary Evaluation

Perform preliminary evaluation on a minimum 100 g sample aliquot. This aliquot will not undergo extraction. These preliminary evaluations include: (1) determination of percent solids by pressure filtration; (2) determination of whether the sample contains insignificant (<0.5%) solids and is therefore its own extract after filtration; (3) determination of whether the solid portion of the sample requires particle size reduction; and for TCLP samples, (4) determination of the appropriate extraction fluid for leaching of the solid fraction.

- 10.2.1.1 Preliminary determination of percent solids - For these samples, percent solids is defined as that fraction of a sample (as a percentage of the total sample) from which no liquid can be forced out by applied pressure.

Exhibit D - Section 10

- 10.2.1.1.1 If a sample will obviously yield no liquid when subjected to pressure filtration (i.e., is 100% solids), proceed to extraction.
- 10.2.1.1.2 If the sample is liquid or multiphasic, liquid/solid separation is required to make a preliminary determination of percent solids.
 - 10.2.1.1.2.1 Pre-weigh the filter and the container that will receive the filtrate.
 - 10.2.1.1.2.2 Assemble the filter holder and filter per the manufacturer's instructions. Place the filter on the support screen and secure.
 - 10.2.1.1.2.3 Weigh out at least 100 g of the sample and record the weight.
 - 10.2.1.1.2.4 Allow slurries to stand to permit the solid phase to settle. Samples that settle slowly may be centrifuged prior to filtration. Centrifugation is to be used only as an aid to filtration. If used, the liquid shall be decanted and filtered, followed by filtration of the solid portion of the sample through the same filtration system.
 - 10.2.1.1.2.5 Quantitatively transfer the sample to the filter holder (both liquid and solid phases). Spread the sample evenly over the surface of the filter. If filtration of the waste material at a temperature of $\leq 6^{\circ}\text{C}$ reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm to room temperature in the device before filtering. If waste material ($>1\%$ of original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Section 10.2.1.1.2.8 to determine the weight of sample that will be filtered.
 - 10.2.1.1.2.6 Gradually apply gentle pressure of 1-10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2-minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2-minute interval, proceed to the next 10 psi increment. When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within any 2-minute period), stop the filtration. Note that instantaneous application of high pressure can damage the filter and may cause premature plugging.
 - 10.2.1.1.2.7 The material retained on the filter is defined as the solid phase of the sample, and the filtrate is defined as the liquid phase. Note that certain oily wastes and paint wastes will contain material that appears to be a liquid. However, this material may not filter under pressure filtration. In this case, the material within the filtration device is defined as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

- 10.2.1.1.2.8 Determine the weight of the liquid phase by subtracting the weight of the filtrate container from the total weight of the filtrate-filled container. Determine the weight of the solid phase by subtracting the weight of the liquid phase from the total weight of the sample. Record the weights of the liquid and solid phases. Calculate the percent solids using Equation 31 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.
- 10.2.1.1.2.9 If the percent solids determined is $\geq 0.5\%$, then proceed to Section 10.2.1.3 to determine whether the solid material requires particle size reduction.
- 10.2.1.1.2.10 If it is noticed that a small amount of the filtrate is entrained in wetting of the filter, remove the solid phase and filter from the filtration apparatus. Dry the filter and solid phase at 100°C ($\pm 20^{\circ}\text{C}$) until two successive weighings yield the same value (within $\pm 1\%$) and record the weight.
- NOTE: Caution shall be taken to ensure that the subject solid will not flash upon heating. It is recommended that the drying oven be vented to a hood or other appropriate device.
- 10.2.1.1.2.11 Calculate the percent dry solids using Equation 32 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.
- 10.2.1.2 If the percent dry solids is $< 0.5\%$, then treat the filtrate as the extract. Store this extract at a temperature of $\leq 6^{\circ}\text{C}$.
- 10.2.1.3 To determine if particle size reduction is required, using a fresh portion of sample, examine the solid portion for particle size. If the material is less than 1 centimeter (cm) in its narrowest dimension (i.e., is capable of passing through a 9.5 mm standard sieve), no particle size reduction is required. Otherwise, prepare the solid portion for extraction by crushing, cutting, or grinding the sample to meet the above criterion.
- 10.2.1.3.1 Special precautions shall be taken when processing solid samples for organic volatiles extraction. Wastes and appropriate reduction equipment shall be refrigerated, if possible, to $\leq 6^{\circ}\text{C}$ prior to particle size reduction. The means used to affect particle size reduction must not generate heat. If reduction of the solid phase of the waste is necessary, exposure of the waste to the atmosphere shall be minimized.
- 10.2.1.4 For samples that are scheduled for extraction with percent solids $\geq 0.5\%$, the appropriate extraction fluid is determined as follows:
- NOTE: TCLP extraction for volatile constituents uses only TCLP Extraction Fluid #1. Therefore, if TCLP extraction only for volatiles is required, proceed to Section 10.2.3.
- 10.2.1.4.1 For samples scheduled for TCLP extraction of non-volatile constituents, remove a small aliquot of the sample and reduce the particle size to less than 1 mm. Transfer 5 g of this material to a 500 mL beaker or Erlenmeyer flask.
- 10.2.1.4.1.1 Add 96.5 mL of reagent water, cover with a watch glass, and stir vigorously for 5 minutes using a magnetic stirrer. Measure and record the pH.

Exhibit D - Section 10

10.2.1.4.1.1.1 If the pH is <5.0, use TCLP Extraction Fluid #1 (Section 7.1.7.1).

10.2.1.4.1.1.2 If the pH is ≥ 5.0 , add 3.5 mL of 1 N HCl (Section 7.1.2), slurry briefly, cover with the watch glass, and heat to 50°C for 10 minutes. Let the solution cool to room temperature and measure the pH. If the pH is <5.0, use TCLP Extraction Fluid #1 (Section 7.1.7.1), otherwise use TCLP Extraction Fluid #2 (Section 7.1.7.2).

NOTE: DO NOT USE TCLP EXTRACTION FLUID #2 FOR ZHE SAMPLES.

10.2.1.4.2 Use the SPLP extraction fluid appropriate to the information provided on the scheduling document.

10.2.1.4.2.1 For soil/sediment samples from east of the Mississippi River, use SPLP Extraction Fluid #1. For samples from west of the Mississippi River, use SPLP Extraction Fluid #2.

10.2.1.4.2.2 For samples scheduled for SPLP ZHE extraction or cyanide, use SPLP Extraction Fluid #3 (Section 7.1.7.5).

10.2.2 TCLP Sample Extraction

Follow this procedure for TCLP leachates that will be analyzed for non-volatile organic, metals, or mercury target analytes. For volatile organic analysis, use the ZHE procedure in Section 10.2.3.

10.2.2.1 A minimum sample size of 100 g is required; however, enough solids shall be extracted to yield a sufficient volume of extract to support all required analyses. In some cases, a larger sample size may be appropriate, depending on the solids content of the waste sample and whether the initial liquid phase of the waste will be miscible with the aqueous extract of the solid. See Section 10.2.2.3 to determine the approximate amount of extract that will be generated for a given mass with the percent solids determined in Section 10.2.1.1.2.11.

10.2.2.1.1 If the sample is 100% solids, then weigh out 100 g of sample and proceed to Section 10.2.2.3.

10.2.2.1.2 If the sample is <0.5% solids, filter enough sample to yield a sufficient volume of extract to support all required analyses if the preliminary percent solids determination did not yield sufficient volume.

10.2.2.1.3 For multiphasic samples with percent solids $\geq 0.5\%$ but <100%, weigh out enough sample to generate a sufficient volume of extract to support all required analyses. Filter the sample using the procedure described in Section 10.2.1. Store the filtrate at $\leq 6^\circ\text{C}$, but not frozen.

10.2.2.2 Prepare the solid portion of the sample for extraction by reducing the particle size as described in Section 10.2.1.3. Quantitatively transfer the material into an extractor bottle and include the filter used to separate the initial liquid from the solid phase.

10.2.2.3 Determine the amount of extraction fluid to add to the extractor bottle using Equation 33 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

- 10.2.2.4 Add the calculated amount of the appropriate extraction fluid (Section 10.2.1.4) to the extractor bottle. Close the bottle tightly (Teflon® tape may be used to ensure a tight seal) and secure it in the rotary agitation apparatus. Rotate the samples at 30 rpm (± 2 rpm) for 18 hours (± 2 hours). Maintain a temperature of 23°C (± 2 °C) in the room where extraction is performed.

NOTE: As agitation continues, pressure may build up within the extractor bottle for some types of samples (e.g., limed or calcium carbonate-containing sample may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be periodically opened (e.g., after 15 minutes, 30 minutes, and 1 hour) and vented into a hood.

- 10.2.2.4.1 Following the 18-hour extraction, separate the material in the extractor bottle into its component liquid and solid phase by filtering through a new glass filter as described in Section 10.2.1.1. For the final filtration of the extract, the glass fiber filter may be changed as necessary during filtration.
- 10.2.2.4.2 If the sample was 100% solids, this filtered liquid is the extract.
- 10.2.2.4.3 For multiphasic samples, combine this extract with the filtrate generated in Section 10.2.2.1.3 if the two liquids are miscible. If the two liquids are not miscible, they shall be prepared and analyzed separately and the analytical results mathematically combined.
- 10.2.2.4.4 Record the pH of the final extract. If organic and inorganic analyses are required on the sample, separate approximately 3/4 of the sample extraction fluid for organic analysis and store in an amber glass bottle.
- 10.2.2.4.5 Preserve extracts for metals and mercury with nitric acid to pH ≤ 2 . Preserve SPLP extracts for cyanide analysis with NaOH to pH ≥ 10 and store at ≤ 6 °C.
- 10.2.2.4.6 DO NOT ACIDIFY OR PRESERVE ANY PORTION OF AN EXTRACT INTENDED FOR ORGANIC ANALYSIS. Do not acidify any non-aqueous portion of the sample.

CAUTION: Nitric acid shall not be mixed with organic compounds because of the possibility of dangerous reaction.

10.2.3 Zero Headspace Extraction

Use ZHE for the TCLP sample extraction for analysis of volatile organic target analytes. For non-volatile organic, metals, and mercury target analytes, follow the TCLP Sample Extraction procedure in Section 10.2.2. Follow the manufacturer's instructions for operation of the ZHE apparatus.

10.2.3.1 Maintaining the ZHE Apparatus

- 10.2.3.1.1 The ZHE vessel and devices shall be free of contaminants and cleaned between TCLP samples. Manufacturer-recommended testing procedures shall be performed to ensure that the apparatus is functioning properly before proceeding with the extraction.

Exhibit D - Section 10

- 10.2.3.1.2 Disassemble and clean the ZHE parts using laboratory detergent. Rinse with methanol and water until there is no visible contamination when surfaces are wiped with a clean paper towel. Bake ZHE metal parts overnight in an oven at 170°C.
- 10.2.3.1.3 Reassemble the ZHE and check that it is clean by adding 250 mL of laboratory reagent water, pressurizing the unit, and tumbling for about 1 hour, making sure it is pressure tight. Collect the laboratory reagent water and analyze as a check sample by Gas Chromatography/Mass Spectrometry (GC/MS) to determine if the ZHE is clean. If any target analytes are detected, disassemble the ZHE and repeat the cleaning.
- 10.2.3.1.4 Record the date, time, and results of each cleaning check in a ZHE laboratory log.
- 10.2.3.1.5 Disassemble, clean, and check the ZHE. Allow the parts to air dry. Cover the ZHE components in aluminum foil and store in the volatile organics analysis laboratory until use.
- 10.2.3.1.6 Check the ZHE for leaks after every extraction. Pressurize the ZHE to 50 psi, allow it to stand unattended for 1 hour, and recheck the pressure. If the ZHE device does not have a pressure gauge, submerge the pressurized ZHE in water and check for air leaks. If the ZHE is leaking, check all fittings, inspect O-rings, and replace if necessary. Retest the device. If the leakage cannot be solved, the ZHE shall be taken off-line and sent to the manufacturer for repairs.
- 10.2.3.1.7 The piston within the ZHE device must be movable with approximately 15 psi or less. If more than 15 psi is required to move the piston, replace the O-rings. If this does not free up the piston, the ZHE shall be taken off-line and sent to the manufacturer for repairs.
- 10.2.3.2 Zero Headspace Extraction of Volatile Compounds
 - 10.2.3.2.1 The ZHE has a 500 mL internal capacity and accommodates a maximum of 25 g of solid based on the need to add an amount of extraction fluid equal to 20 times the weight of the solid phase (fraction of sample from which no additional liquid may be forced out when 50 psi is applied).
 - 10.2.3.2.2 Charge the ZHE with sample only once and do not open the device until the final extract (of the solid) has been collected. Repeated filling of the ZHE to obtain 25 g of solid is not permitted.
 - 10.2.3.2.3 Do not allow the sample, the initial liquid phase, or the extract to be exposed to the atmosphere for any more time than is absolutely necessary.
 - 10.2.3.2.4 Pre-weigh the evacuated filtrate collection container and set aside.
 - 10.2.3.2.5 Place the ZHE piston within the body of the ZHE. Adjust the height of the piston to minimize the travel distance once the ZHE is charged with the sample. Secure bottom flanges. Secure the glass fiber filter between the support screens and set the top flanges according to the manufacturer's instructions.
 - 10.2.3.2.6 If the sample is 100% solids, then weigh a maximum of 25 g and proceed to Section 10.2.3.2.9.

- 10.2.3.2.7 If the sample is <0.5% solids, filter enough sample to yield a sufficient volume of extract to support all volatile analyses required.
- For samples containing $\geq 0.5\%$ solids, use the percent solids determination in Section 10.2.1.1.2.8 to determine the sample size to add to the ZHE using Equation 34 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.
- 10.2.3.2.8 For multiphasic samples, weigh out enough sample to generate a sufficient volume of extract to support all required analyses. Filter the sample using the procedure described in Sections 10.2.1.1.2.7 - 10.2.1.1.2.9. Store the filtrate at a temperature of $\leq 6^{\circ}\text{C}$.
- 10.2.3.2.9 Prepare the solid portion of the sample for extraction by reducing the particle size as described in Section 10.2.1.3.
- 10.2.3.2.10 Determine the amount of TCLP Extraction Fluid #1 to add to the ZHE using Equation 33 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.
- 10.2.3.2.11 Quickly transfer the entire sample (liquid and solid phases) quantitatively to the ZHE. Secure the filter and support screens onto the top flange of the device. Secure the top flange. Tighten all ZHE fittings according to the manufacturer's instructions. Place the ZHE device in vertical position with the gas inlet/outlet flange on the bottom. Do not attach the extract collection device to the top plate at this stage.
- 10.2.3.2.12 Attach a gas line to the gas inlet/outlet valve (bottom flange) and, with the liquid inlet/outlet valve (top flange) open, begin applying gentle pressure of 1-10 psi (or more if necessary) to force all headspace slowly out of the ZHE device into a hood. At the first appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue pressure.
- NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.
- 10.2.3.2.13 Attach the evacuated pre-weighed filtrate collection container (Section 10.2.3.2.4) to the liquid inlet/outlet valve and open the valve. Begin applying gentle pressure of 1-10 psi to force the liquid phase of the sample into the filtrate collection container. If no additional liquid has passed through the filter in any 2-minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. When liquid flow has ceased such that continued pressure filtration at 50 psi does not result in any additional filtrate within a 2-minute period, stop the filtration. Close the liquid inlet/outlet valve, discontinue pressure to the piston, and disconnect and weigh the filtrate collection container.
- 10.2.3.2.14 The material in the ZHE is defined as the solid phase of the sample and the filtrate is defined as the liquid phase.

NOTE: Oily samples and some paint samples may contain material that appears to be a liquid. If after applying pressure filtration the material will not filter, it shall be defined as a solid and is carried through the TCLP extraction as a solid. If the original sample contained <0.5% dry solids, this filtrate shall be defined as the TCLP extract and analyzed directly.

- 10.2.3.2.15 With the ZHE device in the vertical position, attach a line from the extraction fluid reservoir to the liquid inlet/outlet valve. Add the appropriate amount of the TCLP Extraction Fluid #1 to solid material within the ZHE device.
- 10.2.3.2.16 The line used shall contain fresh TCLP Extraction Fluid #1 and shall be pre-flushed with fluid to eliminate any air in the line. Release gas pressure on the ZHE piston (from the gas inlet/outlet valve), open the liquid inlet/outlet valve, and begin transferring extraction fluid (by pumping or similar means) into the ZHE. Continue introducing extraction fluid into the ZHE until the appropriate amount of fluid has been introduced into the device.
- 10.2.3.2.17 Close the liquid inlet/outlet valve and disconnect the extraction fluid line. Check the ZHE to ensure that all valves are in their closed positions. Manually rotate the device in an end-over-end fashion 2 or 3 times. Reposition the ZHE in the vertical position with the liquid inlet/outlet valve on top. Pressurize the ZHE to 5-10 psi (if necessary) and slowly open the liquid inlet/outlet valve to bleed out any headspace (into a hood) that may have been introduced due to the addition of extraction fluid. The bleeding shall be done quickly and stopped at the first appearance of liquid from the valve. Re-pressurize the ZHE with 5-10 psi and check all ZHE fittings to ensure that they are closed.
- 10.2.3.2.18 Secure the ZHE device in the rotary agitation apparatus. Rotate the samples at 30 rpm (± 2 rpm) for 18 hours (± 2 hours). Maintain a temperature of 23°C (± 2 °C) in the room where the extraction is performed.
- 10.2.3.2.19 Following the 18-hour extraction period, check that the ZHE is not leaking by observing the pressure gauge or by quickly opening and closing the gas inlet/outlet valve, and noting the escape of gas. There will be no escape of gas if the device is leaking. If the ZHE device was leaking, perform the extraction again with a new sample.
- 10.2.3.2.20 If the pressure within the device has been maintained, the material in the extractor vessel shall be once again separated into its component liquid and solid phases. If the sample contained an initial liquid phase, the liquid may be filtered directly into the same filtrate collection container holding the initial liquid phase of the sample.
- 10.2.3.2.21 A separate filtrate collection container shall be used if combining would create multiple phases, or there is not enough volume left within the filtrate collection container. Filter through the glass fiber filter, using the ZHE device as discussed. All extracts shall be filtered and collected in the collection container if the extract is multiphasic, or if the sample contained an initial liquid phase.

NOTE: An in-line glass fiber filter may be used to filter the material within the ZHE if it is suspected that the glass fiber filter has been ruptured.

If the original sample contained no initial liquid phase, the filtered liquid material obtained from ZHE procedure shall be defined as the TCLP extract. If the sample contained an initial liquid, the filtered liquid material obtained from the ZHE procedure and the initial liquid phase shall be collectively defined as the TCLP extract.

- 10.2.3.2.22 Following collection of the TCLP extract, immediately prepare the extract for analysis, and store with minimal headspace at a temperature of $\leq 6^{\circ}\text{C}$ until analyzed.

If the individual phases are to be analyzed separately (i.e., are not miscible), determine the volume of the individual phases (to 0.5%), conduct the appropriate analyses, and combine the results mathematically by using the volume-weighted average in Equation 35 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

10.2.4 SPLP Sample Extraction

The Contractor shall follow the procedures in Section 10.2.2 using the appropriate extraction fluid specified in Section 10.2.1.4.2.

11.0 DATA ANALYSIS AND CALCULATIONS

See Section 11.0 in the individual analytical methods for data analysis, and Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations for calculations.

12.0 QUALITY CONTROL

12.1 Leachate Extraction Blank

- 12.1.1 The Leachate Extraction Blank (LEB) shall contain all the reagents and in the same volumes as used in extracting the samples. The LEB shall be carried through the complete extraction procedure.
- 12.1.2 At least one LEB, consisting of the appropriate extraction fluid processed through the extraction procedure, shall be extracted with every SDG scheduled for TCLP or SPLP.
- 12.1.3 Each Complete SDG File (CSF) shall contain the results of all LEB analyses associated with the samples in that SDG.
- 12.1.4 The LEB(s) result(s) is (are) to be reported for each SDG and used in all analyses to ascertain whether sample concentrations reflect contamination.
- 12.1.5 Under no circumstances shall the LEB be analyzed at a dilution.

12.2 Summary of Quality Control Operations

The Quality Control (QC) operations performed are summarized in Section 17.0, Table 1 - Quality Control Operations.

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

See Section 13.0 in Exhibit D - Introduction to Analytical Methods.

Exhibit D - Sections 15-17

15.0 WASTE MANAGEMENT

See Section 14.0 in Exhibit D - Introduction to Analytical Methods.

16.0 REFERENCES

- 16.1 American Water Works Association/American Public Health Association/Water Environment Federation, Standard Methods for the Examination of Water and Wastewater, Method 2540G, Solids, Total, Fixed, and Volatile Solids in Solid and Semisolid Samples.
- 16.2 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 1311, Toxicity Characteristic Leaching Procedure, Revision 0, Update III, July 1992.
- 16.3 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 1312, Synthetic Precipitation Leaching Procedure, Revision 0, Update III, September 1994.
- 16.4 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 9040C, pH Electrometric Measurement, Revision 3, November 2004.
- 16.5 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 9041A, pH Paper Method, Revision 1, July 1992.
- 16.6 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 9045D, Soil and Waste pH, Revision 4, November 2004.
- 17.0 TABLES/DIAGRAMS/FLOWCHARTS

TABLE 1. QUALITY CONTROL OPERATIONS

QC Operation	Frequency
Leachate Extraction Blank (LEB)	For each SDG, an LEB for each extraction procedure.