EXHIBIT D

INTRODUCTION TO INORGANIC ANALYTICAL METHODS

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Exhibit D – Introduction to Inorganic Analytical Methods

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1.0 INTRODUCTION

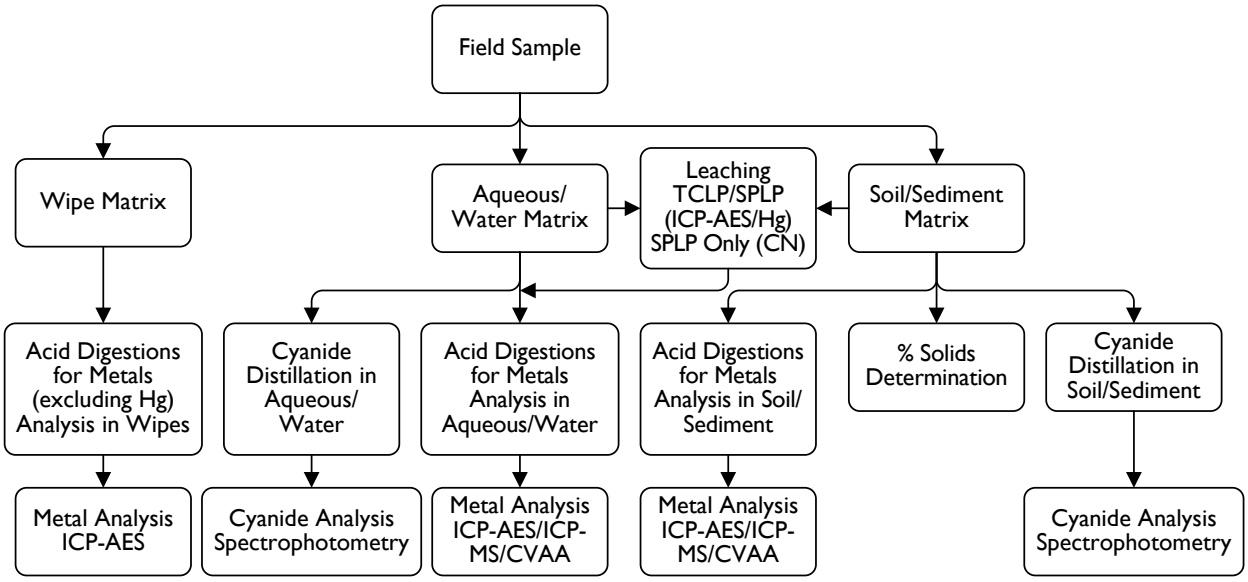
The inorganic analytical service provides a contractual framework for laboratories. This framework applies the U.S. Environmental Protection Agency (EPA) Contract Laboratory Program (CLP) analytical methods for the isolation, detection, and quantitative measurement of 23 metals (including mercury) and cyanide in aqueous/water, soil/sediment, and 22 metals (excluding mercury) in wipe samples.

The analytical methods that follow are designed to analyze aqueous/water, leachate, soil/sediment, and wipe samples from hazardous waste sites for the presence of inorganic analytes contained in the Inorganic Target Analyte List and Contract Required Quantitation Limits (see Exhibit C – Inorganic Target Analyte List and Contract Required Quantitation Limits). The inorganic methods include multiple preparation procedures and Quality Control (QC) requirements. Analytical techniques in the inorganic methodologies include Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES), Inductively Coupled Plasma - Mass Spectrometry (ICP-MS), Cold Vapor Atomic Absorption Spectroscopy (CVAA), and Spectrophotometry.

2.0 INORGANIC METHODS FLOW CHART

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



3.0 GLASSWARE CLEANING

Laboratory glassware to be used within the metals and cyanide analyses must 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. Equivalent procedures are those which meet the Preparation Blank requirements in the Statement of Work (SOW). 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).

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 of Exhibit D. Stock solutions that are past the manufacturer's expiration date shall not be used to prepare analytical standards.

5.0 VERIFICATION OF AQUEOUS/WATER SAMPLE PRESERVATION

5.1 At the time of sample receipt, the Contractor shall check the pH of the sample and note in a sample receipt log if the pH is less than or equal to 2 for metals or is greater than or equal to 10 for a cyanide sample.

5.1.1 If a metals sample has not been properly preserved, the Contractor shall adjust the pH of the sample(s) for metals (according to procedures in Exhibit D) and note this in the Sample Delivery Group (SDG) Narrative.

5.1.2 The Contractor shall not adjust the pH of a sample for cyanide. 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 samples scheduled for Toxicity Characteristic Leaching Procedure (TCLP) or Synthetic Precipitation Leaching Procedure (SPLP) extraction.

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 apprise 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.
- Do not analyze the sample.

6.1.2 If all 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.

- Do not analyze the sample.

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

7.0 SAMPLE DILUTIONS

7.1 All samples for multi-analyte analysis shall be analyzed undiluted, unless the dilution-adjusted detection limits for all analytes are below the Contract Required Quantitation Limits (CRQLs).

7.2 Samples analyzed by ICP-MS (according to procedures in Exhibit D - Inductively Coupled Plasma - Mass Spectrometry) may be analyzed at 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. The Contractor shall use the least dilution necessary to bring the analyte(s) instrument reading within the upper 75% of the calibrated range and report the highest valid value for each analyte as measured from the undiluted and diluted analyses. Unless the Contractor can submit proof that dilution was required to obtain valid results, or to avoid damage to ICP-MS instruments, both diluted and undiluted sample measurements must be contained in the raw data.

7.4 For single analyte analysis, a diluted sample analysis may be the only sample analysis performed if the analyte's instrument result is either greater than fifty (50) times the CRQL, or 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/or duplicate shall initially be analyzed at the same dilution.

7.5 All sample dilutions shall be made with reagent water mixed with the appropriate acid(s) (metals) or base (cyanide) to be consistent with the acid or base concentration in the digestate or distillate.

8.0 DISSOLVED METALS

If dissolved metals are requested by the EPA Regional Offices, the Contractor shall digest the field-filtered samples according to the procedures in Exhibit D of the analytical method and report as dissolved metals.

9.0 REPLICATE INTEGRATIONS/EXPOSURES

If the Contractor analyzes samples using multiple integrations/exposures, the Contractor must 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 deliverable requirements are specified in Exhibit B – Reporting and Deliverables Requirements, Section 2.4. Raw data collected and provided in association with the performance of analyses under this contract shall conform to the appropriate sections of Exhibit B.

11.0 ANALYTICAL STANDARDS REQUIREMENTS

The EPA will not supply analytical reference standards for either direct analytical measurements or the purpose of traceability. All contract laboratories 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 the Neat High Purity Bulk Material

11.1.1 If the laboratory cannot obtain analytical reference standards, the laboratory may prepare its own chemical standards. Laboratories 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 chemicals is essential to safeguard them from decomposition.

11.1.3 The Contractor is responsible for having analytical documentation demonstrating that the purity of each chemical is correctly stated. Purity confirmation, when performed, should use appropriate techniques. 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 the following equation:

EQ. 1 Weight of Impure Compound

$$\text{Weight of Impure Chemical} = \frac{\text{weight of pure chemical}}{(\text{percent purity}/100)}$$

WHERE,

Weight of Pure Chemical = That required to prepare a specific volume of a solution standard of a specified concentration.

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 or analytes, concentration, the standard ID number of the solution, date prepared, solvent, expiration date of the solution, special storage requirements (if any), and initials of the preparer.

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 Contracting Officer's Representative (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

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 Material Safety Data Sheets (MSDS) shall be made available to all personnel involved in the chemical analysis.

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.

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EXHIBIT D

GENERAL INORGANIC ANALYSIS

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Exhibit D - General Inorganic Analysis

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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) (SW-846 Method 1311) or Synthetic Precipitation Leaching Procedure (SPLP) (SW-846 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 - Glossary of Terms 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 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.

5.0 SAFETY

See Section 12.0 in Exhibit D - Introduction to Inorganic 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.

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 (±5°C). Oven shall be in a well-ventilated area.

6.1.3 Balance – Top loader, 300 grams (g) capacity with a minimum sensitivity of ±1.0 milligrams (mg)

The balance calibration must be checked with known masses once per each day of use. This verification consists of a check with two weights covering the range expected (approximately ±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 must 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 E617-97 (2008) or equivalent (e.g., earlier Class 'S' defined masses). All balances must be checked at least once annually by a certified technician. The reference masses used by the Contractor must 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 should be equipped with a means of temperature compensation either manually or automatically.

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 polyethylene or polytetrafluoroethylene (PTFE).

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 ±1°C.

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 rpm.

6.3.2 Extraction Vessels – Jar with sufficient capacity to hold sample and extraction fluid. Vessels may be constructed of PTFE, high-density polyethylene, polypropylene, polyvinyl chloride, or other suitable inert material. It is recommended that borosilicate glass bottles be used instead of other types of glass for the analysis of inorganic constituents.

6.3.3 Filters – Pre-filters must not be used. Borosilicate glass with no binder material with an effective pore size of 0.6–0.8 micrometers (µm). Acid wash with 1N 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.

6.3.4 Filtration Device – Capable of exerting pressures up to 50 psi. Recommend use of units having an internal volume of 1.5 L and capable of accommodating a 142 millimeter (mm) filter.

6.3.5 Beaker – 500 milliliters (mL).

6.3.6 Balance – Any laboratory balance accurate to within ±0.01 grams may be used (all weight measurements are to be within ±0.1 grams). All requirements in Section 6.1.3 shall be met.

6.3.7 pH meter with reference electrode accurate to at least ±0.05 units at 25°C. The pH meter/probe should be equipped with a means of temperature compensation either manually or automatically.

6.3.8 Magnetic stirrer with fluoropolymer-coated stir bar.

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 pH buffer solutions, it may be necessary to boil and cool the water prior to use.

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

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

7.1.4 Sodium Hydroxide, (1N) - Add 40 g reagent grade NaOH to 400 mL 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 conc. sulfuric acid, 95-98% (specific gravity 1.84) with 40 g (approximately 28 mL) conc. 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 should 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 1N NaOH solution, and dilute to 1 L. The pH of this solution should be 4.93 ±0.05.

7.1.7.2 TCLP Extraction Fluid #2 – Dilute 5.7 mL of glacial acetic acid with reagent water to a final volume of 1 L. The pH of this solution should 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 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 shall be separated by at least three pH units.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Sample Collection and Preservation

All aqueous/water and soil/sediment samples must be collected in glass or polyethylene containers. All soil/sediment samples must be iced or refrigerated at ≤6°C, but not frozen, from the time of collection until receipt at the laboratory.

8.2 Sample Storage

All aqueous/water and soil/sediment samples must be stored at ≤6ºC, but not frozen, from the time of sample receipt until preparation.

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 samples must be returned to storage at a temperature of ≤6°C, but not frozen. After all applicable leaching procedures and/or percent solid determination have been completed, the remaining unused portion of the aqueous/water and soil/sediment samples must 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.

8.2.2 Leachate Sample Storage

The remaining unused portion of the preserved TCLP or SPLP leachates must 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.

8.3 Contract Required Holding Time

The holding time for TCLP or SPLP extraction for metals samples is 180 days from Validated Time of Sample Receipt (VTSR). The holding time for TCLP or SPLP extraction for mercury samples is 26 days from VTSR. The holding time for SPLP extraction for cyanide samples 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. These two points shall 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.

10.0 PROCEDURE

10.1 Sample Characterization

10.1.1 Percent Solids Determination

Percent Solids determination is based on Standard Method (SM) 2540G, approved 1997.

10.1.1.1 Transfer 5–10 g of sample to a tared weighing boat and record the total weight to the nearest 0.01 g. Sample handling and drying should 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 1. This value will be used for calculating analytical concentration on a dry weight basis.

EQ. 1 Percent Solids

$$\%\,\text{Solids} = \frac{\text{Sample Dry Weight}}{\text{Sample Wet Weight}} \times 100$$

10.1.1.5 Samples containing percent solids less than or equal to 30% shall be prepared at higher sample weights for all analytical methods to yield a dry weight equivalent to the weight range specified in the analytical preparation method.

NOTE: This requirement does not apply to 7-day turnaround or Preliminary Results samples.

10.1.1.5.1 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 2.

EQ. 2 Required Sample Weight

$$\text{Required Weight} = \frac{\text{Minimal Method Weight}}{\%\text{Solids}/100}$$

10.1.1.6 For samples containing more than 30% solids and less than 50% solids, the Contractor shall proceed with sample analysis and document the issue in the SDG Narrative.

10.1.1.7 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.

10.1.1.8 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. For samples scheduled for Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES), Inductively Coupled Plasma - Mass Spectrometry (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 the Sample Management Office (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.

The Contractor shall follow the procedures for pH measurement based on the EPA SW-846 Method 9041A, Revision 1, July 1992 (pH paper) or the EPA SW-846 Method 9040C, Revision 3, November 2004 [electrometric method (i.e., pH meter and electronic hand-held pen)].

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 must 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 should 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 SW-846 Method 9045D, Revision 4, November 2004 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 must be corrected.

10.2 TCLP and SPLP Extraction Procedures

Extraction methods are based on EPA SW-846 Method 1311, Toxicity Characteristic Leaching Procedure (TCLP), Revision 0, July 1992 or EPA SW-846 Method 1312, Synthetic Precipitation Leaching Procedure (SPLP), Revision 0, September 1994.

TCLP vessel and devices must 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.

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.

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 to make a preliminary determination of percent solids is required.

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 should 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 at a temperature of ≤6°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 vacuum or 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 the following equation:

EQ. 3 Extraction Percent Solids

$$\%\,\text{Solids} = \frac{\text{Weight of solid}}{\text{Total Weight of Sample}} \times 100$$

10.2.1.1.2.9 If the percent solids determined in Equation 3 is equal to or greater than 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 (±20°C) until two successive weighings yield the same value (within ±1%) and record the weight.

NOTE: Caution should 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 the following equation:

EQ. 4 Percent Dry Solids

$$\text{Percent Dry Solids} = \frac{(\text{Wt. of dry waste and filter}) - \text{Tared wt. of filter}}{\text{Initial wt. of waste}} \times 100$$

10.2.1.2 If the percent dry solids is less than 0.5%, then treat the filtrate as the extract. Store this extract at ≤6°C until digestion/distillation.

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.

10.2.1.4 For samples with percent solids greater than 0.5%, determine the appropriate extraction fluid as follows:

10.2.1.4.1 For samples scheduled for TCLP extraction, 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 watchglass, and stir vigorously for 5 minutes using a magnetic stirrer. Measure and record the pH. If the pH is <5.0, use TCLP Extraction Fluid #1 (Section 7.1.7.1). If the pH is ≥5.0, add 3.5 mL 1N HCl (Section 7.1.2), slurry briefly, cover with the watchglass, and heat to 50°C for 10 minutes.

10.2.1.4.1.2 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).

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

10.2.1.4.2.2 For cyanide–containing soil/sediments, use SPLP Extraction Fluid #3 (reagent water) because leaching of cyanide-containing samples under acidic conditions may result in the formation of hydrogen cyanide gas and loss of analyte. Along with being potentially hazardous, this results in loss of analyte and makes results useless.

10.2.2 TCLP Sample Extraction

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 less than 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 greater than or equal to 0.5%, but less than 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 ≤6°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 the following equation:

EQ. 5 Weight of Extraction Fluid

$$\text{Weight of Extraction Fluid} = \frac{20 \times \text{percent solids} \times \text{Weight of sample filtered}}{100}$$

10.2.2.4 Add this 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 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. Preserve extracts for metals (both ICP-AES and Hg) with nitric acid to pH <2. Preserve SPLP extracts for Cyanide analysis with NaOH to pH >10 and store at ≤6°C.

10.2.3 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 individual procedures in Section 11.0 for data analysis and 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 reagent water 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 should the LEB be analyzed at a dilution.

12.2 Summary of Quality Control Operations

The Quality Control (QC) operations performed are summarized 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 Inorganic Analytical Methods.

15.0 WASTE MANAGEMENT

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

16.0 REFERENCES

16.1 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 1311, Revision 0, Update III, July 1992.

16.2 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 1312, Revision 0, Update III, September 1994.

16.3 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 9040C, Revision 3, November 2004.

16.4 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 9041A, Revision 1, July 1992.

16.5 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 9045D, 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.

EXHIBIT D

INDUCTIVELY COUPLED PLASMA - ATOMIC EMISSION SPECTROSCOPY

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Exhibit D – Analytical Methods for Inductively Coupled Plasma – Atomic Emission Spectroscopy

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Exhibit D – Analytical Methods for Inductively Coupled Plasma – Atomic Emission Spectroscopy

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1.0 SCOPE AND APPLICATION

This exhibit provides procedures for the use of Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) to determine the concentration of total recoverable and dissolved metals in aqueous/water, leachate derived from the Toxicity Characteristic Leaching Procedure (TCLP) or Synthetic Precipitation Leaching Procedure (SPLP), soil/sediment, and wipe samples taken from hazardous waste sites. All metals contained in the Inorganic Target Analyte List (TAL) for ICP-AES in Exhibit C - Inorganic Target Analyte List and Contract Required Quantitation Limits are quantitated by this method.

2.0 SUMMARY OF METHOD

2.1 General Method Overview

This method describes the multi-element determination of trace metals by ICP-AES. Aqueous/water, TCLP/SPLP leachate, soil/sediment, and wipe samples are treated with acids and heat to solubilize the metals present. These digestates are then analyzed for trace metals by an atomic emission optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to a plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed and the intensities of the lines are monitored by a photosensitive device. The signals from the photosensitive device are processed by a computer. A background correction technique is required to compensate for variable background contribution to the spectra of trace elements. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result.

2.2 Summary of Digestion Procedures

2.2.1 Hotplate Acid Digestion of Aqueous/Water and TCLP/SPLP Leachate Samples (based on EPA Method 200.7)

2.2.2 Hotplate Acid Digestion of Soil/Sediment Samples (based on EPA Method 3050B)

2.2.3 Hotplate Acid Digestion of Wipe Samples (based on EPA Method 3050B)

3.0 DEFINITIONS

See Exhibit G - Glossary of Terms for a complete list of definitions.

4.0 INTERFERENCES

Several types of interference effects may contribute to inaccuracies in the determination of trace elements in aqueous/waters, TCLP/SPLP leachates, soil/sediments, and wipes by ICP-AES. To prevent this, appropriate steps must be taken in all analyses to ensure that potential interferences are taken into account. This is especially true when dissolved solids exceed 1500 milligrams/Liter (mg/L) and when total elements are determined after the appropriate digestion procedures are performed. Several types of interferences are given in Sections 4.1 through 4.3 below.

4.1 Spectral Interferences

Spectral interferences can be categorized as: (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; (4) and/or background contribution from stray light from the line emission of high concentration elements. The first effect can be compensated by utilizing a computer correction of the raw data. This would require the monitoring and measurement of the interfering element. The second effect may require selection of an alternate wavelength. The third and fourth effects can usually be compensated by a background correction adjacent to the analyte line. In addition, users of simultaneous multi-element instrumentation must assume the responsibility of verifying the absence of spectral interference from an element that could occur in a sample but for which there is no channel in the instrument array.

4.2 Physical Interferences

Physical interferences are generally considered to be effects associated with the sample nebulization and transport processes. Such properties as change in viscosity and surface tension can cause significant inaccuracies, especially in samples which may contain high dissolved solids and/or acid concentrations. The use of a peristaltic pump may minimize these interferences. If these types of interferences are present, they must be reduced by dilution of the sample.

Another problem which can occur from high dissolved solids is salt buildup at the tip of the nebulizer. This affects aerosol flow rate causing instrumental drift. Wetting the argon prior to nebulization, the use of a tip washer, or sample dilution has been used to control this problem. Also, it has been reported that better control of the argon flow rate improves instrument performance. This is accomplished with the use of mass flow controllers.

Internal standardization may be effectively used to compensate for many physical interference effects.

4.3 Chemical Interferences

Chemical interferences are characterized by molecular compound formation, ionization effects, and solute vaporization effects. Normally these effects are not pronounced with ICP-AES technique; however, if observed they can be minimized by careful selection of operating conditions (that is, incident power, observation position, and so forth), by buffering of the sample, and by matrix matching. These types of interferences can be highly dependent on matrix type and the specific element.

5.0 SAFETY

See Section 12.0 in Exhibit D - Introduction to Inorganic 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 Statement of Work (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.

6.1 Glassware/Labware

6.1.1 250 milliliter (mL) beaker or other appropriate digestion vessel (glass or plastic)

6.1.2 Watch glasses (glass or plastic)

6.1.3 Funnels

6.1.4 Graduated cylinders

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

6.1.6 Thermometer that covers a range of 0-200°C

6.1.7 Whatman No. 42 filter paper (or equivalent)

6.1.8 Hotplate, block digester, or other heating source capable of maintaining 95°C (±3°C)

6.1.9 Balances – Top loader balance, 300 gram (g) capacity, and a minimum sensitivity of ±1.0 mg

A balance calibration must be checked with known masses once per each day of use. This verification consists of a check with two weights covering the range expected (approximately ±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 must 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 E617-97 (2008) or equivalent (e.g., earlier Class ‘S’ defined masses). All balances must be checked at least once annually by a certified technician. The reference masses used by the Contractor must 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 Inductively Coupled Plasma - Atomic Emission Spectrometer

The ICP-AES consists of:

- A computer-controlled atomic emission spectrometer with background correction;
- A radio-frequency generator; and
- A supply of Argon gas, welding grade or better.

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.

7.1.2 Hydrochloric acid - Concentrated 32-38% (specific gravity 1.19).

7.1.3 Hydrochloric acid (50% v/v) - Add 500 mL of conc. hydrochloric acid to 400 mL reagent water and dilute to 1 L.

7.1.4 Nitric acid - Concentrated 67-70% (specific gravity 1.41).

7.1.5 Nitric acid (50% v/v) - Add 500 mL conc. nitric acid to 400 mL reagent water and dilute to 1 L.

7.1.6 Hydrogen peroxide (30%).

7.1.7 Nitric acid (2% v/v) - Add 20 mL conc. nitric acid to 500 mL reagent water and dilute to 1 L.

7.2 Standards

7.2.1 Introduction

The Contractor must provide all standards, except as noted, to be used with this contract. These standards may be used only after they have been certified according to the procedure in Exhibit D - Introduction to Inorganic Analytical Methods, Section 11.0. The Contractor must be able to verify that the standards are certified. Manufacturer’s certificates of analysis must be retained by the Contractor and presented upon request.

Samples, sample digestates, and standards must be stored separately.

7.2.2 Stock Standard Solutions

Stock standard solutions may be purchased from a reputable source or prepared from reagent grade chemicals or metals (at least 99.99% pure). All salts must be dried for 1 hour at 105°C unless otherwise specified.

CAUTION: Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling.

7.2.3 Secondary Dilution Standards

Prepare mixed secondary dilution standard solutions by diluting the appropriate volumes of stock standards with 2% (v/v) nitric acid, or as recommended by the manufacturer, to obtain the final volume. Mixed secondary dilution standard solutions may be purchased. The purchased standards shall meet the requirements in Section 7.2.1.

7.2.4 Working Standards

7.2.4.1 Interference Check Sample Solution

7.2.4.1.1 The Interference Check Sample (ICS) consists of two solutions: ICS Solution A (ICSA) and ICS Solution AB (ICSAB). ICSA consists of the interferents and ICSAB consists of the analytes mixed with the interferents. The ICS standards (ICSA for the interferents only and ICSB for the analytes only) shall be obtained from the EPA.

7.2.4.1.1.1 Only if the ICS solutions are not available from the EPA, ICSs shall be prepared with interferent and analyte concentrations at the levels specified in Table 1 - Interferent and Analyte Concentrations Used for ICP-AES Interference Check Sample (ICS).

7.2.4.1.1.2 If the solutions are prepared, the mean value and standard deviation shall be established by initially analyzing the ICSs at least five times repetitively for each analyte listed. Results shall be within the control limits of ±20% of the established mean value or ±1 times the analyte's Contract Required Quantitation Limit (CRQL) of the established mean value, whichever is greater. The mean and standard deviation shall be reported in the raw data.

7.2.4.2 Mixed Calibration Standard Solutions

Care should be taken when preparing the mixed standards that the analytes are compatible and stable. Fresh mixed standards should be prepared as needed with the realization that concentration can change with aging.

Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interferences or the presence of impurities. Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks. Add 2 mL of nitric acid and dilute to 100 mL with reagent water or these standards can be matrix matched to the digested samples. The analyte concentrations in the calibration standards should be sufficient to produce good measurement precision and to accurately define the slope of the response curve. Transfer the mixed standard solutions to Fluorinated Ethylene Propylene (FEP) fluorocarbon or unused polyethylene bottles for storage.

7.2.4.3 Initial Calibration Verification Solutions

7.2.4.3.1 The Initial Calibration Verification (ICV) solution(s) shall be obtained from the EPA.

7.2.4.3.1.1 If the solution(s) is (are) not available from the EPA, then the ICV solution shall be prepared by the laboratory using a certified solution for each analyte from an independent source. An independent source is defined as a standard composed of the analytes from a different source than those used in the standards for the instrument calibration. Analyses shall be conducted at a concentration other than that used for instrument calibration, but near the middle of the calibration range.

7.2.4.3.1.2 The ICV standard shall be prepared in the same acid matrix as the calibration standards and in accordance with the instructions provided by the supplier.

7.3 Blanks

Three types of blanks are required for this method. A Calibration Blank is used to establish the analytical calibration curve, a Preparation Blank (see Section 12.1) is used to assess possible contamination from the sample preparation procedure and to assess spectral background, and a rinse solution is used to flush the instrument between samples to reduce memory interferences.

7.3.1 Calibration Blank - Consists of 2% (v/v) nitric acid in reagent water or matrix matched to the digested samples. The Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB) are identical in composition to the Calibration Blank and are used to monitor for analyte carryover.

7.3.2 Preparation Blank - Must contain all the reagents in the same volumes as used in preparing the samples. The Preparation Blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis. Soil/sediment blanks shall use 1.00 mL (±0.01 mL) of reagent water.

7.3.3 Rinse Solution – Must contain sufficient nitric acid to allow the instrument to return to baseline between the analysis of digested samples, blanks, and standards. The rinse solution would typically consist of 2% (v/v) nitric acid in reagent water.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Sample Collection and Preservation

All aqueous/water and soil/sediment samples must be collected in glass or polyethylene containers. Wipe samples may be placed in zip-top plastic bags, glass, or polyethylene wide-mouth containers for shipment. Wipe samples are not preserved. Aqueous/water samples must be preserved with nitric acid to pH less than or equal to 2 immediately after collection. All soil/sediment samples must be iced or refrigerated at ≤6°C but not frozen from the time of collection until receipt at the laboratory.

8.2 Sample Storage

All aqueous/water and soil/sediment samples must be stored at ≤6°C but not frozen from the time of sample receipt until digestion. Wipe samples shall remain in their original bags until preparation and may be stored at room temperature within the laboratory.

8.2.1 Unused Sample Storage

The Contractor shall retain the unused portion of aqueous/water and soil/sediment samples for a period of 60 days after delivery of a complete, reconciled data package to the EPA. The samples may be stored at room temperature.

8.2.2 Digestate Sample Storage

Sample digestates must be stored until 180 days after delivery of a complete, reconciled data package to the EPA. The Contractor shall store sample ICP-AES digestates in plastic bottles. The bottles shall be labeled with the EPA Sample Number, Case Number, SDG Number, MA No. (if applicable), and digestion date. A logbook of stored digestates, listing the EPA Sample Numbers and associated Case and SDG Numbers, shall be maintained.

8.2.3 Container Storage

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

8.3 Contract Required Holding Time

The holding time for metals is 180 days from Validated Time of Sample Receipt (VTSR) to analysis. The holding time for the analysis of TCLP or SPLP leachates is 180 days from the date of extraction.

9.0 CALIBRATION AND STANDARDIZATION

9.1 Instrument Operating Parameters

Because of the differences between various manufacturers 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. The Method Detection Limit (MDL), precision, and interference effects must be investigated and established for each individual analyte line on that particular instrument. All measurements used to determine interelement corrections must be within the instrument operating range. It is the responsibility of the analyst to verify the instrument configuration and operating conditions used satisfy the analytical requirements and to maintain Quality Control (QC) data confirming instrument performance and analytical results.

9.2 Pre-Calibration Routine

Prior to calibration, the Contractor shall set up each instrument with the operating parameters established in Section 9.1 and conduct any necessary adjustments to the plasma conditions. The instrument must be allowed to become stable (usually 30 minutes) before calibration is performed.

9.3 Instrument Calibration Procedure

9.3.1 Summary of Instrument Calibration

Prior to sample analysis, the Contractor shall calibrate each instrument to determine sensitivity and linearity of the response.

9.3.2 Frequency of Instrument Calibration

Each instrument shall be calibrated each time it is turned on, set up, or after ICV, ICB, Continuing Calibration Verification (CCV), or CCB failure. The instrument calibration date and time shall be included in the raw data.

9.3.3 Procedure for Instrument Calibration

9.3.3.1 Each instrument shall be calibrated according to the manufacturer’s recommended procedures.

9.3.3.2 At least six calibration standards shall be used for each analyte. The calibration standards shall be prepared as in Section 7.2.4.2. One of the standards shall be a blank standard and one shall be at or below the CRQL but greater than the MDL. The rest of the standards shall be uniformly spread out in graduated amounts over the appropriate calibration range of the analyte.

9.3.3.3 A minimum of three replicate integrations are required for data acquisition. The Contractor shall use the average of all the integrations for instrument calibration and data reporting.

9.3.4 Calculations for Instrument Calibration

9.3.4.1 The calibration curve shall be calculated for each analyte using linear regression by plotting the concentration of the standard [in micrograms/Liter (µg/L)] on the X-axis versus the corrected instrument response on the Y-axis. The corrected instrument responses are those corrections [e.g., correction for background, Interelement Corrections (IECs), calibration blank] that may be applied to the raw uncorrected instrument response prior to determining the calibration curve.

9.3.4.2 The Contractor may use standard linear regression, weighted linear regression (1/concentration, 1/square of concentration, variance, 1/variance, standard deviation, 1/standard deviation, or 1/square of standard deviation), or linear regression with zero force calibration models, as appropriate, for the above calculation. No other types of equations (e.g., quadratic) are to be used.

9.3.4.3 The calibration curve for each analyte shall be checked to establish the representativeness of the data that were used to produce it. This check involves re-fitting the data of the non-blank calibration standards back to the calibration curve, and computing the difference between the calculated concentration and the expected concentration for each of these standards. The difference is then divided by the expected concentration of the respective standard and multiplied by 100.

9.3.5 Technical Acceptance Criteria for Instrument Calibration

9.3.5.1 The correlation coefficient of the calibration curve shall be greater than or equal to 0.995.

9.3.5.2 The Percent Difference (%D) for each of the standards shall be within the control limits of ±30%.

9.3.5.3 If a standard is analyzed for a particular analyte at a concentration that is below the CRQL and the %D criteria is not met, that standard can be excluded from the calibration curve as long as the lowest non-zero standard for that analyte is still analyzed at or below the CRQL and all standards included in the calibration curve are continuous and consecutive.

9.3.6 Corrective Action for Instrument Calibration

9.3.6.1 Sample analysis shall not begin until the criteria described in Section 9.3.5 have been met.

9.3.6.2 Any changes or corrections to the analytical system shall be followed by recalibration.

9.4 Initial Calibration Verification

9.4.1 Summary of Initial Calibration Verification

Prior to sample analysis, the Contractor shall demonstrate the accuracy of the instrument calibration for each instrument through the analysis of an ICV standard.

9.4.2 Frequency of Initial Calibration Verification

The ICV shall be analyzed immediately after the instrument has been calibrated.

9.4.3 Procedure for Initial Calibration Verification

9.4.3.1 The ICV shall be analyzed at each wavelength used to report final results for each analyte.

9.4.3.2 The ICV shall reflect the conditions of analysis of the associated analytical samples.

9.4.4 Calculations for Initial Calibration Verification

9.4.4.1 The Percent Recovery (%R) of the ICV shall be calculated using the following equation:

EQ. 1 ICV Percent Recovery

$$\%R = \frac{\text{Found(ICV)}}{\text{True(ICV)}} \times 100$$

WHERE,
Found (ICV) = The found concentration of the analyte in the ICV Solution
True (ICV) = The expected concentration of the analyte in the ICV Solution

9.4.4.2 The Percent Relative Standard Deviation (%RSD) from all replicate integrations shall be calculated for each wavelength used to report final results using Equations 2, 3, and 4.

EQ. 2 Percent Relative Standard Deviation Calculation

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

WHERE,
SD = Standard deviation of ICV replicates (per analyte) from EQ. 3
$\bar{X}$ = Mean value of the ICV replicates (per analyte) from EQ. 4

9.4.4.3 Equation 3 is the general formula for Standard Deviation (SD) for a statistically small set of values.

EQ. 3 Standard Deviation Calculation

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (X_i - \bar{X})^2}{(n-1)}}$$

WHERE,
X_i = Each individual value used to calculate the mean
$\bar{X}$ = The mean of n values from EQ. 4
n = Total number of values

9.4.4.4 Equation 4 is the general formula for the mean of a set of values ($\bar{X}$).

EQ. 4 Mean Value Calculation

$$\bar{X} = \frac{\sum_{i=1}^{n} X_i}{n}$$

WHERE,
X_i = Each individual value used to calculate the mean
n = Total number of values

9.4.5 Technical Acceptance Criteria for Initial Calibration Verification

9.4.5.1 The ICV %R shall be within the control limits of 90-110%.

9.4.5.2 The %RSD of the ICV integrations shall be less than or equal to 5.0%.

9.4.6 Corrective Action for Initial Calibration Verification

If the recovery is outside the control limits of 90% Recovery (low) or 110% Recovery (high), or if the %RSD as calculated from all replicate integrations exceeds 5.0%, the analysis shall be terminated, the problem corrected, the instrument recalibrated, and the calibration verified.

9.5 Continuing Calibration Verification

9.5.1 Summary of Continuing Calibration Verification

Prior to sample analysis, periodically during analysis, and at the conclusion of analysis, the Contractor shall demonstrate the stability of the calibration through the analysis of a CCV standard. The Contractor shall not analyze a blank immediately prior to the analysis of the CCV.

9.5.2 Frequency of Continuing Calibration Verification

9.5.2.1 A CCV shall be analyzed at the beginning of the analytical sequence and after the last analytical sample. A CCV shall also be analyzed at a frequency not to exceed every 2 hours during an analytical sequence. See the example analytical sequence in Section 10.4.5.

9.5.2.2 The analytical sequence can continue indefinitely as long as samples are being continuously analyzed without the instrument being turned off and successive CCV standards meet the technical acceptance criteria in Section 9.5.5.

9.5.3 Procedure for Continuing Calibration Verification

9.5.3.1 The CCV standard shall be prepared using the same source and in the same acid matrix as the calibration standards by combining compatible analytes at a concentration at or near the mid-level of their respective calibration curve.

9.5.3.2 The same CCV standard shall be used throughout the analytical sequences for an SDG.

9.5.3.3 The CCV shall be analyzed at each wavelength used to report final results for each analyte.

9.5.3.4 Each CCV analyzed shall reflect the conditions of analysis of all associated analytical samples (the preceding analytical samples up to the previous CCV as applicable and the analytical samples following this CCV up to the next CCV as applicable).

9.5.4 Calculations for Continuing Calibration Verification

9.5.4.1 The %R of the CCV shall be calculated using the following equation:

EQ. 5 CCV Percent Recovery

$$\%R = \frac{\text{Found (CCV)}}{\text{True(CCV)}} \times 100$$

WHERE,
Found (ICV) = The found concentration of the analyte in the CCV Solution
True (ICV) = The expected concentration of the analyte in the CCV Solution

9.5.4.2 The %RSD from all replicate integrations shall be calculated for each wavelength used to report final results using Equations 2, 3, and 4 above.

9.5.5 Technical Acceptance Criteria for Continuing Calibration Verification

9.5.5.1 The CCV %R shall be within the control limits of 90-110%.

9.5.5.2 The %RSD of the CCV integrations shall be less than or equal to 5.0%.

9.5.5.3 All samples shall be analyzed within 2 hours of an acceptable opening and closing CCV.

9.5.6 Corrective Action for Continuing Calibration Verification

If the deviations of the CCV are greater than the specified control limits of 90% Recovery (low) or 110% Recovery (high), or if the %RSD as calculated from all replicate integrations exceeds 5.0%, the analysis shall be terminated, the problem corrected, the instrument recalibrated, the calibration verified, and reanalysis of all analytical samples analyzed since the last compliant calibration verification shall be performed for the analytes affected.

9.6 Initial and Continuing Calibration Blank

9.6.1 Summary of Calibration Blank

Prior to sample analysis, periodically during analysis, and at the conclusion of analysis, the Contractor shall demonstrate the stability of the calibration baseline through the analysis of an ICB and CCB.

9.6.2 Frequency of Calibration Blank

9.6.2.1 An ICB shall be analyzed immediately after the instrument has been calibrated and the calibration verified by the analysis of the ICV.

9.6.2.2 Each CCB shall be analyzed immediately after the analysis of a CCV.

9.6.3 Procedure for Calibration Blank

9.6.3.1 The ICB and CCB samples shall be analyzed at each wavelength used for reporting final results for each analyte.

9.6.3.2 The ICB analyzed shall reflect the conditions of analysis of the associated analytical samples.

9.6.3.3 Each CCB analyzed shall reflect the conditions of analysis of the associated analytical samples (the preceding analytical samples up to the previous CCB as applicable and the analytical samples following this CCB up to the next CCB as applicable).

9.6.4 Calculations for Calibration Blank

The results for the ICB and CCB samples shall be calculated using Equation 6 in Section 11.0.

9.6.5 Technical Acceptance Criteria for Calibration Blank

The absolute value of each calibration blank result shall be less than or equal to the CRQL for aqueous/water samples for the analyte.

9.6.6 Corrective Action for Calibration Blank

If the absolute value of the calibration blank exceeds the CRQL for aqueous/water samples, the analysis shall be terminated, the problem corrected, the instrument recalibrated, the calibration verified, and reanalysis of all affected analytical samples analyzed since the last compliant calibration blank performed for the analytes affected.

10.0 PROCEDURE

10.1 Aqueous/Water Sample Preparation

Preparation Method 200.7 [based on EPA NERL Method 200.7, Revision 4.4 (1994)]

10.1.1 If the sample pH was ≤2 at the time of sample receipt, the Contractor shall proceed to Section 10.1.2.

If the sample pH was adjusted at the time of sample receipt (see Exhibit D – General Inorganic Analysis, Section 10.1.2.1), the Contractor shall take a second pH measurement, prior to removing an aliquot of the sample for digestion, to verify that the sample was properly preserved upon receipt. If the second pH measurement is ≤2, proceed to Section 10.1.2. If the second pH measurement 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.

10.1.2 For the determination of total recoverable analytes in aqueous/water and leachate samples, transfer a 100 mL (±1 mL) aliquot from a well-mixed, acid-preserved sample to an appropriately sized (approximately 250 mL) digestion vessel (e.g., a beaker or hot block digestion tube). The sample shall not be diluted prior to digestion.

NOTE: A reduced sample volume of 50 mL can be used. If this reduced volume is used, then all other reagents and volumes shall be reduced appropriately.

10.1.3 Add 2 mL 50% (v/v) nitric acid and 1 mL 50% (v/v) hydrochloric acid to the beaker containing the measured volume of sample. Place the beaker on a hotplate, or other comparable heating device, for solution evaporation. The hotplate should be located in a fume hood and previously adjusted to provide evaporation at a temperature of 95°C (±3°C), when covered. The beaker should be covered with an elevated watch glass or other necessary steps should be taken to prevent sample contamination from the fume hood environment.

10.1.4 Reduce the volume of the sample aliquot to about 20 mL by gently heating at 95°C (±3°C). **DO NOT BOIL**. This step takes about 2 hours for a 100 mL aliquot with the rate of evaporation rapidly increasing as the sample volume approaches 20 mL. (A spare beaker containing 20 mL of water can be used as a gauge.)

10.1.5 Cover the beaker with a watch glass to reduce additional evaporation and gently reflux the sample for 30 minutes. (Slight boiling may occur, but vigorous boiling must be avoided to prevent loss of the $HCl-H_2O$ azeotrope.)

10.1.6 Allow the beaker to cool. Quantitatively transfer the sample solution to a 100 mL volumetric flask, make to volume with reagent water, stopper, and mix.

10.1.7 Allow any undissolved material to settle overnight, or centrifuge or filter a portion of the prepared sample until clear to avoid plugging the nebulizer with solid particles.

10.1.8 The sample is now ready for analysis. Because the effects of various matrices on the stability of the samples cannot be characterized, all analyses should be performed as soon as possible after the completed preparation.

10.1.8.1 The digested sample may be diluted if high levels of interferences are noted or if any of the analytes exceed the upper limit of their respective calibration curves, according to Exhibit D – Introduction to Inorganic Analytical Methods, Section 7.0.

10.2 Soil/Sediment Sample Preparation

Preparation Method 3050B [based on EPA Method 3050B, Revision 2, (December 1996)]

10.2.1 Mix the sample thoroughly to achieve homogeneity. Weigh to the nearest 0.01 g and transfer 1.00 – 1.50 g sample (wet weight) to an appropriately sized digestion vessel (e.g., a beaker or hot block digestion tube).

10.2.2 Add 10 mL of 50% (v/v) nitric acid, mix the slurry, and cover with a watch glass. Heat the sample to 95°C (± 3°C) and reflux for 10 to 15 minutes without boiling. Allow the sample to cool, add 5 mL of concentrated nitric acid, replace the cover, and reflux for 30 minutes. If brown fumes are generated, indicating oxidation of the sample by the nitric acid, repeat this step (addition of 5 mL of concentrated nitric acid) until no brown fumes are given off by the sample indicating the complete reaction with nitric acid. Using a watch glass, either allow the solution to evaporate to approximately 5 mL without boiling or heat at 95°C (± 3°C) without boiling for 2 hours. Maintain a covering of solution over the bottom of the vessel at all times.

10.2.3 After the sample has cooled, add 2 mL of reagent water and 3 mL of 30% hydrogen peroxide. Cover the vessel with a watch glass and return the covered vessel to the heat source for warming and to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until the effervescence subsides and cool the vessel. Continue to add 30% hydrogen peroxide in 1-mL amounts with warming until the effervescence is minimal or until the general sample appearance is unchanged. (NOTE: Do not add more than a total of 10 mL of 30% hydrogen peroxide.) Cover the sample with a watch glass and continue heating the acid-peroxide digestate until the volume has been reduced to approximately 5 mL or heat at 95°C (± 3°C) without boiling for 2 hours. Maintain a covering of solution over the bottom of the vessel at all times.

10.2.4 After the sample has cooled, add 10 mL of concentrated hydrochloric acid to the sample digestate and cover with a watch glass. Place the sample on/in the heating source and reflux at 95°C (±3°C) for 15 minutes. Let the sample digestate cool.

10.2.5 Filter the sample digestate through Whatman No. 42 filter paper (or equivalent) and collect the filtrate in a 100-mL volumetric flask. Rinse the filter paper with a small amount of reagent water to complete the quantitative transfer of the analytes and collect the liquid in the same 100-mL volumetric flask. The solution being analyzed must be clear to avoid plugging the nebulizer with solid particles. Make to volume with reagent water, stopper, and mix.

NOTE: In place of filtering, the sample (after dilution and mixing) may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

10.2.6 The sample is now ready for analysis.

10.2.6.1 The digested sample may be diluted if high levels of interferences are noted or if any of the analytes exceed the upper limit of their respective calibration curves, according to Exhibit D – Introduction to Inorganic Analytical Methods, Section 7.0.

10.3 Wipe Sample Preparation

Preparation Method 3050B [based on EPA Method 3050B, Revision 2 (December 1996)]

10.3.1 Transfer the wipe to an appropriately sized digestion vessel (e.g., a beaker or hot block digestion tube). If material remains in the original sample container, use a small (5 mL) portion of reagent water to rinse the material into the digestion vessel.

10.3.2 Follow the procedure as described in Sections 10.2.2 through 10.2.6.

10.4 Sample Analysis

10.4.1 It is recommended that a semi-quantitative analysis be conducted to screen for high element concentrations that may be beyond the calibration range of the instrument or high levels of interferences.

10.4.2 For all sample analyses, a minimum of three replicate integrations are required for data acquisition. Use the average of all the integrations for data reporting.

10.4.3 In accordance with the instrument manufacturer’s instructions, a rinse solution should be used to flush the system between samples. Allow sufficient time to remove traces of the previous sample. Samples should be aspirated for a sufficient period of time to obtain a stable response prior to the collection of data.

10.4.4 Sample digestates having high levels of interferences or concentrations higher than the established calibrated range as determined by the expected concentration of the highest calibration standard shall be diluted into range and reanalyzed, according to procedure in Exhibit D – Introduction to Inorganic Analytical Methods, Section 7.0.

10.4.5 Example Analytical Sequence for ICP-AES Including the Instrument Calibration:

S##
S##
S##
S##
S##
S##
ICV
ICB
ICSA
ICSAB
CCV###
CCB###
samples
CCV###
CCB###
samples
CCV###
CCB###, etc.

11.0 DATA ANALYSIS AND CALCULATIONS

Calculate the Target Analyte concentration using the following equations.

11.1 Aqueous/Water and TCLP/SPLP Leachate Sample Calculation

EQ. 6 Aqueous/Water and TCLP/SPLP Leachate Sample Concentration

$$\text{Concentration}(\mu g/L) = C \times \frac{V_f}{V} \times DF$$

WHERE,
C = Instrument value in µg/L (The average of all replicate exposures)
V_f = Final digestion volume (mL)
V = Initial aliquot amount (mL)
DF = Dilution Factor

NOTE: Convert units to mg/L for TCLP leachates by dividing the final calculated concentration by 1000.

11.2 Soil/Sediment Sample Calculation

The concentrations determined in the digestate are to be reported on the basis of the dry weight of the sample, in units of mg/kg:

EQ. 7 Soil/Sediment Sample Concentration

$$\text{Concentration}\,(\text{mg/kg dry weight}) = C \times \frac{V_f}{W \times S} \times DF \,/\, 1000$$

WHERE,
C = Instrument value in µg/L (The average of all replicate exposures)
V_f = Final digestion volume (mL)
W = Initial aliquot amount (g)
S = % Solids/100 (Exhibit D - General Inorganic Analysis, Section 10.1.1)
DF = Dilution Factor

11.3 Wipe Sample Calculation

EQ. 8 Wipe Mass

$$\text{Mass}(\mu g) = C \times V_f \times DF/1000$$

WHERE,
C = Instrument value in µg/L (The average of all replicate exposures)
V_f = Final digestion volume (mL)
DF = Dilution Factor

11.4 Adjusted Contract Required Quantitation Limit Calculation

11.4.1 Calculate the adjusted CRQL for aqueous/water or TCLP/SPLP leachate samples, by multiplying the CRQL (µg/L) by the sample dilution factor and the V_f/V term as noted in Equation 6. Convert units to mg/L for TCLP leachate samples.

11.4.2 Calculate the adjusted CRQL for soil/sediment samples using the following equation:

EQ. 9 Adjusted Soil/Sediment CRQL

$$\text{Adjusted CRQL}\,(mg/kg) = C \times \frac{W_M}{W \times S} \times \frac{V_f}{V_M} \times DF$$

WHERE,
C = CRQL (mg/kg)
W_M = Minimum method required aliquot amount (g) (1.00 g)
W = Initial aliquot amount (g)
V_M = Method required final sample digestion volume (mL) (100 mL or 50 mL)
V_f = Final digestion volume (mL)
S = % Solids/100 (see Exhibit D – General Inorganic Analysis, Section 10.1.1)
DF = Dilution Factor

11.5 Hardness (Total) Sample Calculation

Total Hardness is defined as the sum of calcium and magnesium concentrations, expressed as calcium carbonate in mg/L. Total Hardness is calculated according to Standard Method 2340 B.

EQ. 10 Calculation of Hardness (Total) in Aqueous/Water Samples

$$\text{Hardness}\,(mg/L) = [\text{Conc. Ca}\,(mg/L) \times 2.497] + [\text{Conc. Mg}\,(mg/L) \times 4.118]$$

WHERE,
Conc. Ca (mg/L) = Calcium concentration (µg/L) ÷ 1000
Conc. Mg (mg/L) = Magnesium concentration (µg/L) ÷ 1000

12.0 QUALITY CONTROL

12.1 Preparation Blank Sample

12.1.1 Summary of Preparation Blank Sample

The Preparation Blank is used to monitor for possible contamination throughout the entire sample preparation and analysis process.

12.1.2 Frequency of Preparation Blank Sample

12.1.2.1 At least one Preparation Blank shall be prepared with every SDG, or with each preparation batch, whichever is more frequent.

12.1.2.2 If sufficient clean wipes are provided by the sampler, an additional Preparation Blank for the wipe samples shall be prepared using a clean wipe.

12.1.3 Procedure for Preparation Blank Sample

The Preparation Blank shall be carried through the complete sample preparation procedure for the matrix and contain the same acid concentration in the final digestate as the samples.

12.1.4 Calculations for Preparation Blank Sample

Calculate the results for aqueous Preparation Blanks by using Equation 6. Calculate the results for soil/sediment Preparation Blanks by using Equation 7. Calculate the results for wipe Preparation Blanks by using Equation 8.

12.1.5 Technical Acceptance Criteria for Preparation Blank Sample

12.1.5.1 The absolute value of the Preparation Blank result shall be less than or equal to the CRQL.

12.1.5.2 For aqueous/water and soil/sediment samples, any analyte concentration in the Preparation Blank may be greater than the CRQL, if the concentration of the analyte in the associated samples is greater than or equal to 10 times the blank concentration.

12.1.5.3 For aqueous/water and soil sediment samples, any analyte concentration in the Preparation Blank may be less than the negative CRQL, if the concentration in the associated samples is greater than or equal to 10 times the CRQL.

12.1.6 Corrective Action for Preparation Blank Sample

12.1.6.1 For aqueous/water and soil/sediment samples, if any analyte concentration in the Preparation Blank is greater than the CRQL, and the concentration of the analyte in any of the associated samples is less than 10 times the blank concentration, then all samples with less than 10 times the blank concentration shall be reprepared and reanalyzed with appropriate new QC for that analyte.

12.1.6.2 For aqueous/water and soil/sediment samples, if any analyte concentration in the Preparation Blank is less than the negative CRQL, and the concentration in the associated samples is less than 10 times the CRQL, then all samples with less than 10 times the CRQL concentration shall be reprepared and reanalyzed with appropriate new QC for that analyte.

12.1.6.3 If the results of the Preparation Blank for wipes exceed either the CRQL or are less than the negative CRQL, the Contractor shall note this in the SDG Narrative, since wipe samples are fully consumed by initial analysis and cannot be reprepared and reanalyzed.

12.2 Interference Check Sample

12.2.1 Summary of Interference Check Sample

The Contractor shall analyze the ICS to verify interelement and background correction factors.

12.2.2 Frequency of Interference Check Sample

The Contractor shall analyze, quantitate, and report the results for all elements on the TAL and for all interferents (target and non-target) immediately after the initial calibration sequence, but not before the ICV/ICB. The analysis of the ICS shall be immediately followed by the analysis of a CCV/CCB pair.

12.2.3 Procedure for Interference Check Sample

12.2.3.1 The ICS solutions (Section 7.2.4.1) shall be analyzed according to the instructions supplied with the ICS.

12.2.3.2 The Contractor shall initially analyze the ICSA and the ICSAB undiluted. Any dilution of the ICS (for the highest concentration elements) necessary to meet the calibrated range values of the instrument shall be analyzed after the undiluted analyses of the ICSA and ICSAB.

12.2.3.3 An ICS analysis consists of analyzing both solutions consecutively, starting with Solution A.

12.2.4 Calculations for Interference Check Sample

12.2.4.1 The ICSA/ICSAB sample concentrations shall be calculated using Equation 6.

12.2.4.2 The %R of the ICSA and ICSAB shall be calculated using the following equations:

EQ. 11 ICSA Percent Recovery

$$\%R = \frac{\text{Found (ICSA)}}{\text{True (ICSA)}} \times 100$$

WHERE,

Found (ICSA) = The found concentration of the analyte in the ICSA Solution

True (ICSA) = The expected concentration of the analyte in the ICSA Solution

EQ. 12 ICSAB Percent Recovery

$$\%R = \frac{\text{Found (ICSAB)}}{\text{True (ICSAB)}} \times 100$$

WHERE,

Found (ICSAB) = The found concentration of the analyte in the ICSAB Solution

True (ICSAB) = The expected concentration of the analyte in the ICSAB Solution

12.2.5 Technical Acceptance Criteria for Interference Check Sample

12.2.5.1 The ICSA and ICSAB %R shall be within the control limits of ±20% of the analyte's true value or the results shall be within ±1 times the CRQL of the analyte's true value, whichever is greater. If the true value for a given analyte is not listed in the certified values for the solution, then the true value shall be assumed to be zero and the ±1 times the CRQL control limits shall apply.

For example, for Chromium (CRQL = 10 µg/L, ICSA true value = 43 µg/L) the correct control window to use would be the greater of ±20% of the true value (0.20 x 43 µg/L = ±8.6 µg/L) or ±1 times the CRQL (±10 µg/L). Therefore, the control window for the found value for Chromium in the ICSA is 43±10, or 33 to 53 µg/L.

12.2.5.2 Only if the ICS solutions are not available from the EPA, the %R of the prepared independent Check Sample results shall be within the control limits of ±20% of the established mean value or the results shall be within ±1 times the analyte's CRQL of the established mean value, whichever is greater.

12.2.6 Corrective Action for Interference Check Sample

If the deviations of the ICSA and/or the ICSAB are greater than the specified control limits, the analysis shall be terminated, the problem corrected, the instrument recalibrated, the calibration verified, and reanalysis of all analytical samples. New IECs may also need to be determined for the failed analyte(s). For analytes with CRQLs less than 1000 µg/L, the ICSA and ICSAB results shall be reported from an undiluted sample analysis.

12.3 Matrix Spike and Post-Digestion Spike Samples

12.3.1 Summary of Matrix Spike and Post-Digestion Spike Sample

The Matrix Spike sample analysis is designed to provide information about the effect of the sample matrix on the digestion and/or measurement methodology.

12.3.2 Frequency of Matrix Spike and Post-Digestion Spike Samples

12.3.2.1 At least one Matrix Spike sample analysis shall be performed on each group of samples of a similar matrix type (i.e., aqueous/water, soil/sediment) or for each SDG, whichever is more frequent.[1]

[1] The EPA may require additional spike sample analyses, upon request from the EPA Regional Contract Laboratory Program Contracting Officer's Representative (EPA Regional CLP COR).

12.3.2.2 Matrix Spike sample analysis is not required for wipe samples.

12.3.2.3 If a Matrix Spike sample does not meet the technical acceptance criteria listed in Section 12.3.5, a Post-Digestion Spike sample shall be performed for those analytes that do not meet the specified criteria (exception: Ag).

12.3.3 Procedure for Matrix Spike and Post-Digestion Spike Samples

12.3.3.1 For a Matrix Spike sample, the spike is added before the digestion (i.e., prior to the addition of other reagents).

12.3.3.2 The analyte spike shall be added in the amount given in Table 2 - Spiking Levels for Matrix Spike Sample Analyses, for each element analyzed. This is the level of spike present in the final digestate.

12.3.3.3 For a Post-Digestion Spike sample, the sample that was initially used for the Matrix Spike sample analysis shall be used for the Post-Digestion Spike analysis. Spike the unspiked aliquot of the undiluted digestate at two times the indigenous level or two times the CRQL, whichever is greater.

12.3.3.4 Samples identified as field blanks and Performance Evaluation (PE) samples shall not be used for Matrix Spike sample analysis. The EPA may require that a specific sample be used for the Matrix Spike sample analysis.

12.3.4 Calculations for Matrix Spike and Post-Digestion Spike Samples

12.3.4.1 If the Matrix Spike analysis is performed on the same sample that is chosen for the Duplicate sample analysis, spike calculations shall be performed using the results of the sample designated as the "original sample" (see Section 12.4). The average of the duplicate results cannot be used for the purpose of determining the %R.

12.3.4.2 Calculate the Matrix Spike and Post-Digestion Spike %R using the following equation:

EQ. 13 Matrix Spike and Post-Digestion Spike Percent Recovery

$$\%R = \frac{SSR - SR}{SA} \times 100$$

WHERE,

SSR = Spiked Sample Result (µg/L or mg/kg) from EQ. 6 or EQ. 7

SR = Sample Result (original) (µg/L or mg/kg) from EQ. 6 or EQ. 7. When the sample concentration is less than the MDL, use SR=0.

SA = Spike Added Theoretical Result (µg/L or mg/kg). This is calculated by substituting the spiking amount used for the 'V_f' term and substituting the spiking standard concentration used for the 'C' term from EQ. 6 or EQ. 7.

NOTE: The units used for reporting SSRs will be identical to those used for reporting SRs.

12.3.5 Technical Acceptance Criteria for Matrix Spike and Post-Digestion Spike Samples

The Matrix Spike and Post-Digestion Spike %R shall be within the control limits of 75-125% (exception: Ag).

12.3.6 Corrective Action for Matrix Spike and Post-Digestion Spike Samples

12.3.6.1 If the Matrix Spike recovery is not at or within the limits of 75-125%, the data for all samples received and associated with that spike sample shall be flagged with "*". An exception to this rule is granted when the sample concentration exceeds the SA concentration by a factor of four or more. In such an event, the data shall be reported unflagged even if the %R does not meet the 75-125% recovery criteria.

12.3.6.2 When the Matrix Spike recovery is outside the control limits and the sample result does not exceed four times the spike added, a Post-Digestion spike shall be performed for those analytes that do not meet the specified criteria (exception: Ag). Follow the procedures in Section 12.3.3.

12.3.6.3 If there is more than one Matrix Spike per matrix, per SDG, if one Matrix Spike sample recovery is not within contract criteria, then flag all the samples of the same matrix and method in the SDG.

12.4 Duplicate Sample

12.4.1 Summary of Duplicate Sample

Duplicates are analyzed to help determine sample homogeneity and laboratory precision.

12.4.2 Frequency of Duplicate Sample

12.4.2.1 One duplicate sample shall be analyzed from each group of samples of a similar matrix type (i.e., aqueous/water, soil/sediment) or for each SDG, whichever is more frequent.[2] Duplicates cannot be averaged for reporting.

12.4.2.2 Duplicate sample analyses are not required for wipe samples.

12.4.3 Procedure for Duplicate Sample

12.4.3.1 Samples identified as field blanks and PE samples shall not be used for duplicate sample analysis. The EPA may require that a specific sample be used for duplicate sample analysis.

12.4.3.2 Prepare a second aliquot of the original sample. The duplicate sample shall be carried through the complete sample preparation procedure.

12.4.4 Calculations for Duplicate Sample

12.4.4.1 The Relative Percent Difference (RPD) for each analyte shall be calculated using the following equation:

EQ. 14 Duplicate Sample Relative Percent Difference

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

WHERE,
S = Sample Result (original) (µg/L or mg/kg) from EQ. 6 or EQ. 7
D = Duplicate Sample Result (µg/L or mg/kg) from EQ. 6 or EQ. 7

[2] The EPA may require additional duplicate sample analyses, upon request from the EPA Regional CLP COR.

12.4.5 Technical Acceptance Criteria for Duplicate Sample

12.4.5.1 The RPD shall be within the control limit of ±20 if the original and duplicate sample values are greater than or equal to five times the CRQL (see Exhibit C – Inorganic Target Analyte List and Contract Required Quantitation Limits).

12.4.5.2 The control limit shall be equal to the CRQL if either the sample or duplicate value are less than five times the CRQL or if one result is above five times the CRQL level and the other is below.

12.4.5.3 If both sample and duplicate values are less than the CRQL, the RPD is not recalculated.

12.4.6 Corrective Action for Duplicate Sample

12.4.6.1 If the duplicate sample results are outside the control limits, flag all the data for samples received associated with that duplicate sample with an "*".

12.4.6.2 If there is more than one duplicate sample per matrix, per SDG, and if one duplicate result is not within contract criteria, flag all samples of the same matrix in the SDG.

12.5 Laboratory Control Sample

12.5.1 Summary of Laboratory Control Sample

Aqueous/water, soil/sediment, and wipe Laboratory Control Samples (LCSs) shall be analyzed for each analyte using the same sample preparations, analytical methods, and Quality Assurance/Quality Control (QA/QC) procedures employed for the samples received.

12.5.2 Frequency of Laboratory Control Sample

12.5.2.1 One LCS shall be prepared for each prepared batch of aqueous/water, soil/sediment, or wipe samples in an SDG.

12.5.2.2 If sufficient clean wipes are provided by the sampler, an additional LCS for the wipe samples shall be prepared by spiking a clean wipe.

12.5.3 Procedure for Laboratory Control Sample

The LCS for aqueous/water, soil/sediment, and wipe samples shall be prepared by spiking an aliquot of reagent water (50-100 mL for aqueous/water, 1 mL for soil/sediment and wipes) such that the final digestate shall contain each analyte at two times the CRQL for the associated matrix.

12.5.4 Calculations for Laboratory Control Sample

Calculate the results for LCS by using Equations 6, 7, or 8 as appropriate.

EQ. 15 LCS Percent Recovery

$$\%R = \frac{\text{Found (LCS)}}{\text{True (LCS)}} \times 100$$

WHERE,

Found (LCS) = The found concentration of each analyte in the LCS (µg/L, mg/kg/ or µg) from EQs. 6, 7, or 8. If the analyte concentration is less than the MDL, a value of zero shall be substituted for the Found (LCS).

True (LCS) = Two times the CRQL for the appropriate matrix (µg/L, mg/kg, µg)

12.5.5 Technical Acceptance Criteria for Laboratory Control Sample

The %R shall be within the control limits of 70-130% for all analytes except Ag and Sb, for which the control limits are 50-150%.

12.5.6 Corrective Action for Laboratory Control Sample

12.5.6.1 If the %R for the LCS for aqueous/water or soil/sediment samples are outside the control limits of 70-130% (exception: Ag and Sb, control limits 50-150%), the analyses shall be terminated, the problem corrected, and the samples associated with that LCS redigested and reanalyzed with appropriate new QC.

12.5.6.2 If the %R for the LCS for wipes are outside the control limits of 70-130% (exception: Ag and Sb, control limits 50-150%), the Contractor shall note this in the SDG Narrative, since wipe samples are fully consumed by initial analysis and cannot be reprepared and reanalyzed.

12.6 ICP-AES Serial Dilution

12.6.1 Summary of ICP-AES Serial Dilution

The Contractor shall perform Serial Dilution analyses to check for interference effects.

12.6.2 Frequency of ICP-AES Serial Dilution

12.6.2.1 The ICP-AES serial dilution analysis shall be performed on a sample from each group of samples of a similar matrix type (i.e., aqueous/water, soil/sediment) or for each SDG, whichever is more frequent, prior to reporting analyte concentration data.

12.6.2.2 Serial Dilution analysis is not required for wipe samples.

12.6.3 Procedure for ICP-AES Serial Dilution

12.6.3.1 Prepare an aliquot of the original sample digestate and dilute it 1:4 (five-fold) with 2% nitric acid. This dilution shall be analyzed as the serial dilution.

12.6.3.2 If the original sample requires dilution for any analyte, a 1:4 (five-fold) dilution of that dilution shall be prepared and analyzed as a serial dilution.

12.6.3.3 Samples identified as field blanks and PE samples shall not be used for serial dilution analysis.

12.6.4 Calculations for ICP-AES Serial Dilution

The percent difference for each component are calculated using the following equation:

EQ. 16 Serial Dilution Percent Difference

$$\%\text{Difference} = \frac{\left| I - S \right|}{I} \times 100$$

WHERE,
I = Initial sample result
S = Serial dilution result. If the analyte concentration is less than the MDL, a value of zero shall be substituted for "S".

12.6.5 Technical Acceptance Criteria for ICP-AES Serial Dilution

If the analyte concentration is sufficiently high (minimally a factor of 50 above the MDL in the original sample), then the serial dilution (a five-fold dilution) shall be within 10% of the original determination after correction for dilution.

12.6.6 Corrective Action for ICP-AES Serial Dilution

12.6.6.1 If the dilution analysis for one or more analytes is not within a control limit of 10%, a chemical or physical interference effect must be suspected, and the data for all affected analytes in the samples received and associated with that serial dilution must be flagged with an "*".

12.6.6.2 In the instance where there is more than one serial dilution per SDG, per matrix, if one serial dilution result is not within contract criteria, flag all the samples of the same matrix in the SDG.

12.7 Method Detection Limit Determination

12.7.1 Before any field samples are analyzed, the MDLs shall be determined for each digestion procedure and instrument used prior to the start of contract analyses and annually thereafter. An MDL study shall also be performed after major instrument maintenance, or changes in instrumentation or instrumental conditions, to verify the current sensitivity of the analysis.

12.7.1.1 To determine the MDLs, the Contractor shall perform MDL studies following the procedures in 40 Code of Federal Regulations (CFR), Part 136.

12.7.1.2 The Contractor shall prepare the MDL samples by each digestion procedure used and shall analyze these samples on each instrument used.

12.7.1.3 The determined concentration of the MDL shall be less than half the concentration of the CRQL listed in Exhibit C – Inorganic Target Analyte List and Contract Required Quantitation Limits.

12.7.1.4 The MDLs for Hardness and TCLP are not required to be determined or reported.

12.8 Interelement Corrections

12.8.1 Before any field samples are analyzed, the IECs factors shall be determined prior to the start of contract analyses and at least annually thereafter following the procedures provided by the instrument manufacturer. Correction factors for spectral interference due to Al, Ca, Fe, and Mg shall be determined for all ICP-AES instruments at all wavelengths used for each analyte reported by ICP-AES. IEC factors shall also be reported for any other elements (including those on the TAL) that have been determined to interfere with the requested target analyte(s).

NOTE: Depending on sample matrix and interferences, it may be necessary to analyze IEC factors at a frequency greater than annually and/or at multiple concentrations comparable to the sample interferent levels.

12.8.2 If the instrument was adjusted in any way that may affect the ICP-AES IEC factors, the factors shall be redetermined and the results submitted for review.

12.8.3 All data used for the determination of the IEC factors shall be available to the EPA during an on-site laboratory evaluation.

12.8.4 Results from the IEC factors determination shall be reported for all ICP-AES analytes in accordance with Exhibit B – Reporting and Deliverables Requirements.

12.9 Summary of Quality Control Operations

The QC operations performed for ICP-AES analysis are summarized in Table 3 – QC Operations for ICP-AES.

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

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

15.0 WASTE MANAGEMENT

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

16.0 REFERENCES

16.1 U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, Method 200.7, Revision 4.4 (1994).

16.2 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 3050B, Revision 2, Third Edition, Update III, December 1996.

16.3 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Test Method 6010D, Revision 4, July 2014.

16.4 U.S. Government Printing Office, 40 Code of Federal Regulations, Part 136, Section 1, Appendix B.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

TABLE 1. INTERFERENT AND ANALYTE CONCENTRATIONS USED FOR ICP-AES INTERFERENCE CHECK SAMPLE (ICS)

Analytes	(µg/L)	Interferents	(µg/L)
Ag	200	Al	250000
As	100	Ca	250000
Ba	500	Fe	100000
Be	500	Mg	250000
Cd	1000		
Co	500		
Cr	500		
Cu	500		
Mn	500		
Ni	1000		
Pb	50		
Sb	600		
Se	50		
Tl	100		
V	500		
Zn	1000		

NOTE: ICSA solution contains the interferents at the indicated concentrations. The ICSA solution may be analyzed at twice the concentration indicated when interferences are present at higher concentrations in the sample. The ICSAB solution contains all of the analytes and interferents listed above at the indicated concentrations.

TABLE 2. SPIKING LEVELS FOR MATRIX SPIKE SAMPLE ANALYSES

Analyte	Water (µg/L)	Soil[1] (mg/kg)
Al	2000	*
Sb	100	20
As	40	8
Ba	2000	400
Be	50	10
Cd	50	10
Ca	*	*
Cr	200	40
Co	500	100
Cu	250	50
Fe	1000	*
Pb	20	4
Mg	*	*
Mn	500	100
Ni	500	100
K	*	*
Se	100	20
Ag	50	10
Na	*	*
Tl	50	10
V	500	100
Zn	500	100

* No spike required.

1 Concentrations in the spike sample when the dry weight of 1 gram of sample is taken for analysis. Adjustment shall be made to maintain these spiking levels when the weight of sample taken deviates by more than 10% of these values.

EQ. 17 Spiking Level Adjustment

$$\text{mg/kg} = \text{µg/L} \times \frac{\text{final volume (L)}}{\text{sample weight (g)}}$$

TABLE 3. QC OPERATIONS FOR ICP-AES

QC Operation	Frequency
Instrument Calibration	Each time instrument is turned on or set up, after ICV or CCV failure, and after major instrument adjustment.
Initial Calibration Verification	Following each instrument calibration for each wavelength used.
Continuing Calibration Verification	For each wavelength used, at a frequency of every 2 hours and at the beginning and end of each analytical sequence.
Initial Calibration Blank	Following each instrument calibration, immediately after the ICV.
Continuing Calibration Blank	Every 2 hours and at the beginning and end of each analytical sequence. Performed immediately after the CCV.
Preparation Blank	For each SDG or each sample preparation and analysis procedure per batch of prepared samples, whichever is more frequent.
Interference Check Sample	At the beginning of each analytical sequence after the ICB but before the CCV.
Matrix Spike Sample	For each matrix type or for each SDG, whichever is more frequent.
Post-Digestion Spike	Each time Matrix Spike Sample Recovery is outside QC limits.
Duplicate Sample Analysis	For each matrix type or for each SDG, whichever is more frequent.
Laboratory Control Sample	For each SDG or each sample preparation and analysis procedure per batch of prepared samples, whichever is more frequent.
Serial Dilution for ICP	For each matrix type or for each SDG, whichever is more frequent.
Method Detection Limit Determination	Prior to start of contract analyses, annually thereafter, and after major instrument adjustment.
Interelement Corrections	Prior to start of contract analyses, annually thereafter, and after major instrument adjustment.

EXHIBIT D

INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY

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Exhibit D – Inductively Coupled Plasma – Mass Spectrometry

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Table of Contents

1.0 SCOPE AND APPLICATION

This exhibit provides procedures for the use of Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) to determine the concentration of total recoverable and dissolved elements in aqueous/water and soil/sediment samples taken from hazardous waste sites. All metals contained in the Inorganic Target Analyte List (TAL) for ICP-MS in Exhibit C - Inorganic Target Analyte List and Contract Required Quantitation Limits are quantitated by this method.

2.0 SUMMARY OF METHOD

2.1 General Method Overview

This method describes the multi-element determination of trace elements by ICP-MS. Sample material in solution is introduced by nebulization into a radio-frequency plasma where energy transfer processes cause desolvation, atomization, and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio. The separated ions are detected and the ion information processed by a data handling system. Interferences related to the technique must be recognized and corrected. Such corrections may include compensation for isobaric elemental interferences and interferences from polyatomic ions derived from plasma gas, reagents, or sample matrix. Instrumental drift, as well as suppressions or enhancements of instrument response, must be corrected for with the use of internal standards.

2.2 Summary of Digestion Procedures

2.2.1 Hotplate Acid Digestion of Aqueous/Water Samples (based on EPA Method 200.8)

2.2.2 Hotplate Acid Digestion of Soil/Sediment Samples (based on EPA Method 200.8)

3.0 DEFINITIONS

See Exhibit G - Glossary of Terms for a complete list of definitions.

4.0 INTERFERENCES

Several types of interferences may contribute to inaccuracies in the determination of trace elements in aqueous/water and soil/sediment samples by ICP-MS. To prevent this, appropriate steps must be taken in all analyses to ensure that potential interferences are taken into account. Several types of interferences are given in Sections 4.1 through 4.5 below.

4.1 Isobaric Elemental Interferences

Isobaric elemental interferences are caused by isotopes of different elements which form singly or doubly charged ions of the same nominal mass-to-charge ratio, and which cannot be resolved by the mass spectrometer. All elements determined by this method have, at minimum, one isotope free of isobaric elemental interference. Of the analytical isotopes recommended for use with this method, only selenium-82 has an isobaric elemental interference (krypton-82). If alternative analytical isotopes having higher natural abundances are selected, in order to achieve greater sensitivity, an isobaric interference may occur. All data obtained under such conditions must be corrected by

measuring the signal from another isotope of the interfering element and subtracting the appropriate signal ratio from the isotope of interest. A record of this correction process shall be included with the data. It should be noted that such corrections will only be as accurate as the accuracy of the isotope ratio used in the elemental equation for data calculations. Relevant isotope ratios should be established prior to the application of any corrections. Interferences from doubly charged ions may not be correctable. The Contractor shall monitor the intensities of the singly charged ions of those isotopes that can cause doubly charged interferences and note high readings in the Sample Delivery Group (SDG) Narrative.

4.2 Abundance Sensitivity

Abundance sensitivity is a property defining the degree to which the wings of a mass peak contribute to adjacent masses. Abundance sensitivity is affected by ion energy and mass filter operating pressure. Wing overlap interferences may result when a small ion peak is being measured adjacent to a large one. The potential for these interferences should be recognized and the spectrometer resolution should be adjusted to minimize them.

4.3 Isobaric Polyatomic Ion Interferences

Isobaric polyatomic ion interferences are caused by ions consisting of more than one atom which have the same nominal mass-to-charge ratio as the isotope of interest, and which cannot be resolved by the mass spectrometer. These ions are commonly formed in the plasma or interface system from support gases or sample components. Most of the common interferences have been identified and are listed in Table 2 - Isobaric Molecular-Ion Interferences, with the target analytes affected. Such interferences must be recognized, and when they cannot be avoided by the selection of alternative analytical isotopes, appropriate corrections must be made to the data. The use of collision cells to reduce these interferences is permitted. Equations for the correction of data should be established at the time of the analytical sequence, since polyatomic ion interferences will be highly dependent on the sample matrix and chosen instrument conditions.

4.4 Physical Interferences

Physical interferences are associated with the physical processes which govern the transport of the sample into the plasma, sample conversion processes in the plasma, and the transmission of ions through the plasma-mass spectrometer interface. These interferences may result in differences between instrument responses for the sample and the calibration standards. Physical interferences may occur in the transfer of solution to the nebulizer (e.g., viscosity effects), at the point of aerosol formation and transport to the plasma (e.g., surface tension), or during the excitation and ionization processes within the plasma itself. High levels of dissolved solids in the sample may contribute to deposits of material on the extraction and/or skimmer cones. Deposits can reduce the effective diameter of the orifices and therefore ion transmission. Dissolved solid levels not exceeding 0.2% (w/v) have been recommended to reduce such effects. Internal standardization may be effectively used to compensate for many physical interference effects. Internal standards ideally should have similar analytical behavior to the elements being determined.

4.5 Memory Interferences

Memory interferences result when isotopes of elements in a previous sample contribute to the signals measured in a new sample. Memory effects, or carryover, can result from sample deposition on the sampler and skimmer cones, as well as from the buildup of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse solution between samples (Section 7.3.3). The possibility of memory interferences should be recognized within an analytical sequence and suitable rinse times or monitoring should be used to reduce them. Memory interferences may also be assessed within an analytical sequence by using a minimum of three replicate integrations for data acquisition. If the integrated signal values drop consecutively, the analyst should be alerted to the possibility of a memory effect, and should examine the analyte concentration in the previous sample to identify if it was high. If a memory interference is suspected, the sample should be reanalyzed after a rinse period.

5.0 SAFETY

See Section 12.0 in Exhibit D - Introduction to Inorganic 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 Statement of Work (SOW) is the responsibility of the Contractor. The Contractor shall document any use of alternate equipment or supplies in the SDG Narrative.

6.1 Glassware/Labware

6.1.1 250 milliliter (mL) beaker or other appropriate vessel (glass or plastic)

6.1.2 Watch glasses (glass or plastic)

6.1.3 Funnels

6.1.4 Graduated cylinders

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

6.1.6 Thermometer that covers range of 0-200°C

6.1.7 Whatman No. 42 filter paper (or equivalent)

6.1.8 Hotplate, block digester, or other heating source capable of maintaining 95°C (±3°C)

6.1.9 Balances – Top loader balance, 300 gram (g) capacity, and a minimum sensitivity of ±1.0 milligram (mg)

A balance calibration must be checked with known masses once per each day of use. This verification consists of a check with two weights covering the range expected (approximately ±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 must 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 E617-97 (2008) or equivalent (e.g., earlier Class 'S' defined masses). All balances must be checked at least once annually by a certified technician. The reference masses used by the Contractor must 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 Inductively Coupled Plasma - Mass Spectrometer

The ICP-MS consists of:

- An instrument capable of scanning the mass range 5-250 atomic mass units (u) with a minimum resolution capability of 1 u peak width at 5% peak height and either a conventional or extended dynamic range detector.
- A radio-frequency generator compliant with Federal Communications Commission (FCC) regulations.
- A high purity (99.99%) argon gas supply.
- A variable speed peristaltic pump to deliver sample solution to the nebulizer.
- A mass-flow controller on the nebulizer gas supply is required.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

Reagents may contain elemental impurities that might affect the integrity of analytical data. Due to the high sensitivity of ICP-MS, high-purity reagents should be used whenever possible. Suitable acids are available from a number of manufacturers or may be prepared by sub-boiling distillation. Nitric acid is preferred for ICP-MS in order to minimize polyatomic ion interferences. Several polyatomic ion interferences result when hydrochloric acid is used; however, it should be noted that hydrochloric acid is required to maintain stability in solutions containing antimony and silver. When hydrochloric acid is used, corrections for the chloride polyatomic ion interferences must be applied to all data.

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.

7.1.2 Hydrochloric acid - Concentrated 32-38% (specific gravity 1.19).

7.1.3 Hydrochloric acid (50% v/v) - Add 500 mL conc. hydrochloric acid to 400 mL reagent water and dilute to 1 Liter (L).

7.1.4 Nitric acid - Concentrated 67-70% (specific gravity 1.41).

7.1.5 Nitric acid (50% v/v) - Add 500 mL conc. nitric acid to 400 mL reagent water and dilute to 1 L.

7.1.6 Nitric acid (2% v/v) – Add 20 mL conc. nitric acid to 400 mL reagent water and dilute to 1 L.

7.1.7 Nitric acid (1% v/v) – Add 10 mL conc. nitric acid to 400 mL reagent water and dilute to 1 L.

7.2 Standards

7.2.1 Introduction

The Contractor must provide all standards, except as noted, to be used with this contract. These standards may be used only after they have been certified according to the procedure in Exhibit D - Introduction to Inorganic Analytical Methods, Section 11.0. The Contractor must be able to verify that the standards are certified. Manufacturer's certificates of analysis must be retained by the Contractor and presented upon request.

Samples, sample digestates, and standards must be stored separately.

7.2.2 Stock Standard Solutions

Stock standard solutions may be purchased from a reputable source or prepared from reagent grade chemicals or metals (at least 99.99% pure). All salts must be dried for 1 hour at 105°C unless otherwise specified. Stock solutions should be stored in Fluorinated Ethylene Propylene (FEP) fluorocarbon bottles. Note that some metals, particularly those which form surface oxides, require cleaning prior to being weighed. This may be achieved by pickling the surface of the metal in acid. An amount in excess of the desired weight should be pickled repeatedly, rinsed with reagent water, dried, and weighed until the desired weight is achieved.

7.2.3 Secondary Dilution Standards

Prepare mixed secondary dilution standard solutions by diluting the appropriate volumes of stock standards with 1% (v/v) nitric acid, or as recommended by the manufacturer, to obtain the final volume. Originating stock standards should be checked for the presence of impurities which might influence the accuracy of the standard. Freshly prepared standards should be transferred to acid-cleaned, not previously used, FEP fluorocarbon bottles for storage and monitored periodically for stability. Mixed secondary dilution standard solutions may be purchased. The purchased standards shall meet the requirements in Section 7.2.1.

7.2.4 Working Standards

7.2.4.1 Mixed Calibration Standard Solutions

Care must be taken in the preparation of mixed calibration standards to ensure that the analytes are compatible and stable. Fresh calibration standards should be prepared from mixed standard solutions every 2 weeks or less.

Prepare the mixed standards to levels appropriate to the operating range of the instrument using 1% (v/v) nitric acid or to match the matrix of the digested samples. The analyte concentrations in the calibration standards should be sufficient to produce good measurement precision and to accurately define the slope of the response curve.

7.2.4.2 Internal Standard Solution

The internal standard solution is to be added to all digested samples, blanks, and standards by the analyst prior to analysis, or it can be added automatically by the instrument during analysis of all digested samples, blanks, and standards. Prepare the mixed internal standard solution by following the manufacturer's guidelines.

7.2.4.3 Tuning Solution

This solution is used for instrument tuning and mass calibration prior to analysis. Prepare a mixed standard by diluting beryllium, magnesium, cobalt, indium, and lead stock standards to 100 micrograms/Liter (µg/L) with 1% (v/v) nitric acid. The concentration of this solution can be reduced based on recommendations from the instrument manufacturer. If indium is also selected as an internal standard, and added automatically, the resulting indium concentration in the tune solution reaching the instrument may exceed 100 µg/L and is allowed for indium only.

7.2.4.4 Interference Check Sample Solution

7.2.4.4.1 The Interference Check Sample (ICS) consists of two solutions: ICS Solution A (ICSA) and ICS Solution AB (ICSAB). ICSA consists of the interferents and ICSAB consists of the analytes mixed with the interferents. The ICS standards (ICSA for the interferents only and ICSB for the analytes only) shall be obtained by the EPA.

7.2.4.4.1.1 Only if the ICS solutions are not available from the EPA, ICSs shall be prepared with interferent and analyte concentrations at the levels specified in Table 1 – Interferent and Analyte Concentrations Used for ICP-MS Interference Check Sample (ICS).

7.2.4.4.1.2 If the solutions are prepared, the mean value and standard deviation shall be established by initially analyzing the ICSs at least five times repetitively for each analyte listed. Results shall be within the control limits of ±20% of the established mean value or ±2 times the analyte’s Contract Required Quantitation Limits (CRQL) of the established mean value, whichever is greater. The mean and standard deviation shall be reported in the raw data.

7.2.4.5 Initial Calibration Verification Solutions

7.2.4.5.1 The Initial Calibration Verification (ICV) solution(s) shall be obtained from the EPA.

7.2.4.5.1.1 If the solution(s) is (are) not available from the EPA, then the ICV solution shall be prepared by the laboratory using a certified solution for each analyte from an independent source. An independent source is defined as a standard composed of the analytes from a different source than those used in the standards for the instrument calibration. Analyses shall be conducted at a concentration other than that used for instrument calibration, but near the middle of the calibration range.

7.2.4.5.1.2 The ICV standard shall be prepared in the same acid matrix as the calibration standards and in accordance with the instructions provided by the supplier.

7.3 Blanks

Three types of blanks are required for this method. A Calibration Blank is used to establish the analytical calibration curve, a Preparation Blank (see Section 12.1) is used to assess possible contamination from the sample preparation procedure and to assess spectral background, and a rinse solution is used to flush the instrument between samples to reduce memory interferences.

7.3.1 Calibration Blank - Consists of 1% (v/v) nitric acid in reagent water or matrix matched to the digested samples. The Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB) are identical in composition to the Calibration Blank and are used to monitor for analyte carryover.

7.3.2 Preparation Blank - Must contain all the reagents in the same volumes as used in preparing the samples. The Preparation Blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis. Soil/sediment blanks shall use 1.00 mL (±0.01 mL) of reagent water.

7.3.3 Rinse Solution – Must contain sufficient nitric acid to allow the instrument to return to baseline between the analysis of digested samples, blanks, and standards. The rinse solution would typically consist of 2% (v/v) nitric acid in reagent water.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Sample Collection and Preservation

All aqueous/water and soil/sediment samples must be collected in glass or polyethylene containers. Aqueous/water samples must be preserved with nitric acid to pH less than or equal to 2 immediately after collection. All soil/sediment samples must be iced or refrigerated at ≤6°C but not frozen from the time of collection until receipt at the laboratory.

8.2 Sample Storage

All aqueous/water and soil/sediment samples must be stored at ≤6°C but not frozen from the time of sample receipt until digestion. If aqueous/water samples are received in glass containers, the Contractor shall note this in the SDG Narrative.

8.2.1 Unused Sample Storage

The Contractor shall retain the unused portion of aqueous/water and soil/sediment samples, for a period of 60 days after delivery of a complete, reconciled data package to the EPA. The samples may be stored at room temperature.

8.2.2 Digestate Sample Storage

Sample digestates must be stored until 180 days after delivery of a complete, reconciled data package to the EPA. The Contractor shall store sample ICP-MS digestates in plastic bottles. The bottles shall be labeled with the EPA Sample Number, Case Number, SDG Numbers, MA No. (if applicable), and digestion date. A logbook of stored digestates, listing the EPA Sample Numbers and associate Case and SDG Numbers, shall be maintained.

8.2.3 Container Storage

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

8.3 Contract Required Holding Time

The holding time for metals is 180 days from Validated Time of Sample Receipt (VTSR).

9.0 CALIBRATION AND STANDARDIZATION

9.1 Instrument Operating Parameters

Because of the differences between various manufacturers 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. The Method Detection Limit (MDL), precision, and interference effects must be investigated and established for each individual analyte on that particular instrument. All measurements must be within the operational range of the instrument where corrections are valid. It is the responsibility of the analyst to verify the instrument configuration and operating conditions used to satisfy the analytical requirements and to maintain Quality Control (QC) data confirming instrument performance and analytical results.

9.2 Pre-Calibration Routine

Prior to calibration, the Contractor shall set up each instrument with the operating parameters established in Section 9.1 and conduct any necessary adjustments to the plasma conditions. The instrument must be allowed to become stable (usually 30 minutes) before calibration is performed.

9.3 Instrument Performance Check

9.3.1 Summary of Instrument Performance Check

The Contractor shall demonstrate instrument stability and precision by analyzing the tuning solution or Instrument Performance Check (IPC) sample.

9.3.2 Frequency of Instrument Performance Check

The tuning solution shall be analyzed prior to instrument calibration.

9.3.3 Procedure for Instrument Performance Check

The Contractor shall analyze the tuning solution as a single analysis with at least five integrations.

9.3.4 Calculations for Instrument Performance Check

The Percent Relative Standard Deviation (%RSD) shall be calculated by the instrument manufacturer’s software.

9.3.5 Technical Acceptance Criteria for Instrument Performance Check

9.3.5.1 The mass calibration shall be within 0.1 u over the range of 6 to 210 u. The peak width shall be measured at the height set by the instrument manufacturer.

9.3.5.2 The %RSD shall be less than or equal to 5.0% for each isotope in the tuning solution.

9.3.5.3 The Contractor shall report the full peak width and the percentage of peak height this full peak width (in u) was measured at for each of the isotope masses in the tuning solution.

9.3.6 Corrective Action for Instrument Performance Check

9.3.6.1 If the mass calibration is not within 0.1 u over the range of 6 to 210 u, the analysis shall be terminated, the problem corrected, and the instrument re-tuned.

9.3.6.2 If the %RSD exceeds 5.0%, the analysis shall be terminated, the problem corrected, and the instrument re-tuned.

9.3.6.3 No sample results may be reported from an analytical sequence associated with a tune that does not meet the technical acceptance criteria.

9.4 Instrument Calibration Procedure

9.4.1 Summary of Instrument Calibration

Prior to sample analysis, the Contractor shall calibrate each instrument to determine sensitivity and linearity of the response.

9.4.2 Frequency of Instrument Calibration

Each instrument shall be calibrated each time it is turned on, set up, or after ICV, ICB, Continuing Calibration Verification (CCV), or CCB failure. The instrument calibration date and time shall be included in the raw data.

9.4.3 Procedure for Instrument Calibration

9.4.3.1 Each instrument shall be calibrated according to the manufacturer’s recommended procedures.

9.4.3.2 At least six calibration standards shall be used for each analyte. The calibration standards shall be prepared as in Section 7.2.4.1. One of the standards shall be a blank standard and one shall be at or below the CRQL but greater than the MDL. The rest of the standards shall be uniformly spread out in graduated amounts over the appropriate calibration range of the analyte.

9.4.3.3 A minimum of three replicate integrations are required for data acquisition. The Contractor shall use the average of all the integrations for instrument calibration and data reporting.

9.4.4 Calculations for Instrument Calibration

9.4.4.1 The calibration curve shall be calculated for each analyte using linear regression by plotting the concentration of the standard (in µg/L) on the X-axis versus the corrected instrument response on the Y-axis. The corrected instrument responses are those corrections (e.g., correction for background, internal standards, interferences, calibration blank) that may be applied to the raw uncorrected instrument response prior to determining the calibration curve.

9.4.4.2 The Contractor may use standard linear regression, weighted linear regression (1/concentration, 1/square of concentration, variance, 1/variance, standard deviation, 1/standard deviation, or 1/square of standard deviation), or linear regression with zero force calibration models, as appropriate, for the above calculation. No other types of equations (e.g., quadratic) are to be used.

9.4.4.3 The calibration curve for each analyte shall be checked to establish the representativeness of the data that were used to produce it. This check involves re-fitting the data of the non-blank calibration standards back to the calibration curve, and

computing the difference between the calculated concentration and the expected concentration for each of these standards. The difference is then divided by the expected concentration of the respective standard and multiplied by 100.

9.4.5 Technical Acceptance Criteria for Instrument Calibration

9.4.5.1 The correlation coefficient of the calibration curve shall be greater than or equal to 0.995.

9.4.5.2 The Percent Difference (%D) for each of the standards shall be within the control limits of ±30%.

9.4.5.3 If a standard is analyzed for a particular analyte at a concentration that is below the CRQL and the %D criteria is not met, that standard can be excluded from the calibration curve as long as the lowest non-zero standard for that analyte is still analyzed at or below the CRQL and all standards included in the calibration curve are continuous and consecutive.

9.4.6 Corrective Action for Instrument Calibration

9.4.6.1 Sample analysis shall not begin until the criteria described in Section 9.4.5 have been met.

9.4.6.2 Any changes or corrections to the analytical system shall be followed by recalibration.

9.5 Initial Calibration Verification

9.5.1 Summary of Initial Calibration Verification

Prior to sample analysis, the Contractor shall demonstrate the accuracy of the instrument calibration for each instrument through the analysis of an ICV standard.

9.5.2 Frequency of Initial Calibration Verification

The ICV shall be analyzed immediately after the instrument has been calibrated.

9.5.3 Procedure for Initial Calibration Verification

9.5.3.1 The ICV shall be analyzed at each mass used to report final results for each analyte.

9.5.3.2 The ICV shall reflect the conditions of analysis of the associated analytical samples.

9.5.4 Calculations for Initial Calibration Verification

9.5.4.1 The Percent Recovery (%R) of the ICV shall be calculated using the following equation:

EQ. 1 ICV Percent Recovery

$$\%R = \frac{\text{Found (ICV)}}{\text{True (ICV)}} \times 100$$

WHERE,

Found (ICV) = The found concentration of the analyte in the ICV Solution

True (ICV) = The expected concentration of the analyte in the ICV Solution

9.5.4.2 The Percent Relative Standard Deviation (%RSD) from all replicate integrations shall be calculated for each mass used to report final results using Equations 2, 3, and 4.

EQ. 2 Percent Relative Standard Deviation Calculation

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

WHERE,

SD = Standard deviation of ICV replicates (per analyte) from EQ. 3

$\bar{X}$ = Mean value of the ICV replicates (per analyte) from EQ. 4

9.5.4.3 Equation 3 is the general formula for Standard Deviation (SD) for a statistically small set of values.

EQ. 3 Standard Deviation Calculation

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (X_i - \bar{X})^2}{(n-1)}}$$

WHERE,

X_i = Each individual value used to calculate the mean

$\bar{X}$ = The mean of n values from EQ. 4

n = Total number of values

9.5.4.4 Equation 4 is the general formula for the mean of a set of values ($\bar{X}$).

EQ. 4 Mean Value Calculation

$$\bar{X} = \frac{\sum_{i=1}^{n} X_i}{n}$$

WHERE,

X_i = Each individual value used to calculate the mean

n = Total number of values

9.5.5 Technical Acceptance Criteria for Initial Calibration Verification

9.5.5.1 The ICV %R shall be within the control limits of 90-110%.

9.5.5.2 The %RSD of the ICV integrations shall be less than or equal to 5.0%.

9.5.6 Corrective Action for Initial Calibration Verification

If the recovery is outside the control limits of 90% Recovery (low) or 110% Recovery (high), or if the %RSD as calculated from all replicate integrations exceeds 5.0%, the analysis shall be terminated, the problem corrected, the instrument recalibrated, and the calibration verified.

9.6 Continuing Calibration Verification

9.6.1 Summary of Continuing Calibration Verification

Prior to sample analysis, periodically during analysis, and at the conclusion of analysis, the Contractor shall demonstrate the stability of the calibration through the analysis of a CCV standard. The Contractor shall not analyze a blank immediately prior to the analysis of the CCV.

9.6.2 Frequency of Continuing Calibration Verification

9.6.2.1 A CCV shall be analyzed at the beginning of the analytical sequence and after the last analytical sample. A CCV shall also be analyzed at a frequency not to exceed every 2 hours during an analytical sequence. See the example analytical sequence in Section 10.3.6.

9.6.2.2 The analytical sequence can continue indefinitely as long as samples are being continuously analyzed without the instrument being turned off and successive CCV standards meet the technical acceptance criteria in Section 9.6.5.

9.6.3 Procedure for Continuing Calibration Verification

9.6.3.1 The CCV standard shall be prepared using the same source and in the same acid matrix as the calibration standards by combining compatible analytes at a concentration at or near the mid-level of their respective calibration curve.

9.6.3.2 The same CCV standard shall be used throughout the analytical sequences for an SDG.

9.6.3.3 The CCV shall be analyzed at each mass used to report final results for each analyte.

9.6.3.4 Each CCV analyzed shall reflect the conditions of analysis of all associated analytical samples (the preceding analytical samples up to the previous CCV as applicable and the analytical samples following this CCV up to the next CCV as applicable).

9.6.4 Calculations for Continuing Calibration Verification

9.6.4.1 The %R of the CCV shall be calculated using the following equation:

EQ. 5 CCV Percent Recovery

$$\%R = \frac{\text{Found (CCV)}}{\text{True (CCV)}} \times 100$$

WHERE,

Found (CCV) = The found concentration of the analyte in the CCV Solution

True (CCV) = The expected concentration of the analyte in the CCV Solution

9.6.4.2 The %RSD from all replicate integrations shall be calculated for each mass used to report final results using Equations 2, 3, and 4 above.

9.6.5 Technical Acceptance Criteria for Continuing Calibration Verification

9.6.5.1 The CCV %R shall be within the control limits of 90-110%.

9.6.5.2 The %RSD of the CCV integrations shall be less than or equal to 5.0%.

9.6.5.3 All samples shall be analyzed within 2 hours of an acceptable opening and closing CCV.

9.6.6 Corrective Action for Continuing Calibration Verification

If the deviations of the CCV are greater than the specified control limits of 90% Recovery (low) or 110% Recovery (high), or if the %RSD as calculated from all replicate integrations exceeds 5.0%, the analysis shall be terminated, the problem corrected, the instrument recalibrated, the calibration verified, and reanalysis of all analytical samples analyzed since the last compliant calibration verification shall be performed for the analytes affected.

9.7 Initial and Continuing Calibration Blank

9.7.1 Summary of Calibration Blank

Prior to sample analysis, periodically during analysis, and at the conclusion of the analysis, the Contractor shall demonstrate the stability of the calibration baseline through the analysis of an ICB and CCB.

9.7.2 Frequency of Calibration Blank

9.7.2.1 An ICB shall be analyzed immediately after the instrument has been calibrated and the calibration verified by the analysis of the ICV.

9.7.2.2 Each CCB shall be analyzed immediately after the analysis of a CCV.

9.7.3 Procedure for Calibration Blank

9.7.3.1 The ICB and CCB samples shall be analyzed at each mass used for reporting final results for each analyte.

9.7.3.2 The ICB analyzed shall reflect the conditions of analysis of the associated analytical samples.

9.7.3.3 Each CCB analyzed shall reflect the conditions of analysis of the associated analytical samples (the preceding analytical samples up to the previous CCB as applicable and the analytical samples following this CCB up to the next CCB as applicable).

9.7.4 Calculations for Calibration Blank

The results for the ICB and CCB samples shall be calculated using Equation 6 in Section 11.0.

9.7.5 Technical Acceptance Criteria for Calibration Blank

The absolute value of each calibration blank result shall be less than or equal to the CRQL for aqueous/water samples for the analyte.

9.7.6 Corrective Action for Calibration Blank

If the absolute value of the calibration blank exceeds the CRQL for aqueous/water samples, the analysis shall be terminated, the problem corrected, the instrument recalibrated, the calibration verified, and reanalysis of all affected analytical samples analyzed since the last compliant calibration blank performed for the analytes affected.

10.0 PROCEDURE

10.1 Aqueous/Water Sample Preparation

Preparation Method 200.8 – Total Recoverable Analytes [based on the EPA NERL Method 200.8, Revision 5.5 (October 1999)]

10.1.1 If the sample pH was ≤2 at the time of sample receipt, the Contractor shall proceed to Section 10.1.2.

If the sample pH was adjusted at the time of sample receipt (see Exhibit D – General Inorganic Analysis, Section 10.1.2.1), the Contractor shall take a second pH measurement, prior to removing an aliquot of the sample for digestion, to verify that the sample was properly preserved upon receipt. If the second pH measurement is ≤2, proceed to Section 10.1.2. If the second pH measurement 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.

10.1.2 For the determination of total recoverable analytes in aqueous/water samples, transfer a 100 mL (±1 mL) aliquot from a well-mixed, acid-preserved sample to an appropriately sized (approximately 250 mL) digestion vessel (e.g., a beaker or hot block digestion tube). The sample shall not be diluted prior to digestion.

NOTE: A reduced sample volume of 50 mL can be used. If this reduced volume is used, then all other reagents and volumes shall be reduced appropriately.

10.1.3 Add 2 mL 50% (v/v) nitric acid and 1 mL 50% (v/v) hydrochloric acid to the beaker containing the measured volume of sample. Place the beaker on a hotplate, or other comparable heating device, for solution evaporation. The hotplate should be located in a fume hood and previously adjusted to provide evaporation at a temperature of 95°C (±3 °C), when covered. The beaker should be covered with an elevated watch glass or other necessary steps should be taken to prevent sample contamination from the fume hood environment.

10.1.4 Reduce the volume of the sample aliquot to about 20 mL by gently heating at 95°C (±3°C). **DO NOT BOIL**. This step takes about 2 hours for a 100 mL aliquot with the rate of evaporation rapidly increasing as the sample volume approaches 20 mL. (A spare beaker containing 20 mL of water can be used as a gauge.)

10.1.5 Cover the beaker with a watch glass to reduce additional evaporation and gently reflux the sample for 30 minutes. (Slight boiling may occur, but vigorous boiling must be avoided to prevent loss of the HCl-H_2O azeotrope.)

10.1.6 Allow the beaker to cool. Quantitatively transfer the sample solution to a 100 mL volumetric flask, make to volume with reagent water, stopper, and mix.

10.1.7 Allow any undissolved material to settle overnight, or centrifuge or filter a portion of the prepared sample until clear to avoid plugging the nebulizer with solid particles.

10.1.8 The sample is now ready for analysis. Because the effects of various matrices on the stability of the samples cannot be characterized, all analyses should be performed as soon as possible after the completed preparation.

10.1.8.1 The digested sample may be further diluted if high levels of interferences (e.g., chloride) are noted or if any of the analytes exceed the upper limit of their respective calibration curves, according to Exhibit D – Introduction to Inorganic Analytical Methods, Section 7.0.

10.2 Soil/Sediment Sample Preparation

Preparation Method 200.8 – Total Recoverable Analytes [based on the EPA NERL Method 200.8, Revision 5.5 (October 1999)]

10.2.1 Mix the sample thoroughly to achieve homogeneity. Weigh to the nearest 0.01 g and transfer 1.0 – 1.5 g sample (wet weight) to an appropriately sized digestion vessel (e.g., a beaker or hot block digestion tube).

10.2.2 Add 4 mL of 50% (v/v) nitric acid and 10 mL of 1:4 HCl, mix the slurry, and cover with a watch glass. Heat the sample to 95°C (±3°C) and reflux for 30 minutes without boiling.

10.2.3 After cooling, transfer the digestate to a 100 mL volumetric flask and dilute to volume with reagent water, stopper, and mix. Allow the sample extract solution to stand overnight to separate insoluble material or centrifuge a portion of the sample until clear. The solution being analyzed must be clear to avoid plugging the nebulizer with solid particles. In place of settling, a portion of the sample (after dilution and mixing) may be filtered through Whatman No. 42 filter paper (or equivalent). Care should be taken to avoid potential contamination from filtration.

10.2.4 Prior to analysis, adjust the chloride concentration by pipetting 20 mL of the prepared solution into a 100 mL volumetric flask, dilute to volume with reagent water, and mix.

10.2.5 The sample is now ready for analysis. Report the final volume as 500 mL and the dilution factor as 1.0 for samples not requiring any additional dilution beyond that specified for chloride adjustment.

10.2.5.1 The digested sample may be further diluted if high levels of interferences are noted, high dissolved solid content, or if any of the analytes exceed the upper limit of their respective calibration curves, according to Exhibit D – Introduction to Inorganic Analytical Methods, Section 7.0.

10.3 Sample Analysis

10.3.1 It is highly recommended that a semi-quantitative analysis be carried out to screen for high element concentrations. This screening procedure can be performed using Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) or some other technique. Information gained from this may be used to prevent potential damage to the detector during sample analysis and to identify elements which may be higher than the calibrated range. Matrix screening may be carried out by diluting the sample by a factor of 500 and analyzing in semi-quantitative mode. The sample should also be screened for background levels of all elements chosen for use as internal standards in order to prevent bias in the calculation of analytical data. Undiluted sample results are not required if elements are present in the undiluted sample digestate at levels which could damage the detector.

10.3.2 For all sample analyses, a minimum of three replicate integrations are required for data acquisition. Use the average of all the integrations for data reporting.

10.3.3 In accordance with the instrument manufacturer's instructions, a rinse solution should be used to flush the system between samples. Allow sufficient time to remove traces of the previous sample. Samples should be aspirated for a sufficient period of time to obtain a stable response prior to the collection of data.

10.3.4 Sample digestates having high levels of interferences or concentrations higher than the established calibrated range as determined by the expected concentration of the highest calibration standard shall be diluted into range and reanalyzed, according to Exhibit D – Introduction to Inorganic Analytical Methods, Section 7.0. The sample digestate should first be analyzed for the trace elements, protecting the detector from the high concentration elements, if necessary, by the selection of appropriate scanning windows. The sample digestate should then be diluted for the determination of the remaining elements.

10.3.5 All masses which might affect data quality must be monitored during the analytical sequence. At a minimum, those masses identified in Table 3 - Recommended Isotopes and Masses for Selected Elements, must be monitored in the same scan that is used for the collection of the data. This information should be used to correct the data for identified interferences.

10.3.6 Example Analytical Sequence for ICP-MS Including the Instrument Calibration:

Tune
S##
S##
S##
S##
S##
S##
ICV
ICB
ICSA
ICSAB
CCV###
CCB###
samples
CCV###
CCB###
samples
CCV###
CCB###, etc.

11.0 DATA ANALYSIS AND CALCULATIONS

11.1 Recommended Elemental Equations

Elemental expressions recommended for sample data calculations are listed in Table 4 - Recommended Elemental Expressions for Isobaric Interferences. Do not report element concentrations below the MDL.

11.2 Data Value Corrections

Data values as produced by the instrument should be corrected for instrument drift or sample matrix induced interferences by the application of internal standardization. Corrections for characterized spectral interferences should be applied to the data. Chloride interference corrections should be made on all samples, regardless of the addition of hydrochloric acid, as the chloride ion is a common constituent of environmental samples.

11.3 Multiple Monitored Isotopes

If an element has more than one monitored isotope, examination of the concentration calculated for each isotope or the isotope ratios will provide useful information in detecting a possible spectral interference. Consideration should therefore be given to both primary and secondary isotopes in the evaluation of sample concentration. In some cases, secondary isotopes may be less sensitive or more prone to interferences than the primary recommended isotopes; therefore, differences between the results do not necessarily indicate a problem with data calculated for the primary isotopes.

11.4 Calculate Target Analyte Concentrations

Calculate the Target Analyte concentration using the following equations.

11.4.1 Aqueous/Water Sample Calculation

EQ. 6 Aqueous/Water Sample Concentration

$$\text{Concentration}\,(\mu g/L) = C \times \frac{V_f}{V} \times DF$$

WHERE,

C = Instrument value in µg/L (The average of all replicate integrations)
V_f = Final digestion volume (mL)
V = Initial aliquot amount (mL)
DF = Dilution Factor

11.4.2 Soil/Sediment Sample Calculation

The concentrations determined in the digestate are to be reported on the basis of the dry weight of the sample, in units of mg/kg:

EQ. 7 Soil/Sediment Sample Concentration

$$\text{Concentration}\,(\text{mg/kg dry weight}) = C \times \frac{V_f}{W \times S} \times DF \,/\, 1000$$

WHERE,
C = Instrument value in µg/L (The average of all replicate integrations)
V_f = Final digestion volume (mL)
W = Initial aliquot amount (g)
S = % Solids/100 (Exhibit D – General Inorganic Analysis, Section 10.1.1)
DF = Dilution Factor

11.5 Adjusted Contract Required Quantitation Limit Calculation

11.5.1 Calculate the adjusted CRQL for aqueous/water samples, by multiplying the CRQL (µg/L) by the sample dilution factor and the V_f/V term as noted in Equation 6.

11.5.2 Calculate the adjusted CRQL for soil/sediment samples using the following equation:

EQ. 8 Adjusted Soil/Sediment CRQL

$$\text{Adjusted CRQL(mg/kg)} = C \times \frac{W_M}{W \times S} \times \frac{V_f}{V_M} \times DF$$

WHERE,
C = CRQL (mg/kg)
W_M = Minimum method required aliquot amount (g) (1.00 g)
W = Initial aliquot amount (g)
V_M = Method required final sample digestion volume (mL) (100 mL)
V_f = Final digestion volume (mL)
S = % Solids/100 (Exhibit D – General Inorganic Analysis, Section 10.1.1)
DF = Dilution Factor

12.0 QUALITY CONTROL

12.1 Preparation Blank Sample

12.1.1 Summary of Preparation Blank Sample

The Preparation Blank is used to monitor for possible contamination throughout the entire sample preparation and analysis process.

12.1.2 Frequency of Preparation Blank Sample

At least one Preparation Blank shall be prepared with every SDG, or with each preparation batch, whichever is more frequent.

12.1.3 Procedure for Preparation Blank Sample

The Preparation Blank shall be carried through the complete sample preparation procedure for the matrix and contain the same acid concentration in the final digestate as the samples.

12.1.4 Calculations for Preparation Blank Sample

Calculate the results for aqueous Preparation Blanks by using Equation 6. Calculate the results for soil/sediment Preparation Blanks by using Equation 7.

12.1.5 Technical Acceptance Criteria for Preparation Blank Sample

12.1.5.1 The absolute value of the Preparation Blank result shall be less than or equal to the CRQL.

12.1.5.2 Any analyte concentration in the Preparation Blank may be greater than the CRQL, if the concentration of the analyte in the associated samples is greater than or equal to 10 times the blank concentration.

12.1.5.3 Any analyte concentration in the Preparation Blank may be less than the negative CRQL, if the concentration in the associated samples is greater than or equal to 10 times the CRQL.

12.1.6 Corrective Action for Preparation Blank Sample

12.1.6.1 If any analyte concentration in the Preparation Blank is greater than the CRQL, and the concentration of the analyte in any of the associated samples is less than 10 times the blank concentration, then all samples with less than 10 times the blank concentration shall be reprepared and reanalyzed with appropriate new QC for that analyte.

12.1.6.2 If any analyte concentration in the Preparation Blank is less than the negative CRQL, and the concentration in the associated samples is less than 10 times the CRQL, then all samples with less than 10 times the CRQL concentration shall be reprepared and reanalyzed with appropriate new QC for that analyte.

12.2 Interference Check Sample

12.2.1 Summary of Interference Check Sample

The Contractor shall analyze the Interference Check Sample to verify elemental and polyatomic corrections. If not available, then the ICS can be prepared by the analyst.

12.2.2 Frequency of Interference Check Sample

The Contractor shall analyze, quantitate, and report the results for all elements on the TAL, and monitor for all interferents, including those caused by these elements, immediately after the initial calibration sequence, but not before the ICV/ICB.

12.2.3 Procedure for Interference Check Sample

12.2.3.1 The ICS solutions (Section 7.2.4.4) shall be analyzed according to the instructions supplied with the ICS.

12.2.3.2 The Contractor shall initially analyze the ICSA and the ICSAB undiluted. Any dilution of the ICS (for the highest concentration elements) necessary to meet the calibrated range values of the instrument shall be analyzed after the undiluted analyses of the ICSA and ICSAB.

12.2.3.3 An ICS analysis consists of analyzing both solutions consecutively, starting with Solution A.

12.2.4 Calculations for Interference Check Sample

12.2.4.1 The ICSA/ICSAB sample concentrations shall be calculated using Equation 6.

12.2.4.2 The %R of the ICSA and ICSAB shall be calculated using the following equations:

EQ. 9 ICSA Percent Recovery

$$\%R = \frac{\text{Found (ICSA)}}{\text{True (ICSA)}} \times 100$$

WHERE,
Found (ICSA) = The found concentration of the analyte in the ICSA Solution
True (ICSA) = The expected concentration of the analyte in the ICSA Solution

EQ. 10 ICSAB Percent Recovery

$$\%R = \frac{\text{Found (ICSAB)}}{\text{True (ICSAB)}} \times 100$$

WHERE,
Found (ICSAB) = The found concentration of the analyte in the ICSAB Solution
True (ICSAB) = The expected concentration of the analyte in the ICSAB Solution

12.2.5 Technical Acceptance Criteria for Interference Check Sample

12.2.5.1 The ICSA and ICSAB %R shall be within the control limits of ±20% of the analyte's true value or the results shall be within ±2 times the CRQL of the analyte's true value, whichever is greater. If the true value for a given analyte is not listed in the certified values for the solution, then the true value shall be assumed to be zero and the ±2 times the CRQL control limits shall apply.

For example, for Chromium (CRQL = 2 µg/L, ICSA true value = 43 µg/L) the correct control window to use would be the greater of ±20% of the true value (0.20 x 43 µg/L = ±8.6 µg/L) or the results shall be within ±2 times the CRQL (±4 µg/L). Therefore, the control window for the found value for Chromium in the ICSA is 43±8.6, or 34.4 to 51.6 µg/L.

12.2.5.2 Only if the ICS solutions are not available from the EPA, the %R of the prepared independent Check Sample results shall be within the control limits of ±20% of the established mean value or the results shall be within ±2 times the analyte's CRQL of the established mean value, whichever is greater.

12.2.6 Corrective Action for Interference Check Sample

If the deviations of the ICSA and/or ICSAB are greater than the specified control limits, the analysis shall be terminated, the problem corrected, the instrument recalibrated, the calibration reverified, and reanalysis of all analytical samples. For analytes with CRQLs less than 1000 µg/L, the ICSA and ICSAB results shall be reported from an undiluted sample analysis.

12.3 Matrix Spike and Post-Digestion Spike Samples

12.3.1 Summary of Matrix Spike and Post-Digestion Spike Samples

The Matrix Spike sample analysis is designed to provide information about the effect of the sample matrix on the digestion and/or measurement methodology.

12.3.2 Frequency of Matrix Spike and Post-Digestion Spike Samples

12.3.2.1 At least one Matrix Spike sample analysis shall be performed on each group of samples of a similar matrix type (i.e., aqueous/water, soil/sediment) or for each SDG, whichever is more frequent.[1]

12.3.2.2 If a Matrix Spike sample does not meet the technical acceptance criteria listed in Section 12.3.5, a Post-Digestion Spike sample shall be performed for those analytes that do not meet the specified criteria.

12.3.3 Procedure for Matrix Spike and Post-Digestion Spike Samples

12.3.3.1 For a Matrix Spike sample, the spike is added before the digestion (i.e., prior to the addition of other reagents).

12.3.3.2 The analyte spike shall be added in the amount given in Table 6 - Spiking Levels for Matrix Spike Sample Analyses, for each element analyzed. This is the level of spike present in the final digestate.

12.3.3.3 For a Post-Digestion Spike sample, the sample that was initially used for the Matrix Spike sample analysis shall be used for the Post-Digestion Spike analysis. Spike the unspiked aliquot of the undiluted digestate at two times the indigenous level or two times the CRQL, whichever is greater.

12.3.3.4 Samples identified as field blanks and Performance Evaluation (PE) samples shall not be used for Matrix Spike sample analysis. The EPA may require that a specific sample be used for the Spike sample analysis.

12.3.4 Calculations for Matrix Spike and Post-Digestion Spike Samples

12.3.4.1 If the Matrix Spike analysis is performed on the same sample that is chosen for the Duplicate sample analysis, spike calculations shall be performed using the results of the sample designated as the "original sample" (see Section 12.4). The average of the duplicate results cannot be used for the purpose of determining %R.

12.3.4.2 Calculate the Matrix Spike and Post-Digestion Spike %R using the following equation:

EQ. 11 Matrix Spike and Post-Digestion Spike Percent Recovery

$$\%R = \frac{SSR - SR}{SA} \times 100$$

WHERE,

SSR = Spiked Sample Result (µg/L or mg/kg) from EQ. 6 or EQ. 7

SR = Sample Result (original) (µg/L or mg/kg) from EQ. 6 or EQ. 7. When the sample concentration is less than the MDL, use SR=0.

SA = Spike Added Theoretical Result (µg/L or mg/kg). This is calculated by substituting the spiking amount used for the 'V_f' term and substituting the spiking standard concentration used for the 'C' term from EQ. 6 or EQ. 7.

NOTE: The units used for reporting SSRs will be identical to those used for reporting SRs.

[1] The EPA may require additional spike sample analyses, upon request from the EPA Regional Contract Laboratory Program Contracting Officer's Representative (EPA Regional CLP COR).

12.3.5 Technical Acceptance Criteria for Matrix Spike and Post-Digestion Spike Samples

The Matrix Spike and Post-Digestion Spike %Rs shall be within the control limits of 75-125%.

12.3.6 Corrective Action for Matrix Spike and Post-Digestion Spike Samples

12.3.6.1 If the Matrix Spike recovery is not at or within the limits of 75-125%, the data for all samples received and associated with that spike sample shall be flagged with "*". An exception to this rule is granted when the sample concentration exceeds the SA concentration by a factor of four or more. In such an event, the data shall be reported unflagged even if the %R does not meet the 75-125% recovery criteria.

12.3.6.2 When the Matrix Spike recovery is outside the control limits and the sample result does not exceed four times the spike added, a Post-Digestion spike shall be performed for those analytes that do not meet the specified criteria. Follow the procedures in Section 12.3.3.

12.3.6.3 If there is more than one Matrix Spike per matrix, per SDG, if one Matrix Spike sample recovery is not within contract criteria, then flag all the samples of the same matrix and method in the SDG.

12.4 Duplicate Sample

12.4.1 Summary of Duplicate Sample

Duplicates are analyzed to help determine sample homogeneity and laboratory precision.

12.4.2 Frequency of Duplicate Sample

One duplicate sample shall be analyzed from each group of samples of a similar matrix type (i.e., aqueous/water, soil/sediment) or for each SDG, whichever is more frequent.[2] Duplicates cannot be averaged for reporting.

12.4.3 Procedure for Duplicate Sample

12.4.3.1 Samples identified as field blanks and PE samples shall not be used for duplicate sample analysis. The EPA may require that a specific sample be used for duplicate sample analysis.

12.4.3.2 Prepare a second aliquot of the original sample. The duplicate sample shall be carried through the complete sample preparation procedure.

12.4.4 Calculations for Duplicate Sample

12.4.4.1 The Relative Percent Difference (RPD) for each analyte shall be calculated using the following equation:

EQ. 12 Duplicate Sample Relative Percent Difference

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

[2] The EPA may require additional duplicate sample analyses, upon request from the EPA Regional CLP COR.

WHERE,
S = Sample Result (original) (µg/L or mg/kg) from EQ. 6 or EQ. 7
D = Duplicate Sample Result (µg/L or mg/kg) from EQ. 6 or EQ. 7

12.4.5 Technical Acceptance Criteria for Duplicate Sample

12.4.5.1 The RPD shall be within the control limits of ±20 if the original and duplicate sample values are greater than or equal to five times the CRQL (see Exhibit C – Inorganic Target Analyte List and Contract Required Quantitation Limits).

12.4.5.2 The control limit shall be equal to the CRQL if either the sample or duplicate value are less than five times the CRQL or if one result is above five times the CRQL level and the other is below.

12.4.5.3 If both sample and duplicate values are less than the CRQL, the RPD is not calculated.

12.4.6 Corrective Action for Duplicate Sample

12.4.6.1 If the duplicate sample results are outside the control limits, flag all the data for samples received associated with that duplicate sample with an "*".

12.4.6.2 If there is more than one duplicate sample per SDG, per matrix, and if one duplicate result is not within contract criteria, flag all samples of the same matrix in the SDG.

12.5 Laboratory Control Sample

12.5.1 Summary of Laboratory Control Sample

Aqueous/water and soil/sediment Laboratory Control Samples (LCSs) shall be analyzed for each analyte using the same sample preparations, analytical methods, and Quality Assurance/Quality Control (QA/QC) procedures employed for the samples received.

12.5.2 Frequency of Laboratory Control Sample

One LCS shall be prepared for each prepared batch of aqueous/water or soil/sediment samples in an SDG.

12.5.3 Procedure for Laboratory Control Sample

The LCS for aqueous/water and soil/sediment samples shall be prepared by spiking an aliquot of reagent water (50-100 mL for aqueous/water, 1 mL for soil/sediment) such that the final digestate shall contain each analyte at two times the CRQL for the associated matrix.

12.5.4 Calculations for Laboratory Control Sample

Calculate the results for LCS by using Equations 6 or 7 as appropriate.

EQ. 13 LCS Percent Recovery

$$\%R = \frac{\text{Found (LCS)}}{\text{True (LCS)}} \times 100$$

WHERE,

Found (LCS)	=	The found concentration of each analyte in the LCS (µg/L or mg/kg) from EQ. 6 or 7. If the analyte concentration is less than the MDL, a value of zero shall be substituted for the Found (LCS).
True (LCS)	=	Two times the CRQL for the appropriate matrix (µg/L or mg/kg)

12.5.5 Technical Acceptance Criteria for Laboratory Control Sample

The %R shall be within the control limits of 70-130% for all analytes.

12.5.6 Corrective Action for Laboratory Control Sample

If the %R for the LCS for aqueous/water or soil/sediment samples are outside the control limits of 70-130%, the analyses shall be terminated, the problem corrected, and the samples associated with that LCS redigested and reanalyzed with appropriate new QC.

12.6 ICP-MS Serial Dilution

12.6.1 Summary of ICP-MS Serial Dilution

The Contractor shall perform Serial Dilution analyses to check for interference effects.

12.6.2 Frequency of ICP-MS Serial Dilution

The ICP-MS serial dilution analysis shall be performed on a sample from each group of samples of a similar matrix type (i.e., aqueous/water, soil/sediment) or for each SDG, whichever is more frequent, prior to reporting analyte concentration data.

12.6.3 Procedure for ICP-MS Serial Dilution

12.6.3.1 Prepare an aliquot of the original sample digestate and dilute it 1:4 (five-fold) with 1% nitric acid. This dilution shall be analyzed as the serial dilution.

12.6.3.2 If the original sample requires dilution for any analyte, a 1:4 (five-fold) dilution of that dilution shall be prepared and analyzed as a serial dilution.

12.6.3.3 Samples identified as field blanks and PE samples shall not be used for serial dilution analysis.

12.6.4 Calculations for ICP-MS Serial Dilution

The percent difference for each component are calculated using the following equation:

EQ. 14 Serial Dilution Percent Difference

$$\%\text{Difference} = \frac{\left| I - S \right|}{I} \times 100$$

WHERE,

I	=	Initial sample result (original)
S	=	Serial dilution result. If the analyte concentration is less than the MDL, a value of zero shall be substituted for "S".

12.6.5 Technical Acceptance Criteria for ICP-MS Serial Dilution

If the analyte concentration is sufficiently high (minimally a factor of 50 above the MDL in the original sample), then the serial dilution (a five-fold dilution) shall be within 10% of the original determination after correction for dilution.

12.6.6 Corrective Action for ICP-MS Serial Dilution

12.6.6.1 If the dilution analysis for one or more analytes is not within a control limit of 10%, a chemical or physical interference effect must be suspected, and the data for all affected analytes in the samples received and associated with that serial dilution must be flagged with an "*".

12.6.6.2 In the instance where there is more than one serial dilution per SDG, per matrix, if one serial dilution result is not within contract criteria, flag all the samples of the same matrix in the SDG.

12.6.6.3 If the internal standard responses for the field sample chosen for serial dilution analysis are not within the limits (identified in Section 12.7.5 – Technical Acceptance Criteria for Internal Standards), and the appropriate corrective action (two-fold dilution and reanalysis) is taken, the following shall apply to the serial dilution analysis:

- If the internal standard responses of the field sample reanalysis are within the limits, the serial dilution results are to be reported from a five-fold dilution of the reanalyzed sample.
- If the internal standard responses of the field sample reanalysis are not within the limits, the serial dilution results are to be reported from a five-fold dilution of the original sample.

12.7 Internal Standards

12.7.1 Summary of Internal Standards

Internal standardization must be used in all analyses to correct the instrument drift and physical interferences. The analyst shall monitor the responses from the internal standards and the ratios of raw uncovered responses between isotopes throughout the sample set being analyzed. This information may be used to correct potential problems caused by mass dependent drift, errors incurred in adding the internal standards, or increases in the concentrations of individual internal standards caused by background contributions from the sample.

12.7.2 Frequency of Internal Standards

Internal standards shall be present in all samples, standards, and blanks (except the tuning solution) at identical levels.

12.7.3 Procedure for Internal Standards

12.7.3.1 A minimum of five internal standards shall be used. A list of acceptable internal standards is provided in Table 5 - Internal Standards.

12.7.3.2 The internal standards selected for an analytical sequence must be consistent throughout the entire analytical sequence.

12.7.3.3 The internal standard may be added directly to an aliquot of each sample, standard, and blank, or by mixing with the sample solution prior to nebulization using a second channel of the peristaltic pump and mixing coil.

12.7.3.4 The concentration of the internal standard should be sufficiently high for good precision and to minimize the possibility of correction errors if the internal standard is naturally present in the sample. Depending on the sensitivity of the instrument, a final concentration range of 20 µg/L to 200 µg/L of each internal standard in each digested sample, standard, and blank is recommended when the internal standards are added manually by the analyst. If the internal standards are added automatically by the instrument prior to analysis, then the manufacturer's guidelines for the appropriate concentration ranges should be followed.

12.7.3.5 If dilutions are performed on the digested samples, then the internal standards must be added after the dilution.

12.7.4 Calculation for Internal Standards

12.7.4.1 Calculate the Percent Relative Intensity using the following equation:

EQ. 15 Percent Relative Intensity

$$\%RI = \frac{I_n}{I_0} \times 100$$

WHERE,

I_n = Raw Uncorrected Intensity of the internal standard in the sample

I_0 = Raw Uncorrected Intensity of the internal standard in the calibration blank (S0)

12.7.5 Technical Acceptance Criteria for Internal Standards

The absolute response of any one internal standard must not deviate more than 60-125% from the original response in the calibration blank.

12.7.6 Corrective Action for Internal Standards

12.7.6.1 If deviations less than 60% or greater than 125% are observed in field samples, matrix spikes, or duplicate samples, the original sample shall be diluted by a factor of two, internal standards added (if not automatically added by the instrument), and the sample reanalyzed for the analyte(s) associated with the noncompliant internal standard(s).

12.7.6.2 If the internal standard responses for the diluted sample analysis are not within the limits, note this in the SDG Narrative and report the results of the undiluted original sample analysis. If the internal standard responses for the diluted sample analysis are within the limits, report the results of this analysis.

12.7.6.3 Target analyte(s) concentration(s) must be within the calibrated range before assessing internal standard response for those internal standard(s) associated with the analyte(s).

12.8 Method Detection Limit Determination

12.8.1 Before any field samples are analyzed, the MDLs shall be determined for each digestion procedure and instrument used prior to the start of contract analyses and annually thereafter. An MDL study shall be performed after major instrument maintenance, or changes in instrumentation or instrumental conditions, to verify the current sensitivity of the analysis.

12.8.1.1 To determine the MDLs, the Contractor shall perform MDL studies following the procedures in 40 Code of Federal Regulations (CFR), Part 136.

12.8.1.2 The Contractor shall prepare the MDL samples by each digestion procedure used and shall analyze these samples on each instrument used.

12.8.1.3 The determined concentration of the MDL shall be less than half the concentration of the CRQL listed in Exhibit C – Inorganic Target Analyte List and Contract Required Quantitation Limits.

12.9 Summary of Quality Control Operations

The QC operations performed for ICP-MS analysis are summarized in Table 7 - QC Operations for ICP-MS.

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

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

15.0 WASTE MANAGEMENT

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

16.0 REFERENCES

16.1 U.S. Environmental Protection Agency, Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Mass Spectrometry, Method 200.8, Revision 5.5, October 1999.

16.2 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 6020B, Revision 2, July 2014.

16.3 U.S. Government Printing Office, 40 Code of Federal Regulations, Part 136, Section 1, Appendix B.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

TABLE 1. INTERFERENT AND ANALYTE CONCENTRATIONS USED FOR ICP-MS INTERFERENCE CHECK SAMPLE (ICS)

Analytes	(µg/L)	Interferents	(µg/L)
Ag	20	Al	100000
As	20	Ca	100000
Ba	20	Fe	100000
Be	20	Mg	100000
Cd	20	K	100000
Co	20	Na	100000
Cr	40	P (as orthophosphate)	100000
Cu	25	S (as sulfate)	100000
Mn	30	C (as citrate)	200000
Ni	25	Cl	1000000
Pb	25	Mo	2000
Sb	20	Ti	2000
Se	20		
Tl	20		
V	20		
Zn	30		

NOTE: ICSA solution contains the interferents at the indicated concentrations. The ICSA solution may be analyzed at twice the concentration indicated when interferences are present at higher concentrations in the sample. The ICSAB solution contains all of the analytes and interferents listed above at the indicated concentrations.

TABLE 2. ISOBARIC MOLECULAR-ION INTERFERENCES

Analyte	Oxygen	Hydroxyl	Nitrogen	Chlorine	Sulfur	Carbon	Other
^{121}Sb	PdO		AgN			AgC	
^{123}Sb	AgO		AgN	SrCl	ZrS	CdC	
^{75}As	CoO	NiOH	NiN	ArCl	CaS	CuC	Nd^{++}, Sm^{++}
^{138}Ba	SnO	SbOH					
^{137}Ba	SbO	SnOH		MoCl			
^{136}Ba	SnO	SnOH				SnC	
^{135}Ba	SnO	SnOH		MoCl			
^{134}Ba	SnO	SnOH	SnN	MoCl		SnC	
^{132}Ba	SnO, CdO	InOH	SnN	MoCl	MoS	SnC	
^{130}Ba	CdO	CdOH	SnN, CdN	MoCl	MoS	SnC	
^{9}Be							
^{114}Cd	MoO	MoOH	MoN	SeCl	SeS		
^{112}Cd	MoO, ZrO	MoOH	MoN	SeCl, AsCl	SeS	MoC	
^{111}Cd	MoO	MoOH	MoN	GeCl			
^{110}Cd	MoO, ZrO		MoN, ZrN	GeCl, AsCl	SeS	MoC	
^{113}Cd	MoO	MoOH		SeCl, AsCl			
^{116}Cd	MoO						
^{106}Cd	ZrO		MoN, ZrN		GeS	MoC, ZrC	
^{108}Cd	MoO, ZrO	ZrOH	MoN, ZrN	GeC1	SeS, GeS	MoC, ZrC	
^{52}Cr	ArO	C1OH				ArC	
^{53}Cr	ClO	ArOH	KN	NCl, OCl		KC	
^{50}Cr	SO		ArN		SO	ArC	Mo^{++}
^{54}Cr		C1OH	ArN, CaN			CaC	
^{59}Co	CaO	CaOH	ScN	MgCl	AlS	TiC	Sn^{++}
^{63}Cu	TiO, PO_2	TiOH	TiN	SiCl, MgCl	PS	VC	ArNa
^{65}Cu	TiO	TiOH	VN	SiCl	S_2, SO_2H	CrC	
^{208}Pb							
^{206}Pb							
^{207}Pb							
^{204}Pb							
^{55}Mn	KO	ArOH	KN		NaS	CaC	Cd^{++}
^{202}Hg	WO						
^{200}Hg	WO	WOH	WN				
^{199}Hg	WO	WOH					
^{201}Hg		WOH					
^{198}Hg	WO	TaOH	WN			WC	
^{204}Hg							
^{196}Hg			WN			WC	

TABLE 2. ISOBARIC MOLECULAR-ION INTERFERENCES (CON'T)

Analyte	Oxygen	Hydroxyl	Nitrogen	Chlorine	Sulfur	Carbon	Other
^{58}Ni	CaO	KOH	CaN	NaCl	MgS	TiC	Cd^{++}, Sn^{++}
^{60}Ni	CaO	CaOH	TiN	MgCl, NaCl	SiS	TiC	Sn^{++}
^{62}Ni	TiO	ScOH	TiN	AlCl, MgCl	SiS	TiC, CrC	Sn^{++}
^{61}Ni	ScO	CaOH	TiN	MgCl	SiS	TiC	Sn^{++}
^{64}Ni	TiO	TiOH	TiN, CrN	SiCl, AlCl	S_2	CrC	
^{80}Se	ZnO	CuOH	ZnN	ScCl, CaCl	TiS	ZnC	Gd^{++}
^{78}Se	NiO	NiOH	ZnN	CaCl, KCl	TiS	ZnC	Sm^{++}, Gd^{++}
^{82}Se	ZnO	CuOH	ZnN	TiCl, ScCl	TiS, CrS		Dy^{++}, Er^{++}
^{76}Se	NiO	CoOH	NiN	KCl	CaS	ZnC	
^{77}Se	NiO	NiOH	CuN	CaCl, ArCl	ScS	CuC	
^{74}Se	NiO	FeOH	NiN	Cl_2, KCl	CaS	NiC	
^{107}Ag	ZrO	ZrOH		GeCl	AsS	MoC	
^{109}Ag		MoOH	MoN	GeCl	SeS	MoC	
^{205}T1							
^{203}T1		WOH					
^{51}V	C1O	SOH	C1N	ClO, ClN	FS	KC	
^{50}V	SO		ArN			ArC	Mo^{++}
^{64}Zn	TiO	TiOH	TiN, CrN	SiCl, AlCl	S_2	CrC	
^{66}Zn	TiO	TiOH	CrN	PCl, SiCl	S_2	FeC	
^{68}Zn	CrO	VOH	FeN	PCl	ArS	FeC	Ba^{++}
^{67}Zn	VO	TiOH	CrN	SCl	ClS	MnC	Ba^{++}
^{70}Zn	FeO	CrOH	GeN	$C1_2$	ArS	NiC	

NOTE: The information provided in this table does not indicate that all of the described interferences need to be tested. However, this table can be consulted if unusual samples are encountered.

TABLE 3. RECOMMENDED ISOTOPES AND MASSES FOR SELECTED ELEMENTS

Element of Interest	**Analyte Masses - Choose One, or More – Calibrated**	**Masses to be Monitored**
Aluminum	27	
Antimony	121	
Arsenic	75	77, 82 (Isobaric Equation Required), 150
Barium	135, 137	
Beryllium	9	
Cadmium	111	106, 108 (Isobaric Equation Required)
Calcium	40, 44	
Chromium	52	
Cobalt	59	
Copper	63, 65	
Iron	54, 56, 57	
Lead	206, 207, 208	
Magnesium	24, 25, 26	
Manganese	55	
Nickel	60	
Potassium	39	
Selenium	78, 82	156, 160, 164
Silver	107, 109	
Sodium	23	
Thallium	203, 205	
Vanadium	51	52, 53 (Isobaric Equation Required)
Zinc	66	
Potential Interferent		
Titanium (TiO on ^{63}Cu)		47 (No Isobaric Equation Required)
Krypton (Kr on ^{82}Se)		83 (No Isobaric Equation Required)
Molybdenum		94, 95, 96, 97, 98
Tin (Sn on ^{115}In)		118 (Isobaric Equation Required)

NOTE: Where possible, alternative isotopes are indicated. At least one of the listed masses shall be used as a quantitation ion. Those isotopes not listed shall not be used as a primary isotope for measurement, although they may be monitored for interference corrections if necessary.

TABLE 4. RECOMMENDED ELEMENTAL EXPRESSIONS FOR ISOBARIC INTERFERENCES

Element	Isobaric Correction	Expression Proportional to Elemental Concentration
As	ArCl, Se	$(1.0000)(^{75}C) - (3.127)[(^{77}C) - (0.815)(^{82}C)]$
Cd	MoO, Pd	$(1.000)(^{111}C) - (1.073)[(^{108}C) - (0.712)(^{106}C)]$
V	ClO, Cr	$(1.0000)(^{51}C) - (3.127)[(^{53}C) - (0.113)(^{52}C)]$
In	Sn	$(1.0000)(^{115}C) - (0.0140)(^{118}C)$

C - Calibration blank subtracted counts at specified mass

The coefficients in correction equations were calculated using natural isotopic abundances, and assuming zero instrumental fractionation. For each particular instrument, these coefficients must be determined experimentally using the procedures or coefficients provided by the instrument manufacturer.

The correction equations shall not be applied if appropriate interference check sample measurement demonstrates absence of interference above the CRQL.

TABLE 5. INTERNAL STANDARDS (MUST USE AT LEAST FIVE)

Internal Standard	Mass	CAS Number
Lithium	6	7439-93-2
Scandium	45	7440-20-2
Yttrium	89	7440-65-5
Rhodium	103	7440-16-6
Indium	115	7440-74-6
Terbium	159	7440-27-9
Holmium	165	7440-60-0
Lutetium	175	7439-94-3
Bismuth	209	7440-69-9

NOTE: Use of Li^{6} requires enriched standard.

TABLE 6. SPIKING LEVELS FOR MATRIX SPIKE SAMPLE ANALYSIS

Analyte	Spike (µg/L)*	Spike (mg/kg)*(1)
Sb	100	10
As	40	4
Ba	2000	200
Be	50	5
Cd	50	5
Cr	200	20
Co	500	50
Cu	250	25
Pb	20	2
Mn	500	50
Ni	500	50
Se	100	10
Ag	50	5
Tl	50	5
V	500	50
Zn	500	50

*Level in the final prepared sample

[1] Concentrations in the spike sample when the dry weight of 1 gram of sample is taken for analysis. Adjustment shall be made to maintain these spiking levels when the weight of sample taken deviates by more than 10% of these values.

EQ. 16 Spiking Level Adjustment

$$\text{mg/kg} = \text{µg/L} \times \frac{\text{final volume (L)}}{\text{sample weight (g)}}$$

TABLE 7. QC OPERATION FOR ICP-MS

QC Operation	Frequency
ICP-MS Tune	Prior to calibration.
Instrument Calibration	Each time instrument is turned on or set up, after ICV or CCV failure, and after major instrument adjustment.
Initial Calibration Verification	Following each instrument calibration for each mass used.
Continuing Calibration Verification	For each mass used, at a frequency of every 2 hours and at the beginning and end of each analytical sequence.
Initial Calibration Blank	Following each instrument calibration, immediately after the ICV.
Continuing Calibration Blank	Every 2 hours and at the beginning and end of each analytical sequence. Performed immediately after the CCV.
Preparation Blank	For each SDG or each sample preparation and analysis procedure per batch of prepared samples, whichever is more frequent.
Interference Check Sample	At the beginning of each analytical sequence after the ICB but before the CCV.
Matrix Spike Sample	For each matrix type or for each SDG, whichever is more frequent.
Post-Digestion Spike	Each time Matrix Spike Sample Recovery is outside QC limits.
Duplicate Sample Analysis	For each matrix type or for each SDG, whichever is more frequent.
Laboratory Control Sample	For each SDG or each sample preparation and analysis procedure per batch of prepared samples, whichever is more frequent.
Serial Dilution for ICP	For each matrix type or for each SDG, whichever is more frequent.
Method Detection Limit Determination	Prior to start of contract analyses, annually thereafter, and after major instrument adjustment.

EXHIBIT D

COLD VAPOR MERCURY ANALYSIS

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Exhibit D – Cold Vapor Mercury Analysis

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Table of Contents

1.0 SCOPE AND APPLICATION

This exhibit provides procedures for the use of a cold vapor technique with Atomic Absorption (AA) to determine total mercury in aqueous/water, leachate derived from the Toxicity Characteristic Leaching Procedure (TCLP) or Synthetic Precipitation Leaching Procedure (SPLP), and soil/sediment samples taken from hazardous waste sites.

In addition to inorganic forms of mercury, organic mercury may also be present. These organo-mercury compounds will not respond to the cold vapor AA technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds, but studies have shown that a number of organo-mercury compounds, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. Potassium persulfate has been found to give approximately 100% recovery when used as the oxidant with these compounds. Therefore, a persulfate oxidation step following the addition of the permanganate has been included in most preparation procedures to ensure that organo-mercury compounds, if present, will be oxidized to the mercuric ion before measurement. A heat step is required for methyl mercuric chloride when present in, or spiked to, a natural system.

2.0 SUMMARY OF METHOD

2.1 General Method Overview

This method is based on the absorption of radiation at 253.7 nanometers (nm) by mercury vapor. Inorganic and some organic forms of mercury are chemically reduced to the free atomic state by reacting the sample with a strong reducing agent like stannous chloride or stannous sulfate in a closed reaction vessel. The volatile free mercury is then driven from the reaction flask by bubbling air through the solution. Mercury atoms are carried in the air stream through tubing connected to an absorption cell, which is placed in the light path of the AA spectrophotometer. Sometimes the cell is heated slightly to avoid water condensation. As the mercury atoms pass into the sampling cell, measured absorbance rises indicating the increasing concentration of mercury atoms in the light path. Some systems allow the mercury vapor to pass from the absorption tube to waste, in which case the absorption peaks and then falls as the mercury is depleted. The highest absorbance observed during the measurement or the associated peak area are usually taken as the analytical signal.

2.2 Summary of Preparation and Analysis Procedures

2.2.1 Heated Acid Digestion and Analysis of Aqueous/Water and TCLP/SPLP Leachate Samples (based on the EPA Method 7470A)

2.2.2 Heated Acid Digestion and Analysis of Soil/Sediment Samples (based on the EPA Method 7471B)

3.0 DEFINITIONS

See Exhibit G - Glossary of Terms for a complete list of definitions.

4.0 INTERFERENCES

4.1 Chlorides

Samples high in chlorides have shown a positive interference, and require additional potassium permanganate [as much as 25 milliliters (mL)]. During the oxidation step, chlorides are converted to free chlorine which will also absorb radiation at 253.7 nm. Care must be taken to assure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL).

4.2 Sulfides

Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations as high as 20 milligrams/Liter (mg/L) of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from reagent water.

4.3 Copper

Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L have no effect on the recovery of mercury from spiked samples.

4.4 Oxidizable Organic Materials

Samples containing high concentrations of oxidizable organic materials, as evidenced by high chemical oxygen demand values, may not be completely oxidized by this procedure. When this occurs, the recovery of organic mercury will be low. The problem can be eliminated by reducing the amount of the original sample or by increasing the amount of potassium persulfate (and consequently stannous chloride) used in the digestion.

5.0 SAFETY

See Section 12.0 in Exhibit D - Introduction to Inorganic 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 Statement of Work (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.

6.1 Glassware/Labware

6.1.1 Graduated cylinders

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

6.1.3 Suitable digestion vessels (300 mL BOD bottles, hot block digestion tubes, etc.), along with a suitable heating source/water bath for heating of the samples to about 95°C

6.1.4 Balances – Top loader balance, 300 gram (g) capacity, and a minimum sensitivity of ±1.0 mg

A balance calibration must be checked with known masses once per each day of use. This verification consists of a check with two weights covering the range expected (approximately ±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 must 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 E617-97 (2008) or equivalent (e.g., earlier Class ‘S’ defined masses). All balances must be checked at least once annually by a certified technician. The reference masses used by the Contractor must 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 Cold Vapor Atomic Absorption Spectrometer

Consisting of an AA spectrometer equipped with a flow-through absorption cell and a mercury hollow cathode lamp or other suitable light source. The analysis system shall also include: a manifold/pump system for mixing reagents with previously digested samples, a liquid-vapor separator, and a vapor dryer. The spectrometer shall have or be linked to a suitable computer system for data processing.

AA Spectrophotometer – Any AA unit having an open sample presentation area in which to mount the absorption cell would be suitable. Instrument settings recommended by the particular manufacturer should be followed. The instrument must be capable of meeting the specified Contract Required Quantitation Limits (CRQLs) for mercury.

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.

7.1.2 Sulfuric acid - Concentrated 95-98% - Reagent grade.

7.1.3 Sulfuric acid, 0.5N - Dilute 14.0 mL of concentrated sulfuric acid to 1 L.

7.1.4 Hydrochloric acid - Concentrated 32-38%. Reagent grade of low mercury content.

7.1.5 Nitric acid - Concentrated 67-70% - Reagent grade of low mercury content. It may be necessary to distill the nitric acid if impurities are detected in blanks.

7.1.6 Aqua regia - Prepare immediately prior to use. Carefully add three volumes of concentrated hydrochloric acid to one volume of concentrated nitric acid.

7.1.7 Sodium chloride-hydroxylamine sulfate solution, 12% solution (w/v) - Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in reagent water and dilute to 100 mL.

NOTE: Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.

7.1.8 Potassium permanganate ($KMnO_4$) - 5% solution (w/v). Dissolve 5 g of potassium permanganate in 100 mL of reagent water.

7.1.9 Potassium persulfate - 5% solution (w/v). Dissolve 5 g of potassium persulfate in 100 mL of reagent water.

7.1.10 Stannous sulfate, (10% w/v) - Dissolve 25 g stannous sulfate to 250 mL of 0.5N sulfuric acid. This mixture is a suspension and should be stirred continuously during use.

NOTE: Stannous chloride may be used in place of stannous sulfate.

7.2 Standards

7.2.1 Introduction

The Contractor must provide all standards, except as noted, to be used with this contract. These standards may be used only after they have been certified according to the procedure in Exhibit D - Introduction to Inorganic Analytical Methods, Section 11.0. The Contractor must be able to verify that the standards are certified. Manufacturer’s certificates of analysis must be retained by the Contractor and presented upon request.

7.2.2 Stock Standard Solutions

Stock standard solutions may be purchased from a reputable source or prepared from reagent grade chemicals or metals (at least 99.99% pure).

CAUTION: Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling.

7.2.2.1 Stock mercury solution - Dissolve 0.1354 g of mercuric chloride in 75 mL of reagent water. Add 10 mL of concentrated nitric acid and adjust the volume to 100.0 mL [1.0 mL = 1.0 mg Hg].

7.2.3 Working Standards

7.2.3.1 Working Mercury Solution

Make successive dilutions of the stock mercury solution (see Section 7.2.2) to obtain a working standard containing 0.1 micrograms/milliliter (µg/mL). This working standard and the dilutions of the stock mercury solution shall be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. Acid should be added to the flask as needed before the addition of the aliquot. From this solution, prepare calibration standards. Standards must be prepared with samples (See Section 10.0).

7.2.4 Initial Calibration Verification Solution

7.2.4.1 The Initial Calibration Verification (ICV) solution shall be obtained from the EPA.

7.2.4.1.1 If the solution is not available from the EPA, then the ICV solution shall be prepared by the laboratory using a certified solution from an independent source. An independent source is defined as a standard from a different source than that used in the standards for instrument calibration. Analyses shall be conducted at a concentration other than that used for instrument calibration, but near the middle of the calibration range.

7.2.4.1.2 The ICV standard shall be prepared in the same acid matrix as the calibration standards and in accordance with the instructions provided by the supplier.

7.3 Blanks

Two types of blanks are required for this method. A Calibration Blank is used to establish the analytical calibration curve and the Preparation Blank (see Section 12.1) is used to assess possible contamination from the sample preparation procedure and to assess spectral background.

7.3.1 Calibration Blank - Must contain all the reagents in the same volumes as used in preparing the samples. The Calibration Blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis. The Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB) are identical in composition to the Calibration Blank and are used to monitor for analyte carryover.

7.3.2 Preparation Blank - Must contain all the reagents in the same volumes as used in preparing the samples. The Preparation Blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis. Soil/sediment blanks shall use 0.5-0.6 mL of reagent water.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Sample Collection and Preservation

All aqueous/water and soil/sediment samples must be collected in glass or polyethylene containers. Aqueous/water samples must be preserved with nitric acid to pH less than or equal to 2 immediately after collection. All soil/sediment samples must be iced or refrigerated at ≤6°C but not frozen from the time of collection until receipt at the laboratory.

8.2 Sample Storage

All aqueous/water and soil/sediment samples must be stored at ≤6°C but not frozen from the time of sample receipt until digestion.

8.2.1 Unused Sample Storage

The Contractor shall retain the unused portion of the aqueous/water and soil/sediment samples for a period of 60 days after delivery of a complete, reconciled data package to the EPA. The unused portion may be stored at room temperature.

8.2.2 Digestate Sample Storage

Digestions shall not be retained. Any reanalyses of the sample shall be performed using a freshly digested aliquot of the sample.

8.2.3 Container Storage

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

8.3 Contract Required Holding Time

The holding time for mercury is 26 days from Validated Time of Sample Receipt (VTSR) to analysis. The holding time for the analysis of TCLP or SPLP leachates is 26 days from the date of extraction.

9.0 CALIBRATION AND STANDARDIZATION

9.1 Instrument Operating Parameters

Because of the differences between various manufacturers 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. The Method Detection Limit (MDL) and precision must be investigated and established for mercury on that particular instrument. All measurements must be within the instrument operating range. It is the responsibility of the analyst to verify the instrument configuration and operating conditions used to satisfy the analytical requirements and to maintain Quality Control (QC) data confirming instrument performance and analytical results.

9.2 Pre-Calibration Routine

Prior to calibration, the Contractor shall set up each instrument with the operating parameters established in Section 9.1 and conduct any necessary adjustments. The instrument must be allowed to become stable (usually 30 minutes) before calibration is performed.

9.3 Instrument Calibration Procedure

9.3.1 Summary of Instrument Calibration

Prior to sample analysis, the Contractor shall calibrate each instrument to determine sensitivity and linearity of the response.

9.3.2 Frequency of Instrument Calibration

Each instrument shall be calibrated daily or once every 24 hours, each time the instrument is set up, or after ICV, ICB, Continuing Calibration Verification (CCV), or CCB failure. The instrument calibration date and time shall be included in the raw data.

9.3.3 Procedure for Instrument Calibration

9.3.3.1 Each instrument shall be calibrated according to the manufacturer's recommended procedures.

9.3.3.2 At least six calibration standards shall be used. The calibration standards shall be prepared as in Section 7.2.3.1. One of the standards shall be a blank standard and one shall be at or below the CRQL, but greater than the MDL. The rest of the standards shall be uniformly spread out in graduated amounts over the appropriate calibration range (typical range is 0.20 to 10.0 µg/L).

9.3.4 Calculations for Instrument Calibration

9.3.4.1 The calibration curve shall be calculated using linear regression by plotting the concentration of the standard (in µg/L) on the X–axis versus the instrument response on the Y-axis. The instrument response is the measured absorbance (displayed as a peak area or height) for each standard.

9.3.4.2 The Contractor may use standard linear regression, weighted linear regression (1/concentration, 1/square of concentration, variance, 1/variance, standard deviation, 1/standard deviation, or 1/square of standard deviation), or linear regression with zero force calibration models, as appropriate, for the above calculation. No other types of equations (e.g., quadratic) are to be used.

9.3.4.3 The calibration curve shall be checked to establish the representativeness of the data that were used to produce it. This check involves re-fitting the data of the non-blank calibration standards back to the calibration curve, and computing the difference between the calculated concentration and the expected concentration for each of these standards. The difference is then divided by the expected concentration of the respective standard and multiplied by 100.

9.3.5 Technical Acceptance Criteria for Instrument Calibration

9.3.5.1 The correlation coefficient of the calibration curve shall be greater than or equal to 0.995.

9.3.5.2 The Percent Difference (%D) for each of the standards shall be within the control limits of ±30%.

9.3.5.3 If a standard is analyzed at a concentration that is below the CRQL and the %D criteria is not met, that standard can be excluded from the calibration curve as long as the lowest non-zero standard is still analyzed at or below the CRQL and all standards included in the calibration curve are continuous and consecutive.

9.3.6 Corrective Action for Instrument Calibration

9.3.6.1 Sample analysis shall not begin until the criteria described in Section 9.3.5 have been met.

9.3.6.2 Any changes or corrections to the analytical system shall be followed by recalibration.

9.4 Initial Calibration Verification

9.4.1 Summary of Initial Calibration Verification

Prior to sample analysis, the Contractor shall demonstrate the accuracy of the instrument calibration for each instrument through the analysis of an ICV standard.

9.4.2 Frequency of Initial Calibration Verification

The ICV shall be analyzed immediately after the instrument has been calibrated.

9.4.3 Procedure for Initial Calibration Verification

9.4.3.1 The ICV shall be analyzed at the wavelength used to report final results.

9.4.3.2 The ICV shall reflect the conditions of analysis of the associated analytical samples.

9.4.4 Calculations for Initial Calibration Verification

The Percent Recovery (%R) of the ICV shall be calculated using the following equation:

EQ. 1 ICV Percent Recovery

$$\%R = \frac{\text{Found (ICV)}}{\text{True (ICV)}} \times 100$$

WHERE,

Found (ICV) = The found concentration of mercury in the ICV Solution

True (ICV) = The expected concentration of mercury in the ICV Solution

9.4.5 Technical Acceptance Criteria for Initial Calibration Verification

The ICV %R shall be within the control limits of 85-115%.

9.4.6 Corrective Action for Initial Calibration Verification

If the recovery is outside the control limits of 85% Recovery (low) or 115% Recovery (high), the analysis shall be terminated, the problem corrected, the instrument recalibrated, and the calibration verified.

9.5 Continuing Calibration Verification

9.5.1 Summary of Continuing Calibration Verification

Prior to sample analysis, periodically during analysis, and at the conclusion of analysis, the Contractor shall demonstrate the stability of the calibration through the analysis of a CCV standard. The Contractor shall not analyze a blank immediately prior to the analysis of the CCV.

9.5.2 Frequency of Continuing Calibration Verification

9.5.2.1 A CCV shall be analyzed at the beginning of the analytical sequence and after the last analytical sample. A CCV shall also be analyzed at a frequency not to exceed 1 hour during an analytical sequence. See the example analytical sequence in Section 10.3.3.

9.5.2.2 The analytical sequence can continue for 24 hours as long as samples are being continuously analyzed without the instrument being turned off and successive CCV standards meet the technical acceptance criteria in Section 9.5.5.

9.5.3 Procedure for Continuing Calibration Verification

9.5.3.1 The CCV standard shall be prepared using the same source and in the same acid matrix as the calibration standards at or near the mid-level of the calibration curve. The CCV shall be prepared according to Section 10.0.

9.5.3.2 The same CCV standard shall be used throughout the analytical sequences for an SDG.

9.5.3.3 The CCV shall be analyzed at the wavelength used to report final results.

9.5.3.4 Each CCV analyzed shall reflect the conditions of analysis of all associated analytical samples (the preceding analytical samples up to the previous CCV as applicable and the analytical samples following this CCV up to the next CCV as applicable).

9.5.4 Calculations for Continuing Calibration Verification

9.5.4.1 The %R of the CCV shall be calculated using the following equation:

EQ. 2 CCV Percent Recovery

$$\%R = \frac{\text{Found (CCV)}}{\text{True (CCV)}} \times 100$$

WHERE,

Found (CCV) = The found concentration of mercury in the CCV Solution

True (CCV) = The expected concentration of mercury in the CCV Solution

9.5.5 Technical Acceptance Criteria for Continuing Calibration Verification

9.5.5.1 The CCV %R shall be within the control limits of 85-115%.

9.5.5.2 All samples shall be analyzed within 1 hour of an acceptable opening and closing CCV.

9.5.6 Corrective Action for Continuing Calibration Verification

If the deviations of the CCV are greater than the specified control limits of 85% Recovery (low) or 115% Recovery (high), the analysis shall be terminated, the problem corrected, the instrument recalibrated, the calibration verified, and reanalysis of all analytical samples analyzed since the last compliant calibration verification shall be performed.

9.6 Initial and Continuing Calibration Blank

9.6.1 Summary of Calibration Blank

Prior to sample analysis, periodically during analysis, and at the conclusion of analysis, the Contractor shall demonstrate the stability of the calibration baseline through the analysis of an ICB and CCB.

9.6.2 Frequency of Calibration Blank

9.6.2.1 An ICB shall be analyzed immediately after the instrument has been calibrated and the calibration verified by the analysis of the ICV.

9.6.2.2 Each CCB shall be analyzed immediately after the analysis of a CCV.

9.6.3 Procedure for Calibration Blank

9.6.3.1 The ICB and CCB samples shall be analyzed at the wavelength used for reporting final results.

9.6.3.2 The ICB analyzed shall reflect the conditions of analysis of the associated analytical samples.

9.6.3.3 Each CCB analyzed shall reflect the conditions of analysis of the associated analytical samples (the preceding analytical samples up to the previous CCB as applicable and the analytical samples following this CCB up to the next CCB as applicable).

9.6.4 Calculations for Calibration Blank

The results for the ICB and CCB samples shall be calculated using Equation 3 in Section 11.0.

9.6.5 Technical Acceptance Criteria for Calibration Blank

The absolute value of each calibration blank result shall be less than or equal to the CRQL for aqueous/water samples.

9.6.6 Corrective Action for Calibration Blank

If the absolute value of the calibration blank exceeds the CRQL for aqueous/water samples, the analysis shall be terminated, the problem corrected, the instrument recalibrated, the calibration verified, and reanalysis of all affected analytical samples analyzed since the last compliant calibration blank performed.

10.0 PROCEDURE

10.1 Aqueous/Water Sample Preparation

10.1.1 If the sample pH was ≤2 at the time of sample receipt, the Contractor shall proceed to Section 10.1.2.

If the sample pH was adjusted at the time of sample receipt (see Exhibit D – General Inorganic Analysis, Section 10.1.2.1), the Contractor shall take a second pH measurement, prior to removing an aliquot of the sample for digestion, to verify that the sample was properly preserved upon receipt. If the second pH measurement is ≤2, proceed to Section 10.1.2. If the second pH measurement 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.

10.1.2 For preparation of the standards, transfer aliquots of the working mercury solution (see Section 7.2.3.1) to a series of suitable digestion vessels. Add enough reagent water to each digestion vessel to make a total volume of 100 mL (±1.0 mL) and mix thoroughly. The acidity of all of the standards should be maintained at 0.15% nitric acid. This acid should be added to the digestion vessel as needed prior to the dilution of the working standard. Standards must be prepared fresh daily.

10.1.3 For preparation of the samples, shake the sample until well mixed and transfer an aliquot of 100 mL (±1.0 mL), containing not more than 1.0 µg of mercury, to a suitable digestion vessel.

10.1.4 Add 5 mL of concentrated sulfuric acid and 2.5 mL of concentrated nitric acid to each of the digestion vessels, mixing after each addition.

10.1.5 Add 15 mL of 5% potassium permanganate solution to each digestion vessel. Some samples (e.g., sewage samples) may require additional potassium permanganate. Shake and add additional portions of potassium permanganate solution, if necessary, until the purple color persists for at least 15 minutes. Ensure that equal amounts of potassium permanganate solution are added to all standards, blanks, and samples.

10.1.6 Add 8 mL of 5% potassium persulfate solution to each digestion vessel and heat for 2 hours in a water bath or block digester maintained at 95°C (±3°C). Allow to cool.

10.1.7 Add 6 mL of 12% sodium chloride-hydroxylamine sulfate solution to reduce the excess potassium permanganate.

10.1.8 All standards and samples must be at the same final volume. Reagent water can be used to make any necessary final volume adjustments.

10.1.9 After digestion, the standards and samples may stand at room temperature for up to 48 hours prior to analysis. However, it is recommended that the digested standards and samples be analyzed as soon as possible. Proceed to Section 10.3 for analysis.

10.1.10 A reduced volume of 50 mL can be used for all standards, blanks, and samples for this digestion procedure. If the reduced volume is used, all standards and reagents used in the digestion process shall be reduced by half of their original required amounts.

10.2 Soil/Sediment Sample Preparation

10.2.1 For preparation of the standards, transfer aliquots of the working mercury solution (see Section 7.2.3.1) to a series of suitable digestion vessels. Add enough reagent water to each digestion vessel to make a total volume of 10 mL (±0.1 mL) and mix thoroughly. The acidity of all of the standards should be maintained at 0.15% nitric acid. This acid should be added to the digestion vessel as needed prior to the dilution of the working standard. Standards must be prepared fresh daily.

10.2.2 For preparation of the samples, mix the sample thoroughly to achieve homogeneity. Weigh (to the nearest 0.01 g) an aliquot amount of 0.50-0.60 g and place in the bottom of a suitable digestion vessel. Add 5 mL of reagent water to each sample.

10.2.3 Add 5 mL of aqua regia to each of the digestion vessels and heat for 2 minutes at 95°C (±3°C) in a water bath or block digester. Allow the contents of each digestion vessel to cool.

10.2.4 Add 50 mL of reagent water and 15 mL of 5% potassium permanganate solution. Mix thoroughly and heat again for 30 minutes at 95°C (±3°C) in a water bath or block digester. Allow to cool.

10.2.5 Add 6 mL of 12% sodium chloride-hydroxylamine solution to each digestion vessel to reduce the excess potassium permanganate.

CAUTION: This addition should be performed under a hood, as chlorine could be evolved.

10.2.6 Add 55 mL of reagent water to each sample or 50 mL of reagent water to each standard. All standards and samples must be at the same final volume. Reagent water can be used to make any final volume adjustments, if necessary.

10.2.7 After digestion, the standards and samples may stand at room temperature for up to 48 hours prior to analysis. However, it is recommended that the digested standards and samples be analyzed as soon as possible. Refer to Section 10.3 for analysis.

10.3 Sample Analysis

10.3.1 Set up the automated analyzer using the recommendations as provided by the manufacturer. Set up the manifold and fill the reagent reservoir with the 10% (w/v) stannous sulfate solution (prepared in 0.5 N sulfuric acid). All reagent and sample lines should be cleaned according to the manufacturer’s recommendations.

10.3.2 Transfer appropriate aliquots of the digested standards and samples to the autosampler in the order as suggested by the manufacturer.

10.3.3 Example Analytical Sequence for Mercury Including the Instrument Calibration:

S##
S##
S##
S##
S##
S##
ICV
ICB
CCV###
CCB###
Samples
CCV###
CCB###
samples
CCV###
CCB###, etc.

10.3.4 Complete the analysis of all of the digested standards and samples and construct the calibration curve. The calibration curve shall be constructed based on the concentration of mercury (in µg/L) in the undigested standards, ignoring the volume of reagents added during the digestion process.

10.3.5 If a sample’s response exceeds the calibrated range of the instrument, the laboratory shall dilute the sample and reanalyze. Dilute a portion of the previously digested sample, which has not been treated with stannous sulfate, using a solution which maintains the same acid and other reagent concentrations as are present in the calibration standards (e.g., one of the calibration blanks). The laboratory shall then promptly analyze the diluted sample.

10.3.6 After the analysis is complete, clean out the system and all of the reagent and sample lines according to the manufacturer’s recommendations.

11.0 DATA ANALYSIS AND CALCULATIONS

Calculate the mercury concentration using the following equations.

11.1 Aqueous/Water and TCLP/SPLP Leachate Sample Calculation

EQ. 3 Aqueous/Water and TCLP/SPLP Leachate Sample Concentration

$$\text{Hg Concentration}\,(\mu g/L) = C \times DF$$

WHERE,
C = Instrument value in µg/L from the calibration curve
DF = Dilution Factor

NOTE: Convert units to mg/L for TCLP leachates by dividing the final calculated concentration by 1000.

11.2 Soil/Sediment Sample Calculation

EQ. 4 Soil/Sediment Sample Concentration

$$\text{Hg Concentration}\,(\text{mg/kg dry weight}) = C \times \frac{1}{W \times S} \times DF \times 0.1$$

WHERE,
C = Instrument value in µg/L from the calibration curve
W = Initial aliquot amount (g)
S = % Solids/100 (Exhibit D – General Inorganic Analysis, Section 10.1.1)
DF = Dilution Factor

11.3 Adjusted Contract Required Quantitation Limit Calculation

11.3.1 Calculate the adjusted CRQL for aqueous/water or TCLP/SPLP leachate samples, by multiplying the CRQL (µg/L) by the dilution factor. Convert units to mg/L for TCLP leachate samples.

11.3.2 Calculate the adjusted CRQL for soil/sediment samples using the following equation:

EQ. 5 Adjusted Soil/Sediment CRQL

$$\text{Adjusted CRQL}\,(\text{mg/kg}) = C \times \frac{W_m}{W \times S} \times DF$$

WHERE,
C = CRQL (mg/kg)
W_m = Method required minimum sample weight (g) (0.50 g)
W = Initial aliquot amount (g)
S = % Solids/100 (Exhibit D - General Inorganic Analysis, Section 10.1.1)
DF = Dilution Factor

12.0 QUALITY CONTROL

12.1 Preparation Blank Sample

12.1.1 Summary of Preparation Blank Sample

The Preparation Blank is used to monitor for possible contamination throughout the entire sample preparation and analysis process.

12.1.2 Frequency of Preparation Blank Sample

At least one Preparation Blank shall be prepared with every SDG, or with each preparation batch, whichever is more frequent.

12.1.3 Procedure for Preparation Blank Sample

The Preparation Blank shall be carried through the complete sample preparation procedure for the matrix and contain the same acid concentration in the final digestate as the samples.

12.1.4 Calculations for Preparation Blank Sample

Calculate the results for aqueous Preparation Blanks by using Equation 3. Calculate the results for soil/sediment Preparation Blanks by using Equation 4.

12.1.5 Technical Acceptance Criteria for Preparation Blank Sample

12.1.5.1 The absolute value of the Preparation Blank result shall be less than or equal to the CRQL.

12.1.5.2 The mercury concentration in the Preparation Blank may be greater than the CRQL, if the concentration of mercury in the associated samples is greater than or equal to 10 times the blank concentration.

12.1.5.3 The mercury concentration in the Preparation Blank may be less than the negative CRQL if the concentration in the associated samples is greater than or equal to 10 times the CRQL.

12.1.6 Corrective Action for Preparation Blank Sample

12.1.6.1 If the mercury concentration in the Preparation Blank is greater than the CRQL, and the concentration of mercury in any of the associated samples is less than 10 times the blank concentration, then all samples with less than 10 times the blank concentration shall be reprepared and reanalyzed with appropriate new QC.

12.1.6.2 If the mercury concentration in the Preparation Blank is less than the negative CRQL and the concentration in the associated samples is less than 10 times the CRQL, then all samples with less than 10 times the CRQL concentration shall be reprepared and reanalyzed with appropriate new QC.

12.2 Matrix Spike Sample

12.2.1 Summary of Matrix Spike Sample

The Matrix Spike sample analysis is designed to provide information about the effect of the sample matrix on the digestion and/or measurement methodology.

12.2.2 Frequency of Matrix Spike Sample

At least one Matrix Spike sample analysis shall be performed on each group of samples of a similar matrix type (i.e., aqueous/water, soil/sediment) or for each SDG, whichever is more frequent.[1]

12.2.3 Procedure for Matrix Spike Sample

12.2.3.1 The spike is added before the digestion (i.e., prior to the addition of other reagents).

12.2.3.2 The analyte spike shall be added at 1 µg/L for aqueous/water and leachate samples, or at 0.5 milligrams/kilogram (mg/kg) for soil/sediment samples. Adjustment shall be made to maintain these spiking levels when the weight of sample taken deviates by more than 10% of these values. This is the level of spike present in the final digestate.

12.2.3.3 Samples identified as field blanks and Performance Evaluation (PE) samples shall not be used for Matrix Spike sample analysis. The EPA may require that a specific sample be used for the Matrix Spike sample analysis.

12.2.4 Calculations for Matrix Spike Sample

12.2.4.1 If the Matrix Spike analysis is performed on the same sample that is chosen for the Duplicate sample analysis, spike calculations shall be performed using the results of the sample designated as the "original sample" (see Section 12.3). The average of the duplicate results cannot be used for the purpose of determining %R.

12.2.4.2 Calculate the Matrix Spike %R using the following equation:

EQ. 6 Matrix Spike Percent Recovery

$$\%R = \frac{SSR - SR}{SA} \times 100$$

WHERE,

SSR = Spiked Sample Result (µg/L or mg/kg) from EQ. 3 or EQ. 4

SR = Sample Result (original) (µg/L or mg/kg) from EQ. 3 or EQ. 4. When the sample concentration is less than the MDL, use SR=0.

SA = Spike Added Theoretical Result (µg/L or mg/kg). This is calculated by substituting the spike concentration specified in Section 12.2.3.2 for the 'C' term from EQ. 3 or EQ.4.

NOTE: The units used for reporting SSRs will be identical to those used for reporting SRs.

12.2.5 Technical Acceptance Criteria for Matrix Spike Sample

The Matrix Spike %R shall be within the control limits of 75-125%.

[1] The EPA may require additional spike sample analyses, upon request from the EPA Regional Contract Laboratory Program Contracting Officer's Representative (EPA Regional CLP COR).

12.2.6 Corrective Action for Matrix Spike Sample

12.2.6.1 If the Matrix Spike recovery is not within the control limits of 75-125%, the data for all samples received and associated with that spike sample shall be flagged with "*". An exception to this rule is granted when the sample concentration exceeds the SA concentration by a factor of four or more. In such an event, the data shall be reported unflagged even if the %R does not meet the 75-125% recovery criteria.

12.2.6.2 If there is more than one Matrix Spike per matrix, per SDG, if one Matrix Spike sample recovery is not within contract criteria, then flag all the samples of the same matrix and method in the SDG.

12.3 Duplicate Sample

12.3.1 Summary of Duplicate Sample

Duplicates are analyzed to help determine sample homogeneity and laboratory precision.

12.3.2 Frequency of Duplicate Sample

12.3.2.1 One duplicate sample shall be analyzed from each group of samples of a similar matrix type (i.e., aqueous/water, soil/sediment) or for each SDG, whichever is more frequent.[2]

12.3.2.2 Duplicate sample analyses cannot be averaged for reporting.

12.3.3 Procedure for Duplicate Sample

12.3.3.1 Samples identified as field blanks and PE samples shall not be used for duplicate sample analysis. The EPA may require that a specific sample be used for duplicate sample analysis.

12.3.3.2 Prepare a second aliquot of the original sample. The duplicate sample shall be carried through the entire sample preparation procedure.

12.3.4 Calculations for Duplicate Sample

12.3.4.1 The Relative Percent Difference (RPD) for each analyte shall be calculated using the following equation:

EQ. 7 Duplicate Sample Relative Percent Difference

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

WHERE,

S = Sample Result (original) (µg/L or mg/kg) from EQ. 3 or EQ. 4

D = Duplicate Sample Result (µg/L or mg/kg) from EQ. 3 or EQ. 4

12.3.5 Technical Acceptance Criteria for Duplicate Sample

12.3.5.1 The RPD shall be within the control limits of ±20 if the original and duplicate sample values are greater than or equal to five times the CRQL (see Exhibit C – Inorganic Target Analyte List and Contract Required Quantitation Limits).

[2] The EPA may require additional duplicate sample analyses, upon request from the EPA Regional CLP COR.

12.3.5.2 The control limit shall be equal to the CRQL if either the sample or duplicate value are less than five times the CRQL or if one result is above five times the CRQL level and the other is below.

12.3.5.3 If both sample and duplicate values are less than the CRQL, the RPD is not calculated.

12.3.6 Corrective Action for Duplicate Sample

12.3.6.1 If the duplicate sample results are outside the control limits, flag all the data for samples received associated with that duplicate sample with an "*".

12.3.6.2 If there is more than one duplicate sample per matrix, per SDG, and if one duplicate result is not within contract criteria, flag all samples of the same matrix in the SDG.

12.4 Method Detection Limit Determination

12.4.1 Before any field samples are analyzed, the MDLs shall be determined for each digestion procedure and instrument used prior to the start of contract analyses and annually thereafter. An MDL study shall be performed after major instrument maintenance, or changes in instrumentation or instrumental conditions, to verify the current sensitivity of the analysis.

12.4.1.1 To determine the MDLs, the Contractor shall perform MDL studies following the procedures in 40 Code of Federal Regulations (CFR), Part 136.

12.4.1.2 The Contractor shall prepare the MDL samples by each digestion procedure used and shall analyze these samples on each instrument used.

12.4.1.3 The determined concentration of the MDL shall be less than half the concentration of the CRQL listed in Exhibit C – Inorganic Target Analyte List and Contract Required Quantitation Limits.

12.5 Summary of Quality Control Operations

The quality control (QC) operations performed for mercury analysis are summarized in Table 1 – QC Operations for Mercury Analysis.

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

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

15.0 WASTE MANAGEMENT

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

16.0 REFERENCES

16.1 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste (SW-846), Method 7470A, Revision 1, September 1994.

16.2 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste (SW-846), Method 7471B, Revision 2, February 2007.

16.3 U.S. Government Printing Office, 40 Code of Federal Regulations, Part 136, Section 1, Appendix B.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

TABLE 1. QC OPERATIONS FOR MERCURY ANALYSIS

QC Operation	Frequency
Instrument Calibration	Daily or each time instrument is turned on or set up, after ICV or CCV failure, and after major instrument adjustment
Initial Calibration Verification	Following each instrument calibration.
Continuing Calibration Verification	At a frequency of every hour of an analytical sequence, and at the beginning and end of each analytical sequence.
Initial Calibration Blank	Following each instrument calibration, immediately after the ICV.
Continuing Calibration Blank	Every hour and at the beginning and end of each analytical sequence. Performed immediately after the CCV.
Preparation Blank	For each SDG or each sample preparation and analysis procedure per batch of prepared samples, whichever is more frequent.
Matrix Spike Sample	For each matrix type or for each SDG, whichever is more frequent.
Duplicate Sample Analysis	For each matrix type or for each SDG, whichever is more frequent.
Method Detection Limit Determination	Prior to start of contract analyses, annually thereafter, and after major instrument adjustment.

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EXHIBIT D

TOTAL CYANIDE ANALYSIS

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Exhibit D – Total Cyanide Analysis

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Table of Contents

1.0 SCOPE AND APPLICATION

This exhibit provides procedures to determine the concentration of total cyanide in aqueous/water, leachate derived from the Synthetic Precipitation Leaching Procedure (SPLP), and soil/sediment samples taken from hazardous waste sites.

2.0 SUMMARY OF METHOD

2.1 General Method Overview

This method describes cyanide determination by spectrophotometry. The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a reflux-distillation, using either a midi- or micro-distillation process, and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined spectrophotometrically.

In the semiautomated spectrophotometric measurement, the cyanide is converted to cyanogen chloride (CNCl), by reaction with chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of pyridine-barbituric acid reagent. The absorbance is read between 570 and 580 nanometers (nm). To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.

2.2 Summary of Distillation Procedures

2.2.1 Midi-Distillation of Aqueous/Water, SPLP Leachate, and Soil/Sediment Samples [based on EPA Method 335.4 (Rev. 1, 1993) and SM 4500-CN E (approved 1999)]

2.2.2 Micro-Distillation of Aqueous/Water, SPLP Leachate, and Soil/Sediment Samples [based on Lachat QuikChem Method 10-204-00-1-X (approved by EPA 3/12/2007)]

3.0 DEFINITIONS

See Exhibit G - Glossary of Terms for a complete list of definitions.

4.0 INTERFERENCES

Several interferences may contribute to inaccuracies in the determination of cyanide in aqueous/water, SPLP leachate, and soil/sediment samples by spectrophotometry. Some of the known interferences are aldehydes, nitrate-nitrite, oxidizing agents such as chlorine, thiocyanate, thiosulfate, and sulfide. Some interferences are eliminated or reduced by using the distillation procedure. Some specific interferences that are commonly encountered are further discussed in Sections 4.1 through 4.4.

4.1 Sulfides

Sulfides adversely affect the spectrophotometric procedure. The sample shall be tested for the presence of sulfides as described in Section 10.1.2.

4.2 Surfactants

The presence of surfactants may cause the sample to foam during refluxing. If this occurs, the addition of an agent such as Dow Corning 544 anti-foam agent, or equivalent, will prevent the foam from collecting in the condenser.

4.3 Oxidizing Agents

Oxidizing agents such as chlorine decompose most of the cyanides. The sample shall be tested for the presence of oxidizing agents as described in Section 10.1.2.

4.4 Nitrates-Nitrites

High results may be obtained for samples that contain nitrate and/or nitrite. During the distillation, nitrate and nitrite will form nitrous acid that will react with some organic compounds to form oximes. These oximes will decompose under test conditions to generate HCN. The samples shall be tested for presence of nitrate and nitrite as described in Section 10.3.1.5.

5.0 SAFETY

See Section 12.0 in Exhibit D - Introduction to Inorganic 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 Statement of Work (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.

6.1 Glassware/Labware

6.1.1 Assorted volumetric glassware (Class A), and calibrated pipettes and micropipettes. Manufacturer’s instructions should be followed for the calibration and maintenance of adjustable pipettes.

6.1.2 Balances - Top loader balance, 300 gram (g) capacity, and a minimum sensitivity of ±1.0 milligram (mg)

A balance calibration must be checked with known masses once per each day of use. This verification consists of a check with two weights covering the range expected (approximately ±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 must 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 E617-97 (2008) or equivalent (e.g., earlier Class ‘S’ defined masses). All balances must be checked at least once annually by a certified technician. The reference masses used by the Contractor must 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 Distillation Apparatus

6.2.1 Midi-Distillation Apparatus

6.2.1.1 Midi-reflux distillation apparatus

6.2.1.2 Heating block - Capable of maintaining 125°C (±5°C)

6.2.2 Micro-Distillation Apparatus

6.2.2.1 Heating block - capable of maintaining 120°C (±5°C)

6.2.2.2 Micro-distillation tubes - Sample tubes and Collector tubes, either pre-filled or user-filled with trapping solution

6.2.2.3 Tube press

6.3 Flow Injection Analyzer with accessories

6.3.1 Sampler

6.3.2 Pump

6.3.3 Cyanide cartridge

6.3.4 Spectrophotometer with 50 millimeter (mm) flow cells and 580 nm filter

6.3.5 Chart recorder or data system

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.

7.1.2 Lead Acetate Test Paper.

7.1.3 Cadmium carbonate (Powdered).

7.1.4 Potassium Iodide – Starch Test Paper.

7.1.5 Ascorbic acid (Crystals).

7.1.6 Midi-Distillation Reagents

7.1.6.1 Sodium hydroxide solution, 0.25N - Dissolve 10.0 g sodium hydroxide in reagent water and dilute to 1 Liter (L).

7.1.6.2 Sodium hydroxide solution, 1.25N - Dissolve 50.0 g sodium hydroxide in reagent water and dilute to 1 L.

7.1.6.3 Sulfuric acid, 50% (v/v) - Carefully add a portion of concentrated (95-98%) sulfuric acid to an equal portion of reagent water.

7.1.6.4 Magnesium chloride solution (2.5M) – Weigh 510 g of $MgCl_2 \cdot 6H_2O$ into a 1000 milliliter (mL) flask, dissolve, and dilute to 1 L with reagent water.

7.1.6.5 Sulfamic acid (Powdered).

7.1.7 Micro-Distillation Reagents

7.1.7.1 Sodium hydroxide solution, 0.25N – Dissolve 10.0 g sodium hydroxide in reagent water and dilute to 1 L.

7.1.7.2 Sodium hydroxide solution, 1.25N - Dissolve 50.0 g sodium hydroxide in reagent water and dilute to 1 L.

7.1.7.3 Sulfuric Acid/Magnesium Chloride solution (7.11 M sulfuric acid/0.79 M magnesium chloride) - In a fume hood, weigh 32.2 g $MgCl_2 \cdot 6H_20$ into a tared 500 mL beaker and add 110.8 g reagent water. Add 139 g concentrated (95-98%) sulfuric acid in 40 g portions with stirring. Allow the solution to cool.

7.1.7.4 Sulfamic acid (Powdered).

7.1.8 Analytical Reagents

7.1.8.1 Chloramine-T solution (0.014M) - Dissolve 0.40 g of chloramine-T in reagent water and dilute to 100 mL. Prepare fresh daily.

7.1.8.2 Sodium dihydrogen Phosphate Buffer – Dissolve 138g of $NaH_2PO_4 \cdot H_2O$ in 1L reagent water.

7.1.8.3 Pyridine-barbituric acid solution - Transfer 15 g of barbituric acid into a 1 L volumetric flask. Add about 100 mL of reagent water and swirl the flask. Add 75 mL of pyridine and mix. Add 15 mL of concentrated hydrochloric acid and mix.

Dilute to about 900 mL with reagent water and mix until the barbituric acid is dissolved. Dilute to 1 L with reagent water. Store at 4°C (±2°C).

7.2 Standards

7.2.1 Introduction

The Contractor must provide all standards, except as noted, to be used with this contract. These standards may be used only after they have been certified according to the procedure in Exhibit D - Introduction to Inorganic Analytical Methods, Section 11.0. The Contractor must be able to verify that the standards are certified. Manufacturer’s certificates of analysis must be retained by the Contractor and presented upon request.

Samples, sample distillates, and standards must be stored separately.

7.2.2 Stock Standard Solutions

7.2.2.1 Stock cyanide solution, 1000 mg/L CN - Dissolve 2.51 g of potassium cyanide and 2.0 g potassium hydroxide in reagent water and dilute 1 L. Standardize with 0.0192N silver nitrate. Standardization is not necessary if this standard is purchased as a certified solution.

7.2.2.2 Intermediate cyanide standard solution, 10 mg/L CN - Dilute 1.0 mL of stock cyanide solution plus 20 mL of 1.25N sodium hydroxide solution to 100 mL with reagent water. Prepare this solution at time of analysis.

7.2.3 Secondary Dilution Standards

Prepare secondary dilution standard solutions by diluting the appropriate volumes of the intermediate cyanide standard solution with 0.25N sodium hydroxide. The final concentration of sodium hydroxide in all standards should be 0.25N.

7.2.4 Initial Calibration Verification Solution

7.2.4.1 The Initial Calibration Verification (ICV) solution shall be obtained from the EPA.

7.2.4.1.1 If the solution is not available from the EPA, then the ICV solution shall be prepared by the laboratory using a certified solution from an independent source. An independent source is defined as a standard from a different source than those used in the standards for the instrument calibration. Analyses shall be conducted at a concentration other than that used for instrument calibration, but near the middle of the calibration range.

7.2.4.1.2 The ICV standard shall be distilled in the same matrix as the calibration standards and in accordance with the instructions provided by the supplier.

7.3 Blanks

Two types of blanks are required for this method. A Calibration Blank is used to establish the analytical calibration curve and the Preparation Blank (see Section 12.1) is used to assess possible contamination from the sample preparation procedure and to assess spectral background.

7.3.1 Calibration Blank - Must contain all the reagents in the same volumes as used in preparing the samples. The Calibration Blank must be carried through the complete procedure and contain the same reagent concentration in the final solution as the sample solution used for analysis. The Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB) are identical in composition to the Calibration Blank and are used to monitor for analyte carryover.

7.3.2 Preparation Blank - Must contain all the reagents in the same volumes as used in preparing the samples. The Preparation Blank must be carried through the complete procedure and contain the same reagent concentration in the final solution as the sample solution used for analysis. Soil/sediment blanks shall use 1.00 mL (±0.01 mL) of reagent water.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Sample Collection and Preservation

All aqueous/water and soil/sediment samples must be collected in polyethylene or glass containers. The aqueous/water samples must be preserved with sodium hydroxide to pH greater than or equal to 10. All samples must be maintained at ≤6ºC but not frozen from the time of collection until receipt at the laboratory.

8.2 Sample Storage

All aqueous/water and soil/sediment samples must be protected from light and refrigerated at ≤6ºC but not frozen from the time of receipt until distillation.

8.2.1 Unused Sample Storage

The Contractor shall retain the unused portion of the aqueous/water and soil/sediment samples for a period of 60 days after delivery of a complete, reconciled data package to the EPA. The unused portion must be protected from light and refrigerated at ≤6ºC but not frozen.

8.2.2 Distillate Sample Storage

Distillates shall not be retained. Any reanalyses of the sample shall be performed using a freshly distilled aliquot of the sample.

8.2.3 Container Storage

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

8.3 Contract Required Holding Time

The sample holding time for cyanide is 12 days from Validated Time of Sample Receipt (VTSR) to analysis. The holding time for the analysis of SPLP leachates is 12 days from the date of extraction.

9.0 CALIBRATION AND STANDARDIZATION

9.1 Instrument Operating Parameters

Because of the difference between various manufacturers 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. The Method Detection Limit (MDL) and precision must be investigated and established for cyanide on that particular instrument. All measurements must be within the operational range of the instrument. It is the responsibility of the analyst to verify the instrument configuration and operating conditions used satisfy the analytical requirements and to maintain Quality Control (QC) data confirming instrument performance and analytical results.

9.2 Pre-Calibration Routine

Prior to calibration, the Contractor shall set up each instrument with the operating parameters established in Section 9.1 and conduct any necessary adjustments. The instrument must be allowed to become stable (usually 30 minutes) before calibration is performed. Establish a steady reagent baseline, adjusting as necessary.

9.3 Instrument Calibration Procedure

9.3.1 Summary of Instrument Calibration

Prior to sample analysis, the Contractor shall calibrate each instrument to determine sensitivity and linearity of the response.

9.3.2 Frequency of Instrument Calibration

Each instrument shall be calibrated daily or once every 24 hours, each time the instrument is set up, or after ICV, ICB, Continuing Calibration Verification (CCV), or CCB failure. The instrument calibration date and time shall be included in the raw data.

9.3.3 Procedure for Instrument Calibration

9.3.3.1 Each instrument shall be calibrated according to the manufacturer’s recommended procedures.

9.3.3.2 At least six calibration standards shall be used. The calibration standards shall be prepared according to Sections 7.2 and 10.2. One of the standards shall be a blank standard and one shall be at or below the Contract Required Quantitation Limit (CRQL), but greater than the MDL. The rest of the standards shall be uniformly spread over the appropriate calibration range.

9.3.3.3 Calibration standards shall be distilled fresh with each calibration performed according to Section 10.2.

9.3.4 Calculations for Instrument Calibration

9.3.4.1 The calibration curve shall be calculated using linear regression by plotting the concentration of the standard [in micrograms/Liter (µg/L)] on the X-axis versus the instrument response (e.g., absorbance) on the Y-axis.

9.3.4.2 The Contractor may use standard linear regression, weighted linear regression (1/concentration, 1/square of concentration, variance, 1/variance, standard deviation, 1/standard deviation, or 1/square of standard deviation), or linear regression with zero force calibration models, as appropriate for the above calculation. No other types of equations (e.g., quadratic) are to be used.

9.3.4.3 The calibration curve shall be checked to establish the representativeness of the data that were used to produce it. This check involves re-fitting the data of the non-blank calibration standards back to the calibration curve, and computing the difference between the calculated concentration and the expected concentration for each of these standards. The difference is then divided by the expected concentration of the respective standard and multiplied by 100.

9.3.5 Technical Acceptance Criteria for Instrument Calibration

9.3.5.1 The correlation coefficient of the calibration curve shall be greater than or equal to 0.995.

9.3.5.2 The Percent Difference (%D) for each of the standards shall be within the control limits of ±30%.

9.3.5.3 If a standard is analyzed at a concentration that is below the CRQL and the %D criteria is not met, that standard can be excluded from the calibration curve as long as the lowest non-zero standard is still analyzed at or below the CRQL and all standards included in the calibration curve are continuous and consecutive.

9.3.6 Corrective Action for Instrument Calibration

9.3.6.1 Sample analysis shall not begin until the criteria described in Section 9.3.5 have been met.

9.3.6.2 Any changes or corrections to the analytical system shall be followed by recalibration.

9.4 Initial Calibration Verification

9.4.1 Summary of Initial Calibration Verification

Prior to sample analysis, the Contractor shall demonstrate the accuracy of the instrument calibration for each instrument through the analysis of an ICV standard.

9.4.2 Frequency of Initial Calibration Verification

The ICV shall be analyzed immediately after the instrument has been calibrated.

9.4.3 Procedure for Initial Calibration Verification

9.4.3.1 The ICV shall be analyzed at the wavelength used to report final results.

9.4.3.2 The ICV shall reflect the conditions of analysis of the associated analytical samples.

9.4.4 Calculations for Initial Calibration Verification

The Percent Recovery (%R) of the ICV shall be calculated using the following equation:

EQ. 1 ICV Percent Recovery

$$\%R = \frac{\text{Found(ICV)}}{\text{True(ICV)}} \times 100$$

WHERE,

Found (ICV) = The found concentration of cyanide in the ICV Solution

True (ICV) = The expected concentration of cyanide in the ICV Solution

9.4.5 Technical Acceptance Criteria for Initial Calibration Verification

The ICV %R shall be within the control limits of 85-115%.

9.4.6 Corrective Action for Initial Calibration Verification

If the recovery is outside the control limits of 85% Recovery (low) or 115% Recovery (high), the analysis shall be terminated, the problem corrected, the instrument recalibrated, and the calibration verified.

9.5 Continuing Calibration Verification

9.5.1 Summary of Continuing Calibration Verification

Prior to sample analysis, periodically during analysis, and at the conclusion of analysis, the Contractor shall demonstrate the stability of the calibration through the analysis of a CCV standard. The Contractor shall not analyze a blank immediately prior to the analysis of the CCV.

9.5.2 Frequency of Continuing Calibration Verification

9.5.2.1 A CCV shall be analyzed at the beginning of the analytical sequence and after the last analytical sample. A CCV shall also be analyzed at a frequency not to exceed 1 hour during an analytical sequence. See the example analytical sequence in Section 10.5.6.

9.5.2.2 The analytical sequence can continue for 24 hours as long as samples are being continuously analyzed without the instrument being turned off and successive CCV standards meet the technical acceptance criteria in Section 9.5.5.

9.5.3 Procedure for Continuing Calibration Verification

9.5.3.1 The CCV standard shall be prepared using the same source and in the same acid matrix as the calibration standards at or near to the mid-level of the calibration curve. The CCV shall be prepared according to Section 10.0.

9.5.3.2 The same CCV standard shall be used throughout the analytical sequences for an SDG.

9.5.3.3 The CCV shall be analyzed at the wavelength used to report final results.

9.5.3.4 Each CCV analyzed shall reflect the conditions of analysis of all associated analytical samples (the preceding analytical samples up to the previous CCV as applicable and the analytical samples following this CCV up to the next CCV as applicable).

9.5.4 Calculations for Continuing Calibration Verification

The %R of the CCV shall be calculated using the following equation:

EQ. 2 CCV Percent Recovery

$$\%R = \frac{\text{Found (CCV)}}{\text{True(CCV)}} \times 100$$

WHERE,

Found (CCV) = The found concentration of cyanide in the CCV Solution

True (CCV) = The expected concentration of cyanide in the CCV Solution

9.5.5 Technical Acceptance Criteria for Continuing Calibration Verification

9.5.5.1 The CCV %R shall be within the control limits of 85-115%.

9.5.5.2 All samples shall be analyzed within 1 hour of an acceptable opening and closing CCV.

9.5.6 Corrective Action for Continuing Calibration Verification

If the deviations of the CCV are greater than the specified control limits of 85% Recovery (low) or 115% Recovery (high), the analysis shall be terminated, the problem corrected, the instrument recalibrated, the calibration verified, and reanalysis of all analytical samples analyzed since the last compliant calibration verification shall be performed.

9.6 Initial and Continuing Calibration Blank

9.6.1 Summary of Calibration Blank

Prior to sample analysis, periodically during analysis, and at the conclusion of analysis, the Contractor shall demonstrate the stability of the calibration baseline through the analysis of an ICB and CCB.

9.6.2 Frequency of Calibration Blank

9.6.2.1 An ICB shall be analyzed immediately after the instrument has been calibrated and the calibration verified by the analysis of the ICV.

9.6.2.2 Each CCB shall be analyzed immediately after the analysis of a CCV.

9.6.3 Procedure for Calibration Blank

9.6.3.1 The ICB and CCB samples shall be analyzed at the wavelength used for reporting final results.

9.6.3.2 The ICB analyzed shall reflect the conditions of analysis of the associated analytical samples.

9.6.3.3 Each CCB analyzed shall reflect the conditions of analysis of the associated analytical samples (the preceding analytical samples up to the previous CCB as applicable and the analytical samples following this CCB up to the next CCB as applicable).

9.6.4 Calculations for Calibration Blank

The results for the ICB and CCB samples shall be calculated using Equation 3 in Section 11.0.

9.6.5 Technical Acceptance Criteria for Calibration Blank

The absolute value of each calibration blank result shall be less than or equal to the CRQL for aqueous/water samples.

9.6.6 Corrective Action for Calibration Blank

If the absolute value of the calibration blank exceeds the CRQL for aqueous/water samples, the analysis shall be terminated, the problem corrected, the instrument recalibrated, the calibration verified, and reanalysis of all affected analytical samples analyzed since the last compliant calibration blank performed.

10.0 PROCEDURE

10.1 Pre-Distillation Sample Preparation

10.1.1 The Contractor shall measure the sample pH at the time of sample receipt to verify that the sample was properly preserved (see Exhibit D – General Inorganic Analysis, Section 10.1.2.1).

10.1.2 Before preparation is initiated for an aqueous/water sample, the Contractor shall test for the presence of sulfides and oxidizing agents (e.g., residual chlorine). The Contractor shall document the presence of sulfides or oxidizing agents in the SDG Narrative. The Contractor shall document the results (positive or negative) of the tests for sulfides and oxidizing agents in the distillation log.

10.1.2.1 The test for sulfides shall be performed by placing a drop of the sample on a strip of lead acetate paper. If the test strip turns black, the Contractor shall contact the Sample Management Office (SMO) for further instructions from the EPA Region before proceeding with sample preparation and analysis.

10.1.2.2 The test for oxidizing agents shall be performed by placing a drop of the sample on a strip of potassium iodide - starch test paper (KI - starch paper). If the test strip turns blue, the Contractor shall contact SMO for further instructions from the EPA Region before proceeding with sample preparation and analysis.

10.2 Standards Preparation

All standards for the midi-distillation and micro-distillation semi-automated spectrophotometric analysis shall be distilled in the same manner as the samples.

10.2.1 Prepare at least five standards and a calibration blank according to Section 9.3.

NOTE: The concentration of one of the calibration standards shall be at or below the CRQL, but greater than the MDL.

10.2.2 For midi-distillation, the standards shall be prepared by pipetting suitable volumes of the secondary dilution standard solution (see Section 7.2.3) into volumetric flasks and diluting to volume with 0.25N sodium hydroxide. Add 50 mL of each standard to a midi-distillation tube and then prepare and distill these standards and the calibration blank in the same manner as the samples.

10.2.3 For micro-distillation, the standards shall be prepared by pipetting suitable volumes of the secondary dilution standard solution (see Section 7.2.3) into volumetric flasks and diluting to volume with 0.25N sodium hydroxide. Add 6 mL of each standard to a sample tube and then prepare and distill these standards and the calibration blank in the same manner as samples.

10.3 Aqueous/Water Sample Preparation

10.3.1 Preparation Method by Midi-Distillation [based on EPA Method 335.4, Revision 1.0 (August 1993)]

10.3.1.1 Pipet 50 mL (±1 mL) of sample into the distillation flask along with 2 or 3 boiling chips (as necessary). The sample shall not be diluted prior to distillation.

10.3.1.2 Add 50 mL (±1 mL) of 0.25N sodium hydroxide to the gas absorbing tube.

10.3.1.3 Connect the boiling flask, condenser, and absorber in the train. The excess cyanide trap contains 0.5N sodium hydroxide.

10.3.1.4 Turn on the vacuum and adjust the gang (Whitney) valves to give a flow of between 2 to 3 bubbles per second from the impingers in each reaction vessel.

10.3.1.5 Test sample for nitrate and/or nitrite using an appropriate test strips or kits. Record method, manufacturer information, and results on the Distillation Log and in the SDG Narrative. If the samples contain nitrate and/or nitrite, add 0.2 g of sulfamic acid through the air inlet tube. The interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid prior to the distillation. Mix for 3 minutes prior to adding the sulfuric acid.

10.3.1.6 After 5 minutes of vacuum flow, inject 5 mL of 50% (v/v) sulfuric acid through the top air inlet tube of the distillation head into the reaction vessel. Allow the airflow to mix the reaction vessel contents for 5 minutes.

NOTE: The acid volume must be sufficient to bring the sample/solution pH to below 2.0.

10.3.1.7 Add 2 mL of the 2.5M magnesium chloride solution through the top air inlet tube of the distillation head into the reaction vessel. Excessive foaming from samples containing surfactants may be quelled by the addition of either another 2 mL of the 2.5M magnesium chloride solution or a few drops of a commercially available anti-foam agent. The Contractor shall document the addition of magnesium chloride solution or anti-foam agent in the SDG Narrative.

10.3.1.8 Turn on the heating block and set for 125°C (±3°C). Heat the solution to boiling, taking care to prevent solution backup by periodic adjustment of the vacuum flow.

10.3.1.9 After 1 1/2 hours of refluxing, turn off the heat and continue the vacuum for an additional 15 minutes. The flasks should be cool at this time.

10.3.1.10 After cooling, close off the vacuum at the gang valve and remove the absorber. Seal the distillate and store at 4°C until analyzed.

10.3.2 Preparation Method by Micro-Distillation (based on Lachat QuikChem Method 10.204-00-1-X)

10.3.2.1 Preheat the heater block to 120°C (±3°C).

10.3.2.2 Add 6 mL (±0.1 mL) of sample to the sample tube. The sample shall not be diluted prior to distillation. If the Contractor is not using the prefilled collector tubes, add 2 mL (±0.1 mL) of the 0.25N absorbing solution to each collector tube. Add 0.75 mL of the (7.11M/0.79M) sulfuric acid/magnesium chloride solution to each sample tube and immediately cap with a collector tube and press to seal.

10.3.2.3 Place the assembled tubes into the heater block and heat for 30 minutes. After 30 minutes, remove each tube from the block and immediately pull off the sample tube.

10.3.2.4 Invert each collector tube and allow to cool. Mix the distillate and detach the upper portion. Dilute the distillate to 6 mL (±0.1 mL) with absorbing solution and mix. Seal the distillate and store at 4°C until analyzed.

10.4 Soil/Sediment Sample Preparation

10.4.1 Preparation Method by Midi-Distillation [based on EPA Method 335.4, Revision 1.0 (August 1993)]

10.4.1.1 Mix the sample thoroughly to achieve homogeneity. Weigh to the nearest 0.01 g and transfer 1.00-1.50 g of sample (wet weight) into the reaction vessel and add 50 mL of reagent water. Add 2 or 3 boiling chips (as necessary).

10.4.1.2 Add 50 mL (±1 mL) of 0.25N sodium hydroxide to the gas absorbing impinger.

10.4.1.3 Connect the reaction vessel, condenser, and absorber in the train. The excess cyanide trap contains 0.5N sodium hydroxide.

10.4.1.4 Turn on the vacuum and adjust the gang (Whitney) valves to give a flow of between 2 to 3 bubbles per second from the impingers in each reaction vessel.

10.4.1.5 After 5 minutes of vacuum flow, inject 5 mL of 50% (v/v) sulfuric acid through the top air inlet tube of the distillation head into the reaction vessel. Allow the airflow to mix the reaction vessel contents for 5 minutes.

NOTE: The acid volume must be sufficient to bring the sample/solution pH to below 2.0.

10.4.1.6 Add 2 mL of the 2.5M magnesium chloride solution through the top air inlet tube of the distillation head into the reaction vessel. Excessive foaming from samples containing surfactants may be quelled by the addition of either another 2 mL of the 2.5M magnesium chloride solution or a few drops of a commercially available anti-foam agent. The Contractor shall document the addition of the magnesium chloride solution or anti-foam agent in the SDG Narrative.

10.4.1.7 Turn on the heating block and set for 125°C (±3°C). Heat the solution to boiling, taking care to prevent solution backup by periodic adjustment of the vacuum flow.

10.4.1.8 After 1 1/2 hours of refluxing, turn off the heat and continue the vacuum for an additional 15 minutes. The flasks should be cool at this time.

10.4.1.9 After cooling, close off the vacuum at the gang valve and remove the absorber. Seal the distillate and store at 4°C until analyzed.

10.4.2 Preparation Method by Micro-Distillation (based on Lachat QuikChem Method 10-204-00-1-X)

10.4.2.1 Preheat the heater block to 120°C (±3°C).

10.4.2.2 Add 0.50-1.00 g (±0.01 g) of sample (wet weight) and 5 mL of reagent water to the sample tube. If the Contractor is not using the prefilled collector tubes, add 2 mL (±0.1 mL) of the 0.25N absorbing solution to the collector tube. Add 0.75 mL of the (7.11M/0.79M) sulfuric acid/magnesium chloride solution to each sample tube and immediately cap with collector tube and press to seal.

10.4.2.3 Place the assembled tubes into the heater block and heat for 30 minutes. After 30 minutes, remove each tube from the block and immediately pull off the sample tube.

10.4.2.4 Invert each collector tube and allow to cool. Mix the distillate and detach the upper portion. Dilute the distillate to 6 mL (±0.1 mL) with absorbing solution and mix. Seal the distillate and store at 4°C until analyzed.

10.5 Sample Analysis

10.5.1 Set up the manifold. Pump the reagents through the system until a steady baseline is obtained.

10.5.2 Place the distilled calibration standards, blanks, and control standards in the sampler tray, followed by the distilled samples, duplicates, standards, spikes, and blanks. See example sequence provided in Section 10.5.6.

10.5.3 Allow all standards and samples to come to ambient room temperature prior to analysis.

10.5.4 When a steady reagent baseline is obtained and before starting the sampler, adjust the baseline using the appropriate knob on the spectrophotometer. Aspirate the distilled blank calibration standard and adjust the spectrophotometer until the desired signal is obtained. Establish the baseline and proceed to analyze the remainder of the distilled standards and distilled samples.

10.5.5 Sample distillates having concentrations higher than the established calibration range as determined by the expected concentration of the highest calibration standard shall be diluted into range with the absorbing solution and reanalyzed.

10.5.6 Example Analytical Sequence for Cyanide Including the Instrument Calibration:

S##
S##
S##
S##
S##
S##
ICV
ICB
CCV###
CCB###
samples
CCV###
CCB###
samples
CCV###
CCB###, etc.

11.0 DATA ANALYSIS AND CALCULATIONS

Calculate the Cyanide concentration using the following equations.

11.1 Aqueous/Water and SPLP Leachate Sample Calculation

EQ. 3 Aqueous/Water and SPLP Leachate Sample Concentration

$$\text{CN Concentration}\,(\mu g/L) = C \times \frac{V_f}{V} \times DF$$

WHERE,
C = Instrument response in µg/L CN from the calibration curve
V_f = Final prepared (absorbing solution) volume (mL)
V = Initial aliquot amount (mL)
DF = Dilution Factor

11.2 Soil/Sediment Sample Calculation

The concentrations in the distillates are to be reported on the basis of the dry weight of the sample, in units of milligram/kilogram (mg/kg):

EQ. 4 Soil/Sediment Sample Concentration

$$\text{CN Concentration}\,(\text{mg/kg dry weight}) = C \times \frac{V_f}{W \times S} \times (1/1000) \times DF$$

WHERE,
C = Instrument response in µg/L CN from the calibration curve
V_f = Final prepared (absorbing solution) volume (mL)
W = Initial aliquot amount (g)
S = % Solids/100 (see Exhibit D – General Inorganic Analysis, Section 10.1.1)
DF = Dilution Factor

11.3 Adjusted Contract Required Quantitation Limit Calculation

11.3.1 Calculate the adjusted CRQL for aqueous/water or SPLP leachate samples by multiplying the CRQL (µg/L) by the sample dilution factor and the V_f/V terms as noted in Equation 3.

11.3.2 Calculate the adjusted CRQL for soil/sediment using the following equation:

EQ. 5 Adjusted Soil/Sediment CRQL

$$\text{Adjusted CRQL (mg/kg)} = C \times \frac{W_M}{W \times S} \times DF$$

WHERE,
C = CRQL (mg/kg)
W_M = Minimum method required aliquot amount (1.00 g for midi or 0.50 g for micro)
W = Initial aliquot amount (g)
S = % Solids/100 (see Exhibit D - General Inorganic Analysis, Section 10.1.1)
DF = Dilution Factor

12.0 QUALITY CONTROL

12.1 Preparation Blank Sample

12.1.1 Summary of Preparation Blank Sample

The Preparation Blank is used to monitor for possible contamination throughout the entire sample preparation and analysis process.

12.1.2 Frequency of Preparation Blank Sample

At least one Preparation Blank shall be prepared with every SDG, or with each preparation batch, whichever is more frequent.

12.1.3 Procedure for Preparation Blank Sample

The Preparation Blank shall be carried through the complete sample preparation procedure for the matrix and contain the same reagent concentration in the final distillate as the samples.

12.1.4 Calculations for Preparation Blank Sample

Calculate the results for aqueous Preparation Blanks by using Equation 3. Calculate the results for soil/sediment Preparation Blanks by using Equation 4.

12.1.5 Technical Acceptance Criteria for Preparation Blank Sample

12.1.5.1 The absolute value of the Preparation Blank result shall be less than or equal to the CRQL.

12.1.5.2 The cyanide concentration in the Preparation Blank may be greater than the CRQL, if the concentration of cyanide in the associated samples is greater than or equal to 10 times the blank concentration.

12.1.5.3 The cyanide concentration in the Preparation Blank may be less than the negative CRQL if the concentration in the associated samples is greater than or equal to 10 times the CRQL.

12.1.6 Corrective Action for Preparation Blank Sample

12.1.6.1 If the cyanide concentration in the Preparation Blank is greater than the CRQL, and the concentration of cyanide in any of the associated samples is less than 10 times the blank concentration, then all samples with less than 10 times the blank concentration shall be reprepared and reanalyzed with appropriate new QC.

12.1.6.2 If the cyanide concentration in the Preparation Blank is less than the negative CRQL and the concentration in the associated samples is less than 10 times the CRQL, then all samples with less than 10 times the CRQL concentration shall be reprepared and reanalyzed with appropriate new QC.

12.2 Matrix Spike and Post-Distillation Spike Samples

12.2.1 Summary of Matrix Spike and Post-Distillation Spike Samples

The Matrix Spike sample analysis is designed to provide information about the effect of the sample matrix on the distillation and/or measurement methodology.

12.2.2 Frequency of Matrix Spike and Post-Distillation Spike Samples

12.2.2.1 At least one Matrix Spike sample analysis shall be performed on each group of samples of a similar matrix type (i.e., aqueous/water, soil/sediment) or for each SDG, whichever is more frequent.[1]

12.2.2.2 If a Matrix Spike sample does not meet the technical acceptance criteria listed in Section 12.2.5, a Post-Distillation Spike Sample shall be performed for those analytes that do not meet the specified criteria.

12.2.3 Procedure for Matrix Spike and Post-Distillation Spike Samples

12.2.3.1 For a Matrix Spike sample, the spike is added before the distillation (i.e., prior to the addition of other reagents).

12.2.3.2 The analyte spike shall be added to achieve a concentration of 100 µg/L in the final sample solution prepared for analysis (i.e., post-distillation). For example, the midi-distillation procedure would require the addition of 5 µg of cyanide to the sample prior to distillation (based on the final distillation volume of 50 mL). For a typical 50 mL aqueous/water sample, this would be equivalent to a concentration of 100 µg/L in the original sample. For a typical 1.00 g soil/sediment sample, this would be equivalent to a concentration of 5 mg/kg in the original dry sample. Adjustments shall be made to maintain these spiking levels when the weight of the sample taken deviates by more than 10% of these values.

12.2.3.3 For a Post-Distillation Spike sample, the sample that was initially used for the Matrix Spike analysis shall be used for the Post-Distillation Spike analysis. Spike the unspiked aliquot of the original distillate at two times the indigenous level of two times the CRQL, whichever is greater.

12.2.3.4 Samples identified as field blanks and Performance Evaluation (PE) samples shall not be used for Matrix Spike sample analysis. The EPA may require that a specific sample be used for the Matrix Spike sample analysis.

[1] The EPA may require additional spike sample analyses, upon request from the EPA Regional Contract Laboratory Program Contracting Officer’s Representative (EPA Regional CLP COR).

12.2.4 Calculations for Matrix Spike and Post-Distillation Spike Samples

12.2.4.1 If the Matrix Spike analysis is performed on the same sample that is chosen for the Duplicate sample analysis, spike calculations shall be performed using the results of the sample designated as the "original sample" (see Section 12.3). The average of the duplicate results cannot be used for the purpose of determining %R.

12.2.4.2 Calculate the Matrix Spike and Post-Distillation Spike %R using the following equation:

EQ. 6 Matrix Spike and Post-Distillation Spike Percent Recovery

$$\%R = \frac{SSR - SR}{SA} \times 100$$

WHERE,

SSR = Spiked sample result (original) (µg/L or mg/kg) from EQ. 3 or EQ. 4

SR = Sample result (original) (µg/L or mg/kg) from EQ. 3 or EQ. 4. When the sample concentration is less than the MDL, use SR=0.

SA = Spike Added Theoretical Result (µg/L or mg/kg). This is calculated by using the spike concentration specified in Section 12.2.3.2 and applying all corrections used in calculating the sample concentration.

NOTE: The units used for reporting SSRs will be identical to those used for reporting SRs.

12.2.5 Technical Acceptance Criteria for Matrix Spike and Post-Distillation Spike Samples

The Matrix Spike and Post-Distillation Spike %R shall be within the control limits of 75-125%.

12.2.6 Corrective Action for Matrix Spike Sample

12.2.6.1 If the Matrix Spike recovery is not within the control limits of 75-125%, the data for all samples received and associated with that spike sample shall be flagged with "*". An exception to this rule is granted when the sample concentration exceeds the SA concentration by a factor of four or more. In such an event, the data shall be reported unflagged even if the %R does not meet the 75-125% recovery criteria.

12.2.6.2 When the Matrix Spike recovery is outside the control limits and the sample result does not exceed four times the spike added, a Post-Distillation spike shall be performed following procedures in Section 12.2.3.

12.2.6.3 If there is more than one Matrix Spike per matrix, per SDG, if one Matrix Spike sample recovery is not within contract criteria, then flag all the samples of the same matrix and method in the SDG.

12.3 Duplicate Sample

12.3.1 Summary of Duplicate Sample

Duplicates are analyzed to help determine sample homogeneity and laboratory precision.

12.3.2 Frequency of Duplicate Sample

12.3.2.1 One duplicate sample shall be analyzed from each group of samples of a similar matrix type (i.e., aqueous/water, soil/sediment) or for each SDG, whichever is more frequent.[2]

12.3.2.2 Duplicate sample analyses cannot be averaged for reporting.

12.3.3 Procedure for Duplicate Sample

12.3.3.1 Samples identified as field blanks and PE samples shall not be used for duplicate sample analysis. The EPA may require that a specific sample be used for duplicate sample analysis.

12.3.3.2 Prepare a second aliquot of the original sample. The duplicate sample shall be carried through the complete sample preparation procedure.

12.3.4 Calculations for Duplicate Sample

12.3.4.1 The Relative Percent Difference (RPD) for each analyte shall be calculated using the following equation:

EQ. 7 Duplicate Sample Relative Percent Difference

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

WHERE,
S = Sample Result (original) (µg/L or mg/kg) from EQ. 3 or EQ. 4
D = Duplicate Sample Result (µg/L or mg/kg) from EQ. 3 or EQ. 4

12.3.5 Technical Acceptance Criteria for Duplicate Sample

12.3.5.1 The RPD shall be within the control limits of ±20 if the original and duplicate sample values are greater than or equal to five times the CRQL (see Exhibit C – Inorganic Target Analyte List and Contract Required Quantitation Limits).

12.3.5.2 The control limit shall be equal to the CRQL if either the sample or duplicate value are less than five times the CRQL, or if one result is above five times the CRQL level and the other is below.

12.3.5.3 If both sample and duplicate values are less than the CRQL, the RPD is not calculated.

12.3.6 Corrective Action for Duplicate Sample

12.3.6.1 If the duplicate sample results are outside the control limits, flag all the data for samples received associated with that duplicate sample with an "*".

12.3.6.2 If there is more than one duplicate sample per matrix per SDG, and if one duplicate result is not within contract criteria, flag all samples of the same matrix in the SDG.

[2] The EPA may require additional duplicate sample analyses, upon request from the EPA Regional CLP COR.

12.4 Method Detection Limit Determination

12.4.1 Before any field samples are analyzed, the MDLs shall be determined for each distillation procedure and instrument used prior to the start of contract analyses and annually thereafter. An MDL study shall be performed after major instrument maintenance, or changes in instrumentation or instrumental conditions, to verify the current sensitivity of the analysis.

12.4.1.1 To determine the MDLs, the Contractor shall perform MDL studies following the procedures in 40 Code of Federal Regulations (CFR), Part 136.

12.4.1.2 The Contractor shall prepare the MDL samples by each distillation procedure used and shall analyze these samples on each instrument used.

12.4.1.3 The determined concentration of the MDL shall be less than half the concentration of the CRQL listed in Exhibit C – Inorganic Target Analyte List and Contract Required Quantitation Limits.

12.5 Summary of Quality Control Operations

The QC operations performed for cyanide analysis are summarized in Table 1 – QC Operations for Cyanide Analysis.

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

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

15.0 WASTE MANAGEMENT

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

16.0 REFERENCES

16.1 U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, Method 335.4, Revision 1.0, August 1993.

16.2 American Water Works Association/American Public Health Association/Water Environment Federation, Standard Methods for the Examination of Water and Wastewater, Method 4500-CN E.

16.3 U.S. Government Printing Office, 40 Code of Federal Regulations, Part 136, Section 1, Appendix B.

16.4 Lachat QuikChem Method 10-204-00-1-X.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

TABLE 1. QC OPERATIONS FOR CYANIDE ANALYSIS

QC Operation	Frequency
Instrument Calibration	Daily or each time instrument is turned on or set up, after ICV or CCV failure, and after major instrument adjustment.
Initial Calibration Verification	Following each instrument calibration.
Continuing Calibration Verification	At a frequency of every hour of an analytical sequence, and at the beginning and end of each analytical sequence.
Initial Calibration Blank	Following each instrument calibration, immediately after the ICV.
Continuing Calibration Blank	Every hour and at the beginning and end of each analytical sequence. Performed immediately after the CCV.
Preparation Blank	For each SDG or each sample preparation and analysis procedure per batch of prepared samples, whichever is more frequent.
Matrix Spike Sample	For each matrix type or for each SDG, whichever is more frequent.
Post-Distillation Spike	Each time Spike Sample Recovery is outside QC limits.
Duplicate Sample Analysis	For each matrix type or for each SDG, whichever is more frequent.
Method Detection Limit Determination	Prior to start of contract analyses, annually thereafter, and after major instrument adjustment.