

EXHIBIT D

INDUCTIVELY COUPLED PLASMA -
ATOMIC EMISSION SPECTROSCOPY METALS ANALYSIS

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Exhibit D - Inductively Coupled Plasma - Atomic Emission Spectroscopy
Metals Analysis

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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, waste, and wipe samples collected from hazardous waste sites. All metals contained in the Inorganic Target Analyte List (TAL) for ICP-AES in Exhibit C - 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, waste, 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 shall 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 and Waste 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 - List of Abbreviations & Acronyms, Glossary of Terms, and Equations for a complete list of definitions.

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4.0 INTERFERENCES

Several types of interference effects may contribute to inaccuracies in the determination of trace elements in aqueous/waters, TCLP/SPLP leachates, soils/sediments, wastes, and wipes by ICP-AES. Therefore, appropriate steps shall 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 described 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; and/or (4) 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 shall 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 the 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 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, demonstration of equivalent performance that meets 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.

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

6.1 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) - Ribbed and non-ribbed, or equivalent.
- 6.1.3 Funnels.
- 6.1.4 Graduated cylinders.
- 6.1.5 Assorted volumetric glassware (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 ($\pm 3^\circ\text{C}$).
- 6.1.9 Balances - Top-loader balance, 300 gram (g) capacity, and a minimum sensitivity of $\pm 1.0\text{ mg}$.

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

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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 compliant with Federal Communications Commission (FCC) regulations.
- 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), ACS Reagent grade or better.
- 7.1.3 Hydrochloric acid (50% v/v) - Add 500 mL of concentrated hydrochloric acid to 400 mL reagent water and dilute to 1 L.
- 7.1.4 Nitric acid - Concentrated 67-70% (specific gravity 1.41), ACS Reagent grade or better.
- 7.1.5 Nitric acid (50% v/v) - Add 500 mL of concentrated nitric acid to 400 mL of reagent water and dilute to 1 L.
- 7.1.6 Hydrogen peroxide (30%).
- 7.1.7 Nitric acid (2% v/v) - Add 20 mL of concentrated nitric acid to 500 mL of reagent water and dilute to 1 L.

7.2 Standards

7.2.1 Introduction

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

Samples, sample digestates, and standards shall 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 shall 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 must 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 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 Exhibit D - ICP-AES, Table 1.

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 must be within the control limits of $\pm 15\%$ 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 shall be taken in the preparation of mixed calibration standards to ensure that the analytes are compatible and stable. Fresh mixed calibration standards should be prepared as needed with the realization that concentration can change with aging.

Prior to preparing the mixed calibration 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 matrix-match these standards 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 calibration 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.

7.2.4.3.2 If the solution(s) are not available from the EPA, the ICV solution shall be prepared by the Contractor using a certified solution for each analyte from an independent source, which is defined as a standard from a different source than that used for the instrument calibration. Analyses shall be conducted at a concentration other than that used for instrument calibration, but near the middle (within $\pm 30\%$) of the calibration range.

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7.2.4.3.3 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 and a rinse solution are required for this method. A Calibration Blank is used to establish the analytical calibration curve as well as to verify the calibration initially and continually during the analysis, 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 shall 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 and waste 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, STORAGE, AND HOLDING TIMES

8.1 Sample Collection and Preservation

- 8.1.1 All aqueous/water, soil/sediment, and waste samples should 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 should be preserved with nitric acid to a pH ≤ 2 immediately after collection. All soil/sediment and waste samples should be iced or refrigerated at $\leq 6^{\circ}\text{C}$, but not frozen, from the time of collection until receipt at the laboratory.
- 8.1.2 The Contractor shall measure the sample pH at the time of sample receipt to verify that the samples were properly preserved. 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. If the pH is > 9 at the time of receipt, the Contractor should consider the possibility that the labels for the metals and cyanide samples were switched in the field. Do not add acid to samples designated for metals analysis and with a pH > 9 unless the pH of the samples designated for cyanide analysis has been checked and is acceptable for cyanide analysis.

8.2 Sample Storage

All aqueous/water samples preserved to pH ≤2 may be stored at ambient temperature from the time of sample receipt until digestion. All soil/sediment and waste samples shall 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. Samples shall be stored in an upright position.

8.2.1 Unused Sample Storage

The Contractor shall retain the unused portions of aqueous/water, soil/sediment, and waste samples for a period of 60 days after the 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 shall 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 Times

The holding time for metals samples is 180 days from the 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.

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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 shall 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 shall be allowed to become stable 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 the 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 target 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 ($\mu\text{g}/\text{L}$)] 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. See Equation 15 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.3.5 Technical Acceptance Criteria for Instrument Calibration

- 9.3.5.1** The correlation coefficient of the calibration curve must be greater than or equal to 0.995.
- 9.3.5.2** The Percent Difference (%D) for each of the non-blank standards must be within the control limits of $\pm 30\%$.
- 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. No standard analyzed for a particular analyte with a concentration greater than or equal to the CRQL shall be excluded from the calibration curve.

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.

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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 Equation 16 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

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 1, 2, and 3 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.4.5 Technical Acceptance Criteria for Initial Calibration Verification

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

9.4.5.2 The %RSD of the ICV integrations must 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 any CCV after the analysis of the initial CCV following the ICB.

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 ($\pm 30\%$ of mid-range) 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 down 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 Equation 16 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.
- 9.5.4.2 The %RSD from all replicate integrations shall be calculated for each wavelength used to report final results using Equations 1, 2, and 3 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.5.5 Technical Acceptance Criteria for Continuing Calibration Verification

- 9.5.5.1 The CCV %R must be within the control limits of 90-110%.
- 9.5.5.2 The %RSD of the CCV integrations must 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.

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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 down 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 4E in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.6.5 Technical Acceptance Criteria for Calibration Blank

The absolute value of each calibration blank result must 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/TCLP Leachate/SPLP Leachate Sample Preparation

Preparation Method 200.7 (based on EPA Method 200.7)

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 - ICP-AES, Section 8.1.2), 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 a ribbed 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 ($\pm 3^\circ\text{C}$). **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-H₂O 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 Analytical Methods, Section 7.0.

10.2 Soil/Sediment and Waste Sample Preparation

Preparation Method 3050B (based on EPA Method 3050B)

- 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). The Contractor shall not add or remove sample material once the mass range (i.e., 1.00 – 1.50 g) is achieved to ensure that the aliquot amount is representative of the sample.
- 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 ($\pm 3^\circ\text{C}$) 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 ($\pm 3^\circ\text{C}$) without boiling for 2 hours. Maintain a covering of solution over the bottom of the vessel at all times.

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- 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 shall 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 ribbed watch glass and continue heating the acid-peroxide digestate until the volume has been reduced to approximately 5 mL or heat at 95°C ($\pm 3^\circ\text{C}$) 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 ($\pm 3^\circ\text{C}$) 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 Analytical Methods, Section 7.0.

10.3 Wipe Sample Preparation

Preparation Method 3050B (based on EPA Method 3050B)

- 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 shall 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 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

11.1 Target Analyte Concentrations

Calculate the target analyte concentrations or amounts using Equation 4E, 5H, or 5I in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

11.2 Contract Required Quantitation Limit Calculations

Calculate the adjusted CRQLs using Equation 6E or 7H in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

11.3 Hardness (Total) Sample Calculation

Calculate Total Hardness using Equation 4F in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

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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. If no clean wipe is provided, prepare the Preparation Blank without a 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/water Preparation Blanks using Equation 4E in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations. Calculate the results for soil/sediment and waste Preparation Blanks by using Equation 5H in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations. Calculate the results for wipe Preparation Blanks by using Equation 5I in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.1.5 Technical Acceptance Criteria for Preparation Blank Sample

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

12.1.5.2 For aqueous/water, soil/sediment, and waste 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, soil/sediment, and waste 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, soil/sediment, and waste 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, soil/sediment, and waste samples, if any analyte concentration in the Preparation Blank is less than the negative CRQL, and the concentration in any of 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 Prior to the analysis of samples, 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 4E in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.2.4.2 The %R of the ICSA and ICSAB shall be calculated using Equation 16 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.2.5 Technical Acceptance Criteria for Interference Check Sample

12.2.5.1 The ICSA and ICSAB %R must be within the control limits of $\pm 15\%$ of the analyte's true value or the results must 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.

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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 ±15% of the true value ($0.15 \times 43 \text{ } \mu\text{g/L} = \pm 6.5 \text{ } \mu\text{g/L}$) or ±1 times the CRQL ($\pm 10 \text{ } \mu\text{g/L}$). 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 must be within the control limits of ±15% of the established mean value or the results must 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 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, waste) or for each SDG, whichever is more frequent.¹

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 Exhibit D - ICP-AES, Table 2, 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 original unspiked concentration or two times the CRQL, whichever is greater.

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).

12.3.3.4 Samples identified as field blanks or 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 selected 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 Equation 23 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

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

The Matrix Spike %R must 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 for an analyte is not at or within the limits of 75-125%, the data for that analyte in all the samples received and associated with that spike sample shall be flagged with an **. An exception to this rule is granted when the sample concentration exceeds the Spike Added (SA) concentration by a factor of four or more. In such an instance, 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 analysis 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, and one Matrix Spike sample recovery for an analyte is not within contract criteria, flag the data for that analyte in 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, waste) or for each SDG, whichever is more frequent.² Duplicate sample analyses cannot be averaged for reporting.

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

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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 or 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

The Relative Percent Difference (RPD) for each analyte shall be calculated using Equation 24B in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.4.5 Technical Acceptance Criteria for Duplicate Sample

12.4.5.1 The RPD must 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 - Target Analyte List and Contract Required Quantitation Limits, Table 5).

12.4.5.2 The control limit must 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 for an analyte are outside the control limits, flag the data for that analyte in all the 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 one duplicate analyte result is not within contract criteria, flag the data for that analyte in all the 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, waste, and wipe Laboratory Control Samples (LCSSs) 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, leachate, soil/sediment, waste, 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. If no clean wipe is provided, prepare the LCS without a wipe.

12.5.3 Procedure for Laboratory Control Sample

The LCS for aqueous/water, TCLP/SPLP leachates, soil/sediment, waste, and wipe samples shall be prepared by spiking an aliquot of reagent water (50-100 mL for aqueous/water and leachates; 1 mL for soil/sediment, waste, 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

12.5.4.1 Calculate the results for the LCS using Equation 4E, 5H, or 5I in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations as appropriate.

12.5.4.2 Calculate the %R for the LCS using Equation 26B in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.5.5 Technical Acceptance Criteria for Laboratory Control Sample

The LCS %R must 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, soil/sediment, or waste samples is outside the control limits of 70-130% (exception: Ag and Sb; control limits of 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 is outside the control limits of 70-130% (exception: Ag and Sb; control limits of 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, waste) 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.

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12.6.4 Calculations for ICP-AES Serial Dilution

The percent difference for each analyte is calculated using Equation 27 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

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) must be within 20% 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 20%, a chemical or physical interference effect must be suspected, and the data for all affected analytes in all the samples received and associated with that Serial Dilution shall be flagged with an "*".

12.6.6.2 In the instance where there is more than one Serial Dilution per SDG, per matrix, and one serial dilution result for an analyte is not within contract criteria, flag the data for the analyte in 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 under the contract, the MDL for each analyte shall be determined for each digestion procedure, and for each instrument under the same conditions used for analysis, used prior to the start of contract analyses and verified annually thereafter. MDL determination is matrix-specific (i.e., the MDL shall be determined for aqueous/water and soil/sediment samples. The MDL determined for aqueous/water samples shall be used for TCLP and SPLP leachates. For wipe samples, the results of the MDL performed for soil/sediment samples shall be used and reported in the appropriate units. The MDL determined for soil/sediment samples shall be used for waste samples.). 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 Title 40 of the Code of Federal Regulations (CFR), Part 136, Appendix B, Revision 2.

12.7.1.2 The determined concentration of the MDL must be less than half the concentration of the CRQL listed in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 5.

12.7.1.3 The MDL for Hardness is not required to be determined or reported.

12.7.1.4 The delivery requirements for the MDL values are specified in Exhibit B - Reporting and Deliverables Requirements, Table 1.

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.

12.9 Summary of Quality Control Operations

The QC operations performed for ICP-AES analysis are summarized in Exhibit D - ICP-AES, Table 3.

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

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

15.0 WASTE MANAGEMENT

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

16.0 REFERENCES

- 16.1 U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, Method 200.7, Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma - Atomic Emission Spectrometry, Revision 4.4, 1994.
- 16.2 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 3050B, Acid Digestion of Sediments, Sludges, and Soil, 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), Method 6010D, Inductively Coupled Plasma - Optical Emission Spectrometry, Revision 5, July 2018.
- 16.4 U.S. Government Printing Office, Title 40 of the Code of Federal Regulations, Chapter 1, Subchapter D, Part 136, Appendix B, Definition and Procedure for the Determination of the Method Detection Limit, Revision 2.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

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

Analytes	($\mu\text{g/L}$)	Interferents	($\mu\text{g/L}$)
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	Aqueous/Water Spike ($\mu\text{g/L}$)	Soil/Sediment and Waste Spike (mg/kg) ⁽¹⁾
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.

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, after ICB or CCB 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 METALS ANALYSIS

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Exhibit D - Inductively Coupled Plasma - Mass Spectrometry Metals Analysis

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Exhibit D - Inductively Coupled Plasma - Mass Spectrometry Metals Analysis

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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, soil/sediment, and waste samples collected from hazardous waste sites. All metals contained in the Inorganic Target Analyte List (TAL) for ICP-MS in Exhibit C - 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 shall 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, shall 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 and Waste Samples (based on EPA Method 200.8)

3.0 DEFINITIONS

See Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations 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, soil/sediment, and waste samples by ICP-MS. Therefore, appropriate steps shall be taken in all analyses to ensure that potential interferences are taken into account. Several types of interferences are described in Sections 4.1 through 4.5 below.

Exhibit D - Section 4

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 a 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 shall 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 Exhibit D - ICP-MS, Table 1. Such interferences must be recognized, and when they cannot be avoided by the selection of alternative analytical isotopes, appropriate corrections shall 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 Analytical Methods.

Exhibit D - Section 6

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, demonstration of equivalent performance that meets 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.

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

6.1 Glassware/Labware

- 6.1.1 250 milliliter (mL) beaker or other appropriate vessel (glass or plastic).
- 6.1.2 Watch glasses (glass or plastic) - Ribbed and non-ribbed, or equivalent.
- 6.1.3 Funnels.
- 6.1.4 Graduated cylinders.
- 6.1.5 Assorted volumetric glassware (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 ($\pm 3^\circ\text{C}$).
- 6.1.9 Balances - Top-loader balance, 300 gram (g) capacity, and a minimum sensitivity of ± 1.0 milligram (mg).

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

6.2 Inductively Coupled Plasma - Mass Spectrometer

The ICP-MS consists of:

- An instrument capable of scanning the mass range of 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 (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 shall 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), ACS Reagent grade or better.
- 7.1.3 Hydrochloric acid (50% v/v) - Add 500 mL of concentrated hydrochloric acid to 400 mL of reagent water and dilute to 1 Liter (L).
- 7.1.4 Nitric acid - Concentrated 67-70% (specific gravity 1.41), ACS Reagent grade or better.
- 7.1.5 Nitric acid (50% v/v) - Add 500 mL of concentrated nitric acid to 400 mL of reagent water and dilute to 1 L.
- 7.1.6 Nitric acid (2% v/v) - Add 20 mL of concentrated nitric acid to 400 mL of reagent water and dilute to 1 L.
- 7.1.7 Nitric acid (1% v/v) - Add 10 mL of concentrated nitric acid to 400 mL of reagent water and dilute to 1 L.

Exhibit D - Section 7

7.2 Standards

7.2.1 Introduction

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

Samples, sample digestates, and standards shall 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 shall 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 must meet the requirements in Section 7.2.1.

7.2.4 Working Standards

7.2.4.1 Mixed Calibration Standard Solutions

Care shall be taken in the preparation of mixed calibration standards to ensure that the analytes are compatible and stable. Fresh mixed calibration standards should be prepared as needed with the realization that concentration can change with aging.

Prepare the mixed calibration 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 ($\mu\text{g}/\text{L}$) 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 $\mu\text{g}/\text{L}$ 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 and ICSB for the analytes only) shall be obtained from the EPA.

7.2.4.4.1.1 Only if the ICS solutions are not available from the EPA, the ICSS shall be prepared with interferent and analyte concentrations at the levels specified in Exhibit D - ICP-MS, Table 2.

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 must be within the control limits of $\pm 15\%$ 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 shall be obtained from the EPA.

7.2.4.5.2 If the solution(s) are not available from the EPA, the ICV solution shall be prepared by the Contractor using a certified solution for each analyte from an independent source, which is defined as a standard from a different source than that used for the instrument calibration. Analyses shall be conducted at a concentration other than that used for instrument calibration, but near the middle (within $\pm 30\%$) of the calibration range.

7.2.4.5.3 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 and a rinse solution are required for this method. A Calibration Blank is used to establish the analytical calibration curve as well as to verify the calibration initially and continually during the analysis, 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.

Exhibit D - Sections 7-8

- 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 shall 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 and waste 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, STORAGE, AND HOLDING TIMES

8.1 Sample Collection and Preservation

- 8.1.1 All aqueous/water, soil/sediment, and waste samples should be collected in glass or polyethylene containers. Aqueous/water samples should be preserved with nitric acid to a pH ≤ 2 immediately after collection. All soil/sediment and waste samples should be iced or refrigerated at $\leq 6^{\circ}\text{C}$, but not frozen, from the time of collection until receipt at the laboratory.
- 8.1.2 The Contractor shall measure the sample pH at the time of sample receipt to verify that the samples were properly preserved. 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. If the pH is > 9 at the time of receipt, the Contractor should consider the possibility that the labels for the metals and cyanide samples were switched in the field. Do not add acid to samples designated for metals analysis and with a pH > 9 unless the pH of the samples designated for cyanide analysis has been checked and is acceptable for cyanide analysis.

8.2 Sample Storage

All aqueous/water samples preserved to pH ≤ 2 may be stored at ambient temperature from the time of sample receipt until digestion. All soil/sediment and waste samples shall be stored at $\leq 6^{\circ}\text{C}$, but not frozen, from the time of sample receipt until digestion. Samples shall be stored in an upright position. 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 portions of aqueous/water, soil/sediment, and waste samples for a period of 60 days after the 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 shall 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 Times

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

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 shall 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 shall be allowed to become stable 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.

Exhibit D - Section 9

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 must 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 must 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 the 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 target 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 $\mu\text{g/L}$) 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. See Equation 15 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.4.5 Technical Acceptance Criteria for Instrument Calibration

- 9.4.5.1 The correlation coefficient of the calibration curve must be greater than or equal to 0.995.
- 9.4.5.2 The Percent Difference (%D) for each of the non-blank standards must be within the control limits of $\pm 30\%$.
- 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. No standard analyzed for a particular analyte with a concentration greater than or equal to the CRQL shall be excluded from the calibration curve.

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.

Exhibit D - Section 9

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 Equation 16 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

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 1, 2, and 3 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.5.5 Technical Acceptance Criteria for Initial Calibration Verification

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

9.5.5.2 The %RSD of the ICV integrations must 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 any CCV after the analysis of the initial CCV following the ICB.

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 ($\pm 30\%$ of mid-range) 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 down 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 Equation 16 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.
 - 9.6.4.2 The %RSD from all replicate integrations shall be calculated for each mass used to report final results using Equations 1, 2, and 3 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.
- 9.6.5 Technical Acceptance Criteria for Continuing Calibration Verification
 - 9.6.5.1 The CCV %R must be within the control limits of 90-110%.
 - 9.6.5.2 The %RSD of the CCV integrations must 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.

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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 down 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 4E in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.7.5 Technical Acceptance Criteria for Calibration Blank

The absolute value of each calibration blank result must 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 (based on the EPA Method 200.8)

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 - ICP-MS, Section 8.1.2), 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 ($\pm 3^\circ\text{C}$), when covered. The beaker should be covered with a ribbed 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 ($\pm 3^\circ\text{C}$). **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-H₂O 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 Analytical Methods, Section 7.0.

10.2 Soil/Sediment and Waste Sample Preparation

Preparation Method 200.8 (based on the EPA Method 200.8)

- 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). The Contractor shall not add or remove sample material once the mass range (e.g., 1.00 - 1.50 g) is achieved to ensure that the aliquot amount is representative of the sample.
- 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 ($\pm 3^\circ\text{C}$) 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 shall 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.

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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 Analytical Methods, Section 7.0.

10.3 Sample Analysis

- 10.3.1 It is highly recommended that a semi-quantitative analysis be conducted 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 shall 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 Analytical Methods, Section 7.0. If possible, the sample digestate should first be analyzed for the trace elements determined by screening, 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 shall be monitored during the analytical sequence. At a minimum, those masses identified in Exhibit D - ICP-MS, Table 3, shall 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##
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 Exhibit D - ICP-MS, Table 4. 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 Target Analyte Concentrations

Calculate the target analyte concentrations using Equation 4E or 5H in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

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11.5 Contract Required Quantitation Limit Calculations

Calculate the adjusted CRQLs using Equation 6E or 7H in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

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/water Preparation Blanks using Equation 4E in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations. Calculate the results for soil/sediment and waste Preparation Blanks by using Equation 5H in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.1.5 Technical Acceptance Criteria for Preparation Blank Sample

12.1.5.1 The absolute value of the Preparation Blank result must 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 any of 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 ICS to verify elemental and polyatomic corrections.

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. The Contractor shall also analyze the ICS every 12 hours during an analytical sequence. 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 Prior to the analysis of samples, the ICS solutions (Section 7.2.4.4) shall be analyzed.

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 4E in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.2.4.2 The %R of the ICSA and ICSAB shall be calculated using Equation 16 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.2.5 Technical Acceptance Criteria for Interference Check Sample

12.2.5.1 The ICSA and ICSAB %R must be within the control limits of $\pm 15\%$ of the analyte's true value or the results must 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 $\mu\text{g/L}$, ICSA true value = 43 $\mu\text{g/L}$), the correct control window to use would be the greater of $\pm 15\%$ of the true value ($0.15 \times 43 \mu\text{g/L} = \pm 6.5 \mu\text{g/L}$) or ± 2 times the CRQL ($\pm 4 \mu\text{g/L}$). Therefore, the control window for the found value for chromium in the ICSA is 43 ± 6.5 , or 36.5 to 49.5 $\mu\text{g/L}$.

12.2.5.2 Only if the ICS solutions are not available from the EPA, the %R of the prepared independent Check Sample results must be within the control limits of $\pm 15\%$ of the established mean value or the results must be within ± 2 times the analyte's CRQL of the established mean value, whichever is greater.

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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, waste) 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 Exhibit D - ICP-MS, Table 5, 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 original unspiked concentration or two times the CRQL, whichever is greater.

12.3.3.4 Samples identified as field blanks or 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 selected 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 Equation 23 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

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 %R must 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 for an analyte is not at or within the limits of 75-125%, the data for that analyte in all the samples received and associated with that spike sample shall be flagged with an "*". An exception to this rule is granted when the sample concentration exceeds the Spike Added (SA) concentration by a factor of four or more. In such an instance, 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 analysis 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, and one Matrix Spike sample recovery for an analyte is not within contract criteria, flag the data for that analyte in 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, waste) or for each SDG, whichever is more frequent.² Duplicate sample analyses cannot be averaged for reporting.

12.4.3 Procedure for Duplicate Sample

12.4.3.1 Samples identified as field blanks or 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

The Relative Percent Difference (RPD) for each analyte shall be calculated using Equation 24B in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.4.5 Technical Acceptance Criteria for Duplicate Sample

12.4.5.1 The RPD must 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 - Target Analyte List and Contract Required Quantitation Limits, Table 5).

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

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12.4.5.2 The control limit must 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 for an analyte are outside the control limits, flag the data for that analyte in all the 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 one duplicate analyte result is not within contract criteria, flag the data for that analyte in all the 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 waste 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, soil/sediment, or waste samples in an SDG.

12.5.3 Procedure for Laboratory Control Sample

The LCS for aqueous/water, soil/sediment, and waste samples shall be prepared by spiking an aliquot of reagent water (50-100 mL for aqueous/water; 1 mL for soil/sediment and waste) 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

12.5.4.1 Calculate the results for the LCS using Equation 4E or 5H in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations as appropriate.

12.5.4.2 Calculate the %R for the LCS using Equation 26B in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.5.5 Technical Acceptance Criteria for Laboratory Control Sample

The LCS %R must 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, soil/sediment, or waste samples is 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, waste) 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 analyte is calculated using Equation 27 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

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) must be within 20% 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 20%, 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 shall be flagged with an "*".

12.6.6.2 In the instance where there is more than one Serial Dilution per SDG, per matrix, and one serial dilution result for an analyte is not within contract criteria, flag that analyte for all the samples of the same matrix in the SDG.

12.6.6.3 If the internal standard responses for the field sample selected for Serial Dilution analysis are not within the limits (identified in Section 12.7.5), 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.

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12.7 Internal Standards

12.7.1 Summary of Internal Standards

Internal standardization shall 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 uncorrected 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 Exhibit D - ICP-MS, Table 6.

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 shall 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 shall be added after the dilution.

12.7.4 Calculation for Internal Standards

Calculate the Percent Relative Intensity (%RI) using the Equation 28 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.7.5 Technical Acceptance Criteria for Internal Standards

The absolute response of any one internal standard, calculated as %RI, must not deviate more than ±30% from the original response in the calibration blank.

12.7.6 Corrective Action for Internal Standards

- 12.7.6.1 If deviations greater/less than 30% for the %RI 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 under the contract, the MDL for each analyte shall be determined for each digestion procedure, and for each instrument under the same conditions used for analysis, used prior to the start of contract analyses and verified annually thereafter. MDL determination is matrix-specific (i.e., the MDL shall be determined for aqueous/water and soil/sediment samples. The MDL determined for soil/sediment samples shall be used for waste samples.). 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 Title 40 of the Code of Federal Regulations (CFR), Part 136, Appendix B, Revision 2.
- 12.8.1.2 The determined concentration of the MDL must be less than half the concentration of the CRQL listed in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 5.
- 12.8.1.3 The delivery requirements for the MDL values are specified in Exhibit B - Reporting and Deliverables Requirements, Table 1.

12.9 Summary of Quality Control Operations

The QC operations performed for ICP-MS analysis are summarized in Exhibit D - ICP-MS, Table 7.

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

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

15.0 WASTE MANAGEMENT

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

Exhibit D - Section 16

16.0 REFERENCES

- 16.1 U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, Method 200.8, Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Mass Spectrometry, Revision 5.4, 1994.
- 16.2 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 6020B, Inductively Coupled Plasma - Mass Spectrometry, Revision 2, July 2014.
- 16.3 U.S. Government Printing Office, Title 40 of the Code of Federal Regulations, Chapter 1, Subchapter D, Part 136, Appendix B, Definition and Procedure for the Determination of the Method Detection Limit, Revision 2.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

TABLE 1. 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	GeCl	SeS, GeS	MoC, ZrC	
⁵² Cr	ArO	C1OH				ArC	
⁵³ Cr	C1O	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 ₂ H	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			WN			WC	
¹⁹⁶ Hg							

Exhibit D - Section 17

TABLE 1. 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		BrH ⁺ , 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 Tl							
²⁰³ Tl		WOH					
⁵¹ V	ClO	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	Cl 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 2. INTERFERENT AND ANALYTE CONCENTRATIONS USED FOR ICP-MS
INTERFERENCE CHECK SAMPLE (ICS)

Analytes	($\mu\text{g/L}$)	Interferents	($\mu\text{g/L}$)
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.

Exhibit D - Section 17

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, 81, 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	81, 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	$(1.0000)(^{75}\text{C}) - (3.127)[(^{77}\text{C}) - (0.815)(^{82}\text{C})]$
Cd	MoO, Pd	$(1.000)(^{111}\text{C}) - (1.073)[(^{108}\text{C}) - (0.712)(^{106}\text{C})]$
V	ClO, Cr	$(1.0000)(^{51}\text{C}) - (3.127)[(^{53}\text{C}) - (0.113)(^{52}\text{C})]$
In	Sn	$(1.0000)(^{115}\text{C}) - (0.0140)(^{118}\text{C})$

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 shall 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. SPIKING LEVELS FOR MATRIX SPIKE SAMPLE ANALYSES

Analyte	Aqueous/Water Spike ($\mu\text{g/L}$)*	Soil/Sediment and Waste 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.

TABLE 6. 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 Li⁶ requires enriched standard.

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, after ICB or CCB 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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1.0 SCOPE AND APPLICATION

This exhibit provides procedures for the use of a cold vapor technique with Atomic Absorption (AA) to determine the concentration of total mercury in aqueous/water, leachate derived from the Toxicity Characteristic Leaching Procedure (TCLP) or Synthetic Precipitation Leaching Procedure (SPLP), soil/sediment, and waste samples collected 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 is 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 EPA Method 7470A)
- 2.2.2 Heated Acid Digestion and Analysis of Soil/Sediment and Waste Samples (based on EPA Method 7471B)

3.0 DEFINITIONS

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

Exhibit D - Sections 4-5

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 shall 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 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, demonstration of equivalent performance that meets 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.

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

6.1 Glassware/Labware

- 6.1.1 Graduated cylinders.
- 6.1.2 Assorted volumetric glassware (Class A) and calibrated pipettes. 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.

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

6.2 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.

Exhibit D - Section 7

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%, ACS Reagent grade or better.
- 7.1.3 Sulfuric acid, 0.5 N - 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 of stannous sulfate to 250 mL of 0.5 N 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 shall provide all standards, except as noted, to be used with the contract. These standards may be used only after they have been certified according to the procedure in Exhibit D - Introduction to Analytical Methods, Section 11.0. The Contractor shall be able to verify that the standards are certified. Manufacturer's certificates of analysis shall be retained by the Contractor and presented upon request.

Samples, sample digestates, and standards shall 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).

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 ($\mu\text{g/mL}$). 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. Prepare calibration standards using this solution. Standards shall be prepared with the 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.

7.2.4.2 If the solution is not available from the EPA, the ICV solution shall be prepared by the Contractor using a certified solution from an independent source, which is defined as a standard from a different source than that used for the instrument calibration. Analyses shall be conducted at a concentration other than that used for instrument calibration, but near the middle (within $\pm 30\%$) of the calibration range.

7.2.4.3 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 and a rinse solution are required for this method. A Calibration Blank is used to establish the analytical calibration curve as well as to verify the calibration initially and continually during the analysis, 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 other calibration standards. The Calibration Blank shall be carried through the complete sample preparation procedure and contain the same acid concentration in the final solution as the sample solution used for analysis (see Section 10.0). 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 shall be carried through the complete sample preparation procedure and contain the same acid concentration in the final solution as the sample solution used for analysis (see Section 10.0). Soil/sediment and waste blanks shall use 0.5-0.6 mL of reagent water.

7.3.3 Rinse Solution - Prepare the rinse solution based on the instrument manufacturer's instruction.

Exhibit D - Section 8

8.0 SAMPLE COLLECTION, PRESERVATION, STORAGE, AND HOLDING TIMES

8.1 Sample Collection and Preservation

- 8.1.1 All aqueous/water, soil/sediment, and waste samples should be collected in glass or polyethylene containers. Aqueous/water samples should be preserved with nitric acid to a pH ≤2 immediately after collection. All soil/sediment and waste samples should be iced or refrigerated at ≤6°C, but not frozen, from the time of collection until receipt at the laboratory.
- 8.1.2 The Contractor shall measure the sample pH at the time of sample receipt to verify that the samples were properly preserved. 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. If the pH is >9 at the time of receipt, the Contractor should consider the possibility that the labels for the metals and cyanide samples were switched in the field. Do not add acid to samples designated for metals analysis and with a pH >9 unless the pH of the samples designated for cyanide analysis has been checked and is acceptable for cyanide analysis.

8.2 Sample Storage

All aqueous/water samples preserved to pH ≤2 may be stored at ambient temperature from the time of sample receipt until digestion. All soil/sediment and waste samples shall be stored at ≤6°C, but not frozen, from the time of sample receipt until digestion. Samples shall be stored in an upright position.

8.2.1 Unused Sample Storage

The Contractor shall retain the unused portion of the aqueous/water, soil/sediment, and waste samples for a period of 60 days after the 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

Digestates 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 Times

The holding time for mercury samples is 26 days from the 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 shall be investigated and established for mercury on that particular instrument. All measurements shall 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 shall be allowed to become stable 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 the 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 Section 7.2.3.1 and digested according to Section 10.0. One of the standards shall be a blank standard (see Section 7.3.1), 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.

Exhibit D - Section 9

- 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. See Equation 15 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.
- 9.3.5 Technical Acceptance Criteria for Instrument Calibration
- 9.3.5.1 The correlation coefficient of the calibration curve must be greater than or equal to 0.995.
- 9.3.5.2 The Percent Difference (%D) for each of the non-blank standards must be within the control limits of $\pm 30\%$.
- 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. No standard analyzed with a concentration greater than or equal to the CRQL shall be excluded from the calibration curve.
- 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 prepared according to Section 7.2.4 and digested in a similar manner as the calibration standards (see Section 10.0). 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 Equation 16 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.4.5 Technical Acceptance Criteria for Initial Calibration Verification

The ICV %R must 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 any CCV after the analysis of the initial CCV following the ICB.

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 ($\pm 30\%$ of midrange) of the calibration curve. The CCV shall be prepared according to Section 7.2.3.1 and digested 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 down to the next CCV as applicable).

9.5.4 Calculations for Continuing Calibration Verification

The %R of the CCV shall be calculated using Equation 16 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

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9.5.5 Technical Acceptance Criteria for Continuing Calibration Verification

9.5.5.1 The CCV %R must 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 shall be prepared according to Section 7.3.1 and digested according to Section 10.0. The ICB and CCB 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 down 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 4G in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.6.5 Technical Acceptance Criteria for Calibration Blank

The absolute value of each calibration blank result must 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/TCLP Leachate/SPLP Leachate 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 - Mercury, Section 8.1.2), 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 To prepare 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 shall be prepared fresh daily.
- 10.1.3 To prepare the calibration blanks (including ICB and CCB) and the Preparation Blank, transfer 100 mL (± 1.0 mL) of reagent water acidified at 0.15% nitric acid to a suitable digestion vessel.
- 10.1.4 To prepare the samples, shake the sample until well-mixed and transfer an aliquot of 100 mL (± 1.0 mL) to a suitable digestion vessel.
- 10.1.5 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.
- 10.1.6 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.
- 10.1.7 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 ($\pm 3^\circ\text{C}$). Allow to cool.
- 10.1.8 Add 6 mL of 12% sodium chloride-hydroxylamine sulfate solution to reduce the excess potassium permanganate.
- 10.1.9 All standards, samples, and blanks must be at the same final volume. Reagent water can be used to make any necessary final volume adjustments.
- 10.1.10 The digestates may stand at room temperature for up to 48 hours prior to analysis. However, it is recommended that they be analyzed as soon as possible. Refer to Section 10.3 for analysis.
- 10.1.11 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.

Exhibit D - Section 10

10.2 Soil/Sediment and Waste Sample Preparation

- 10.2.1 To prepare 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 shall be prepared fresh daily.
- 10.2.2 To prepare the calibration blanks (including ICB and CCB), transfer 10 mL (± 0.1 mL) of reagent water acidified at 0.15% nitric acid to a suitable digestion vessel.
- 10.2.3 To prepare 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. To prepare the Preparation Blank, add 5 mL of reagent water to a suitable digestion vessel.
- 10.2.4 Add 5 mL of aqua regia to each of the digestion vessels and heat for 2 minutes at 95°C ($\pm 3^\circ\text{C}$) in a water bath or block digester. Allow the contents of each digestion vessel to cool.
- 10.2.5 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 ($\pm 3^\circ\text{C}$) in a water bath or block digester. Allow to cool.
- 10.2.6 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.
- 10.2.7 Add 55 mL of reagent water to each sample or 50 mL of reagent water to each standard. All standards, samples, and blanks must be at the same final volume. Reagent water can be used to make any final volume adjustments, if necessary.
- 10.2.8 The digestates may stand at room temperature for up to 48 hours prior to analysis. However, it is recommended that they 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, samples, and blanks 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, samples, and blanks and construct the calibration curve. The calibration curve shall be constructed based on the concentration of mercury (in $\mu\text{g/L}$) 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 Contractor 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 Contractor 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

11.1 Target Analyte Concentration

Calculate the mercury concentration using Equation 4G or 5H in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

11.2 Contract Required Quantitation Limit Calculations

Calculate the adjusted CRQL using Equation 6F or 7I in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

Exhibit D - Section 12

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/water Preparation Blanks by using Equation 4G in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations. Calculate the results for soil/sediment and waste Preparation Blanks using Equation 5H in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.1.5 Technical Acceptance Criteria for Preparation Blank Sample

12.1.5.1 The absolute value of the Preparation Blank result must 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 any of 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, waste) or for each SDG, whichever is more frequent.¹

12.2.3 Procedure for Matrix Spike Sample

12.2.3.1 For a Matrix Spike sample, 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 TCLP/SPLP leachate samples, or at 0.5 milligrams/kilogram (mg/kg) for soil/sediment and waste 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 or 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 selected 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 the %R.

12.2.4.2 Calculate the Matrix Spike %R using Equation 23 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.2.5 Technical Acceptance Criteria for Matrix Spike Sample

The Matrix Spike %R must 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 the samples received and associated with that spike sample shall be flagged with an **. An exception to this rule is granted when the sample concentration exceeds the Spike Added (SA) concentration by a factor of four or more. In such an instance, 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, and 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.

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).

Exhibit D - Section 12

12.3.2 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, waste) or for each SDG, whichever is more frequent.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 or 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

The Relative Percent Difference (RPD) for mercury shall be calculated using Equation 24B in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.3.5 Technical Acceptance Criteria for Duplicate Sample

12.3.5.1 The RPD must 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 - Target Analyte List and Contract Required Quantitation Limits, Table 6).

12.3.5.2 The control limit must 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 the 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 one duplicate result is not within contract criteria, flag all the samples of the same matrix in the SDG.

12.4 Method Detection Limit Determination

12.4.1 Before any field samples are analyzed under the contract, the MDLs shall be determined for each digestion procedure, and for each instrument under the same conditions used for analysis, used prior to the start of contract analyses and verified annually thereafter. MDL determination is matrix-specific (i.e., the MDL shall be determined for aqueous/water and soil/sediment samples. The MDL determined for aqueous/water samples shall be used for TCLP and SPLP leachates. The MDL determined for soil/sediment samples shall be used for waste samples.). 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.

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

- 12.4.1.1 To determine the MDLs, the Contractor shall perform MDL studies following the procedures in Title 40 of the Code of Federal Regulations (CFR), Part 136, Appendix B, Revision 2.
- 12.4.1.2 The determined concentration of the MDL must be less than half the concentration of the CRQL listed in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 6.
- 12.4.1.3 The delivery requirements for the MDL values are specified in Exhibit B - Reporting and Deliverables Requirements, Table 1.

12.5 Summary of Quality Control Operations

The QC operations performed for mercury analysis are summarized in Exhibit D - Mercury, Table 1.

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

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

15.0 WASTE MANAGEMENT

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

16.0 REFERENCES

- 16.1 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste (SW-846), Method 7470A, Mercury in Liquid Waste (Manual Cold-Vapor Technique), Revision 1, September 1994.
- 16.2 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste (SW-846), Method 7471B, Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique), Revision 2, February 2007.
- 16.3 U.S. Government Printing Office, Title 40 of the Code of Federal Regulations, Chapter 1, Subchapter D, Part 136, Appendix B, Definition and Procedure for the Determination of the Method Detection Limit, Revision 2.

Exhibit D - Section 17

17.0 TABLES/DIAGRAMS/FLOWCHARTS

TABLE 1. QC OPERATIONS FOR MERCURY ANALYSIS

QC Operation	Frequency
Instrument Calibration	Daily or each time instrument is set up, after ICV or CCV failure, after ICB or CCB 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.

EXHIBIT D
TOTAL CYANIDE ANALYSIS

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Exhibit D - Total Cyanide Analysis

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1.0 SCOPE AND APPLICATION

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

2.0 SUMMARY OF METHOD

2.1 General Method Overview

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 semi-automated spectrophotometric measurement, the cyanide is converted to cyanogen chloride (CNCl), by reaction with chloramine-T at a pH <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, Soil/Sediment, and Waste Samples (based on EPA Method 335.4 and Standard Method 4500-CN E)

2.2.2 Micro-Distillation of Aqueous/Water, SPLP Leachate, Soil/Sediment, and Waste Samples (based on Lachat QuikChem Method 10-204-00-1-X)

3.0 DEFINITIONS

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

Exhibit D - Sections 4-5

4.0 INTERFERENCES

Several interferences may contribute to inaccuracies in the determination of cyanide in aqueous/water, SPLP leachate, soil/sediment, and waste 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 and treated with sulfamic acid as necessary.

5.0 SAFETY

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

6.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here; however, demonstration of equivalent performance that meets 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.

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

6.1 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).

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

6.2 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 ($\pm 5^{\circ}\text{C}$).

6.2.2 Micro-Distillation Apparatus

6.2.2.1 Heating block - Capable of maintaining 120°C ($\pm 5^{\circ}\text{C}$).

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.

Exhibit D - Section 7

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 Nitrate-Nitrite Test Strips or Test Kits.

7.1.7 Midi-Distillation Reagents

7.1.7.1 Sodium hydroxide solution, 0.25 N - Dissolve 10.0 g of sodium hydroxide in reagent water and dilute to 1 Liter (L).

7.1.7.2 Sodium hydroxide solution, 1.25 N - Dissolve 50.0 g of sodium hydroxide in reagent water and dilute to 1 L.

7.1.7.3 Sulfuric acid, 50% (v/v) - Carefully add a portion of concentrated (95-98%) sulfuric acid to an equal portion of reagent water.

7.1.7.4 Magnesium chloride solution (2.5 M) - Weigh 510 g of $MgCl_2 \cdot 6H_2O$ into a 1000-milliliter (mL) flask, dissolve, and dilute to 1 L with reagent water.

7.1.7.5 Sulfamic acid (Powdered).

7.1.8 Micro-Distillation Reagents

7.1.8.1 Sodium hydroxide solution, 0.25 N - Dissolve 10.0 g of sodium hydroxide in reagent water and dilute to 1 L.

7.1.8.2 Sodium hydroxide solution, 1.25 N - Dissolve 50.0 g of sodium hydroxide in reagent water and dilute to 1 L.

7.1.8.3 Sulfuric acid/Magnesium chloride solution (7.11 M sulfuric acid/0.79 M magnesium chloride) - In a fume hood, weigh 32.2 g of $MgCl_2 \cdot 6H_2O$ into a tared 500-mL beaker and add 110.8 g reagent water. Add 139 g of concentrated (95-98%) sulfuric acid in 40 g portions with stirring. Allow the solution to cool.

7.1.8.4 Sulfamic acid (Powdered).

7.1.9 Analytical Reagents

7.1.9.1 Chloramine-T solution (0.014 M) - Dissolve 0.40 g of chloramine-T in reagent water and dilute to 100 mL. Prepare fresh daily.

7.1.9.2 Sodium dihydrogen phosphate buffer - Dissolve 138 g of $NaH_2PO_4 \cdot H_2O$ in 1 L of reagent water.

7.1.9.3 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 ($\pm 2^\circ C$).

7.2 Standards

7.2.1 Introduction

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

Samples, sample distillates, and standards shall 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 of potassium hydroxide in reagent water and dilute to 1 L. Standardize with 0.0192 N 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 1.25 N sodium hydroxide solution to 100 mL with reagent water. Prepare this solution at the 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 0.25 N sodium hydroxide. The final concentration of sodium hydroxide in all standards should be 0.25 N. Prepare the calibration standards using this solution.

7.2.4 Initial Calibration Verification Solution

- 7.2.4.1 The Initial Calibration Verification (ICV) solution shall be obtained from the EPA.
- 7.2.4.2 If the solution is not available from the EPA, the ICV solution shall be prepared by the Contractor using a certified solution from an independent source, which is defined as a standard from a different source than that used for the instrument calibration. Analyses shall be conducted at a concentration other than that used for instrument calibration, but near the middle (within $\pm 30\%$) of the calibration range.
- 7.2.4.3 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 as well as to verify the calibration initially and continually during the analysis, and the Preparation Blank (see Section 12.1) is used to assess possible contamination from the sample preparation procedure and to assess spectral background.

Exhibit D - Sections 7-8

- 7.3.1 Calibration Blank - Must contain all the reagents in the same volumes as used in preparing the other calibration standards. The Calibration Blank shall be carried through the complete sample preparation 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 shall be carried through the complete sample preparation procedure and contain the same reagent concentration in the final solution as the sample solution used for analysis. Soil/sediment and waste blanks shall use 1.00 mL (± 0.01 mL) of reagent water.

8.0 SAMPLE COLLECTION, PRESERVATION, STORAGE, AND HOLDING TIMES

8.1 Sample Collection and Preservation

- 8.1.1 All aqueous/water, soil/sediment, and waste samples should be collected in polyethylene or glass containers. The aqueous/water samples should be preserved with sodium hydroxide to a pH ≥ 10 . All samples must be maintained at $\leq 6^{\circ}\text{C}$, but not frozen, from the time of collection until receipt at the laboratory.
- 8.1.2 The Contractor shall measure the sample pH at the time of sample receipt to verify that the samples were properly preserved. 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.

8.2 Sample Storage

All aqueous/water, soil/sediment, and waste samples shall be protected from light and refrigerated at $\leq 6^{\circ}\text{C}$, but not frozen, from the time of receipt until distillation. Samples shall be stored in an upright position.

8.2.1 Unused Sample Storage

The Contractor shall retain the unused portion of the aqueous/water, soil/sediment, and waste samples for a period of 60 days after the delivery of a complete, reconciled data package to the EPA. The unused portion shall be protected from light and refrigerated at $\leq 6^{\circ}\text{C}$ 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 Times

The holding time for cyanide samples is 12 days from the 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 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 shall be investigated and established for cyanide on that particular instrument. All measurements shall 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. The instrument shall be allowed to become stable 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 the 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 Section 7.2 and distilled according to Section 10.2. One of the standards shall be a blank standard (see Section 7.3.1), 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.

Exhibit D - Section 9

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 ($\mu\text{g}/\text{L}$)] 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. See Equation 15 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.3.5 Technical Acceptance Criteria for Instrument Calibration

- 9.3.5.1 The correlation coefficient of the calibration curve must be greater than or equal to 0.995.
- 9.3.5.2 The Percent Difference (%D) for each of the non-blank standards must be within the control limits of $\pm 30\%$.
- 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. No standard analyzed with a concentration greater than or equal to the CRQL shall be excluded from the calibration curve.

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 be prepared according to Section 7.2.4 and distilled in the same manner as the calibrations standards (see Section 10.2). 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 Equation 16 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.4.5 Technical Acceptance Criteria for Initial Calibration Verification

The ICV %R must 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 any CCV after the analysis of the initial CCV following the ICB.

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 matrix as the calibration standards at or near to the mid-level ($\pm 30\%$ of midrange) of the calibration curve. The CCV shall be prepared according to Section 7.2 and distilled according to Section 10.2.

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 down to the next CCV as applicable).

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9.5.4 Calculations for Continuing Calibration Verification

The %R of the CCV shall be calculated using Equation 16 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.5.5 Technical Acceptance Criteria for Continuing Calibration Verification

9.5.5.1 The CCV %R must 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 shall be prepared according to Section 7.3.1 and distilled according to Section 10.2. The ICB and CCB 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 down 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 4E in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.6.5 Technical Acceptance Criteria for Calibration Blank

The absolute value of each calibration blank result must 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 - Cyanide, Section 8.1.2).
- 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 on 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, indicating the presence of sulfides, the Contractor shall contact 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, indicating the presence of oxidizing agents, the Contractor shall contact SMO for further instructions from the EPA Region before proceeding with sample preparation and analysis.

10.2 Standards and Calibration Blanks Preparation

All standards and calibration blanks 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 0.25 N sodium hydroxide. Add 50 mL of each standard to a midi-distillation flask and then prepare and distill these standards and the calibration blank in the same manner as the samples.

The calibration blanks (including ICB and CCB) shall be prepared by adding 50 mL (± 1.0 mL) of the 0.25 N sodium hydroxide solution (see Section 7.1.7.1) to a midi-distillation flask, and distilled in the same manner as the samples.

Exhibit D - Section 10

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 0.25 N 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.

The calibration blanks (including ICB and CCB) shall be prepared by adding 6 mL (± 0.1 mL) of the 0.25 N sodium hydroxide solution (see Section 7.1.7.1) to a sample tube, and distilled in the same manner as the samples.

10.3 Aqueous/Water/SPLP Leachate Sample Preparation

10.3.1 Preparation Method by Midi-Distillation (based on EPA Method 335.4)

10.3.1.1 Pipet 50 mL (± 1.0 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. To prepare the Preparation Blank, add 50 mL (± 1.0 mL) of the 0.25 N sodium hydroxide solution (see Section 7.1.7.1) to the midi-distillation flask.

10.3.1.2 Add 50 mL (± 1.0 mL) of 0.25 N 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 0.5 N 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 the sample for nitrate and/or nitrite using an appropriate test strip or kit. 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. 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 2.5 M 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 reduced by the addition of either another 2 mL of the 2.5 M 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.

10.3.1.8 Turn on the heating block and set for 125°C ($\pm 3^\circ\text{C}$). 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 ($\pm 3^\circ\text{C}$).
- 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. To prepare the Preparation Blank, add 6 mL (± 0.1 mL) of the 0.25 N sodium hydroxide solution (see Section 7.1.7.1) to the sample tube. If the Contractor is not using the prefilled collector tubes, add 2 mL (± 0.1 mL) of the 0.25 N absorbing solution to each collector tube.
- 10.3.2.3 Test the sample for nitrate and/or nitrite using an appropriate test strip or kit. Record method, manufacturer information, and results on the Distillation Log and in the SDG Narrative. If the samples contain nitrate and/or nitrite, add 120 μL of 20% sulfamic acid directly to the 6 mL of sample in the distillation tube. Mix for 3 minutes prior to adding the sulfuric acid/magnesium chloride solution.
- 10.3.2.4 Add 0.75 mL of the sulfuric acid/magnesium chloride solution (7.11 M/0.79 M) to each sample tube and immediately cap with a collector tube and press to seal.
- 10.3.2.5 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.
- 10.3.2.6 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 and Waste Sample Preparation

- 10.4.1 Preparation Method by Midi-Distillation (based on EPA Method 335.4)
- 10.4.1.1 Mix the sample thoroughly to achieve homogeneity. Weigh to the nearest 0.01 g, 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). To prepare the Preparation Blank, add 50 mL of reagent water to the reaction vessel.
- 10.4.1.2 Add 50 mL (± 1 mL) of 0.25 N 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 0.5 N 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.

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- 10.4.1.6 Add 2 mL of the 2.5 M 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 reduced by the addition of either another 2 mL of the 2.5 M 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 ($\pm 3^\circ\text{C}$). 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 ($\pm 3^\circ\text{C}$).
 - 10.4.2.2 Mix the sample thoroughly to achieve homogeneity. Add 0.50-1.00 g (± 0.01 g) of sample (wet weight) and 5 mL of reagent water to the sample tube. To prepare the Preparation Blank, add 6 mL (± 0.1 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 0.25 N absorbing solution to the collector tube. Add 0.75 mL of the sulfuric acid/magnesium chloride solution (7.11 M/0.79 M) 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 standards, samples, and blanks in the sampler tray in the appropriate sequence. See example sequence provided in Section 10.5.6.
- 10.5.3 Allow all distillates 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

11.1 Target Analyte Concentration

Calculate the cyanide concentration using Equation 4E or 5H in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

11.2 Contract Required Quantitation Limit Calculations

Calculate the adjusted CRQL using Equation 6E or 7I in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

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/water Preparation Blanks using Equation 4E in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations. Calculate the results for soil/sediment and waste Preparation Blanks by using Equation 5H in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

Exhibit D - Section 12

12.1.5 Technical Acceptance Criteria for Preparation Blank Sample

- 12.1.5.1 The absolute value of the Preparation Blank result must 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 any of 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, waste) 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.

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 or SPLP leachate sample, this would be equivalent to a concentration of 100 µg/L in the original sample. For a typical 1.00 g soil/sediment or waste sample, this would be equivalent to a concentration of 5 mg/kg in the original dry sample. Adjustments

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).

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 original unspiked concentration or two times the CRQL, whichever is greater.
- 12.2.3.4 Samples identified as field blanks or 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 and Post-Distillation Spike Samples
- 12.2.4.1 If the Matrix Spike analysis is performed on the same sample that is selected 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 the %R.
- 12.2.4.2 Calculate the Matrix Spike and Post-Distillation Spike %R using Equation 23 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.
- 12.2.5 Technical Acceptance Criteria for Matrix Spike and Post-Distillation Spike Samples
- The Matrix Spike %R must be within the control limits of 75-125%.
- 12.2.6 Corrective Action for Matrix Spike and Post-Distillation Spike Samples
- 12.2.6.1 If the Matrix Spike recovery is not within the control limits of 75-125%, the data for all the samples received and associated with that spike sample shall be flagged with an **. An exception to this rule is granted when the sample concentration exceeds the Spike Added (SA) concentration by a factor of four or more. In such an instance, 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 analysis 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, and 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.

Exhibit D - Section 12

12.3.2 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, waste) or for each SDG, whichever is more frequent.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 or 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

The Relative Percent Difference (RPD) for cyanide shall be calculated using Equation 24B in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.3.5 Technical Acceptance Criteria for Duplicate Sample

12.3.5.1 The RPD must 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 - Target Analyte List and Contract Required Quantitation Limits, Table 7).

12.3.5.2 The control limit must 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 the 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 one duplicate result is not within contract criteria, flag all the samples of the same matrix in the SDG.

12.4 Method Detection Limit Determination

12.4.1 Before any field samples are analyzed under the contract, the MDLs shall be determined for each distillation procedure, and for each instrument under the same conditions used for analysis, used prior to the start of contract analyses and verified annually thereafter. MDL determination is matrix-specific (i.e., the MDL shall be determined for aqueous/water and soil/sediment samples. The MDL determined for aqueous/water samples shall be used for SPLP leachates. The MDL determined for soil/sediment samples shall be used for waste samples.). 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.

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

- 12.4.1.1 To determine the MDLs, the Contractor shall perform MDL studies following the procedures in Title 40 of the Code of Federal Regulations (CFR), Part 136, Appendix B, Revision 2.
- 12.4.1.2 The determined concentration of the MDL must be less than half the concentration of the CRQL listed in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 7.
- 12.4.1.3 The delivery requirements for the MDL values are specified in Exhibit B - Reporting and Deliverables Requirements, Table 1.

12.5 Summary of Quality Control Operations

The QC operations performed for cyanide analysis are summarized in Exhibit D - Cyanide, Table 1.

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

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

15.0 WASTE MANAGEMENT

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

16.0 REFERENCES

- 16.1 American Water Works Association/American Public Health Association/Water Environment Federation, Standard Methods for the Examination of Water and Wastewater, Method 4500-CN E, Colorimetric Method.
- 16.2 Lachat QuikChem Method 10-204-00-1-X, Digestion and Distillation of Total Cyanide in Drinking and Wastewaters using MICRO DIST and Determination of Cyanide by Flow Injection Analysis.
- 16.3 U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, Method 335.4, Determination of Total Cyanide by Semi-Automated Colorimetry, Revision 1.0, August 1993.
- 16.4 U.S. Government Printing Office, Title 40 of the Code of Federal Regulations, Chapter 1, Subchapter D, Part 136, Appendix B, Definition and Procedure for the Determination of the Method Detection Limit, Revision 2.

Exhibit D - Section 17

17.0 TABLES/DIAGRAMS/FLOWCHARTS

TABLE 1. QC OPERATIONS FOR CYANIDE ANALYSIS

QC Operation	Frequency
Instrument Calibration	Daily or each time instrument is set up, after ICV or CCV failure, after ICB or CCB 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.

EXHIBIT D
ANIONS BY ION CHROMATOGRAPHY

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Exhibit D - Anions by Ion Chromatography

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1.0 SCOPE AND APPLICATION

This exhibit provides procedures for the use of ion chromatography to determine the concentration of Chloride (Cl^-), Fluoride (F^-), Bromide (Br^-), Nitrate (NO_3^-), Nitrite (NO_2^-), Orthophosphate (PO_4^{3-}), and Sulfate (SO_4^{2-}) in aqueous/water samples and extracts of soil/sediment samples collected from hazardous waste sites.

2.0 SUMMARY OF METHOD

2.1 General Method Overview

This method describes the determination of multiple anions by ion chromatography. A small volume of sample or extract is injected onto an ion chromatograph via a constant volume sample loop. The anions of interest are separated and measured using a system that comprises: a guard column; an analytical column packed with an anion exchange resin; a suppressor device to reduce background conductivity and convert the anions to the more conductive acid form; and a conductivity detector. Anion identification is based on comparison of the analyte signal peak retention times in the samples relative to known standards. Quantitation is achieved by comparing the measurement of the peak area in the samples to calibration standards.

3.0 DEFINITIONS

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

4.0 INTERFERENCES

Several interferences may contribute to inaccuracies in the determination of anions in aqueous/water and soil/sediment samples by ion chromatography. Interferences can be divided into three different categories: (1) direct chromatographic coelution, where an analyte response is observed at very nearly the same retention time as the target anion; (2) concentration dependent coelution, which is observed when the response of higher than typical concentrations of the neighboring peak overlap into the retention window of the target anion; and (3) ionic character displacement, where retention times may significantly shift due to the influence of high ionic strength matrices (high mineral content or hardness) overloading the exchange sites on the column and significantly shortening target analyte's retention times. Some specific interferences that are commonly encountered are further discussed in Sections 4.1 through 4.4.

4.1 Direct Chromatographic Coelution

- 4.1.1 Direct chromatographic coelution may be solved by changing columns, eluent strength, modifying the eluent with organic solvents (if compatible with IC columns), changing the detection systems, or selective removal of the interference with pretreatment. Sample dilution will have little to no effect.
- 4.1.2 Sample dilution may resolve some of the difficulties if the interference is the result of either concentration dependent coelution or ionic character displacement, so long as the specified Contract Required Quantitation Limits (CRQLs) can be met after dilution.

Exhibit D - Sections 4-6

4.2 Reagents and Equipment

Method interferences may be caused by contaminants in the reagent water, reagents, glassware, sample handling apparatus, and in the ion chromatographic system that may lead to discrete artifacts or elevated baselines. These interferences can lead to false positive results for the target analytes.

4.3 Organic Acids

Formate, acetate, and other monovalent organic acid anions elute early in the run and can interfere with fluoride, and can shift the retention times of other anions when these are present in large amounts.

4.4 Particulates

Samples and extracts shall be filtered through a 0.45 micrometer (μm) filter prior to injection. It is recommended to filter any eluent reagents through a 0.20 μm filter to remove particulate matter to prevent damage to the columns and flow system.

5.0 SAFETY

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

6.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here; however, demonstration of equivalent performance that meets 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.

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

6.1 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).

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

- 6.1.3 Autosampler Vials - Sized for autosampler (if applicable).
- 6.1.4 Syringes - Plastic, disposable, 10 mL. Equipped with valves with Luer-Lok ends.
- 6.1.5 Syringe Filters - 0.45 µm pore diameter.

6.2 Ion Chromatograph

A system consisting of a pump, an autosampler, a sample injector, and the following components:

- 6.2.1 Precolumn - A guard column placed before the separator column to protect the separator column from particulates or organic constituents.
- 6.2.2 Separator (or analytical) column - A column packed with an anion exchange resin, suitable for resolving the target anions.
- 6.2.3 Conductivity suppressor - An ion exchange-based device that is capable of converting the eluent and separated anions to their respective acid forms. The device may also be used to regenerate the eluent, reducing the volume of eluent prepared and allowing continuous operation of the instrument.
- 6.2.4 Conductivity detector - A flow-through, temperature-compensated, electrical conductivity cell capable of linearly reading from 0 to at least 1000 Siemens/centimeter.
- 6.2.5 Chromatographic data system - Capable of integrating the conductivity detector signal output and storing it as chromatographic data.

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 Eluent - Per column manufacturer's guidance. A bicarbonate/carbonate solution is recommended. For example, 1.7 millimolar (mM) NaHCO₃/1.8 mM Na₂CO₃ - dissolve 0.2856 g NaHCO₃ and 0.3816 g Na₂CO₃ in reagent water and dilute to 2 L with reagent water. It is recommended that this solution be purged with helium prior to use to remove micro-bubbles.
- 7.1.3 Conductivity suppressor regenerant solution - Per manufacturer's guidance. A sulfuric acid regenerant may be used. For example, 25 mM sulfuric acid - add 2.8 mL of concentrated sulfuric acid to 4 L of reagent water.

7.2 Standards

7.2.1 Introduction

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

Samples, extracts, and standards shall be stored separately.

Exhibit D - Section 7

7.2.2 Stock Standard Solutions

Stock standard solutions may be purchased as certified solutions or prepared from ACS reagent grade salts as listed below. Salts shall be dried to constant weight and stored in a desiccator prior to weighing. Bromide and chloride salts shall be dried at 150°C. Fluoride, nitrate, orthophosphate, and sulfate salts shall be dried at 105°C. Nitrite salts shall be dried at room temperature in a desiccator containing concentrated H₂SO₄.

- 7.2.2.1 Bromide stock solution, 1000 milligrams/Liter (mg/L) Br⁻ - Dissolve 1.2877 g of dried sodium bromide (NaBr) in reagent water and dilute to 1 L.
- 7.2.2.2 Chloride stock solution, 1000 mg/L Cl⁻ - Dissolve 1.6484 g of dried sodium chloride (NaCl) in reagent water and dilute to 1 L.
- 7.2.2.3 Fluoride stock solution, 1000 mg/L F⁻ - Dissolve 2.2100 g of dried sodium fluoride (NaF) in reagent water and dilute to 1 L.
- 7.2.2.4 Nitrate stock solution, 1000 mg/L NO₃⁻ - Dissolve 1.3707 g of dried sodium nitrate (NaNO₃) in reagent water and dilute to 1 L.
- 7.2.2.5 Nitrite stock solution, 1000 mg/L NO₂⁻ - Dissolve 1.4998 g of dried sodium nitrite (NaNO₂) in reagent water and dilute to 1 L. Store in a sterilized bottle and refrigerate.
- 7.2.2.6 Orthophosphate stock solution, 1000 mg/L PO₄³⁻ - Dissolve 1.4330 g of dried potassium dihydrogen phosphate (KH₂PO₄) in reagent water and dilute to 1 L.
- 7.2.2.7 Sulfate stock solution, 1000 mg/L SO₄²⁻ - Dissolve 1.8141 g of dried potassium sulfate (K₂SO₄) in reagent water and dilute to 1 L.

NOTE: Stock standards for most anions are stable for at least 1 month when stored at ≤6°C, but not frozen. Dilute working standards shall be prepared fresh daily when analyzing for nitrate, nitrite, or orthophosphate.

7.2.3 Calibration Standard Solutions

Prepare a blank and at least five combination anion calibration standards containing the target analytes. The concentrations in the standards shall be sufficient to produce good measurement precision and to accurately define the slope of the calibration curve. Prepare calibration standards daily or as required.

7.2.4 Initial Calibration Verification Solution

- 7.2.4.1 The Initial Calibration Verification (ICV) solution may be obtained from the EPA, or it shall be a mixed standard prepared by the Contractor using a certified solution for each analyte from an independent source, which is defined as a standard from a different source than that used for the instrument calibration. Analyses shall be conducted at a concentration other than that used for instrument calibration, but near the middle (within ±30%) of the calibration range.
- 7.2.4.2 The ICV standard shall be prepared in the same matrix as the calibration standards and in accordance with the instructions provided by the supplier(s).

7.3 Blanks

Two types of blanks are required for this method. A Calibration Blank is used to establish the analytical calibration curve as well as to verify the calibration initially and continually during the analysis, and a Preparation Blank (see Section 12.1) is used to assess possible contamination from any sample preparation procedure.

- 7.3.1 Calibration Blank - Must contain all the reagents in the same volumes as used in preparing the other calibration standards. 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 and baseline drift.
- 7.3.2 Preparation Blank - Must contain all the reagents in the same volumes as used in preparing the samples. The Preparation Blank shall be carried through the complete procedure and contain the same reagent concentration in the final solution as the sample solution used for analysis. For soil extractions, add a mass of reagent water equal to the mass of the soils being extracted to the Preparation Blank before extraction.

8.0 SAMPLE COLLECTION, PRESERVATION, STORAGE, AND HOLDING TIMES

8.1 Sample Collection and Preservation

All aqueous/water and soil/sediment samples should be collected in polytetrafluoroethylene (PTFE), polyethylene or glass containers. Samples for fluoride should be collected in PTFE or polyethylene containers. All aqueous/water and soil/sediment samples should be iced or refrigerated at $\leq 6^{\circ}\text{C}$, but not frozen, from the time of collection until receipt at the laboratory.

8.2 Sample Storage

All aqueous/water and soil/sediment samples shall be protected from light and stored at $\leq 6^{\circ}\text{C}$, but not frozen, from the time of receipt until analysis or extraction. Samples for orthophosphate analysis shall not be held at room temperature for more than 12 cumulative hours. Samples shall be stored in an upright position.

8.2.1 Unused Sample Storage

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

8.2.2 Extract Sample Storage

Soil/sediment extracts shall not be retained. Any reanalyses of the sample shall be performed using a freshly extracted 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 Times

- 8.3.1 The holding time for nitrate, nitrite, and orthophosphate samples is 24 hours from the Validated Time of Sample Receipt (VTSR).

Exhibit D - Sections 8-9

8.3.2 The holding time for bromide, chloride, fluoride, and sulfate samples is 26 days from the 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. Target anion elution order and approximate retention times shall be determined by analysis of appropriate standards on the instrument and column used for analysis to allow the identification of the target anions. The Method Detection Limit (MDL) and precision shall be investigated and established for each anion on that particular instrument. All measurements shall 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 shall be allowed to become stable 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 the sensitivity and linearity of the response.

9.3.2 Frequency of Instrument Calibration

The instrument shall be calibrated at least weekly. If an analytical sequence ends and a new analytical sequence starts later within a week of the calibration, an ICV, ICB, Continuing Calibration Verification (CCV), and CCB are again required prior to sample analysis. The instrument shall be immediately recalibrated after ICV, ICB, CCV, or Laboratory Control Sample (LCS) 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 five calibration standards shall be used. The calibration standards shall be prepared according to Section 7.2.3. One of the standards shall be a blank standard (see Section 7.3.1) and one shall be at or below the CRQL, but greater than the MDL. The rest of the standards shall be uniformly spread over the appropriate calibration range.

- 9.3.3.3 For instruments subject to the "water dip" caused by water in the sample rapidly passing through the columns potentially interfering with early eluting fluoride or chloride, the analyst may add concentrated eluent to each calibration standard to make the solution equivalent to the eluent concentration. The Contractor shall document the amount and concentration of eluent added to each calibration standard in the SDG Narrative.
- 9.3.3.4 Calibration standards shall be prepared fresh with each calibration performed.
- 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 mg/L) on the X-axis versus the instrument peak area response on the Y-axis. It is the analyst's responsibility to review all chromatograms to ensure accurate baseline integration of target analytes.
- 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. See Equation 15 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.
- 9.3.5 Technical Acceptance Criteria for Instrument Calibration
- 9.3.5.1 The correlation coefficient of the calibration curve must be greater than or equal to 0.995.
- 9.3.5.2 The Percent Difference (%D) for each of the non-blank standards must be within the control limits of $\pm 30\%$.
- 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 at or below the CRQL and all standards included in the calibration curve are continuous and consecutive. No standard analyzed for a particular analyte with a concentration greater than or equal to the CRQL shall be excluded from the calibration curve.
- 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.

Exhibit D - Section 9

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 settings 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 Equation 16 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.4.5 Technical Acceptance Criteria for Initial Calibration Verification

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

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), 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 any CCV after the analysis of the initial CCV following the ICB.

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 10 samples during an analytical sequence. See the example analytical sequence in Section 10.2.6.

9.5.2.2 The analytical sequence can continue for up to a week as long as samples are being continuously analyzed and successive CCV standards meet the technical acceptance criteria in Section 9.5.5. If an analytical sequence ends and a new analytical sequence starts later within a week of the calibration, an ICV, ICB, CCV, and CCB are again required prior to sample analysis.

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 matrix as the calibration standards by combining the analytes at a concentration at or near the mid-level ($\pm 30\%$ of mid-range) 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 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 down to the next CCV as applicable).

9.5.4 Calculations for Continuing Calibration Verification

The %R of the CCV shall be calculated using Equation 16 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.5.5 Technical Acceptance Criteria for Continuing Calibration Verification

- 9.5.5.1 The CCV %R must be within the control limits of 90-110%.
- 9.5.5.2 Up to 10 samples may be analyzed between 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), 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 analyte(s) 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 analyzed shall reflect the conditions of analysis of the associated analytical samples.
- 9.6.3.2 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 down to the next CCB as applicable).

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9.6.4 Calculations for Calibration Blank

The results for the ICB and CCB samples shall be calculated using Equation 4H in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.6.5 Technical Acceptance Criteria for Calibration Blank

The absolute value of each calibration blank result must 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 analyte(s) affected.

10.0 PROCEDURE

10.1 Sample Preparation

For instruments subject to the "water dip" caused by the water in the sample rapidly passing through the columns potentially interfering with early eluting fluoride or chloride, the analyst may add concentrated eluent to each sample or extract to make the solution equivalent to the eluent concentration. The Contractor shall document the amount and concentration of eluent added to each sample in the SDG Narrative.

10.1.1 Aqueous Sample Preparation

Allow the samples to reach room temperature. Filter each sample through a 0.45 µm filter prior to injection onto the sample loop. The use of a syringe filter is acceptable.

10.1.2 Soil/Sediment Sample Preparation

Extract the soil/sediment samples by adding an aliquot of the sample to a beaker or flat-bottomed flask. Add an amount of reagent water equal to 10 times the weight of the sample. Mix the slurry for 10 minutes using a magnetic stirring device. Filter the slurry through a 0.45 µm filter.

10.2 Sample Analysis

10.2.1 Establish ion chromatograph operating parameters exactly equivalent to those used for calibration. Establish a stable baseline.

10.2.2 Place the calibration standards, samples, and blanks in the sampler tray in the appropriate sequence. See example sequence provided in Section 10.2.6.

10.2.3 Allow all standards, samples, and blanks to come to ambient room temperature prior to analysis.

10.2.4 Complete the analysis of all the standards, samples, and blanks and construct a calibration curve for each anion. The calibration curve shall be constructed based on the concentration of the anion (in mg/L) in the standards.

- 10.2.5 Samples having concentrations higher than the established calibration range for any anion(s) as determined by the expected concentration of the highest calibration standard shall be diluted into range with reagent water (or with reagent water and eluent if eluent was added to samples and standards) according to procedure in Exhibit D - Introduction to Analytical Methods, Section 7.0 and reanalyzed for the affected anion(s). The Contractor shall then promptly analyze the diluted sample.
- 10.2.6 Example Analytical Sequence for Anions Including the Instrument Calibration:

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

11.0 DATA ANALYSIS AND CALCULATIONS

11.1 Target Analyte Concentrations

Calculate the target analyte concentration using Equation 4H or 5J in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

11.2 Contract Required Quantitation Limit Calculation

Calculate the adjusted CRQLs using Equation 6G or 7J in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

11.3 Data Processing Procedure

Target analytes identified shall be quantitated using the peak area response. It is expected that situations will arise where the automated quantitation procedures in the ion chromatography software provide inappropriate quantitation. This can occur when there is compound coelution, baseline noise, or matrix interferences. In these circumstances, the Contractor shall perform a manual quantitation by integrating the area of the peak of the target analyte. This integration shall only include the area attributable to the specific target analyte. The area integrated shall not include baseline background noise. The area integrated shall also not extend past the point where the sides of the peak intersect with the baseline noise. Manual integration is not to be used solely to meet QC criteria, nor is it to be used as a substitute for corrective action on the chromatographic system. Any instances of manual integration shall be documented in the SDG Narrative.

Exhibit D - Sections 11-12

In all circumstances where the data system has been edited, or where manual integration or quantitation has been performed, the ion chromatograph instrument operator shall identify such procedures by initialing and dating the changes made to the report, and shall include the integration scan range.

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 concentrations as the samples.

12.1.4 Calculations for Preparation Blank Sample

Calculate the results for aqueous/water Preparation Blanks using Equation 4H in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations. Calculate the results for soil/sediment Preparation Blanks using Equation 5J in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.1.5 Technical Acceptance Criteria for Preparation Blank Sample

12.1.5.1 The absolute value of the Preparation Blank result for each analyte must be less than or equal to the CRQL for that analyte.

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

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

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 for that analyte, and the concentration of that 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 for that analyte, and the concentration in any of the associated samples is less than 10 times the CRQL for that analyte, 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 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 For a Matrix Spike sample, the spike is added prior to the addition of other reagents and filtration.
- 12.2.3.2 The analyte spike shall be added to achieve the concentration in Exhibit D - Anions by Ion Chromatography, Table 2, in the final sample solution prepared for analysis.
- 12.2.3.3 Samples identified as field blanks or 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 selected 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 the %R.
- 12.2.4.2 Calculate the Matrix Spike %R using Equation 23 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.2.5 Technical Acceptance Criteria for Matrix Spike Sample

The Matrix Spike %R must be within the control limits of 80-120%.

12.2.6 Corrective Action for Matrix Spike Sample

- 12.2.6.1 If the Matrix Spike recovery for an analyte is not within the control limits of 80-120%, the data for that analyte in all the 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 Spike Added (SA) concentration by a factor of four or more. In such an instance, the data shall be reported unflagged even if the %R does not meet the 80-120% recovery criteria.
- 12.2.6.2 If there is more than one Matrix Spike per matrix, per SDG, and one Matrix Spike sample recovery for an analyte is not within contract criteria, then flag the data for that analyte in all the samples of the same matrix and method in the SDG.

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).

Exhibit D - Section 12

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

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 Duplicate sample analyses cannot be averaged for reporting.

12.3.3 Procedure for Duplicate Sample

12.3.3.1 Samples identified as field blanks or 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

The Relative Percent Difference (RPD) for each analyte shall be calculated using Equation 24B in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.3.5 Technical Acceptance Criteria for Duplicate Sample

12.3.5.1 The RPD must be within the control limits of $\pm 20\%$ if the original and Duplicate sample values are greater than or equal to five times the CRQL (see Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 8).

12.3.5.2 The control limit must 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 for an analyte are outside the control limits, flag the data for that analyte in all the 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 one duplicate analyte result is not within contract criteria, flag the data for that analyte in all the samples of the same matrix in the SDG.

12.4 Laboratory Control Sample

12.4.1 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.

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

12.4.2 Frequency of Laboratory Control Sample

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

12.4.3 Procedure for Laboratory Control Sample

The LCS for aqueous/water and soil/sediment samples shall be prepared by spiking an aliquot of reagent water such that the final preparation shall contain each analyte at two times the CRQL for the associated matrix.

12.4.4 Calculations for Laboratory Control Sample

12.4.4.1 Calculate the results for the LCS using Equation 4H or 5J in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.4.4.2 Calculate the %R for the LCS using Equation 26B in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations

12.4.5 Technical Acceptance Criteria for Laboratory Control Sample

The %R must be within the control limits of 80-120% for all analytes.

12.4.6 Corrective Action for Laboratory Control Sample

If the %R for the LCS for aqueous/water or soil/sediment samples is outside the control limits of 80-120%, the analyses shall be terminated, the problem corrected, and the samples associated with that LCS reprepared and reanalyzed with appropriate new QC.

12.5 Method Detection Limit Determination

12.5.1 Before any field samples are analyzed under the contract, the MDL for each analyte shall be determined for each preparation procedure, and for each instrument under the same conditions used for analysis, used prior to the start of contract analyses and verified annually thereafter. MDL determination is matrix-specific (i.e., the MDL shall be determined for aqueous/water and soil/sediment samples). 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.

12.5.1.1 To determine the MDLs, the Contractor shall perform MDL studies following the procedures in Title 40 of the Code of Federal Regulations (CFR), Part 136, Appendix B, Revision 2.

12.5.1.2 The determined concentration of the MDL must be less than half the concentration of the CRQL listed in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 8.

12.5.1.3 The delivery requirements for the MDL values are specified in Exhibit B - Reporting and Deliverables Requirements, Table 1.

12.6 Summary of Quality Control Operations

The QC operations performed for anion analysis are summarized in Exhibit D - Anions by Ion Chromatography, Table 1.

Exhibit D - Sections 13-16

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

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

15.0 WASTE MANAGEMENT

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

16.0 REFERENCES

- 16.1 U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, Method 300.0, Determination of Inorganic Anions by Ion Chromatography, Revision 2.1, August 1993.
- 16.2 U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Waste, Method 300.1, Determination of Inorganic Anions in Drinking Water by Ion Chromatography, Revision 1.0, 1997.
- 16.3 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 9056A, Determination of Inorganic Anions by Ion Chromatography, Revision 1, Third Edition, Update IV-B, February 2007.
- 16.4 U.S. Government Printing Office, Title 40 of the Code of Federal Regulations, Chapter 1, Subchapter D, Part 136, Appendix B, Definition and Procedure for the Determination of the Method Detection Limit, Revision 2.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

TABLE 1. QC OPERATIONS FOR ANION ANALYSIS

QC Operation	Frequency
Instrument Calibration	Weekly or, after ICV or CCV failure, after ICB or CCB failure, after LCS failure, and after major instrument adjustment.
Initial Calibration Verification	Following each instrument calibration. If an analytical sequence ends and a new analytical sequence starts later within a week of the calibration, an ICV is again required prior to sample analysis.
Continuing Calibration Verification	At a frequency of every 10 samples 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. If an analytical sequence ends and a new analytical sequence starts later within a week of the calibration, an ICB is again required prior to sample analysis.
Continuing Calibration Blank	At a frequency of every 10 samples, 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.
Laboratory Control Sample	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/Verification	Prior to start of contract analyses, annually thereafter, and after major instrument adjustment.

TABLE 2. SPIKING LEVELS FOR SPIKE SAMPLE ANALYSIS

Analyte	Aqueous/Water (mg/L)	Soil/Sediment (mg/kg)
Bromide	5.0	50
Chloride	5.0	50
Fluoride	2.0	20
Nitrate	2.0	20
Nitrite	2.0	20
Orthophosphate	2.0	20
Sulfate	5.0	50

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EXHIBIT D

HEXAVALENT CHROMIUM BY ION CHROMATOGRAPHY

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Exhibit D - Hexavalent Chromium by Ion Chromatography

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1.0 SCOPE AND APPLICATION

This exhibit provides procedures for the use of ion chromatography to determine the concentration of Hexavalent Chromium [Cr(VI)] as the chromate ion CrO₄²⁻ in aqueous/water samples collected from hazardous waste sites.

2.0 SUMMARY OF METHOD

2.1 General Method Overview

This method describes hexavalent chromium determination by ion chromatography followed by post-column derivatization and Ultraviolet-Visible (UV-Vis) spectroscopy. A small volume of sample is injected onto an ion chromatograph via a constant volume sample loop. The hexavalent chromium is separated and measured using a system comprised of: a guard column; an analytical column packed with an anion exchange resin; a post-column reactor that uses 1,5-Diphenylcarbazide to derivatize the chromate ions present; a UV-Vis absorbance detector to measure the derivative at a wavelength of 530 nm; and a chromatography data system. Cr(VI) identification is based on the comparison of the analyte signal peak retention time in the samples relative to known calibration standards. Quantitation is achieved by comparing the measurement of the peak area in the samples to that in calibration standards.

3.0 DEFINITIONS

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

4.0 INTERFERENCES

Due to the chromatographic separation of chromate from other ionic species and the specificity of the derivatizing agent to chromate, there are minimal interferences from other anions. However, reduction of Cr(VI) and oxidation of Cr(III) must be prevented. Therefore, samples are preserved by buffering to a pH >8 to minimize reduction of Cr(VI), and a dechlorinating agent is added to minimize oxidation of Cr(III).

4.1 Particulates

Samples shall be filtered through at least a 0.45 micrometer (μm) filter (polytetrafluoroethylene recommended) prior to injection. It is also recommended that any eluent reagents be filtered through a 0.20 μm filter to remove particulate matter to prevent damage to the columns and flow system.

4.2 Reagents and Equipment

Method interferences may be caused by contaminants in the reagent water, reagents (including the method preservative), glassware, sample handling apparatus, and in the ion chromatographic system that may lead to discrete artifacts or elevated baselines. These interferences can lead to false positive results for the target analyte.

4.3 Matrix Interferences

Sample ionic strength may enhance or suppress Cr(VI) response.

Exhibit D - Sections 4-6

4.4 Oxidation-Reduction (Redox)

To ensure sample integrity, Cr(VI) must be protected from reduction, and Cr(III) if present, must not oxidize to Cr(VI) during sample storage. Buffering the sample to at least pH 8 will stabilize the CrO₄²⁻ ion form. Free chlorine oxidizes Cr(III) to Cr(VI), therefore the preservative is designed to complex free chlorine by forming chloramines and minimize the oxidation of Cr(III).

5.0 SAFETY

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

6.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here; however, demonstration of equivalent performance that meets 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.

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

6.1 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).

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

6.1.3 Autosampler Vials - Sized for autosampler (if applicable).

6.1.4 Syringes - Plastic, disposable, 10 mL. Equipped with valves with Luer-Lok ends.

6.1.5 Syringe Filters - 0.45 μ m pore diameter.

6.1.6 Chlorine Test Kit - Capable of detecting below 0.10 mg/L free chlorine.

6.2 Ion Chromatograph

A system consisting of a pump, an autosampler, a sample injector, and the following components:

- 6.2.1 Precolumn - A guard column placed before the separator column to protect the separator column from particulates or organic constituents.
- 6.2.2 Separator (or analytical) column - A column packed with an anion exchange resin, suitable for resolving hexavalent chromium from other anions. Maintain at a stable temperature.
- 6.2.3 Post-column reactor - Consisting of a pulse-free reagent pump, mixing tee, and reaction coil.
- 6.2.4 UV-Vis spectrometer - Absorbance detector set to monitor a wavelength of 530 nm.
- 6.2.5 Chromatographic data system - Capable of integrating the detector signal output and storing it as chromatographic data.

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 - 93-98%, trace metal grade. For preparing the post-column reagent.
- 7.1.3 Methanol - Liquid Chromatography/Mass Spectrometry (LC/MS) grade or equivalent. For preparing the post-column reagent.
- 7.1.4 1,5-Diphenylcarbazide - For preparing the post-column reagent.
- 7.1.5 Eluent - Per column manufacturer's guidance for constituents and concentrations. Both bicarbonate/carbonate and ammonium hydroxide/ammonium sulfate solutions have been shown to be suitable eluents. Follow manufacturer's guidance on stability of specified eluents.
- 7.1.6 Post-column reagent - 2 millimolar (mM) 1,5-diphenylcarbazide, 10% methanol, and 0.5 M (1N) sulfuric acid. In a 1 liter (L) volumetric flask, add 500 mL of reagent water and 28 mL of sulfuric acid (see Section 7.1.2). Mix and allow the solution to cool to room temperature. Weigh out 0.50 g of 1,5-diphenylcarbazide in a 100 mL beaker, add 75 mL of methanol, and sonicate for 5 minutes to dissolve the solid. Transfer the methanol solution to a 100 mL volumetric flask, bring up to volume with methanol, add to the cooled sulfuric acid solution and dilute to 1 L. This reagent solution is stable for approximately 5 days.
- 7.1.7 Ammonium Hydroxide (NH_4OH), 28-30% NH_3 (w/w) - For preparing $\text{NH}_4\text{OH}/(\text{NH}_4)_2\text{SO}_4$ (liquid) preservative and eluent.
- 7.1.8 Ammonium Sulfate $(\text{NH}_4)_2\text{SO}_4$, reagent grade - For preparing preservatives (liquid and solid) and eluent.
- 7.1.9 Sodium Bicarbonate (NaHCO_3), reagent grade - For preparing solid preservative and eluent.
- 7.1.10 Sodium Carbonate (Na_2CO_3), anhydrous reagent grade - For preparing solids preservative and eluent.

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- 7.1.11 Liquid Preservative - Dissolve 3.3 g $(\text{NH}_4)_2\text{SO}_4$ in 75 mL of reagent water. Add 6.5 mL ammonium hydroxide and dilute to 100 mL final volume with reagent water.
- 7.1.12 Solid preservative - For every 100-mL sample, Mix 13.3 mg Na_2CO_3 , 10.5 mg NaHCO_3 , and 33 mg $(\text{NH}_4)_2\text{SO}_4$.

7.2 Standards

7.2.1 Introduction

The Contractor must provide all standards, except as noted, to be used with the contract. These standards may be used only after they have been certified according to the procedure in Exhibit D - Introduction to 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 and standards must be stored separately.

7.2.2 Stock Standard Solutions

- 7.2.2.1 Stock standard solutions may be purchased from a reputable source or prepared from reagent grade chemicals.
- 7.2.2.2 Stock hexavalent chromium solution, 1000 mg/L - Dry the potassium dichromate salt ($\text{K}_2\text{Cr}_2\text{O}_7$) at 100°C to constant weight, weigh out 0.283 g, dissolve in reagent water and dilute to 100 mL with reagent water. Store the standard at room temperature.

7.2.3 Working Standards

- 7.2.3.1 Working hexavalent chromium solution, 1 mg/L - Dilute the stock hexavalent chromium solution (see Section 7.2.2.2) 1:1000 with reagent water to which the preservative used for the field samples has been added (see Section 8.1). Store this solution in a polyethylene or polypropylene bottle at room temperature. The solution is stable for 14 days.

7.2.3.2 Calibration Standards

Prepare standards by transferring suitable volumes of the working hexavalent chromium solution (see Section 7.2.3.1) into volumetric flasks, add the appropriate preservative (see Section 8.1), and dilute with reagent water. The concentrations in the standards should be sufficient to produce good measurement precision and to accurately define the slope of the calibration curve. Prepare calibration standards daily or as needed.

7.2.4 Initial Calibration Verification Solution

- 7.2.4.1 The Initial Calibration Verification (ICV) solution may be obtained from the EPA, or it shall be prepared by the Contractor using a certified solution from an independent source, which is defined as a standard composed of the analytes from a different source than that used for the instrument calibration. Analyses shall be conducted at a concentration other than that used for instrument calibration, but near the middle (within $\pm 30\%$) of the calibration range.
- 7.2.4.2 The ICV standard shall be prepared 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 as well as to verify the calibration initially and continually during the analysis, and the Preparation Blank (see Section 12.1) is used to assess possible contamination from any sample preparation procedure.

- 7.3.1 Calibration Blank - Must contain the same preservative in the same volume as used in preparing the other calibration standards. 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 and baseline drift.
- 7.3.2 Preparation Blank - Must contain the same preservative in the same volume as used in the samples. The Preparation Blank shall be carried through the complete sample preparation procedure, including filtration if field samples are filtered in the laboratory.

8.0 SAMPLE COLLECTION, PRESERVATION, STORAGE, AND HOLDING TIMES

8.1 Sample Collection and Preservation

- 8.1.1 All samples should be collected in high-density polyethylene or polypropylene copolymer containers. Samples should be preserved in the field to pH >8 with a combination buffer/dechlorinating agent, using either a liquid mixture of NH₄OH/(NH₄)₂SO₄ (1 mL per 100 mL of sample) or a solid mixture of Na₂CO₃/NaHCO₃/(NH₄)₂SO₄ (13.3 mg Na₂CO₃, 10.5 mg NaHCO₃, and 33 mg (NH₄)₂SO₄ per 125 mL bottle). All samples should be iced or refrigerated at ≤6°C, but not frozen, from the time of collection until receipt at the laboratory. If the preservative used is not listed on the Traffic Report/Chain of Custody, contact the Sample Management Office (SMO) with this information. SMO will contact the EPA Region to determine the preservative used. The preservative used will determine how to prepare the calibration standards and Quality Control (QC) samples.
- 8.1.2 The Contractor shall measure and record the sample pH and test for free chlorine at the time of sample receipt to verify that the samples were properly preserved. If the pH of the sample is ≤8, or if free chlorine is detected at a concentration ≥0.10 mg/L, the Contractor shall immediately contact SMO and notify them of the problem. SMO will contact the EPA Region. The EPA Region may require the Contractor to either proceed with analysis or to not analyze the sample. If the sample is to be analyzed, the EPA Region may direct the Contractor to preserve the sample with either the liquid or solid preservative. The EPA resolution shall be documented in the SDG Narrative.

8.2 Sample Storage

All samples shall be protected from light and refrigerated at ≤6°C, but not frozen, from the time of receipt until analysis. Samples shall be stored in an upright position.

8.2.1 Unused Sample Storage

The Contractor shall retain the unused portions of the samples for a period of 60 days after the delivery of a complete, reconciled data package to the EPA. The unused portions must be protected from light and refrigerated at ≤6°C but not frozen.

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8.2.2 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 Times

The holding time for preserved hexavalent chromium samples is 12 days from the 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) and precision must be investigated and established for hexavalent chromium on that particular instrument. All measurements shall 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 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 shall be allowed to become stable 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 the sensitivity and linearity of the response.

9.3.2 Frequency of Instrument Calibration

Each instrument shall be calibrated each time it is set up, after eluent concentration or constituent change, or after ICV, ICB, Continuing Calibration Verification (CCV), CCB, or Laboratory Control Sample (LCS) 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 Section 7.2.3.2. One of the standards shall be a blank standard (see Section 7.3.1) 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 prepared fresh with each calibration performed.
- 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 $\mu\text{g}/\text{L}$) on the X-axis versus the instrument response (e.g., peak area) on the Y-axis. It is the analyst's responsibility to review all chromatograms to ensure accurate baseline integration of target analytes.
- 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. Forcing the calibration curve through the origin is not recommended. 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. See Equation 15 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.
- 9.3.5 Technical Acceptance Criteria for Instrument Calibration
- 9.3.5.1 The correlation coefficient of the calibration curve must be greater than or equal to 0.995.
- 9.3.5.2 The Percent Difference ($\%D$) for each of the non-blank standards must be within the control limits of $\pm 30\%$.
- 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. No standard analyzed with a concentration greater than or equal to the CRQL shall be excluded from the calibration curve.
- 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.

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9.4.3 Procedure for Initial Calibration Verification

9.4.3.1 The ICV shall be analyzed at the settings 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 Equation 16 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.4.5 Technical Acceptance Criteria for Initial Calibration Verification

The ICV %R must 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 any CCV after the analysis of the initial CCV following the ICB.

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 10 samples during an analytical sequence. See the example analytical sequence in Section 10.2.6.

9.5.2.2 The analytical sequence can continue indefinitely for 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 matrix as the calibration standards at or near to the mid-level ($\pm 30\%$ of mid-range) of the calibration curve.

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

9.5.3.3 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 down to the next CCV as applicable).

9.5.4 Calculations for Continuing Calibration Verification

The %R of the CCV shall be calculated using Equation 16 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.5.5 Technical Acceptance Criteria for Continuing Calibration Verification

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

9.5.5.2 Up to 10 samples may be analyzed between 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 analyzed shall reflect the conditions of analysis of the associated analytical samples.

9.6.3.2 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 down 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 4H in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.6.5 Technical Acceptance Criteria for Calibration Blank

The absolute value of each calibration blank result must be less than or equal to the CRQL.

9.6.6 Corrective Action for Calibration Blank

If the absolute value of the calibration blank exceeds the CRQL, 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.

Exhibit D - Section 10

10.0 PROCEDURE

10.1 Sample Preparation

Allow the samples to reach room temperature. Filter each sample through a 0.45 µm filter prior to injection onto the sample loop. The use of a syringe filter is acceptable.

10.2 Sample Analysis

- 10.2.1 Establish ion chromatograph operating parameters exactly equivalent to those used for calibration. Establish a stable baseline.
- 10.2.2 Place the calibration standards, samples, and blanks in the sampler tray in the appropriate sequence. See example sequence provided in Section 10.2.6.
- 10.2.3 Allow all standards, samples, and blanks to come to ambient room temperature prior to analysis.
- 10.2.4 Complete the analysis of all the standards, samples, and blanks and construct the calibration curve. The calibration curve shall be constructed based on the concentration of hexavalent chromium (in µg/L) in the standards.
- 10.2.5 Samples having concentrations higher than the established calibration range for hexavalent chromium as determined by the expected concentration of the highest calibration standard shall be diluted into range according to the procedure in Exhibit D - Introduction to Analytical Methods, Section 7.0 and reanalyzed. Dilute a portion of the sample using a solution which maintains the same reagent concentrations as are present in the calibration standards (e.g., one of the calibration blanks). The Contractor shall then promptly analyze the diluted sample.
- 10.2.6 Example Analytical Sequence for Hexavalent Chromium 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

11.1 Target Analyte Concentrations

Calculate the hexavalent chromium concentration using Equation 4H in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

11.2 Contract Required Quantitation Limit Calculation

Calculate the adjusted CRQL by using Equation 6G in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

11.3 Data Processing Procedure

Hexavalent chromium shall be quantitated using the peak area response. It is expected that situations will arise where the automated quantitation procedures in the ion chromatography software provide inappropriate quantitation. This can occur when there is compound coelution, baseline noise, or matrix interferences. In these circumstances, the Contractor shall perform a manual quantitation by integrating the area of the peak of the target analyte. This integration shall only include the area attributable to the target analyte. The area integrated shall not include baseline background noise. The area integrated shall also not extend past the point where the sides of the peak intersect with the baseline noise. Manual integration is not to be used solely to meet QC criteria, nor is it to be used as a substitute for corrective action on the chromatographic system. Any instances of manual integration shall be documented in the SDG Narrative.

In all circumstances where the data system has been edited, or where manual integration or quantitation has been performed, the ion chromatograph instrument operator shall identify such procedures by initialing and dating the changes made to the report, and shall include the integration scan range.

Exhibit D - Section 12

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, and contain the same preservative concentrations as the samples.

12.1.4 Calculations for Preparation Blank Sample

Calculate the results for Preparation Blanks using Equation 4H in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.1.5 Technical Acceptance Criteria for Preparation Blank Sample

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

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

12.1.5.3 The hexavalent chromium 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 concentration in the Preparation Blank is greater than the CRQL, and the concentration 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 reanalyzed with appropriate new QC.

12.1.6.2 If the concentration in the Preparation Blank is less than the negative CRQL, and the concentration in any of the associated samples is less than 10 times the CRQL, then all samples with less than 10 times the CRQL concentration shall be 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 measurement methodology.

12.2.2 Frequency of Matrix Spike Sample

At least one Matrix Spike sample analysis shall be performed for each SDG.¹

12.2.3 Procedure for Matrix Spike Sample

12.2.3.1 For a Matrix Spike sample, the spike is added prior to the addition of other reagents and filtration.

12.2.3.2 The analyte spike shall be added to achieve the concentration of 1.0 µg/L in the final sample solution prepared for analysis.

12.2.3.3 Samples identified as field blanks or 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 selected 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 the %R.

12.2.4.2 Calculate the Matrix Spike %R using Equation 23 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.2.5 Technical Acceptance Criteria for Matrix Spike Sample

The Matrix Spike %R must fall 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 the 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 Spike Added (SA) concentration by a factor of four or more. In such an instance, 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 SDG, and one Matrix Spike sample recovery is not within contract criteria, then flag all the samples 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

One Duplicate sample shall be analyzed for each SDG.² Duplicate sample analyses cannot be averaged for reporting.

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).

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

Exhibit D - Section 12

12.3.3 Procedure for Duplicate Sample

12.3.3.1 Samples identified as field blanks or 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

The Relative Percent Difference (RPD) for the analyte shall be calculated using equation 24B in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.3.5 Technical Acceptance Criteria for Duplicate Sample

12.3.5.1 The RPD must be within the control limits of $\pm 20\%$ if the original and Duplicate sample values are greater than or equal to five times the CRQL (see Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 9).

12.3.5.2 The control limit must 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 the samples received associated with that Duplicate sample with an "*".

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

12.4 Laboratory Control Sample

12.4.1 Summary of Laboratory Control Sample

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

12.4.2 Frequency of Laboratory Control Sample

One LCS shall be prepared for each prepared batch of samples in an SDG.

12.4.3 Procedure for Laboratory Control Sample

The LCS shall be prepared by spiking an aliquot of reagent water containing the appropriate preservative (see Section 8.1) such that the final preparation shall contain chromate at 2 times the CRQL.

12.4.4 Calculations for Laboratory Control Sample

12.4.4.1 Calculate the results for the LCS by using Equation 4H in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.4.4.2 Calculate the %R for the LCS using Equation 26B in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.4.5 Technical Acceptance Criteria for Laboratory Control Sample

The LCS %R must be within the control limits of 70-130%.

12.4.6 Corrective Action for Laboratory Control Sample

If the %R for the LCS is outside the control limits of 70-130%, the analysis shall be terminated, the problem corrected, and the samples associated with that LCS reanalyzed with appropriate new QC.

12.5 Method Detection Limit Determination

12.5.1 Before any field samples are analyzed under the contract, the MDLs shall be determined for each preparation procedure, and for each instrument under the same conditions used for analysis, used prior to the start of contract analyses and verified 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.

12.5.1.1 To determine the MDLs, the Contractor shall perform MDL studies following the procedures given in Title 40 of the Code of Federal Regulations (CFR), Part 136, Appendix B, Revision 2.

12.5.1.2 The determined concentration of the MDL must be less than the CRQL listed in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 9.

12.5.1.3 The delivery requirements for the MDL values are specified in Exhibit B - Reporting and Deliverables Requirements, Table 1.

12.6 Summary of Quality Control Operations

The QC operations performed for hexavalent chromium analysis are summarized in Exhibit D - Hexavalent Chromium, Table 1.

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

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

15.0 WASTE MANAGEMENT

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

16.0 REFERENCES

16.1 U.S. Environmental Protection Agency, Office of Drinking Water, Method 218.6, Determination of Dissolved Hexavalent Chromium in Drinking Water, Groundwater, and Industrial Wastewater Effluent by Ion Chromatography, Revision 3.3, May 1994.

16.2 U.S. Environmental Protection Agency, Office of Water, Method 218.7, Determination of Hexavalent Chromium in Drinking Water by Ion Chromatography with Post-Column Derivatization and UV-Vis Spectroscopic Detection, November 2011.

16.3 U.S. Government Printing Office, Title 40 of the Code of Federal Regulations, Chapter 1, Subchapter D, Part 136, Appendix B, Definition and Procedure for the Determination of the Method Detection Limit, Revision 2.

Exhibit D - Section 17

17.0 TABLES/DIAGRAMS/FLOWCHARTS

TABLE 1. QC OPERATIONS FOR HEXAVALENT CHROMIUM ANALYSIS

QC Operation	Frequency
Instrument Calibration	Daily or each time instrument is turned on or set up, after ICV or CCV failure, after ICB or CCB failure, after LCS failure, and after major instrument adjustment.
Initial Calibration Verification	Following each instrument calibration.
Continuing Calibration Verification	At a frequency of every 10 samples 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	At a frequency of every 10 samples, 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.
Laboratory Control Sample	For each SDG or each sample preparation and analysis procedure per batch of prepared samples, whichever is more frequent.
Matrix Spike Sample	For each SDG.
Duplicate Sample Analysis	For each SDG.
Method Detection Limit Determination	Prior to start of contract analyses, annually thereafter, and after major instrument adjustment.

EXHIBIT D
TOTAL ORGANIC CARBON ANALYSIS

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Exhibit D - Total Organic Carbon Analysis

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Exhibit D - Total Organic Carbon Analysis

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1.0 SCOPE AND APPLICATION

This exhibit provides procedures for the use of either a nondispersive infrared (IR) technique or a membrane conductimetric technique to determine total organic carbon (TOC) in aqueous/water and soil/sediment samples collected from hazardous waste sites. Aqueous/water samples are analyzed using either a persulfate digestion with ultraviolet and/or heat oxidation technique, or a combustion technique to generate carbon dioxide. Soil/sediment samples are analyzed for total organic carbon using pyrolysis to generate carbon dioxide and the same detection techniques listed above for aqueous/water samples.

Instruments for soil/sediment samples may also use detection systems that convert the carbon dioxide to methane and use gas chromatography detectors such as flame ionization or thermal conductivity.

In addition to organic forms of carbon, inorganic carbon may also be present. This is typically removed by treatment of the samples with acid prior to analysis, unless total carbon is to be analyzed for.

2.0 SUMMARY OF METHOD

2.1 General Method Overview

This method is based on the oxidation and measurement by IR or conductimetry of the organic carbon present in samples. Aqueous/water samples are treated to remove inorganic carbon and the organic carbon present is oxidized with persulfate in the presence of ultraviolet (UV) radiation and/or heat, or processed through a combustion system using heat with or without a catalyst to oxidize the organic carbon present to carbon dioxide. Soil/sediment samples are treated to remove any inorganic carbon present in the sample and the organic carbon is oxidized by pyrolysis using oxygen to generate carbon dioxide. The carbon dioxide generated from the aqueous/water and soil/sediment samples is measured by either a nondispersive IR detector, a membrane conductimetric detector, or is catalytically converted to methane and detected by a flame ionization or thermal conductivity detector.

3.0 DEFINITIONS

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

Exhibit D - Sections 4-5

4.0 INTERFERENCES

4.1 Carbonate and Bicarbonate

Inorganic carbon in the form of carbonates and bicarbonates will generate carbon dioxide under analysis conditions. The inorganic carbon is removed by pre-treating the sample with acid. Aqueous/water samples are sparged after acidification to remove the resulting carbon dioxide.

4.2 Chloride

Chloride concentrations exceeding 250 mg/L may interfere with persulfate oxidation methods. Samples high in chloride may require increased persulfate concentration and extended oxidation times. Follow the instrument manufacturer's guidance for samples with high chloride.

4.3 Volatile Organic Compounds

Volatile organic compounds may be lost from soil samples during the removal of inorganic carbon.

4.4 Particulates

Particles large enough to clog syringes or pipettes will affect the analysis. Samples may be homogenized, or allowed to settle. Filtration is generally reserved for the determination of dissolved organic carbon.

5.0 SAFETY

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

6.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here; however, demonstration of equivalent performance that meets 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.

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

6.1 Glassware/Labware

- 6.1.1 Graduated cylinders.
- 6.1.2 Assorted volumetric glassware (Class A), and calibrated pipettes and micropipettes. Manufacturer's instructions should be followed for the calibration and maintenance of adjustable pipettes.
- 6.1.3 Sample vials - 40-milliliter (mL) glass with caps and polytetrafluoroethylene (PTFE)/silicone septa.
- 6.1.4 Balances - Top-loader balance, 300 gram (g) capacity, and a minimum sensitivity of ± 1.0 milligram (mg).

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

6.2 Total Organic Carbon (TOC) Analyzer

The instrument shall consist of a module to convert the organic carbon present in aqueous/water samples into carbon dioxide. This module may be either a persulfate digestion system with ultraviolet and/or heat oxidation capabilities, or a combustion system using heat with or without a catalyst. The instrument shall also be equipped with a pyrolysis module that uses oxygen or carbon dioxide-free air to convert the organic carbon present in soil/sediment samples into carbon dioxide. In addition, the instrument shall include either a nondispersive IR or a membrane conductimetric detector, or a flame ionization or thermal conductivity GC detector. The instrument shall have, or be linked to, a suitable computer system for data processing.

Instrument settings recommended by the particular manufacturer should be followed. The instrument must be capable of storing and producing the settings used for each analytical sequence. The instrument must be capable of meeting the specified Contract Required Quantitation Limits (CRQLs) for TOC.

Exhibit D - Section 7

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 Persulfate reagent - Prepare this solution according to the instrument manufacturer's instructions or purchase from the instrument manufacturer.
- 7.1.3 O-Phosphoric Acid (85%) - ACS reagent grade or better.
- 7.1.3.1 Phosphoric acid 1:1 - Carefully add 500 mL of O-Phosphoric acid to 400 mL of reagent water and dilute to 1 liter (L).
- 7.1.3.2 Phosphoric acid solution - Prepare this solution according to the instrument manufacturer's instructions or purchase from the instrument manufacturer.
- 7.1.4 Sulfuric Acid - Concentrated 95-98% - ACS reagent grade or better.
- 7.1.4.1 Sulfuric acid solution - Prepare this solution according to the instrument manufacturer's instructions or purchase from the instrument manufacturer.
- 7.1.5 Potassium hydrogen phthalate (C8H5O4K) - Anhydrous, ACS reagent grade or better.
- 7.1.6 Oxygen, carbon dioxide-free air, nitrogen - Ultra high purity, either compressed or lab-generated for combustion, carrier gas, or sparging.

7.2 Standards

7.2.1 Introduction

The Contractor shall provide all standards, except as noted, to be used with the contract. These standards may be used only after they have been certified according to the procedure in Exhibit D - Introduction to Analytical Methods, Section 11.0. The Contractor shall be able to verify that the standards are certified. Manufacturer's certificates of analysis shall be retained by the Contractor and presented upon request. Standards shall be prepared in the same matrix (acid preservative) as the samples.

Samples and standards shall 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.

- 7.2.2.1 Stock organic carbon solution - Dissolve 1.063 g of potassium hydrogen phthalate (see Section 7.1.5) in 500 mL of reagent water to which 1 mL of the appropriate concentrated acid has been added. Dilute to 1 L final volume [1.0 mL = 0.5 mg organic carbon]. Store this solution in an amber glass bottle at room temperature. This solution is stable for at least 6 months.

7.2.3 Calibration Standards Solutions

- 7.2.3.1 Aqueous/Water Solutions - Make successive dilutions of the stock organic carbon solution (see Section 7.2.2) with reagent water acidified with the appropriate acid to obtain a range of calibration standards. Store these solutions in amber glass bottles. These solutions are stable for 30 days.

- 7.2.3.2 Soil/Sediment Solutions - Make successive dilutions of the stock organic carbon solution (see Section 7.2.2) with reagent water to obtain a range of calibration standards. Store these solutions in amber glass bottles.
- 7.2.4 Initial Calibration Verification Solution
- 7.2.4.1 The Initial Calibration Verification (ICV) solution shall be obtained from the EPA.
- 7.2.4.2 If the solution is not available from the EPA, the ICV solution shall be prepared by the Contractor using a certified solution from an independent source, which is defined as a standard from a different source than that used for instrument calibration. Analyses shall be conducted at a concentration other than that used for instrument calibration, but near the middle (within $\pm 30\%$) of the calibration range.
- 7.2.4.3 The ICV standard shall be prepared in the same reagent 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 as well as to verify the calibration initially and continually during the analysis, and the Preparation Blank (see Section 12.1) is used to assess possible contamination from the sample preparation procedures.

- 7.3.1 Calibration Blank - Must contain all the reagents in the same volumes as used in preparing the other calibration standards. 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 shall be carried through the complete sample preparation procedure and contain the same reagent concentration in the final solution as the sample solution used for analysis.

Exhibit D - Section 8

8.0 SAMPLE COLLECTION, PRESERVATION, STORAGE, AND HOLDING TIMES

8.1 Sample Collection and Preservation

8.1.1 All aqueous/water and soil/sediment samples should be collected in amber glass containers. The lids should be lined with foil or PTFE. Aqueous/water samples must be preserved with acid (sulfuric or phosphoric) to pH ≤2 immediately after collection. All aqueous/water and soil/sediment samples should be iced or refrigerated at ≤6°C, but not frozen, from the time of collection until receipt at the laboratory. If the preservative used is not listed on the Traffic Report/Chain of Custody, contact the Sample Management Office (SMO) with this information. SMO will contact the EPA Region to determine the preservative used. The preservative used will determine how to prepare the calibration standards and Quality Control (QC) samples.

8.1.2 The Contractor shall measure the sample pH at the time of sample receipt to verify that the samples were properly preserved. If the pH is >2, the Contractor shall immediately notify SMO of the affected sample(s) and pH value(s). SMO will contact the EPA Region. The EPA Region may require the Contractor to either proceed with the analysis or to not analyze the sample(s). The EPA resolution shall be documented in the SDG Narrative.

8.2 Sample Storage

All aqueous/water and soil/sediment samples shall be stored at ≤6°C, but not frozen, from the time of sample receipt until preparation. Samples shall be stored in an upright position.

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 the delivery of a complete, reconciled data package to the EPA. The unused portions may be stored at room temperature.

8.2.2 Digestate Sample Storage

Not applicable.

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 TOC is 26 days from the 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) and precision must be investigated and established for TOC on that particular instrument. All measurements shall 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 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 shall be allowed to become stable 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 the 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 it is set up, or after ICV, ICB, Continuing Calibration Verification (CCV), CCB, or Laboratory Control Sample (LCS) 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 five calibration standards shall be used. The calibration standards shall be prepared according to Section 7.2.3.1. One of the standards shall be a blank standard (see Section 7.3.1) and one shall be at or below the CRQL, but greater than the MDL. The rest of the standards shall be uniformly spread over the appropriate calibration range.

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 mg/L) on the X-axis versus the instrument response 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.

Exhibit D - Section 9

- 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. See Equation 15 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.
- 9.3.5 Technical Acceptance Criteria for Instrument Calibration
- 9.3.5.1 The correlation coefficient of the calibration curve must be greater than or equal to 0.995.
- 9.3.5.2 The Percent Difference (%D) for each of the non-blank standards must be within the control limits of $\pm 30\%$.
- 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. No standard analyzed with a concentration greater than or equal to the CRQL shall be excluded from the calibration curve.
- 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
- 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 Equation 16 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.
- 9.4.5 Technical Acceptance Criteria for Initial Calibration Verification
- The ICV %R must be within the control limits of 80-120%.
- 9.4.6 Corrective Action for Initial Calibration Verification
- If the recovery is outside the control limits of 80% Recovery (low) or 120% 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 any CCV after the analysis of the initial CCV following the ICB.

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 of every 10 samples during an analytical sequence. See the example analytical sequence in Section 10.3.2.

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 ($\pm 30\%$ of mid-range) 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 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 down to the next CCV as applicable).

9.5.4 Calculations for Continuing Calibration Verification

The %R of the CCV shall be calculated using Equation 16 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.5.5 Technical Acceptance Criteria for Continuing Calibration Verification

9.5.5.1 The CCV %R must be within the control limits of 80-120%.

9.5.5.2 Up to 10 samples may be analyzed between 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 80% Recovery (low) or 120% 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.

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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 analyzed shall reflect the conditions of analysis of the associated analytical samples.

9.6.3.2 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 down 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 4H in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.6.5 Technical Acceptance Criteria for Calibration Blank

The absolute value of each calibration blank result must 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 Allow the samples to reach room temperature.
- 10.1.2 Transfer a portion of the sample to a 40 mL sampling vial. Add 40 μ L of the appropriate acid to the vial. If the instrument has the capability to sparge the carbon dioxide resulting from the reaction of the acid with the inorganic carbon, set the instrument to perform this operation. If not, sparge the vial with nitrogen at 100 - 200 mL/min for 20 minutes.
- 10.1.3 If the samples show evidence that humic/fulvic substances have precipitated due to the low pH, it may be necessary to split the sparged sample into two vials and adjust the pH of one of them to 5.0 - 7.0. Allow the vials to sit capped for 30 minutes to re-dissolve any hydrophobic substances. Document this in the SDG Narrative.

10.2 Soil/Sediment Sample Preparation

Mix the sample thoroughly to achieve homogeneity. Weigh an aliquot amount of up to 0.50 g (to the nearest 0.01 g) and place in the bottom of the combustion cup or boat. Soil/sediment blanks shall use 0.5 - 0.6 mL of reagent water. Add 1:1 phosphoric acid (See Section 7.1.3.1) to each sample one drop at a time until effervescence stops. Heat the sample to 75°C.

10.3 Sample Analysis

- 10.3.1 Set up the analyzer using the recommended settings provided by the manufacturer for TOC analysis. All reagent and sample lines should be cleaned according to the manufacturer's recommendations.
- 10.3.2 Example Analytical Sequence for Total Organic Carbon Including the Instrument Calibration:

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

- 10.3.3 Complete the analysis of all the standards, samples, and blanks and construct the calibration curve. The calibration curve shall be constructed based on the concentration of TOC in the standards, ignoring the volume of reagents added during the analysis process.

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- 10.3.4 Samples having concentrations higher than the established calibration range as determined by the concentration of the highest calibration standard shall be diluted into range according to the procedure in Exhibit D - Introduction to Analytical Methods, Section 7.0 and reanalyzed. Dilute a portion of the sample using a solution that maintains the same reagent concentrations as in the calibration standards (e.g., one of the calibration blanks). The Contractor shall then promptly analyze the diluted sample.
- 10.3.5 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

11.1 Target Analyte Concentration

Calculate the TOC concentration using Equation 4H or 5J in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

11.2 Contract Required Quantitation Limit Calculation

Calculate the adjusted CRQL using Equation 6G or 7J in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

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 concentrations as the samples.

12.1.4 Calculations for Preparation Blank Sample

Calculate the results for aqueous/water Preparation Blanks using Equation 4H in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations. Calculate the results for soil/sediment Preparation Blanks using Equation 5J in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.1.5 Technical Acceptance Criteria for Preparation Blank Sample

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

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

12.1.5.3 The TOC concentration in the Preparation Blank may be less than the negative CRQL, if the concentration of 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 TOC concentration in the Preparation Blank is greater than the CRQL, and the concentration of total organic carbon 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 TOC concentration in the Preparation Blank is less than the negative CRQL, and the concentration in any of 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 preparation 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 For a Matrix Spike sample, the spike is added prior to the addition of other reagents.

12.2.3.2 The analyte spike shall be added at 5.0 mg/L for aqueous/water samples, or at 1000 mg/kg for soil/sediment samples in the final sample.

12.2.3.3 Samples identified as field blanks or 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 selected 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 the %R.

12.2.4.2 Calculate the Matrix Spike %R using Equation 23 in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.2.5 Technical Acceptance Criteria for Matrix Spike Sample

The Matrix Spike %R must be within the control limits of 70-130%.

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).

Exhibit D - Section 12

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 70-130%, the data for all the 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 Spike Added (SA) concentration by a factor of four or more. In such an instance, the data shall be reported unflagged even if the %R does not meet the 70-130% recovery criteria.
- 12.2.6.2 If there is more than one Matrix Spike per matrix, per SDG, and 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

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 Duplicate sample analyses cannot be averaged for reporting.

12.3.3 Procedure for Duplicate Sample

12.3.3.1 Samples identified as field blanks or 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

The Relative Percent Difference (RPD) for each analyte shall be calculated using Equation 24B in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.3.5 Technical Acceptance Criteria for Duplicate Sample

12.3.5.1 The RPD must be within the control limits of $\pm 20\%$ if the original and Duplicate sample values are greater than or equal to five times the CRQL (see Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 10).

12.3.5.2 The control limit must 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 the samples received associated with that Duplicate sample with an "*".

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

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

12.4 Laboratory Control Sample

12.4.1 Summary of Laboratory Control Sample

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

12.4.2 Frequency of Laboratory Control Sample

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

12.4.3 Procedure for Laboratory Control Sample

The LCS for aqueous/water or soil/sediment samples shall be prepared by spiking an aliquot of reagent water (40 mL for aqueous/water, 0.5 mL for soil/sediment) such that the solution shall contain total organic carbon at two times the CRQL for the associated matrix.

12.4.4 Calculations for Laboratory Control Sample

12.4.4.1 Calculate the results for the LCS using Equation 4H or 5J in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.4.4.2 Calculate the %R for the LCS using Equation 26B in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.4.5 Technical Acceptance Criteria for Laboratory Control Sample

The %R must be within the control limits of 75-125%.

12.4.6 Corrective Action for Laboratory Control Sample

If the %R for the LCS for aqueous/water or soil/sediment samples is outside the control limits of 75-125%, the analyses shall be terminated, the problem corrected, and the samples associated with that LCS reprepared and reanalyzed with appropriate new QC.

12.5 Method Detection Limit Determination

12.5.1 Before any field samples are analyzed under the contract, the MDLs shall be determined for each preparation procedure, and for each instrument under the same conditions used for analysis, used prior to the start of contract analyses and verified annually thereafter. MDL determination is matrix specific (i.e., the MDL shall be determined for aqueous/water and soil/sediment samples). 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.

12.5.1.1 To determine the MDLs, the Contractor shall perform MDL studies following the procedures in Title 40 of the Code of Federal Regulations (CFR), Part 136, Appendix B, Revision 2.

12.5.1.2 The determined concentration of the MDL must be less than half the concentration of the CRQL listed in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 10.

12.5.1.3 The delivery requirements for the MDL values are specified in Exhibit B - Reporting and Deliverables Requirements, Table 1.

Exhibit D - Sections 12-16

12.6 Summary of Quality Control Operations

The QC operations performed for TOC analysis are summarized in Exhibit D - Total Organic Carbon, Table 1.

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

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

15.0 WASTE MANAGEMENT

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

16.0 REFERENCES

- 16.1 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste (SW-846), Method 9060A, Total Organic Carbon, Revision 1, November 2004.
- 16.2 U.S. Environmental Protection Agency, Region 2, Determination of Total Organic Carbon in Sediment (Lloyd Kahn Method), July 1988.
- 16.3 U.S. Environmental Protection Agency, Nation Exposure Research Laboratory, Office of Research and Development, Method 415.3, Determination of Total Organic Carbon and Specific UV Absorbance at 254 nm in Source Water and Drinking Water, Revision 1.2, September 2009.
- 16.4 Standard Methods for the Examination of Water and Wastewater, Method 5310 B, Total Organic Carbon Combustion Method.
- 16.5 Standard Methods for the Examination of Water and Wastewater, Method 5310 C, Total Organic Carbon Persulfate-Ultraviolet Oxidation Method.
- 16.6 Standard Methods for the Examination of Water and Wastewater, Method 5310 D, Total Organic Carbon Wet-Oxidation Method.
- 16.7 U.S. Government Printing Office, Title 40 of the Code of Federal Regulations, Chapter 1, Subchapter D, Part 136, Appendix B, Definition and Procedure for the Determination of the Method Detection Limit, Revision 2.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

TABLE 1. QC OPERATIONS FOR TOTAL ORGANIC CARBON ANALYSIS

QC Operation	Frequency
Instrument Calibration	Daily or each time instrument is turned on or set up, after ICV or CCV failure, after ICB or CCB failure, after LCS failure, and after major instrument adjustment.
Initial Calibration Verification	Following each instrument calibration.
Continuing Calibration Verification	At a frequency of every 10 samples 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	At a frequency of every 10 samples, 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.
Laboratory Control Sample	For each SDG or each sample preparation and analysis procedure per batch of prepared samples, 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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