EXHIBIT D

INTRODUCTION TO ANALYTICAL METHODS

Exhibit D - Analytical Methods

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1.0 INTRODUCTION

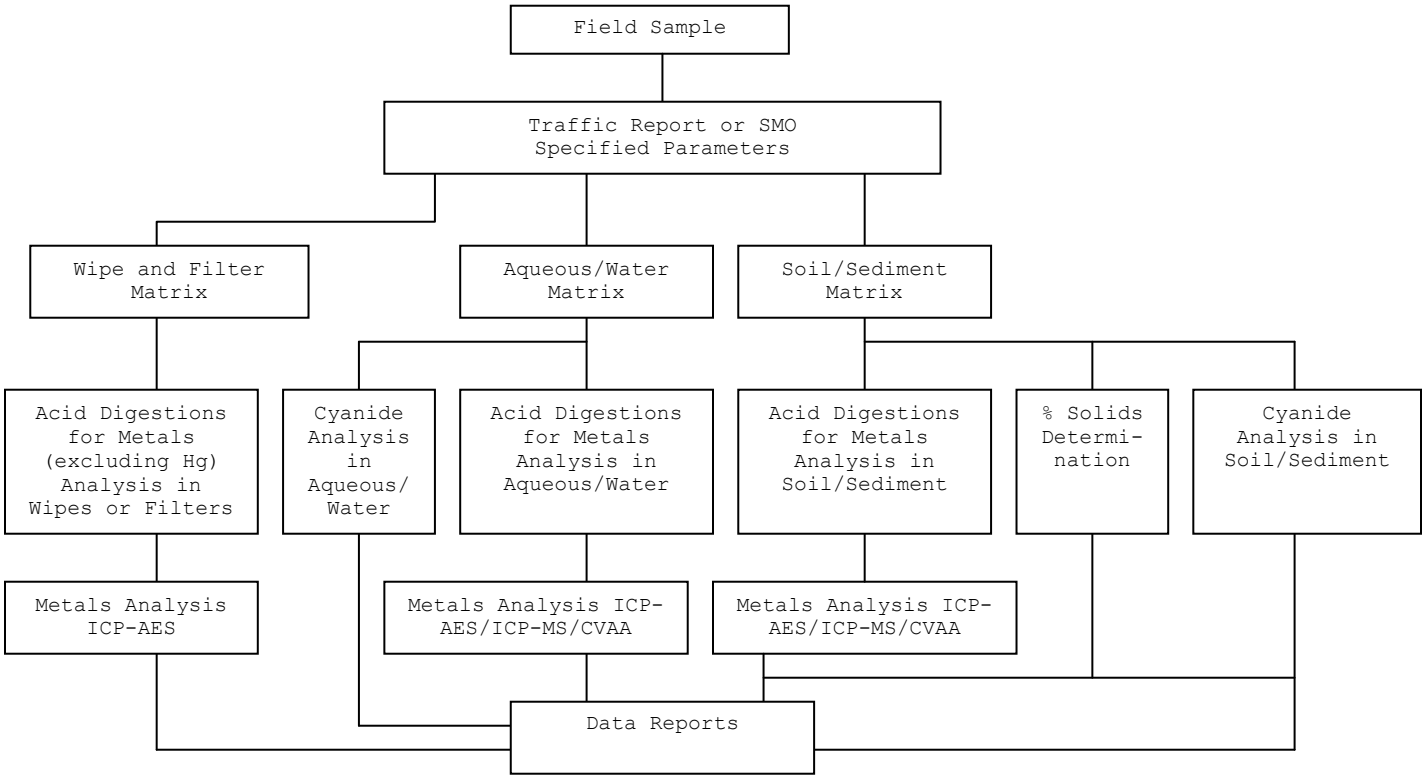
The inorganic analytical service provides a contractual framework for laboratories. This framework applies U.S. Environmental Protection Agency (USEPA) Contract Laboratory Program (CLP) analytical methods for the isolation, detection, and quantitative measurement of 23 metals (including mercury) and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

The analytical methods that follow are designed to analyze aqueous/water, soil/sediment, surface wipe, and air filter samples from hazardous waste sites for the presence of inorganic analytes contained on the Inorganic Target Analyte List (TAL) (see Exhibit C). The inorganic methods include alternative analysis procedures for some analytes, multiple preparation procedures, and Quality Control (QC) requirements. A default preparation method is provided for each matrix, with alternative methods available for USEPA Regional use. Analytical techniques in the inorganic methodologies include Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES), Inductively Coupled Plasma - Mass Spectrometry (ICP-MS), Cold Vapor Atomic Absorption Spectroscopy (CVAA), and Spectrophotometry.

1.1 Inorganic Methods Flow Chart

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

1.2 Figure 1 – Inorganic Methods Flow Chart



1.3 Glassware Cleaning

Lab glassware to be used within the metals analysis must be acid cleaned according to USEPA's manual, Methods for Chemical Analysis of Water and Wastes (EPA Manual 600479020) or an equivalent procedure. Equivalent procedures are those which meet the Preparation Blank requirements in the Statement of Work (SOW). An electronic version of this manual can be found via USEPA's National Environmental Publications Internet Site (NEPIS) at http://nepis.epa.gov/EPA/html/Pubs/pubtitleORD.htm (search on EPA Manual 600479020).

1.4 Standard Stock Solutions

Stock solutions to be used for preparing instrument or method standards may be purchased or prepared as described in the individual methods of Exhibit D, Section 7 (Reagents and Standards).

1.5 Verification of Aqueous/Water Sample Preservation

1.5.1 At the time of sample receipt, the Contractor shall check the pH of the sample and note in a sample receipt log if the pH is less than or equal to 2 for metals. In addition, it should be noted if the pH is greater than or equal to 12 for a cyanide sample. If a metals sample has not been properly preserved, the Contractor may adjust the pH of a sample for metals, allow time for the sample to equilibrate prior to digestion, and note this in the Sample Delivery Group (SDG) Narrative. The Contractor shall not adjust the pH of a sample for cyanide. If the pH of a cyanide sample is <12, contact the Sample Management Office (SMO) for further instructions before proceeding with the preparation and analysis. The determination of pH for soil/sediment samples is not required.

1.5.2 Before preparation is initiated for an aqueous/water cyanide sample, the Contractor shall test for the presence of sulfides and oxidizing agents (e.g., residual chlorine). The test for sulfides shall be performed by placing a drop of the sample on a strip of lead acetate paper. If the test strip turns black, the Contractor shall treat the total volume of sample with powdered cadmium carbonate. Yellow cadmium sulfide precipitates when the sample contains sulfide. This operation shall be repeated until a drop of the treated sample solution does not darken the lead acetate test paper. The solution shall be filtered through a dry filter paper into a dry beaker, and the volume of sample to be used for analysis shall be measured from the filtrate. It is recommended that the Contractor avoid a large excess of cadmium carbonate and a long contact time in order to minimize a loss by complexation or occlusion of cyanide on the precipitated material. The test for oxidizing agents shall be performed by placing a drop of the sample on a strip of potassium iodide - starch test paper (KI - starch paper). If the test strip turns blue, the Contractor shall contact SMO for further instructions from the Region before proceeding with sample preparation and analysis. The Contractor shall document the presence of sulfides or oxidizing agents in the SDG Narrative.

1.6 Percent Solids Determination Procedure

1.6.1 Immediately following the weighing of the sample to be processed for analysis, add 5-10 g of sample to a tared disposable weigh boat. Weigh and record the weight to the nearest 0.01 g.

1.6.2 Place weigh boat plus sample, with the cover tipped to allow for moisture escape, in a drying oven maintained at 105°C (±5°C). Sample handling and drying should be conducted in a well-ventilated area.

1.6.3 Dry the sample overnight (12-24 hours) but no longer than 24 hours. If dried less than 12 hours, it must be documented that constant weight was attained.[1] Remove the sample from the oven and cool in a desiccator with the weigh boat cover in place before weighing. Weigh and record weight to nearest 0.01 g. Do not analyze the dried sample. Calculate percent solids by the formula below. The value thus obtained will be reported on the appropriate Forms IA-IN and IB-IN and, where applicable, Forms VA-IN and VI-IN. This value will be used for calculating analytical concentration on a dry weight basis.

EQ. 1 Percent Solids

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

1.6.4 If the sample contains less than 50% solids, the Contractor shall notify SMO immediately of the samples impacted. After notification to SMO, the Contractor shall proceed with sample analysis and document the issue in the SDG Narrative except as noted below.

1.6.5 For 14- and 21-day turnaround samples without Preliminary Results, the Contractor is required to perform the percent solids determination prior to sample preparation and analysis. Samples containing percent solids less than or equal to 30% are required to be prepared at higher sample weights to yield a dry weight equivalent to the weight range specified in the preparation method. Calculate the required sample weight by dividing the minimal method weight by the percent solids expressed as a decimal. This requirement does not apply to 7-day turnaround or Preliminary Results samples.

EQ. 2 Required Sample Weight

$$\text{Req. Wt} = \frac{\text{Minimal Method Wt}}{\%\text{Solids}/100}$$

1.7 Insufficient Sample Volume

If insufficient sample volume (less than the required amount) is received to perform the analysis, the Contractor shall contact SMO

[1] Drying time is defined as the elapsed time in the oven; thus raw data must record the time in and out of the oven to document the 12-hour drying time minimum. In the event it is necessary to demonstrate the attainment of constant weight, data must be recorded for a minimum of two repetitive weigh/dry/desiccate/weigh cycles with a minimum of 1-hour drying time in each cycle. Constant weight would be defined as a loss in weight of no greater than 0.01 g between the start weight and final weight of the last cycle.

to apprise them of the problem. SMO will contract the USEPA Region for instructions. The Region will either approve that no sample analysis be performed or will require that a reduced volume be used for the sample analysis. No other changes in the analysis will be permitted. SMO will notify the Contractor of the Region's decision. The Contractor shall document the Region's decision in the SDG Narrative.

1.8 Sample Mixing

Unless instructed otherwise by the USEPA Regional CLP Project Officer (CLP PO), all samples shall be mixed thoroughly prior to aliquoting for digestion. There is no specific procedure provided herein for homogenization of soil/sediment samples; however, an effort should be made to obtain a representative aliquot. Coarse stones, twigs, or debris that are not representative of the soil/sediment should be excluded from the aliquot. For multi-phase samples, see Exhibit D, Section 10.1.

1.9 Undiluted Analysis

1.9.1 Unless the dilution-adjusted detection limits for all analytes are below the Contract Required Quantitation Limits (CRQLs), all samples for multi-analyte analysis shall be run undiluted. When an analyte concentration exceeds the calibrated range, appropriate dilution (but not below the CRQL) and re-analysis is required. The Contractor shall use the least dilution necessary to bring the analyte(s) instrument reading within the upper 75% of the calibrated range and report the highest valid value for each analyte as measured from the undiluted and diluted analyses. Unless the Contractor can submit proof that dilution was required to obtain valid results, or to avoid damage to ICP-MS instruments, both diluted and undiluted sample measurements must be contained in the raw data.

1.9.2 For single analyte analysis, a diluted sample analysis may be the only sample analysis performed if the analyte's instrument result is in the upper 75% of the calibrated range. An undiluted sample analysis does not have to be performed in this case. The sample and its associated matrix spike and duplicate shall initially be run at the same dilution.

1.9.3 All sample dilutions shall be made with reagent water appropriately acidified (except for cyanide) to maintain constant acid strength.

1.10 Dissolved Metals

For samples filtered in the field, the Contractor shall digest the samples designated as dissolved metals. If dissolved metals are requested by USEPA Regional Offices, the Contractor shall digest the field-filtered samples designated as dissolved metals. Only if requested as a Modified Analysis shall the Contractor filter samples prior to digestion or perform direct analysis.

1.11 Replicate Integrations/Exposures

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

1.12 Raw Data Requirements

The Contractor is reminded and cautioned that the collection and provision of raw data may or may not be referred to within the individual methods of Exhibit D or the Quality Assurance (QA) protocol of Exhibit E. The raw data deliverable requirements are specified in Exhibit B, Section 2.5.2.3. Raw data collected and provided in association with the performance of analyses under this contract shall conform to the appropriate provisions of Exhibit B.

1.13 Quality Control Samples

If the Sampler designated two (or more) samples as QC for the same matrix, and the QC samples are not specifically labeled with the analysis they are to be used for (dissolved metals and total metals), then the Contractor is to contact SMO to report the issue. SMO shall then contact the USEPA Region and notify the Contractor of the Regional decision. If the Sampler did not designate QC samples, then the Contractor is to select a sample for QC and to contact SMO to report the issue.

1.14 Safety

The toxicity or carcinogenicity of each reagent used in this SOW has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of chemicals specified in this method. A reference file of material handling data sheets should also be made available to all personnel involved in the chemical analysis.

1.15 Pollution Prevention

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

1.16 Waste Management

USEPA requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. USEPA urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions.

EXHIBIT D - PART A

ANALYTICAL METHODS
FOR
INDUCTIVELY COUPLED PLASMA -
ATOMIC EMISSION SPECTROSCOPY

Exhibit D – Analytical Methods for ICP-AES

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1.0 SCOPE AND APPLICATION

This method provides procedures for the use of Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) to determine the concentrations of total recoverable and dissolved elements in aqueous/water, soil/sediment, surface wipe, and air filter samples taken from hazardous waste sites. All metals (except mercury) contained in the Inorganic Target Analyte List (TAL) in Exhibit C 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 Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES). Aqueous/water, soil/sediment, wipe, and air filter samples are treated with acids and heat to solubilize the metals present. These digestates are then analyzed for trace metals by an atomic emission optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to a plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed and the intensities of the lines are monitored by a photosensitive device. The signals from the photosensitive device are processed by a computer. A background correction technique is required to compensate for variable background contribution to the spectra of trace elements. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result.

2.2 Summary of Digestion Procedures

2.2.1 Hotplate Acid Digestion of Aqueous/Water Samples (based on USEPA 200.7)

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

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

2.2.4 Hotplate Acid Digestion of Filter Samples (based on a modified version of NIOSH 7300)

2.2.5 Alternative digestion procedures are included in Section 18 of this Exhibit.

3.0 DEFINITIONS

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

4.0 INTERFERENCES

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

4.1 Spectral Interferences

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

4.2 Physical Interferences

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

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

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

4.3 Chemical Interferences

Chemical interferences are characterized by molecular compound formation, ionization effects, and solute vaporization effects. Normally these effects are not pronounced with the Inductively Coupled Plasma - Atomic Emission Spectroscopy (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 1.14 in Exhibit D - Introduction to Analytical Methods.

6.0 EQUIPMENT AND SUPPLIES

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

6.1 Glassware/Labware

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

6.1.2 Watch glasses (glass or plastic)

6.1.3 Funnels

6.1.4 Graduated cylinders

6.1.5 Various volumetric flasks and pipets (Class A)

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

6.1.7 Whatman No. 41 filter paper (or equivalent)

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

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

6.2 Equipment and Supplies for Microwave Digestion

The equipment and supplies listed in this section are used if one of the alternate microwave sample preparation procedures was approved for use by the USEPA Region.

6.2.1 Whatman No. 41 filter paper (or equivalent)

6.2.2 Disposable polypropylene filter funnel

6.2.3 Polyethylene bottles, 125 mL, with caps

6.2.4 Microwave oven with programmable power settings up to at least 600 watts.

6.2.5 The system must use polytetrafluoroethylene perfluoroalkoxy (PTFE PFA) digestion vessels (120 mL capacity) capable of withstanding pressure of up to 110 (±10) psi [7.5 (±0.7) atm]. These vessels are capable of controlled pressure relief at pressures exceeding 110 psi.

6.2.6 A rotating turntable must be used to ensure homogeneous distribution of microwave radiation within the oven. The speed of the turntable must be a minimum of 3 revolutions per minute (rpm).

6.3 Inductively Coupled Plasma - Atomic Emission Spectrometer (ICP-AES)

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

7.0 REAGENTS AND STANDARDS

7.1 Reagents

7.1.1 Reagent water - The purity of this water must be equivalent to ASTM Type II water (ASTM D1193-06). Use this water for all reagents, standards, and dilutions.

7.1.2 Hydrochloric acid - Concentrated (specific gravity 1.19).

7.1.3 Hydrochloric acid, (50% v/v) - Add 500 mL conc. hydrochloric acid (specific gravity 1.19) to 400 mL reagent water and dilute to 1 L.

7.1.4 Nitric acid - Concentrated (specific gravity 1.41).

7.1.5 Nitric acid, (50% v/v) - Add 500 mL conc. nitric acid (specific gravity 1.41) to 400 mL reagent water and dilute to 1 L.

7.1.6 Hydrogen peroxide (30%)

7.1.7 Nitric acid, (5% v/v) - Add 50 mL conc. nitric acid (specific gravity 1.41) to 500 mL reagent water and dilute to 1 L.

7.2 Standards

7.2.1 Introduction

The Contractor must provide all standards, except as noted, to be used with this contract. These standards may be used only after they have been certified according to the procedure in Exhibit E, Section 8.0. The Contractor must be able to verify that the standards are certified. Manufacturer's certificates of analysis must be retained by the Contractor and presented upon request.

7.2.2 Stock Standard Solutions

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

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

7.2.3 Secondary Dilution Standards

7.2.3.1 Mixed Secondary Dilution Standards

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

7.2.4 Working Standards

7.2.4.1 Interference Check Sample (ICS) Solution

The ICS consists of two solutions: Solution A (ICSA) and Solution AB (ICSAB). ICSA consists of the interferents and ICSAB consists of the analytes mixed with the interferents. The ICS standards (ICSA for the interferents only and ICSB for the analytes only) are normally supplied by USEPA.

7.2.4.2 Mixed Calibration Standard Solutions

7.2.4.2.1 Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks. Add 2 mL of nitric acid and dilute to 100 mL with reagent water or these standards can be matrix matched to the digested samples. The analyte concentrations in the calibration standards should be sufficient to produce good measurement precision and to accurately define the slope of the response curve. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards that the analytes are compatible and stable. Transfer the mixed standard solutions to fluorinated ethylene propylene (FEP) fluorocarbon or unused polyethylene bottles for storage. Fresh mixed standards should be prepared as needed with the realization that concentration can change with aging.

7.2.4.2.2 Protect all standards from light. Samples, sample digestates, and standards must be stored separately.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Sample Collection and Preservation

All aqueous/water and soil/sediment samples must be collected in glass or polyethylene containers. Aqueous/water samples must be preserved with nitric acid to pH less than or equal to 2 immediately after collection. All aqueous/water and soil/sediment samples must be iced or refrigerated at 4°C (±2°C) from the time of collection until digestion. Wipes and air filter samples shall remain in their original bags or cassettes until preparation and may be stored at room temperature within the laboratory.

8.1.1 Dissolved Metals

For the determination of dissolved metals, the sample must be filtered through a 0.45 micrometer (µm) pore diameter membrane filter at the time of collection or as soon as possible. Use a portion of the sample to rinse the filter flask, discard this portion, and collect the required volume of filtrate. Preserve the filtrate with nitric acid to pH less than or equal to 2 immediately after filtration.

8.2 Procedures for Sample Storage and Disposal

Following digestion, the remaining unused portion of aqueous/water and soil sediment samples may be stored at room temperature within the laboratory until 60 days after delivery of a complete, reconciled data package to USEPA. After 60 days, the samples may be disposed of in a manner that complies with all applicable regulations.

8.3 Procedure for Sample Digestate Storage

Sample digestates must be stored until 6 months after delivery of a complete, reconciled data package to USEPA.

8.4 Contract Required Holding Time

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

9.0 CALIBRATION AND STANDARDIZATION

9.1 Instrument Operating Parameters

Because of the differences between various makes and models of satisfactory instruments, no detailed operating instructions can be provided. Instead, the analyst should follow the instructions provided by the manufacturer of the particular instrument. The Method Detection Limit (MDL), precision, and interference effects must be investigated and established for each individual analyte line on that particular instrument. All measurements used to determine interelement corrections must be within the instrument operating range. It is the responsibility of the analyst to verify the instrument configuration and operating conditions used satisfy the analytical requirements and to maintain Quality Control (QC) data confirming instrument performance and analytical results.

9.2 Inductively Coupled Plasma - Atomic Emission Spectrometer (ICP-AES) Instrument Calibration Procedure

9.2.1 Instruments shall be calibrated each time the instrument is turned on, set up, or after Initial Calibration Verification (ICV) or Continuing Calibration Verification (CCV) failure. The instrument standardization date and time shall be included in the raw data.

9.2.2 The calibration standards shall be prepared as in Section 7.2.4.2.

9.2.3 Calibrate the ICP-AES instruments according to instrument manufacturer's recommended procedures. At least six standards shall be used for ICP-AES calibration. One of the standards shall be a blank standard and one shall be at or below the Contract Required Quantitation Limit (CRQL). The rest of the standards shall be uniformly spread out in graduated amounts over the appropriate calibration range for each metal. A minimum of three replicate integrations are required for data acquisition. Use the average of all the integrations for instrument calibration and data reporting. 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 corrected instrument response on the Y-axis. The corrected instrument response are those corrections (e.g., such as correction for background, internal standards, Interelement Corrections (IECs), calibration blank) that may be applied to the raw uncorrected instrument response prior to determining the calibration curve. A standard linear regression, a weighted linear regression (e.g., 1/concentration or 1/concentration^2), or a linear regression with zero force calibration model can be used as appropriate. No other types of equations (e.g., quadratic) are to be used. The acceptance criteria for the calibration curve is a correlation coefficient greater than or equal to 0.995. Sample analysis shall not begin until this criteria and the criteria described in Sections 9.2.4 and 9.2.5 have been met.

9.2.4 The calibration equation must be checked to establish the representativeness of the data that were used to produce the calibration equation. This check involves the re-fitting of the non-blank calibration data back to the calibration equation or the comparison of the calculated concentration of each of the standards against the expected concentration of the associated standard. This difference is related to the actual residual. For this calculation, the Percent Difference shall be used where the above difference is

further divided by the expected amount or concentration of the respective standard. If these Percent Differences for each of the standards do not fall within ±30%, then the calibration equation is not acceptable and must be corrected. If a standard is analyzed for a particular analyte at a concentration that is below the CRQL and the above criteria is not met, that value can be excluded from the calibration equation as long as the lowest non-zero standard for each of the remaining standards for each analyte is still analyzed at or below the CRQL and all standards included in the calibration equation are continuous and consecutive.

9.2.5 The y-intercept from the linear regression initial calibration equation shall also be evaluated. If the y-intercept is not below the CRQL for each of the analyte initial calibration curves, the calibration is not acceptable and must be corrected. Samples are not to be analyzed until the y-intercept for each analyte's initial calibration curve meets the acceptance criteria.

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

9.3 Initial Calibration Verification (ICV)

9.3.1 Immediately after each instrument has been calibrated, the accuracy of the initial calibration shall be verified and documented for every analyte by the analysis of the ICV solution(s) at each wavelength used to report final results. The percent Relative Standard Deviation (%RSD) shall also be calculated from all replicate integrations and reported for each wavelength used to report final results.

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

9.3.3 The ICV solution(s) shall be run at each wavelength used for reporting final results.

9.4 Continuing Calibration Verification (CCV)

To ensure calibration accuracy during each analytical run sequence, a CCV shall be analyzed and reported for every wavelength used for reporting final results for each analyte, at a frequency not to exceed every 2 hours during an analytical run sequence. The standard shall be analyzed and reported for every wavelength used for reporting final results for each analyte at the beginning of the analytical run sequence and after the last analytical sample. The %RSD shall be calculated from all integrations and reported for each wavelength used to report final results. See the example analytical run sequence in Section 12.11. This analytical run sequence can continue indefinitely as long as samples are being continuously analyzed without the instrument being turned off and successive CCVs and their associated %RSDs meet the stated criteria. This CCV standard(s) shall be prepared from the same source and at or near the same mid-level concentration as used during the initial calibration.

The same CCV standard shall be used throughout the analytical run sequences for a Sample Delivery Group (SDG) of samples received.

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

9.5 Initial and Continuing Calibration Blank (ICB/CCB)

An ICB or CCB shall be analyzed at each wavelength used for reporting final results for each analyte immediately after every ICV and CCV.

10.0 PROCEDURE

10.1 Sample Preparation

10.1.1 If insufficient sample amount (less than 90% of the required amount) is received to perform the analyses, the Contractor shall contact the Sample Management Office (SMO) to inform them of the problem. SMO will contact the USEPA Region for instructions. The USEPA Region will either require that no sample analyses be performed or will require that a reduced volume be used for the sample analysis. No other changes in the analyses will be permitted. The Contractor shall document the USEPA Region's decision in the Sample Delivery Group (SDG) Narrative.

10.1.2 If multiphase samples (e.g., two-phase liquid sample, oily sludge/sandy soil/sediment sample) are received by the Contractor, the Contractor shall contact SMO to apprise them of the type of sample received. SMO will contact the USEPA Region. If all phases of the sample are amenable to analysis, the USEPA Region may require the Contractor to do any of the following:

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

10.1.2.1 If all of the phases are not amenable to analysis (i.e., outside scope), the USEPA Region may require the Contractor to do any of the following:

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

10.1.2.2 No other changes in the analyses will be permitted. The Contractor shall document the USEPA Region's decision in the SDG Narrative.

10.1.3 The primary sample preparation procedures to be used for this method are described in the following Sections (10.1.4, 10.1.5, 10.1.6, and 10.1.7). These methods are to be used without deviation. Alternative sample preparation procedures are listed in Section 18 of this method and may be requested by the USEPA Region. No other changes in the analyses will be permitted.

10.1.4 Aqueous/Water Sample Preparation

10.1.4.1 Preparation Method 200.7 - Total Recoverable Analytes [based on USEPA NERL Method 200.7, Revision 4.4 (1994)]

10.1.4.1.1 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) beaker or other comparable digestion vessel. The sample shall not be diluted prior to digestion.

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

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

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

10.1.4.1.5 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.

10.1.4.1.6 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. 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.

10.1.4.1.7 The concentrations as determined by this method shall be reported as "Total". 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. The digested sample can be diluted if high levels of interferences are noted or if any of the analytes exceed the upper limit of their respective calibration curves.

10.1.5 Soil/Sediment Sample Preparation

10.1.5.1 Preparation Method 3050B (based on USEPA OSW Method 3050B, Revision 2, December 1996)

10.1.5.1.1 Mix the sample thoroughly to achieve homogeneity (see Exhibit D - Introduction to Analytical Methods, Section 1.8). For each digestion procedure, weigh to the nearest 0.01 g and transfer 1.00 – 1.50 g sample (wet weight) to an appropriately sized digestion vessel (e.g., a beaker or hot block digestion tube).

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

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

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

10.1.5.1.5 Filter the sample digestate through Whatman No. 41 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. The sample is now ready for analysis.

10.1.5.1.6 The digested sample can be diluted if high levels of interferences are noted or if any of the analytes exceed the upper limit of their respective calibration curves.

10.1.6 Wipe Sample Preparation

10.1.6.1 Preparation Method 3050B [based on USEPA OSW Method 3050B, Revision 2 (December 1996)]

10.1.6.1.1 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.

10.1.6.1.2 Follow the procedure as described in Sections 10.1.5.1.2 through 10.1.5.1.6.

10.1.7 Filter Sample Preparation

10.1.7.1 Preparation Method 7300 (based on a modified version of NIOSH method 7300 from the Fourth Edition of the NIOSH Manual of Analytical Methods, Issue 3, dated 15 March 2003). This procedure is for small (e.g., 37 mm MCEF) filters. The method is not suitable for high-volume filters.

10.1.7.1.1 The method was modified by removing the use of all perchloric acid during the sample preparation due to safety issues. If the Contractor has the necessary equipment to safely work with and perform perchloric acid digestions, then the Contractor should contact SMO. SMO will then contact the USEPA Region and decide if this modified method or the original method should be used for the samples within this specific SDG.

10.1.7.1.2 Remove the filter from the cassette and transfer to a 50 mL beaker.

10.1.7.1.3 Add 3 mL of concentrated nitric acid and 1 mL of 30% of hydrogen peroxide and cover with a watch glass. Heat the sample to 95°C (±3°C) on a hotplate, block digester, or equivalent heat source and reflux until the volume has been reduced to approximately 0.5 mL.

10.1.7.1.4 Rinse the watch glass and the sides of the beaker with 3 mL of 5% (v/v) nitric acid and heat until the sample volume has been reduced to approximately 0.5 mL.

10.1.7.1.5 Add 1 mL of concentrated hydrochloric acid and heat for 10 minutes at 95°C (±3°C). Allow the sample to cool.

10.1.7.1.6 Adjust the final volume to 10.0 mL (±0.1 mL) with reagent water. The sample may be filtered to remove solid particles. The sample is now ready for analysis.

10.2 Sample Analysis

10.2.1 For every new or unusual matrix, 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.

10.2.2 Set up the instrument with proper operating parameters established in Section 9.1. The instrument must be allowed to become thermally stable before beginning. This usually requires at least 30 minutes of operation prior to calibration.

10.2.3 Initiate appropriate operating configuration of the computer.

10.2.4 Profile and calibrate the instrument according to instrument manufacturer's recommended procedures. The initial calibration curve shall be established using mixed calibration standard solutions such as those described in Section 7.2.4.2.

10.2.5 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.

10.2.6 The rinse blank should be used to flush the system between samples. Allow sufficient time to remove traces of the previous sample. Samples should be aspirated for a sufficient period of time to obtain a stable response prior to collection of data.

10.2.7 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.

11.0 DATA ANALYSIS AND CALCULATIONS

11.1 Aqueous/Water Sample Calculation

EQ. 1 Aqueous/Water Sample Concentration

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

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

11.2 Soil/Sediment Sample Calculation

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

EQ. 2 Soil/Sediment Sample Concentration

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

WHERE,
- C = Instrument value in µg/L (The average of all replicate exposures)
- V_f = Final digestion volume (mL)
- W = Initial aliquot amount (g)
- S = % Solids/100 (see Exhibit D - Introduction to Analytical Methods, Section 1.6)
- DF = Dilution Factor

11.3 Adjusted Method Detection Limit (MDL)/Adjusted Contract Required Quantitation Limit (CRQL) Calculation

To calculate the adjusted MDL or adjusted CRQL for aqueous/water samples, multiply the value of the MDL or CRQL (µg/L) by the sample dilution factor and the V_f/V term as noted in Equation 1.

Calculate the adjusted MDL or adjusted CRQL for soil/sediment samples as follows:

EQ. 3 Adjusted Soil/Sediment MDL or CRQL Concentration

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

WHERE,
- C = MDL or CRQL Concentration (mg/kg)
- W_M = Minimum method required aliquot amount (g) (1.00 g or 0.50 g)
- W = Initial aliquot amount (g)
- V_M = Method required final sample digestion volume (mL) (100 mL or 50 mL)
- V_f = Final digestion volume (mL)
- S = % Solids/100 (see Exhibit D - Introduction to Analytical Methods, Section 1.6)
- DF = Dilution Factor

11.4 Wipe/Filter Mass

EQ. 4 Wipe/Filter Mass

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

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

12.0 QUALITY CONTROL (QC)

12.1 Initial Calibration Verification (ICV)

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. If measurements exceed the control limits of 90% Recovery (low) or 110% Recovery (high), or if the percent Relative Standard Deviation (%RSD) as calculated from all replicate exposures exceeds 5.0%, the analysis shall be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified. The results of the ICV analysis shall be reported.

12.2 Continuing Calibration Verification (CCV)

The CCV standard shall be prepared in the same acid matrix as the calibration standards by combining compatible analytes at a concentration equivalent to the mid-levels of their respective calibration curves. If the measurements exceed the control limits specified of 90% Recovery (low) or 110% Recovery (high), or if the %RSD as calculated from all replicate exposures exceeds 5.0%, the analysis shall be stopped, 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. The results of all CCV analyses shall be reported.

12.3 Blank Analyses

There are two different types of blanks required by this method. The calibration blank is used in establishing the analytical curve. The Initial and Continuing Calibration Blanks (ICB/CCB) are identical in composition to the calibration blank and are analyzed immediately after the ICV/CCV to monitor for potential carryover of analytes. The Preparation Blank is used to monitor for possible contamination throughout the entire sample preparation and analysis process.

12.3.1 Initial and Continuing Calibration Blank (ICB/CCB)

The ICB and CCB are identical in composition to the Calibration Blank as used to establish the initial calibration curve. If the absolute value of the calibration blank (ICB/CCB) result exceeds the Contract Required Quantitation Limit (CRQL) (see Exhibit C), 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 blank shall be performed for the analytes affected. The results of the ICB and CCB analyses shall be reported.

12.3.2 Preparation Blank

12.3.2.1 The Preparation Blank shall contain all the reagents and in the same volumes as used in processing 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.

12.3.2.2 At least one Preparation Blank, consisting of reagent water, a clean wipe, or a clean air filter, processed through each sample preparation and analysis procedure (see Section 10), shall be prepared and analyzed with every Sample Delivery Group (SDG), or with each batch[1] of samples digested, whichever is more frequent. For wipes and filters, the sampler should provide clean wipes or filters. In the event that they are not provided by the sampler, the Contractor shall use reagent water and note this in the SDG Narrative.

12.3.2.3 The first batch of samples in an SDG is to be assigned to Preparation Blank one, the second batch to Preparation Blank two, etc. Each Complete SDG File (CSF) shall contain the results of all Preparation Blank analyses associated with the samples in that SDG.

12.3.2.4 The Preparation Blank(s) is (are) to be reported for each SDG and used in all analyses to ascertain whether sample concentrations reflect contamination in the following manner:

12.3.2.4.1 If the absolute value of the concentration of the blank is less than or equal to the CRQL (see Exhibit C), no further action is required.

12.3.2.4.2 For aqueous/water and soil/sediment samples, if any analyte concentration in the blank is above the CRQL, the lowest concentration of that analyte in the associated samples (except those identified as field blanks) shall be greater than or equal to 10 times the blank concentration. Otherwise, all samples (except those identified as field blanks) associated with the blank, with the analyte concentration less

[1] A group of samples prepared at the same time.

than 10 times the blank concentration and above the CRQL, shall be redigested and reanalyzed with appropriate new Quality Control (QC) for that analyte. The sample concentration is not to be corrected for the blank value.

12.3.2.4.3 For aqueous/water and soil/sediment samples, if the concentration of the blank is below the negative CRQL, then all samples reported below 10 times the CRQL associated with the blank shall be redigested and reanalyzed with appropriate new QC.

12.3.2.4.4 The results for the Preparation Blank shall be reported.

12.4 Interference Check Sample (ICS)

12.4.1 The ICS solutions shall be obtained from USEPA. If not available, then the ICS can be prepared by the analyst.

12.4.2 To verify interelement and background correction factors, the Contractor shall analyze and report the results for the ICS for all elements on the Target Analyte List (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. The ICS solutions shall be obtained from USEPA, if available, and analyzed according to the instructions supplied with the ICS. The Contractor shall always initially run the ICS undiluted. Dilution of the ICS (for the highest concentration elements) may be necessary to meet the calibrated range values of the instrument.

12.4.3 The ICS consists of two solutions: Solution A and Solution AB. Solution A consists of the interferents; Solution AB consists of the analytes mixed with the interferents. Even though no analytes have been added to Solution A, low levels of some of the analytes may be present due to the purity of the materials used. An ICS analysis consists of analyzing both solutions consecutively, starting with Solution A.

12.4.4 The analytical results of ICS Solution A (ICSA) shall fall within the control limit of ±20% of the analyte's true value or ±1 times the CRQL of the analyte's true value, whichever is greater. If the true value for a given analyte is not listed in the certified values for the solution, then the true value shall be assumed to be zero and the ±1 times the CRQL control limits shall apply. For example, for Chromium (CRQL = 10 µg/L, ICSA true value = 43 µg/L) the correct control window to use would be the greater of ±20% of the true value (0.20 x 43 µg/L = ±8.6 µg/L) or ±1 times the CRQL (±10 µg/L). Therefore, the control window for the found value for Chromium in the ICSA is 43±10, or 33 to 53 µg/L. If the analytical results of the ICSA do not fall within the control limits, the analysis shall be terminated, the problem corrected, and the instrument recalibrated. New Interelement Corrections (IECs) may also need to be determined for the failed analyte(s). For analytes with CRQLs less than 1000 µg/L, the ICSA results shall be reported from an undiluted sample analysis.

12.4.5 Results for the ICS Solution AB (ICSAB) during the analytical runs shall fall within the control limit of ±20% of the true value or ±1 times the CRQL of the true value, whichever is greater, for the analytes included in the ICSAB. If the analytical results of the ICSAB do not fall within the control limits, the analysis shall be

terminated, the problem corrected, and the instrument recalibrated. New IEC's may also need to be determined for the failed analyte(s). For analytes with CRQLs less than 1000 µg/L, the ICSAB shall be reported from an undiluted sample analysis.

NOTE: The control limits and concentrations for the ICSAB are being monitored. These may be adjusted to provide greater control of interferences.

12.4.6 If true values for analytes contained in the ICS are not supplied with the solutions, the mean shall be determined by initially analyzing the ICS at least five times repetitively for the particular analytes. This mean determination shall be made during an analytical run where the results for the previously supplied ICS met all contract specifications. Additionally, the results of this initial mean determination shall be used as the true value for the lifetime of that solution (i.e., until the solution is exhausted). Only if the ICS solutions are not available from USEPA, independent Check Samples shall be prepared with interferent and analyte concentrations at the levels specified in Table 1 - Interferent and Analyte Elemental Concentrations Used for ICP-AES Interference Check Sample (ICS). The mean value and standard deviation shall be established by initially analyzing the Check Samples at least five times repetitively for each parameter. Results shall fall within the control limit of ±20% of the established mean value or ±1 times the analyte's CRQL of the established mean value, whichever is greater. The mean and standard deviation shall be reported in the raw data.

12.4.7 The results of ICS analyses shall be reported.

12.5 Spike Sample Analysis

12.5.1 The spike sample analysis is designed to provide information about the effect of the sample matrix on the digestion and/or measurement methodology. The spike is added before the digestion (i.e., prior to the addition of other reagents). At least one spike sample analysis (matrix spike) 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.[2] Spike sample analysis is not required for wipe samples or air filter samples.

12.5.2 If the spike analysis is performed on the same sample that is chosen for the duplicate sample analysis, spike calculations shall be performed using the results of the sample designated as the "original sample" (see Section 12.6). The average of the duplicate results cannot be used for the purpose of determining percent recovery. Samples identified as field blanks and Performance Evaluation (PE) samples shall not be used for spiked sample analysis. USEPA may require that a specific sample be used for the spike sample analysis.

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

NOTE: See Table 2 footnotes for concentration levels and applications.

[2] USEPA may require additional spike sample analyses, upon USEPA Regional CLP Project Officer (CLP PO) request.

12.5.4 If the spike recovery is not at or within the limits of 75-125%, the data for all samples received and associated with that spike sample shall be flagged with the letter "N". 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 event, the data shall be reported unflagged even if the percent recovery does not meet the 75-125% recovery criteria.

12.5.5 When the matrix spike recovery falls outside the control limits and the sample result does not exceed four times the spike added, a post-digestion spike shall be performed for those analytes that do not meet the specified criteria (exception: Ag). Note that if a post-digestion spike analysis is required for an analyte, the same EPA sample that was used for the matrix spike analysis shall be used for the post-digestion spike analysis. Spike the unspiked aliquot of the undiluted digestate at two times the indigenous level or two times the CRQL, whichever is greater.

12.5.6 In the instance where there is more than one spike sample per matrix per SDG, if one spike sample recovery is not within contract criteria, then flag all the samples of the same matrix and method in the SDG. Individual component percent recoveries are calculated as follows:

EQ. 5 Matrix Spike and Post-Digestion Spike Percent Recovery

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

WHERE, SSR = Spiked Sample Result (µg/L or mg/kg) from EQ. 1 or EQ. 2
SR = Sample Result (µg/L or mg/kg) from EQ. 1 or EQ. 2
SA = Spike Added Theoretical Result (µg/L or mg/kg). This is calculated by substituting the spiking amount used for the 'V_f' term and substituting the spiking standard concentration used for the 'C' term from EQ. 1 or EQ. 2.

12.5.7 When sample concentration is less than the Method Detection Limit (MDL), use SR = 0 only for purposes of calculating the percent recovery. The Spike Sample Results (SSRs), Sample Results (SRs), Spike Added Theoretical Results (SA), and percent recovery (positive or negative) shall be reported.

12.5.8 The units used for reporting Spiked Sample Results (SSRs) will be identical to those used for reporting Sample Results (SRs).

12.6 Duplicate Sample Analysis

12.6.1 One duplicate sample shall be analyzed from each group of samples of a similar matrix type (i.e., aqueous/water, soil/sediment) or for each SDG, whichever is more frequent.[3] Duplicates cannot be averaged for reporting. Duplicate samples are not required for wipe samples or air filter samples.

[3] USEPA may require additional duplicate sample analyses, upon USEPA Regional CLP PO request.

12.6.2 Duplicate sample analyses are not required for percent solids. Samples identified as field blanks and PE samples shall not be used for duplicate sample analysis. USEPA may require that a specific sample be used for duplicate sample analysis. The Relative Percent Difference (RPD) for each analyte is calculated as follows:

EQ. 6 Duplicate Sample Relative Percent Difference

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

WHERE, RPD = Relative Percent Difference
S = Sample Result (original) (µg/L or mg/kg) from EQ. 1 or EQ. 2
D = Duplicate Sample Result (µg/L or mg/kg) from EQ. 1 or EQ. 2

12.6.3 The results of the duplicate sample analyses shall be reported. A control limit of 20 for RPD shall be used for original and duplicate sample values greater than or equal to five times the CRQL (see Exhibit C). A control limit equal to the CRQL shall be entered in the "Control Limit" column if either the sample or duplicate value is less than five times the CRQL. If the sample and duplicate values are greater than or equal to five times the CRQL, or if the sample and duplicate values are less than the CRQL, the "Control Limit" field is left empty.

12.6.4 If one result is above five times the CRQL level and the other is below, use the CRQL criteria to determine if the duplicate analysis is in control. If both sample and duplicate values are less than the CRQL, the RPD is not calculated. For soil/sediment sample or soil/sediment duplicate results less than five times the CRQL, enter the value of the CRQL, corrected for sample weight and percent solids (i.e., original, not duplicate sample weight), in the "Control Limit" column. If the duplicate sample results are outside the control limits, flag all the data for samples received associated with that duplicate sample with an "*". In the instance where there is more than one duplicate sample per SDG, if one duplicate result is not within contract criteria, flag all samples of the same matrix in the SDG. The percent difference data will be used by USEPA to evaluate the long-term precision of the methods for each analyte. Specific control limits for each analyte will be added at a later date based on these precision results.

12.7 Laboratory Control Sample (LCS) Analysis

12.7.1 Aqueous/water, soil/sediment, wipe, and filter 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 EPA samples received.

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

12.7.1.2 The LCS for the wipe samples shall be prepared by spiking a clean wipe provided by the sampler such that the final digestate shall contain each analyte at two times the CRQL. One wipe LCS shall be prepared and analyzed for every group of wipe samples in an SDG, or for each batch of wipe samples digested, whichever is more frequent. If a clean wipe is not provided by the sampler, prepare the LCS using reagent water and note this in the SDG Narrative.

12.7.1.3 The LCS for the air filter samples shall be prepared by spiking a clean air filter provided by the sampler such that the final digestate shall contain each analyte at two times the CRQL. One filter LCS shall be prepared and analyzed for every group of filter samples in an SDG, or for each batch of filter samples digested, whichever is more frequent. If a clean filter is not provided by the sampler, prepare the LCS using reagent water and note this in the SDG Narrative.

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

12.7.3 If the results for the LCS for wipes or filters fall outside the control limits of 70-130%, the Contractor shall note this in the SDG Narrative, since wipe and filter samples are fully consumed by initial analysis and cannot be reprepared and reanalyzed.

12.8 ICP-AES Serial Dilution Analysis

12.8.1 Prior to reporting concentration data for the analytes, the Contractor shall analyze and report the results of the ICP-AES serial dilution analysis. 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, wipe, filter) or for each SDG, whichever is more frequent. Samples identified as field blanks and PE samples shall not be used for serial dilution analysis.

12.8.2 If the analyte concentration is sufficiently high (minimally a factor of 50 above the MDL in the original sample), the serial dilution (a five-fold dilution) shall then agree within 10% of the original determination after correction for dilution. If the dilution analysis for one or more analytes is not within a control limit of 10%, a chemical or physical interference effect must be suspected, and the data for all affected analytes in the samples received and associated with that serial dilution must be flagged with an "E".

12.8.3 The percent differences for each component are calculated as follows:

EQ. 7 Serial Dilution Percent Differences

$$\%\text{Difference} = \frac{\left| SR - SDSR \right|}{SR} \times 100$$

WHERE, SR = Sample Result (µg/L or mg/kg) from EQ. 1 or EQ. 2
SDSR = Serial Dilution Sample Result (µg/L or mg/kg) from EQ. 1 or EQ. 2

12.8.4 In the instance where there is more than one serial dilution per SDG, if one serial dilution result is not within contract criteria, flag all the samples of the same matrix in the SDG. Serial dilution results and "E" flags shall be reported.

12.9 MDL Determination

12.9.1 Before any field samples are analyzed under this contract, the MDLs shall be determined for each digestion procedure and instrument used prior to the start of contract analyses and annually thereafter. The MDLs shall meet the levels specified in Exhibit C. 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.

12.9.1.1 To determine the MDLs, the Contractor shall run MDL studies following the procedures given in 40 CFR, Part 136. The Contractor shall prepare the MDL samples by each digestion procedure used and shall analyze these samples on each instrument used.

12.9.1.2 The determined concentration of the MDL shall be less than half the concentration of the CRQL listed in Exhibit C.

12.9.1.3 The results of the MDL determination studies shall be forwarded to the USEPA Regional CLP PO, Sample Management Office (SMO), and Quality Assurance Technical Support (QATS).

12.9.1.4 The MDL results shall be reported on Form IX-IN.

12.10 Interelement Corrections

12.10.1 Before any field samples are analyzed under this contract, the interelement correction factors shall be determined prior to the start of contract analyses and at least annually thereafter. 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. Interelement correction 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 interelement correction factors at a frequency greater than annually and/or at multiple concentrations comparable to the sample interferent levels.

If the instrument was adjusted in any way that may affect the ICP-AES interelement correction factors, the factors shall be redetermined and the results submitted for use. In addition, all data used for the determination of the interelement correction factors shall be available to the USEPA during an on-site laboratory evaluation. Results from the interelement correction factors determination shall be reported for all ICP-AES analytes.

12.11 Example Analytical Sequence for ICP-AES Including the Initial Calibration

S0
S
S
S
S
S
ICV
ICB
ICSA
ICSAB
CCV
CCB
samples
CCV
CCB
samples
CCV
CCB, etc.

12.12 Summary of QC Operations

The QC operations performed for ICP-AES analysis are summarized in the table below.

QC Operation	**Frequency**
Instrument Calibration	Each time instrument is turned on or set up, after ICV or CCV failure, and after major instrument adjustment.
Initial Calibration Verification	Following each instrument calibration for each wavelength or mass used.
Initial Calibration Blank	Following each instrument calibration, immediately after the ICV.
Continuing Calibration Verification	For each wavelength or mass used, at a frequency of every 2 hours of a run, at the beginning of each day, and at the beginning and end of each run.
Continuing Calibration Blank	Every 2 hours of a run, at the beginning of each day, and at the beginning and end of each run. Performed immediately after the last CCV.
Interference Check Sample	At the beginning of each run.
Serial Dilution for ICP	For each matrix type or for each SDG, whichever is more frequent.
Preparation Blank	For each SDG or each sample preparation and analysis procedure per batch of prepared samples, whichever is more frequent.

QC Operation	Frequency
Laboratory Control Sample	For each SDG or each sample preparation and analysis procedure per batch of prepared samples, whichever is more frequent.
Spike Sample	For each matrix type or for each SDG, whichever is more frequent.
Post-Digestion/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.
Determination of Method Detection Limits	Prior to contract award, annually thereafter, and after major instrument adjustment.
Interelement Corrections	Prior to contract award, annually thereafter, and after major instrument adjustment.

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

See Section 1.15 in Exhibit D - Introduction to Analytical Methods.

15.0 WASTE MANAGEMENT

See Section 1.16 in Exhibit D - Introduction to Analytical Methods.

16.0 REFERENCES

16.1 US Environmental Protection Agency. Methods for Chemical Analysis of Water and Wastes. Draft Method 200.7, Revision 5 (2001).

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

16.3 US Environmental Protection Agency. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846). Method 3015A, Revision 1, Update IVa. January 1998.

16.4 US Environmental Protection Agency. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846). Method 3051A, Revision 1, Update IVa. January 1998.

16.5 National Institute for Occupational Safety and Health (NIOSH). NIOSH Manual of Analytical Methods, Fourth Edition. Method 7300, Issue 3, March 2003.

16.6 US Government Printing Office. 40 Code of Federal Regulations, Part 136. Section 1. Appendix B.

16.7 US Environmental Protection Agency. Test Methods for Evaluating Solid Waste, Physical/Chemical methods (SW-846). Test Method 6010C, Revision 3, February 2007.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

TABLE 1: Interferent and Analyte Elemental Concentrations Used for ICP-AES Interference Check Sample (ICS)

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

NOTE: ICS Solution A (ICSA) contains the interferents at the indicated concentrations. The ICSA may be analyzed at twice the concentration indicated when interferences are present at higher concentrations in the sample. ICS Solution AB (ICSAB) contains all of the analytes and interferents listed above at the indicated concentrations. The ICS solutions are normally provided by USEPA along with the established concentrations for each of the analytes and interferents.

TABLE 2: Spiking Levels for Spike Sample Analysis

Analyte	Water (µg/L)	Soil[(1)] (mg/kg)	Analyte	Water (µg/L)	Soil[(1)] (mg/kg)
Aluminum	2000	*	Magnesium	*	*
Antimony	100	20	Manganese	500	100
Arsenic	40	8	Nickel	500	100
Barium	2000	400	Potassium	*	*
Beryllium	50	10	Selenium	50	10
Cadmium	50	10	Silver	50	10
Calcium	*	*	Sodium	*	*
Chromium	200	40	Thallium	50	10
Cobalt	500	100	Vanadium	500	100
Copper	250	50	Zinc	500	100
Iron	1000	*			
Lead	20	4			

[*] No spike required. NOTE: Analytes without spike levels, and not designated with an asterisk, shall be spiked at appropriate levels.

[1] The levels shown indicate 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. Appropriate adjustments shall be made for the alternative microwave digestion procedures where 0.5 grams of sample or 50 mL (45 mL of sample plus 5 mL of acid) of aqueous/water sample are required for analysis.

EQ. 8 Spiking Level Adjustment

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

18.0 ALTERNATIVE SAMPLE PREPARATION PROCEDURES

18.1 Regionally-Selected Alternative Sample Preparation Procedures

Due to the variability of the matrices received and the interferences encountered, the sample preparation procedures described in Sections 10.1.4 through 10.1.7 may not always produce valid and/or reliable results. Sample preparation procedures are given in this section that describe alternative procedures that can be used if interferences or other issues are noted with the primary procedures. If the Contractor feels that one of these alternative sample preparation procedures would provide better results than the primary methods, then the Contractor shall contact the Sample Management Office (SMO). SMO will contact the USEPA Region for instructions. The Contractor shall document the USEPA Region's decision in the Sample Delivery Group (SDG) Narrative along with populating the Forms and the electronic data deliverable with the valid values that described the actual sample preparation procedures used by the Contractor.

18.2 Alternative Aqueous/Water Sample Preparation Procedures

18.2.1 Preparation Method 3015A – Nitric Acid Digestion (based on USEPA OSW Method 3015A, Revision 1, January 1998)

18.2.1.1 This method describes a sample preparation procedure for the determination of total analytes in various aqueous/water matrices using a microwave technique with a nitric acid only digestion.

18.2.1.2 Measure a 45.0 mL (±0.1 mL) aliquot of a well-shaken, homogenized sample using an appropriate volumetric delivery device, and quantitatively transfer the aliquot to an appropriate vessel equipped with a controlled pressure relief mechanism. The sample shall not be diluted prior to digestion.

18.2.1.3 Add 5.0 mL (±0.1 mL) of concentrated nitric acid to the digestion vessel.

18.2.1.4 Seal the digestion vessel according to the manufacturer's directions. Properly place the digestion vessels in the microwave system according to the manufacturer's recommended specifications and, when applicable, connect appropriate temperature and pressure monitoring equipment to the digestion vessels according to the manufacturer's specifications.

18.2.1.5 The Preparation Blank must have 45.0 mL of reagent water and the same amount (5.0 mL) of acid that was added to the samples.

18.2.1.6 The microwave program is then started. The temperature of each sample should rise to 170°C (±5°C) in approximately 10 minutes and remain at 170°C (±5°C) for 10 minutes, or for the remainder of the 20-minute digestion period. When using temperature feedback control, the number of samples that may be simultaneously digested may vary, from one sample up to the maximum number of digestion vessels that can be heated by the magnetron of the microwave unit. Whenever fewer than the recommended number of samples are to be digested, the remaining digestion vessels should be filled with 45.0 mL of water and 5.0 mL of acid so that the full complement of vessels is achieved. This provides an energy balance, since the microwave power absorbed is proportional to the total absorbing mass in the cavity.

18.2.1.7 At the end of the microwave program, allow the digestion vessels to cool for a minimum of 5 minutes before removing them from the microwave system. When the vessels have cooled to near room temperature, determine if the digestion vessels have maintained their seal throughout the digestion. For vessels that are sealed as discrete separate entities, the digestion vessel weight may be taken before and after digestion to evaluate seal integrity. If the weight loss of the sample exceeds 1% of the weight of the sample and reagents, then the sample is considered compromised and the sample must be redigested. For digestion vessels with burst disks, a careful visual inspection of the disk, in addition to weighing, may identify compromised digestion vessels.

18.2.1.8 Complete the preparation of the sample by carefully uncapping and venting each digestion vessel in a fume hood. Quantitatively transfer the sample to an acid-cleaned bottle. If the digested sample contains particulates which may clog nebulizers or interfere with the injection of the sample into the instrument, the sample may be centrifuged, allowed to settle, or filtered through Whatman No. 41 (or equivalent) filter paper.

18.2.1.9 The final solution typically requires nitric acid to maintain appropriate sample solution acidity and stability of the elements. Commonly, a 2% (v/v) nitric acid concentration is desirable.

18.2.1.10 Transfer or decant the digested sample into a 50 mL volumetric flask and dilute to volume. The samples are now ready for analysis. Concentrations so determined shall be reported as "Total".

18.2.1.11 The digested sample can be diluted if high levels of interferences are noted or if any of the analytes exceed the upper limit of their respective calibration curves.

18.2.2 Preparation Method 3015A – Nitric Acid and Hydrochloric Acid Digestion (based on USEPA OSW Method 3015A, Revision 1, January 1998)

18.2.2.1 This method describes a sample preparation procedure for the determination of total analytes in various aqueous/water matrices using a microwave technique with a nitric acid and hydrochloric acid digestion. The addition of the concentrated hydrochloric acid to the nitric acid is appropriate for the stabilization of certain analytes (such as silver, barium, and antimony) and high concentrations of iron and aluminum in solution. The addition of hydrochloric acid may, however, limit the detection techniques or increase the difficulties of analysis for some detection systems.

18.2.2.2 Measure a 45.0 mL (±0.1 mL) aliquot of a well-shaken, homogenized sample using an appropriate volumetric measurement device, and quantitatively transfer the aliquot to an appropriate vessel equipped with a controlled pressure relief mechanism. The sample shall not be diluted prior to digestion.

18.2.2.3 Add 4.0 mL (±0.1 mL) of concentrated nitric acid and 1.0 mL (±0.1 mL) of concentrated hydrochloric acid to the digestion vessel.

18.2.2.4 The analyst should be aware of the potential for a vigorous reaction, especially with samples containing suspended solids composed of volatile or easily oxidized organic species. When digesting a matrix of this type, if a vigorous reaction occurs upon the addition of reagent(s), this sample represents a safety

hazard. Do not leach the sample as described in this method due to the high potential for unsafe and uncontrollable reactions.

18.2.2.5 Follow the procedure as described in Sections 18.2.1.4 through 18.2.1.11.

18.3 Alternative Soil/Sediment Sample Preparation Procedures

18.3.1 Preparation Method 3050B – Optional Procedure (based on USEPA OSW Method 3050B, Revision 2, December 1996)

18.3.1.1 This method describes an optional sample preparation procedure that may be used to improve the solubilities and recoveries of antimony, barium, lead, and silver when necessary. This procedure should not be required on a routine basis.

18.3.1.2 Mix the sample thoroughly to achieve homogeneity (See Exhibit D - Introduction to Analytical Methods, Section 1.8). For each digestion procedure, weigh to the nearest 0.01 g and transfer 1.0 – 1.5 g sample (wet weight) to an appropriately sized digestion vessel (e.g., a beaker or hot block digestion tube).

18.3.1.3 Add 2.5 mL of concentrated nitric acid and 10 mL of concentrated hydrochloric acid and cover with a watch glass or vapor recovery device. Heat the sample to 95°C (±3°C) and reflux for 15 minutes without boiling.

18.3.1.4 Filter the digestate through Whatman No. 41 filter paper (or equivalent) and collect the filtrate in a 100-mL volumetric flask. Wash the filter paper, while still in the funnel, with no more than 5 mL of hot (approximately 95°C) concentrated hydrochloric acid, and then with 20 mL of hot (approximately 95°C) reagent water. Collect the washings in the same 100-mL volumetric flask.

18.3.1.5 Remove the filter and residue from the funnel and place them back in the digestion vessel. Add 5 mL of concentrated hydrochloric acid, place the digestion vessel back on the heating source, and heat at 95°C (±3°C) until the filter paper dissolves. Remove the digestion vessel from the heating source and wash the cover and sides with reagent water. Filter the residue and collect the filtrate in the same 100 mL volumetric flask. Allow the filtrate to cool and then dilute to volume. NOTE: High concentrations of metal salts with temperature-sensitive solubilities can result in the formation of precipitates upon cooling of primary and/or secondary filtrates. If precipitation occurs in the flask upon cooling, do not dilute to volume.

18.3.1.6 If a precipitate forms on the bottom of the flask, add up to 10 mL of concentrated hydrochloric acid to dissolve the precipitate. After the precipitate is dissolved, dilute to volume with reagent water, stopper, and mix. The sample is now ready for analysis.

18.3.1.7 The digested sample can be diluted if high levels of interferences are noted or if any of the analytes exceed the upper limit of their respective calibration curves.

18.3.2 Preparation Method 3051A – Nitric Acid Digestion (based on USEPA OSW Method 3051A, Revision 1, January 1998)

18.3.2.1 This method describes a sample preparation procedure for the determination of total recoverable analytes in various soil/sediment matrices using a microwave technique with a nitric acid only digestion.

18.3.2.2 Mix the sample thoroughly to achieve homogeneity (See Exhibit D - Introduction to Analytical Methods, Section 1.8). For each digestion procedure, weigh to the nearest 0.001 g and transfer a 0.50 g sample (wet weight) to an appropriate digestion vessel equipped with a controlled pressure relief mechanism.

18.3.2.3 Add 10 mL (±0.1 mL) of concentrated nitric acid to the digestion vessel in a fume hood.

18.3.2.4 The analyst should be aware of the potential for a vigorous reaction especially with samples containing volatile or easily oxidized organic species. When digesting a matrix of this type, initially use no more than 0.10 g (±0.001 g) of sample. If a vigorous reaction occurs upon the addition of the acid(s), allow the sample to predigest in the uncapped digestion vessel until the reaction ceases. Heat may be added in this step for safety considerations (e.g., the rapid release of carbon dioxide from carbonates, easily oxidized organic matter, etc.). Once the initial reaction has ceased, the sample may continue through the digestion procedure.

18.3.2.5 Seal the digestion vessel according to the manufacturer's directions. Properly place the digestion vessels in the microwave system according to the manufacturer's recommended specifications and, when applicable, connect appropriate temperature and pressure monitoring equipment to the digestion vessels according to the manufacturer's specifications.

18.3.2.6 The Preparation Blank must have 0.50 g (±0.001 g) of reagent water and the same amount of acid(s) that was added to the samples.

18.3.2.7 The microwave program is then started. The temperature of each sample should rise to 175°C (±5°C) in approximately 5.5 (±0.25) minutes and remain at 175°C (±5°C) for 4.5 minutes, or for the remainder of the 10-minute digestion period. When using temperature feedback control, the number of samples that may be simultaneously digested may vary, from one sample up to the maximum number of digestion vessels that can be heated by the magnetron of the microwave unit. Whenever fewer than the recommended number of samples are to be digested, the remaining digestion vessels should be filled with 0.50 g of water and the same amount of acid(s) so that the full complement of vessels is achieved. This provides an energy balance, since the microwave power absorbed is proportional to the total absorbing mass in the cavity.

18.3.2.8 At the end of the microwave program, allow the digestion vessels to cool for a minimum of 5 minutes before removing them from the microwave system. When the vessels have cooled to near room temperature, determine if the digestion vessels have maintained their seal throughout the digestion. For vessels that are sealed as discrete separate entities, the digestion vessel weight may be taken before and after digestion to evaluate seal integrity. If the weight loss of the sample exceeds 1% of the weight of the sample and reagents, then the sample is considered compromised and the sample must be redigested. For digestion vessels with burst disks, a careful visual inspection of the disk, in addition to weighing, may identify compromised digestion vessels.

18.3.2.9 Complete the preparation of the sample by carefully uncapping and venting each digestion vessel in a fume hood. Quantitatively transfer the sample to an acid-cleaned bottle. Filter the digested sample through Whatman No. 41 (or equivalent) filter paper to remove particulates which may clog nebulizers or otherwise interfere with the injection of the digested sample into the instrument.

18.3.2.10 The final solution typically requires nitric acid to maintain appropriate sample solution acidity and stability of the elements. Commonly, a 2% (v/v) nitric acid concentration is desirable.

18.3.2.11 Transfer or decant the digested sample into a 50 mL volumetric flask and dilute to volume. The samples are now ready for analysis.

18.3.2.12 The digested sample can be diluted if high levels of interferences are noted or if any of the analytes exceed the upper limit of their respective calibration curves.

18.3.3 Preparation Method 3051A – Nitric Acid and Hydrochloric Acid Digestion (based on USEPA OSW Method 3051A, Revision 1, January 1998)

18.3.3.1 This method describes a sample preparation procedure for the determination of total recoverable analytes in various soil/sediment matrices using a microwave technique with a nitric acid and hydrochloric acid digestion. The addition of the concentrated hydrochloric acid to the nitric acid is appropriate for the stabilization of certain analytes (such as silver, barium, and antimony) and high concentrations of iron and aluminum in solution. Improvements are also noted with the recoveries of antimony, iron, and silver. The addition of hydrochloric acid may, however, limit the detection techniques or increase the difficulties of analysis for some detection systems.

18.3.3.2 Mix the sample thoroughly to achieve homogeneity (See Exhibit D - Introduction to Analytical Methods, Section 1.8). For each digestion procedure, weigh to the nearest 0.001 g and transfer a 0.50 g sample (wet weight) to an appropriate digestion vessel equipped with a controlled pressure relief mechanism.

18.3.3.3 Add 9 mL (±0.1 mL) of concentrated nitric acid and 3 mL (±0.1 mL) of concentrated hydrochloric acid to the digestion vessel in a fume hood.

18.3.3.4 Follow the procedure as described in Sections 18.3.2.4 through 18.3.2.12.

18.4 Microwave Calibration Procedure

18.4.1 The calibration procedure is a critical step prior to the use of any microwave unit. The microwave unit must be calibrated every 6 months. The data for each calibration must be available for review during on-site audits. In order that absolute power settings may be interchanged from one microwave unit to another, the actual delivered power must be determined.

18.4.2 Calibration of a laboratory microwave unit depends on the type of electronic system used by the manufacturer. If the unit has a precise and accurate linear relationship between the output power and the scale used in controlling the microwave unit, then the calibration can be a two-point calibration at maximum and 40% power. If the unit is not accurate or precise for some portion of the controlling scale, then a multiple-point calibration is necessary. If the unit power calibration needs a multiple-point calibration, then the point where linearity begins must be identified. For example: a calibration at 100, 99, 98, 97, 95, 90, 80, 70, 60, 50, and 40% power settings can be applied and the data plotted. The non-linear portion of the calibration curve can be excluded or restricted in use. Each percent is equivalent to approximately 5.5-6 watts and becomes the smallest unit of power that can be controlled. If 20-40 watts are contained from 99-100%, that portion of the microwave calibration is not controllable by 3-7 times that of the linear portion of the control scale and will prevent duplication of precise power conditions specified in that portion of the power scale.

18.4.3 The power available for heating is evaluated so that the absolute power setting (watts) may be compared from one microwave to another. This is accomplished by measuring the temperature rise in 1 kilogram (kg) of water exposed to microwave radiation for a fixed period of time. The water is placed in a polytetrafluoroethylene (PTFE) beaker (or a beaker that is made of some other material that does not absorb microwave energy) and stirred before measuring the temperature. Glass beakers absorb microwave energy and may not be used. The initial temperature of the water must be between 19°C and 25°C. The beaker is circulated continuously through the field for at least 2 minutes at full power. The beaker is removed from the microwave, the water is stirred vigorously, and the final temperature is recorded. The final reading is the maximum temperature reading after each energy exposure. These measurements must be accurate to ±0.1°C and made within 30 seconds of the end of heating. If more measurements are needed, do not use the same water until it has cooled down to room temperature. Otherwise, use a fresh water sample.

The absorbed power is determined by the following formula:

EQ. 9 Absorbed Power

$$P = \frac{(K)(C_p)(m)(DT)}{t}$$

WHERE,
- P = The apparent power absorbed by the sample in watts (joules per second)
- K = The conversion factor for thermochemical calories per second to watts (4.184)
- C_p = The heat capacity, thermal capacity, or specific heat (cal. $g^{-1}\,°C^{-1}$) of water (1.0)
- m = The mass of the sample in grams (g)
- DT = The final temperature minus the initial temperature (°C)
- t = The time in seconds (s)

Using 2 minutes and 1 kg of reagent water, the calibration equation simplifies to:

$$P = (DT)(34.87)$$

The microwave user can now relate power in watts to the percent power setting of the microwave.

18.5 Microwave Digestion Cleaning Procedure

18.5.1 Initial Cleaning of the Polytetrafluoroethylene Perfluoroalkoxy (PTFE PFA) Digestion Vessels

18.5.1.1 Prior to first use - new vessels must be annealed before they are used. A pretreatment/cleaning procedure must be followed. This procedure calls for heating the vessels for 96 hours at 200°C. The vessels must be disassembled during annealing and the sealing surfaces (the top of the vessel or its rim) must not be used to support the vessel during annealing.

18.5.1.2 Rinse in reagent water.

18.5.1.3 Immerse in 50% (v/v) hydrochloric acid for a minimum of 3 hours after the cleaning bath has reached a temperature just below boiling.

18.5.1.4 Rinse in reagent water.

18.5.1.5 Immerse in 50% (v/v) nitric acid for a minimum of 3 hours after the cleaning bath has reached a temperature just below boiling.

18.5.1.6 The vessels are then rinsed with copious amounts of reagent water prior to use for any analyses under this contract.

18.5.2 Cleaning Procedure between Sample Digestions

18.5.2.1 Wash entire vessel in hot water using laboratory-grade non-phosphate detergent.

18.5.2.2 Rinse with 50% (v/v) nitric acid.

18.5.2.3 Rinse 3 times with reagent water.

EXHIBIT D - PART B

ANALYTICAL METHODS FOR INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY

Exhibit D – Analytical Methods for ICP-MS

Table of Contents

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1.0 SCOPE AND APPLICATION

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

2.0 SUMMARY OF METHOD

2.1 General Method Overview

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

2.2 Summary of Digestion Procedures

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

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

2.2.3 Alternative digestion procedures are included in Section 18 of this Exhibit.

3.0 DEFINITIONS

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

4.0 INTERFERENCES

Several types of interferences may cause inaccuracies in the determination of trace elements by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS). To prevent this, appropriate steps must be taken in all analyses to ensure that potential interferences are taken into account. Possible interferences are given in Sections 4.1 through 4.5.

4.1 Isobaric Elemental Interferences

Isobaric elemental interferences are caused by isotopes of different elements which form singly or doubly charged ions of the same nominal mass-to-charge ratio, and which cannot be resolved by the mass spectrometer. All elements determined by this method have, at minimum, one isotope free of isobaric elemental interference. Of the analytical isotopes recommended for use with this method, only selenium-82 has an isobaric elemental interference (krypton-82). If alternative analytical isotopes having higher natural abundances are selected, in order to achieve greater sensitivity, an isobaric interference may occur. All data obtained under such conditions must be corrected by measuring the signal from another isotope of the interfering element and subtracting the appropriate signal ratio from the isotope of interest. A record of this correction process shall be included with the data. It should be noted that such corrections will only be as accurate as the accuracy of the isotope ratio used in the elemental equation for data calculations. Relevant isotope ratios should be established prior to the application of any corrections.

4.2 Abundance Sensitivity

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

4.3 Isobaric Polyatomic Ion Interferences

Isobaric polyatomic ion interferences are caused by ions consisting of more than one atom which have the same nominal mass-to-charge ratio as the isotope of interest, and which cannot be resolved by the mass spectrometer. These ions are commonly formed in the plasma or interface system from support gases or sample components. Most of the common interferences have been identified and are listed in Table 2 - Isobaric Molecular-Ion Interferences, with the target analytes affected. Such interferences must be recognized, and when they cannot be avoided by the selection of alternative analytical isotopes, appropriate corrections must be made to the data. Equations for the correction of data should be established at the time of the analytical run 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 blank between samples (see Section 7.3.3). The possibility of memory interferences should be recognized within an analytical run and suitable rinse times or monitoring should be used to reduce them. Memory interferences may also be assessed within an analytical run 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 1.14 in Exhibit D - Introduction to Analytical Methods.

6.0 EQUIPMENT AND SUPPLIES

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

6.1 Glassware/Labware

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

6.1.2 Watch glasses (glass or plastic)

6.1.3 Funnels

6.1.4 Graduated cylinders

6.1.5 Various volumetric flasks and pipets (Class A)

6.1.6 Thermometer that covers range of 0-200°C

6.1.7 Whatman No. 41 filter paper (or equivalent)

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

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

6.2 Equipment and Supplies for Microwave Digestion

The equipment and supplies listed in this section are used if one of the alternate microwave sample preparation procedures was approved for use by the USEPA Region.

6.2.1 Whatman No. 41 filter paper (or equivalent)

6.2.2 Disposable polypropylene filter funnel

6.2.3 Polyethylene bottles, 125 mL, with caps

6.2.4 Microwave oven with programmable power settings up to at least 600 watts.

6.2.5 The system must use polytetrafluoroethylene perfluoroalkoxy (PTFE PFA) digestion vessels (120 mL capacity) capable of withstanding pressure of up to 110 (±10) psi [7.5 (±0.7) atm]. These vessels are capable of controlled pressure relief at pressures exceeding 110 psi.

6.2.6 A rotating turntable must be used to ensure homogeneous distribution of microwave radiation within the oven. The speed of the turntable must be a minimum of 3 revolutions per minute (rpm).

6.3 Inductively Coupled Plasma-Mass Spectrometer (ICP-MS)

6.3.1 The ICP-MS consists of:

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

7.0 REAGENTS AND STANDARDS

7.1 Reagents

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

7.1.1 Reagent water - The purity of this water must be equivalent to ASTM Type II water (ASTM D1193-06). Use this water for all reagents, standards, and dilutions.

7.1.2 Nitric acid - Concentrated (specific gravity 1.41).

7.1.3 Nitric acid (50% v/v) - Add 500 mL conc. nitric acid (specific gravity 1.41) to 400 mL of reagent water and dilute to 1 L.

7.1.4 Nitric acid (10% v/v) - Add 100 mL conc. nitric acid (specific gravity 1.41) to 400 mL of reagent water and dilute to 1 L.

7.1.5 Nitric acid (2% v/v) – Add 20 mL conc. nitric acid (specific gravity 1.41) to 400 mL of reagent water and dilute to 1 L.

7.1.6 Nitric acid (1% v/v) – Add 10 ml conc. nitric acid (specific gravity 1.41) to 400 mL of reagent water and dilute to 1 L.

7.1.7 Hydrochloric acid - Concentrated (specific gravity 1.19).

7.1.8 Hydrochloric acid (50% v/v) - Add 500 mL conc. hydrochloric acid (specific gravity 1.19) to 400 mL of reagent water and dilute to 1 L.

7.1.9 Hydrochloric acid (HCl) (20% v/v) - Add 200 mL conc. hydrochloric acid (specific gravity 1.19) to 400 mL reagent water and dilute to 1 L.

7.2 Standards

7.2.1 Introduction

The Contractor must provide all standards, except as noted, to be used with this contract. These standards may be used only after they have been certified according to the procedure in Exhibit E, Section 8.0. The Contractor must be able to verify that the standards are certified. Manufacturer's certificates of analysis must be retained by the Contractor and presented upon request.

7.2.2 Stock Standard Solutions

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

7.2.3 Secondary Dilution Standards

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

7.2.4 Working Standards

7.2.4.1 Mixed Calibration Standard Solutions

Care must be taken in the preparation of mixed calibration standards to ensure that the analytes are compatible and stable. Fresh calibration standards should be prepared from mixed standard solutions every 2 weeks or less. Prepare the mixed standards to levels appropriate to the operating range of the instrument using 1% (v/v) nitric acid or to match the matrix of the digested samples. The analyte concentrations in the calibration standards should be sufficient to produce good measurement precision and to accurately define the slope of the response curve. Protect all standards from light. Samples, sample digestates, and standards must be stored separately.

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 µg/L with 1% (v/v) nitric acid. The concentration of this solution can be reduced based on recommendations from the instrument manufacturer.

7.2.4.4 Interference Check Sample (ICS) Solution

The ICS consists of two solutions: Solution A (ICSA) and Solution AB (ICSAB). ICSA consists of the interferents and ICSAB consists of the analytes mixed with the interferents. The ICS standards (ICSA for the interferents only and ICSB for the analytes only) are normally supplied by USEPA.

7.3 Blanks

Three types of blanks are required for this method. A Calibration Blank is used to establish the analytical calibration curve, the Preparation Blank (see Section 12.4.2) is used to assess possible contamination from the sample preparation procedure and to assess spectral background, and the Rinse Blank is used to flush the instrument between samples to reduce memory interferences.

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

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

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

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Sample Collection and Preservation

All aqueous/water and soil/sediment samples must be collected in glass or polyethylene containers. Aqueous/water samples must be preserved with nitric acid to pH less than or equal to 2 immediately after collection. All samples must be iced or refrigerated at 4°C (±2°C) from the time of collection until digestion. If aqueous/water samples are received in glass containers, please note this in the Sample Delivery Group (SDG) Narrative.

8.1.1 Dissolved Metals

For the determination of dissolved metals, the sample must be filtered through a 0.45 micrometer (µm) pore diameter membrane filter at the time of collection or as soon as possible. Use a portion of the sample to rinse the filter flask, discard this portion, and collect the required volume of filtrate. Preserve the filtrate with nitric acid to pH less than or equal to 2 immediately after filtration.

8.2 Procedures for Sample Storage and Disposal

Following digestion, the remaining unused portion of aqueous/water and soil/sediment samples may be stored at room temperature within the laboratory until 60 days after delivery of a complete, reconciled data package to USEPA. After 60 days, the samples may be disposed of in a manner that complies with all applicable regulations.

8.3 Procedure for Sample Digestate Storage

Sample digestates must be stored until 6 months after delivery of a complete, reconciled data package to USEPA.

8.4 Contract Required Holding Time

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

9.0 CALIBRATION AND STANDARDIZATION

9.1 Instrument Operating Parameters

Because of the differences between various makes and models of satisfactory instruments, no detailed operating instructions can be provided. Instead, the analyst should follow the instructions provided by the manufacturer of the particular instrument. The Method Detection Limit (MDL), precision, and interference effects must be investigated and established for each individual analyte on that particular instrument. All measurements must be within the operational range of the instrument where corrections are valid. It is the responsibility of the analyst to verify the instrument configuration and operating conditions used to satisfy the analytical requirements and to maintain Quality Control (QC) data confirming instrument performance and analytical results.

9.2 Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) Instrument Calibration Procedure

9.2.1 Precalibration routine - The following precalibration routine must be completed prior to calibrating the instrument.

Set up the instrument with proper operating parameters established in Section 9.1. The instrument must be allowed to become stable prior to calibration. Conduct any necessary mass calibration and resolution routines to bring peak width within the manufacturer's specifications and adjust mass calibration to within 0.1 amu over the range of 6 to 210 amu.

Demonstrate instrument stability and precision by analyzing the tuning solution as a single analysis with at least five integrations. The percent relative standard deviation of the absolute signals for all the multiple integrations in the tuning solution, as calculated by the instrument, must be less than 5.0% for each analyte.

9.2.2 Internal Standardization

Internal standardization must be used in all analyses to correct the instrument drift and physical interferences. A list of acceptable internal standards is provided in Table 5 - Internal Standards. For full range mass scans, a minimum of five internal standards shall be used. The internal standards selected for a run must be consistent throughout the entire run. Internal standards shall be present in all samples, standards, and blanks (except the tuning solution) at identical levels. This may be achieved by directly adding an aliquot of the internal standard solution to 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. The concentration of the internal standard should be sufficiently high for good precision and to minimize the possibility of correction errors if the internal standard is naturally present in the sample. Depending on the sensitivity of the instrument, a final concentration range of 20 µg/L to 200 µg/L of each internal standard in each digested sample, blank, and standard is recommended when the internal standards are added manually by the analyst. If dilutions are performed on the digested samples, then the internal standards must be added after the dilution. 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.

9.2.3 Calibration

Instruments shall be calibrated each time the instrument is set up, or after Initial Calibration Verification (ICV) or Continuing Calibration Verification (CCV) failure. The instrument standardization date and time shall be included in the raw data. Calibration standards shall be prepared as in Section 7.2.4.1. Calibrate the instrument with at least six standards, one of which shall be a blank standard and one shall be at or below the Contract Required Quantitation Limit (CRQL). The rest of the standards shall be uniformly spread out in graduated amounts over the appropriate calibration range for each metal. A minimum of three replicate integrations are required for data acquisition. Use the average of all the integrations for instrument calibration and data reporting. 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 corrected instrument response on the Y-axis. The corrected instrument response are those corrections (e.g., such as correction for background, internal standards, Interelement Corrections (IECs), calibration blank) that may be applied to the raw uncorrected instrument response prior to determining the calibration curve. A standard linear regression, a weighted linear regression (e.g., 1/concentration or 1/concentration^2), or a linear regression with zero force calibration model can be used as appropriate. No other types of equations (e.g., quadratic) are to be used. The acceptance criteria for the calibration curve is a correlation coefficient greater than or equal to 0.995. Sample analysis shall not begin until this criteria and the criteria described in Sections 9.2.4 and 9.2.5 have been met.

9.2.4 The calibration equation must be checked to establish the representativeness of the data that were used to produce the calibration equation. This check involves the re-fitting of the non-blank calibration data back to the calibration equation or the comparison of the calculated concentration of each of the standards against the expected concentration of the associated standard. This difference is related to the actual residual. For this calculation, the Percent Difference shall be used where the above difference is further divided by the expected amount or concentration of the respective standard. If these Percent Differences for each of the standards do not fall within ±30%, then the calibration equation is not acceptable and must be corrected. If a standard is analyzed for a particular analyte at a concentration that is below the CRQL and the above criteria is not met, that value can be excluded from the calibration curve as long as the lowest non-zero standard for each analyte is still analyzed at or below the CRQL and all standards included in the calibration curve are continuous and consecutive.

9.2.5 The y-intercept from the linear regression initial calibration equation shall also be evaluated. If the y-intercept is not below the CRQL for each of the analyte initial calibration curves, the calibration is not acceptable and must be corrected. Samples are not to be analyzed until the y-intercept for each analyte’s initial calibration curve meets the acceptance criteria.

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

9.3 Initial Calibration Verification (ICV)

9.3.1 Immediately after each instrument has been calibrated, the accuracy of the initial calibration shall be verified and documented for every analyte by the analysis of the ICV solution(s) for each mass used to report final results. The percent Relative Standard Deviation (%RSD) shall also be calculated from all replicate integrations and reported for each mass used to report final results.

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

9.3.3 The ICV solution(s) shall be run at each mass used for reporting final results.

9.4 Continuing Calibration Verification (CCV)

9.4.1 To ensure calibration accuracy during each analytical run sequence, a CCV shall be analyzed and reported for each mass used for reporting final results for each analyte, at a frequency not to exceed every 2 hours during an analytical run sequence. The standard shall be analyzed and reported for each mass used for reporting final results for each analyte at the beginning of the analytical run sequence and after the last analytical sample. The %RSD shall be calculated from all integrations and reported for each mass used to report final results. See the example sample analysis sequence in Section 12.12. This analytical run sequence can continue indefinitely as long as samples are being continuously analyzed without the instrument being turned off and successive CCVs and their associated %RSDs meet the stated criteria.

This CCV standard(s) shall be prepared from the same source and at or near the mid-level concentration as used during the initial calibration.

The same CCV standard shall be used throughout the analytical run sequences for a Sample Delivery Group (SDG) of samples received.

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

9.5 Initial and Continuing Calibration Blank (ICB/CCB)

An ICB or CCB shall be analyzed for each mass used for reporting final results for each analyte immediately after every ICV and CCV.

10.0 PROCEDURE

10.1 Sample Preparation

10.1.1 If insufficient sample amount (less than 90% of the required amount) is received to perform the analyses, the Contractor shall contact the Sample Management Office (SMO) to inform them of the problem. SMO will contact the USEPA Region for instructions. The USEPA Region will either require that no sample analysis be performed or will require that a reduced volume be used for the sample analysis. No other changes in the analysis will be permitted. The Contractor shall document the USEPA Region's decision in the Sample Delivery Group (SDG) Narrative.

10.1.2 If multiphase samples (e.g., two-phase liquid sample, oily sludge/sandy soil/sediment sample) are received by the Contractor, the Contractor shall contact SMO to apprise them of the type of sample received. SMO will contact the USEPA Region. If all phases of the sample are amenable to analysis, the USEPA Region may require the Contractor to do any of the following:

- Mix the sample and analyze an aliquot from the homogenized sample.
- Separate the phases of the sample and analyze one or more of the phases, separately. SMO will provide EPA sample numbers for the additional phases, if required.

- Do not analyze the sample.

10.1.2.1 If all of the phases are not amenable to analysis (i.e., outside scope), the USEPA Region may require the Contractor to do any of the following:

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

10.1.2.2 No other changes in the analyses will be permitted. The Contractor shall document the USEPA Region's decision in the SDG Narrative.

10.1.3 The primary sample preparation procedures to be used for this method are described in the following Sections (10.1.4 and 10.1.5). These methods are to be used without deviation. Alternative sample preparation procedures are listed in Section 18 of this method and may be requested by the USEPA Region. No other changes in the analyses will be permitted.

10.1.4 Aqueous/Water Sample Preparation

10.1.4.1 Preparation Method 200.8 – Total Recoverable Analytes [based on USEPA NERL Method 200.8 Rev 5.5 (October 1999)]

10.1.4.1.1 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) beaker or other comparable digestion vessel. The sample shall not be diluted prior to digestion.

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

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

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

10.1.4.1.5 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.

10.1.4.1.6 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.

10.1.4.1.7 Prior to analysis, if the chloride concentration interferes with the analysis, then the solution can be diluted to reduce the chloride concentration. 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.

10.1.4.1.8 The concentrations as determined by this method shall be reported as "Total". 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. The digested sample can be further diluted if high levels of interferences are noted or if any of the analytes exceed the upper limit of their respective calibration curves.

10.1.5 Soil/Sediment Sample Preparation

10.1.5.1 Preparation Method 3050B (based on USEPA OSW Method 3050B, Revision 2, December 1996)

10.1.5.1.1 Mix the sample thoroughly to achieve homogeneity (see Exhibit D - Introduction to Analytical Methods, Section 1.8). For each digestion procedure, weigh to the nearest 0.01 g and transfer 1.0 – 1.5 g sample (wet weight) to an appropriately sized digestion vessel (e.g., a beaker or hot block digestion tube).

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

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

10.1.5.1.4 After cooling, transfer the digestate to a 100 mL volumetric flask through Whatman No. 41 filter paper (or equivalent). 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. Dilute to volume with reagent water, stopper, and mix. The sample is now ready for analysis.

10.1.5.1.5 Prior to analysis, the digested sample can be diluted (e.g., 1:4 would be suggested) with 1% nitric acid if high levels of chloride are present which may cause problems with some instruments and interfere with the analysis. Dilution of the digestate may also be necessary if high levels of interferences are noted or if any of the analytes exceed the upper limit of their respective calibration curves.

10.2 Sample Analysis

10.2.1 For every new or unusual matrix, it is highly recommended that a semi-quantitative analysis be carried out to screen for high element concentrations. This screening procedure can be performed using 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.

10.2.2 Initiate instrument operating configuration. Tune and calibrate the instrument for the analytes of interest. Establish instrument software run procedures for quantitative analysis. 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.

10.2.3 The rinse blank should be used to flush the system between samples. Allow sufficient time to remove traces of the previous sample. Samples should be aspirated for a sufficient period of time to obtain a stable response prior to the collection of data.

10.2.4 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. The sample digestate should first be analyzed for the trace elements, protecting the detector from the high concentration elements, if necessary, by the selection of appropriate scanning windows. The sample digestate should then be diluted for the determination of the remaining elements.

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

11.0 DATA ANALYSIS AND CALCULATIONS

11.1 Recommended Elemental Equations

Elemental expressions recommended for sample data calculations are listed in Table 4 - Recommended Elemental Expressions for Isobaric Interferences. Do not report element concentrations below the Method Detection Limit (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 Aqueous/Water Sample Calculation

EQ. 1 Aqueous/Water Sample Concentration

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

WHERE,
- C = Instrument value in µg/L (The average of all replicate integrations)
- V_f = Final digestion volume (mL)
- V = Initial Aliquot Amount (mL)
- DF = Dilution Factor

11.5 Adjusted MDL/Adjusted Contract Required Quantitation Limit (CRQL) Calculation for Aqueous/Water Samples

To calculate the adjusted MDL or adjusted CRQL for aqueous/water samples, multiply the value of the MDL or CRQL(µg/L) by the sample dilution factor and the V_f/V term as noted in Equation 1.

11.6 Soil/Sediment Sample Calculation

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

EQ. 2 Soil/Sediment Sample Concentration

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

WHERE,
- C = Instrument value in µg/L (The average of all replicate integrations)
- V_f = Final digestion volume (mL)
- W = Initial aliquot amount (g)
- S = % Solids/100 (see Exhibit D - Introduction to Analytical Methods, Section 1.6)
- DF = Dilution Factor

11.7 Adjusted MDL/Adjusted CRQL Calculation for Soil/Sediment Samples

Calculate the adjusted MDL or adjusted CRQL for soil/sediment samples as follows:

EQ. 3 Adjusted Soil/Sediment MDL or CRQL Concentration

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

WHERE,
- C = MDL or CRQL (mg/kg)
- W_M = Minimum method required aliquot amount (g) (1.00g or 0.50g)
- W = Initial aliquot amount (g)
- V_M = Method required final sample digestion volume (mL) (100 mL)
- V_f = Final digestion volume (mL)
- S = % Solids/100 (see Exhibit D - Introduction to Analytical Methods, Section 1.6)
- DF = Dilution Factor

12.0 QUALITY CONTROL (QC)

12.1 Tune Standard

The Tune Standard shall be prepared in the same acid matrix as the calibration standards and analyzed as a single analysis with at least five integrations. If the mass calibration is not within 0.1 amu over the range of 6 to 210 amu, or the percent Relative Standard Deviation (%RSD) of all the integrations of the absolute signals of the analytes exceeds 5.0%, the analysis shall be terminated, the problem corrected, and the instrument re-tuned. In addition, the laboratory must also monitor the resolution by measuring and reporting the full peak width (in amu) and the percentage of the peak height this full peak width was measured at for each of the analyte masses in the tune solution. All sample results reported must be associated with an instrument tune that meets these requirements.

12.2 Initial Calibration Verification (ICV)

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. If the measurements exceed 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 reverified. The results of the ICV analysis shall be reported.

12.3 Continuing Calibration Verification (CCV)

The CCV standard shall be prepared in the same acid matrix as the calibration standards by combining compatible analytes at a concentration equivalent to the mid-levels of their respective calibration curves. If the deviation of the CCV is 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 stopped, 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. The results of all CCV analyses shall be reported.

12.4 Blank Analyses

There are two different types of blanks required by this method. The calibration blank is used in establishing the analytical curve. The Initial and Continuing Calibration Blanks (ICB/CCB) are identical in composition to the calibration blank and are analyzed immediately after the ICV/CCV to monitor for potential carryover of analytes. The preparation blank is used to monitor for possible contamination throughout the entire sample preparation and analysis process.

12.4.1 Initial and Continuing Calibration Blank (ICB/CCB)

The ICB and CCB are identical in composition to the Calibration Blank as used to establish the initial calibration curve. If the absolute value of the calibration blank (ICB/CCB) result exceeds the Contract Required Quantitation Limit (CRQL) (see Exhibit C), 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 blank shall be performed for the analytes affected. The results of the ICB and CCB analyses shall be reported.

12.4.2 Preparation Blank

12.4.2.1 The Preparation Blank shall contain all the reagents and in the same volumes as used in processing 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.

12.4.2.2 At least one Preparation Blank, consisting of reagent water processed through each sample preparation and analysis procedure (see Section 10), shall be prepared and analyzed with every Sample Delivery Group (SDG), or with each batch[1] of samples digested, whichever is more frequent.

12.4.2.3 The first batch of samples in an SDG is to be assigned to Preparation Blank one, the second batch to Preparation Blank two, etc. Each Complete SDG File (CSF) shall contain the results of all Preparation Blank analyses associated with the samples in that SDG.

12.4.2.4 The Preparation Blank(s) is (are) to be reported for each SDG and used in all analyses to ascertain whether sample concentrations reflect contamination in the following manner:

12.4.2.4.1 If the absolute value of the concentration of the blank is less than or equal to the CRQL (see Exhibit C), no further action is required.

12.4.2.4.2 If the analyte concentration in the blank is above the CRQL, the lowest concentration of that analyte in the associated samples (except those identified as field blanks) shall be greater than or equal to 10 times the blank concentration. Otherwise, all samples (except those identified as field blanks) associated with the blank, with the analyte concentration less than 10 times the blank concentration and above the CRQL, shall be redigested and reanalyzed with appropriate new Quality Control (QC) for that analyte. The sample concentration is not to be corrected for the blank value.

12.4.2.4.3 If the concentration of the blank is below the negative CRQL, then all samples reported below 10 times the CRQL associated with the blank shall be redigested and reanalyzed with appropriate new QC.

12.4.2.4.4 The results for the Preparation blank shall be reported.

12.5 Interference Check Sample (ICS)

12.5.1 The ICS is obtained from USEPA. If not available, then the ICS can be prepared by the analyst.

12.5.2 To verify corrections for elemental and polyatomic isobaric interferences, the Contractor shall analyze and report the results for the ICS for all elements on the Target Analyte List (TAL) and

[1] A group of samples prepared at the same time.

monitor for all interferents, 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. The ICS solutions shall be obtained from USEPA, if available, and analyzed according to instructions supplied with the ICS. The Contractor shall always initially run the ICS undiluted. Dilution of the ICS (for the higher concentration elements) may be necessary to meet the calibrated range values of the instrument.

12.5.3 The ICS consists of two solutions: Solution A and Solution AB. Solution A consists of the interferents; Solution AB consists of the analytes mixed with the interferents. Even though no analytes have been added to Solution A, low levels of some of the analytes may be present due to the purity of the materials used. An ICS analysis consists of analyzing both solutions consecutively, starting with Solution A.

12.5.4 The analytical results of ICS Solution A (ICSA) shall fall within the control limit ±20% of the analyte's true value or ±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 Copper (CRQL = 2 µg/L, ICSA true value = 8 µg/L) the correct control window to use would be the greater of ±20% of the true value (0.20 x 8 µg/L = ±1.6 µg/L) or ±2 times the CRQL (±4 µg/L). Therefore, the control window for the found value for Chromium in the ICSA is 8±4, or 4 to 12 µg/L. If the analytical results of the ICSA do not fall within the control limits, the analysis shall be terminated, the problem corrected, and the instrument recalibrated.

12.5.5 Results for the ICS Solution AB (ICSAB) shall fall within the control limit of ±20% of the true value or ±2 times the CRQL of the true value, whichever is greater. If the analytical results of the ICSAB do not fall within the control limits, the analysis shall be terminated, the problem corrected, and the instrument recalibrated.

NOTE: The control limits and concentrations for the ICSAB are being monitored. These may be adjusted to provide greater control of interferences.

12.5.6 If true values for analytes contained in the ICS are not supplied with the solutions, the mean shall be determined by initially analyzing the ICS at least five times repetitively for the particular analytes. This mean determination shall be made during an analytical run where the results for a previously supplied ICS met all contract specifications. Additionally, the results of this initial mean determination shall be used as the true value for the lifetime of that solution (i.e., until the solution is exhausted). Only if the ICS solutions are not available from USEPA, independent Check Samples shall be prepared with interferent and analyte concentrations at the levels specified in Table 1 – Interferent and Analyte Elemental Concentrations Used for ICP-MS Interference Check Sample (ICS). The mean value and standard deviation shall be established by initially analyzing the Check Samples at least five times repetitively for each analyte listed. Results shall fall within the control limit of ±20% of the established mean value or ±2 times the analyte's CRQL of the established mean value, whichever is greater. The mean and standard deviation shall be reported in the raw data. Results from the ICS analyses shall be reported for all ICP-MS target analytes.

12.5.7 The results of the ICS analysis shall be reported.

12.6 Spike Sample Analysis

12.6.1 The spike sample analysis is designed to provide information about the effect of sample matrix on the digestion and/or measurement methodology. The spike is added before the digestion (i.e., prior to the addition of other reagents). At least one spike sample analysis (matrix spike) 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.[2]

12.6.2 If the spike analysis is performed on the same sample that is chosen for the duplicate sample analysis, spike calculations shall be performed using the results of the sample designated as the "original sample" (see Section 12.7). The average of the duplicate results cannot be used for the purpose of determining percent recovery. Samples identified as field blanks and Performance Evaluation (PE) samples shall not be used for spiked sample analysis. USEPA may require that a specific sample be used for the spike sample analysis.

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

12.6.4 If the spike recovery is not at or within the limits of 75-125%, the data for all samples received and associated with that spike sample shall be flagged with the letter "N". 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 event, the data shall be reported unflagged even if the percent recovery does not meet the 75-125% recovery criteria.

12.6.5 When the matrix spike recovery falls outside the control limits and the sample result does not exceed four times the spike added, a post-digestion spike shall be performed for those analytes that do not meet the specified criteria. Note that if a post-digestion spike analysis is required for an analyte, the same EPA sample that was used for the matrix spike analysis shall be used for the post-digestion spike analysis. Spike the unspiked aliquot of the undiluted digestate at two times the indigenous level or two times the CRQL, whichever is greater.

12.6.6 In the instance where there is more than one spike sample per matrix per SDG, if one spike sample recovery is not within contract criteria, then flag all the samples of the same matrix and method in the SDG. Individual component percent recoveries are calculated as follows:

[2] USEPA may require additional spike sample analyses, upon USEPA Regional CLP Project Officer (CLP PO) request.

EQ. 4 Matrix Spike and Post-Digestion Spike Percent Recovery

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

WHERE, SSR = Spike Sample Result (µg/L or mg/kg) from EQ. 1 or EQ. 2
SR = Sample Result (µg/L or mg/kg) from EQ. 1 or EQ. 2
SA = Spike Added Theoretical Result (µg/L or mg/kg). This is calculated by substituting the spiking amount used for the 'V_f' term and substituting the spiking standard concentration used for the 'C' term from EQ. 1 or EQ. 2.

12.6.7 When sample concentration is less than the Method Detection Limit (MDL), use SR = 0 only for purposes of calculating the percent recovery. The Spike Sample Results (SSRs), Sample Results (SRs), Spike Added Theoretical Results (SA), and Percent Recovery (positive or negative) shall be reported.

12.6.8 The units used for reporting Spiked Sample Results (SSRs) will be identical to those used for reporting Sample Results (SRs).

12.7 Duplicate Sample Analysis

12.7.1 One duplicate sample shall be analyzed for each group of samples of a similar matrix type (i.e., aqueous/water, soil/sediment) or for each SDG, whichever is more frequent.[3] Duplicates cannot be averaged for reporting.

12.7.2 Duplicate sample analyses are not required for percent solids. Samples identified as field blanks and PE samples shall not be used for duplicate sample analysis. USEPA may require that a specific sample be used for duplicate sample analysis. The Relative Percent Difference (RPD) for each analyte is calculated as follows:

EQ. 5 Duplicate Sample Relative Percent Difference

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

WHERE, RPD = Relative Percent Difference
S = Sample Result (original) (µg/L or mg/kg) from EQ.1 or EQ. 2
D = Duplicate Sample Result (µg/L or mg/kg) from EQ.1 or EQ. 2

12.7.3 The results of the duplicate sample analyses shall be reported. A control limit of 20 for RPD shall be used for original and duplicate sample values greater than or equal to five times the CRQL (see Exhibit C). A control limit equal to the CRQL shall be entered in the "Control Limit" column if either the sample or duplicate value is less than five times the CRQL. If the sample and duplicate values are greater than or equal to five times the CRQL, or if the sample and duplicate values are less than the CRQL, the "Control Limit" field is left empty.

12.7.4 If one result is above five times the CRQL level and the other is below, use the CRQL criteria to determine if the duplicate analysis is in control. If both sample and duplicate values are less than

[3] USEPA may require additional duplicate sample analyses, upon USEPA Regional CLP PO request.

the CRQL, the RPD is not calculated. For soil/sediment sample or soil/sediment duplicate results less than five times the CRQL, enter the value of the CRQL, corrected for sample weight and percent solids (i.e., original, not duplicate sample weight), in the "Control Limit" column. If the duplicate sample results are outside the control limits, flag all the data for samples received associated with that duplicate sample with an "*". In the instance where there is more than one duplicate sample per SDG, if one duplicate result is not within contract criteria, flag all samples of the same matrix in the SDG. The percent difference data will be used by USEPA to evaluate the long-term precision of the methods for each analyte. Specific control limits for each analyte may be added at a later date based on these precision results.

12.8 Laboratory Control Sample (LCS) Analysis

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

12.8.2 All LCS and percent recovery results shall be reported. If the percent recovery for the LCS falls 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.

12.9 ICP-MS Serial Dilution Analysis

12.9.1 Prior to reporting concentration data for the analytes, the Contractor shall analyze and report the results of the ICP-MS serial dilution analysis. The ICP-MS serial dilution analysis shall be performed on a sample from each group of samples of a similar matrix type (i.e., aqueous/water, soil/sediment) or for each SDG, whichever is more frequent. Samples identified as field blanks and PE samples shall not be used for serial dilution analysis.

12.9.2 If the analyte concentration is sufficiently high (minimally a factor of 50 above the MDL in the original sample), the serial dilution (a five-fold dilution) shall then agree within 10% of the original determination after correction for dilution. If the dilution analysis for one or more analytes is not within a control limit of 10%, and the internal standards in the original sample met the contract criteria, an interference effect must be suspected, and the data for all affected analytes in the samples received and associated with that serial dilution must be flagged with an "E".

12.9.3 The percent differences for each component are calculated as follows:

EQ. 6 Serial Dilution Percent Difference

$$\%\text{Difference} = \frac{\left| SR - SDSR \right|}{SR} \times 100$$

WHERE, SR = Sample Result (µg/L or mg/kg) from EQ.1 or EQ. 2
SDSR = Serial Dilution Sample Result (µg/L or mg/kg) from EQ.1 or EQ.2

12.9.4 In the instance where there is more than one serial dilution per SDG, if one serial dilution result is not within the contract criteria, flag all samples of the same matrix in the SDG. Serial dilution results and "E" flags shall be reported.

12.9.5 If the internal standard responses for the field sample chosen for serial dilution analysis are not within the limits and the appropriate corrective action (two-fold dilution and reanalysis) is taken, the following shall apply to the serial dilution analysis: if the internal standard responses of the field sample reanalysis are within the limits, the serial dilution results are to be reported from a five-fold dilution of the reanalyzed sample. If the internal standard responses of the field sample reanalysis are not within the limits, the serial dilution results are to be reported from a five-fold dilution of the original sample.

12.10 Internal Standards

The analyst shall monitor the responses from the internal standards throughout the sample set being analyzed. Ratios of the raw uncorrected internal standard responses between isotopes should also be routinely monitored. 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. The absolute response of any one internal standard must not deviate more than 60-125% from the original response in the calibration blank.

Calculate the Percent Relative Intensity as follows:

EQ. 7 Percent Relative Intensity

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

WHERE, I_n = Raw Uncorrected Intensity of the internal standard in the sample
I_0 = Raw Uncorrected Intensity of the internal standard in the calibration blank (S0)

If deviations greater than these 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 non-compliant internal standard(s). If the internal standard responses for the diluted sample analysis are within the limits, report the results of this analysis on the appropriate Summary Form. 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 on the appropriate Summary Form.

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).

12.11 MDL Determination

12.11.1 Before any field samples are analyzed under this contract, the MDLs shall be determined for each digestion procedure and instrument used prior to the start of contract analyses and annually thereafter. The MDLs shall meet the levels specified in Exhibit C. 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.

12.11.1.1 To determine the MDLs, the Contractor shall run MDL studies following the procedures given in 40 CFR, Part 136. The Contractor shall prepare the MDL samples by each digestion procedure used and shall analyze these samples on each instrument used.

12.11.1.2 The determined concentration of the MDL shall be less than half the concentration of the CRQL listed in Exhibit C.

12.11.1.3 The results of the MDL determination studies shall be forwarded to the USEPA Regional CLP PO, Sample Management Office (SMO), and Quality Assurance Technical Support (QATS).

12.11.1.4 The MDL results shall be reported on Form IX-IN.

12.12 Example Analytical Sequence for ICP-MS Including the Initial Calibration

Tune
S0
S
S
S
S
S
ICV
ICB
ICSA
ICSAB
CCV
CCB
samples
CCV
CCB
samples
CCV
CCB, etc.

12.13 Summary of QC Operations

The QC operations performed for ICP-MS analysis are summarized in the table below.

QC Operation	Frequency
Instrument Calibration	Each time instrument is turned on or set up, after ICV or CCV failure, and after major instrument adjustment.
Initial Calibration Verification	Following each instrument calibration for each wavelength or mass used.
Initial Calibration Blank	Following each instrument calibration, immediately after the ICV.
Continuing Calibration Verification	For each wavelength or mass used, at a frequency of every 2 hours of a run, at the beginning of each day, and at the beginning and end of each run.
Continuing Calibration Blank	Every 2 hours of a run, at the beginning of each day, and at the beginning and end of each run. Performed immediately after the last CCV.
Interference Check Sample	At the beginning of the run after the ICB but before the CCV.
Serial Dilution for ICP	For each matrix type or for each SDG, whichever is more frequent.
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.
Spike Sample	For each matrix type or for each SDG, whichever is more frequent.
Post-Digestion/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.
ICP-MS Tune	Prior to calibration.
Determination of Method Detection Limits	Prior to contract award, annually thereafter, and after major instrument adjustment.

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

See Section 1.15 in Exhibit D - Introduction to Analytical Methods.

15.0 WASTE MANAGEMENT

See Section 1.16 in Exhibit D - Introduction to Analytical Methods.

16.0 REFERENCES

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

16.2 US Environmental Protection Agency. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846). Method 6020A. Third Edition, 1986, Update IV-A. 1998.

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

16.4 US Environmental Protection Agency. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846). Method 3015A, Revision 1, Update IVa. January 1998.

16.5 US Environmental Protection Agency. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846). Method 3051A, Revision 1, Update IVa. January 1998.

16.6 US Government Printing Office. 40 Code of Federal Regulations, Part 136. Section 1. Appendix B.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

TABLE 1: Interferent and Analyte Elemental Concentrations Used for ICP-MS Interference Check Sample (ICS)

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

NOTE: ICS Solution A (ICSA) contains the interferents at the indicated concentrations. The ICSA may be analyzed at twice the concentration indicated when interferences are present at higher concentrations in the sample. ICS Solution AB (ICSAB) contains all of the analytes and interferents listed above at the indicated concentrations. The ICS solutions are normally provided by USEPA along with the established concentrations of each of the analytes and interferents.

TABLE 2: Isobaric Molecular-Ion Interferences

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

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	
^{78}Se	NiO	NiOH	ZnN	CaCl,KCl	TiS	ZnC	
^{82}Se	ZnO	CuOH	ZnN	TiCl, ScCl	TiS, CrS		
^{76}Se	NiO	CoOH	NiN	KCl	CaS	ZnC	
^{77}Se	NiO	NiOH	CuN	CaCl, ArCl	ScS	CuC	
^{74}Se	NiO	FeOH	NiN	Cl_2, KCl	CaS	NiC	
^{107}Ag	ZrO	ZrOH		GeCl	AsS	MoC	
^{109}Ag		MoOH	MoN	GeCl	SeS	MoC	
$^{205}T1$							
$^{203}T1$		WOH					
^{51}V	C1O	SOH	C1N	ClO, ClN	FS	KC	
^{50}V	SO		ArN			ArC	Mo^{++}
^{64}Zn	TiO	TiOH	TiN, CrN	SiCl, AlCl	S_2	CrC	
^{66}Zn	TiO	TiOH	CrN	PCl, SiCl	S_2	FeC	
^{68}Zn	CrO	VOH	FeN	PCl	ArS	FeC	Ba^{++}
^{67}Zn	VO	TiOH	CrN	SCl	ClS	MnC	Ba^{++}
^{70}Zn	FeO	CrOH	GeN	$C1_2$	ArS	NiC	

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

TABLE 3: Recommended Isotopes and Masses for Selected Elements

Element of Interest	**Analyte Masses - Choose One, or More - Calibrated**	**Masses to be Monitored**
Aluminum	27	
Antimony	121	
Arsenic	75	77, 82 (Isobaric Equation Required)
Barium	135, 137	
Beryllium	9	
Cadmium	111	106, 108 (Isobaric Equation Required)
Calcium	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	
Silver	107, 109	
Sodium	23	
Thallium	203, 205	
Vanadium	51	52, 53 (Isobaric Equation Required)
Zinc	66	
Potential Interferent		
Titanium (TiO on 63Cu)		47 (No Isobaric Equation Required)
Krypton (Kr on 82Se)		83 (No Isobaric Equation Required)
Molybdenum		94, 95, 96, 97, 98
Tin (Sn on 115In)		118 (Isobaric Equation Required)

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

TABLE 4: Recommended Elemental Expressions for Isobaric Interferences

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

C - Calibration blank subtracted counts at specified mass

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

The correction equations shall not be applied if appropriate interference check sample measurement demonstrates absence of interference above the Contract Required Quantitation Limit (CRQL).

TABLE 5: Internal Standards (must use at least five)

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

NOTE: Use of Li^6 requires enriched standard.

TABLE 6: Spiking Levels for Spike Sample Analysis

Analyte	Spike (µg/L)*	Spike (mg/kg)*
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	10	1
Ag	50	5
Tl	50	5
V	500	50
Zn	500	50

*Level in the final prepared sample

18.0 ALTERNATIVE SAMPLE PREPARATION PROCEDURES

18.1 Regionally-Selected Alternative Sample Preparation Procedure

Due to the variability of the matrices received and the interferences encountered, the sample preparation procedures described in Sections 10.1.4 and 10.1.5 may not always produce valid and/or reliable results. Sample preparation procedures are given in this section that describe alternative procedures that can be used if interferences or other issues are noted with the primary procedures. If the Contractor feels that one of these alternative sample preparation procedures would provide better results than the primary methods, then the Contractor shall contact the Sample Management Office (SMO). SMO will contact the USEPA Region for instructions. The Contractor shall document the USEPA Region's decision in the Sample Delivery Group (SDG) Narrative along with populating the Forms and the electronic data deliverable with the valid values that described the actual sample preparation procedures used by the Contractor.

18.2 Alternative Aqueous/Water Sample Preparation Procedures

18.2.1 Preparation Method 3015A – Nitric Acid Digestion (based on USEPA OSW Method 3015A, Revision 1, January 1998)

18.2.1.1 This method describes a sample preparation procedure for the determination of total analytes in various aqueous/water matrices using a microwave technique with a nitric acid only digestion.

18.2.1.2 Measure a 45.0 mL (±0.1 mL) aliquot of a well-shaken, homogenized sample using an appropriate volumetric delivery device, and quantitatively transfer the aliquot to an appropriate vessel equipped with a controlled pressure relief mechanism. The sample shall not be diluted prior to digestion.

18.2.1.3 Add 5.0 mL (±0.1 mL) of concentrated nitric acid to the digestion vessel.

18.2.1.4 Seal the digestion vessel according to the manufacturer's directions. Properly place the digestion vessels in the microwave system according to the manufacturer's recommended specifications and, when applicable, connect appropriate temperature and pressure monitoring equipment to the digestion vessels according to the manufacturer's specifications.

18.2.1.5 The Preparation Blank must have 45.0 mL of reagent water and the same amount (5.0 mL) of acid that was added to the samples.

18.2.1.6 The microwave program is then started. The temperature of each sample should rise to 170°C (±5°C) in approximately 10 minutes and remain at 170°C (±5°C) for 10 minutes, or for the remainder of the 20-minute digestion period. When using temperature feedback control, the number of samples that may be simultaneously digested may vary, from one sample up to the maximum number of digestion vessels that can be heated by the magnetron of the microwave unit. Whenever fewer than the recommended number of samples are to be digested, the remaining digestion vessels should be filled with 45.0 mL of water and 5.0 mL of acid so that the full complement of vessels is achieved. This provides an energy balance, since the microwave power absorbed is proportional to the total absorbing mass in the cavity.

18.2.1.7 At the end of the microwave program, allow the digestion vessels to cool for a minimum of 5 minutes before removing them from the microwave system. When the vessels have cooled to near room temperature, determine if the digestion vessels have maintained their seal throughout the digestion. For vessels that are sealed as discrete separate entities, the digestion vessel weight may be taken before and after digestion to evaluate seal integrity. If the weight loss of the sample exceeds 1% of the weight of the sample and reagents, then the sample is considered compromised and the sample must be redigested. For digestion vessels with burst disks, a careful visual inspection of the disk, in addition to weighing, may identify compromised digestion vessels.

18.2.1.8 Complete the preparation of the sample by carefully uncapping and venting each digestion vessel in a fume hood. Quantitatively transfer the sample to an acid-cleaned bottle. If the digested sample contains particulates which may clog nebulizers or interfere with the injection of the sample into the instrument, the sample may be centrifuged, allowed to settle, or filtered through Whatman No. 41 (or equivalent) filter paper.

18.2.1.9 The final solution typically requires nitric acid to maintain appropriate sample solution acidity and stability of the elements. Commonly, a 2% (v/v) nitric acid concentration is desirable.

18.2.1.10 Transfer or decant the digested sample into a 50 mL volumetric flask and dilute to volume. The samples are now ready for analysis. Concentrations so determined shall be reported as "Total".

18.2.1.11 The digested sample can be diluted if high levels of interferences are noted or if any of the analytes exceed the upper limit of their respective calibration curves.

18.3 Alternative Soil/Sediment Sample Preparation Procedures

18.3.1 Preparation Method 3051A – Nitric Acid Digestion (based on USEPA OSW Method 3051A, Revision 1, January 1998)

18.3.1.1 This method describes a sample preparation procedure for the determination of total recoverable analytes in various soil/sediment matrices using a microwave technique with a nitric acid only digestion.

18.3.1.2 Mix the sample thoroughly to achieve homogeneity (See Exhibit D - Introduction to Analytical Methods, Section 1.8). For each digestion procedure, weigh to the nearest 0.001 g and transfer a 0.50 g sample (wet weight) to an appropriate digestion vessel equipped with a controlled pressure relief mechanism.

18.3.1.3 Add 10 mL (±0.1 mL) of concentrated nitric acid to the digestion vessel in a fume hood.

18.3.1.4 The analyst should be aware of the potential for a vigorous reaction especially with samples containing volatile or easily oxidized organic species. When digesting a matrix of this type, initially use no more than 0.10 g (±0.001 g) of sample. If a vigorous reaction occurs upon the addition of the acid(s), allow the sample to predigest in the uncapped digestion vessel until

the reaction ceases. Heat may be added in this step for safety considerations (e.g., the rapid release of carbon dioxide from carbonates, easily oxidized organic matter, etc.). Once the initial reaction has ceased, the sample may continue through the digestion procedure.

18.3.1.5 Seal the digestion vessel according to the manufacturer's directions. Properly place the digestion vessels in the microwave system according to the manufacturer's recommended specifications and, when applicable, connect appropriate temperature and pressure monitoring equipment to the digestion vessels according to the manufacturer's specifications.

18.3.1.6 The Preparation Blank must have 0.50 g (±0.001 g) of reagent water and the same amount of acid(s) that was added to the samples.

18.3.1.7 The microwave program is then started. The temperature of each sample should rise to 175°C (±5°C) in approximately 5.5 (±0.25) minutes and remain at 175°C (±5°C) for 4.5 minutes, or for the remainder of the 10-minute digestion period. When using temperature feedback control, the number of samples that may be simultaneously digested may vary, from one sample up to the maximum number of digestion vessels that can be heated by the magnetron of the microwave unit. Whenever fewer than the recommended number of samples are to be digested, the remaining digestion vessels should be filled with 0.50 g of water and the same amount of acid(s) so that the full complement of vessels is achieved. This provides an energy balance, since the microwave power absorbed is proportional to the total absorbing mass in the cavity.

18.3.1.8 At the end of the microwave program, allow the digestion vessels to cool for a minimum of 5 minutes before removing them from the microwave system. When the vessels have cooled to near room temperature, determine if the digestion vessels have maintained their seal throughout the digestion. For vessels that are sealed as discrete separate entities, the digestion vessel weight may be taken before and after digestion to evaluate seal integrity. If the weight loss of the sample exceeds 1% of the weight of the sample and reagents, then the sample is considered compromised and the sample must be redigested. For digestion vessels with burst disks, a careful visual inspection of the disk, in addition to weighing, may identify compromised digestion vessels.

18.3.1.9 Complete the preparation of the sample by carefully uncapping and venting each digestion vessel in a fume hood. Quantitatively transfer the sample to an acid-cleaned bottle. Filter the digested sample through Whatman No. 41 (or equivalent) filter paper to remove particulates which would clog the nebulizer or otherwise interfere with the injection of the digested sample into the instrument.

18.3.1.10 The final solution typically requires nitric acid to maintain appropriate sample solution acidity and stability of the elements. Commonly, a 2% (v/v) nitric acid concentration is desirable.

18.3.1.11 Transfer or decant the digested sample into a 50 mL volumetric flask and dilute to volume. The samples are now ready for analysis.

18.3.1.12 The digested sample can be diluted if high levels of interferences are noted or if any of the analytes exceed the upper limit of their respective calibration curves.

18.4 Microwave Calibration Procedure

18.4.1 The calibration procedure is a critical step prior to the use of any microwave unit. The microwave unit must be calibrated every six months. The data for each calibration must be available for review during on-site audits. In order that absolute power settings may be interchanged from one microwave unit to another, the actual delivered power must be determined.

18.4.2 Calibration of a laboratory microwave unit depends on the type of electronic system used by the manufacturer. If the unit has a precise and accurate linear relationship between the output power and the scale used in controlling the microwave unit, then the calibration can be a two-point calibration at maximum and 40% power. If the unit is not accurate or precise for some portion of the controlling scale, then a multiple-point calibration is necessary. If the unit power calibration needs a multiple-point calibration, then the point where linearity begins must be identified. For example: a calibration at 100, 99, 98, 97, 95, 90, 80, 70, 60, 50, and 40% power settings can be applied and the data plotted. The non-linear portion of the calibration curve can be excluded or restricted in use. Each percent is equivalent to approximately 5.5-6 watts and becomes the smallest unit of power that can be controlled. If 20-40 watts are contained from 99-100%, that portion of the microwave calibration is not controllable by 3-7 times that of the linear portion of the control scale and will prevent duplication of precise power conditions specified in that portion of the power scale.

18.4.3 The power available for heating is evaluated so that the absolute power setting (watts) may be compared from one microwave to another. This is accomplished by measuring the temperature rise in 1 kilogram (kg) of reagent water exposed to microwave radiation for a fixed period of time. The reagent water is placed in a polytetrafluoroethylene (PTFE) beaker (or a beaker that is made of some other material that does not absorb microwave energy) and stirred before measuring the temperature. Glass beakers absorb microwave energy and may not be used. The initial temperature of the reagent water must be between 19°C and 25°C. The beaker is circulated continuously through the field for at least 2 minutes at full power. The beaker is removed from the microwave, the reagent water is stirred vigorously, and the final temperature is recorded. The final reading is the maximum temperature reading after each energy exposure. These measurements must be accurate to ±0.1°C and made within 30 seconds of the end of heating. If more measurements are needed, do not use the same reagent water until it has cooled down to room temperature. Otherwise, use a fresh reagent water sample.

The absorbed power is determined by the following formula:

EQ. 8 Absorbed Power

$$P = \frac{(K)(C_p)(m)(DT)}{t}$$

WHERE,
- P = The apparent power absorbed by the sample in watts (joules per second)
- K = The conversion factor for thermochemical calories per second to watts (4.184)
- C_p = The heat capacity, thermal capacity, or specific heat (cal. $g^{-1}\,°C^{-1}$) of reagent water (1.0)
- m = The mass of the sample in grams (g)
- DT = The final temperature minus the initial temperature (°C)
- t = The time in seconds (s)

Using 2 minutes and 1 kg of reagent water, the calibration equation simplifies to:

$$P = (DT)(34.87)$$

The microwave user can now relate power in watts to the percent power setting of the microwave.

18.5 Microwave Digestion Cleaning Procedure

18.5.1 Initial Cleaning of the Polytetrafluoroethylene Perfluoroalkoxy (PTFE PFA) Digestion Vessels

18.5.1.1 Prior to first use - new vessels must be annealed before they are used. A pretreatment/cleaning procedure must be followed. This procedure calls for heating the vessels for 96 hours at 200°C. The vessels must be disassembled during annealing and the sealing surfaces (the top of the vessel or its rim) must not be used to support the vessel during annealing.

18.5.1.2 Rinse in reagent water.

18.5.1.3 Immerse in 50% (v/v) hydrochloric acid for a minimum of 3 hours after the cleaning bath has reached a temperature just below boiling.

18.5.1.4 Rinse in reagent water.

18.5.1.5 Immerse in 50% (v/v) nitric acid for a minimum of 3 hours after the cleaning bath has reached a temperature just below boiling.

18.5.1.6 The vessels are then rinsed with copious amounts of reagent water prior to use for any analyses under this contract.

18.5.2 Cleaning Procedure between Sample Digestions

18.5.2.1 Wash entire vessel in hot water using laboratory-grade non-phosphate detergent.

18.5.2.2 Rinse with 50% (v/v) nitric acid.

18.5.2.3 Rinse 3 times with reagent water.

EXHIBIT D - PART C

ANALYTICAL METHODS
FOR
COLD VAPOR MERCURY ANALYSIS

Exhibit D – Analytical Methods for Cold Vapor Mercury Analysis

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1.0 SCOPE AND APPLICATION

The analytical method that follows is designed to analyze aqueous/water, soil/sediment, and sludge samples taken from hazardous waste sites using a cold vapor technique with Atomic Absorption (AA) for total mercury.

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 Atomic Absorption (AA) spectrophotometer. Sometimes the cell is heated slightly to avoid water condensation. As the mercury atoms pass into the sampling cell, measured absorbance rises indicating the increasing concentration of mercury atoms in the light path. Some systems allow the mercury vapor to pass from the absorption tube to waste, in which case the absorption peaks and then falls as the mercury is depleted. The highest absorbance observed during the measurement or the associated peak area are usually taken as the analytical signal.

2.2 Summary of Preparation and Analysis Procedures

2.2.1 Heated Acid Digestion and Analysis of Aqueous/Water Samples (based on USEPA 7470A) – Manual Preparation Method Followed by an Automated Analysis Method

2.2.2 Heated Acid Digestion and Analysis of Soil/Sediment Samples (based on USEPA 7471B) – Manual Preparation Method Followed by an Automated Analysis Method

2.2.3 Alternative digestion procedures are included in Section 18 of this Exhibit.

3.0 DEFINITIONS

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

4.0 INTERFERENCES

4.1 Aqueous/Water

4.1.1 Some sea waters and wastewaters high in chlorides have shown a positive interference, and require additional 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 nanometers (nm). Care must be taken to assure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). Both inorganic and organic mercury spikes have been quantitatively recovered from the sea water using this technique.

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

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

4.1.4 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.

4.2 Soil/Sediment

4.2.1 The same types of interferences that may occur in aqueous/water samples are also possible with soil/sediment samples (i.e., sulfides, high copper, high chlorides, etc.).

5.0 SAFETY

See Section 1.14 in Exhibit D - Introduction to Analytical Methods.

6.0 EQUIPMENT AND SUPPLIES

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

6.1 Glassware/Labware

6.1.1 Graduated cylinders

6.1.2 Various volumetric flasks and pipets (Class A)

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 milligram (mg)

6.2 General Instrumentation Information for the Automated Analysis of Previously Digested Aqueous/Water and Soil/Sediment Samples

6.2.1 Sampler for the uptake of the previously digested samples

6.2.2 Manifold/Pump system for the addition and mixing of reagents with the previously digested samples

6.2.3 Liquid-Vapor separator

6.2.4 Vapor dryer

6.2.5 Suitable absorption cell

6.2.6 Atomic Absorption (AA) Spectrophotometer – Any AA unit having an open sample presentation area in which to mount the absorption cell would be suitable. AA unit must also be equipped with a Mercury Hollow Cathode Lamp or other suitable light source. 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.

6.2.7 Suitable computer system for data processing

7.0 REAGENTS AND STANDARDS

7.1 Reagents for the Manual Digestion of Aqueous/Water and Soil/Sediment Samples

7.1.1 Aqueous/Water and Soil/Sediment by Manual Digestion Technique

7.1.1.1 Reagent water - The purity of this water must be equivalent to ASTM Type II water (ASTM D1193-06). Use this preparation for all reagents, standards, and dilutions of solutions.

7.1.1.2 Sulfuric acid, concentrated - Reagent grade.

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

7.1.1.3 Nitric acid, concentrated - Reagent grade of low mercury content. If a high Preparation Blank is obtained, it may be necessary to distill the nitric acid.

7.1.1.4 Sodium chloride-hydroxylamine sulfate solution, 12% solution (w/v) - Add 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.

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

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

7.1.1.7 Aqua regia - Prepare immediately prior to use by carefully adding three volumes of concentrated hydrochloric acid to one volume of concentrated nitric acid.

7.1.2 Reagents for the Automated Analysis of Aqueous/Water and Soil/Sediment Digested Samples

7.1.2.1 Stannous sulfate - Add 25 g stannous sulfate to 250 mL of 0.5N sulfuric acid. This mixture is a suspension and should be stirred continuously during use.

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

7.1.2.2 Additional reagents may be needed according to the manufacturer's instructions (e.g., for rinsing out sample and reagent lines).

7.2 Standards

7.2.1 Introduction

The Contractor must provide all standards, except as noted, to be used with this contract. These standards may be used only after they have been certified according to the procedure in Exhibit E, Section 8.0. The Contractor must be able to verify that the standards are certified. Manufacturer's certificates of analysis must be retained by the Contractor and presented upon request.

7.2.1.1 Stock standard solutions may be purchased from a reputable source or prepared from reagent grade chemicals or metals. (CAUTION: Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling.)

7.2.1.2 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 milligram (mg) Hg].

7.2.1.3 Working mercury solution - Make successive dilutions of the stock mercury solution (see Section 7.2.1.2) to obtain a working standard containing 0.1 µg/mL. This working standard and the dilutions of the stock mercury solution shall be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot. From this solution, prepare standards.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Sample Collection and Preservation

All aqueous/water and soil/sediment samples must be collected in glass or polyethylene containers. Aqueous/water samples must be preserved with nitric acid to pH less than or equal to 2 immediately after collection. All samples must be iced or refrigerated at 4°C (±2°C) from the time of collection until digestion.

8.1.1 Dissolved Metals

For the determination of dissolved metals, the sample must be filtered through a 0.45 micrometer (um) pore diameter membrane filter at the time of collection or as soon as possible. Use a portion of the sample to rinse the filter flask, discard this portion, and collect the required volume of filtrate. Preserve the filtrate with nitric acid to pH less than or equal to 2 immediately after filtration.

8.2 Procedure for Sample Storage and Disposal

Following digestion, the remaining unused portion of aqueous/water and soil sediment samples may be stored at room temperature within the laboratory until 60 days after delivery of a complete, reconciled data package to USEPA. After 60 days, the samples may be disposed of in a manner that complies with all applicable regulations.

8.3 Contract Required Holding Time

The maximum holding time for mercury is 26 days from Validated Time of Sample Receipt (VTSR).

9.0 CALIBRATION AND STANDARDIZATION

9.1 Instrument Operating Parameters

Because of the differences between various makes and models of satisfactory instruments, no detailed operating instructions can be provided. Instead, the analyst should follow the instructions provided by the manufacturer of that particular instrument. The Method Detection Limit (MDL) and precision must be investigated and established for mercury on that particular instrument. All measurements must be within the operational range of the instrument. It is the responsibility of the analyst to verify the instrument configuration and operating conditions used satisfy the analytical requirements and to maintain Quality Control (QC) data confirming instrument performance and analytical results.

9.2 Cold Vapor Atomic Absorption (AA) Instrument Calibration Procedure

9.2.1 Instruments shall be calibrated daily or once every 24 hours, each time the instrument is set up, or after Initial Calibration Verification (ICV) or Continuing Calibration Verification (CCV) failure. The instrument standardization date and time shall be included in the instrument output.

9.2.2 The date and time of preparation and analysis shall be given in the laboratory logs (preparation) and instrument output (analysis).

9.2.3 Calibration standards shall be prepared fresh with each calibration performed. Calibrate the instrument with at least six standards, one of which must be a blank standard and one shall be at or below the Contract Required Quantitation Limit (CRQL), in graduated amounts in the appropriate range (Typical range is 0.20 to 10.0 µg/L). Standards and samples must be prepared in the same way on the same day.

9.2.4 The calibration curve shall be calculated using linear regression by plotting the concentration of mercury in the standard (in µg/L) on the X-axis versus the instrument response on the Y-axis. The instrument response is typically the measured Absorbance (displayed as peak area or peak height) for each standard. A standard linear regression, a weighted linear regression (e.g., 1/concentration or $1/concentration^2$), or a linear regression with zero force calibration model can be used as appropriate. No other types of equations (e.g., quadratic) are to be used. The acceptance criteria for the initial calibration curve is a correlation coefficient greater than or equal to 0.995. Sample analysis shall not begin until this criteria and the criteria described in Sections 9.2.5 and 9.2.6 have been met.

9.2.5 The calibration equation must be checked to establish the representativeness of the data that were used to produce the calibration equation. This check involves the re-fitting of the non-blank calibration data back to the calibration equation or the comparison of the calculated concentration of each of the standards against the expected concentration of the associated standard. This difference is related to the actual residual. For this calculation, the Percent Difference shall be used where the above difference is further divided by the expected amount or concentration of the respective standard. If these Percent Differences for each of the standards do not fall within ±30%, then the calibration equation is not acceptable and must be corrected. If a standard is analyzed at

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

9.2.6 The y-intercept from the linear regression initial calibration equation shall also be evaluated. If the y-intercept is not below the CRQL for the initial calibration curve, the calibration is not acceptable and must be corrected. Samples are not to be analyzed until the y-intercept for the initial calibration curve meets the acceptance criteria.

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

9.3 Initial Calibration Verification (ICV)

9.3.1 Immediately after the AA system has been calibrated, the accuracy of the initial calibration shall be verified and documented for mercury by the analysis of the ICV solution at the wavelength used for analysis.

9.3.2 The ICV solution is obtained from USEPA. If the ICV solution is not available, then the ICV solution can be prepared by the laboratory using a certified solution of the analyte from an independent source. Analyses shall be conducted at a concentration other than that used for instrument calibration, but near the middle of the calibration range. An independent source is defined as a standard composed of the analyte from a different source than that used in the standards for instrument calibration. The ICV shall be prepared and analyzed in the same manner as the other samples and standards.

9.3.3 The ICV solution shall be run at the wavelength used for reporting final results.

9.4 Continuing Calibration Verification (CCV)

9.4.1 To ensure calibration accuracy during each analytical run sequence, a CCV shall be analyzed and reported at a frequency not to exceed every 1 hour during an analytical run sequence. The standard shall be analyzed and reported at the beginning of the analytical run sequence and after the last analytical sample. See the example sample analytical run sequence in Section 12.7. This CCV standard shall be prepared from the same source and at the same mid-level concentration as used during the initial calibration.

The same CCV standard shall be used throughout the analytical run sequences for a Sample Delivery Group (SDG) of samples received.

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

9.5 Initial and Continuing Calibration Blank (ICB/CCB)

An ICB or CCB shall be analyzed at the wavelength used for reporting final results for mercury immediately after every ICV and CCV. The ICB and CCB(s) shall be prepared and analyzed in the same manner as the other samples and standards.

NOTE: The results for the ICB and CCBs shall be reported.

10.0 PROCEDURE

10.1 Sample Preparation and Analysis Procedures

10.1.1 If insufficient sample amount (less than 90% of the required amount) is received to perform the analyses, the Contractor shall contact the Sample Management Office (SMO) to inform them of the problem. SMO will contact the USEPA Region for instructions. The USEPA Region will either require that no sample analyses be performed or will require that a reduced volume be used for the sample analysis. No other changes in the analyses will be permitted. The Contractor shall document the USEPA Region's decision in the Sample Delivery Group (SDG) Narrative.

10.1.2 If multiphase samples (e.g., two-phase liquid sample, oily sludge/sandy soil/sediment sample) are received by the Contractor, the Contractor shall contact SMO to apprise them of the type of sample received. SMO will contact the USEPA Region. If all phases of the sample are amenable to analysis, the USEPA Region may require the Contractor to do any of the following:

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

10.1.2.1 If all of the phases are not amenable to analysis (i.e., outside the scope), the USEPA Region may require the Contractor to do any of the following:

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

10.1.2.2 No other changes in the analyses will be permitted. The Contractor shall document the USEPA Region's decision in the SDG Narrative.

10.1.3 The primary sample preparation procedures to be used for this method are described in the following Sections (10.1.4 and 10.1.5). These methods are to be used without deviation. Alternative sample preparation procedures are listed in Section 18 of this method and may be requested by the USEPA Region. No other changes in the analyses will be permitted.

10.1.4 Aqueous/Water Preparation and Analysis of Standards and Samples (For the Manual Preparation Method Followed by an Automated Analysis Method - based on USEPA OSW Method 7470A, Revision 1, September 1994)

10.1.4.1 Manual Technique for the Preparation of Standards and Samples

10.1.4.1.1 For preparation of the standards, transfer aliquots of the working mercury solution (see Section 7.2.1.3) 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 working standard and the dilutions prepared

from this working standard should be prepared fresh daily. 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.

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

10.1.4.1.3 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. 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. Add 8 mL of 5% potassium persulfate solution to each digestion vessel and heat for 2 hours in a water bath or block digester maintained at 95°C (±3°C). Cool and add 6 mL of 12% sodium chloride-hydroxylamine sulfate solution to reduce the excess potassium permanganate. All standards and samples must be at the same final volume. Reagent water can be used to make any necessary final volume adjustments.

10.1.4.1.4 At this point, the digested standards and samples can be allowed to stand at room temperature for up to 48 hours prior to analysis. However, it is recommended that the digested standards and samples be analyzed as soon as possible. Proceed to Section 10.1.4.2 for analysis.

10.1.4.1.5 A reduced volume of 50 mL can be used for all standards, blanks and samples for this digestion procedure. All standards and reagents used in the digestion process shall be scaled back by half of their original required amounts when this reduced volume is used. However, it is the responsibility of the laboratory to confirm that the resultant data meets the CRQL requirements for mercury.

10.1.4.2 Automated Technique for the Analysis of the Digested Standards and Samples

10.1.4.2.1 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.

Transfer appropriate aliquots of the digested standards and samples to the autosampler in the order as suggested by the manufacturer. Complete the analysis of all of the digested standards and samples and construct the calibration curve. The calibration curve shall be constructed based on the concentration of mercury (in µg/L) in the undigested standards, ignoring the volume of reagents added during the digestion process.

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

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

10.1.5 Soil/Sediment Preparation and Analysis of Standards and Samples (For the Manual Preparation Method Followed by an Automated Analysis Method - Based on USEPA OSW Method 7471B, Revision 2, January 1998)

10.1.5.1 Manual Technique for the Preparation of Standards and Samples

10.1.5.1.1 For preparation of the standards, transfer aliquots of the working mercury solution (see Section 7.2.1.3) 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. This working standard and the dilutions prepared from this working standard shall be prepared fresh daily. 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.

10.1.5.1.2 For preparation of the samples, mix the sample thoroughly to achieve homogeneity (See Exhibit D - Introduction to Analytical Methods, Section 1.8). For each digestion procedure, weigh (to the nearest 0.01 g) an aliquot amount of 0.50-0.60 g and place in the bottom of a suitable digestion vessel. Add 5 mL of reagent water to each sample.

10.1.5.1.3 Add 5 mL of aqua regia to each of the digestion vessels and heat for 2 minutes at 95°C (±3°C) in a water bath or block digester. Allow the contents of each digestion vessel to cool and add 50 mL of reagent water and 15 mL of 5% potassium permanganate solution. Mix thoroughly and heat again for 30 minutes at 95°C (±3°C) in a water bath or block digester. Cool and 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. Add 55 mL of reagent water to each sample or 50 mL of reagent water to each standard. All standards and samples must be at the same final volume. Reagent water can be used to make any final volume adjustments, if necessary.

10.1.5.1.4 At this point, the digested standards and samples can be allowed to stand at room temperature for up to 48 hours prior to analysis. However, it is recommended that the digested standards and samples be analyzed as soon as possible. Refer to Section 10.1.4.2 for analysis.

11.0 DATA ANALYSIS AND CALCULATIONS

11.1 Aqueous/Water Sample Calculation

11.1.1 Prepare a standard curve by plotting the instrument response (e.g., peak area or peak height) of the processed standards against their true concentrations (in µg/L) using linear regression as discussed in Section 9.2.4. Determine the instrument response (e.g., peak area or peak height) of the processed field and Quality Control (QC) samples and determine the concentration of mercury (in µg/L) from the standard curve.

11.1.2 Calculate the mercury concentration in the sample by the following formula:

EQ. 1 Aqueous/Water Sample Concentration

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

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

11.2 Soil/Sediment Sample Calculation

11.2.1 Prepare a standard curve by plotting the instrument response (e.g., peak area or peak height) of the processed standards against their true concentrations (in µg/L) using linear regression as discussed in Section 9.2.4. Determine the instrument response (e.g., peak area or peak height) of the processed field and Quality Control (QC) samples and determine the concentration of mercury (in µg/L) from the standard curve.

11.2.2 Calculate the mercury concentration in the sample by the formula:

EQ. 2 Soil/Sediment Sample Concentration

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

WHERE,
- C = Instrument value in µg/L from the calibration curve
- W = Initial aliquot amount (g)
- S = % Solids/100 (see Exhibit D - Introduction to Analytical Methods, Section 1.6)
- DF = Dilution Factor

11.3 Adjusted Method Detection Limit (MDL)/Adjusted Contract Required Quantitation Limit (CRQL) Calculation

To calculate the adjusted MDL or adjusted CRQL for aqueous/water samples, multiply the value of the MDL or CRQL (µg/L) by the Dilution Factor.

Calculate the adjusted MDL or CRQL for soil/sediment samples as follows:

EQ. 3 Adjusted Soil/Sediment MDL or CRQL Concentration

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

WHERE,

C = MDL or CRQL (mg/kg)
W_m = Method required minimum sample weight (g) (0.50 g)
W = Initial aliquot amount (g)
S = % Solids/100 (see Exhibit D - Introduction to Analytical Methods, Section 1.6)
DF = Dilution Factor

12.0 QUALITY CONTROL (QC)

12.1 Initial Calibration Verification (ICV)

The ICV standard shall be prepared in accordance with the instructions provided by the supplier, and carried through the entire preparation and analysis procedure. If measurements exceed 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 reverified. The results of the ICV analysis shall be reported.

12.2 Continuing Calibration Verification (CCV)

The CCV Standard shall be prepared in the same acid matrix as the calibration standards and at a concentration equivalent to the mid-level of the calibration curve using the same standards that were used to prepare the initial calibration curve and carried through the entire preparation and analysis procedure. If the measurements exceed the control limits of 85% Recovery (low) or 115% Recovery (high), the analysis shall be stopped, 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. The results of the CCV analyses shall be reported.

12.3 Blank Analyses

There are two different types of blanks required by this method. The calibration blank is used in establishing the analytical curve. The Initial and Continuing Calibration Blanks (ICB/CCB) are identical in composition to the calibration blank and are analyzed immediately after the ICV/CCV to monitor for potential carryover. The Preparation Blank is used to monitor for possible contamination throughout the entire sample preparation and analysis process.

12.3.1 Initial and Continuing Calibration Blank (ICB/CCB)

The ICB and CCB are prepared with acids and reagent water, and are identical in composition to the Calibration Blank as used to establish the initial calibration curve and carried through the entire preparation and analysis procedure. If the absolute value of the ICB/CCB exceeds the Contract Required Quantitation Limit (CRQL) (see Exhibit C), 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 blank shall be performed. The results of the ICB and CCB analyses shall be reported.

12.3.2 Preparation Blank

12.3.2.1 The Preparation Blank shall contain all the reagents and in the same volumes as used in processing 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.

12.3.2.2 At least one Preparation Blank, consisting of reagent water processed through each sample preparation and analysis procedure (see Section 10), shall be prepared and analyzed with every Sample Delivery Group (SDG), or with each batch[1] of samples digested, whichever is more frequent.

12.3.2.3 The first batch of samples in an SDG is to be assigned to Preparation Blank one, the second batch to Preparation Blank two, etc. Each Complete SDG File (CSF) shall contain the results of all Preparation Blank analyses associated with the samples in that SDG.

12.3.2.4 The Preparation Blank(s) is (are) to be reported for each SDG and used in all analyses to ascertain whether sample concentrations reflect contamination in the following manner:

12.3.2.4.1 If the absolute value of the concentration of the blank is less than or equal to the CRQL (see Exhibit C), no further action is required.

12.3.2.4.2 If the analyte concentration in the blank is above the CRQL, the lowest concentration of the analyte in the associated samples (except those identified as field blanks) shall be greater than or equal to 10 times the blank concentration. Otherwise, all samples (except those identified as field blanks) associated with that blank, with the analyte concentration less than 10 times the blank concentration and above the CRQL, shall be redigested and reanalyzed with appropriate new Quality Control (QC). The sample concentration is not to be corrected for the blank value.

12.3.2.4.3 If the concentration of the blank is below the negative CRQL, then all samples reported below 10 times the CRQL associated with the blank shall be redigested and reanalyzed with appropriate new QC.

12.3.2.4.4 The results for the Preparation Blank shall be reported.

12.4 Spike Sample Analysis

12.4.1 The spike sample analysis is designed to provide information about the effect of the sample matrix on the digestion and/or measurement methodology. The spike is added before the digestion (i.e., prior to the addition of other reagents) and prior to any sample dilutions. At least one spike sample analysis (matrix spike) 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.[2] The sample and its associated spike sample shall initially be run at the same dilution.

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[1] A group of samples prepared at the same time.

[2] USEPA may require additional spike sample analyses, upon USEPA Regional CLP Project Officer (CLP PO) request.

12.4.2 If the spike analysis is performed on the same sample that is chosen for the duplicate sample analysis, spike calculations shall be performed using the results of the sample designated as the "original sample" (see Section 12.5). The average of the duplicate results cannot be used for the purpose of determining percent recovery. Samples identified as field blanks and Performance Evaluation (PE) samples shall not be used for spiked sample analysis. USEPA may require that a specific sample be used for the spike sample analysis.

12.4.3 The analyte spike shall be added at 1 µg/L (aqueous/water) or 0.5 mg/kg (soil/sediment). Adjustment shall be made to maintain these spiking levels when the weight of sample taken deviates by more than 10% of these values.

12.4.4 If the spike recovery falls outside the control limits, the data of all samples received and associated with that spike sample shall be flagged with the letter "N". 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 event, the data shall be reported unflagged even if the percent recovery does not meet the 75-125% recovery criteria.

12.4.5 In the instance where there is more than one spike sample per matrix, per method, per SDG, if one spike sample recovery is not within contract criteria, then flag all the samples of the same matrix and method in the SDG. Individual component percent recoveries (%R) are calculated as follows:

EQ. 4 Matrix Spike Percent Recovery

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

WHERE, SSR = Spiked Sample Result (in µg/L or mg/kg) from EQ. 1 or EQ. 2
SR = Sample Result (in µg/L or mg/kg) from EQ. 1 or EQ. 2
SA = Spike Added Theoretical Result (in µg/L or mg/kg)

12.4.6 When sample concentration is less than the Method Detection Limit (MDL), use SR = 0 only for purposes of calculating the percent recovery. The Spike Sample Results (SSRs), Sample Results (SRs), Spike Added Theoretical Results (SA), and Percent Recovery (positive or negative) shall be reported.

12.4.7 The units used for reporting Spiked Sample Results (SSRs) will be identical to those used for reporting Sample Results (SRs).

12.5 Duplicate Sample Analysis

12.5.1 One duplicate sample shall be analyzed from each group of samples of a similar matrix type (i.e., aqueous/water, soil/sediment) or for each SDG, whichever is more frequent.[3] Duplicates cannot be averaged for reporting.

[3] USEPA may require additional duplicate sample analyses, upon USEPA Regional CLP PO request.

12.5.2 Duplicate sample analyses are not required for percent solids. Samples identified as field blanks and PE samples shall not be used for duplicate sample analysis. USEPA may require that a specific sample be used for duplicate sample analysis. The Relative Percent Difference (RPD) is calculated as follows:

EQ. 5 Duplicate Sample Relative Percent Difference

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

WHERE, RPD = Relative Percent Difference
S = Sample Result (original) (in µg/L or mg/kg) from EQ. 1 or EQ. 2
D = Duplicate Sample Result (in µg/L or mg/kg) from EQ. 1 or EQ. 2

12.5.3 The results of the duplicate sample analyses shall be reported. A control limit of 20 for RPD shall be used for original and duplicate sample values greater than or equal to five times the CRQL (see Exhibit C). A control limit equal to the CRQL shall be entered in the "Control Limit" column if either the sample or duplicate value is less than five times the CRQL. If the sample and duplicate values are greater than or equal to five times the CRQL, or if the sample and duplicate values are less than the CRQL, the "Control Limit" field is left empty.

12.5.4 If one result is above five times the CRQL level and the other is below, use the CRQL criteria to determine if the duplicate analysis is in control. If both sample and duplicate values are less than the CRQL, the RPD is not calculated. For soil/sediment sample or soil/sediment duplicate results less than five times the CRQL, enter the value of the CRQL, corrected for sample weight and percent solids (i.e., original, not duplicate sample weight), in the "Control Limit" column. If the duplicate sample results are outside the control limits, flag all the data for samples received associated with that duplicate sample with an "*". In the instance where there is more than one duplicate sample per SDG, if one duplicate result is not within contract criteria, flag all samples of the same matrix in the SDG. The percent difference data will be used by USEPA to evaluate the long-term precision of the method. Specific control limits for the analyte will be added at a later date based on these precision results.

12.6 MDL Determination

12.6.1 Before any field samples are analyzed under this contract, the MDLs shall be determined for each digestion procedure and instrument used, prior to the start of contract analyses and annually thereafter. The MDLs shall meet the levels specified in Exhibit C. 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.

12.6.1.1 To determine the MDLs, the Contractor shall run MDL studies following the procedures given in 40 CFR, Part 136. The Contractor shall prepare the MDL samples by each digestion procedure used and shall analyze these samples on each instrument used.

12.6.1.2 The determined concentration of the MDL shall be less than half the concentration of the CRQL listed in Exhibit C.

12.6.1.3 The results of the MDL determination studies shall be forwarded to the USEPA Regional CLP PO, Sample Management Office (SMO), and Quality Assurance Technical Support (QATS).

12.6.1.4 The MDL results shall be reported on Form IX-IN.

12.7 Example Analytical Sequence for Mercury

S0
S0.20
S1.0
S2.0
S5.0
S10.0
ICV
ICB
CCV
CCB
samples
CCV
CCB
samples
CCV
CCB, etc.

12.8 Summary of QC Operations

The QC operations performed for mercury analysis are summarized in the table below.

QC Operation	Frequency
Instrument Calibration	Daily or each time instrument is turned on or set up, after ICV or CCV failure, and after major instrument adjustment
Initial Calibration Verification	Following each instrument calibration.
Initial Calibration Blank	Following each instrument calibration, immediately after the ICV.
Continuing Calibration Verification	At a frequency of every hour of a run, and at the beginning and end of each run.
Continuing Calibration Blank	Every hour of a run, and at the beginning and end of each run. Performed immediately after the last CCV.
Preparation Blank	For each SDG or each sample preparation and analysis procedure per batch of prepared samples, whichever is more frequent.
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.
Determination of Method Detection Limits	Prior to contract award, annually thereafter, and after major instrument adjustment.

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

See Section 1.15 in Exhibit D - Introduction to Analytical Methods.

15.0 WASTE MANAGEMENT

See Section 1.16 in Exhibit D - Introduction to Analytical Methods.

16.0 REFERENCES

16.1 US Environmental Protection Agency. Methods for Chemical Analysis of Water and Wastes. Method 245.1. 1974.

16.2 US Environmental Protection Agency. Methods for Chemical Analysis of Water and Wastes. Method 245.2. 1974.

16.3 US Environmental Protection Agency. Methods for Chemical Analysis of Water and Wastes. Method 245.5. 1974.

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

16.5 US Environmental Protection Agency. Test Methods for Evaluating Solid Waste (SW-846), Method 7471B, Revision 2, January 1998.

16.6 US Government Printing Office. 40 Code of Federal Regulations, Part 136. Section 1. Appendix B.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

Not applicable.

18.0 ALTERNATIVE SAMPLE PREPARATION PROCEDURES

18.1 Regionally-Selected Alternative Sample Preparation Procedures

Due to the variability of the matrices received and the interferences encountered, the sample preparation and analysis procedures described in Sections 10.1.4 and 10.1.5 may not always produce valid and/or reliable results. Sample preparation procedures are given in this section that describe alternative procedures that can be used if interferences or other issues are noted with the primary procedures. If the Contractor feels that one of these alternative sample preparation procedures would provide better results than the primary methods, then the Contractor shall contact the Sample Management Office (SMO). SMO will contact the USEPA Region for instructions. The Contractor shall document the USEPA Region's decision in the Sample Delivery Group (SDG) Narrative along with populating the Forms and the electronic data deliverable with the valid values that described the actual sample preparation procedures used by the Contractor.

18.2 Soil/Sediment Preparation and Analysis of Standards and Samples (Manual Technique - Based on modified version of USEPA OSW Method 7471B, Revision 2, January 1998)

18.2.1 This method was modified by using sulfuric acid in combination with nitric acid rather than using aqua regia, which is a combination of hydrochloric acid and nitric acid, as the digestion acid. This method is consistent with how soil/sediment standards and samples were digested in the previous Statements of Work and may provide better consistency of results for certain project samples that were prepared by the older method.

18.2.2 Manual Technique for the Preparation of Standards and Samples

18.2.2.1 For preparation of the standards, transfer aliquots of the working mercury solution (see Section 7.2.1.3) 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. This working standard and the dilutions prepared from this working standard shall be prepared fresh daily. The acidity of all 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.

18.2.2.2 For preparation of the samples, mix the samples thoroughly to achieve homogeneity (see Exhibit D - Introduction to Analytical Methods, Section 1.8). For each digestion procedure, weigh (to the nearest 0.01 g) an aliquot 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.

18.2.2.3 Add 5 mL of concentrated sulfuric acid and 2.5 mL of concentrated nitric acid and heat for 2 minutes at 95°C (±3°C) in a water bath or block digester. Cool, then add 50 mL reagent water, 15 mL potassium permanganate solution, and 8 mL of potassium persulfate solution to each sample. Mix thoroughly, then heat for an additional 30 minutes at 95°C (±3°C) in a water bath or block digester. Cool and add 6 mL of sodium chloride- hydroxylamine sulfate to each digestion vessel to reduce the excess potassium permanganate. CAUTION: Do this addition under a hood, as chlorine could be evolved. Add 55 mL of reagent water to each

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

18.2.2.4 At this point, the digested standards and samples can be allowed to stand for up to 48 hours prior to analysis. However, it is recommended that the digested standards and samples be analyzed as soon as possible. Refer to Section 10.1.4.2 for analysis.

EXHIBIT D - PART D

ANALYTICAL METHODS
FOR
TOTAL CYANIDE ANALYSIS

Exhibit D – Analytical Methods For Total Cyanide Analysis

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1.0 SCOPE AND APPLICATION

The method is designed to determine the concentration of total cyanide in aqueous/water and soil/sediment samples taken from hazardous waste sites.

2.0 SUMMARY OF METHOD

2.1 Aqueous/Water and Soil/Sediment

2.1.1 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.

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

3.0 DEFINITIONS

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

4.0 INTERFERENCES

Several interferences are encountered with this method. 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 should be tested in the field for the presence of sulfides as described in Section 8.1.1.

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 antifoam 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 should be tested in the field for the presence of oxidizing agents as described in Section 8.1.1.

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 interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid prior to the distillation process.

5.0 SAFETY

See Section 1.14 in Exhibit D - Introduction to Analytical Methods.

6.0 EQUIPMENT AND SUPPLIES

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

6.1 Midi-Distillation of Aqueous/Water and Soil/Sediment Samples

6.1.1 Midi-reflux distillation apparatus

6.1.2 Heating block - Capable of maintaining 125°C (±5°C)

6.1.3 Auto analyzer system with accessories:

6.1.3.1 Sampler

6.1.3.2 Pump

6.1.3.3 Cyanide cartridge

6.1.3.4 Spectrophotometer with 50 mm flow cells and 580 nm filter

6.1.3.5 Chart recorder or data system

6.1.4 Assorted volumetric glassware, pipets, and micropipets (Class A)

6.1.5 Top loader balance, 300 g capacity, and a minimum sensitivity of ±1.0 mg

6.2 Micro-Distillation of Aqueous/Water and Soil/Sediment Samples

6.2.1 Micro-distillation apparatus

6.2.1.1 Heating block - capable of maintaining 120°C (±5°C)

6.2.1.2 Micro-distillation tubes - Sample tubes and Collector tubes, either pre-filled or user-filled with trapping solution

6.2.1.3 Tube press

6.2.2 Flow Injection Analyzer with accessories

6.2.2.1 Spectrophotometer with 580 nm filters

6.2.3 Assorted volumetric glassware, pipets, and micropipets (Class A)

6.2.4 Top loader balance, 300 g capacity and sensitivity of ±1.0 mg

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 preparation for all reagents, standards, and dilutions of solutions.

7.1.2 Lead acetate Test Paper.

7.1.3 Cadmium carbonate (Powdered).

7.1.4 Potassium Iodide – Starch Test Paper.

7.1.5 Ascorbic acid (Crystals).

7.1.6 Midi-Distillation and Preparation Reagents for Aqueous/Water and Soil/Sediment Samples

7.1.6.1 Sodium hydroxide absorbing solution and sample wash solution, 0.25N - Dissolve 10.0 g sodium hydroxide in reagent water and dilute to 1 L.

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

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

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

7.1.6.5 Sulfamic acid (Powdered).

7.1.7 Micro-Distillation and Preparation Reagents for Aqueous/Water and Soil/Sediment Samples

7.1.7.1 Sodium hydroxide absorbing solution and sample wash solution, 0.25N – Dissolve 10.0 g sodium hydroxide in reagent water and dilute to 1 L.

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

7.1.7.3 Sulfuric Acid/Magnesium Chloride solution (7.11 M sulfuric acid/0.79 M magnesium chloride) - In a fume hood, weigh 32.2 g $MgCl_2 \cdot 6H_20$ into a tared 500 mL beaker and add 110.8 g reagent water. Add 139 g concentrated sulfuric acid in 40 g portions with stirring. Allow the solution to cool.

7.1.7.4 Sulfamic acid (Powdered).

7.1.8 Spectrophotometric Reagents for Midi- and Micro-Distillation of Aqueous/Water and Soil/Sediment Samples

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

7.1.8.2 Acetate Buffer - Dissolve 410 g of $NaC_2H_3O_2 \cdot 3H_2O$ in 500 mL of reagent water. Add sufficient glacial acetic acid to adjust pH to 4.5 (approximately 500 mL). An equivalent phosphate buffer may be substituted for the acetate buffer.

7.1.8.3 Pyridine-barbituric acid solution - Transfer 15 g of barbituric acid into a 1 Liter volumetric flask. Add about 100 mL of reagent water and swirl the flask. Add 75 mL of pyridine and mix. Add 15 mL of concentrated hydrochloric acid and mix.

Dilute to about 900 mL with reagent water and mix until the barbituric acid is dissolved. Dilute to 1 L with reagent water. Store at 4°C (±2°C).

7.2 Standards

7.2.1 Introduction

The Contractor must provide all standards, except as noted, to be used with this contract. These standards may be used only after they have been certified according to the procedure in Exhibit E, Section 8.0. The Contractor must be able to verify that the standards are certified. Manufacturer's certificates of analysis must be retained by the Contractor and presented upon request.

7.2.2 Stock Standard Solutions

7.2.2.1 Stock cyanide solution, 1000 mg/L CN - Dissolve 2.51 g of potassium cyanide and 2.0 g potassium hydroxide in reagent water and dilute 1 L. Standardize with 0.0192N silver nitrate. Standardization is not necessary if this standard is purchased as a certified solution.

7.2.2.2 Intermediate cyanide standard solution, 10 mg/L CN - Dilute 1.0 mL of stock cyanide solution plus 20 mL of 1.25N sodium hydroxide solution to 100 mL with reagent water. Prepare this solution at time of analysis.

7.2.3 Secondary Dilution Standards

7.2.3.1 Secondary Dilution Standards

Prepare secondary dilution standard solutions by diluting the appropriate volumes of the intermediate cyanide standard solution with 0.25N sodium hydroxide. The final concentration of sodium hydroxide in all standards should be 0.25N.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Sample Collection and Preservation

8.1.1 Aqueous/Water Sample Preservation

Collection of total cyanide must be in polyethylene or glass containers. The sample must be tested for sulfides and oxidizing agents, and preserved by the sampler immediately upon sample collection. Place a drop of the sample on lead acetate test paper to detect the presence of sulfides. If sulfides are present (test strip turns black), the sample volume required for the cyanide determination should be increased by 25 milliliters (mL). The total volume of sample should then be treated with powdered cadmium carbonate. Yellow cadmium sulfide precipitates if the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper. Filter the solution through dry filter paper into a dry beaker, and from the filtrate measure the sample to be used for analysis. Avoid a large excess of cadmium carbonate and a long contact time in order to minimize a loss by complexation or occlusion of cyanide on the precipitated material. If no sulfides are present, test for the presence of oxidizing agents by placing a drop of the sample on a strip of potassium iodide - starch test paper (KI - starch paper); a blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on

the indicator paper. Then add an additional 0.6 g of ascorbic acid for each liter of sample volume. Preserve the sample with sodium hydroxide to pH greater than or equal to 12 and maintain at 4°C (±2°C) until distillation.

8.1.2 Soil/Sediment Sample Preservation

Samples shall be kept at 4°C (±2°C) from the time of collection until distillation.

8.2 Procedure for Sample Storage and Disposal

8.2.1 Aqueous/water samples must be protected from light and refrigerated at 4°C (±2°C) from the time of receipt until 60 days after delivery of a complete, reconciled data package to the U.S. Environmental Protection Agency (USEPA). After distillation, soil/sediment samples may be stored at room temperature within the laboratory until 60 days after delivery of a complete, reconciled data package to USEPA. After 60 days, the samples may be disposed of in a manner that complies with all applicable regulations.

8.2.2 The samples must be stored in an atmosphere demonstrated to be free of all potential contaminants.

8.2.3 Samples, sample distillates, and standards must be stored separately.

8.3 Contract Required Holding Time

The maximum sample holding time for cyanide is 12 days from Validated Time of Sample Receipt (VTSR).

9.0 CALIBRATION AND STANDARDIZATION

9.1 Instrument Operating Parameters

Because of the difference between various makes and models of satisfactory instruments, no detailed operating instructions can be provided. Instead, the analyst should follow the instructions provided by the manufacturer of the particular instrument. The Method Detection Limit (MDL) and precision must be investigated and established for cyanide on that particular instrument. All measurements must be within the operational range of the instrument. It is the responsibility of the analyst to verify the instrument configuration and operating conditions used satisfy the analytical requirements and to maintain Quality Control (QC) data confirming instrument performance and analytical results.

9.2 General Procedure

The following general procedure applies to most semi-automated spectrophotometers. Set up the manifold and complete system per manufacturer's instructions. Allow the spectrophotometer and recorder to warm up for at least 30 minutes prior to use. Establish a steady reagent baseline, feeding reagent water through the sample line and appropriate reagents (see Section 7.1.8) through reagent lines. Adjust the baseline using the appropriate control on the spectrophotometer. Prepare a standard curve by plotting the instrument response (e.g., absorbance) of standard on the Y-axis vs. concentration of the standard (in µg/L) on the X-axis.

9.3 Spectrophotometric Instrument Calibration Procedure

9.3.1 Instruments shall be calibrated daily or once every 24 hours, each time the instrument is set up, or after Initial Calibration Verification (ICV) or Continuing Calibration Verification (CCV) failure. The instrument standardization date and time shall be included in the instrument output.

9.3.2 The date and time of preparation and analysis shall be given in the laboratory logs (preparation) or instrument output (analysis).

9.3.3 Calibration standards shall be prepared fresh with each calibration performed. Calibrate the instrument with at least six standards, one of which must be a blank standard and one shall be at or below the Contract Required Quantitation Limit (CRQL), in graduated amounts in the appropriate range. The calibration curve shall be calculated using linear regression by plotting the concentration of cyanide in the standard (in µg/L) on the X-axis versus the instrument response (e.g., Absorbance) on the Y-axis. A standard linear regression, a weighted linear regression (e.g., $1/\text{concentration}$ or $1/\text{concentration}^2$), or a linear regression with zero force calibration model can be used as appropriate. No other types of equations (e.g., quadratic) are to be used. The acceptance criteria for the calibration curve is a correlation coefficient greater than or equal to 0.995. Sample analysis shall not begin until this criteria and the criteria in Sections 9.3.4 and 9.3.5 have been met.

9.3.4 The calibration equation must be checked to establish the representativeness of the data that were used to produce the calibration equation. This check involves the re-fitting of the non-blank calibration data back to the calibration equation or the comparison of the calculated concentration of each of the standards against the expected concentration of the associated standard. This difference is related to the actual residual. For this calculation the Percent Difference shall be used where the above difference is further divided by the expected amount or concentration of the respective standard. If these Percent Differences for each of the standards do not fall within ±30%, then the calibration equation is not acceptable and must be corrected. If a standard is analyzed at a concentration that is below the CRQL and the above criteria is not met, that value can be excluded from the calibration curve as long as the lowest non-zero standard is still analyzed at or below the CRQL and all standards included in the calibration curve are continuous and consecutive.

9.3.5 The y-intercept from the linear regression initial calibration equation shall also be evaluated. If the y-intercept is not below the CRQL for the initial calibration curve, the calibration is not acceptable and must be corrected. Samples are not to be analyzed until the y-intercept for the initial calibration curve meets the acceptance criteria.

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

9.4 Initial Calibration Verification (ICV)

9.4.1 Immediately after each cyanide system has been calibrated, the accuracy of the initial calibration shall be verified and documented for cyanide by the analysis of the ICV Solution at the wavelength used for analysis.

9.4.2 The ICV Solution is obtained from USEPA. If the solution is not available, the ICV solution can be prepared by the laboratory using a certified solution of the analyte from an independent source. Analyses shall be conducted at a concentration other than that used for instrument calibration, but near the middle of the calibration range. An independent source is defined as a standard composed of the analyte from a different source than those used in the standards for the instrument calibration.

9.4.3 The ICV shall be processed in the same manner as the standards used for the initial calibration for the method used.

9.5 Continuing Calibration Verification (CCV)

9.5.1 To ensure calibration accuracy during each analytical run sequence, a CCV shall be analyzed and reported at a frequency not to exceed every 1 hour during an analytical run sequence. The standard shall also be analyzed and reported at the beginning of the analytical run sequence and after the last analytical sample. See the example sample analytical run sequence in Section 12.7. This CCV standard shall be prepared from the same source and at the same mid-level concentration as the standards used during the initial calibration.

The same CCV standard shall be used throughout the analytical run sequences for a Sample Delivery Group (SDG) of samples received.

9.5.2 Each CCV analyzed shall be processed in the same manner as the standards used for the initial calibration for the method used.

10.0 PROCEDURE

10.1 Sample Preparation

10.1.1 If insufficient sample amount (less than 90% of the required amount) is received to perform the analyses, the Contractor shall contact the Sample Management Office (SMO) to inform them of the problem. SMO will contact the USEPA Region for instructions. The USEPA Region will either require that no sample analyses be performed or will require that a reduced volume be used for the sample analysis. No other changes in the analyses will be permitted. The Contractor shall document the USEPA Region's decision in the Sample Delivery Group (SDG) Narrative.

10.1.2 If multi-phase samples (e.g., two-phase liquid sample, oily sludge/sandy soil/sediment sample) are received by the Contractor, the Contractor shall contact SMO to apprise them of the type of sample received. SMO will contact the USEPA Region. If all phases of the sample are amenable to analysis, the USEPA Region may require the Contractor to do any of the following:

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

10.1.2.1 If all of the phases are not amenable to analysis (i.e., outside scope), the USEPA Region may require the Contractor to do any of the following:

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

10.1.2.2 No other changes in the analyses will be permitted. The Contractor shall document the USEPA Region's decision in the SDG Narrative.

10.1.3 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 test for sulfides shall be performed by placing a drop of the sample on a strip of lead acetate paper. If the test strip turns black, the Contractor shall treat the total volume of sample with powdered cadmium carbonate. Yellow cadmium sulfide precipitates when the sample contains sulfide.

This operation shall be repeated until a drop of the treated sample solution does not darken the lead acetate test paper. The solution shall be filtered through dry filter paper into a dry beaker, and the volume of sample to be used for analysis shall be measured from the filtrate. It is recommended that the Contractor avoid a large excess of cadmium carbonate and a long contact time in order to minimize a loss by complexation or occlusion of cyanide on the precipitated material. The test for oxidizing agents shall be performed by placing a drop of the sample on a strip of potassium iodide - starch test paper (KI - starch paper). If the test strip turns blue, the Contractor shall contact SMO for further instructions from the USEPA Region before proceeding with sample preparation and analysis. The Contractor shall document the presence of sulfides or oxidizing agents in the SDG Narrative. The Contractor shall document the results (positive or negative) of the tests for sulfides and oxidizing agents in the distillation log.

10.2 Aqueous/Water and Soil/Sediment Preparation of Standards and Samples

10.2.1 Standards Preparation

10.2.1.1 All standards for the midi-distillation and micro-distillation semi-automated spectrophotometric analysis shall be distilled in the same manner as the samples.

10.2.1.2 Standards for Midi-Distillation Preparation and Semi-Automated Spectrophotometric Analysis of Aqueous/Water and Soil/Sediment Samples

Calibration standards - Prepare a minimum of five standards and a calibration blank over the range of the analysis. These standards shall be prepared by pipetting suitable volumes of the secondary dilution standard solution (see Section 7.2.3.1) into volumetric flasks and diluting to volume with 0.25N sodium hydroxide. Add 50 mL of each standard to a midi-distillation tube and then prepare and distill these standards and the calibration blank in the same manner as the samples.

NOTE: The concentration of one of the calibration standards shall be at or below the Contract Required Quantitation Limit (CRQL).

10.2.1.3 Standards for Micro-Distillation Preparation and Semi-Automated Spectrophotometric Analysis of Aqueous/Water and Soil/Sediment Samples

Calibration Standards - Prepare a minimum of five standards and a calibration blank over the range of the analysis. These standards shall be prepared by pipetting suitable volumes of the secondary dilution standard solution (see Section 7.2.3.1) into volumetric flasks and diluting to volume with 0.25N sodium hydroxide. Add 6 mL of each standard to a sample tube and then prepare and distill these standards and the calibration blank in the same manner as samples.

NOTE: The concentration of one of the calibration standards shall be at or below the CRQL.

10.2.2 Aqueous/Water Samples Preparation

10.2.2.1 Preparation Method for Aqueous/Water Samples by Midi-Distillation

10.2.2.1.1 The procedure described here utilizes a midi-distillation apparatus and requires a sample aliquot of 50 mL for aqueous/water samples. The sample shall not be diluted prior to distillation.

10.2.2.1.2 Pipet 50 mL (±1 mL) of sample into the distillation flask along with 2 or 3 boiling chips.

10.2.2.1.3 Add 50 mL (±1 mL) of 0.25N sodium hydroxide to the gas absorbing tube.

10.2.2.1.4 Connect the boiling flask, condenser, and absorber in the train. The excess cyanide trap contains 0.5N sodium hydroxide.

10.2.2.1.5 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.

10.2.2.1.6 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.

10.2.2.1.7 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.

10.2.2.1.8 Add 2 mL of the 2.5M magnesium chloride solution through the top air inlet tube of the distillation head into the reaction vessel. Excessive foaming from samples containing surfactants may be quelled by the addition of either another 2 mL of the 2.5M magnesium chloride solution or a few drops of a commercially available anti-foam agent. The Contractor shall document the addition of magnesium chloride solution or anti-foam agent in the SDG Narrative.

10.2.2.1.9 Turn on the heating block and set for 125°C (±3°C). Heat the solution to boiling, taking care to prevent solution backup by periodic adjustment of the vacuum flow.

10.2.2.1.10 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.

10.2.2.1.11 After cooling, close off the vacuum at the gang valve and remove the absorber. Seal the receiving solutions and store them at 4°C until analyzed.

10.2.2.2 Preparation Method for Aqueous/Water Samples by Micro-Distillation

10.2.2.2.1 Preheat the heater block to 120°C (±3°C). Add 6 mL (±0.1 mL) of sample to the sample tube. The sample shall not be diluted prior to distillation. If the Contractor is not using the prefilled collector tubes, add 2 mL (±0.1 mL) of the 0.25N absorbing solution to each collector tube. Add 0.75 mL of the (7.11M/0.79M) sulfuric acid/magnesium chloride solution to each sample tube and immediately cap with a collector tube and press to seal.

10.2.2.2.2 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.

10.2.2.2.3 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. The distillate is now ready for analysis. Seal the distillate and store at 4°C until analyzed.

10.2.3 Soil/Sediment Samples Preparation

10.2.3.1 Preparation Method for Soil/Sediment Samples by Midi-Distillation

10.2.3.1.1 The procedure described here utilizes a midi-distillation apparatus and requires a sample aliquot of at least 1 g for soil/sediment.

10.2.3.1.2 Mix the sample thoroughly to achieve homogeneity (see Exhibit D - Introduction to Analytical Methods, Section 1.8). For each digestion procedure, weigh to the nearest 0.01 g and transfer 1.00 - 1.50 g of sample (wet weight) into the reaction vessel and add 50 mL of reagent water. Add 2 or 3 boiling chips.

10.2.3.1.3 Add 50 mL (±1 mL) of 0.25N sodium hydroxide to the gas absorbing impinger.

10.2.3.1.4 Connect the reaction vessel, condenser, and absorber in the train. The excess cyanide trap contains 0.5N sodium hydroxide.

10.2.3.1.5 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.

10.2.3.1.6 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 to mix for 5 minutes.

NOTE: The acid volume must be sufficient to bring the sample/solution pH to below 2.0.

10.2.3.1.7 Add 2 mL of the 2.5M magnesium chloride solution through the top air inlet tube of the distillation head into the reaction vessel. Excessive foaming from samples containing surfactants may be quelled by the addition of either another 2 mL of the 2.5M magnesium chloride solution or a few drops of a

commercially available anti-foam agent. The Contractor shall document the addition of the 2.5M magnesium chloride solution or anti-foam agent in the SDG Narrative.

10.2.3.1.8 Turn on the heating block and set for 125°C (±3°C). Heat the solution to boiling, taking care to prevent solution backup by periodic adjustment of the vacuum flow.

10.2.3.1.9 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.

10.2.3.1.10 After cooling, close off the vacuum at the gang valve and remove the absorber. Seal the receiving solutions and store them at 4°C until analyzed.

10.2.3.2 Preparation Method for Soil/Sediment Samples by Micro-Distillation

10.2.3.2.1 Preheat the heater block to 120°C (±3°C). Add 0.50-1.00 g (±0.01 g) of sample (wet weight) and 5 mL of reagent water to the sample tube. If the Contractor is not using the prefilled collector tubes, add 2 mL (±0.1 mL) of the 0.25N absorbing solution to the collector tube. Add 0.75 mL of the (7.11M/0.79M) sulfuric acid/magnesium chloride solution to each sample tube and immediately cap with collector tube and press to seal.

10.2.3.2.2 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.

10.2.3.2.3 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. The distillate is now ready for analysis. Seal the distillate and store at 4°C until analyzed.

10.3 Sample Analysis

10.3.1 Semi-Automated Spectrophotometric Determination of Distillates

10.3.1.1 Set up the manifold. Pump the reagents through the system until a steady baseline is obtained.

10.3.1.2 Place the distilled calibration standards, blanks, and control standards in the sampler tray, followed by the distilled samples, duplicates, standards, spikes, and blanks. Allow all standards and samples to come to ambient room temperature prior to analysis.

10.3.1.3 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.

10.3.1.4 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.

11.0 DATA ANALYSIS AND CALCULATIONS

11.1 Calculations for Midi- and Micro-Distillation of Aqueous/Water and Soil/Sediment Samples

11.1.1 Calculations for Semi-automated Spectrophotometric Determination

11.1.1.1 Prepare a standard curve by plotting the instrument response of the standards against their true concentrations in µg/L using linear regression as discussed in Section 9.3.3. This standard curve is then used to determine the concentration of cyanide in the field and Quality Control (QC) samples.

11.1.1.2 Calculate the cyanide concentration in aqueous/water samples by the formula:

EQ. 1 Aqueous/Water Sample Concentration

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

WHERE,
- C = Instrument response in µg/L CN from the calibration curve
- V_f = Final prepared (absorbing solution) volume (mL)
- V = Initial aliquot amount (mL)
- DF = Dilution Factor

11.1.1.3 Calculate the cyanide concentration in soil/sediment samples by the formula:

EQ. 2 Soil/Sediment Sample Concentration

$$\text{CN Concentration (mg/kg)} = C \times \frac{V_f}{W \times S} \times (1/1000) \times DF$$

WHERE,
- C = Instrument response in µg/L CN from the calibration curve
- V_f = Final prepared (absorbing solution) volume (mL)
- W = Initial aliquot amount (g)
- S = % Solids/100 (see Exhibit D - Introduction to Analytical Methods, Section 1.6)
- DF = Dilution Factor

11.1.1.4 Adjusted Method Detection Limit (MDL)/Adjusted Contract Required Quantitation Limit (CRQL) Calculation

To calculate the adjusted aqueous/water MDL or CRQL for the midi and micro methods, multiply the MDL or CRQL (µg/L) by the sample Dilution Factor.

The adjusted soil/sediment MDL or CRQL for the midi- and micro-distillation methods shall be calculated as follows:

EQ. 3 Adjusted Soil/Sediment MDL or CRQL

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

WHERE,
- C = MDL or CRQL (mg/kg)
- W_M = Minimum method required aliquot amount (1.00 g for midi or 0.50 g for micro)
- W = Initial aliquot amount (g)
- S = % Solids/100 (see Exhibit D - Introduction to Analytical Methods, Section 1.6)
- DF = Dilution Factor

12.0 QUALITY CONTROL (QC)

12.1 Initial Calibration Verification (ICV)

The ICV standard shall be prepared in the same matrix as the calibration standards and in accordance with the instructions provided by the supplier. The ICV standard shall be processed in the same manner as the standards used for the initial calibration for the method used. If measurements exceed 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 reverified. The results of the ICV analysis shall be reported.

12.2 Continuing Calibration Verification (CCV)

The CCV standard shall be prepared in the same matrix as the calibration standards by the analyst at a concentration equivalent to the mid-point of the calibration curve using the same standards that were used to prepare the initial calibration curve. The CCV standard shall be processed in the same manner as the standards used for the initial calibration for the method used. If the measurement exceeds the control limits of 85% Recovery (low) or 115% Recovery (high), the analysis shall be stopped, 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. The results of all CCV analyses shall be reported.

12.3 Blank Analyses

There are two different types of blanks required by this method. The calibration blank is used in establishing the analytical curve. The Initial and Continuing Calibration Blanks (ICB/CCB) are identical in composition to the calibration blank and are analyzed immediately after the ICV/CCV to monitor for potential carryover of the analyte. The Preparation Blank is used to monitor for possible contamination throughout the entire sample preparation and analysis process.

12.3.1 Initial and Continuing Calibration Blank (ICB/CCB)

The ICB and CCB are identical in composition to the Calibration Blank as used to establish the initial calibration curve. The ICB/CCB shall be processed in the same manner as the standards used for the initial calibration for the method used. If the absolute value of the calibration blank (ICB/CCB) result exceeds the Contract Required Quantitation Limit (CRQL) (see Exhibit C), 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 blank shall be performed. Results of the ICB and CCB analyses shall be reported.

12.3.2 Preparation Blank

12.3.2.1 The Preparation Blank shall contain all the reagents and in the same volumes as used in processing the samples. The Preparation Blank shall be carried through the complete preparation, distillation, and analysis method process.

12.3.2.2 At least one Preparation Blank, consisting of reagent water processed through each sample preparation and analysis procedure (see Section 10), shall be prepared and analyzed with every Sample Delivery Group (SDG), or with each batch[1] of samples distilled, whichever is more frequent.

12.3.2.3 The first batch of samples in an SDG is to be assigned to Preparation Blank one, the second batch of samples to Preparation Blank two, etc. Each Complete SDG File (CSF) shall contain the results of all the Preparation Blank analyses associated with the samples in that SDG.

12.3.2.4 The Preparation Blank(s) is (are) to be reported for each SDG and used in all analyses to ascertain whether sample concentrations reflect contamination in the following manner:

12.3.2.4.1 If the absolute value of the concentration of the blank is less than or equal to the CRQL (see Exhibit C), no further action is required.

12.3.2.4.2 If the analyte concentration in the blank is above the CRQL, the lowest concentration of the analyte in the associated samples (except those identified as field blanks) shall be greater than or equal to 10 times the blank concentration. Otherwise, all samples (except those identified as field blanks) associated with the blank, with the analyte concentration less than 10 times the blank concentration and above the CRQL, shall be redistilled and reanalyzed with appropriate new QC. The sample concentration is not to be corrected for the blank value.

12.3.2.4.3 If the concentration of the blank is below the negative CRQL, then all samples associated with the blank and reported below 10 times CRQL shall be reprepared and reanalyzed with appropriate new QC.

12.3.2.4.4 The results for the Preparation Blank shall be reported.

12.4 Spike Sample Analysis

12.4.1 The spike sample analysis is designed to provide information about the effect of the sample matrix on the distillation and/or measurement methodology. The spike is added before the distillation step and prior to the addition of other reagents. At least one spike sample analysis (matrix spike) 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.[2] The sample and its associated spike sample shall initially be run at the same dilution.

12.4.2 If the spike analysis is performed on the same sample that is chosen for the duplicate sample analysis, spike calculations shall be performed using the results of the sample designated as the "original sample" (see Section 12.5). The average of the duplicate results cannot be used for the purpose of determining percent recovery. Samples identified as field blanks and Performance Evaluation (PE) samples shall not be used for spiked sample

[1] A group of samples prepared at the same time.

[2] USEPA may require additional spike sample analyses, upon USEPA Regional CLP Project Officer (CLP PO) request.

analysis. USEPA may require that a specific sample be used for the spike sample analysis.

12.4.3 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 distillate volume of 50 mL). For a typical 50 mL aqueous/water sample, this would be equivalent to a concentration of 100 µg/L in the original sample. For a typical 1.00 g soil/sediment sample, this would be equivalent to a concentration of 5 mg/kg in the original dry sample. Adjustments shall be made to maintain these spiking levels when the weight of the sample taken deviates by more than 10% of these values.

12.4.4 If the spike recovery is not at or within the limits of 75-125%, the data for all samples received and associated with that spike sample and determined by the same analytical method shall be flagged with the letter "N". 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 event, the data shall be reported unflagged even if the percent recovery does not meet the 75-125% recovery criteria.

12.4.5 When the matrix spike recovery falls outside the control limits and the sample result does not exceed four times the spike added, a post-distillation spike shall be performed. Note that if a post-distillation spike analysis is required, the same USEPA sample that was used for the matrix spike analysis shall be used for the post-digestion spike analysis. Spike the unspiked aliquot of the undiluted distillate at two times the indigenous level or two times the CRQL, whichever is greater.

12.4.6 In the instance where there is more than one spike sample per matrix, per method, per SDG, if one spike sample recovery is not within contract criteria, flag all the samples of the same matrix and method in the SDG. Individual component percent recoveries are calculated as follows:

EQ. 4 Matrix Spike and Post-Digestion Spike Percent Recovery

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

WHERE, SSR = Spiked Sample Result (µg/L or mg/kg) from EQ. 1 or EQ. 2
SR = Sample Result (µg/L or mg/kg) from EQ. 1 or EQ. 2
SA = Spike Added Theoretical Result (µg/L or mg/kg). This is calculated by substituting the spiking amount used for the 'V_f' term and substituting the spiking standard concentration used for the 'C' term from EQ. 1 or EQ.2.

12.4.7 When the sample concentration is less than the Method Detection Limit (MDL), use SR = 0 only for purposes of calculating the percent recovery. The Spike Sample Results (SSRs), Sample Results (SRs), Spike Added (SA), and percent recovery (positive or negative) shall be reported.

12.4.8 The units used for reporting Spike Sample Results (SSRs) will be identical to those used for reporting Sample Results (SRs).

12.5 Duplicate Sample Analysis

12.5.1 One duplicate sample shall be analyzed from each group of samples of a similar matrix type (i.e., aqueous/water, soil/sediment) or for each SDG, whichever is more frequent.[3] Duplicates cannot be averaged for reporting.

12.5.2 Duplicate sample analyses are not required for percent solids. Samples identified as field blanks and PE samples shall not be used for duplicate sample analysis. USEPA may require that a specific sample be used for duplicate sample analysis. The Relative Percent Difference (RPD) is calculated as follows:

EQ. 5 Duplicate Sample Relative Percent Difference

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

WHERE, RPD = Relative Percent Difference
S = Sample Result (original) (µg/L or mg/kg) from EQ. 1 or EQ. 2
D = Duplicate Sample Result (µg/L or mg/kg) from EQ. 1 or EQ. 2

12.5.3 The results of the duplicate sample analyses shall be reported. A control limit of 20 for RPD shall be used for original and duplicate sample values greater than or equal to five times the CRQL (see Exhibit C). A control limit equal to the CRQL value shall be entered in the "Control Limit" column if either the sample or duplicate value is less than five times the CRQL. If the sample and duplicate values are greater than or equal to five times the CRQL, or if the sample and duplicate values are less than the CRQL, the "Control Limit" field is left empty.

12.5.4 If one result is above five times the CRQL level and the other is below, use the CRQL criteria to determine if the duplicate analysis is in control. If both sample and duplicate values are less than the CRQL, the RPD is not calculated. For soil/sediment sample or soil/sediment duplicate results less than five times the CRQL, enter the value of the CRQL, corrected for sample weight and percent solids, (i.e., original, not duplicate sample weight), in the "Control Limit" column. If the duplicate sample results are outside the control limits, flag all the data for samples received and associated with that duplicate sample with an "*". In the instance where there is more than one duplicate sample per SDG, if one duplicate result is not within contract criteria, flag all samples of the same matrix and method in the SDG. The percent difference data will be used by USEPA to evaluate the long-term precision of the method. Specific control limits for this analyte will be added at a later date based on the precision results.

[3] USEPA may require additional duplicate sample analyses, upon USEPA Regional CLP PO request.

12.6 MDL Determination

12.6.1 Before any field samples are analyzed under this contract, the MDLs shall be determined for each distillation procedure and instrument used, prior to the start of contract analyses, and annually thereafter. The MDLs shall meet the levels specified in Exhibit C. 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.

12.6.1.1 To determine the MDLs, the Contractor shall run MDL studies following the procedures given in 40 CFR, Part 136. The Contractor shall prepare the MDL samples by each digestion procedure used and shall analyze these samples on each instrument used.

12.6.1.2 The determined concentration of the MDL shall be less than half the concentration of the CRQL listed in Exhibit C.

12.6.1.3 The results of the MDL determination studies shall be forwarded to the USEPA Regional CLP PO, Sample Management Office (SMO), and Quality Assurance Technical Support (QATS).

12.6.1.4 The MDL results shall be reported on Form IX-IN.

12.7 Example Analytical Sequence for Cyanide

S0
S10
S50
S100
S200
S400
ICV
ICB
CCV
CCB
samples
CCV
CCB
samples
CCV
CCB, etc.

12.8 Summary of QC Operations

The QC operations performed for cyanide analysis are summarized in the table below.

QC Operation	Frequency
Instrument Calibration	Daily or each time instrument is turned on or set up, after ICV or CCV failure, and after major instrument adjustment.
Initial Calibration Verification	Following each instrument calibration.
Initial Calibration Blank	Following each instrument calibration, immediately after the ICV.

QC Operation	Frequency
Continuing Calibration Blank	Every hour of a run, and at the beginning and end of each run. Performed immediately after the last CCV.
Continuing Calibration Verification	At a frequency of every hour of a run, and at the beginning and end of each run.
Preparation Blank	For each SDG or each sample preparation and analysis procedure per batch of prepared samples, whichever is more frequent.
Spike Sample	For each matrix type or for each SDG, whichever is more frequent.
Post-Digestion/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.
Determination of Method Detection Limits	Prior to contract award, annually thereafter, and after major instrument adjustment.

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

See Section 1.15 in Exhibit D - Introduction to Analytical Methods.

15.0 WASTE MANAGEMENT

See Section 1.16 in Exhibit D - Introduction to Analytical Methods.

16.0 REFERENCES

16.1 US Environmental Protection Agency. Methods for Chemical Analysis of Water and Wastes. Method 335.4, Revision 1.0, August 1993.

16.2 American Water Works Association/American Public Health Association/Water Environment Federation. Standard Methods for the Examination of Water and Wastewater. Method 4500. 18th Edition.

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

17.0 TABLES/DIAGRAMS/FLOWCHARTS

Not applicable.