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CCP
Determination of Mercury by CVAA for TRU Waste Characterization

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1. ABSTRACT

This Central Characterization Project (CCP) procedure defines equipment, materials, and operating instructions for the determination of mercury in wastes by Cold Vapor Atomic Absorption Spectroscopy (CVAA). This method implements analytical requirements defined in the Waste Isolation Pilot Plant (WIPP) Waste Analysis Plan (WAP) for characterization of homogeneous solids and soil/gravel.

Appendix D contains acronyms and abbreviations applicable to this method.

2. APPLICABILITY

This method is applicable to homogeneous solids and soil/gravel transuranic waste samples. This method is based upon the determination of mercury as described in Method 7471A, "Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique)" from the EPA publication, Test Methods for Evaluating Solid Waste, Third Edition (SW-846). Additional quality control elements described in Chapter One, Chapter Three, and Method 7000A of SW-846 are also implemented in this procedure.

This procedure functions as an ICP Use Type 2 document for performing operations within the ALD facilities.

Personnel performing this procedure will be trained and qualified in accordance with CCP-QP-002, *CCP Training and Qualification Plan*, prior to performing this procedure.

2.1 Interferences

Free chorine also absorbs light at 253.7 nm. Excess of sodium chloride-hydroxylamine hydrochloride reagent is added to ensure that free chlorine is absent before the mercury is reduced and swept into the cell.

2.2 Range of Method

The lower concentration limit for the procedure is the demonstrated instrument detection limit (IDL). The upper concentration limit is the concentration of the highest calibration standard. The upper limit of the method range is extended by the analysis of sample dilutions.

2.3 Precision Attainable Over the Range of the Method

The precision of the method is expected to be ±20% for mercury concentrations which exceed the IDL by a factor of ten or more.

3. DISCUSSION

The cold-vapor atomic absorption (CVAA) technique is a physical method based on the absorption of light at 253.7 nm by atomic mercury vapor. Samples are treated prior to analysis so that all forms of mercury within the sample are in aqueous solution and are in a suitable oxidation state. Treated sample solutions are introduced into the instrument where the mercury is reduced to the elemental state and aerated from solution. The mercury vapor passes through a cell positioned in the light path of a spectrophotometer. The concentration of mercury in samples is determined by comparing the reduction in signal or absorption caused by samples to that caused by a known set of standards.

All samples must be subjected to an oxidation step to ensure that all mercury compounds present in the sample will be reduced to elemental mercury at the aeration step. For example, organo-mercury compounds will not respond to the cold-vapor atomic absorption technique unless they are first broken down and converted to mercuric ions.

EPA Method 7471A states: “Instruments designed specifically for the measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.” This method utilizes a Flow Injection Mercury System (FIMS), which is a CVAA instrument that has been specifically configured for mercury determinations. Amounts of reagents used and calibration standard concentrations have been adjusted for use with the FIMS.

The mercury vapor production and absorption measurements are performed using the FIMS. Figure 1 in Appendix E shows a general schematic of the technique. The reactions necessary for production of the atomic mercury vapor take place after the sample is introduced into the FIMS. The mercury-bearing sample solution is pumped into the system where reducing agents and a carrier are introduced. The resulting solution passes into a mixing block, where the mercury in solution is converted to mercury vapor. This vapor is then carried by argon gas into a gas/liquid separator block where the vapor is separated from the liquid. The mercury vapor is then carried by the argon gas through tubing into the absorption cell positioned in the light path of an atomic absorption spectrophotometer. Absorption of light at 253.7 nm by the vapor is measured as a function of mercury concentration. From the cell, the potentially toxic vapors are vented into the laboratory hood exhaust system.

4. SAFETY PRECAUTIONS

4.1 Chemical Handling

4.1.1 Handle all chemicals per MCP-3635, “Chemical Hygiene Plan.”

4.1.2 Wear the following standard laboratory PPE in the lab:

A. Lab coat

B. Safety glasses with side shields

C. Substantial footwear

D. Appropriate gloves.

4.1.3 Change gloves immediately upon chemical contact.

4.1.4 Handle corrosives per ACLP-0.27, "Routine Handling of Corrosives."

4.1.5 Handle all spills per ACLP-0.24, "Laboratory Spill Cleanup."

4.2 Radiological Hazards

4.2.1 Perform all work under an applicable RWP per MCP-7, "Radiological Work Permit."

4.2.2 Handle nonroutine samples per ACLP-0.21, "Work Control Procedure for the Analysis of Nonroutine Samples."

4.3 Thermal Hazards

4.3.1 Avoid contact with hot surfaces on hot plates and heating blocks.

4.3.2 Use leather or heat-resistant gloves, rubber safety grips, or tongs to move thermally hot materials and equipment.

4.4 Waste Disposition

4.4.1 Manage all waste per ACLP-0.40, "Analytical Laboratories Waste Management."

5. APPARATUS AND REAGENTS

5.1 Apparatus

5.1.1 Perkin-Elmer model, FIMS-100 stand-alone flow injection mercury analysis system or equivalent with associated electronics

5.1.2 Sample Loop for FIMS-100, 500-, 200-, or 100-µL

5.1.3 Absorption cell, 4-mm ID., 260-mm path

5.1.4 Balance, resolution ≤1-mg and 100-g minimum capacity

5.1.5 Computer, industry standard with color monitor, hard disk drive and printer

5.1.6 Light source, low-pressure mercury lamp

5.1.7 Peristaltic pump, adjustable-speed, external or incorporated into the analysis system, with two or more channels

5.1.8 Autosampler tubes, glass or plastic, 15-mL and 50-mL, or equivalent

5.1.9 Polyvinyl chloride (PVC) peristaltic pump tubing as listed in the following table:

Function	I.D., inches	I.D., mm	Color Code
Nitric acid carrier uptake	0.060	1.52	Yellow-Blue
Sample loop to drain	0.060	1.52	Yellow-Blue
Stannous chloride reductant uptake	0.045	1.14	Red-Red
Separator drain to waste	0.125	3.17	Black-White

NOTE: *Alternate peristaltic pump tubing sizes are allowed. Use of uptake tubing sizes other than those listed above are documented in the IDL Determination Record or on the documentation for IDL determinations.*

5.1.10 Mechanical Pipets, 0.01- to 10-mL with disposable tips, verified according to ACLP-2.06, "Mechanical Pipettor Calibration Verification Procedure for Spectrochemistry."

5.1.11 High density polyethylene (HDPE) bottles; assorted sizes

5.1.12 Spatula

5.1.13 Volumetric flasks, assorted sizes

NOTE: *Only one of the following digestion systems, block or hot plate, is required for this analysis.*

5.1.14 Block digestion system, ModBlock™ or equivalent including:

5.1.14.1 External temperature controller unit

5.1.14.2 Graphite block heating unit with lifting jig

5.1.14.3 Digestion tubes. Tubes of disposable, graduated, metal-free, polypropylene, 70-mL capacity or other appropriate volume with caps are used and must be compatible with the graphite block heating unit.

5.1.14.4 Covers for digestion tubes

<u>OR</u>

5.1.15 Water bath digestion system including:

5.1.15.1 Hot water bath, heated with a hot plate or equivalent

5.1.15.2 Graduated cylinder, 50-or 100-mL

5.1.15.3 Volumetric Flasks, 50- and 100-mL, or equivalent

5.1.15.4 High density polyethylene (HDPE) bottles, 60- or 120-mL

5.1.16 Filter for stannous chloride reductant (optional)

5.1.16.1 Filter housing, reusable, sized for easy placement in the reductant bottle

5.1.16.2 Filter media, glass fiber, diameter appropriate to housing, pore size ≥0.45 µm

5.1.16.3 Syringe filters, 0.45 µm pore size, Nalgene or equivalent

5.1.16.4 Plastic syringes, various sizes, with male luer-lock fitting

5.1.16.5 Syringe filters, with female luer-lock fitting, 0.45 µm, Acrodisc or equivalent

5.2 Reagents

Use Trace Metals Grade acids throughout this procedure unless another grade is specified. Use Analytical Reagent Grade or better chemicals for preparation of all other reagents.

Use ASTM Type II water (with respect to conductivity) or better for preparation of all reagents and samples.

NOTE: *A volume other than specified can be prepared if the specified reagent ratios are maintained.*

5.2.1 Aqua regia. Prepare immediately before use by carefully adding three volumes of concentrated hydrochloric acid to one volume of concentrated nitric acid. Prepare only the amount of aqua regia needed. Do not store excess aqua regia.

5.2.2 Argon, welder's grade or better

5.2.3 Hydrochloric acid, concentrated, Trace Metal Grade

5.2.4 Hydrochloric acid, 10%v/v, for tubing rinse. Add approximately 250 mL of water to the mixing vessel. Add 50 mL of concentrated HCl and bring the total volume to 500 mL with water.

5.2.5 Nitric acid, concentrated, Trace Metal Grade

5.2.6 Nitric acid, 3%. Add about 500 mL water to the mixing vessel. Add 30 mL of concentrated nitric acid and bring to a total volume of 1000 mL with water.

5.2.7 Potassium permanganate, suitable for mercury analysis. Analyzed mercury concentration must be ≤0.050 mg/kg.

5.2.8 Potassium Permanganate, 5% Solution (w/v). Dissolve 5 g of potassium permanganate in 100 mL of water.

5.2.9 Sodium Chloride 12 % (w/v) - Hydroxylamine Hydrochloride 12% (w/v) solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine hydrochloride in water and dilute to 100 mL.

5.2.10 Solid Laboratory Control Sample: Purchased from Environmental Resource Associates or other NIST-traceable source. Preferred concentration range 0.1 to 5 mg/kg. Solid LCS materials must be used within the manufacturer-provided shelf life, if applicable. If the manufacturer does not provide a shelf life, then use within 5 years of receipt date.

5.2.11 Stannous chloride ($SnCl_2 \cdot 2H_2O$), reagent grade

5.2.12 Stannous Chloride Solution, 10% (w/v) in 10% (v/v) HCl: Prepare by dissolving 10 grams stannous chloride ($SnCl_2 \cdot 2H_2O$) in 10 mL concentrated HCl for each 100 mL. After the stannous chloride is dissolved, take to volume with water, adding the water very slowly at first.

5.2.13 Dilution Solution for Solid Samples (DSS)

5.2.13.1 Fill a marked or graduated 1-liter plastic bottle or container approximately half full of water.

5.2.13.2 Add the following to the container and mix:

A. 30 mL of concentrated hydrochloric acid

B. 10 mL of concentrated nitric acid

C. 100 mL of Potassium Permanganate ($KMnO_4$) Solution.

WARNING

Chlorine gas could be evolved in the following step. Chlorine gas is toxic by inhalation, ingestion, and through skin contact. Inhalation can cause serious lung damage and may be fatal.

5.2.13.3 Cap the bottle, place in a hood, mix, then add 40 mL of Sodium Chloride-Hydroxylamine Hydrochloride Solution.

5.2.13.4 Mix carefully, loosening the cap frequently to allow pressure to vent. Shake the solution until it is clear.

5.2.13.5 Add water to the 1.0-L mark.

5.2.14 Standard Stock Solutions and Standards Prepared by the Quality Control Laboratory

NOTE: *The primary standards, secondary standards, and QC solutions listed in this section are provided by the Quality Control Laboratory (QCL) in accordance with ACLP-1.01, "Preparation of Quality Control Reagents and Standards" and tracked and used by the Spectrochemistry Group (SCG) in accordance to ACLP-2.05, "Control, Distribution and Use of Spectrochemical Standards." Instructions for preparing working standards from these standards and solutions are provided in Section 7.2, "Preparation of Working Standards."*

5.2.14.1 Stock Hg Solution: A solution containing a known concentration of mercury traceable NIST. This solution is used to prepare calibration standards.

5.2.14.2 10.0 mg/L Hg Standard: Prepare by diluting an appropriate aliquot of Stock Hg Solution to volume with nitric acid, minimum concentration 1%.

5.2.14.3 Independent Calibration Verification Stock Hg Solution (ICVSt): A solution containing a known concentration of mercury. The ICV Stock Hg Solution must be independent of the Stock Hg Solution.

5.2.14.4 10.0 mg/L Hg ICV Solution: Prepare by diluting an appropriate aliquot of ICVSt to volume with nitric acid, minimum concentration 1%.

6. SAMPLE HANDLING

6.1 Refrigerate samples at 4 °C between receipt and analysis.

NOTE: *SW-846 allows a range of ±2 °C around the specified storage temperature.*

6.2 Prepare and analyze samples within 28 days of sample collection.

6.3 Group samples into analytical batches. The analytical batch is a suite of samples of similar matrix that are processed as a unit, using the same analytical method within a specific time period. An analytical batch must not exceed 20 samples, all of which must be received by the laboratory within 14 days of the validated time of sample receipt (VTSR) of the first sample of the batch.

NOTE: *Field blanks, field duplicates, and all other samples supplied by the client are counted toward the 20-sample maximum. Laboratory quality control samples, such as, LB, ICV, S, SD and Calibration Standards are not counted toward the 20-sample maximum.*

7. PROCEDURES

NOTE: *Sections 1., 7.3, 7.5, and 7.8 provide general instructions to be used concurrently with other procedure sections.*

7.1 Labware Cleaning

Clean all reusable labware according to ACLP-0.25, "Labware Cleaning for Environmental Samples," before use in this procedure. Subsequent cleaning to ACLP-0.25 is not required when labware is reused for identical QC or rinse solutions.

NOTE: *It is suggested that the ASTM Type II water rinse be repeated on stored labware just prior to use.*

7.2 Preparation of Working Standards

7.2.1 Standard Control

7.2.1.1 Control all primary, secondary, and working standards per ACLP-2.05.

7.2.1.2 Prepare working standards daily.

NOTE: *IWS must be independent of CWS.*

7.2.2 Preparation of CWS (200 µg/L Hg Working Standard)

7.2.2.1 Add approximately 25 mL of water to a 50-mL volumetric flask.

7.2.2.2 Add 1 to 2 mL of concentrated HNO_3 and 1.00 mL of 10.0 mg/L Hg Standard (see Item 5.2.14.2).

7.2.2.3 Dilute to volume with water.

7.2.2.4 Label this flask *CWS*. The mercury concentration is 200 µg/L in this solution.

7.2.3 Preparation of IWS (200 µg/L Hg ICV Working Standard)

7.2.3.1 Add approximately 25 mL of water to a 50-mL volumetric flask.

7.2.3.2 Add 1 to 2 mL of concentrated HNO_3 and 1.00 mL of 10.0 mg/L Hg ICV Solution (See Item 5.2.14.4).

7.2.3.3 Dilute to volume with water.

7.2.3.4 Label this flask IWS. The mercury concentration is 200 µg/L in this solution.

7.3 Sample Preparation General Instructions

7.3.1 Reagent Control

Various chemicals used in this procedure contain trace amounts of metals that show up as a consistent level of contamination in the analysis. All solutions in the batch must be treated with the same reagents so that the contribution of this contamination to sample results can be estimated. For this reason, check that a single container of each chemical with enough for the entire batch is available before adding it to any samples and standards.

7.3.2 Standard Control

Control all primary, secondary, and working standards per ACLP-2.05.

7.3.3 Naming Batch-Specific Quality Control (QC) Samples

Label prepared QC samples such as laboratory blanks (LB), digested Initial Calibration Verification (ICV) solutions, and laboratory control samples (LCS) with unique identifiers. Label ICVs and LBs as *ICV LLL-pp* and *LB LLL-pp* where *LLL-pp* denotes the location of the digestion record. *LLL* is the logbook ALD number and *pp* is the page number.

7.3.4 Alternate Sample Loop Sizes

The linear range of the FIMS can be extended by decreasing the size of the sample loop. Instructions in this method are for the system configured with a 500 µL loop. Use of alternate loop sizes (200 µL or 100 µL) is allowed. Use of loop sizes other than 500 µL must be documented in the sample run logbook or in the instrument maintenance logbook. If alternate loop sizes are used, calibration standard and spiking standard concentrations may be increased. The IDL must be redetermined if the loop size is changed.

7.4 Preparation of Soil, Sediments, Sludges, Solid or Semi-solid Samples

NOTE 1: *The Laboratory Blank, LCS, Samples, MS Samples, and MSD samples are taken through the complete digestion process together as an analytical batch. ICB, ICV, CCB, CCV, and calibration standards are digested as directed in this section, but their digestion does not need to be processed concurrently with the analytical batch. However, the same reagent lots should be used for preparation of standards and samples.*

NOTE 2: *Initial weights and final volumes other than those specified in the following sections may be used for sample preparation. All reagent volumes added during preparation must be adjusted in proportion to the final sample volume. The use of volumes other than those specified is to be documented in the preparation log. Actual initial and final sample volumes are recorded in the preparation log.*

NOTE 3: *This* digestion method may be performed using either the block or hot plate digestion systems, see Section *5.1*, Apparatus. The instructions have been written for the block digestion method and may be directly converted to hot plate instructions by substituting a hot plate, beakers, and volumetric containers when blocks and vials are referenced below.

7.4.1 Select an analytical batch of samples for digestion according to the definition of analytical batch in Step 6.3.

7.4.2 IF calibration standards are to be prepared with this batch, THEN label tubes as in Table 7.4. Preparation of the S8, S12, OR the S20 calibration standard may be omitted. All other calibration standards must be prepared.

NOTE 1: *The calibration curve must include a blank and a minimum of five non-zero standards.*

NOTE 2: *Calibration standards do not have to be prepared and digested as a unit with samples.*

7.4.3 Label a digestion tube “LB LLL-pp” (see Step 7.3.3) for the laboratory blank (LB).

7.4.4 Label a digestion tube “ICV LLL-pp” (see Step 7.3.3) for the initial calibration verification solution (ICV).

NOTE: *The amount of solid LCS added in the next step is dependent upon the concentration of mercury in the LCS material.*

7.4.5 Prepare a Laboratory Control Sample (LCS) by transferring 0.20 ± 0.05 grams of the Solid Laboratory Control Sample (see Item 5.2.10) to a digestion tube. Label this tube “LCS LLL-pp” (see Step 7.3.3). Record this initial weight in the preparation log.

7.4.6 To prepare sample matrix spikes (S) and matrix spike duplicates (SD), choose one sample for each sample matrix included in this batch, and label one tube with the Lab ID, label a second tube with the lab ID plus the suffix “S”, and label a third tube with the lab ID plus the suffix “SD.” Weigh 0.50 ± 0.05 g of this sample to each of the three labeled tubes.

NOTE: *MS and MSD aliquots must be included for every matrix type in a digestion batch. The supervision should be consulted whenever there is a question regarding matrix spike assignment.*

7.4.7 Label additional tubes for all remaining samples in the analytical batch, and transfer 0.5 ±0.05 g of sample into each tube and record this initial amount added in the preparation log.

7.4.8 Add 3.0 mL water to all labeled tubes.

7.4.9 Add 1.00 mL of IWS to the ICV tube.

7.4.10 Add 1.00 mL of CWS to each of the tubes labeled *S* and *SD*.

NOTE: *The instructions above are for a spike value of 4 µg/L mercury as run through the instrument. Spike amounts may be adjusted when justified by project requirements. Deviations from specified spike amounts are to be recorded in the sample preparation log. To ensure reliable volume transfers, spike volumes of less than 0.100 mL should be avoided.*

7.4.11 Add the volumes of CWS listed in Table 7.4 to each of the calibration standard digestion tubes.

Table 7.4: Standards Preparation Chart

Tube Label	Solution Name(s)	Amount of CWS, mL
S0	S0, ICB, CCB	None
S0.2	S0.2	0.05
S1	S1	0.25
S4	S4, CCV	1.00
S8	S8	2.00
S12	S12	3.00
S20	S20	5.00

7.4.12 Add 2.0 mL of aqua regia, to all labeled tubes, mixing after each addition while the sample tubes are in a hood.

7.4.13 Cover the tubes and heat them for 2 minutes in the block digester maintained at a temperature just below boiling.

NOTE: *Due to the high altitude of the INL Site, "at a temperature just below boiling" is as close to 95 °C as is achievable without boiling the sample (the boiling point of water here is slightly under 95 °C). Boiling the sample is undesirable due to the potential for loss of mercury as volatile chlorides.*

7.4.14 Use the lifting jig to remove the tubes from the digestion block after the digestion is complete.

7.4.15 Add 15 mL of water and 5 mL of Potassium Permanganate Solution to each tube. Mix thoroughly.

7.4.16 IF the purple color persists for all samples,
THEN GO TO Step 7.4.19.

7.4.17 IF the purple color does NOT persist,
THEN add an additional portion of Potassium Permanganate Solution. Add additional portions of Potassium Permanganate Solution until the purple color persists.

7.4.18 IF additional Potassium Permanganate Solution is added to one sample, THEN add the same amount to ALL solutions including calibration standards.

7.4.19 Return the tubes to the block digester in the fume hood and heat them for a minimum of 30 minutes at a temperature just below boiling.

NOTE: *Due to the high altitude of the INL Site, "at a temperature just below boiling" is as close to 95 °C as is achievable without boiling the sample (the boiling point of water here is slightly under 95 °C). Boiling the sample is undesirable due to the potential for loss of mercury as volatile chlorides.*

7.4.20 Use the lifting jig to remove the tubes from the digestion block after the digestion is complete and allow the tubes to cool.

WARNING

Chlorine gas could be evolved in the following step. Chlorine gas is toxic by inhalation, ingestion, and through skin contact. Inhalation can cause serious lung damage and may be fatal.

7.4.21 Just prior to analysis add 2 mL of Sodium Chloride-Hydroxylamine Hydrochloride to reduce the excess permanganate while the sample tubes are in a hood.

7.4.22 Swirl the solution until it is clear. Mix carefully, taking care that pressure does not build within the tube.

7.4.23 IF the solution remains purple,
THEN add additional Sodium Chloride-Hydroxylamine Hydrochloride solution to reduce the extra permanganate.

7.4.24 IF additional Sodium Chloride-Hydroxylamine Hydrochloride solution is added to one sample,
THEN add the same amount to ALL solutions including calibration standards.

7.4.25 IF the hotplate digestion is performed,
THEN quantitatively transfer the solution into a volumetric container.

7.4.26 Bring all samples to 50 mL total volume with water.

7.4.27 Record 50 mL as the final sample volume.

7.4.28 Remove particulates in the digestate which may clog the sample introduction tubing by filtration or by allowing the sample to settle. Filtering, when required, is typically performed using a syringe and disposable filter. Collect enough liquid for analysis.

7.5 Analytical Run Overview

Appendix A, Typical Run Sequence, provides an overview of the analysis procedure. Instructions for the completion of each task are included in the indicated step.

The term *analytical sample* includes any solution or media introduced into the instrument on which an analysis is performed, excluding instrument calibrations, initial calibration verifications, and continuing calibration verifications. Note that the following are all defined as analytical samples: spiked samples, laboratory control samples (LCSs), field blanks, laboratory blanks, and all method of standard addition (MSA) solutions. However a rinse typically does NOT count as an analytical sample because no analysis is performed on the rinse. Re-analysis of any solution must be counted as an additional analytical sample. When multiple analytical batches are combined in one run, it is suggested that the sequence start at “ICV Analysis” for each analytical batch.

7.6 Spectrometer Setup

NOTE: *Steps 7.6.1 through 7.6.5 may be completed in any order.*

7.6.1 Daily or with use, check the condition of the system sample introduction tubing and peristaltic pump tubing. Replace tubing as necessary.

7.6.2 Dispense 3% nitric acid (Item 5.2.6) into the carrier reservoir.

7.6.3 Dispense stannous chloride solution, 10% (w/v) in 10% (v/v) HCl (Item 5.2.12) into the reductant reservoir.

7.6.4 Set up the FIMS as shown in Appendix E, Figures 2 and 3, placing the carrier tube into the 3% nitric acid reservoir and the reductant tube into the stannous chloride solution reservoir.

7.6.5 Allow the system to warm up for a minimum of 30 minutes.

7.6.6 Feed all reagents through the system (see Appendix E, Figures 1 and 2).

7.7 Calibration

7.7.1 Watch the drain tubing while the first few readings are made with the system. Check that liquid is moving through the drain tubing and not accumulating in the liquid/gas separator. If the system is not draining properly, check the position, condition, and clamp tightness for the drain tubing through the peristaltic pump and adjust if needed.

7.7.2 Calibrate the instrument daily by performing the steps in Section 7.8 using the calibration standards prepared according to the instructions in Section 7.2.

7.7.3 IF the resulting correlation coefficient, r, is not ≥0.995,
THEN repeat all or part of the calibration.
DO NOT proceed with the analysis until this criterion is met.

NOTE 1: *The calibration curve must include a blank and a minimum of five non-zero standards. If you prepared six non-zero standards, then one non-zero standard may be deleted from the calibration curve and the curve recalculated. A calibration curve with at least five non-zero standards and a blank with correlation coefficient ≥ 0.995 must be demonstrated before analysis can continue.*

NOTE 2: *The concentration of at least one QC or calibration standard is required to be at or below the solution-equivalent of the PRQL in Appendix B. Since all of the calibration standards and the ICV standard fulfill this requirement no additional QC standard is needed to meet this requirement.*

7.8 Sample Analysis

NOTE: *This section provides universal instructions for sample introduction into the flow injection mercury analysis system.*

7.8.1 Place the probe in the sample solution either manually or using the autosampler.

7.8.2 Respond to the software prompts to begin the flow injection sequence either manually or through the autosampler.

7.8.3 Place the probe in water between each sample analysis.

7.9 ICV Analysis

7.9.1 Analyze the ICV solution as if it were a sample.

7.9.2 IF the ICV result obtained is within ±10% of the ICV 'true' value, THEN continue with the next analysis in the run sequence in Appendix A.

7.9.3 IF the ICV result obtained is NOT within ±10% of the ICV 'true' value, THEN recalibrate or reslope the calibration curve and re-analyze the ICV.

NOTE: *The ICV result must be within 20% of the true value for data to be reported. However, it is highly desirable to maintain the ICV within 10%. For this reason, Steps 7.9.2 and 7.9.3 instruct the analyst to first evaluate the ICV against the 10% criterion before proceeding with the analysis.*

7.9.4 IF the second analysis of the ICV is within ±20% of the ICV 'true' value,
THEN continue to the next task in the analysis sequence (see Appendix A).

7.9.5 IF the second analysis of the ICV is NOT within ±20% of the ICV 'true' value,
THEN correct the problem, recalibrate, and reanalyze the ICV.

7.10 Initial Calibration Blank (ICB) Analysis

7.10.1 Analyze the calibration blank solution as if it were a sample, naming this solution ICB.

7.10.2 IF the ICB result is 0 ± the Project Required Detection Limit (PRDL), THEN continue to the next task in the analysis sequence (see Appendix A).

NOTE: *Since the PRDL is > 0.2 µg/L, it is suggested that the ICB result be compared to 0 ± 0.2 µg/L rather than the PRDL.*

7.10.3 IF the ICB fails to meet this criterion,
THEN correct the problem and repeat the analysis of the ICV and ICB.

7.10.4 IF both ICV and ICB subsequently pass,
THEN continue to the next task in the analysis sequence (see Appendix A).

7.10.5 IF either ICV or ICB subsequently fail,
THEN correct the problem, recalibrate, and reanalyze the ICV and ICB.

7.11 CCV Analysis

7.11.1 Analyze the 4 µg/L calibration standard solution as if it were a sample, naming this solution CCV.

7.11.2 IF CCV results are within 20% of the true value,
THEN proceed to the analysis of CCB.

7.11.3 IF the value obtained for CCV is not within 20% of the true value,
THEN terminate the analysis; correct the problem, recalibrate, and verify the calibration curve by repeating the CCV and CCB analysis tasks. Re-analyze all analytical samples analyzed since the last compliant CCV/CCB pair.

7.12 CCB Analysis

7.12.1 Analyze the calibration blank solution as if it were a sample, naming this solution CCB.

7.12.2 IF the CCB result is 0 ± the Project Required Detection Limit (PRDL),
THEN continue to the next task in the analysis sequence.

NOTE: *Since the PRDL is > 0.2 µg/L, it is suggested that the CCB result be compared to 0 ± 0.2 µg/L rather than the PRDL.*

7.12.3 IF the CCB fails to meet this criterion,
THEN terminate the analysis; correct the problem, recalibrate, and verify the calibration curve by repeating the CCV and CCB analysis tasks. Re-analyze all analytical samples analyzed since the last compliant CCV/CCB pair.

7.13 Laboratory Blank Analysis

7.13.1 Analyze the laboratory blank (LB) solution as if it were a sample and continue to the next task in the analysis sequence (see Appendix A).

NOTE: *LB results are evaluated in Section 7.20.*

7.14 Laboratory Control Sample (LCS) Analysis

7.14.1 Analyze the prepared LCS solution as if it were a sample.

7.14.2 IF the result obtained for the LCS is within the limits set by the manufacturer's Certificate of Analysis,
THEN continue to the next task in the analysis sequence (see Appendix A).

7.14.3 IF the LCS result does not meet these limits,
THEN reanalyze the LCS.

7.14.4 IF the LCS fails a second time,
THEN terminate the analysis. The samples associated with this batch must be redigested and reanalyzed. Consult with supervision for direction prior to proceeding.

7.15 Matrix Spike (MS) and Matrix Spike Duplicate (MSD) Analysis

7.15.1 Analyze the MS and MSD as samples, and continue to the next task in the analysis sequence (see Appendix A).

NOTE: *MS and MSD results are evaluated in Section 7.17.*

7.16 Dilutions

7.16.1 Dilute and reanalyze samples that exceed the calibration range. The mercury concentration in diluted samples must be greater than 100 × the IDL OR greater than 0.25 times the concentration of the highest calibration standard, whichever is less.

NOTE: *For example, if the IDL is 0.1 µg/L and the highest calibration standard is 12 µg/L, dilution concentration must be greater than 0.1 × 100 = 10 µg/L OR 12 × 0.25 = 3 µg/L. You will dilute so that the dilution result is >3 µg/L.*

7.16.1.1 Use dilution solution for solid samples (DSS) (see Item 5.2.13) as the diluent.

7.17 Evaluation of MS and MSD Results

7.17.1 Calculate the percent recovery (%R) of the mercury spike for the MS and MSD samples using the equation in Section 9.1.

7.17.2 IF the calculated %R of the MS and MSD is 100 ± 20,
THEN post-digestion spike and serial dilution tests are not required.

7.17.3 IF the calculated %R of the MS or MSD is NOT 100 ± 20,
AND at least one sample in the batch contains Hg greater than 10 times the IDL,
THEN prepare and analyze a serial dilution of one sample (see Section 7.18). If possible, select a sample from the batch with Hg at > 25 times the IDL for the serial dilution test.

7.17.4 IF the calculated %R of the MS OR MSD is NOT 100 ± 20,
AND the serial dilution test is performed,
AND the calculated %D for the serial dilution test is greater than 10,
THEN prepare and analyze a post-digestion spike (PDS) test (see Section 7.19).

7.17.5 IF the calculated %R of the MS or MSD is NOT 100 ± 20, AND Hg is below 10 times the IDL for all of the samples in the batch, THEN perform the post-digestion spike (PDS) test. (See Section 7.19.)

7.18 Serial Dilution Test

NOTE 1: *A Serial Dilution is NOT REQUIRED if:*

A. %R of the S and SD are 100 ± 20 OR

B. Hg is below 10 times the IDL for all of the samples in the batch.

NOTE 2: *The serial dilution is a five-fold dilution of the sample solution. If the sample is diluted to bring it into calibration range, the serial dilution is a five-fold dilution of the diluted sample. For example, if a ten-fold dilution is needed to bring the sample into calibration range, then the serial dilution is a five-fold dilution of the ten-fold dilution.*

7.18.1 Select a sample for serial dilution. If possible, select a sample from the batch with Hg at > 25 times the IDL. If no samples contain > 25 times the IDL, select a sample with concentration > 10 times the IDL.

7.18.2 Prepare a five-fold dilution of the sample using dilution solution for solid samples (DSS) as diluent.

7.18.3 Analyze the serial dilution, entering the sample ID plus the suffix 'L' as the sample name.

7.18.4 IF the calculated %D of the serial dilution test is ≤10, THEN continue to the next task in the analysis sequence.

7.18.5 IF the calculated %D of the serial dilution test is >10, THEN repeat the serial dilution test.

7.18.6 IF the calculated %D of the repeated serial dilution test is ≤10, THEN continue to the next task in the analysis sequence.

7.18.7 IF the calculated %D of the repeated test is >10, THEN perform the PDS test (see Section 7.19).

7.19 Post-Digestion Spike (PDS) Test

NOTE 1: *A PDS is NOT REQUIRED if:*

A. %R of the S and SD are 100 ± 20 OR

B. %D is ≤10 for a serial dilution test. (See Section 7.18.)

NOTE 2: *Post digestion spikes (PDS) are also known as analytical spikes.*

7.19.1 Add prepared, unspiked sample (or diluted sample) and **CWS** to a tube according to the following table and mix.

"As Run" Sample Concentration Range	Sample added	CWS added	PDS Spike Added Amount as analyzed
0 to 2 µg/L	10 mL	0.10 mL	1.98 µg/L
2 to 5 µg/L	10 mL	0.25 mL	4.88 µg/L
5 to 10 µg/L	10 mL	0.50 mL	9.52 µg/L

NOTE: *Other sample and CWS volumes may be used. The relative volumes of sample (or diluted sample) and CWS added should result in a spike added amount that is between 1 and 4 times the amount present in the sample. Spike added should be approximately 2 µg/L for samples containing ≤2 µg/L Hg.*

7.19.2 Analyze the PDS, entering the unspiked sample ID plus the suffix 'A' as the sample name.

7.19.3 IF the calculated %R of the PDS is 85-115%,
THEN continue to the next task in the analysis sequence.

7.19.4 IF the calculated %R of the PDS is NOT 85-115%,
THEN repeat the PDS test.

7.19.5 IF the calculated %R of the repeated PDS test is NOT 85-115%,
THEN continue to the next task in the analysis sequence.

NOTE: *PDS and other QC sample data will be evaluated for MSA quantitation in Section 7.21.*

7.20 Laboratory Blank Evaluation

7.20.1 IF the laboratory blank mercury concentration is > 3 × PRDL,
THEN redigest and reanalyze all samples with mercury concentrations ≤ 10 times the laboratory blank concentration and ≥0.5 times the PRQL.

7.20.2 Do NOT correct sample results for analyte found in laboratory blanks.

7.21 Evaluating Data for Method of Standard Addition (MSA) Quantification

7.21.1 IF matrix spike OR matrix spike duplicate recovery fails to meet the acceptance criteria listed in Appendix C
AND serial dilution %D (if required) fails to meets the acceptance criteria
AND PDS recovery (if required) fails to meet the acceptance criteria,
THEN quantitate by MSA (see Section 7.22).

NOTE: *MSA is NOT required if any one of the following three conditions is true:*

A. Matrix spike and matrix spike duplicate recoveries meet the acceptance criteria listed in Appendix C

B. Serial dilution %D (if required) meets the acceptance criteria

C. PDS recovery (if required) meets the acceptance criteria.

7.22 Determination of Mercury by the Method of Standard Additions (MSA)

NOTE: *The standard addition technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards.*

7.22.1 Pipet four identical aliquots of the sample solution into volumetric flasks (suggested minimum flask size is 10-mL).

NOTE: *Known amounts of CWS will be added to three of these aliquots. The fourth aliquot will be unspiked unknown.*

7.22.2 IF the diluted sample concentration is ≤2 µg/L,
THEN use 2 µg/L as the expected concentration of the diluted sample.

7.22.3 Prepare the first addition by adding an appropriate volume of **CWS** so that the resulting spike added amount is approximately 50% of the expected concentration of the diluted sample.

7.22.4 Prepare the second addition by adding twice the volume of **CWS** added in Step 7.22.3. The amount added will be approximately equal to 100% of the expected concentration of the diluted sample.

7.22.5 Prepare the third addition by adding three times the volume of **CWS** added in Step 7.22.3. The amount added will be approximately equal to 150% of the expected concentration of the diluted sample.

7.22.6 Bring all four aliquots to volume by adding the appropriate dilution solution (DSS, Item 5.2.13). Dilute as needed to maintain the signals in the linear range of the method.

7.22.7 Analyze all four aliquots.

7.22.8 Plot the analyzed (or calibration derived) concentration of each solution determined on the vertical axis (y-axis) of a graph, with the concentrations of the added known standards plotted on the horizontal axis (x-axis).

7.22.9 Extrapolate the resulting line to zero concentration.

7.22.10 Record the point of interception of the horizontal axis as the found concentration of mercury in the diluted sample.

7.22.11 Apply all preparation dilutions, run time dilutions, and unit factors to this concentration and report as the sample concentration.

7.23 End of Run

7.23.1 End the run with a calibration verification. In other words, the last solutions analyzed in the run must be the CCV followed by a CCB. Check that no more than ten analytical samples (see Section 7.5), including MSA, PDS, serial dilutions, spikes, dilutions, duplicates, LCS, and LB, were analyzed between calibration verifications. Count each re-analysis of an analytical sample as an additional analytical sample.

7.23.2 <u>IF</u> more than 10 analytical samples were analyzed between calibration verification,
<u>THEN</u> reanalyze those samples using no more than 10 analytical samples between calibration verifications, and report only the reanalyzed values.

7.23.3 Evaluate the data for compliance to acceptance criteria and required corrective actions in Appendix C.

7.23.4 <u>IF</u> QC sample results associated with the reported samples do not meet Appendix C acceptance criteria
<u>AND</u> the QC failure is not due to sample matrix,
<u>THEN</u> initiate a nonconformance report (NCR) per CCP-QP-005, *CCP TRU Nonconforming Item Reporting and Control* .

7.23.5 Verify that the Instrument Performance Check was recorded.

7.23.6 Generate a hard copy print out of the solution run sequence for addition to the run logbook.

7.24 FIMS Shutdown

7.24.1 At the completion of the analysis sequence, remove the two reagent intake tubes from the reagents and place them in water along with the sample tube. The stannous chloride reductant intake tube may be placed in 10% HCl for one to 5 minutes prior to the water rinse. Allow water to pump through the system for approximately five minutes.

7.24.2 Place the dilute nitric acid carrier solution intake tube into a separate water rinse vessel.

7.24.3 Transfer the stannous chloride reductant solution intake tube into a water rinse vessel.

7.24.4 Allow the water rinse to pump through the system for about five minutes.

7.24.5 Remove the carrier, reductant, and sample tubes from the rinse vessels and allow the tubing to flush with air.

7.24.6 Turn off the pump and release the pump tension on all tubing.

7.24.7 Turn off the mercury lamp.

7.25 IDL Determination

NOTE: *Section 8.1 provides requirements for the frequency for determining IDLs.*

7.25.1 Prepare or obtain a solution of calibration blank matrix containing mercury at a concentration of approximately 2 to 5 times the estimated IDL.

7.25.2 Perform at least seven analyses of this standard solution. Perform each measurement as though it were a separate analytical sample (that is, follow each measurement with a rinse and/or any other procedure normally performed between the analysis of separate samples).

NOTE: *Analyses performed for IDL determinations must meet all calibration verification requirements for the analysis of samples. Acceptable ICV and ICB or CCV and CCB readings must bracket all data used to determine IDLs.*

7.25.3 Calculate the IDL by the equation in Section 9.7, Instrument Detection Limit (IDL) Calculation.

7.25.4 Round the calculated value UP (away from zero) to the nearest 0.1 µg/L.

NOTE: *For example, if an IDL calculated according to Section 9.7 is 0.12 µg/L, the IDL is reported as 0.2 µg/L.*

7.26 Reporting

7.26.1 Report sample results in mg/kg wet weight.

7.26.2 Report sample concentrations less than the IDL as the IDL multiplied by any applicable dilution and conversion factors along with a qualifier which indicates that the analyte was not detected.

7.26.3 Report sample results using two significant figures.

7.26.4 Report analysis results per CCP-TP-188.

7.26.5 When applicable, discuss the use of MSA quantitation in the batch data report narrative.

8. QUALITY CONTROL REQUIREMENTS

Quality Control (QC) requirements and detailed instructions for meeting these requirements are included in Section 7 of this procedure.

8.1 Determination of IDLs

8.1.1 Determine IDLs every six months.

8.1.2 Determine IDLs for each instrument used to obtain reported data and for each specific set of operating conditions.

8.1.3 If instrument conditions are adjusted in any way that may affect the IDL, re-determine the IDLs for that instrument and use the results as the established IDLs for all subsequent reporting.

8.1.4 If IDLs are determined using a sample loop size other than 500 µL, ensure that IDL documentation clearly states the loop size used for IDL determination.

8.2 Method Performance Demonstration (Precision and Accuracy)

8.2.1 Demonstrate method performance initially before analyzing any samples.

8.2.2 Demonstrate initial method performance by preparing seven replicate aliquots of a control standard having all target analytes at quantifiable concentration.

8.2.2.1 Digest method performance samples (the solid LCS may be used for this purpose) according to Section 7.4.

8.2.3 Analyze digested method performance samples.

8.2.4 Calculate average percent recovery and the percent relative standard deviation of the results. Initial and continuing method performance demonstrations are acceptable if the average percent recovery meets the acceptance criteria for LCSs and the percent relative standard deviation is ≤ 30.

8.2.5 If the method performance demonstration is not acceptable, terminate sample analysis until acceptable method performance has been demonstrated. Repeat the demonstration until acceptance criteria are met.

8.2.6 Demonstrate continuing method performance semiannually using a minimum of four (4) method performance samples.

8.3 Preparation Quality Control Elements

8.3.1 Prepare and analyze at least one laboratory blank with each analytical batch to assess contamination from the analytical process (Section 7.4).

8.3.2 Prepare and analyze at least one matrix spike (MS) and one matrix spike duplicate (MSD) sample pair with each analytical batch to access analytical recovery for a specific matrix. The MSD is used in lieu of a laboratory duplicate to assess the precision of the method for a specific matrix. (Section 7.4).

8.3.3 Prepare and analyze at least one laboratory control sample (LCS) with each analytical batch. (Section 7.4).

8.4 Analysis Quality Control Elements

8.4.1 Calibrate the instrument daily with use, with a minimum of a calibration blank and five standards (Section 7.7).

8.4.2 Analyze an Independent Calibration Verification at least daily and with each batch (Section 7.9).

8.4.3 Analyze periodic calibration verifications at a minimum frequency of 10% (Section 7.11). A nonconformance report (NCR) is required per CCP-QP-005, if reported data are associated with calibration verifications that do not meet the minimum 10% frequency.

8.4.4 Perform a serial dilution test with each batch when MS or MSD results do not meet acceptance criteria and at least one sample concentration exceeds a specified level (Section 7.18).

8.4.5 Perform a post digestion spike (PDS) test with each batch when MS or MSD results do not meet acceptance criteria and a serial dilution test is not performed or does not meet acceptance criteria (Section 7.19).

8.4.6 Determine mercury by Method of Standard Addition (MSA) if MS and MSD recoveries are not 80-120% and neither the PDS or serial dilution tests meet acceptance criteria (Section 7.22).

9. CALCULATIONS

Use internally consistent units wherever units are not specified in the following calculations. For example, in the matrix spike recovery calculation SSR, SR, SA must all be in the same units.

9.1 Matrix Spike and Post Digestion Spike Recovery

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

where:

SSR = Measured concentration in the spiked sample in mg/kg

SR = Measured concentration in the unspiked sample in mg/kg (SR=0 if the analyte was not detected in the unspiked sample)

SA = Known concentration of the spike in the sample in mg/kg

NOTE: *For post digestion spikes, SR may be adjusted to compensate for dilution due to spike addition. See Section 9.3 for calculating SA for post digestion spikes.*

9.2 Matrix Spike Duplicate/Matrix Duplicate Agreement

$$RPD = \left|\frac{S - D}{0.5\left(S + D\right)}\right| \times 100 = \left|\frac{S - D}{(S + D)}\right| \times 200$$

where:

RPD = Relative Percent Difference

S = Concentration of first spike sample or duplicate sample in mg/kg

D = Concentration of second spike sample or duplicate sample in mg/kg

9.3 PDS (Post Digestion Spike) Spike Added Calculation

$$SA = \frac{s \times C_{st}}{(a+s))}$$

where:

SA = Post Digestion Spike Added in µg/L

s = Volume of stock spiking solution added to the aliquot, mL

C_{st} = Stock spiking solution concentration in µg/L

a = Post-preparation sample aliquot taken, mL

9.4 Sample Result Calculation

$$C_S = \frac{X_C \times V}{W} \times \frac{(a+d)}{a}$$

where:

Cs = Sample concentration in mg/kg

X_c = Sample concentration from the instrument readout in µg/L

V = Final preparation volume, in liters

a = Post-preparation sample aliquot taken

d = Volume of diluent added to the post-preparation aliquot

W = Initial weight of sample, in g

9.5 Percent Recovery for ICV, CCV, and LCS

$$\%R = \frac{C_m}{C_t} \times 100$$

where:

%R = % Recovery

C_m = Measured concentration in the unspiked sample in µg/L (or mg/kg for LCS)

C_t = Known concentration of the spike in the sample in µg/L (or mg/kg for LCS)

9.6 Percent Difference (%D) for Serial Dilutions

$$\%D = \frac{SR - SDR}{SR} \times 100$$

where:

%D = Percent difference

SR = Undiluted sample result, in µg/L

SDR = Serial dilution sample result, corrected for the five-fold dilution, in µg/L

9.7 Instrument Detection Limit (IDL) Calculation

$$IDL = t_{(n-1,1-\alpha=.99)} \times s$$

where:

IDL = Instrument Detection Limit.

s = The standard deviation of the replicate measurements

$t_{(n-1,1-\alpha=.99)}$ = The t-distribution value appropriate to a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom

n = The number of replicate measurements obtained

t Distribution Values for n=7 to n=11

n	n-1	$t_{(n-1,1-\alpha=.99)}$		n	n-1	$t_{(n-1,1-\alpha=.99)}$
7	6	3.143		10	9	2.821
8	7	2.998		11	10	2.764
9	8	2.896				

10. RECORDS

Records generated during the performance of this procedure are maintained as QA records in accordance with CCP-QP-008, *CCP Records Management*. The records are the following:

QA/Nonpermanent

- Instrument Detection Limit (IDL) Determination File
- Precision and Accuracy (P&A) Demonstration File

The following records generated during the performance of this procedure will be compiled into the Supporting Data Package, in accordance with CCP-TP-188, *CCP Analytical Data Recording, Review and Reporting.*

QA/Nonpermanent

- Copy of applicable pages of Sample Preparation Logbook
- Copy of applicable pages of Instrument Run Logbook
- Instrument Printouts/Raw Data

11. REFERENCES

11.1 ACLP-0.21, “Work Control Procedure for the Analysis of Nonroutine Samples”

11.2 ACLP-0.24, “Laboratory Spill Cleanup”

11.3 ACLP-0.25, “Labware Cleaning For Environmental Samples”

11.4 ACLP-0.27, “Routine Handling of Corrosives”

11.5 ACLP-0.40, “Analytical Laboratories Waste Management”

11.6 ACLP-1.01, “Preparation of Quality Control Reagents and Standards”

11.7 ACLP-2.04, “Calibration and Maintenance Procedures for Spectrochemistry Instruments”

11.8 ACLP-2.05, “Control, Distribution and Use of Spectrochemical Standards”

11.9 ACLP-2.06, “Mechanical Pipettor Calibration Verification Procedure for Spectrochemistry”

11.10 Annual Book of ASTM Standards, Part 31

11.11 CCP-QP-002, *CCP Training and Qualification Plan*

11.12 CCP-QP-005, *CCP TRU Nonconforming Item Reporting and Control*

11.13 CCP-QP-008, *CCP Records Management*

11.14 CCP-TP-188, *CCP Analytical Data Recording, Review, and Reporting*

11.15 EPA. 1996. *Test Methods for Evaluating Solid Waste, Physical /Chemical Methods.* SW-846, Fourth Edition, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response.

11.16 MCP-3635, “Chemical Hygiene Plan”

11.17 MCP-7, “Radiological Work Permit”

11.18 New Mexico Environment Department, 1999. *Hazardous Waste Facility Permit Issued to Waste Isolation Pilot Plant*, EPA No. NM4890139088, New Mexico Environment Department.

Appendix A – Typical Run Sequence

Task	Section	Notes
Spectrometer Setup	7.6	
Calibration	7.7	
ICV analysis	7.9	
ICB analysis	7.10	
CCV analysis	7.11	
CCB analysis	7.12	
Laboratory blank analysis [b]	7.13	
LCS analysis [b]	7.14	
Sample 1 [b]	7.8, 7.16	
Sample 1 S [b]	7.15	Matrix Spike (MS)
Sample 1 SD [b]	7.15	Matrix Spike Duplicate (MSD)
Analysis of up to 5 additional analytical samples [a]		See Note a.
CCV analysis	7.11	
CCB analysis	7.12	
**Analysis of up to 10 analytical samples [a, b]		See Note a.
**CCV analysis	7.11	
**CCB analysis	7.12	
At this point, repeat the three steps preceded by ** in order until all samples and analytical samples [a, b] are analyzed and followed by a final CCV and CCB.		
Analysis of Diluted Samples (if required) [a, b]	7.16	
Serial Dilution Analysis [a, b]	7.18	(if required see Step 7.17)
Post Digestion Spike (PDS) Analysis [a, b]	7.19	(if required see Step 7.17)
Evaluation for MSA Quantification [a, b]	7.21	
Quantification by MSA [a, b]	7.22	(if required see Step 7.21)
End of Run	7.23	Includes analysis of CCV and CCB.
Instrument Shutdown	7.24	
Laboratory Blank Evaluation[c]	7.20	See Note c.

a The term 'Analytical Samples' in the above table is as defined in Section 7.5. No more than ten analytical samples can be analyzed between calibration verifications. Re-analysis of any analytical sample must be counted as an additional analytical sample.

b Indicates a suggested sequence. Any Analytical Sample may be substituted (one-for-one) for another Analytical Sample.

c Laboratory blank evaluation can be performed at any time between the analysis of the LB and completion of Section 7.

Appendix B – Quality Assurance Objectives

Precision (%RSD or RPD)	Accuracy (%R)[a]	PRDL[b] (µg/L)	PRQL (mg/kg)	Completeness (%)
≤30	80-120	4.0	4.0	90

a Applies to laboratory control samples, laboratory matrix spikes, and PDP blind audit samples. If a solid laboratory control material which has established statistical control limits is used, then the established control limits for that material should be used for accuracy requirements.

b PRDL set such that it is a factor of 10 below the PRQL for 100 percent solid samples, assuming a 100× dilution during digestion.

Appendix C – Summary of Laboratory Quality Control Samples and Frequencies

QC Sample	Minimum Frequency	Acceptance Criteria	Corrective Action [a]
Method performance samples	Seven (7) samples initially and four (4) semiannually	Meet Appendix B QAOs	Repeat until acceptable
Laboratory blanks	One (1) per analytical batch	≤3 × PRDL	Redigest and reanalyze any samples with analyte concentrations which are ≤10 × blank value and ≥ 0.5 × PRQL
Matrix spikes	One (1) per analytical batch	Meet Appendix B accuracy QAOs	Nonconformance if %R outside the range specified in Appendix B.
Matrix spike duplicates	One (1) per analytical batch	Meet Appendix B accuracy and precision QAOs	Nonconformance if RPDs > values and % R outside range specified in Appendix B.
Initial Calibration 1 blank, 5 standards	Daily	80-120 %R for ICV, Regression coefficient ≥0.995.	Correct problem and recalibrate; repeat initial calibration
Continuing Calibration	Every 10 samples and beginning and end of run	80-120% for CCV	Correct problem and recalibrate; rerun last 10 samples
Laboratory Control Samples	One (1) per analytical Batch	Appendix B accuracy QAOs	Redigest and reanalyze. Non conformance if not reanalyzed

a Corrective action when final reported QC samples do not meet the acceptance criteria. Nonconformances do not apply to matrix related exceedances.

Appendix D – Acronyms and Abbreviations

CCB	Continuing Calibration Blank
CCV	Continuing Calibration Verification
CVAA	Cold Vapor Atomic Absorption Spectroscopy
CWS	200 µg/L Hg Working Standard. See Step 7.2.2
DSS	Dilution Solution for Solid Samples. See Item 5.2.13
FIMS	Flow Injection Mercury System
HDPE	High density polyethylene
ICB	Initial Calibration Blank
ICV	Independent Calibration Verification
IDL	Instrument Detection Limit
IWS	200 µg/L Hg ICV Working Standard. See Step 7.2.3
LB	Laboratory Blank
LCS	Laboratory Control Sample
MS	Matrix Spike Sample
MSA	Method of Standard Addition
MSD	Matrix Spike Duplicate Sample
PDS	Post-Digestion Spike
PRDL	Program Required Detection Limit
PRQL	Program Required Quantitation Limit
PVC	Polyvinyl chloride
QC	Quality Control
RWP	Radiological Work Permit
SW-846	*Test Methods for Evaluating Solid Waste*, Third Edition

TRU	Transuranic
VTSR	Validated Time of Sample Receipt
WIPP	Waste Isolation Pilot Plant
WAP	Waste Analysis Plan

Appendix E – FIMS Setup Diagrams

Figure 1: General Schematic of Flow Injection.

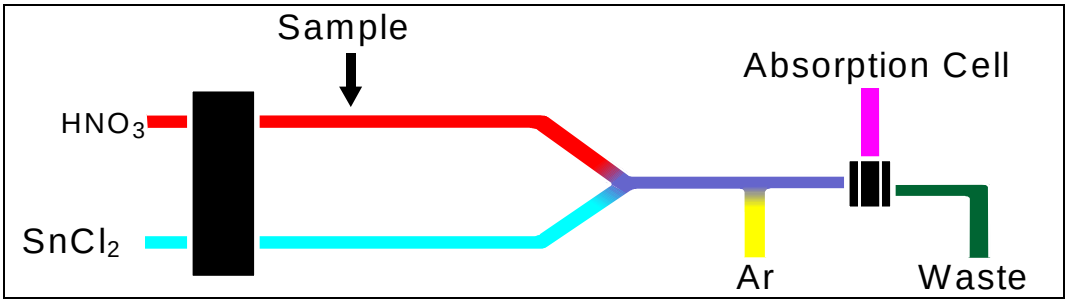
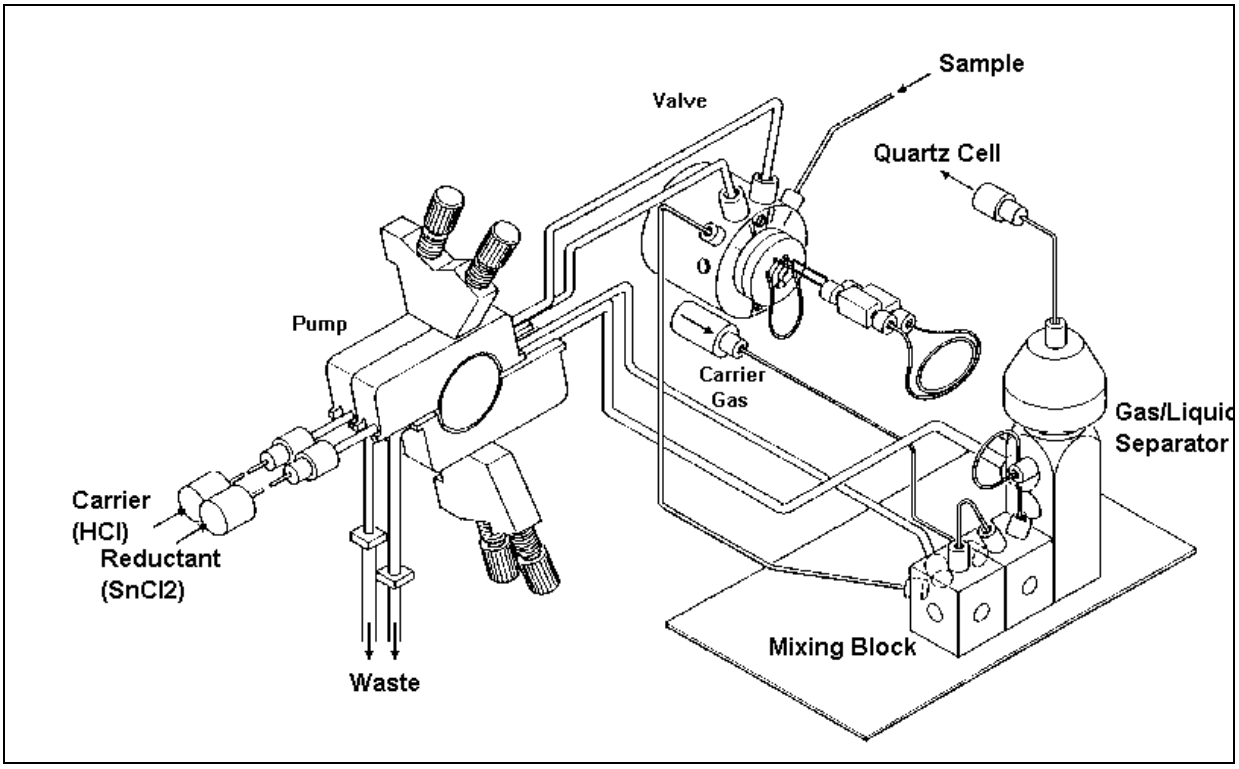


Figure 2: Tubing Set-up for Flow Injection System.



NOTE: *Figure 2 designates HCl as the carrier, however, dilute nitric acid is used as the carrier for this method. An additional gas/liquid separation device may be installed between the Gas/Liquid Separator and the Quartz Cell in Figure 2.*

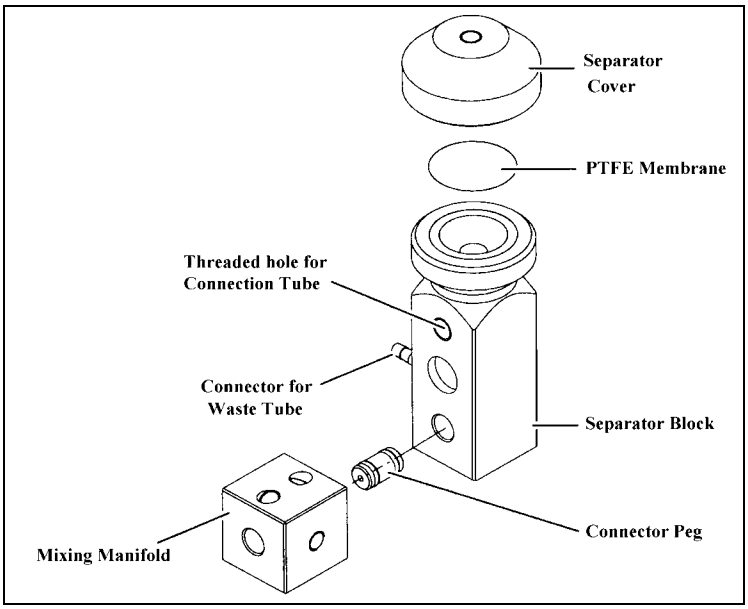



Figure 3: Mixing Manifold and Gas/Liquid Separator