STANDARD OPERATING PROCEDURE APPROVAL AND CHANGE FORM

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STANDARD OPERATING PROCEDURE
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DIGESTION AND ANALYSIS OF MERCURY BY COLD-VAPOR ATOMIC ABSORPTION (CVAA) (EPA/SW-846 Methods 7000B/7470A/7471B)

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DIGESTION AND ANALYSIS OF MERCURY BY COLD-VAPOR ATOMIC ABSORPTION (CVAA) (EPA/SW-846 Methods 7000B/7470A/7471B)

1.0 SCOPE AND APPLICATION

This standard operating procedure (SOP) is based on Environmental Protection Agency (EPA) SW-846 Methods 7000B, 7470A and 7471B and those requirements set forth in the latest approved version of The NELAC Institute (TNI) standard. Mercury (Hg) in solution may be readily determined by cold-vapor atomic absorption (CVAA) spectroscopy. Method 7470A is applicable for determining the Hg concentrations in mobility-procedure extracts (i.e., Toxicity Characteristic Leaching Procedure [TCLP], Synthetic Precipitation Leaching Procedure [SPLP], Multiple Extraction Procedure [MEP]), ground waters and aqueous wastes. Method 7471B is applicable for determining Hg concentrations in soils, sediments, sludges and other solid matrices including tissues.

The typical reporting limit (RL) is 0.200 micrograms per liter (µg/L) for water samples and 0.0400 milligrams per kilogram (mg/kg) for solid samples without correcting for moisture. **NOTE:** The reporting limit (RL) is analogous to the limit of quantitation (LOQ) based on the low standard.

This method may not be changed without the expressed approval of the Analytical Support Leader and the Quality Assurance/Quality Control (QA/QC) Officer. Only those versions issued through the Scientific, Engineering, Response and Analytical Services (SERAS) document control system may be used. Modifications made to the procedure due to interferences in the samples or for any other reason must be documented in the case narrative and on a nonconformance memo.

2.0 METHOD SUMMARY

Prior to analysis, aqueous and solid samples must be prepared according to the procedures outlined in Section 7.3. The prepared sample with Hg present enters the automated mercury system and is mixed with a reducing agent (stannous chloride) to form elemental Hg vapor. The mixture flows into a liquid-gas mixer where an inert gas is introduced to carry the Hg vapor. The gaseous-liquid mixture enters the liquid-gas separator where the liquid is drained away and the Hg-containing gas continues to the drying tube that dehumidifies the gaseous mixture. The dry vapor then enters the dual beam optical cell that has been optimized for fast response time and high sensitivity. A Hg lamp controlled by the error signal of the reference beam delivers a stable source of emission at 253.7 nanometers (nm). Absorbance by the Hg cold vapor is measured using a solid state detector with a wide dynamic range.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

Sample holding times, suggested collection volume, preservative, and type of containers are as follows:

Mercury Measurement	Collection Amount Required	Containers	Type of Preservative	Holding Time
Total	1000 mL	P, G	HNO_3 to pH < 2	28days
Dissolved	1000 mL	P, G	Filter; HNO_3 to pH <2	28 days
Solids	200 g	G	none/≤6°C	28 days
Tissues	10 g	G	none/≤ -10°C	28 days (once thawed)

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P - plastic, G - glass, g - grams, mL - milliliters, ^{o}C - degrees Celsius, HNO_3 - nitric acid, < - less than

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

Although the method minimizes dilution and sample matrix effects, the technique is not completely interference free. Inorganic and organic Hg compounds may cause a positive interference. Interferences have been reported for samples containing sulfide, chloride, and copper. Organic compounds which have broad-band ultraviolet (UV) absorbance (around 253.7 nm) will interfere. Certain volatile organic materials that absorb at this wavelength may also cause interference. Potassium permanganate is added to eliminate possible interference from sulfide. Samples high in chlorides require additional permanganate because chlorine also absorbs at 253.7 nm. The concentration levels for interfering elements/compounds are difficult to define; therefore, quality control (QC) procedures (section 9.0) must be strictly followed.

Cross-contamination and contamination of the sample can be major sources of error due to the sensitivities achieved with the CVAA spectroscopy technique. The sample preparation work area should be kept scrupulously clean. All glassware should be cleaned as specified in Section 7.1.

5.0 EQUIPMENT/APPARATUS

- Leeman Labs, Inc., HydraAA Automated Mercury Analysis System equipped with WinHg software, autosampler, personal computer, printer and monitor
- Water Bath or Hot Plate, commercially available, capable of maintaining water temperature at 95 ± 3^{o}C
- Syringes, commercially available, Henke SASS plastic or equivalent. Alternatively, disposable glass or plastic funnels may be used.
- Funnels, plastic or equivalent.
- Filters, 0.45 microns (µm), Corning SCFA or equivalent. Alternatively, glass wool may be used.
- Autopipettors, 50 to 1000 microliters (µL) and 500 to 5000 µL, calibrated quarterly
- Volumetric flasks, Class A, 100 milliliters (mL)
- Glass dispensers, 2-liter (L), 1-L, 1-gallon, checked quarterly for accuracy
- Bottles, 30-mL or 60 mL, Nalgene or equivalent
- Polypropylene round-bottom tubes, 14-mL, for samples
- Graduated cylinder, Class A, 100 mL

- Polypropylene round-bottom tubes, 50-mL, for standards
- BOD bottles, 300 mL, with ground glass stoppers for digestion of samples and standards
- Bottles, Nalgene or equivalent, miscellaneous volumes for reagent storage
- Tube rack
- Balance, capable of weighing samples to 0.01 grams (g), calibrated annually by an outside vendor

6.0 REAGENTS

- Deionized (DI) water, Type I Water (American Society for Testing and Materials [ASTM] D1193), for the preparation of all reagents and calibration standards and as dilution water
- Nitric Acid (HNO_3), concentrated, trace metal grade
- 2 Percent (%) HNO_3, Dilute 20 mL of concentrated trace metal grade HNO_3 to 1-L with DI water in a Class A volumetric flask.
- Hydrochloric Acid (HCl), concentrated, trace metal grade
- Sulfuric Acid (H_2SO_4), concentrated, trace metal grade
- Aqua Regia - Add 3 parts of concentrated HCl to 1 part of concentrated HNO_3.
- Stock Hg Calibration Standard 10 micrograms per milliliter (µg/mL), commercially available, accompanied by a certificate of analysis.
- Intermediate Hg Calibration Standard, 100µg/L - Dilute 1.0 mL of the stock calibration standard with 2% HNO_3 on a 100-mL in a Class A volumetric flask. Alternatively, use serial dilutions with 2% HNO_3 to achieve a final concentration of 100µg/L.
- Intermediate Hg Calibration Standard, 10µg/L - Dilute 10 mL of the 100 µg/L intermediate Hg calibration standard with 2% HNO_3 in a 100-mL in a Class A volumetric flask.
- Stock Hg Initial Calibration Verification/Continuing Calibration Verification Standard (ICV/CCV), Laboratory Control Sample (LCS), Matrix Spike/Matrix Spike Duplicate (MS/MSD) standard, 10 µg/mL, commercially available, accompanied by a certificate of analysis - must be a source different than that used for calibration
- Intermediate Hg ICV/CCV/LCS/MS/MSD Standard, 100µg/L - Dilute 1.0 mL of the stock Hg

ICV/CCV/LCS/MS/MSD standard with 2% HNO_3 in a 100-mL in a Class A volumetric flask. Alternatively, use serial dilutions using 2% HNO_3 to achieve a final concentration of 100µg/L.

- Working Hg ICV/CCV Standard, 2µg/L - Dilute 2 mL of the 100µg/L intermediate Hg ICV/CCV/LCS/MS/MSD standard with DI water in a 100-mL in a Class A volumetric flask.

- Stannous Chloride Solution - Dissolve 20g reagent grade stannous chloride ($SnCl_2$) in 40 mL of concentrated HCl. Slowly add this solution to 100 mL DI water. Dilute to final volume (200 mL) with DI water and mix well. Prepare fresh daily or each time calibration standards are prepared.

- Potassium Permanganate Solution, 5% weight/volume (w/v) - Dissolve 100g of Hg-free reagent grade potassium permanganate ($KMnO_4$) in 2000 mL DI water.

- Sodium Chloride-Hydroxylamine Hydrochloride Solution - Dissolve 12.0 g of reagent grade hydroxylamine hydrochloride [$(NH_2OH)_2 \cdot HCl$] and 12.0 g of sodium chloride (NaCl) in DI water and dilute to 100 mL.

- Potassium Persulfate Solution, 5% w/v - Dissolve 5 g reagent grade potassium persulfate ($K_2S_2O_8$) in 100 mL DI water.

NOTE: Premixed certified standards will be stored according to the manufacturer's documented storage requirements. These standards may be kept in storage up to the manufacturer's stated expiration date. Once dilutions are made, the standards will be stored for a period not to exceed six months or the manufacturer's expiration date, whichever is less.

NOTE: All calibration standards and spiking solutions will be prepared and documented in accordance with SERAS SOP #1012, *Preparation of Standard Solutions and Reagents.*

NOTE: Stock concentrations may vary depending on the vendor; thus, the concentration of intermediate standards may also vary. Preparation instructions may differ based on the volumes prepared and the concentrations of standards available. Any reagent may be prepared at any volume as long as the weight/volume ratios are maintained.

7.0 PROCEDURES

Preliminary treatment of waste water, ground water, extracts/leachates, and industrial waste is always necessary because of the complexity and variability of sample matrices. Tissue samples, solids, slurries, and suspended material must be subjected to a solubilization process before analysis. This process may vary depending on the nature of the sample being analyzed. **NOTE**: All chemicals must be added in the order indicated in section 7.3.

7.1 Glassware Preparation

All glassware, polypropylene, or Teflon containers, including sample bottles, volumetric flasks and

graduated cylinders, should be washed in the following sequence: detergent, tap water, 1:1 HNO_3, tap water, 1:1 HCl, tap water, and DI water. If it can be documented through an active analytical QC program using spiked samples and reagent blanks, that certain steps in the cleaning procedure are not required for routine samples, those steps may be eliminated from the procedure.

7.2 Total Solids

A total solids analysis must be conducted for soil, sediment, solid, semi-solid and tissue samples to report data on a dry weight basis. See detailed instructions in Appendix A.

7.3 Sample Preparation

7.3.1 Soil, Sediment, Solid and Semisolid Samples

Weigh 0.2 to 0.8 g (wet) portions of untreated sample and place in the bottom of a BOD bottle. Add 5mL of DI water and 5mL of aqua regia. Heat the solution for two minutes in a water bath at 95 ± 3°C. Cool; then add 50mL DI water and 15 mL potassium permanganate solution to each bottle. Mix thoroughly and place in the water bath for 30 minutes at 95 ± 3°C.

NOTE: Record the digestion time in and the digestion time out on the digestion log.

Cool and add 6 mL sodium chloride-hydroxylamine hydrochloride solution to reduce excess permanganate. Transfer the sample through a disposable polypropylene funnel into a 100-mL Class A volumetric flask and dilute to final volume with DI water. Filter an aliquot of the sample using a plastic syringe and a 0.45 µm filter into a Nalgene bottle (or equivalent) prior to analysis.

7.3.2 Aqueous Samples

Check the pH of the water sample to ensure that the pH is < 2. If the pH is not <2, adjust the sample pH to <2 by adding additional HNO_3 not to exceed 1% of the total volume of sample. Measure 100 mL of sample using a dedicated Class A device or an aliquot of the sample diluted to 100 mL and transfer to a 300-mL BOD bottle. Add 5 mL H_2SO_4 and then 2.5 mL HNO_3, mixing after each addition. Add 15 mL potassium permanganate solution to each sample bottle. Shake and add additional permanganate as necessary, until purple color persists for at least 15 minutes. Sewage samples may require additional permanganate solution. Add the same volume of permanganate solution to all standards, blanks and samples. Add 8 mL of potassium persulfate to each bottle and heat for 2 hours in a water bath at 95 ± 3°C.

NOTE: Record the digestion time in and the digestion time out on the digestion log.

Cool and then add 6 mL of sodium chloride-hydroxylamine hydrochloride to reduce excess permanganate. If necessary, filter an aliquot of the sample using a plastic syringe and a 0.45 µm filter into a Nalgene bottle (or equivalent) prior to analysis.

NOTE: For TCLP and other extract samples, take aliquots for MS/MSD analysis first and then adjust the pH of the remaining sample to pH<2 with HNO_3 prior to digestion.

7.3.3 Tissue Samples

Carefully weigh out a 0.2 to 0.8 g (wet) portion of each sample into a BOD bottle. Do not allow any of the samples to adhere to the sides of the bottle. Add 5mL aqua regia and 5mL DI water to each bottle and place in a water bath at 95 ± 3°C until the tissue is completely dissolved (if necessary, do not dilute aqua regia with 5mL of DI water in this first step). Cool and then add 50 mL DI water and 15 mL potassium permanganate solution to each sample bottle. Add additional (10 mL maximum) permanganate solution, as necessary, to maintain oxidizing conditions. Add the same volume of permanganate solution to all standards, blanks and samples. Heat the resulting solution in a water bath at 95 ± 3°C for 30 minutes to solubilize the tissue samples.

NOTE: Record the digestion time in and the digestion time out on the digestion log.

Cool the samples and reduce with 6 mL of sodium chloride-hydroxylamine hydrochloride. Transfer the sample through a disposable polypropylene funnel with glass wool into a 100-mL Class A volumetric flask and dilute to final volume with DI water. Filter an aliquot of the sample using a plastic syringe and a 0.45 µm filter into a Nalgene bottle (or equivalent) prior to analysis.

7.4 Preparation of Working Calibration Standards

For those instruments which do not read out directly in concentration, a calibration curve will be prepared to cover the appropriate concentration range. For best results, working standards should be prepared fresh each time a batch of samples is analyzed. A blank and a minimum of five working standards will be used to calibrate the Hg instrument. Working standards are typically prepared as follows:

From the 10 µg/L intermediate calibration standard, prepare the following working standards:

Standard Concentration µg/L	10 µg/L Intermediate Cal Standard, mL	Final Volume, mL
0.2	2	100
0.5	5	100
1.0	10	100

From the 100 µg/L intermediate calibration standard, prepare the following working standards:

Standard Concentration, µg/L	100µg/L Intermediate Cal Standard, mL	Final Volume, mL
2.0	2	100
5.0	5	100

The working calibration standards are digested along with the samples using the procedure outlined in Section 7.3.

For soil/tissue samples, pipet an appropriate volume (as specified above) of the intermediate standards into BOD bottles, add the appropriate volume of reagents and dilute to 100 mL with DI water after digestion.

NOTE: Any standard may be prepared from any stock or intermediate standard or any volume as long as the appropriate factor is applied and the correct v/v ratio is maintained. Calibration standards should be prepared fresh each time a batch of samples is analyzed.

7.5 Preparation of Initial and Continuing Calibration Verification Standards

For water samples, transfer 100 mL of the working Hg ICV/CCV standard into a 300-mL BOD bottle and add the appropriate volumes of reagents. For soil/tissue samples, pipet 2 mL of the 100µg/L ICV/CCV/LCS/MS/MSD intermediate Hg standard in to a BOD bottle, add the appropriate volumes of reagents and dilute to 100 mL after digestion. The ICV/CCV standards are digested along with the samples using the procedure outlined in Section 7.3. The ICV will be run immediately following instrument calibration. The CCV will be run after every 10 samples and at the end of the analytical run.

NOTE: Standards may be prepared using alternate intermediate standards as long as the final concentration is 2µg/L and the v/v ratios are maintained.

7.6 Preparation of the Laboratory Control Sample

The LCS is-prepared by spiking a blank with a known amount of Hg (at or near midrange of the calibration curve) using a second source Hg standard. Prepare the LCS for water samples by spiking 2 mL of the 100µg/L ICV/CCV/LCS/MS/MSD intermediate Hg standard to 100 mL of DI water for a concentration of 2µg/L. Prepare the LCS for solid samples by either using a minimum of 0.2 g of a certified solid sample or by adding 2 mL of the 100µg/L ICV/CCV/LCS/MS/MSD intermediate Hg standard to a clean BOD bottle. The LCS will be analyzed at the frequency of one per batch of 20 samples batch of the same matrix. Digest the LCS along with the samples (Section 7.3).

7.7 Preparation of Method and Initial/Continuing Calibration Blanks

A 100 mL DI water method blank (MB) must be prepared for each analytical batch of 20 samples. This blank is also used for dilution water, the initial calibration blank (ICB), the continuing calibration blank (CCB) and as the "zero" point for the initial calibration. Digest as in Section 7.3.

7.8 Preparation of the Matrix Spike/Matrix Spike Duplicate Samples

Prepare a MS/MSD sample by spiking a sample with a known amount of Hg approximately midrange of the calibration curve at a frequency of one in 20 samples or per project. Prepare the MS/MSD for water samples by spiking 2 mL of the 100µg/L ICV/CCV/LCS/MS/MSD intermediate Hg standard to 100 mL of water sample for a final concentration of 2µg/L. Prepare the MS/MSD for solid samples by spiking 2 mL of the 100µg/L ICV/CCV/LCS/MS/MSD intermediate Hg standard to 0.2 to 0.8 g of sample. Digest using the procedures outlined in Section 7.3.

7.9 Calibration and Measurement

Detailed operating instructions for the atomic absorption (AA) instruments and cold-vapor generators are precluded from this SOP due to differences in various models. Follow instructions stated in the instrument manual.

Analyze the full set of working calibration standards using two replicates of each standard at the beginning of the run to establish the initial calibration curve. The average of each standard's response is used to generate the linear curve *((y = mx + b) where m=slope, y= absorbance, b= y-intercept and x=calculated concentration.)*. The WinHg Runner software is used to generate the linear curve.The relative percent difference (%RPD) must be <10% for all standards with the exception of the zero point and the two lowest standards (up to 0.2 µg/L) due to poor system response.

Analyze calibration verification standards (ICV/CCV) and calibration blanks (ICB/CCB) during sample analysis to confirm instrument response at the frequency in Section 9.0. Method blanks, samples and QC samples are analyzed using two replicates during the run and the average value is reported. At the end of the analytical sequence, the ENDCCV, RL and CCB standards must be analyzed. For environmental samples, the Percent Relative Standard Deviation (%RSD) between replicate injections should be ≤20% as a guideline. Refer to Section 9.0 for QC criteria.

Samples containing Hg concentrations greater than the highest calibration standard must be diluted into the linear calibration range (see Section 9.8). All sample dilutions will be documented on the "Dilution Preparation and Analysis for Hg" log included in the data package.

8.0 CALCULATIONS

8.1 Mercury Concentrations

The Hg concentration in µg/L which is calculated using the instrument linear fit software is displayed on the instrument panel. The final Hg concentration in the sample is calculated by the system as follows:

$$A = \mu g/L = Hg\ in\ sample = B\ x \frac{D+C}{D}$$

where:

B = Concentration of Hg from the calibration (µg/L)
C = Amount of acid blank matrix used for dilution (mL)
D = Sample aliquot used for dilution (mL)

NOTE: If no dilution was required, C = 0, and A = B.

For solid samples, calculate concentrations as mg/kg based on wet weight:

$$mg/kg\ Hg\ in\ sample\ (wet\ basis) = \frac{B\,x\,V}{W\ x1000}\ x\ DF$$

where:

B = Concentration of Hg from the calibration (µg/L)
V = Final volume of the processed sample (mL)
W = Weight of sample (grams)
DF = Dilution factor for diluted samples (1.00 with no sample dilution)

For solid samples, report Hg concentrations as mg/kg based on dry weight:

$$mg/kg\ Hg\ in\ sample\ (dry\ basis) = \frac{mg/kg\ (wet\ basis)}{(S/100)}$$

where:

S = percent total solids in the sample

8.2 MS/MSD Sample Recoveries and Relative Percent Difference

MS/MSD percent recoveries (%R) are calculated as follows:

$$\text{Spike Recovery (\%R)} = \frac{\text{MS - SR}}{\text{SA}} \text{ x } 100$$

where:

MS= Matrix Spike (MS) or Matrix Spike Duplicate (MSD)
SR = Sample result
SA = Spike added

The Relative Percent Difference (RPD) for the MS/MSD sample is calculated as follows:

$$\text{RPD} = \frac{|\text{MS - MSD}|}{(\text{MS} + \text{MSD})/2} \text{ x}100$$

where:

MS = concentration of the Matrix Spike sample
MSD = concentration of the Matrix Spike Duplicate sample

8.3 LCS Recoveries

The recoveries of each of the compounds in the LCS are calculated using the following equation:

$$\textit{Laboratory Control Sample}\,\text{Recovery}\,(\%R) = \left(\frac{LCS - BLK}{SA}\right) x\,100$$

where:

LCS = Concentration of target analyte in LCS
SA = Concentration of spike added or certified value of target analyte
BLK = Method Blank results, (µg/L or mg/Kg)

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9.0 QUALITY ASSURANCE/QUALITY CONTROL

All quality control data should be documented and available for reference or inspection at the SERAS facility.

9.1 Instrument Calibration

A minimum correlation coefficient (r) of 0.995 must be achieved for the linear calibration to be valid. If r is <0.995, a new calibration curve must be run.

9.2 Initial Calibration Verification

The calibration curve must be verified by the analysis of an ICV standard (at or near mid-range) from an independent source. The ICV result must be within 10% of the true value for the calibration to be considered valid. If the ICV result is .outside 10% acceptance criterion, the ICV analysis must be repeated. If the ICV is still outside QC limits, the instrument must be re-calibrated.

9.3 Continuing Calibration Verification

The working standard curve must be verified by analyzing the CCV standard (at or near the mid-range) after every 10 samples or 20 injections. CCV results must be within 10% of the true value, or the previous ten samples must be reanalyzed.

9.4 Initial/Continuing Calibration Blanks

The ICB/CCB results must be less than the RL for the sequence to continue. A total of two attempts for the ICB are allowed. If the second attempt fails, refill with fresh ICB/CCB solution and re-calibrate prior to analysis.

9.5 Method Blank

A 100 mL DI water method blank must be prepared for each analytical batch of 20 samples. The method blank result must be less than the RL. If the method blank result is above the RL, the system must be recalibrated and samples re-analyzed. A method blank containing an analyte concentration >RL may be used in instances when the sample concentrations are at least 10 times the method blank concentration. For all samples with a concentration less than 10x the method blank result, the lab must re-digest and reanalyze. If there is insufficient sample, estimate the reported results of those samples.

9.6 Laboratory Control Sample

The LCS (Section 7.6) must be prepared with each batch of 20 samples. LCS results for mercury must be within the specifications supplied by the vendor or within 80 - 120% of the true value and are calculated as in Section 8.3. If the LCS does not meet the criterion, the LCS should be re-run once

and, if still unacceptable, all samples after the last acceptable LCS should be re-prepared and reanalyzed. The laboratory must compile historical data and develop control chart limits. Under no circumstances must the laboratory accept %R outside of the ±20% criterion.

9.7 Matrix Spike/Matrix Spike Duplicate

At least one MS and one MSD sample must be digested with every 20 samples or with each project type to verify the accuracy of the method. The spike level should be at or near mid-range of the calibration. The MS/MSD samples should be spiked at the same level as the corresponding LCS. In the event that there is insufficient sample available to run a MS/MSD in the batch, a LCS/laboratory control sample duplicate (LCSD) must be run. Recoveries are calculated as in Sections 8.2 (MS/MSD) or 8.3 (LCS/LCSD) and must be within 80-120% for the MS/MSD and LCS/LCSD. Under no circumstances must the laboratory accept %R outside of the ±20% criterion. If MS/MSD recoveries are out of the acceptance range but the LCS recovery is acceptable, analysis will continue.

The Relative Percent Difference (RPD) for the MS/MSD or LCS/LCSD samples must be within ±20% (see Section 8.2).

9.8 Dilution Analysis

If the sample Hg concentration exceeds the initial calibration range, the sample must be diluted and reanalyzed. Use the results of the original analysis to determine the approximate dilution factor required to get Hg concentration within the initial linear calibration range. Dilute the sample and analyze the diluted sample aliquot. Report Hg results from the lowest dilution factor which is in the linear calibration range (see Section 8.0). Increase the RL by the same dilution factor as the samples.

9.9 System Routine Maintenance

Routine maintenance is conducted using the guidelines provided by the manufacturer as follows:

Maintenance	Frequency
Clean optical cell	As needed
Clean optical windows	As needed
Adjust Hg lamp	Every 3 months or as needed
Replace pump, waste drain and process tubing	As needed
Check pump head	As needed

9.10 Demonstration of Capability

Prior to running a method or any time there is a change in instrument type, personnel or test method or any time a method or analyst has not performed a method in a twelve-month period, an analyst must demonstrate acceptable performance for that method. This is known as the initial demonstration of capability (DOC). Four aliquots of a QC standard (second source) must be prepared and analyzed according to the method over one or a period of days. If the method does not specify a concentration to be used for the DOC, then the concentration must be prepared at 1-4 times the RL. Using Excel, the analyst must provide a table containing the following: Results of the 4 replicates, Mean Concentration, Mean Recovery, Standard Deviation and %RSD with the LCS acceptance limits.

On-going demonstration of capability on an annual basis may be satisfied by the analyst successfully passing a performance testing (PT) sample or a minimum of 4 consecutive LCS samples with acceptable precision and accuracy levels or another initial DOC. Results of tabulated QC samples (i.e., control chart data) that are analyst-specific accompanied by precision and accuracy criteria agreed upon by the Analytical Support Leader and the QA/QC Officer may also be used.

9.11 Limit of Detection/Limit of Quantitation Studies

The Limit of Detection (LOD) must be determined for each target analyte on every instrument used for the analysis and reporting of samples. The LOD must be determined initially and each time there is a change in the method that affects how the test is performed or when there is a change in instrumentation. The LOD must be verified for each matrix, method and analyte. If concentrations less than the low standard on the calibration curve are not reported, then an annual LOD study is not required. The LOD will be run using a minimum of seven replicates of a sample prepared from the calibration source at 4 times the LOD for multiple analyte tests. Each of these 7 aliquots must be subjected to the entire analytical procedure. Calculate the mean, mean recovery, variance and standard deviation of the replicate measurements. The LOD is calculated by multiplying the standard deviation times the Students t-Value of 3.143. If more than 7 replicates are used, the Students t-Value must be adjusted accordingly.

The Limit of Quantitation (LOQ) must be confirmed by the successful analysis of a secondary source QC sample containing each target analyte in each matrix at 1-2 times the claimed LOQ (typically the low standard). The recoveries must fall within ±30%. Alternately, a control chart with recoveries established from previously analyzed LOQ samples may be used. The LOQ must be subjected to the entire analytical procedure. The LOQ must be verified annually for each matrix, method and analyte. If a LOD is performed, then the LOD/LOQ must be determined at the same time.

If the laboratory will not be reporting concentrations less than the lowest standard on the calibration curve (i.e., the RL), then an annual LOD is not required.

9.12 System Troubleshooting

If the instrument will not start, check to make sure the power supplies are ON, argon gas is ON and at the correct pressure, exhaust is ON, sample tubing is connected and correct tension on the pump winding tubing. After making these adjustments and the instrument will still not start, power down the instrument, wait a few minutes and then power up. If repeated attempts fail to start the analyzer, contact the manufacturer for assistance.

If high RSDs are encountered during analysis, recheck pump winding tubing, sample uptake probe, stannous chloride line from the solution to the pump, drying tube and points of tubing connection. Adjust and re-calibrate instrument prior to any analysis.

For any hardware/software problems, contact the manufacturer for assistance.

9.13 Nonconformance Memo

A nonconformance memo will be generated any time the analyst notices a deficiency suspected of being a nonconformance. This nonconformance memo will be included in the data package for verification of corrective action.

10.0 DATA VALIDATION

Data will be assessed for usability by the Data Validation and Report Writing Group using the most current version of SERAS SOP #1017, *Data Validation Procedure for Routine Inorganic Analysis.* However, data are considered satisfactory for submission purposes when all of the requirements listed in the method are met.

11.0 HEALTH AND SAFETY

The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. The laboratory is responsible for following the chemical hygiene plan and laboratory safety program regarding the safe handling of the chemicals specified in this method.

When working with potentially hazardous materials, refer to EPA, Occupational Safety and Health Administration (OSHA) and corporate health and safety practices. More specifically, refer to SERAS SOP #3013, *SERAS Chemical Hygiene Plan* and SERAS SOP #1501, *Hazardous Waste Management*. The analyst should consult all appropriate MSDS information prior to running an analysis for the first time.

12.0 REFERENCES

Teledyne Leeman Labs. 2003. *HydraAA Automated Mercury Analyzer Manual*, 150-00210, Revision C.

Teledyne Leeman Labs. 2001. *HydraAA Automated Mercury Analyzer Operation Manual*, 150-00213, Revision A.

The NELAC Institute, 2009. TNI Standard, Volume 1Management and Technical Requirements for Laboratories Performing Environmental Analysis, EL-V1-2009-ISO.

U.S. EPA, Office of Solid Waste and Emergency Response. 2007. *Test Methods for Evaluating Solid Waste*, SW-846, 3rd ed. Update I. Method 7000B.

U.S. EPA, Office of Solid Waste and Emergency Response. 1994. *Test Methods for Evaluating Solid Waste*, SW-846, 3rd ed. Update II. Method 7470A.

U.S. EPA, Office of Solid Waste and Emergency Response. 2007. *Test Methods for Evaluating Solid Waste*, SW-846, 3rd ed. Revision 2. Method 7471B.

U.S. EPA. 1984. Federal Register, 40 Code of Federal Regulations (CFR) Part 136, Appendix B, *Definition and Procedure of the Determination of the Method Detection Limit - Revision 1.11*, October 26, 1984.

13.0 APPENDICES

This section is not applicable to this SOP.

DIGESTION AND ANALYSIS OF MERCURY BY COLD-VAPOR ATOMIC ABSORPTION (CVAA) (EPA/SW-846 Methods 7000B/7470A/7471B)

APPENDIX A
Procedure for Determination of Total Percent (%) Solids
SOP#1832
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DIGESTION AND ANALYSIS OF MERCURY BY COLD-VAPOR ATOMIC ABSORPTION (CVAA) (EPA/SW-846 Methods 7000B/7470A/7471B)

PROCEDURE FOR DETERMINATION OF TOTAL PERCENT (%) SOLIDS

1.0 APPLICABILITY

This procedure applies to soil, sediment, and other solid samples received for laboratory analysis of total percent solid at the Scientific, Engineering, Response and Analytical Services (SERAS) Laboratory.

2.0 PURPOSE

A step by step procedure is outlined for the determination of total percent solids in soil, sediment and other solid samples.

3.0 REFERENCES

Standard Methods for the Examination of Water and Wastewater, Ed. by L. S. Clesceri, A. E. Greenberg, and A. D. Eaton, APHA, AWWA, WEF, Washington, D.C., latest online edition, Method 2540 G. (With modification-instead of repeating drying, cooling and weighing cycle; overnight drying followed by cooling is allowed to achieve constant weight).

4.0 EQUIPMENT:

-Laboratory oven with temperature control capable of maintaining 103 - 105^{o}C

-Desiccator with a desiccant containing a color indicator for moisture content.

-Aluminum weighing dishes for weighing/drying samples.

-Spatulas or equivalent for transferring samples to the aluminum weighing dishes.

-Analytical balance, capable of weighing samples to 0.01 grams (g), calibrated annually by an outside vendor

Note: The drying oven should be monitored so that proper temperature is maintained during the drying process and care should be taken to avoid excessively high temperatures. The oven must be well ventilated to prevent potentially harmful vapors from escaping to the surrounding air.

5.0 PROCEDURE

The analyst should determine if there is sufficient mass for % solids determination on a sample to sample basis.

1. Sample Preparation

   Samples should be homogenized (as much as possible) and at room temperature prior to % Solids determination.

2. Balance Preparation

Check the balance using class S weights at 0.1, 1.0, and 10.0 g prior to weighing samples.

3 Total % Solids Determination

- Weigh a labeled, empty aluminum weighing dish on the balance; record weight (to the nearest 0.01 g).

- Transfer 10-25 g sample to the dish and record weight (to the nearest 0.01 g) for wet sample plus dish.

- Place the sample dish in the drying oven for a minimum of eight hours at 103 - 105^{o}C.

- Record the initial and final oven temperatures, dates and time in the percent solids log book.

- Cool the samples in a desiccator (to room temperature)

- Record the weight of the dry sample plus dish (to the nearest 0.01g).

- Calculate % solids as described below.

Note: The analyst should adjust the amount of sample used and/or drying time based on the condition of the sample; very wet materials will require larger sample amounts and drying times to get accurate % solids results.

6.0 CALCULATIONS FOR PERCENT SOLIDS

The result for total percent solids is calculated as follows:

$$\%S = [(C - A) / (B - A)] * 100$$

Where:

%S = Percent Solids
A = weight of empty dish (g)
B = weight of wet sample plus dish (g)
C = weight of dry sample plus dish (g)

Record the value in the percent solids log (to the appropriate number of significant figures).

NOTE: Alternatively, the calculation may be performed using a verified spreadsheet on a computer and/or using a Laboratory Information Management System (LIMS).