

STANDARD OPERATING PROCEDURE

TITLE: Mercury Analysis of Aqueous Samples by CVAA

DEPARTMENT: Wet Chemistry

MATRICES: Ground waters, Wastewaters, Drinking Waters, Leach Test Extracts, Seawater, and Brines

DETECTION LIMITS: The method detection limit is 0.088 ug/L and the EQL is 0.20 ug/L.

SCOPE AND APPLICATION: This procedure measures total Mercury (organic and inorganic) in drinking water, surface water, ground waters, leaching extracts, industrial wastewaters, and domestic wastewaters.

REFERENCE: EPA Method 245.1, 600 4-82-055, December 1982
USEPA Test Methods for Evaluating Solid Waste SW-846, 3rd Edition, Method 7470A
USEPA Test Methods for Evaluating Solid Waste SW-846, 3rd Edition, Method 7000, Section 8.7

PROCEDURE SUMMARY:

Cold vapor atomic absorption utilizes the volatile property of elemental mercury at the 253.7 nm wavelength. To release mercury from organic complexes, the sample is digested with oxidizing reagents and acids in a hot water bath. After digestion, the oxidizing reagents are neutralized. Stannous chloride is added to reduce ionic mercury to the ground state. A Flow Injection Analysis System sweeps the volatile elemental mercury out of the sample and into the cell of an atomic absorption spectrophotometer. The absorbance signal is proportional to the amount of mercury in the sample.

REVIEWED BY: Michael J. Helmann 3/12/02
Michael J. Helmann
Wet Chemistry Supervisor
Date

Julie A. Trivedi 3/12/02
Julie A. Trivedi
Quality Assurance Officer
Date

APPROVED BY: Glen A. Coder 3/12/02
Glen A. Coder
Laboratory Manager
Date

Annual Review

Date:						
Initials:						

DEFINITIONS:

Calibration Blank-A volume of reagent water acidified with the same acid matrix as in the calibration standards. The calibration blank is a zero standard and is used to auto-zero the instrument.

Calibration Standard-A solution prepared from the dilution of stock standard solutions. The calibration solutions are used to calibrate the instrument response with respect to analyte concentration.

Laboratory Control Sample (LCS)- An aliquot of reagent water or other blank matrices to which a known quantity of the method analyte is added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate measurements.

Laboratory Control Sample Duplicate (LCSD)-A second aliquot of reagent water or other blank matrices to which a known quantity of the method analyte is added in the laboratory. . The LCSD is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

Linear Range-The concentration range over which the instrument response to an analyte is linear.

Matrix Spike (MS)-An aliquot of an environmental sample to which a known quantity of the method analyte is added in the laboratory. The MS is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentration of the analyte in the sample matrix must be determined in a separate aliquot a bias to the analytical results. The background concentration of the analyte in the sample matrix must be determined in a separate aliquot and the measured values in the MSD are corrected for background concentrations.

Method Blank- An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The method blank is used to determine if the method analyte or other interferences are present in the laboratory environment, reagents, or apparatus.

Method Detection Limit (MDL)-The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

Method of Standard Addition (MSA)-The addition of a known amount of analyte to the sample in order to determine the relative response of the detector to the analyte within the sample matrix. The relative response is then used to assess either an operative matrix effect or the sample analyte concentration.

Stock Standard-A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

INTERFERENCES:

Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide as NaS do not interfere with the recovery of added inorganic mercury from D.I. water.

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

Seawaters, brines and industrial effluents high in chlorides require additional permanganate, as much as 25 mL, because during the oxidation step, chlorides are converted to free chlorine which also absorbs radiation at 253.7 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine hydrochloride reagent, 6 mL.

Certain volatile organic materials that absorb at this wavelength may also interfere. A preliminary run without reagents would determine if this type of interference is present.

SAFETY:

The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Laboratory staff should observe all safety procedures as outlined in the Laboratory Health and Safety Manual. Staff should consult Material Safety Data Sheets (MSDS) for information on specific chemicals.

EQUIPMENT AND SUPPLIES:

Balance
BOD bottles: 300 mL
Graduated cylinders: 50 mL, 100 mL
Glass beaker: 1000 mL
Volumetric flasks: 200 mL, 1000 mL, 2000 mL
Volumetric pipets: 20 mL
Eppendorf pipettor and tips
Acid and reagent repipettors
Water bath(s)
Stir bar
Stir plate
Oxford pipettor and tips

REAGENTS AND STANDARDS:

Deionized (D.I.) water
Certified standard solution: 1000 mg/L (1000 ppm)
Second Source Certified standard solution: 1000 mg/L (1000 ppm)
Sulfuric acid (H₂SO₄): concentrated, reagent grade
Nitric acid (HNO₃): concentrated, distilled or mercury-free
Hydrochloric acid (HCL): concentrated, trace grade
Potassium permanganate, low mercury, 5% solution (w/v)

Potassium persulfate, 5% solution (w/v)
Sodium chloride
Hydroxylamine hydrochloride
Stannous chloride

Prepare Potassium permanganate, 5% solution (w/v):

- Dissolve 100 grams potassium permanganate (KMnO_4) in 2 liters D.I. water.

Prepare Potassium persulfate, 5% solution (w/v):

- Dissolve 50 grams potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$) with D.I. water in a 1 liter volumetric flask.
- Warm to dissolve.

Prepare Sodium chloride - hydroxylamine hydrochloride Solution:

- Dissolve 120 grams sodium chloride (NaCl) and 120 grams hydroxylamine hydrochloride ($\text{NH}_2\text{OH} \cdot \text{HCl}$) in 1 liter D.I. water.

Prepare Stannous chloride Solution:

- Add 11 grams stannous chloride ($\text{SnCl}_2 \cdot 2 \text{H}_2\text{O}$) and 30 mL conc. HCL to 500 mL D.I. water in a 1 liter volumetric flask.
- Dissolve and dilute to volume with D.I. water.

NOTE: These solutions should be prepared fresh monthly.

Prepare Intermediate Calibration Standard, 1 ppm:

- Acid rinse a 100 mL volumetric flask, first with 1:1 HNO_3 , then with D.I. water.
- Add 50 - 70 mL D.I. water.
- Add 0.5 mL HNO_3 . Wash down with D.I. water.
- Pipet 0.1 mL standard solution (1000 ppm) into the flask using a calibrated Eppendorf pipettor.
- Bring to volume with D.I. water, invert 6 times, and label as 1 ppm Hg intermediate standard.

Prepare Working Calibration Standard, 0.1 ppm:

- Acid rinse a 50 mL volumetric flask.
- Add 0.3 mL HNO_3 to flask. Rinse down with D.I. water and swirl.
- Pipet 5 mL 1 ppm Hg intermediate standard into the flask using a glass or calibrated pipettor.
- Bring to volume with D.I. water, invert 6 times, and label as 0.1 ppm Hg working standard.

Prepare Calibration Standards

- Label one BOD bottle as a blank.

- Label one bottle as a zero standard and one bottle each as 0.2, 1.0, 5.0, 10.0 ppb standards. Using a calibrated pipettor, transfer 0.2, 1.0, 5.0 and 10.0 mL, respectively, of 0.1 ppm working standard into each bottle of the pair. A 2.0 ppb standard (0.20 mL of 1.0 ppm working standard) is necessary for EPT digestions.
- Fill with D.I. water so that the total volume in each bottle equals 100 mL. Use a graduated cylinder.

Prepare Laboratory Control Sample (LCS)

- Transfer 100 mL D.I. water into a BOD bottle using a graduated cylinder.
- Pipet 0.5 mL Hg intermediate standard into bottle using a calibrated Eppendorf pipettor. Label as LCS.

Prepare ICB, CCB and MB (Initial Calibration Blank, Continuing Calibration Blank and Method Blank)

- Transfer 100 mL D.I. water into BOD bottles using a graduated cylinder. Label as ICB, CCB, or MB.

Prepare ICV and CCV (Initial Calibration Verification and Continuing Calibration Verification)

- Acid rinse a 100 mL volumetric flask, first with 1:1 HNO₃, then with D.I. water.
- Add 50 - 70 mL D.I. water.
- Add 0.5 mL HNO₃. Wash down with D.I. water and swirl.
- Pipet 0.1 mL second source standard solution (1000 ppm) into the flask using a calibrated Eppendorf pipettor.
- Bring to volume with D.I. water, invert 6 times, and label as 1 ppm Hg intermediate standard.
- Transfer 100 mL D.I. water into BOD bottles using a graduated cylinder.
- Pipet 0.4 mL 1 ppm Hg intermediate into each BOD bottle using a calibrated Eppendorf pipettor. Label as ICV - 4 ppb or pipette 0.5 mL 1 ppm Hg intermediate standard into each BOD bottle. Label as CCV.

SAMPLE COLLECTION, PRESERVATION, AND STORAGE:

Samples may be collected in glass or plastic bottles. Samples are preserved by adjusting the pH to < 2 with nitric acid (HNO₃). The holding time for preserved samples is 28 days.

QUALITY CONTROL:

Quality Control, Quantified by Comparison to Standard Curve

Correlation Coefficient (r-value)

The correlation coefficient, the measure of linearity of a standard curve, must be 0.995 or greater. If the value is less than 0.995 recalibrate the instrument.

Initial Calibration Verification (ICV)

The ICV is prepared from a source independent from the calibration standards and must be analyzed immediately after calibration. The ICV must meet the rejection criteria of $\pm 10\%$ of the true value. Recalibrate if the ICV fails. The concentration of the ICV should be near the mid-point of the calibration curve.

Initial Calibration Blank (ICB)

The ICB must be analyzed after the ICV. The absolute value must be \leq EQL. Recalibrate if it fails.

Continuing Calibration Verification (CCV)

The CCV is analyzed after every 10 samples. Rejection criteria is $\pm 10\%$ of true value. If the CCV fails, the problem must be corrected and the previous 10 samples between the CCV and last CCB must be reanalyzed. Concentration of the CCV should be near the mid-point of the calibration curve.

Continuing Calibration Blank (CCB)

The CCB is analyzed after every CCV. The absolute value must be \leq EQL. If the CCB fails, the problem must be corrected and the previous 10 samples between the last CCB and the CCV must be reanalyzed.

Laboratory Control Sample (LCS)

The LCS is carried through all preparation procedures and analyzed for each matrix type with a frequency of 5%. See current QC charts for control ranges. In cases where the LCS is outside of acceptable ranges all samples prepared in that batch must be re-prepared and re-analyzed.

Method Blank (MB)

A MB is carried through all prep procedures and analyzed with a frequency of 5%. Rejection criteria is $<$ LOD. Other criteria may apply, such as regulatory limit and the analyte concentration in the samples.

Matrix Spike/Matrix Spike Duplicate

One matrix spike and matrix spike duplicate are analyzed for each group of samples that are similar in matrix at a frequency of 5%. Both QC samples must be calculated for accuracy. See current QC charts for control range.

If the both spike recoveries are outside of the specified control limit, the corresponding parent sample is to be post-spiked and the reported result shall be flagged with the "N" qualifier. The control limits for a post-spike are 75-125%. If the post-spike recovery is out-of-control, dilute the corresponding sample and perform a post-spike on the diluted aliquot of sample. Dilute appropriately until an acceptable recovery is obtained.

If the analyte of interest is greater than the linear range, dilute appropriately and post-spike the sample; however, the "N" qualifier is not required. Also, if the analyte of interest is greater than 4x the level of the spike concentration, accuracy calculations are not necessary.

The relative percent difference (RPD) is used to determine whether the precision criteria have been met. Please refer to the current list of control limits. If the RPD is outside of the acceptable control limits, the reported sample result is to be qualified with the "*" flag.

If there is insufficient sample volume to perform a matrix spike and a matrix spike duplicate, an LCS and LCS DUP must be performed.

For EPA METHOD 245.1:

Warm up the lamp at least 30 minutes prior to analysis.

Perform a matrix spike at a minimum of 10% of the samples or one per sample batch, whichever is more frequent.

CALIBRATION AND STANDARDIZATION:

Please refer to EnChem SOP MET-57 for instrument calibration and standardization procedures.

PROCEDURE:

1. Collect samples and bring to room temperature. (Use tubs of hot water if necessary).
2. Heat water bath(s) to 95°C. Water in bath should reach above liquid level in BOD bottles. Note temperature of bath into water bath log book.
3. Prepare reagents as necessary.
4. Write up run on digestion bench sheet and CVAA aqueous bench sheet. Identify the samples for Quality Control..
5. Collect and label acid-washed BOD bottles and acid-washed glassware.
6. Transfer 100 mL, or an aliquot diluted to 100 mL with D.I. water, of each well-mixed sample into a BOD bottle using a graduated cylinder.
7. Spike designated samples by pipetting 0.5 mL 1 ppm Hg intermediate standard into BOD bottles using a calibrated Eppendorf pipettor.
8. All BOD bottles should contain 100 mL volume before adding reagents. Keep stoppers on bottles to avoid contamination problems.

CAUTION: CONTINUE DIGESTION IN HOOD. WEAR SAFETY GLASSES AND GLOVES.

NOTE: All reagents should be added in equal amounts to standards and samples.

9. Add 5 mL concentrated H₂SO₄ using an acid repipettor and mix.
10. Add 2.5 mL concentrated distilled HNO₃ using acid repipettor and mix.
11. Add 15 mL potassium permanganate solution using a calibrated pipettor. Mix, adding additional potassium permanganate crystals if necessary until purple color persists.

12. Add 8 mL potassium persulfate using a calibrated pipettor and mix.
13. Heat BOD bottles in 95°C water bath for 2 hours. (Check to ensure purple color is maintained. Add potassium permanganate crystals if needed. The same amount of crystals must be added to all samples, standards, and QC samples.)
14. Cool bottles to room temperature before analysis.
15. Set up AA instrument for cold vapor analysis. See EN CHEM METHOD MET-57.
16. Add 6 mL sodium chloride-hydroxylamine hydrochloride solution to each BOD bottle using an repipettor. Swirl until no color persists.

CALCULATIONS:

Aqueous Sample Calculation:

$$\text{Raw Data result (ug/L)} \times \text{DF} = \text{Final Result (ug/L)}$$

DF = Dilution Factor

$$\text{Spike Percent Recovery} = \frac{\text{SSR} - \text{SR}}{\text{SA}}$$

SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

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

MS = Method Spike Value
MSD = Method Spike Duplicate Value

POLLUTION PREVENTION:

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Laboratory staff should order and prepare only those quantities of reagents that will be used prior to the expiration date. Other appropriate measures to minimize waste generation should be brought to the attention of laboratory management. All laboratory waste shall be handled as directed by the Laboratory Waste Management Plan and Hazardous Waste Contingency Plan.

WASTE MANAGEMENT:

USEPA requires that laboratory waste handling practices conducted be consistent with all applicable rules and regulations. Excess reagents, samples, and method process wastes should be characterized and disposed of in an appropriate manner. Please refer to the EnChem Standard Operating Procedures GEN-5 and GEN-12 for additional information on the disposal of environmental samples and other laboratory wastes.