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Mercury in Sediments

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1 Scope and Application

Method 245.5 is used to prepare and analyze samples for Mercury analysis by Cold Vapor Atomic Absorption Spectroscopy in soils, sediments, sludges, and bottom deposits. Due to volume limitations in the digestion equipment, all digestion volumes are reduced to 25%.

Compound	CAS No.
Mercury	7439-97-6

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1.2 Restricted Procedure

This procedure is restricted to use by an analyst experienced in the operation of atomic absorption spectrometers. Additionally, the analyst must complete the requirements of the GAEPD Initial Demonstration of Analyst Proficiency prior to the analysis of actual samples. Analysts are further warned that performance of this analysis involves the use of potentially hazardous chemicals; refer to the GAEPD Chemical Hygiene Plan for additional information regarding chemicals required by this method.

2 Definitions

Refer to Chapter 3 of the Georgia EPD Laboratory Quality Assurance Manual for Quality Control Definitions.

3 Interferences

3.1 Potassium Permanganate is added to the samples to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide (as sodium sulfide) do not interfere with the recovery of added inorganic mercury from reagent water.

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

3.3 Certain volatile organic materials that absorb at 253.7 nm may also interfere. Analyzing the sample without reagents shall validate a positive mercury result. The presence of mercury in the sample without reagents confirms the presence of interference and the concentration of mercury present in the treated sample is commented.

4 Safety

Refer to Laboratory Chemical Hygiene Plan, online revision

5 Apparatus and Equipment

5.1 Complete cold vapor mercury analyzer system and controller.
5.2 Autosampler tubes.
5.3 50 mL hot block digestion vessels with screw caps.
5.4 Hot block digestion system.
5.5 Assorted volume graduated cylinders.
5.6 Magnetic stirrer and magnetic stir bars.
5.7 Pipettors capable of delivering the required volumes of reagents
5.8 Assorted high quality pipette tips
5.9 Top loading balance capable of measuring 0.1 g ± 0.01 g.

6 Reagents and Standards

All reagents or standards that are prepared must be logged into the standard log notebook, the standard number must be written on the sample prep log, and the container must be labelled with the standard number, standard name, initials and the expiration date.

6.1 Reagent water: 18MΩ water.
6.2 Concentrated reagent grade sulfuric acid.
6.3 Concentrated reagent grade nitric acid.
6.4 Stannous chloride: add 11 g stannous chloride ($SnCl_2 \cdot 2H_2O$) to a graduated cylinder, add 3% (v/v) HCl to bring the final volume to 1000 mL. Place the graduated cylinder on a magnetic stirrer, add a magnetic stir bar to the cylinder, and stir continuously during use
6.5 Sodium chloride-hydroxylamine hydrochloride solution: Dissolve 12 g of sodium chloride and 12 g hydroxylamine sulfate in 18MΩ water and bring to 100 mL.
6.6 Potassium permanganate, mercury-free, 5% solution (w/v): Dissolve 5 g potassium permanganate in 18MΩ water and bring to 100 mL.
6.7 Aqua regia: Mix 3 volumes concentrated hydrochloric acid to 1 volume concentrated nitric acid, mix thoroughly.
6.8 3% Hydrochloric Acid: bring 30 mL concentrated hydrochloric acid to 1000 mL with 18 MΩ water.
6.9 Concentrated reagent grade hydrochloric acid.

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7 Sample Collection

Soil and sediment samples for mercury analysis are collected in 500 mL wide mouth plastic (HDPE) bottles. Sample bottles must be cooled to 4^0C after sample collection. Mercury analysis must be performed within 28 days.

8 Calibration

8.1 Calibration Curve
The Mercury analyzer is calibrated daily using a multipoint calibration curve. The concentrations of the calibration standards are (in mg/kg): 0.0, 0.0002, 0.0005, 0.001, 0.002, 0.003, and 0.006. Minimum acceptable correlation coefficient is 0.995 using linear regression.

8.2 Calibration Verification
An ICV, CCC, and CCB are analyzed immediately after calibration. A CCC and CCB are also analyzed after calibration, every ten samples, and as the last samples in an analytical batch.

9 Quality Control

Refer to Table 13.1 for Reporting Limits (PQLs), Table 13.2 for Quality Control Acceptance Criteria, and Table 13.3 for Quality Control Procedures associated with this method.

9.1 Record all reagents used, volumes, standard or lot numbers, time, temperature, and sample IDs on the digestion log. Fill out a run log with every use of the instrument. The run log must include all samples and standards analyzed in the order they were analyzed.

9.2 Verify the pipette calibration by weighing 100 ul and 500 ul of MillQ water. Acceptable weights are 0.100g ±0.019g for 100 ul and 0.500g ± 0.05g for 500 ul. Record the pipette number, the volumes and the weights on the digestion sheet.

10 Procedure

10.1 Weigh a 0.15-gram portion of the dried sample into a 50 mL hot block digestion vessel use Ottawa Sand for the MB, LCS, and LCSD.

10.2 Add 1.25 mL 18MΩ water and 1.25 mL aqua regia to each vessel. Mix thoroughly. Add the LCS, LCSD, MS, and MSD spikes..

10.3 Place each vessel into the hot block and heat at 95ºC for 2 minutes. Do not heat the standards.

10.4 Remove the vessels from the hot block, allow to cool to room temperature, add 12 mL 18MΩ water and 3.75 mL potassium permanganate solution to each vessel. Mix thoroughly.

10.5 Place each vessel into the hot block and heat at 95ºC for 30 minutes. Do not heat the standards.

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10.6 Remove the vessels from the hot block, cool to room temperature, and add 1.5 mL sodium chloride-hydroxylamine hydrochloride to each vessel. Bring all to 40 mL with 18 MΩ water..

10.7 Any sample with a Hg concentration > LDR must be diluted to bring the Hg concentration between the RL and LDR. If the sample was spiked, then both the spike and spike duplicate must be diluted by the same amount.

10.8 Calibration and QC standard preparation

Standard	Preparation	Final concentration (mg/kg)
Hg intermediate standard	Dilute 0.1mL 1000 ppm stock solution to 100 mL with 1% nitric acid.	1.0
Hg calibration blank	18 MΩ water	<RL
Hg calibration standard 1	Weigh out 0.15 g Ottowa Sand and add 0.0080 mL Hg intermediate standard. Continue with step 10.2.	0.0002
Hg calibration standard 2	Weigh out 0.15 g Ottowa Sand and add 0.020 mL Hg intermediate standard. Continue with step 10.2.	0.0005
Hg calibration standard 3	Weigh out 0.15 g Ottowa Sand and add 0.040 mL Hg intermediate standard. Continue with step 10.2.	0.001
Hg calibration standard 4	Weigh out 0.15 g Ottowa Sand and add 0.080 mL Hg intermediate standard. Continue with step 10.2.	0.002

Standard	Preparation	Final concentration (mg/kg)
Hg calibration standard 5	Weigh out 0.15 g Ottowa Sand and add 0.120 mL Hg intermediate standard. Continue with step 10.2.	0.003
Hg calibration standard 6	Weigh out 0.15 g Ottowa Sand and add 0.240 mL Hg intermediate standard. Continue with step 10.2.	0.006
HgICV	Weigh out 0.15 g Ottowa Sand and add 0.120 mL of a Hg 1000 ug/L second source intermediate standard to hot block tube. Continue with step 10.2.	0.003
HgLCS/LCSD	Weigh out 0.15 g Ottowa Sand and add 0.120 mL Hg intermediate stock to hot block tube. Continue with step 10.2. Use the same stock as the calibration blank.	0.003
HgCCC	Weigh out 0.15 g Ottowa Sand and add 0.120 mL of intermediate Hg standard to a digestion vessel. Continue with step 10.2.	0.003
CCB	Weigh out 0.15 g Ottowa Sand. Continue with step 10.2. Analyze after calibration, after every 10 samples, and at the end of the batch.	<RL
HgMS/HgMSD	Weigh out 0.15 grams of the sample and add 0.120 mL of a 1000 ug/L intermediate Hg standard to hot block tube. Continue with step 10.2	0.003

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Table 10.1 Reagent preparation.

Reagent	Preparation
Stannous chloride	Mix 11g stannous sulfate, bring to 1000 mL in 3% hydrochloric acid. Mix well with a stir bar during use.
Sodium chloride-hydroxylamine hydrochloride	Mix 12g sodium chloride and 12g hydroxylamine hydrochloride together and bring to 100 mL in 18MΩ water.
Aqua Regia	Mix 3 volumes concentrated hydrochloric acid with 1 volume concentrated nitric acid.
5% (w/v) Potassium permanganate	Add 5g potassium permanganate and bring to 100mL with 18MΩ water.
3% HCl carrier solution	Bring 30 mL concentrated hydrochloric acid to 1000 mL with18MΩ water.
1% Nitric Acid	Bring 10 mL concentrated nitric acid to 1000 mL with 18MΩ water.

Table 10.2 Procedure summary

Step	Reagent	Amount
10.2.1	Sample	0.15 g
10.2.2	18MΩ water	1.25 mL
10.2.2	Aqua Regia	1.25 mL
10.2.3	95ºC hot block	2 minutes
10.2.4	18MΩ water	12.0 mL
10.2.4	5% (w/v) potassium permanganate	3.75 mL
10.2.5	95ºC hot block	30 min
10.2.6	Sodium chloride-hydroxylamine hydrochloride	1.5 mL
	18MΩ water	Bring all to 40 mL

10.9 FIMS 400 Operating Parameters

FIMS 400 Parameter	FIMS 400 Setting
Carrier gas	Argon
Wavelength	253.7nm
Carrier solution	3.0% (v/v) HCl
Sample diluent	3.0% (v/v) HCl
Reductant	1.1% $SnCl_2$ in 3.0% (v/v) HCl
Carrier gas flow rate	50mL/min
Sample Volume	0.5mL
Reaction coil	110mm length, 1.0mm i.d.
Pump #1 speed	100
Pump # 2 speed	120

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11 Evaluation of the Linearity of the Initial Calibration

Print the calibration curve and the linear correlation coefficient. The minimum acceptable linear correlation coefficient is 0.995.

11.1 Sample Concentration

$$\text{Concentration} = \frac{CVD_f}{DW}$$

Where C = concentration from instrument in mg/L.

V = final digestion volume in L.

D_f = dilution factor.

DW = sample weight in kg after drying to constant weight at 60°C ± 5°C.

Use the following formula if there is insufficient sample to dry for digestion: Concentration = $\frac{CVD_F P_s}{WW}$ Where C = concentration from instrument in mg/L V = final digestion volume in L. D_f = dilution factor. WW = wet weight of sample (not dried). P_s = percent solids Percent Solids = $\frac{DW}{WW}$ Where DW = sample weight in kg after drying to constant weight at 60°C ± 5°C WW = wet weight of sample (not dried).	Waste Concentration Calculation: Concentration= $\frac{CVD_F}{WW}$ Where C= concentration from instrument in mg/L V = final digestion volume in L. D_f= dilution factor WW = wet weight of sample.

Sample results are expressed in mg/kg.

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12 References

12.1 *Methods for the Determination of Metals in Environmental Samples, Supplement I*, Environmental Monitoring Systems Laboratory, Office of Research and Development, USEPA, Cincinnati, Ohio, 45268.

13 Reporting Limits (RL), Precision and Accuracy Criteria, and Quality Control Approach

Table 13.1 RLs for Method 245.5

Parameter/Method	Analyte	Matrix (Solid)	
		RL	Unit
Mercury by Cold Vapor Atomic Absorption Spectrometry	Mercury	0.1	mg/Kg

Table 13.2 Acceptance Criteria for Method 245.5

Method	Analyte	Accuracy Solids (%R)	Precision Solids (RPD)
Mercury by Cold Vapor Atomic Absorption Spectrometry	Mercury	85-115%	≤15

Table 13.3 Summary of Calibration and QC Procedures for Method 245.5

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
245.5	Mercury	Analyst Initial Demonstration.	Once per analyst	Average of 4 LCS recoveries between 85-115%. Recovery of unknown sample between 70% and 130%.	Recalculate results, correct problem, then rerun the initial demonstration for those analytes that did not meet criteria.	
		Continuing Demonstration	Every 6 Months	Average of 4 LCS recoveries between 85%-115%, mb<RL, Unknown or PE.	Correct the problem.	
		MDL study.	Once every 12 months.	All analyte MDLs must be < RL.	Correct the problem.	
		Analysis of PE sample.	Once every 12 months	All analyte results acceptable per the auditing agency.	Correct the problem	
		Initial Calibration. Minimum of 4 standards.	Daily initial calibration prior to sample analysis.	Correlation coefficient ≥ 0.995	Correct the problem and recalibrate	
		Initial Calibration Verification (ICV)	Daily after calibration.	All analyte recoveries between 90% and 110% of the true value.	Correct the problem and recalibrate.	
		Continuing Calibration Blank (CCB).	Daily after calibration, after every 10 samples, and at end of analysis sequence.	All analyte concentrations must be < RL.	Correct the problem, recalibrate, and reanalyze all samples since the last acceptable CCB.	If unable to re-analyze, flag with a "B"
		Continuing Calibration Check (CCC).	Daily after calibration, after every 10 samples, and at end of analysis sequence.	Initial analyte recoveries between 80% and 120% subsequent recoveries between 80%-120%	Correct the problem, recalibrate, and reanalyze all samples since the last acceptable CCC.	
		Laboratory Control Sample (LCS).	Once per batch.	All analyte recoveries between 85-115%.	Correct the problem, redigest, and reanalyze all samples in the batch.	If unable to re-analyze, flag with a "J"

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Table 13.3 Summary of Calibration and QC Procedures for Method 245.5

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
245.5	Mercury	Laboratory Control Sample Duplicate (LCSD).	Once per batch.	≤ 15 RPD	Correct the problem, redigest, and reanalyze all samples in the batch.	If unable to re-analyze, flag with a "J"
		Matrix Blank	Once per batch.	All analyte concentrations must be < RL.	Correct the problem, redigest, and reanalyze all samples in the batch.	If unable to re-analyze, flag with a "B"
		Matrix Spike	Every 10 samples.	All analyte recoveries between 70% and 130%.	Comment sample report	
		Matrix Spike Duplicate.	Every 10 samples.	≤ 15 RPD	Comment sample report .	

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