Georgia Department of Natural Resources
Environmental Protection Division Laboratory

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Mercury in Solid or Semisolid Waste

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1 Scope and Application

Method 7471A is used to prepare and analyze samples for Mercury analysis by Cold Vapor Atomic Absorption Spectroscopy in soils, sediments, and sludges. Due to volume limitations in the digestion equipment, all digestion volumes are reduced to 50%.

Compound	CAS No.
Mercury	7439-97-6

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.

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 hydrochloride in 18MΩ water and dilute to 100 mL.
6.6 Potassium permanganate, mercury-free, 5% solution (w/v): Dissolve 5 g potassium permanganate in 100 mL of 18MΩ water.
6.7 Aqua Regia: Mix 3 volumes of concentrated hydrochloric acid and 1 volume of concentrated nitric acid.
6.8 3% Hydrochloric Acid: Bring 30 mL concentrated hydrochloric acid to 1000 mL with 18MΩ water.
6.9 1% Nitric Acid: bring 30 mL concentrated Nitric Acid to 1000 mL with 18MΩ water.
6.10 Concentrated Hydrochloric Acid.

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.

8.2 Calibration Verification

An ICV, CCC, and CCB are analyzed immediately after calibration. A CCC and CCB are analyzed after calibration, before each batch after every ten samples, after each batch and at the end of an analytical sequence.

9 Quality Control

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

9.2 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.

9.3 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 0.10 gram triplicate portions of an untreated (not dried) sample into a 50 mL hot block tube for a total weight of approximately 0.30g. Record the actual weight to two significant figures on the digestion sheet.

10.2 Add 2.5 mL 18MΩ water and 2.5 mL aqua regia to each vessel.

10.3 Place each vessel into the hot block and heat to 95ºC for 2 minutes. Heat the standards as well as the samples.

10.4 Remove the vessels from the hot block, cool to room temperature add 20 mL of 18MΩ water and 7.5 mL potassium permanganate solution to each vessel. Mix thoroughly.

10.5 Place each vessel into the hot block and heat to 95ºC for 30 minutes. Heat the standards as well as the samples.

10.6 Remove the vessels from the hot block and cool to room temperature. Add 3.0 mL sodium chloride-hydroxylamine hydorchloride to each vessel. Bring to 40 mL with 18MΩ water.

10.7 Any sample with Hg concentration >LDR must be diluted to bring the Hg concentration between the PQL 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: Prepare calibration standards according to table 10.1.

10.9 All standards and intermediate dilutions must be logged into the standard log book.

Table 10.1 Standard preparation

Standard	**Preparation**	**Final concentration (mg/Kg)**
Hg intermediate standard	Dilute 0.1 mL 1000 ppm stock solution to 100 mL with 1% nitric acid.	1.00
Hg calibration blank	18MΩ water.	<RL
Hg calibration standard 1	Add 0.30 g Ottowa Sand, 0.008 mL Hg intermediate standard to hot block tube. Continue with step 10.2	0.0002
Hg calibration standard 2	Add 0.30 g Ottowa Sand, 0.02 mL Hg intermediate standard to hot block tube. Continue with step 10.2.	0.0005
Hg calibration standard 3	Add 0.30 g Ottowa Sand, 0.04 mL Hg intermediate standard to hot block tube. Continue with step 10.2.	0.001
Hg calibration standard 4	Add 0.30 g Ottowa Sand, 0.08 mL Hg intermediate standard to hot block tube. Continue with step 10.2.	0.002
Hg calibration standard 5	Add 0.30 g Ottowa Sand, 0.120 mL Hg intermediate standard to hot block tube. Continue with step 10.2.	0.003

Standard	**Preparation**	**Final concentration (mg/Kg)**
Hg calibration standard 6	Add 0.30 g Ottowa Sand, 0.24 mL Hg intermediate standard to hot block tube. Continue with step 10.2.	0.006
HgICV	Add 0.30 g Ottowa Sand, 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	Add 0.30 g Ottowa Sand, 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	Add 0.30 g Ottowa Sand, 0.120 mL of intermediate Hg standard to a digestion vessel. Continue with step 10.2.	0.003
CCB	Add 0.30 g Ottowa Sand to a hot block tube, after calibration, after every 10 samples, and at the end of the batch. Continue with step 10.2.	<RL
HgMS/HgMSD	Add 0.30 grams of the sample and 0.120 mL of a 1000 ug/L intermediate Hg standard to hot block tube. Continue with step 10.2.	0.003

Table 10.2 Reagent preparation

Reagent	Preparation
Stannous chloride	Mix 11g stannous chloride, Bring to 1000 mL with 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 of concentrated hydrochloric acid with 1 volume of concentrated nitric acid.
5% (w/v) Potassium permanganate	Add 5g potassium permanganate and bring to 100 mL in 18MΩ water.
1% Nitric Acid	Bring 10 mL concentrated nitric acid to 1000 mL with 18 MΩ water.
3% Hydrochloric Acid	Bring 30 mL concentrated hydrochloric acid to 1000 mL with 18 MΩ water.

Table 10.3 Procedure summary

Step	**Reagent**	**Amount**
10.1	Sample	0.30 g
10.2	18 MΩ water	2.5 mL
10.2	Aqua Regia	2.5 mL
10.3	95ºC hot bock	2 minutes
10.4	18 MΩ water	20 mL
10.5	5% (w/v) Potassium permanganate	7.5 mL
10.6	95ºC hot block	30 minutes

Step	Reagent	Amount
10.7	Sodium Chloride-hydroxylamine chloride	3.0 mL
10.8	18 MΩ water	Bring 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	50 mL/min
Sample Volume	0.5 mL
Reaction coil	110mm length, 1.0mm i.d.
Pump #1 speed	100
Pump # 2 speed	120

11 Evaluation of the Linearity of the Initial Calibration.
Print the calibration curve. The FIMS 400 software calculates and prints the linear correlation coefficient. The minimum acceptable linear correlation coefficient is 0.995.

11.1 Sample Concentration
Multiply sample concentration by the percent solids. Sample results are expressed in ug/kg for TAL samples or mg/kg for all other samples.

Solids Concentration Calculation

Use the following formula if there is insufficient sample to dry for digestion:

$$\text{Concentration} = \frac{CVD_F P_s}{WW}$$

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.

$$\text{Percent Solids} = \frac{DW}{WW}$$

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:

$$\text{Concentration} = \frac{CVD_F}{WW}$$

Where C= concentration from instrument in mg/L.
V = final digestion volume in L.

D_f = dilution factor.
WW = wet weight of sample.

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 (RLs), Precision and Accuracy Criteria, and Quality Control Approach

Table 13.1 RLs for Method SW846-7471A

Parameter/Method	Analyte	Matrix Solid		Matrix TAL Solids	
		RL	Unit	RL	Unit
Mercury by Cold Vapor Atomic Absorption Spectrometry	Mercury	0.1	mg/Kg	100	ug/kg

Table 13.2 Acceptance RL for Method SW846-7471A

Method	Analyte	LCS Accuracy (%R)	LCSD Precision (%RPD)	MS Accuracy (%R)	MS Precision (%RPD)
7471A Mercury by Cold Vapor Atomic Absorption Spectrometry	Mercury	85-115	≤ 15	70-130	≤ 15

Table 13.3 Summary of Calibration QC Procedures for Method SW846-7471A

Method	Appliciable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
7471A	Mercury	Analyst Initial Demonstration.	Once per analyst.	Average of 4 LCS recoveries between 85-115%. Recovery of unknown sample between 75%-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.	Analyte MDLs must be < RL.	Correct the problem.	
		Linear Dynamic Range	Once every year.			

Table 13.3 Summary of Calibration QC Procedures for Method SW846-7471A

Method	Appliciable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
7471A	Mercury	Analysis of PE sample.	Once every 12 months.	Analyte results acceptable per the auditing agency.	Correct the problem.	
		Initial Calibration. Using 7 standards.	Daily initial calibration prior to sample analysis.	Correlation coefficient ≥ 0.995	Correct the problem and recalibrate.	
		Initial Calibration Verification (ICV).	Daily after calibration.	Analyte recoveries between 90% and 110% of true value.	Correct the problem and recalibrate.	
		Continuing Calibration Blank (CCB).	Daily after calibration, before each batch, after every 10 samples, after each batch and at end of analysis sequence.	Analyte concentrations must be < RL.	Correct the problem, recalibrate, and reanalyze all samples since the last acceptable CCB.	
		Continuing Calibration Check (CCC).	Daily after calibration, after every 10 samples, and at end of analysis sequence.	Initial analyte recovery between 90% and 110%, subsequent recoveries between 80% and 120%.	Correct the problem, recalibrate, and reanalyze all samples since the last acceptable CCC.	
		Laboratory Control Sample (LCS).	Once per batch.	Analyte recovery between 85% and 115%.	Correct the problem, recalibrate, and reanalyze all samples in the batch.	If unable to re-analyze, flag with a "J".
		Laboratory Control Sample Duplicate (LCSD).	Once per batch.	≤ 15 RPD.	Correct the problem, recalibrate, and reanalyze all samples in the batch.	If unable to re-analyze, flag with a "J".
		Laboratory Control Samples Duplicate Recovery	Once per batch	Analyte recovery between 85% and 115%.	Comment Sample Report.	
		Matrix Blank.	Once per batch.	Analyte concentrations must be < RL.	Correct the problem, recalibrate, and reanalyze all samples in the batch.	If unable to re-analyze, flag with a "B".
		Matrix Spike.	Every 10 samples.	Analyte recovery between 70% and 130%.	Comment Sample Report.	
		Matrix Spike Duplicate.	Every 10 samples.	≤ 15 RPD.	Comment Sample Report.	
		Matrix Spike Duplicate Recovery.	Every 10 samples.	Analyte recovery between 70% and 130%.	Comment Sample Report.	

Appendix A-Quality Assurance Criteria for EPA Method 7471A Mercury in Solid or Semisolid Waste

Table A.1 Mercury (HG7471A)

QC Type	Analyte	Accuracy (%R) LCL	 UCL	Precision (%RPD)
LCS/LCSD	**Mercury**	**85**	**115**	**15**
MS/MSD	**Mercury**	**70**	**130**	**15**

Control Limits are static by EPA Method/EPD Lab default. Static Limits are generated for trend monitoring purposes.