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Mercury in Liquid Waste-EPA Method 7470A

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1 Scope and Application

Method SW846-7470A is used to prepare samples for Mercury analysis by Cold Vapor Atomic Absorption Spectroscopy in TCLP extracts, aqueous wastes, ground waters and sludge wastes. Due to volume limitations in the digestion equipment, all digestion volumes are reduced to 25%.

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.

3.1 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 Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 6.25ml) to oxidize the high concentration of chloride to free chlorine. Excess hydroxylamine hydrochloride reagent (up to 6.25 ml) must then be added to eliminate the excess free chlorine. Free chlorine absorbs at 253.7 nm.

3.4 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

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 volume of reagents
5.8 Assorted high quality pipet 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 in the sample prep log, and the container must be labeled with the standard name, standard number, 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 to a graduated container and bring to 1000ml in 3% hydrochloric acid. Place the container on a magnetic stirrer, add a stir bar, and mix continuously during use. Log the stannous chloride solution into the standard log and write the standard number on the sample prep sheet.
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 Potassium persulfate, 5% solution (w/v): Dissolve 5 g of potassium persulfate in 100 ml of 18MΩ water.
6.8 1% Nitric Acid: Bring 10 ml concentrated nitric acid to 1000 ml with 18MΩ water.
6.9 3% Hydrochloric Acid: Bring 30 ml concentrated hydrochloric acid to 1000 ml with 18MΩ water.

Water samples and liquid waste samples for mercury analysis are collected in 500 ml narrow mouth plastic (HDPE) bottles. Samples are preserved with sufficient HNO_3 to lower the pH below 2. One to two bottles are required for each sample. 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 ug/L): 0.0, 0.2, 0.4, 1.0, 2.0, 3.0, and 6.0.

8.2 Calibration Verification

An ICV, CCC, and CCB are analyzed immediately after calibration. A CCC and CCB are also analyzed after calibration, before each batch, every ten samples, after each batch and as the last sample in an analytical sequence.

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 Transfer 25 ml of sample to a 50 ml hot block tube.

10.2 Add 1.3 ml concentrated sulfuric acid and 0.65ml concentrated nitric acid to each digestion tube, mixing after each addition.

10.3 Add 3.75 ml of 5% (w/v) potassium permanganate solution to each digestion tube.

10.4 Shake and add if necessary additional 1.25 ml aliquots of potassium permanganate to each sample until the purple color persists for at least 15 minutes. Sewage, seawater, brines, and industrial effluents high in chlorides require additional potassium permanganate (up to 6.25 ml). Ensure that equal amounts of potassium permanganate are added to the samples, blanks, and calibration standards.

10.5 Add 2.0 ml potassium persulfate solution to each vessel, cap tightly and shake well to mix. Loosen the cap.

10.6 Place each digestion vessel into the hot block and heat at 95º C for 2 hours. Heat the standards as well as the samples.

10.7 Remove the vessels from the hot block, cool to room temperature, and add 1.5 ml sodium chloride-hydroxylamine sulfate to reduce the excess potassium permanganate. Bring all to 40 mL with 18MΩ water

10.8 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 also be diluted by the same amount.

10.9 Calibration and QC standard preparation: Prepare standards according to table 10.1. All standards and intermediate dilutions must be logged into the standard logbook.

Table 10.1 Standard preparation

Reagent	Preparation	Final conc. (ug/L)
Hg intermediate standard	Dilute 0.1ml 1000 ppm stock solution to 100 ml with 1% nitric acid.	1000
Hg calibration blank	Aliquot 25 ml of 1% nitric acid. Continue with Step 10.2	<PQL
Hg calibration	Dilute 0.005 ml Hg intermediate standard to 25 ml	0.2

standard 1	with 1% nitric acid. Continue with Step 10.2	
Hg calibration standard 2	Dilute 0.010ml Hg intermediate standard to 25 ml with 1% nitric acid. Continue with Step 10.2	0.4
Hg calibration standard 3	Dilute 0.025 ml Hg intermediate standard to 25 ml with 1% nitric acid. Continue with Step 10.2	1.0
Hg calibration standard 4	Dilute 0.05 ml Hg intermediate standard to 25 ml with 1% nitric acid. Continue with Step 10.2	2.0
Hg calibration standard 5	Dilute 0.075 ml Hg intermediate standard to 25 ml with 1% nitric acid. Continue with Step 10.2	3.0
Hg calibration standard 6	Dilute 0.150ml Hg intermediate standard to 25 ml with 1% nitric acid. Continue with Step 10.2	6.0
HgICV	Dilute 0.075 ml of a Hg 1000 ug/L 2nd source intermediate standard to 25 ml with 1% nitric acid. Continue with Step 10.2	3.0
HgLCS	Dilute 0.075 ml Hg intermediate stock to 25 ml with 1% nitric acid. Use the same stock as the calibration blank. Continue with Step 10.2	3.0
HgCCC	Dilute 0.075 ml of a 1000 ug/L Hg solution to 25 ml with 1% nitric acid. Use the same stock as your calibration stock. Continue with Step 10.2	3.0
HgMS	Dilute 0.075 ml of a 1000 ug/L Hg stock 1o 25 ml with a sample. Continue with Step 10.2	3.0
HgMSD	Prepare a spike duplicate using another aliquot of the same sample. Continue with Step 10.2	3..0
Hg CCB	Aliquot 25 ml of 1% nitric acid. Continue with Step 10.2	<PQL
Hg MB	Aliquot 25 ml of 1% nitric acid. Continue with Step 10.2	<PQL

Table 10.2 Reagent preparation

Reagent	Preparation
10% (w/v) Stannous chloride	Weigh11g stannous chloride ,mix with 1000 mL of 3 % HCl. 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 with 18MΩ water.
5% (w/v) Potassium persulfate	Add 5g potassium persulfate and bring to 100 ml with18MΩ water.
5% (w/v) Potassium permanganate	Add 5g potassium permanganate and bring to 100ml with 18MΩ water.
1% Nitric Acid	Bring 10 ml concentrated nitric acid to 1000ml with 18 MΩ water.
3% HCl carrier solution	Bring 30 ml concentrated hydrochloric acid to 1000ml with 18 MΩ water.

Table 10.3 Procedure summary

Step	Reagent	Amount
10.1	Sample	25 ml

10.2	Concentrated sulfuric acid	1.3 m l
10.2	Concentrated nitric acid	0.65ml
10.3	5% (w/v) Potassium permanganate	3.75 ml
10.4	5% (w/v) Potassium permanganate	1.25 ml until purple stays 15 minutes (max 6.25 ml)
10.5	5% (w/v) Potassium persulfate	2.0 ml
10.6	Hot block, 95°C	2 hours
10.7	Sodium Chloride-hydroxylamine sulfate	1.5 ml
10.8	18 MΩ water	Bring all to 40 mL with 18 M water

10.10 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

11 Evaluation of the Linearity of the Initial Calibration.
Print the calibration curve, the FIMS 400 software to calculate and print the linear correlation coefficient. The minimum acceptable linear correlation coefficient is 0.995.

11.1 Sample Concentration

Concentration = CD_f

Where C = concentration from instrument

D_f = dilution factor

$$D_f = \frac{D}{S}$$

D = dilution volume in liters.

S = Sample aliquot volume in liters.

Sample results are expressed in ug/L.

12 References

12.1 *Test Methods for Evaluating Solid Waste Physical/Chemical Methods* (SW846) Third Edition, Update IIB, March 1995.

13 Practical Quantitation Limits (PQLs), Precision and Accuracy Criteria, and Quality Control Approach

Table 13.1 RLs for Method SW846-7470A

Parameter/Method	Analyte	Matrix Aqueous	
		RL	Unit
Mercury by Cold Vapor Atomic Absorption Spectrometry	Mercury	0.2	ug/L

Table 13.2 Acceptance RL for Method SW846-7470A

Method	Analyte	LCS Accuracy (%R)	LCSD Precision (%RPD)	MS Accuracy (%R)	MSD Precision (%RPD)
7470 Mercury by Cold Vapor Atomic Absorption Spectrometry	Mercury	85-115	≤15	70-130	≤15

Table 13.3 Summary of Calibration QC Procedures for method SW846-7470A

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
7470	Mercury	Analyst Initial Demonstration.	Once per analyst	Average of 4 LCS recoveries between 85-115%. Recovery of unknown sample between 70%-130%, TCLP recoveries between 50%-150%.	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.	
		Linear Dynamic Range (LDR)	Once a year.			
		Analysis of PE sample.	Once every 12 months	All 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.	All analyte recoveries between 90% and 110% of true value.	Correct the problem and recalibrate.	
7470	Mercury	Continuing Calibration Blank (CCB).	Daily after calibration, before each batch, after every 10 samples, after each batch and at end of analysis sequence.	All analyte concentrations < RL.	Correct the problem, recalibrate, and reanalyze all samples since the last acceptable CCB.	

Table 13.3 Summary of Calibration QC Procedures for method SW846-7470A

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
		Continuing Calibration Check (CCC).	Daily after calibration, after every 10 samples, and at end of analysis sequence.	Initial analyte recovery between 80%-120%, 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.	All analyte recoveries between 85-115%.	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.	RPD ≤ 15	Correct the problem, recalibrate, and reanalyze all samples in the batch.	If unable to re-analyze, flag with a “J”.
		Laboratory Control Sample Duplicate Recovery	Once per batch.	All analyte recoveries between 85-115%	Comment Report.	
		Low Standard	During Calibration	Low Standard Recovery < RL		
		Matrix Blank	Once per batch.	All 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.	All analyte recoveries between 70%-130%. TCLP recoveries between 50%-150%.	Comment Sample Report	
		Matrix Spike Duplicate.	Every 10 samples.	≤ 15 RPD	Comment Sample Report	
		Matrix Spike Duplicate Recovery	Every 10 samples.	All analyte recoveries between 70%-130%.	Comment Sample Report.	

Appendix A-Quality Assurance Criteria for EPA Method 7470A Mercury in Liquid Waste

Table A.1 Mercury (HG7470A)

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.

Table A.2 Mercury (HGTCLP)

QC Type	Analyte	Accuracy (%R) LCL	 UCL	Precision (%RPD)
LCS/LCSD	Mercury	85	115	15
MS/MSD	Mercury	50	150	15

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