Laboratory Manager Approval: Shene A. Jones / 08/19/2021

QA Manager Approval: Jeffney Moore / 08/19/2021

EPA Method 245.1: Mercury in Water

Access to this SOP shall be available within the laboratory for reference purposes; the official copy of this SOP resides on the official Georgia EPD website at https://epd.georgia.gov/about-us/epd-laboratory-operations. Printed copies of this SOP will contain a watermark indicating the copy is an uncontrolled copy.

1 Scope and Application

Method 245.1 is used to prepare samples for Mercury analysis by Cold Vapor Atomic Absorption Spectroscopy in drinking, surface, ground, sea, brackish waters, industrial and domestic wastewater. Due to volume limitations in the digestion equipment, all volumes are reduced to 25%.

This method is used to analyze the follow metal:

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

2.1 Refer to Section 3 and Section 4 of the Georgia EPD Laboratory Quality Assurance Manual for Quality Control Definitions. (See SOP reference 13.7)

2.2 MDL standard (ML) = Method Detection Limit Spike Standard ($MDLs_{pike}$): An MDLspike is analyzed with every batch of samples and is carried through the same procedure as the samples being analyzed. One or more MDL_{spikes} may be used per batch if needed. ML_{spike} is a standard equal to the concentration of lowest calibration curve standard.

2.3 MDL_{blank} is analyzed with every batch of samples and is carried through the same procedure as the samples being analyzed. One or more MDL_{blanks} may be used per batch is needed.

2.4 Lower Level Check Standard (LLCS): LLCS is a standard equal to the lowest concentration on the calibration curve and digestion is not required.

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 Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 15 mL) to oxidize the high concentration of chloride into free chlorine. Excess hydroxylamine hydrochloride reagent 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 lack of interference and the concentration of mercury present in the treated sample is reported.

4 Safety

Refer to Laboratory Chemical Hygiene Plan, online revision. (See SOP reference 13.8)

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 Air displacement pipettes of capable of delivering volumes ranging from 0.1-2500uL., auto-pipettors, and pipette tips in various sizes. Air displacement pipettes and auto-pipettors may also be described as mechanical pipettes.

5.7.1 Each day of use, the volume dispensed by each mechanical pipette must be verified for the specific volume for which the pipette is being used.

5.7.1.1 Mechanical pipette volumes are verified by measuring the weight of a volume of water dispensed by the unit. At room temperature, 1 ml of water is equal to 1 g. Pipettes must be capable of ± 2.5% accuracy and within 2.5% precision RSD.

5.7.1.2 Auto-pipettors may be verified by measuring the volume dispensed with a graduated cylinder. The volume dispensed must be within ±2.5% of the nominal weight.

5.7.1.3 Air displacement pipettes must be professionally calibrated every 6 months.

5.8 Assorted high quality pipette tips

6 Reagents and Standards

Note: 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 labeled with the standard number, standard name, initials, and the expiration date.

6.1 Reagent water: 18MΩ water – Purified water which does not contain any measurable quantities of target elements or interfering elements for each element of interest. Milli-Q water is used by the EPD Metals Lab. Milli-Q water is used by the EPD Metals Lab. Milli-Q water has a resistivity of

18.2 [MΩ.cm] @ 25°C and a TOC of 50µg/L or less.

6.2 Concentrated reagent grade sulfuric acid.

6.3 Concentrated reagent grade nitric acid.

6.4 Concentrated reagent grade hydrochloric acid

6.5 Stannous chloride: weigh 11 g stannous chloride into a graduated container, bring to 1L with 3% hydrochloric acid. Place on a magnetic stirrer, add a magnetic stir bar, and stir continuously during use. This solution is made according the instrument manufacturer's recommended conditions.

6.6 Sodium chloride-hydroxylamine hydrochloride solution: Dissolve 12 g of sodium chloride and 12 g hydroxylamine hydrochloride in 18MΩ water and dilute to 100 mL.

6.7 Potassium permanganate, mercury-free, 5% solution (w/v): Dissolve 5 g of potassium permanganate in 100 mL of 18MΩ water.

6.8 Potassium persulfate, 5% solution (w/v): Dissolve 5 g of potassium persulfate in 100 mL of 18MΩ water.

6.9 1% Nitric acid: Bring 10 mL concentrated nitric acid to 1000 mL with 18MΩ water. This blank solution is stored in a HDPE bottle.

6.10 3% Hydrochloric acid: Bring 30 mL concentrated hydrochloric acid to 1000 mL with 18MΩ water.

Note: Refer to table 10.10.1 for summary of reagent preparation for sections 6.5 – 6.10.

7 Sample Collection

Water samples and liquid waste samples for mercury and IOC analysis are collected in a 500 mL narrow mouth/or wide mouth plastic (HDPE) bottle for WQ samples. For IOC samples, the samples are collected in 500 ml wide mouth plastic (HDPE) bottles. Samples are preserved with sufficient HNO3 to lower the pH below 2. One to two bottles are required for each sample. Mercury analysis must be performed within 28 days of sample collection.

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 analyzed at the beginning of the run, before each batch after every ten samples, after each batch, and as the last samples in an analytical sequence.

9 Quality Control –

Refer to Table 14.1 for Reporting Limits (PQLs), Table 14.2 for Quality Control Procedures associated with this method. See Appendix A, Table A.1 for Quality Control Acceptance Criteria.

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 following procedure outlined in section 5.7. Record the pipette number, the volumes and the weights on the digestion sheet.

9.3 Control Limits

9.3.1 The default control limits from EPA Method 245.1 are 85 – 115% recovery for Mercury for LCS recoveries. The EPD Laboratory applies LCS recovery limits to LCSDs. Note, unless specified by method, the EPD Laboratory does not validate batch quality based on LCSD recoveries.

9.3.2 By default, the EPD Laboratory sets LCS/LCSD precision control limits to be 0 – 15% RPD.

9.3.3 10% of all routine samples must be spiked. See Section 9.4 modification below. EPA Method 245.1 requires recovery control limits of 70 – 130% for matrix spikes. The EPD Laboratory applies MS recovery limits to MSDs.

9.3.4 By default, the EPD Laboratory sets default MS/MSD precision control limits to be 0 – 15% RPD. MS/MSD precision limits are not dependent on control charting results.

9.3.5 Recovery and precision control limits are updated through the use of control charts. MS/MSD control limits are static at the default limit.

9.3.6 See Administrative SOP for Control Charting and Control Limits for further details.

9.4 Batch samples in groups of 20. For each batch, analyze a Matrix Spike (MS) and a Matrix Spike Duplicate (MSD) for a minimum of 10% of routine samples**.**

9.4.1 For batches of 1 to 10 routine samples, one MS/MSD pair must be spiked. For batches of 11 to 20 routine samples, two MS/MSD pairs must be spiked using different samples for each pair.

9.5 Method Detection Limit (MDL) is the minimum concentration of a substance that can be measured and reported with 99% confidence that the values is above zero.

9.5.1 The actual MDL varies depending on the instrument matrix.

9.5.2 The MDL study must be determined annually for each instrument prior to results being reported for that instrument. The MDL determined for each analyte must be less than the reporting limit for that analyte.

9.5.3 The MDL study for all analytes must be performed initially on a new instrument, after major instrument repairs, changes to the procedures and with Drinking Water Initial Demonstrations (see 9.5.3.1). There are two ways to perform the MDL study. The first is by analyzing seven MDL_{spike} samples (ML) and seven MDL_{blanks} over 3 separate days. *MDLs for new instrument start-up, must be performed over 3 separate days.* The second way is by analyzing the MDL_{spike} sample with every batch.

9.5.3.1 To perform the seven MDL_{spike} and seven MDL_{blank} MDL study over 3 separate days, prepare seven blanks and seven spike blanks. The seven spiked blanks are spiked at the lowest calibration point on the curve. Please note, digested samples must be digested over 3 separate days.

9.5.3.2 A continuous MDL study format: One blank is spiked per batch and identified as the ML_{sample}. The ML_{sample} is at the lowest point on the calibration curve. The Method Blank is the $MDL_{blank.}$

9.6 The result of MDL_{blank} will be entered into Labworks using the Method Blank test code. The MDL_{spike} result will be entered using the prefix $ML followed by the test code. The instrument used for the MDL_{sample} and $MDL_{blank,}$ will be selected using the prefix INSTR followed by the instrument number.

Note: The default control limits are presented to assist in defining control limits established with control charts and are not used as batch acceptance criteria.

Table 9.3.1. – Default Quality Assurance Criteria for Method EPA 245.1

QC Type	Analyte	Accuracy(%R) LCL	UCL	Precision (%RPD)
LCS/LCSD	Mercury	85 – 115		0 – 15
MS/MSD	Mercury	70 – 130		0 – 15

10 Procedure

10.1 Invert sample several times to mix. Then transfer 25 mL of sample to a 50 mL hot block digestion tube.

10.2 Add 1.30 mL concentrated sulfuric acid and 0.650 mL concentrated nitric acid to each digestion tube, mixing after each addition.

10.3 Add 3.75 mL 5% (w/v) potassium permanganate solution to each digestion vessel.

10.3.1 Shake and if necessary add additional 1.25 mL aliquots of potassium permanganate to each sample until the purple color persists for at least 15 minutes (up to 3.75 mL). If the purple color does not persist, transfer a reduced sample volume to another digestion vessel and dilute to 25 ml with 1% nitric acid and repeat sections 10.2 and 10.3. Sewage, seawaters, brines, and industrial effluents high in chlorides require additional potassium permanganate solution. Ensure that equal amounts of potassium permanganate are added to the samples, blanks, and calibration standards.

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

10.5 Place sample digestion vessels (including LCS, LCSD, MS, MSD, MB and ML) into the hot block and heat at 95ºC ± 5ºC for 2 hours. Do not heat the calibration standards.
Note: Be sure to alternate positions of the QC samples in the hotblock for each digestion batch. This allows for all positions of the hotblock to be evaluated over time.

10.6 Remove the vessels from the hot block, cool to room temperature.

10.7 Add 1.5 mL sodium chloride-hydroxylamine hydrochloride to reduce the excess potassium permanganate. Add additional 1.5 ml aliquots until the solution is no longer purple but do not add more than 6.0 ml total. Bring all to 40 mL with 18MΩ water.
Note: Final volume cannot exceed 40 ml. So if the purple color still persists after the 40 ml final volume is reach see Supervisor/Manager about repeating the procedure with a smaller sample aliquot.

10.8 Any sample with a Hg concentration or area/height response greater than the highest standard concentration on the curve must be diluted to bring the Hg concentration at or below the highest standard concentration in the curve. The response of the dilution must be between the reporting limit and the high standard in the curve, adjusted for the dilution. If it is not, adjust the dilution ratio accordingly and reanalyze. Dilute sample above Linear Detection Range (LDR) with calibration blank. The upper LDR limit should be an observed signal no more than 10% below the level extrapolated from the lower standard. Determined sample analyte concentrations that are greater than 90% of the determined upper LDR limit must be diluted and reanalyzed. If the sample was spiked, then both the spike and spike duplicate must be diluted by the same amount.
Note: Refer to Table 10.10.2 for a summary of procedure sections 10.1 – 10.8.

10.9 Calibration and QC standard preparation: Prepare calibration standards according to Table 10.9.1

10.9.1 All standards and intermediate dilutions must be logged into the standard logbook.

Table 10.9.1 - Standard Preparation

Standard	Preparation	Final concentration (ug/L)
Hg intermediate standard	Dilute 0.1mL 1000 ppm stock solution to 100 mL with 1% nitric acid.	1000
Hg calibration blank	Aliquot 25mL 1% nitric acid. Continuing from step 10.2-10.4. Do not heat. Continue to step 10.7. Dilute to final volume of 40ml with 18MΩ water.	<PQL
Hg calibration standard 1	Dilute 0.005 mL Hg intermediate standard to 25 mL with 1% nitric acid. Continuing from step 10.2.-10.4. Do not heat. Continue to step 10.7. Dilute to final volume of 40ml with 18MΩ water.	0.2
Hg calibration standard 2	Dilute 0.01 mL Hg intermediate standard to 25 mL with 1% nitric acid. Continuing from step 10.2-10.4. Do not heat. Continue to step 10.7. Dilute to final volume of 40ml with 18MΩ water.	0.4
Hg calibration standard 3	Dilute 0.025 mL Hg intermediate standard to 25 mL with 1% nitric acid. Continuing from step 10.2-10.4. Do not heat. Continue to step 10.7. Dilute to final volume of 40ml with 18MΩ water.	1.0
Hg calibration standard 4	Dilute 0.050 mL Hg intermediate standard to 25 mL with 1% nitric acid. Continuing from step 10.2-10.4. Do not heat. Continue to step 10.7. Dilute to final volume of 40ml with 18MΩ water.	2.0
Hg calibration standard 5	Dilute 0.075 mL Hg intermediate standard to 25 mL with 1% nitric acid. Continuing from step 10.2-10.4. Do not heat. Continue to step 10.7. Dilute to final volume of 40ml with 18MΩ water.	3.0
Hg calibration standard 6	Dilute 0.150 mL Hg intermediate standard to25 mL with 1% nitric acid. Continuing from step 10.2-10.4. Do not heat. Continue to step 10.7. Dilute to final volume of 40ml with 18MΩ water.	6.0
HgICV	Dilute 0.075 mL of Hg 1000 ug/L from a second source intermediate standard to 25 mL with 1% nitric acid. Continue from step 10.2-10.4. Do not heat. Continue to step 10.7. Dilute to final volume of 40ml with 18MΩ water.	3.0

Table 10.9.1 - Standard Preparation

Standard	Preparation	Final concentration (ug/L)
HgLCS/HgLCSD	Dilute 0.075 mL Hg intermediate stock to 25 mL with 1% nitric acid. Use the same stock as the calibration blank. Continue from step 10.2-10.5. Digest according to step 10.6-10.8. Dilute to final volume of 40ml with 18MΩ water.	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. Continuing from step 10.2-10.4. Do not heat. Continue to step 10.7. Dilute to final volume of 40ml with 18MΩ water.	3.0
Hg CCB	Aliquot 25 mL of 1% HNO3. Continuing from step 10.2-10.4. Do not heat. Continue to step 10.7. Dilute to final volume of 40ml with 18MΩ water.	< RL
Hg MB	Aliquot 25 mL of 1% HNO3. Continue from step 10.2-10.5. Digest according to step 10.6-10.8. Dilute to final volume of 40ml with 18MΩ water.	< RL
HgMS	Dilute 0.075 mL of a 1000 ug/L Hg stock to 25 mL with a sample. Continue from step 10.2-10.5. Digest according to step 10.6-10.8. Dilute to final volume of 40ml with 18MΩ water.	3.0
HgMSD	Prepare a spike duplicate using another aliquot of the same sample. Continue from step 10.2-10.5. Digest according to step 10.6-10.8. Dilute to final volume of 40ml with 18MΩ water.	3.0
Hg LLCS	Re-analyze Hg calibration standard 1 once per calibration.	0.2
Hg MDL Standard (ML)	Dilute 0.005 mL Hg intermediate standard to 25 mL with 1% nitric acid. Continuing from step 10.2.-10.5. Digest according to step 10.6-10.8. Dilute to final volume of 40ml with 18MΩ water.	0.2

10.10 Reagent Preparation and Procedure Summary

Table 10.10.1 Reagent Preparation

Reagent	Preparation
Stannous chloride	Weigh 11g stannous chloride into a 1 L graduated cylinder, and bring to a volume of 1L 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.

Table 10.10.1 Reagent Preparation

Reagent	Preparation
5% (w/v) Potassium persulfate	Add 5g potassium persulfate and bring to 100 mL in 18MΩ water.
5% (w/v) Potassium permanganate	Add 5g potassium permanganate and bring to 100mL in 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 10.10.2 Procedure summary

Step	Reagent	Amount
1	Sample	25 mL
2	Concentrated sulfuric acid	1.30mL
3	Concentrated nitric acid	0.65 mL
4	5% (w/v) Potassium permanganate	3.75 mL
5	5% (w/v) Potassium permanganate	1.25 mL until purple stays 15 minutes (max 3.75 mL)
6	5% (w/v) Potassium persulfate	2.0 mL
7	Hot block, 95ºC ±5 ºC	2 hours
8	Sodium Chloride-hydroxylamine hydrochloride	1.5 mL until purple color disappears. (Max 6.0 mL)
9	18MΩ water	Bring to 40 mL with 18MΩ water.

10.11 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 Calculations

11.1 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.

11.2 Sample Concentration

Concentration = CD_f (ug/L)

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.

12 Waste Management

12.1 See GA EPD Laboratory SOP-EPD Laboratory Waste Management Standard Operating procedures, SOP 6-015, online revision.

13 References

13.1 EPA Method 245.1 – Determination of Mercury in Water by Cold Vapor Atomic Absorption Spectrometry, Revision 3, 1994.

13.2 GA EPD Laboratory SOPs – Initial Demonstration of Capability SOP 6-001, online revision or later and/or Continuing Demonstration of Capability SOP 6-002, online revision.

13.3 GA EPD Laboratory SOP - EPD Laboratory Procedures for Control Charting and Control Limits SOP, SOP 6-025, online revision.

13.4 GA EPD Laboratory SOP – EPD Laboratory Waste Management SOP, SOP 6-015, online revision.

13.5 Manual for the Certification of Laboratories Analyzing Drinking Water, EPA/815-R-05-004, January 2005.

13.6 GA EPD Laboratory SOP – Determination of Method Detection Limit, SOP 6-007, online revision.

13.7 GA EPD Laboratory Quality Assurance Plan, online revision.

13.8 GA EPD Laboratory Safety/Chemical Hygiene Plan & Fire Safety Plan, online revision.

14 Reporting Limits (RLs), Precision and Accuracy Criteria, and Quality Control Approach

14.1 Refer to Appendix A, Table A.1 for precision and accuracy criteria.

Table 14.1 RLs for Method 245.1

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

Table 14.2 Summary of Calibration and QC Procedures for Method EPA 245.1

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
EPA Method 245.1	Mercury	Analyst Initial Demonstration: Demonstrate ability to generate acceptable accuracy and precision using four analysis of 4 LCS samples and one method blank. In addition, the analyst must prepare at least one standard. For drinking water samples, and MDL study must be performed over 3 days. See 9.5.3.1	Once per analyst.	Matrix blank<RL plus 4 LCS recoveries between 85-115%. Recovery of unknown sample within 85-115%. Perform 3 day initial MDL study for drinking water.	Recalculate results, correct problem, then rerun the initial demonstration for those analytes that did not meet criteria.	
		Continuing Demonstration: Demonstrate ability to generate acceptable accuracy and precision using a variety of analysis options of a QC sample (s).	Every 6 Months after IDC	Matrix blank<RL plus 4 LCS recoveries or Unknown sample between 85-115%. Passing PE sample may also be used. For drinking water samples: matrix blank plus 4 LCS recoveries or 1 unknown between control charting limits. See App. A.	Correct the problem. Then rerun the continuing demonstration for those analytes that did not meet criteria.	
		MDL Study Initial	New instrument start-up, major instrument repair and analyst demonstration for drinking water analysis	Minimum detection limits established shall be <RLs in table 14.1. All spiked MDLs must have a value greater than 0	Redo MDL study	None
		MDL Study Continuous	Generated yearly over a two- year period	All analyte concentrations must be <RL	Redo initial MDL study	Corrective Action Report
		MDLspike	Once per analytical batch or as needed to acquire data points per SOP.MDL6-007. Online version	All batch QC must meet established criteria. All spiked MDLs must have value greater than 0	Rerun the MDL once and initiate a corrective action. If the MDL fails a second time, do not use MDL data. Update corrective action and use associated sample data	None
		MDLblank Can be combined with Matrix Blank.	Once per analytical batch or as needed to acquire data points per SOP MDL6-007, online version	All batch QC must meet established criteria. All MDL blanks must be <RL. Any result without a positive or negative response must be entered as "ND"	Rerun once, if still out of limits, correct the problem and reanalyze affected batch if MDLblank is matrix blank	MDLblank Can be combined with Matrix Blank.

Table 14.2 Summary of Calibration and QC Procedures for Method EPA 245.1

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
EPA Method 245.1	Mercury	Linear Dynamic Range (LDR)	Once every 12 months or whenever major maintenance is performed on the instrument that might affect the instruments detector.	Consecutive levels of increasing concentrations must be within 10% of expected value. See 10.8.		
		Analysis of PT sample.	Once every 12 months	All analyte results acceptable per the auditing agency.	Correct the problem.	
		Initial Calibration using a blank and 7 standards.	Daily initial calibration prior to sample analysis.	Correlation coefficient ≥ 0.995.	Correct the problem and recalibrate.	
		Low Level Check Standard (LLCS)	Daily after calibration before sample analysis.	Low Level Check Standard at reporting limit. Recovery between 50-150%.	Rerun once, if still outside of control limits, correct the problem and recalibrate.	
		Initial Calibration Verification (ICV)	Daily after calibration.	Analyte recovery between 90% and110% .	Rerun once, if still out of control correct the problem and recalibrate.	
		Continuing Calibration Blank (CCB).	Daily after calibration, before each batch after every 10 samples, at the end of each batch, and at end of analysis sequence.	Analyte concentration ≤ RL.	Rerun once, if still out of control limits, 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, before each batch after every 10 samples, at the end of each batch, and at end of analysis sequence.	Initial recovery between 95-105%, subsequent recoveries between 90%-110%.	Rerun once, if still out of control, correct the problem, recalibrate, and reanalyzes all samples since the last acceptable CCC.	
		Laboratory Control Sample (LCS) and Laboratory Control Sample Duplicate (LCSD)	Once each per batch.	See Appendix A for recovery and control limits.	LCS: If LCS recovery fails, rerun once, correct the problem, and recalibrate. If still outside of control limits re-digest and reanalyze all samples in the batch. LCSD: The EPD Laboratory does not validate results based on LCSD recoveries. LCS/LCSD: If precision fails, correct the problem, redigest and reanalyze all samples in the batch.	If unable to re-analyze, flag with a "J".

Table 14.2 Summary of Calibration and QC Procedures for Method EPA 245.1

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
EPA Method 245.1	Mercury	Matrix Blank	Once per batch.	Analyte concentration <RL	Rerun once if still outside of control limits, correct the problem and recalibrate. If still outside of control limits, redigest, and reanalyze all samples in the batch.	If unable to re-analyze, flag with a "B".
		Matrix Spike (MS) and Matrix Spike Duplicate (MSD)	Minimum frequency each at 10% of samples	See Appendix A for recovery and precision control limits.	Comment sample report.	

Appendix A-Quality Assurance Criteria for Method EPA 245.1 Mercury in Water

Table A.1 Mercury (HG2451)

QC Type	Analyte	Accuracy (%R) LCL		UCL	Precision (%RPD)
LCS/LCSD*	**Mercury**	**85**	**-**	**115**	**10**
MS/MSD**	**Mercury**	**70**	**-**	**130**	**15**

* LCS/LCSD recovery and precision limits based on control charts of data collected from 1/1/2019 - 1/1/2021

** Method 245.1 specifies 70-130% recovery limits for Mercury. The EPD Lab sets a static range of 0-15% for matrix spike precision. Static limits are generated for trend monitoring purposes.

Updates:
Appendix A added.
Updated for online revision.