

## 9.0 Quality Control

9.1 Each laboratory that uses this Method is required to operate a formal quality assurance program (Reference 17). The minimum requirements of this program consist of an initial demonstration of laboratory capability, ongoing analysis of standards and blanks as a test of continued performance, and the analysis of matrix spikes (MS) and matrix spike duplicates (MSD) to assess accuracy and precision. Laboratory performance is compared to established performance criteria to determine that the results of analyses meet the performance characteristics of the Method.

9.1.1 The laboratory shall make an initial demonstration of the ability to generate acceptable accuracy and precision with this Method. This ability is established as described in Section 9.2.

9.1.2 In recognition of advances that are occurring in analytical technology, the laboratory is permitted certain options to improve results or lower the cost of measurements. These options include automation of the dual-amalgamation system, single-trap amalgamation (Reference 18), direct electronic data acquisition, calibration using gas-phase elemental Hg standards, changes in the bubbler design (including substitution of a flow-injection system), or changes in the detector (i.e., CVAAS) when less sensitivity is acceptable or desired. Changes in the principle of the determinative technique, such as the use of colorimetry, are not allowed. If an analytical technique other than the CVAFS technique specified in this Method is used, that technique must have a specificity for mercury equal to or better than the specificity of the technique in this Method.

9.1.2.1 Each time this Method is modified, the laboratory is required to repeat the procedure in Section 9.2 to demonstrate that an MDL (40 CFR Part 136, Appendix B) less than or equal to one-third the regulatory compliance level or less than or equal to the MDL of this Method, whichever is greater, can be achieved. If the change will affect calibration, the instrument must be recalibrated according to Section 10.

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- 9.1.2.2 The laboratory is required to maintain records of modifications made to this Method. These records include the following, at a minimum:
- 9.1.2.2.1 The names, titles, addresses, and telephone numbers of the analyst(s) who performed the analyses and modification, and the quality control officer who witnessed and will verify the analyses and modification
  - 9.1.2.2.2 A narrative stating the reason(s) for the modification(s)
  - 9.1.2.2.3 Results from all quality control (QC) tests comparing the modified method to this Method, including the following:
    - (a) Calibration (Section 10)
    - (b) Initial precision and recovery (Section 9.2)
    - (c) Analysis of blanks (Section 9.4)
    - (d) Matrix spike/matrix spike duplicate analysis (Section 9.3)
    - (e) Ongoing precision and recovery (Section 9.5)
    - (f) Quality control sample (Section 9.6)
    - (g) Method detection limit (Section 9.2.1)
  - 9.1.2.2.4 Data that will allow an independent reviewer to validate each determination by tracking the instrument output to the final result. These data are to include the following:
    - (a) Sample numbers and other identifiers
    - (b) Processing dates
    - (c) Analysis dates
    - (d) Analysis sequence/run chronology
    - (e) Sample weight or volume
    - (f) Copies of logbooks, chart recorder, or other raw data output
    - (g) Calculations linking raw data to the results reported
- 9.1.3 Analyses of MS and MSD samples are required to demonstrate the accuracy and precision and to monitor matrix interferences. Section 9.3 describes the procedure and QC criteria for spiking.
- 9.1.4 Analyses of blanks are required to demonstrate acceptable levels of contamination. Section 9.4 describes the procedures and criteria for analyzing blanks.
- 9.1.5 The laboratory shall, on an ongoing basis, demonstrate through analysis of the ongoing precision and recovery (OPR) sample and the quality control sample (QCS) that the system is in control. Sections 9.5 and 9.6 describe these procedures, respectively.
- 9.1.6 The laboratory shall maintain records to define the quality of the data that are generated. Sections 9.3.7 and 9.5.3 describe the development of accuracy statements.
- 9.1.7 The determination of Hg in water is controlled by an analytical batch. An analytical batch is a set of samples oxidized with the same batch of reagents, and analyzed during the same 12-hour shift. A batch may be from 1 to as many as 20 samples. Each batch must be accompanied by at least three bubbler blanks (Section 9.4), an OPR sample,

and a QCS. In addition, there must be one MS and one MSD sample for every 10 samples (a frequency of 10%).

## 9.2 Initial demonstration of laboratory capability

9.2.1 Method detection limit—To establish the ability to detect Hg, the laboratory shall achieve an MDL that is less than or equal to the MDL listed in Section 1.5 or one-third the regulatory compliance limit, whichever is greater. The MDL shall be determined according to the procedure at 40 CFR 136, Appendix B using the apparatus, reagents, and standards that will be used in the practice of this Method. This MDL shall be used for determination of laboratory capability only, and should be determined when a new operator begins work or whenever, in the judgment of the laboratory, a change in instrument hardware or operating conditions would dictate reevaluation of capability.

9.2.2 Initial precision and recovery (IPR)—To establish the ability to generate acceptable precision and recovery, the laboratory shall perform the following operations:

9.2.2.1 Analyze four replicates of the IPR solution (5 ng/L, Section 7.10) according to the procedure beginning in Section 11.

9.2.2.2 Using the results of the set of four analyses, compute the average percent recovery (X), and the standard deviation of the percent recovery (s) for Hg.

9.2.2.3 Compare s and X with the corresponding limits for initial precision and recovery in Table 2. If s and X meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If, however, s exceeds the precision limit or X falls outside the acceptance range, system performance is unacceptable. Correct the problem and repeat the test (Section 9.2.2.1).

9.3 Matrix spike (MS) and matrix spike duplicate (MSD)—To assess the performance of the Method on a given sample matrix, the laboratory must spike, in duplicate, a minimum of 10% (1 sample in 10) from a given sampling site or, if for compliance monitoring, from a given discharge. Therefore, an analytical batch of 20 samples would require two pairs of MS/MSD samples (four spiked samples total).

9.3.1 The concentration of the spike in the sample shall be determined as follows:

9.3.1.1 If, as in compliance monitoring, the concentration of Hg in the sample is being checked against a regulatory compliance limit, the spiking level shall be at that limit or at 1–5 times the background concentration of the sample (as determined in Section 9.3.2), whichever is greater.

9.3.1.2 If the concentration of Hg in a sample is not being checked against a limit, the spike shall be at 1–5 times the background concentration or at 1–5 times the ML in Table 2, whichever is greater.

9.3.2 To determine the background concentration (B), analyze one sample aliquot from each set of 10 samples from each site or discharge according to the procedure in Section 11.

If the expected background concentration is known from previous experience or other knowledge, the spiking level may be established a priori.

- 9.3.2.1 If necessary, prepare a standard solution to produce an appropriate level in the sample (Section 9.3.1).
- 9.3.2.2 Spike two additional sample aliquots with the spiking solution and analyze these aliquots as described in Section 11.1.2 to determine the concentration after spiking (A).
- 9.3.3 Calculate the percent recovery (R) in each aliquot using the following equation:

$$\% R = 100 \frac{(A-B)}{T}$$

where:

*A* = Measured concentration of analyte after spiking  
*B* = Measured concentration of analyte before spiking  
*T* = True concentration of the spike

- 9.3.4 Compare percent recovery (R) with the QC acceptance criteria in Table 2.
- 9.3.4.1 If results of the MS/MSD are similar and fail the acceptance criteria, and recovery for the OPR standard (Section 9.5) for the analytical batch is within the acceptance criteria in Table 2, an interference is present and the results may not be reported or otherwise used for permitting or regulatory compliance purposes. If the interference can be attributed to sampling, the site or discharge should be resampled. If the interference can be attributed to a method deficiency, the laboratory must modify the method, repeat the test required in Section 9.1.2, and repeat analysis of the sample and MS/MSD. However, during the development of Method 1631, very few interferences have been noted in the determination of Hg using this Method. (See Section 4.4 for information on interferences.)
- 9.3.4.2 If the results of both the spike and the OPR test fall outside the acceptance criteria, the analytical system is judged to be not in control, and the results may not be reported or used for permitting or regulatory compliance purposes. The laboratory must identify and correct the problem and reanalyze all samples in the sample batch.
- 9.3.5 Relative percent difference between duplicates—Compute the relative percent difference (RPD) between the MS and MSD results according to the following equation using the concentrations found in the MS and MSD. Do not use the recoveries calculated in Section 9.3.3 for this calculation because the RPD is inflated when the background concentration is near the spike concentration.

$$RPD = 200 \times \frac{(|D1-D2|)}{(D1+D2)}$$

Where:

*D1* = concentration of Hg in the MS sample  
*D2* = concentration of Hg in the MSD sample

- 9.3.6 The RPD for the MS/MSD pair must not exceed the acceptance criterion in Table 2. If the criterion is not met, the system is judged to be out of control. The problem must be identified and corrected immediately, and the analytical batch reanalyzed.
- 9.3.7 As part of the QC program for the laboratory, method precision and accuracy for samples should be assessed and records maintained. After analyzing five samples in which the recovery passes the test in Section 9.3.4, compute the average percent recovery ( $R_a$ ) and the standard deviation of the percent recovery ( $s_r$ ). Express the accuracy assessment as a percent recovery interval from  $R_a - 2s_r$  to  $R_a + 2s_r$ . For example, if  $R_a = 90\%$  and  $s_r = 10\%$  for five analyses, the accuracy interval is expressed as 70–110%. Update the accuracy assessment regularly (e.g., after every five to ten new accuracy measurements).
- 9.4** Blanks—Blanks are critical to the reliable determination of Hg at low levels. The sections below give the minimum requirements for analysis of blanks. However, it is suggested that additional blanks be analyzed as necessary to pinpoint sources of contamination in, and external to, the laboratory.
- 9.4.1 Bubbler blanks—Bubbler blanks are analyzed to demonstrate freedom from system contamination. At least three bubbler blanks must be run per analytical batch. One bubbler blank must be analyzed following each OPR. The mean bubbler blank for an analytical batch, if within acceptance criteria, is subtracted from all raw data for that batch prior to the calculation of results.
- 9.4.1.1 Immediately after analyzing a sample for Hg, place a clean gold trap on the bubbler, purge and analyze the sample a second time using the procedure in Section 11, and determine the amount of Hg remaining in the system.
- 9.4.1.2 If the bubbler blank is found to contain more than 50 pg Hg, the system is out of control. The problem must be investigated and remedied, and the samples run on that bubbler must be reanalyzed. If the blanks from other bubblers contain less than 50 pg Hg, the data associated with those bubblers remain valid.
- 9.4.1.3 The mean result for all bubbler blanks (from bubblers passing the specification in Section 9.4.1.2) in an analytical batch (at least three bubbler blanks) is calculated at the end of the batch. The mean result must be < 25 pg with a standard deviation of < 10 pg for the batch to be considered valid. If the mean is < 25 pg, the average peak measurement value is subtracted from all raw data before results are calculated.
- 9.4.1.4 If Hg in the bubbler blank exceeds the acceptance criteria in Section 9.4.1.3, the system is out of control, and the problem must be resolved and the samples reanalyzed. Usually, the bubbler blank is too high for one of the following reasons:
- (a) Bubblers need rigorous cleaning;
  - (b) Soda-lime is contaminated; or
  - (c) Carrier gas is contaminated.

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- 9.4.2 Reagent blanks—The Hg concentration in reagent blanks must be determined on solutions of reagents by adding these reagents to previously purged reagent water in the bubbler.
- 9.4.2.1 Reagent blanks are required when the batch of reagents (bromine monochloride plus hydroxylamine hydrochloride) are prepared, with verification in triplicate each month until a new batch of reagents is needed.
- 9.4.2.2 Add aliquots of BrCl (0.5 mL), NH<sub>2</sub>OH (0.2 mL) and SnCl<sub>2</sub> (0.5 mL) to previously purged reagent water in the bubbler. Samples high in organic materials may require additional BrCl. In order to evaluate the reagents as a potential source of contamination, the amount of reagent added to the reagent blank(s) must be the same as the amount of reagent added to the sample(s).
- 9.4.2.3 The presence of more than 25 pg of Hg indicates a problem with the reagent solution. The purging of certain reagent solutions, such as SnCl<sub>2</sub> or NH<sub>2</sub>OH with mercury-free nitrogen or argon can reduce Hg to acceptable levels. Because BrCl cannot be purified, a new batch should be made from different reagents and should be tested for Hg levels if the level of Hg in the BrCl solution is too high.
- 9.4.3 Field blanks
- 9.4.3.1 Analyze the field blank(s) shipped with each set of samples (samples collected from the same site at the same time, to a maximum of 10 samples). Analyze the blank immediately before analyzing the samples in the batch.
- 9.4.3.2 If Hg or any potentially interfering substance is found in the field blank at a concentration equal to or greater than the ML (Table 2), or greater than one-fifth the level in the associated sample, whichever is greater, results for associated samples may be the result of contamination and may not be reported or otherwise used for regulatory compliance purposes.
- 9.4.3.3 Alternatively, if a sufficient number of field blanks (three minimum) are analyzed to characterize the nature of the field blank, the average concentration plus two standard deviations must be less than the regulatory compliance limit or less than one-half the level in the associated sample, whichever is greater.
- 9.4.3.4 If contamination of the field blanks and associated samples is known or suspected, the laboratory should communicate this to the sampling team so that the source of contamination can be identified and corrective measures taken before the next sampling event.
- 9.4.4 Equipment blanks—Before any sampling equipment is used at a given site, the laboratory or cleaning facility is required to generate equipment blanks to demonstrate that the sampling equipment is free from contamination. Two types of equipment blanks are required: bottle blanks and sampler check blanks.
- 9.4.4.1 Bottle blanks—After undergoing the cleaning procedures in this Method, bottles should be subjected to conditions of use to verify the effectiveness of the cleaning procedures. A representative set of sample bottles should be filled with reagent

water acidified to pH <2 and allowed to stand for a minimum of 24 h. Ideally, the time that the bottles are allowed to stand should be as close as possible to the actual time that the sample will be in contact with the bottle. After standing, the water should be analyzed for any signs of contamination. If a bottle shows contamination at or above the level specified for the field blank (Section 9.4.3), the problem must be identified, the cleaning procedures corrected or cleaning solutions changed, and all affected bottles recleaned.

9.4.4.2 Sampler check blanks—Sampler check blanks are generated in the laboratory or at the equipment cleaning facility by processing reagent water through the sampling devices using the same procedures that are used in the field (see Sampling Method). Therefore, the "clean hands/dirty hands" technique used during field sampling should be followed when preparing sampler check blanks at the laboratory or cleaning facility.

9.4.4.2.1 Sampler check blanks are generated by filling a large carboy or other container with reagent water (Section 7.1) and processing the reagent water through the equipment using the same procedures that are used in the field (see Sampling Method, Reference 9). For example, manual grab sampler check blanks are collected by directly submerging a sample bottle into the water, filling the bottle, and capping. Subsurface sampler check blanks are collected by immersing a submersible pump or intake tubing into the water and pumping water into a sample container.

9.4.4.2.2 The sampler check blank must be analyzed using the procedures in this Method. If mercury or any potentially interfering substance is detected in the blank at or above the level specified for the field blank (Section 9.4.3), the source of contamination or interference must be identified, and the problem corrected. The equipment must be demonstrated to be free from mercury and interferences before the equipment may be used in the field.

9.4.4.2.3 Sampler check blanks must be run on all equipment that will be used in the field. If, for example, samples are to be collected using both a grab sampling device and a subsurface sampling device, a sampler check blank must be run on both pieces of equipment.

9.5 Ongoing precision and recovery (OPR)—To demonstrate that the analytical system is within the performance criteria of this Method and that acceptable precision and accuracy is being maintained within each analytical batch, the laboratory shall perform the following operations:

9.5.1 Analyze the OPR solution (5 ng/L, Section 7.11) followed by a bubbler blank prior to the analysis of each analytical batch according to the procedure beginning in Section 11. An OPR also must be analyzed at the end of an analytical run or at the end of each 12-hour shift. Subtract the peak height (or peak area) of the bubbler blank from the peak height (or area) of the OPR and calculate the concentration for the blank-subtracted OPR.

9.5.2 Compare the concentration recovery with the limits for ongoing precision and recovery in Table 2. If the recovery is in the range specified, the analytical system is control and

analysis of samples and blanks may proceed. If, however, the concentration is not in the specified range, the analytical process is not in control. Correct the problem and repeat the ongoing precision and recovery test. All reported results must be associated with an OPR that meets the Table 2 performance criteria at the beginning and end of each batch.

- 9.5.3 The laboratory should add results that pass the specification in Section 9.5.2 to IPR and previous OPR data and update QC charts to form a graphic representation of continued laboratory performance. The laboratory also should develop a statement of laboratory data quality by calculating the average percent recovery ( $R_a$ ) and the standard deviation of the percent recovery ( $s_r$ ). Express the accuracy as a recovery interval from  $R_a - 2s_r$  to  $R_a + 2s_r$ . For example, if  $R_a = 95\%$  and  $s_r = 5\%$ , the accuracy is 85–105%.
- 9.6 Quality control sample (QCS)—The laboratory must obtain a QCS from a source different from the Hg used to produce the standards used routinely in this Method (Sections 7.7–7.10). The QCS should be analyzed as an independent check of system performance.
- 9.7 Depending on specific program requirements, the laboratory may be required to analyze field duplicates and field spikes collected to assess the precision and accuracy of the sampling, sample transportation, and storage techniques. The relative percent difference (RPD) between field duplicates should be less than 20%. If the RPD of the field duplicates exceeds 20%, the laboratory should communicate this to the sampling team so that the source of error can be identified and corrective measures taken before the next sampling event.

## 10.0 Calibration and Standardization

- 10.1 Establish the operating conditions necessary to purge Hg from the bubbler and to desorb Hg from the traps in a sharp peak. Further details for operation of the purge and trap and desorption and analysis systems is given in Sections 11.3 and 11.4, respectively. The entire system is calibrated using standards traceable to NIST standard reference material, as follows:

### 10.1.1 Calibration

- 10.1.1.1 The calibration must contain five or more non-zero points and the results of analysis of two bubbler blanks. The lowest calibration point must be at the Minimum Level (ML).
- 10.1.1.2 Standards are analyzed by the addition of aliquots of Hg working standard A (Section 7.9) and Hg working standard B (Section 7.10) directly into the bubblers. Add 0.50 mL of working standard B and 0.5 mL SnCl<sub>2</sub> to the bubbler. Swirl to produce a standard of 0.5 ng/L. Purge under the optimum operating conditions (Section 10.1). Sequentially follow with the addition of aliquots of 0.05, 0.25, 0.50 and 1.0 mL of working standard A plus 0.5 mL SnCl<sub>2</sub> to produce standards of 5.0, 25.0, 50.0 and 100.0 ng/L.
- 10.1.1.3 For each point, subtract the mean peak height or area of the bubbler blanks for the analytical batch from the peak height or area for the standard. Calculate the calibration factor ( $CF_x$ ) for Hg in each of the five standards using the mean bubbler-blank-subtracted peak height or area and the following equation:

$$CF_x = \frac{(A_x) - (A_{BB})}{(C_x)}$$

Where:

- $A_x$  = peak height or area for Hg in standard  
 $A_{BB}$  = peak height or area for Hg in bubbler blank  
 $C_x$  = concentration of standard analyzed (ng/L)

- 10.1.1.4 Calculate the mean calibration factor ( $CF_m$ ), the standard deviation of the calibration factor (SD), and the relative standard deviation (RSD) of the calibration factor, where  $RSD = 100 \times SD/CF_m$ .
- 10.1.1.5 If  $RSD \leq 15\%$ , calculate the recovery for the lowest standard (0.5 ng/L) using  $CF_m$ . If the  $RSD \leq 15\%$  and the recovery of the lowest standard is in the range of 75-125%, the calibration is acceptable and  $CF_m$  may be used to calculate the concentration of Hg in samples. If  $RSD > 15\%$  or if the recovery of the lowest standard is not in the range of 75-125%, recalibrate the analytical system and repeat the test.

- 10.2 Ongoing precision and recovery—Perform the ongoing precision and recovery test (Section 9.5) to verify calibration prior to and after analysis of samples in each analytical batch.

## 11.0 Procedure

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*NOTE: The following procedures for analysis of samples are provided as guidelines. Laboratories may find it necessary to optimize the procedures, such as drying time or potential applied to the Nichrome wires, for the laboratory's specific instrumental set-up.*

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### 11.1 Sample Preparation

- 11.1.1 Pour a 100-mL aliquot from a thoroughly shaken, acidified sample, into a 125-mL fluoropolymer bottle. If BrCl was not added as a preservative (Section 8.5), add the amount of BrCl solution (Section 7.6) given below, cap the bottle, and digest at room temperature for a 12 h minimum.
- 11.1.1.1 For clear water and filtered samples, add 0.5 mL of BrCl; for brown water and turbid samples, add 1.0 mL of BrCl. If the yellow color disappears because of consumption by organic matter or sulfides, more BrCl should be added until a permanent (12-h) yellow color is obtained.
- 11.1.1.2 Some highly organic matrices, such as sewage effluent, will require high levels of BrCl (i.e., 5 mL/100 mL of sample), and longer oxidation times, or elevated temperatures (i.e., place sealed bottles in oven at 50 °C for 6 h). The amount of reagent (including BrCl) added to a sample must be the same as the amount added to a blank to detect contamination in the reagents (see Section 9.4.2.2). The oxidation must be continued until it is complete. Complete oxidation can be determined by either observation of a permanent yellow color remaining in the

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sample or the use of starch iodide indicating paper to test for residual free oxidizer.

- 11.1.2 Matrix spikes and matrix spike duplicates—For every 10 or fewer samples, pour two additional 100-mL aliquots from a randomly selected sample, spike at the level specified in Section 9.3, and process in the same manner as the samples. There should be 2 MS/MSD pairs for each analytical batch of 20 samples.
- 11.2 Hg reduction and purging—Place 100 mL of reagent water in each bubbler, add 1.0 mL of SnCl<sub>2</sub>, and purge with Hg-free N<sub>2</sub> for 20 min at 300–400 mL/min (Figure 1).
- 11.2.1 Connect a gold sand trap to the output of the soda lime pretrap, and purge the water another 20 min to obtain a bubbler blank.
- 11.2.2 Add 0.2 mL of 30% NH<sub>2</sub>OH to the BrCl-oxidized sample in the 125-mL fluoropolymer bottle. Cap the bottle and swirl the sample. The yellow color will disappear, indicating the destruction of the BrCl. Allow the sample to react for 5 min with periodic swirling to be sure that no traces of halogens remain.

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**NOTE:** *Purging of free halogens onto the gold trap will result in damage to the trap and low or irreproducible results.*

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- 11.2.3 After discarding the water from the standards, connect a fresh trap to the bubbler, pour the reduced sample into the bubbler, add 0.5 mL of 20% SnCl<sub>2</sub> solution, and purge the sample onto a gold sand trap with N<sub>2</sub> for 20 min.
- 11.2.4 When analyzing Hg samples, the recovery is quantitative, and organic interferents are destroyed. Thus, standards, bubbler blanks, and small amounts of high-level samples may be run directly in the water of previously purged samples. After very high samples, a small degree of carryover (<0.01%) may occur. Bubblers that contain such samples should be blanked prior to proceeding with low level samples.
- 11.3 Desorption of Hg from the gold trap
- 11.3.1 Remove the sample trap from the bubbler, place the Nichrome wire coil around the trap and connect the trap into the analyzer train between the incoming Hg-free argon and the second gold-coated (analytical) sand trap (Figure 2).
- 11.3.2 Pass argon through the sample and analytical traps at a flow rate of approximately 30 mL/min for approximately 2 min to drive off condensed water vapor.
- 11.3.3 Apply power to the coil around the sample trap for 3 minutes to thermally desorb the Hg (as Hg(0)) from the sample trap onto the analytical trap.
- 11.3.4 After the 3-min desorption time, turn off the power to the Nichrome coil, and cool the sample trap using the cooling fan.
- 11.3.5 Turn on the chart recorder or other data acquisition device to start data collection, and apply power to the Nichrome wire coil around the analytical trap. Heat the analytical trap for 3 min (1 min beyond the point at which the peak returns to baseline).

- 11.3.6 Stop data collection, turn off the power to the Nichrome coil, and cool the analytical trap to room temperature using the cooling fan.
- 11.3.7 Place the next sample trap in line and proceed with analysis of the next sample.

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**NOTE:** Do not heat a sample trap while the analytical trap is still warm; otherwise, the analyte may be lost by passing through the analytical trap.

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- 11.4 Peaks generated using this technique should be very sharp and almost symmetrical. Mercury elutes at approximately 1 minute and has a width at half-height of about 5 seconds.
- 11.4.1 Broad or asymmetrical peaks indicate a problem with the desorption train, such as improper gas flow rate, water vapor on the trap(s), or an analytical trap damaged by chemical fumes or overheating.
- 11.4.2 Damage to an analytical trap is also indicated by a sharp peak, followed by a small, broad peak.
- 11.4.3 If the analytical trap has been damaged, the trap and the fluoropolymer tubing downstream from it should be discarded because of the possibility of gold migration onto downstream surfaces.
- 11.4.4 Gold-coated sand traps should be tracked by unique identifiers so that any trap producing poor results can be quickly recognized and discarded.

## 12.0 Data Analysis and Calculations

- 12.1 Calculate the mean peak height or area for bubbler blanks, "BB" (n = at least 3)
- 12.2 Calculate the concentration of Hg in ng/L (parts-per-trillion; ppt) in each sample according to the following equation:

$$[\text{Hg}] \text{ (ng/L)} = \frac{A_s - A_{BB}}{CF_m}$$

where:

$A_s$  = peak height (or area) for Hg in sample

$A_{BB}$  = peak height (or area) for Hg in bubbler blank

$CF_m$  = mean calibration factor (Section 10.1.1.5)

- 12.3 Calculate the concentration of Hg in the reagent blank ( $C_{RB}$ ), in ng/L, using the equation in Section 12.2 and substituting the peak height or area resulting from the reagent blank for  $A_s$ . If the Hg in the reagent blank is attributable to Hg in the BrCl, correct the concentration of Hg in the reagent blank by the volume of BrCl used for the particular sample (Section 11.1.1.2) using the following correction factor:

$$C_{RB} = \frac{V_{BS}}{V_{BRB}}$$

where:

$V_{BS}$  = volume of BrCl solution used in sample (Section 11.1.1.2)

$V_{BRB}$  = volume of BrCl solution used in reagent blank (Section 9.4.2.2)

## 12.4 Reporting

- 12.4.1 Report results for Hg at or above the ML, in ng/L, to three significant figures. Report results for Hg in samples below the ML as <0.5 ng/L, or as required by the regulatory authority or in the permit. Report results for Hg in reagent blanks and field blanks at or above the ML, in ng/L, to three significant figures. Report results for Hg in reagent blanks or field blanks below the ML but at or above the MDL to two significant figures. Report results for Hg not detected in reagent blanks or field blanks as <0.2 ng/L, or as required by the regulatory authority or in the permit.
- 12.4.2 Report results for Hg in samples, reagent blanks and field blanks separately, unless otherwise requested or required by a regulatory authority or in a permit. If blank correction is requested or required, subtract the concentration of Hg in the reagent blank from the concentration of Hg in the sample to obtain the net sample Hg concentration.
- 12.4.3 Results from tests performed with an analytical system that is not in control must not be reported or otherwise used for permitting or regulatory compliance purposes, but does not relieve a discharger or permittee of reporting timely results.

## 13.0 Method Performance

- 13.1 This method was tested in 12 laboratories using reagent water, freshwater, marine water and effluent (Reference 19). The quality control acceptance criteria listed in Table 2 were verified by data gathered in the interlaboratory study, and the method detection limit (MDL) given in Section 1.5 was verified in all 12 laboratories. In addition, the techniques in this Method have been intercompared with other techniques for low-level mercury determination in water in a variety of studies, including ICES-5 (Reference 20) and the International Mercury Speciation Intercomparison Exercise (Reference 21).
- 13.2 Precision and recovery data for reagent water, freshwater, marine water, and secondary effluent are given in Table 3.

## 14.0 Pollution Prevention

- 14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Many opportunities for pollution prevention exist in laboratory

operation. EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address waste generation. When wastes cannot be reduced feasibly at the source, the Agency recommends recycling as the next best option. The acids used in this Method should be reused as practicable by purifying by electrochemical techniques. The only other chemicals used in this Method are the neat materials used in preparing standards. These standards are used in extremely small amounts and pose little threat to the environment when managed properly. Standards should be prepared in volumes consistent with laboratory use to minimize the disposal of excess volumes of expired standards.

- 14.2 For information about pollution prevention that may be applied to laboratories and research institutions, consult *Less is Better: Laboratory Chemical Management for Waste Reduction*, available from the American Chemical Society's Department of Governmental Relations and Science Policy, 1155 16th Street NW, Washington DC 20036, 202/872-4477.

## 15.0 Waste Management

- 15.1 The laboratory is responsible for complying with all Federal, State, and local regulations governing waste management, particularly hazardous waste identification rules and land disposal restrictions, and for protecting the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required. An overview of requirements can be found in *Environmental Management Guide for Small Laboratories* (EPA 233-B-98-001).
- 15.2 Acids, samples at pH <2, and BrCl solutions must be neutralized before being disposed of, or must be handled as hazardous waste.
- 15.3 For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* and *Less is Better: Laboratory Chemical Management for Waste Reduction*, both available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington, DC 20036.

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## 17.0 Glossary

The definitions and purposes below are specific to this Method, but have been conformed to common usage as much as possible.

- 17.1 **Ambient Water**—Waters in the natural environment (e.g., rivers, lakes, streams, and other receiving waters), as opposed to effluent discharges.
- 17.2 **Analytical Batch**—A batch of up to 20 samples that are oxidized with the same batch of reagents and analyzed during the same 12-hour shift. Each analytical batch must also include at least three bubbler blanks, an OPR, and a QCS. In addition, MS/MSD samples must be prepared at a frequency of 10% per analytical batch (one MS/MSD for every 10 samples).
- 17.3 **Bubbler Blank**—Analyzed to demonstrate freedom from system contamination. Immediately after analyzing a sample, water in the bubbler is purged and analyzed using the same procedure as for the samples to determine Hg. The blank is somewhat different between days, and a minimum of three bubbler blanks must be analyzed per analytical batch. The average of the results for the three bubbler blanks is subtracted from the result of analysis of each sample to produce a final result.
- 17.4 **Intercomparison Study**—An exercise in which samples are prepared and split by a reference laboratory, then analyzed by one or more testing laboratories and the reference laboratory. The intercomparison, with a reputable laboratory as the reference laboratory, serves as the best test of the precision and accuracy of the analyses at natural environmental levels.
- 17.5 **Matrix Spike (MS) and Matrix Spike Duplicate (MSD)**—Aliquots of an environmental sample to which known quantities of the analyte(s) of interest is added in the laboratory. The MS and MSD are analyzed exactly like a sample. Their purpose is to quantify the bias and precision caused by the sample matrix. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS and MSD corrected for these background concentrations.
- 17.6 **May**—This action, activity, or procedural step is allowed but not required.
- 17.7 **May not**—This action, activity, or procedural step is prohibited.
- 17.8 **Minimum Level (ML)**—The lowest level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed. The ML is calculated by

multiplying the MDL by 3.18 and rounding the result to the number nearest to  $(1, 2, \text{ or } 5) \times 10^n$ , where  $n$  is an integer.

- 17.8 Must**—This action, activity, or procedural step is required.
- 17.9 Quality Control Sample (QCS)**—A sample containing Hg at known concentrations. The QCS is obtained from a source external to the laboratory, or is prepared from a source of standards different from the source of calibration standards. It is used as an independent check of instrument calibration.
- 17.10 Reagent Water**—Water demonstrated to be free of mercury at the MDL of this Method. It is prepared from 18 MΩ ultrapure deionized water starting from a prepurified source. Reagent water is used to wash bottles, as trip and field blanks, and in the preparation of standards and reagents.
- 17.11 Regulatory Compliance Limit**—A limit on the concentration or amount of a pollutant or contaminant specified in a nationwide standard, in a permit, or otherwise established by a regulatory authority.
- 17.12 Shall**—This action, activity, or procedure is required.
- 17.13 Should**—This action, activity, or procedure is suggested, but not required.
- 17.14 Stock Solution**— A solution containing an analyte that is prepared from a reference material traceable to EPA, NIST, or a source that will attest to the purity and authenticity of the reference material.
- 17.15 Ultraclean Handling**— A series of established procedures designed to ensure that samples are not contaminated during sample collection, storage, or analysis.

## 18.0 Tables and Figures

**Table 1**

**Lowest Ambient Water Quality Criterion for Mercury and the Method Detection Limit and Minimum Level of Quantitation for EPA Method 1631**

Metal	Lowest Ambient Water Quality Criterion <sup>(1)</sup>	Method Detection Limit (MDL) and Minimum Level (ML)	
		MDL <sup>(2)</sup>	ML <sup>(3)</sup>
Mercury (Hg)	1.3 ng/L	0.2 ng/L	0.5 ng/L

1. Lowest water quality criterion for the Great Lakes System (Table 4, 40 CFR 132.6). The lowest Nationwide criterion is 12 ng/L (40 CFR 131.36).
2. Method detection limit (40 CFR 136, Appendix B)
3. Minimum level of quantitation (see Glossary)



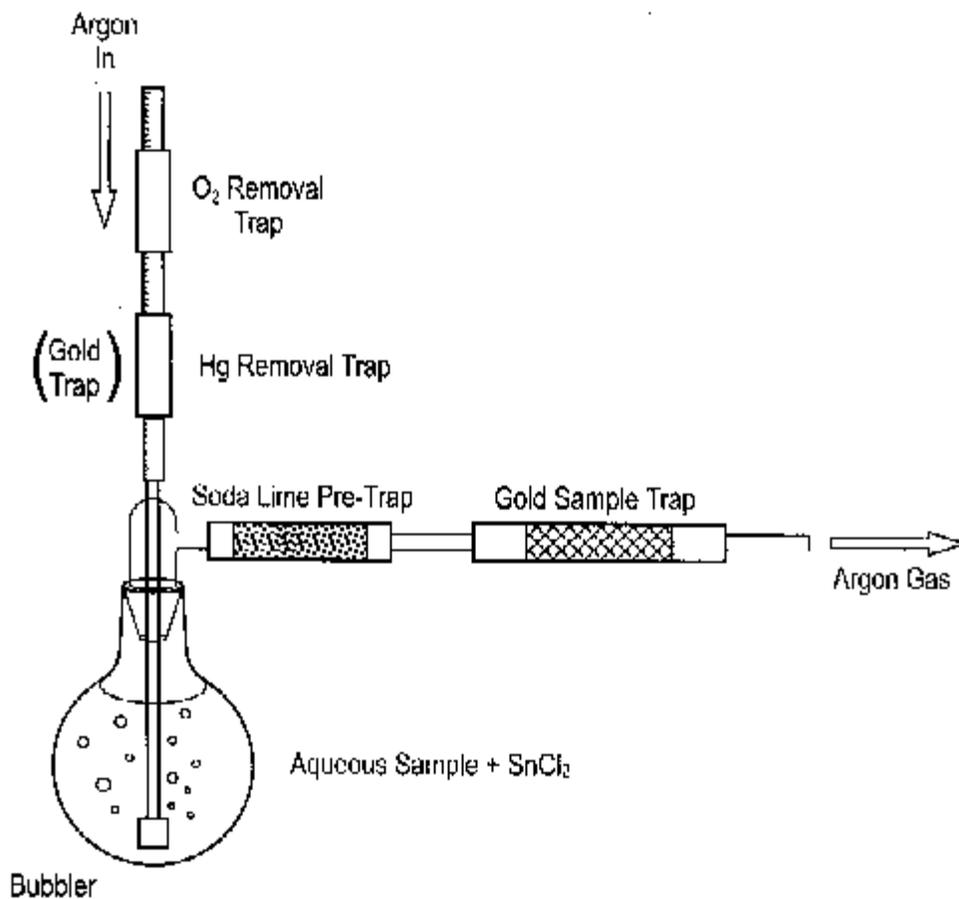
**Table 2****Quality Control Acceptance Criteria for Performance Tests in EPA Method 1631**

Acceptance Criteria	Section	Limit (%)
Initial Precision and Recovery (IPR)	9.2.2	
Precision (RSD)	9.2.2.3	21
Recovery (X)	9.2.2.3	79-121
Ongoing Precision and Recovery (OPR)	9.5.2	77-123
Matrix Spike/Matrix Spike Duplicate (MS/MSD)	9.3	
Recovery	9.3.4	71-125
Relative Percent Difference (RPD)	9.3.5	24

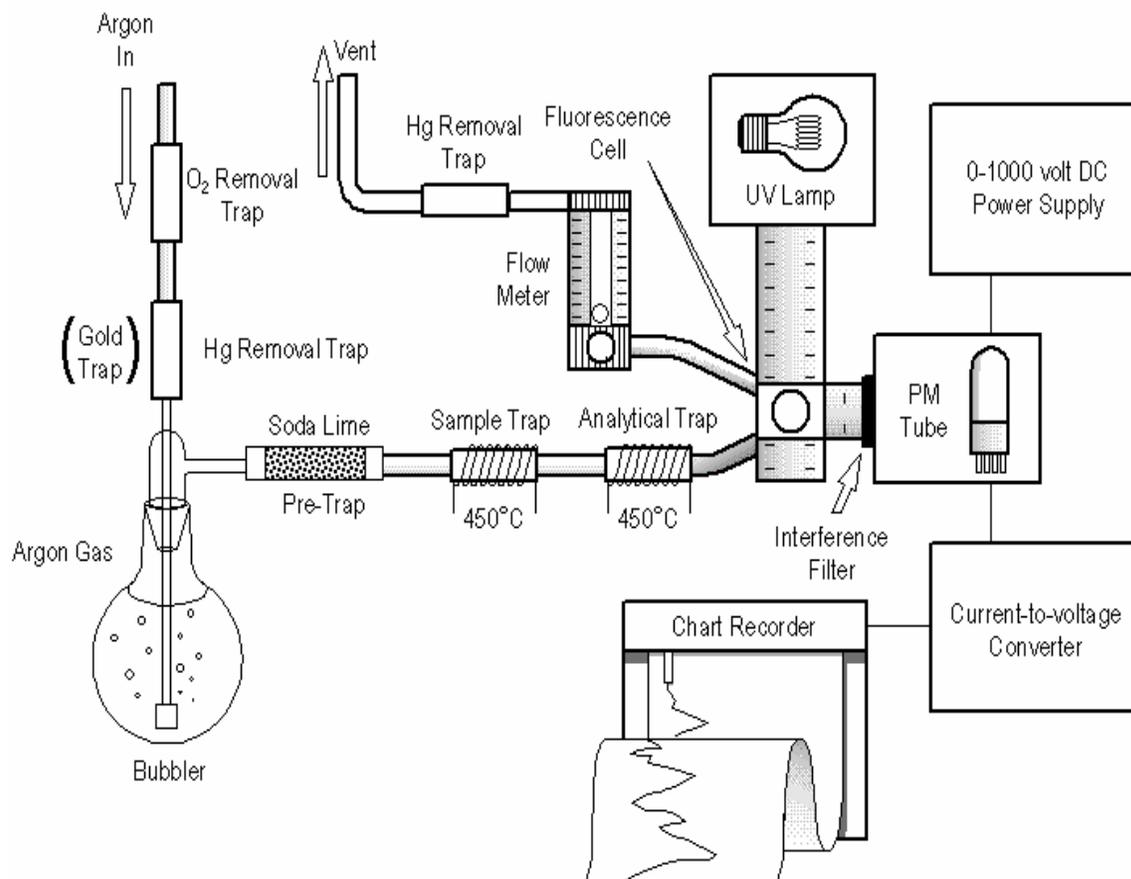
**Table 3****Precision and Recovery for Reagent Water, Fresh Water, Marine Water, and Effluent Water Using Method 1631**

Matrix	*Mean Recovery (%)	*Precision (% RSD)
Reagent Water	98.0	5.6
Fresh Water (Filtered)	90.4	8.3
Marine Water (Filtered)	92.3	4.7
Marine Water (Unfiltered)	88.9	5.0
Secondary Effluent (Filtered)	90.7	3.0
Secondary Effluent (Unfiltered)	92.8	4.5

\*Mean percent recoveries and RSDs are based on expected Hg concentrations.



**Figure 1.** Schematic Diagram of Bubbler Setup



**Figure 2.** Schematic Diagram of the Cold Vapor Atomic Fluorescence Spectrometer (CVAFS) System