METHOD 245.1

DETERMINATION OF MERCURY IN WATER BY COLD VAPOR ATOMIC ABSORPTION SPECTROMETRY

Revision 3.0
EMMC Version

J.F. Kopp, M.C. Longbottom, and L.B. Lobring - Mercury in Water (Cold Vapor Technique), Revision 1.0, (1972)

J.F. Kopp and L.B. Lobring - Method 245.1, Revision 2.0 (1979)

L.B. Lobring and B.B. Potter - Method 245.1, Revision 2.3 (1991)

J.W. O'Dell, B.B. Potter, L.B. Lobring, and T.D. Martin - Method 245.1, Revision 3.0 (1994)

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METHOD 245.1

DETERMINATION OF MERCURY IN WATER
BY COLD VAPOR ATOMIC ABSORPTION SPECTROMETRY

1.0 SCOPE AND APPLICATION

1.1 This procedure[1] measures total mercury (organic + inorganic) in drinking, surface, ground, sea, brackish waters, industrial and domestic wastewater.

Analyte	Chemical Abstracts Service Registry Number (CASRN)
Mercury	7439-97-6

1.2 The range of the method is 0.2-10 µg Hg/L. The range may be extended above or below the normal range by increasing or decreasing sample size. However, the actual method detection limit and linear working range will be dependent on the sample matrix, type of instrumentation configuration, and selected operating conditions.

1.3 Reduced volume or semi-automated versions of this method, that use the same reagents and molar ratios, are acceptable provided they meet the quality control and performance requirements stated in the method (Section 9.0).

1.4 For reference where this method is approved for use in compliance monitoring programs [e.g., Clean Water Act (NPDES) or Safe Drinking Water Act (SDWA)] consult both the appropriate sections of the Code of Federal Regulation (40 CFR Part 136 Table 1B for NPDES, and Part 141 § 141.23 for drinking water), and the latest Federal Register announcements.

2.0 SUMMARY OF METHOD

2.1 A known portion of a water sample is transferred to a BOD bottle, equivalent ground glass stoppered flask or other suitable closed container. It is digested in diluted potassium permanganate-potassium persulfate solutions and oxidized for two hours at 95°C. Mercury in the digested water sample is reduced with stannous chloride to elemental mercury and measured by the conventional cold vapor atomic absorption technique.

3.0 DEFINITIONS

3.1 **Calibration Blank** - A volume of reagent water acidified with the same acid matrix as in the calibration standards. The calibration blank is a zero standard and is used to auto-zero the instrument.

3.2 **Calibration Standard (CAL)** - A solution prepared from the dilution of stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.3 **Field Reagent Blank (FRB)** - An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to the sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

3.4 **Instrument Performance Check (IPC) Solution** - A solution of the method analyte, used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.5 **Laboratory Duplicates (LD1 and LD2)** - Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.6 **Laboratory Fortified Blank (LFB)** - An aliquot of LRB to which a known quantity of the method analyte is added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

3.7 **Laboratory Fortified Sample Matrix (LFM)** - An aliquot of an environmental sample to which a known quantity of the method analyte is added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.8 **Laboratory Reagent Blank (LRB)** - An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The LRB is used to determine if the method analyte or other interferences are present in the laboratory environment, reagents, or apparatus.

3.9 **Linear Dynamic Range (LDR)** - The concentration range over which the instrument response to an analyte is linear.

3.10 **Method Detection Limit (MDL)** - The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

3.11 **Quality Control Sample (QCS)** - A solution of the method analyte of known concentration which is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check either laboratory or instrument performance.

3.12 **Standard Addition** - The addition of a known amount of analyte to the sample in order to determine the relative response of the detector to an analyte within the sample matrix. The relative response is then used to assess either an operative matrix effect or the sample analyte concentration.

3.13 **Stock Standard Solution** - A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

4.0 INTERFERENCES

4.1 Interferences have been reported for waters containing sulfide, chloride, copper and tellurium. Organic compounds which have broad band UV absorbance (around 253.7 nm) are confirmed interferences. The concentration levels for interferants are difficult to define. This suggests that quality control procedures (Section 9.0) must be strictly followed.

4.2 Volatile materials (e.g., chlorine) which absorb at 253.7 nm will cause a positive interference. In order to remove any interfering volatile materials, the dead air space in the digestion vessel (BOD bottle) should be purged before addition of stannous chloride solution.

4.3 Low level mercury sample preparation, digestion, and analysis may be subject to environmental contamination if preformed in areas with high ambient backgrounds where mercury was previously employed as an analytical reagent in analyses such as total Kjeldahl nitrogen (TKN) or chemical oxygen demand (COD).

5.0 SAFETY

5.l The toxicity and carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices[1]. Normal accepted laboratory safety practices should be followed during reagent preparation and instrument operation. Always wear safety glasses or full-face shield for eye protection when working with these reagents. Each laboratory is responsible for maintaining a current safety plan, a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method.[3,4]

5.2 Mercury compounds are highly toxic if swallowed, inhaled, or absorbed through the skin. Analyses should be conducted in a laboratory exhaust hood. The analyst should use chemical resistant gloves when handling concentrated mercury standards.

5.3 The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples should be done in a fume hood.

5.4 All personnel handling environmental samples known to contain or to have been in contact with human waste should be immunized against known disease causative agents.

6.0 EQUIPMENT AND SUPPLIES

6.1 Atomic Absorption Cold Vapor System

6.1.1 Atomic Absorption Spectrophotometer - Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. The use of background correction is recommended, but is not mandatory.

6.1.2 Mercury Hollow Cathode Lamp - Single element hollow cathode lamp or electrodeless discharge lamp and associated power supply.

6.1.3 Absorption Cell - Standard spectrophotometer cells 10-cm long, having quartz windows may be used. Suitable cells may be constructed from plexiglass tubing, 1 in. O.D. by 4 ½ in. long. The ends are ground perpendicular to the longitudinal axis and quartz windows (1 in. diameter by 1/16 in. thickness) are cemented in place. Gas inlet and outlet ports (also of plexiglass but ¼ in. O.D.) are attached approximately ½ in. from each end. The cell is strapped to a burner for support and aligned in the light beam to give the maximum transmittance.

6.1.4 Aeration Tubing - Inert mercury-free tubing is used for passage of mercury vapor from the sample bottle to the absorption cell. In some systems, mercury vapor is recycled. Straight glass tubing terminating in a coarse porous glass aspirator is used for purging mercury released from the water sample in the BOD bottle.

6.1.5 Air Pump - Any pump (pressure or vacuum system) capable of passing air 1 L/min. is used. Regulated compressed air can be used in an open one-pass system.

6.1.6 Drying Tube - Tube (6 in. x ¾ in. O.D.) containing 20 g of magnesium perchlorate. The filled tube is inserted (in-line) between the BOD bottle and the absorption tube. In place of the magnesium perchlorate drying tube, a small reading lamp is positioned to radiate heat (about 10°C above ambient) on the absorption cell. Heat from the lamp prevents water condensation in the cell.

6.1.7 Recorder - Any multi-range variable speed recorder or data system that is compatible with the UV detection system is suitable.

Note: Instruments designed specifically for mercury measurement using the cold vapor technique are commercially available and may be substituted for the atomic absorption cold vapor system described above.

6.2 Flowmeter, capable of measuring an air flow of 1 L/min.

6.3 A water bath with a covered top and capacity to maintain a water depth of 2-3 in. at 95°C.

6.4 Analytical balance, with capability to measure to 0.1 mg, for use in weighing reagents and preparing standards.

6.5 Labware - All reusable labware should be sufficiently clean for the task objectives. Particular attention should be given to all ground glass surfaces during cleaning. Routinely all items should be soaked in 30% HNO_3 and rinsed three times in reagent water. Digestion containers used in sample preparation that do not rinse clean of the previous sample should be washed with a detergent solution prior to acid cleaning.

6.5.1 Glassware - Volumetric flasks and graduated cylinders.

6.5.2 BOD bottles (or other equivalent suitable closed containers).

6.5.3 Assorted calibrated pipettes.

7.0 REAGENTS AND STANDARDS

7.1 Reagents may contain elemental impurities which bias analytical results. All reagents should be assayed by the chemical manufacturer for mercury and meet ACS specifications. The assayed mercury level of all solid reagents used in this method should not exceed 0.05 ppm. It is recommended that the laboratory analyst assay all reagents for mercury.

7.2 Reagent Water, ASTM Type II[5].

7.3 Nitric Acid (HNO_3), concentrated (sp.gr. 1.41), assayed mercury level is not to exceed 1 µg/L.

7.3.1 Nitric acid (1+1) - Add 500 mL concentrated HNO_3 to 400 mL reagent water and dilute to 1 L.

7.4 Sulfuric Acid (H_2SO_4), concentrated (sp.gr. 1.84), assayed mercury level is not to exceed 1 µg/L.

7.4.1 Sulfuric acid, 0.5 N - Slowly add 14.0 mL of conc. H_2SO_4 to 500 mL of reagent water and dilute to 1 L with reagent water.

7.5 Mercury standard, stock, 1 mL = 100 µg Hg: DO NOT DRY. **CAUTION:** highly toxic element. Dissolve 0.1354 g $HgCl_2$ in 75 mL reagent water. Add 50.0 mL concentrated HNO_3 (Section 7.3) and dilute to volume in 1 L volumetric flask with reagent water.

7.6 Mercury calibration standard (CAL) - To each volumetric flask used for serial dilutions, acidify with (0.1-0.2% by volume) HNO_3 (Section 7.3). Using mercury stock standard (Section 7.5), make serial dilutions to obtain a concentration of 0.1 µg Hg/mL.

7.7 Potassium permanganate solution - Dissolve 5 g of $KMnO_4$ in 100 mL of reagent water.

7.8 Potassium persulfate solution - Dissolve 5 g of $K_2S_2O_8$ in 100 mL of reagent water.

7.9 Sodium chloride-hydroxylammonium chloride solution - Dissolve 12 g of NaCl and 12 g of hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) in 100 mL reagent water. (Hydroxylamine sulfate $(NH_2OH)_2 \cdot H_2SO_4$ may be used in place of hydroxylamine hydrochloride.)

7.10 Stannous chloride solution - Add 25 g of $SnCl_2 \cdot 2H_2O$ to 250 mL of 0.5 N H_2SO_4 (Section 7.4.1). This mixture is a suspension and should be stirred continuously during use.

7.11 Blanks - Three types of blanks are required for the analysis. The calibration blank is used in establishing the analytical curve, the laboratory reagent blank is used to assess possible contamination from the sample preparation procedure, and the laboratory fortified blank is used to assess routine laboratory performance.

7.11.1 The calibration blank must contain all reagents in the same concentrations and in the same volume as used in preparing the calibration solutions.

7.11.2 The laboratory reagent blank (LRB) is prepared in the manner as the calibration blank except the LRB must be carried through the entire sample preparation scheme.

7.11.3 The laboratory fortified blank (LFB) is prepared by fortifying a sample size volume of laboratory reagent blank solution with mercury to a suitable

concentration of >10X the MDL, but less than the midpoint concentration of the calibration curve. The LFB must be carried through the entire sample preparation scheme.

7.12 Instrument Performance Check (IPC) Solution - The IPC solution is used to periodically verify instrument performance during analysis. It must contain all reagents in the same concentration as the calibration solutions and mercury at an appropriate concentration to approximate the midpoint of the calibration curve. The IPC solution should be prepared from the same CAL standard (Section 7.6) as used to prepare the calibration solutions. Agency programs may specify or request that additional instrument performance check solutions be prepared at specified concentrations in order to meet particular program needs.

7.13 Quality Control Sample (QCS) - For initial and periodic verification of calibration standards and instrument performance, analysis of a QCS is required. The QCS must be obtained from an outside source different from the standard stock solution, but prepared in the same manner as the calibration solutions. The concentration of the mercury in the QCS solution should be such that the resulting solution will provide an absorbance reading near the midpoint of the calibration curve. The QCS should be analyzed quarterly or more frequently as needed to meet data-quality needs.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Because of the extreme sensitivity of the analytical procedure and the presence of mercury in a laboratory environment, care must be taken to avoid extraneous contamination. Sampling devices, sample containers and plastic items should be determined to be free of mercury; the sample should not be exposed to any condition in the laboratory that may result in contamination from airborne mercury vapor.

8.2 For the determination of total mercury (inorganic + organic) in aqueous samples, samples are **not** filtered, but acidified with (1+1) nitric acid (Section 7.3.1) to pH <2 (normally, 3 mL of (1+1) acid per liter of sample is sufficient for most ambient and drinking water samples). Preservation may be done at the time of collection, however, to avoid the hazards of strong acids in the field, transport restrictions, and possible contamination it is recommended that the samples be returned to the laboratory as soon as possible after collection and acid preserved upon receipt in the laboratory. Following acidification, the sample should be mixed, held for 16 hours, and then verified to be pH <2 just prior withdrawing an aliquot for processing. If for some reason such as high alkalinity the sample pH is verified to be >2, more acid must be added and the sample held for additional 16 hours until verified to be pH <2. The preserved sample should be analyzed within 28 days of collection.

Note: When the nature of the sample is either unknown or is known to be hazardous, acidification should be done in a fume hood. See Section 5.2.

8.3 A field blank should be prepared and analyzed as required by the data user. Use the same container and acid as used in sample collection.

9.0 QUALITY CONTROL

9.1 Each laboratory using this method is required to operate a formal quality control (QC) program. The minimum requirements of this program consist of an initial demonstration of laboratory capability by analysis of laboratory reagent blanks, fortified blanks and samples used for continuing check on method performance. Commercially available water quality control samples are acceptable for routine laboratory use. The laboratory is required to maintain performance records that define the quality of the data generated.

9.2 Initial Demonstration of Performance (mandatory).

9.2.1 The initial demonstration of performance is used to characterize instrument performance (determination of linear dynamic ranges and analysis of quality control samples) and laboratory performance (determination of method detection limits) prior to analyses conducted by this method.

9.2.2 Linear dynamic range (LDR) - The upper limit of the LDR must be established. It must be determined from a linear calibration prepared from a minimum of three different concentration standards, one of which is close to the upper limit of the linear range. The LDR should be determined by analyzing succeedingly higher standard concentrations of mercury until the observed analyte concentration is no more than 10% below the stated concentration of the standard. The determined LDR must be documented and kept on file. The LDR which may be used for the analysis of samples should be judged by the analyst from the resulting data. Determined sample analyte concentrations that are greater than 90% of the determined upper LDR limit must be diluted and reanalyzed. The LDR should be verified annually or whenever, in the judgement of the analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions would dictate they be redetermined.

9.2.3 Quality control sample (QCS) - When beginning the use of this method, on a quarterly basis, after the preparation of stock or calibration standard solutions or as required to meet data-quality needs, verify the calibration standards and acceptable instrument performance with the preparation and analyses of a QCS (Section 7.13). To verify the calibration standards, the determined concentration of the QCS must be within ±10% of the stated value. If the calibration standard cannot be verified, performance of the determinative step of the method is unacceptable. The source of the problem must be identified and corrected before either proceeding on with the initial determination of method detection limits or continuing with on-going analyses.

9.2.4 Method detection limit (MDL) - A mercury MDL must be established using an LRB solution fortified at a concentration of two to three times the estimated detection limit.[5] To determine MDL values, take seven replicate aliquots of the fortified LRB and process through the entire analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

$$MDL = (t) \times (S)$$

where:

t = Student's t value for n-1 degrees of freedom at the 99% confidence level; t = 3.143 for six degrees of freedom

S = standard deviation of the replicate analyses

Note: If the relative standard deviation (RSD) from the analyses of the seven aliquots is <10%, the concentration used to determine the mercury MDL may have been inappropriately high for the determination. If so, this could result in the calculation of an unrealistically low MDL. Concurrently, determination of MDL in an LRB solution represents a best case situation and does not reflect possible matrix effects of real world samples. However, successful analyses of LFMs (Section 9.4) can give confidence to the MDL value determined in LRB solution.

The MDL must be sufficient to detect mercury at the required level according to compliance monitoring regulation (Section 1.2). The mercury MDL should be determined annually, when a new operator begins work or whenever, in the judgement of the analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions would dictate they be redetermined.

9.3 Assessing Laboratory Performance (mandatory)

9.3.1 Laboratory reagent blank (LRB) - The laboratory must analyze at least one LRB (Section 7.11.2) with each batch of 20 or fewer samples of the same matrix. LRB data are used to assess contamination from the laboratory environment. LRB values that exceed the MDL indicate laboratory or reagent contamination should be suspected. When LRB values constitute 10% or more of the analyte level determined for a sample or is 2.2 times the analyte MDL whichever is greater, fresh aliquots of the samples must be prepared and analyzed again for the affected analytes after the source of contamination has been corrected and acceptable LRB values have been obtained.

9.3.2 Laboratory fortified blank (LFB) - The laboratory must analyze at least one LFB (Section 7.11.3) with each batch of samples. Calculate accuracy as percent recovery using the following equation:

$$R = \frac{LFB - LRB}{s} \times 100$$

where:

R = percent recovery
LFB = laboratory fortified blank
LRB = laboratory reagent blank
s = concentration equivalent of mercury added to fortify the LRB solution.

If the recovery of mercury falls outside the required control limits of 85-115%, the analysis is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

9.3.3 The laboratory must use LFB analyses data to assess laboratory performance against the required control limits of 85-115% (Section 9.3.2). When sufficient internal performance data become available (usually a minimum of 20-30 analyses), optional control limits can be developed from the mean percent recovery (x) and the standard deviation (S) of the mean percent recovery. These data can be used to establish the upper and lower control limits as follows:

UPPER CONTROL LIMIT = x + 3S
LOWER CONTROL LIMIT = x - 3S

The optional control limits must be equal to or better than the required control limits of 85-115%. After each five to ten new recovery measurements, new control limits can be calculated using only the most recent 20-30 data points. Also, the standard deviation (S) data should be used to establish an on-going precision statement for the level of concentrations included in the LFB. These data must be kept on file and be available for review.

9.3.4 Instrument performance check (IPC) solution - For all determinations the laboratory must analyze the IPC solution (Section 7.12) and a calibration blank immediately following each calibration, after every 10th sample (or more frequently, if required) and at the end of the sample run. Analysis of the calibration blank should always be less than the MDL. Analysis of the IPC solution immediately following calibration must verify that the instrument is within ±5% of calibration. Subsequent analyses of the IPC solution must be within ±10 % of calibration. If the calibration cannot be

verified within the specified limits, analysis must be discontinued, the cause determined and/or in the case of drift the instrument recalibrated. All samples following the last acceptable IPC solution must be reanalyzed. The analysis data of the calibration blank and IPC solution must be kept on file with the sample analyses data.

9.4 Assessing Analyte Recovery and Data Quality

9.4.1 Sample homogeneity and the chemical nature of the sample matrix can affect mercury recovery and the quality of the data. Taking separate aliquots from the sample for replicate and fortified analyses can in some cases assess the effect. Unless otherwise specified by the data user, laboratory or program, the following laboratory fortified matrix (LFM) procedure (Section 9.4.2) is required.

9.4.2 The laboratory must add a known amount of mercury to a minimum of 10% of samples or one sample per sample set, whichever is greater. In each case the LFM aliquot must be a duplicate of the aliquot used for sample analysis. Select a sample with a low mercury background that is representative of the type of water samples being analyzed. It is recommended that this sample be analyzed prior to fortification. The concentration of mercury added may vary based on the nature of samples being analyzed. When possible, the concentration should be the same as that added to the LRB, but should not exceed the midpoint concentration of the calibration curve. Over time, samples from all routine sample sources should be fortified.

9.4.3 Calculate the percent recovery, corrected for background concentration measured in the unfortified sample aliquot, and compare these values to the control limits to the designated LFM recovery range of 70-130%. Percent recovery may be calculated using the following equation:

$$R = \frac{C_s - C}{s} \times 100$$

where:

R = percent recovery
C_s = fortified sample concentration
C = sample background concentration
s = concentration equivalent of mercury added to water sample

9.4.4 If mercury recovery falls outside the designated range, and the laboratory performance is shown to be in control (Section 9.3), the recovery problem encountered with the fortified water sample is judged to be matrix related, not system related. The result for mercury in the unfortified sample must

be labelled to inform the data user that the results are suspect due to matrix effects.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Conveniently arrange and connect the various components of the instrument system using one of the options shown in Figure 1. If adjustable, the monochromator should be set to 253.65 nm. Prior to the use of this method the air flow should be optimized. (The recommended air flow rate through the system is 1 L/min.) For all determinations allow an instrument and hollow cathode lamp warm up period of not less than 15 minutes. When an instrument designed specifically for the determination of mercury by the cold vapor technique is being utilized, the analyst should follow the instructions provided by the manufacturer.

10.2 Before using the procedure (Section 11.0) to analyze samples, there must be data available documenting initial demonstration of performance. The required data and procedure is described in Section 9.2. This data must be generated using the same instrument operating conditions and calibration routine used for sample analysis. These documented data must be kept on file and be available for review by the data user.

10.3 The recommended calibration routine is given in Section 11.2.

11.0 PROCEDURE

11.1 Sample Preparation

11.1.1 Transfer 100 mL of the water sample [or an aliquot diluted with reagent water (Section 7.2) to 100 mL] into a sample container.

Note: For reduced volume analysis, adjust sample and reagent volumes to maintain the required sample to reagent ratios.

11.1.2 Add 5 mL of H_2SO_4 (Section 7.4) and 2.5 mL of HNO_3 (Section 7.3) to the container.

11.1.3 To each container add 15 mL $KMnO_4$ solution (Section 7.7). For sewage or industry wastewaters, additional $KMnO_4$ may be required. Shake and add additional portions of $KMnO_4$ solution, if necessary, until the purple color persists for at least 15 minutes. Add 8 mL of $K_2S_2O_8$ solution (Section 7.8) to each container. Mix thoroughly, cap and cover the top of the sample container (if required) with aluminum foil or other appropriate cover. Heat for two hours in a water bath at 95°C.

11.1.4 Remove the sample containers from the water bath and cool to room temperature. (During the cool down period proceed with instrument warm up and calibration.)

11.1.5 When the samples are at room temperature, to each container, add 6 mL of NaCl-$(NH_2OH)_2H_2SO_4$ solution (Section 7.9) to reduce the excess permanganate.

11.2 Sample Analysis

11.2.1 Before beginning daily calibration the instrument should be reconfigured to the optimized conditions. Turn on the instrument and circulating pump. Adjust pump rate to 1 L/min. or as required. Allow system to stabilize.

11.2.2 Prepare calibration standards by transferring 0.5, 1.0, 2.0, 5.0, and 10 mL aliquots of the 0.1 µg/mL CAL (Section 7.6) to a series of sample containers (Section 6.5.2). Dilute the standard aliquots to 100 mL with reagent water (Section 7.2) and process as described in Sections 11.1.2, 11.1.3 (without heating), and 11.1.5. These solutions contain 0.05-1.0 µg of Hg. (Other appropriate calibration standards, volumes, and ranges may also be used.)

11.2.3 Treating each standard solution container individually, add 5 mL of $SnCl_2$ solution (Section 7.10) and immediately attach the container to the aeration apparatus. The absorbance, as exhibited either on the instrument or recording device, will increase and reach maximum within 30 sec. As soon as the maximum response is obtained, approximately one minute, open the bypass value (or optionally remove aspirator from the sample container if it is vented under the hood) and continue aeration until the absorbance returns to its minimum value.

11.2.4 Close the by-pass value, remove the aspirator from the standard solution container and continue aeration. Repeat (Section 11.2.3) until data from all standards have been collected.

11.2.5 Construct a standard curve by plotting peak height, area or maximum response obtained from each standard solution, versus micrograms of mercury in the container. The standard curve must comply with Section 9.2.2. Calibration using computer or calculator based regression curve fitting techniques on concentration/response data is acceptable.

11.2.6 Following calibration the digested samples are analyzed in the same manner as the standard solutions described in Section 11.2.3. However, prior to the addition of the $SnCl_2$ solution, place the aspirator inside the container above the liquid, and purge the head space (20-30 seconds) to remove possible gaseous interference.

11.2.7 During the analysis of samples, the laboratory must comply with the required quality control described in Sections 9.3 and 9.4.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 From the prepared calibration curve (Section 11.2.4) compute sample values by comparing response with the standard curve.

12.2 Calculate the mercury concentration in the sample by the formula:

$$\mu g\ Hg/L = \left(\begin{array}{c}\mu g\ Hg\ in \\ aliquot\end{array}\right)\left(\frac{1{,}000}{mL\ of\ aliquot}\right)$$

12.3 Report mercury concentrations to the proper significant figures in mg/L, µg/L or ng/L as required.

13.0 METHOD PERFORMANCE

13.1 In a single laboratory (EMSL), using an Ohio River composite sample with a background mercury concentration of 0.35 µg/L Hg and fortified with concentration of 1.0, 3.0, and 4.0 µg/L Hg, the standard deviations were ±0.14, ±0.10, and ±0.08 µg/L Hg, respectively. Standard deviation at the 0.35 µg/L Hg level was ±0.16 µg/L Hg. Percent recoveries at the three levels were 89%, 87%, and 87%, respectively.

13.2 In a joint EPA/ASTM interlaboratory study of the cold vapor technique for total mercury in water, increments of organic and inorganic mercury were added to natural waters. Recoveries were determined by difference. A statistical summary of this study is found in Table 1.

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. Numerous opportunities for pollution prevention exist in laboratory operation. The 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 their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions, consult “Less is Better: Laboratory Chemical Management for Waste Reduction, available from the American Chemical Society's Department of Government Relations and Science Policy”, 1155 16th Street N.W., Washington D.C. 20036, (202)872-4477.

15.0 WASTE MANAGEMENT

15.1 The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rule and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and

controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult "The Waste Management Manual for Laboratory Personnel", available from the American Chemical Society at the address listed in the Section 14.2.

16.0 REFERENCES

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2. "Safety in Academic Chemistry Laboratories", American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

3. "OSHA Safety and Health Standards, General Industry", (29CFR 1910), Occupational Safety and Health Administration, OSHA 2206, revised January 1976.

4. "Proposed OSHA Safety and Health Standards, Laboratories", Occupational Safety and Health Administration, Federal Register, July 24, 1986.

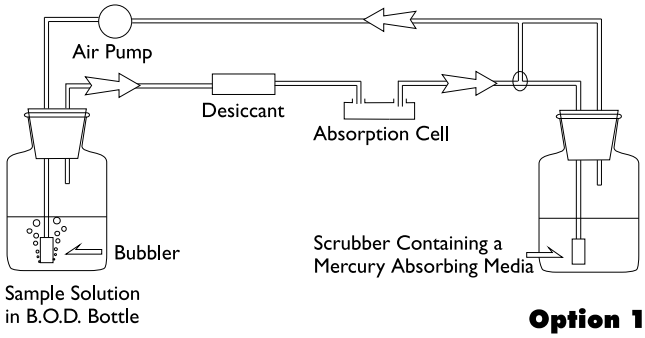
5. "Specification for Reagent Water", D1193, Annual Book of ASTM Standards, Vol. 11.01, 1990.

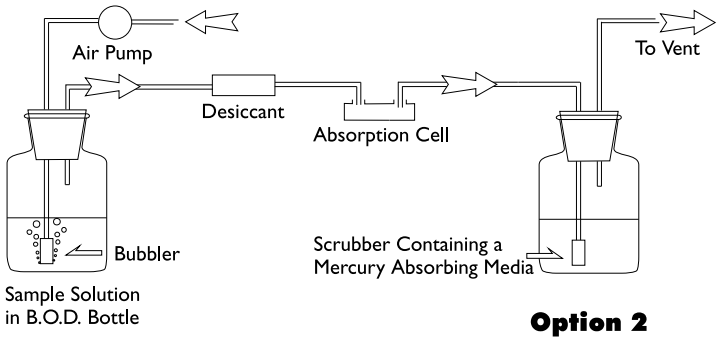
6. Code of Federal Regulations 40, Ch. 1, Pt. 136 Appendix B.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

TABLE 1. INTERLABORATORY PRECISION AND ACCURACY DATA FOR FLAMELESS ATOMIC ABSORPTION

Number of Labs	True Values µg/L	Mean Value µg/L	Standard Deviation µg/L	RSD %	Mean Accuracy as % Bias
76	0.21	0.349	0.276	89	66
80	0.27	0.414	0.279	67	53
82	0.51	0.674	0.541	80	32
77	0.60	0.709	0.390	55	18
82	3.4	3.41	1.49	44	0.34
79	4.1	3.81	1.12	29	-7.1
79	8.8	8.77	3.69	42	-0.4
78	9.6	9.10	3.57	39	-5.2





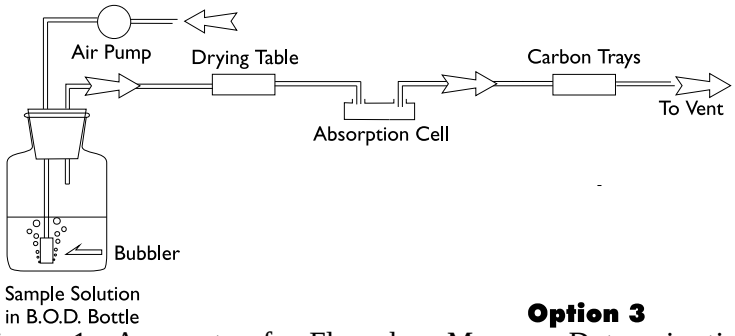


Figure 1. Apparatus for Flameless Mercury Determination

Because of the toxic nature of mercury vapor, inhalation must be avoided. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as:

a) equal volumes of 0.1 N $KMnO_4$ and 10% H_2SO_4
b) 0.25% iodine in a 3% KI solution.

A specially treated charcoal that will absorb mercury vapor is also available from Barnebey and Cheney, P.O. Box 2526, Columbus, OH 43216, Catalog No. 580-13 or 580-22.