



Designation: D3223 – 02(Reapproved 2007)^{ε1}

Standard Test Method for Total Mercury in Water¹

This standard is issued under the fixed designation D3223; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense.

^{ε1} NOTE—Reference to Practice D2777 – 77 was editorially updated to D2777 – 06 in August 2007.

1. Scope

1.1 This test method² covers the determination of total mercury in water in the range from 0.5 to 10.0 $\mu\text{g Hg/L}$ (**1**).³ The test method is applicable to fresh waters, saline waters, and some industrial and sewage effluents. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

1.1.1 The analyst should recognize that the precision and bias of this standard may be affected by the other constituents in all waters, as tap, industrial, river, and wastewaters. The cold vapor atomic absorption measurement portion of this method is applicable to the analysis of materials other than water (sediments, biological materials, tissues, etc.) if, and only if, an initial procedure for digesting and oxidizing the sample is carried out, ensuring that the mercury in the sample is converted to the mercuric ion, and is dissolved in aqueous media (**2,3**).

1.2 Both organic and inorganic mercury compounds may be analyzed by this procedure if they are first converted to mercuric ions. Using potassium persulfate and potassium permanganate as oxidants, and a digestion temperature of 95°C, approximately 100 % recovery of organomercury compounds can be obtained (**2,4**).

1.3 The range of the test method may be changed by instrument or recorder expansion or both, and by using a larger volume of sample.

1.4 A method for the disposal of mercury-containing wastes is also presented (**Appendix X1**) (**5**).

¹ This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

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² Adapted from research investigations by the U. S. Environmental Protection Agency's Analytical Quality Control Laboratory, Cincinnati, OH, and Region IV Surveillance and Analysis Division, Chemical Services Branch, Athens, GA.

³ The boldface numbers in parentheses refer to the references at the end of this test method.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see 7.8 and 10.8.2.

2. Referenced Documents

2.1 ASTM Standards:⁴

D512 Test Methods for Chloride Ion In Water

D1129 Terminology Relating to Water

D1193 Specification for Reagent Water

D1245 Practice for Examination of Water-Formed Deposits by Chemical Microscopy

D1252 Test Methods for Chemical Oxygen Demand (Dichromate Oxygen Demand) of Water

D1426 Test Methods for Ammonia Nitrogen In Water

D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water

D3370 Practices for Sampling Water from Closed Conduits

D4691 Practice for Measuring Elements in Water by Flame

Atomic Absorption Spectrophotometry

D4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents

D5810 Guide for Spiking into Aqueous Samples

D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis

3. Terminology

3.1 *Definitions:* For definitions of terms used in this test method, refer to Terminology D1129.

4. Summary of Test Method

4.1 The test method consists of a wet chemical oxidation which converts all mercury to the mercuric ion; reduction of mercuric ions to metallic mercury, followed by a cold vapor

⁴ For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

atomic absorption analysis (1,2). A general guide for flame and vapor generation atomic absorption applications is given in Practice D4691.

4.2 Cold vapor atomic absorption analysis is a physical method based on the absorption of ultraviolet radiation at a wavelength of 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in either a closed recirculating system or an open one-pass system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance is measured as a function of mercury concentration.

5. Significance and Use

5.1 The presence of mercury in industrial discharge, domestic discharge, and potable water is of concern to the public because of its toxicity. Regulations and standards have been established that require the monitoring of mercury in water. This test method provides an analytical procedure to measure total mercury in water.

6. Interference

6.1 Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from distilled water (2).

6.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L have no effect on the recovery of mercury from spiked samples (2).

6.3 Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 mL). During the oxidation step chlorides are converted to free chlorine which will also absorb radiation at 253.7 nm. Care must be taken to assure that free chlorine is absent before mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). The dead air space in the reaction flask must also be purged before the addition of stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from sea water using this technique (2).

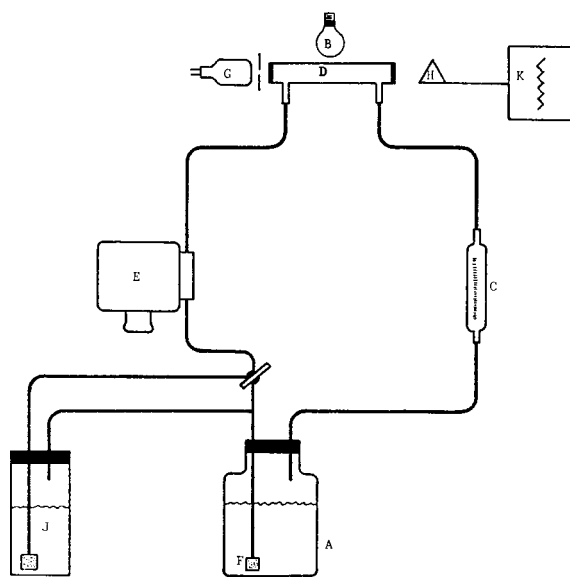
6.4 Volatile organic materials that could interfere will be removed with sample digestion as described in 11.2 through 11.4.

7. Apparatus

NOTE 1—Take care to avoid contamination of the apparatus with mercury. Soak all glass apparatus, pipets, beakers, aeration tubes, and reaction flasks in nitric acid (HNO₃) (1 + 1), and rinse with mercury-free water before use.

7.1 The schematic arrangement of the closed recirculating system is shown in Fig. 1 and the schematic arrangement of the open one-pass system is shown in Fig. 2.

7.2 *Atomic Absorption Spectrophotometer*—A commercial atomic absorption instrument is suitable if it has an open-burner head area in which to mount an absorption cell, and if it provides the sensitivity and stability for the analyses. Also instruments designed specifically for the measurement of



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|---------------------------------------|--|
| A—Reaction flask | G—Hollow cathode mercury lamp |
| B—60-W light bulb | H—Atomic absorption detector |
| C—Rotameter, 1 L of air per minute | J—Gas washing bottle containing 0.25 % iodine in a 3 % potassium iodide solution |
| D—Absorption cell with quartz windows | K—Recorder, any compatible model |
| E—Air pump, 1 L of air per minute | |
| F—Glass tube with fritted end | |

FIG. 1 Schematic Arrangement of Equipment for Mercury Measurement by Cold Vapor Atomic Absorption Technique Closed Recirculating System

mercury using the cold vapor technique in the working range specified may be used.

7.2.1 *Mercury Hollow Cathode Lamp*.

7.2.2 *Simultaneous Background Correction*—Background correction may be necessary to compensate for molecular absorption that can occur at this mercury wavelength. It is the analyst's responsibility to determine the applicable use.

7.3 *Recorder*—Any multirange variable speed recorder that is compatible with the ultraviolet (UV) detection system is suitable.

7.4 *Absorption Cell*—The cell (Fig. 3) is constructed from glass 25.4-mm outside diameter by 114 mm (Note 2). The ends are ground perpendicular to the longitudinal axis and quartz windows (25.4-mm diameter by 1.6 mm thickness) are cemented in place. Gas inlet and outlet ports (6.4-mm diameter) are attached approximately 12 mm from each end. The cell is strapped to a support and aligned in the light beam to give maximum transmittance.

NOTE 2—An all-glass absorption cell, 18 mm in outside diameter by 200 mm, with inlet 12 mm from the end, 18-mm outside diameter outlet in the center, and with quartz windows has been found suitable. Methyl methacrylate tubing may also be used.

7.5 *Air Pump*—A peristaltic pump, with electronic speed control, capable of delivering 1 L of air per minute may be used. Regulated compressed air can be used in the open one-pass system.

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

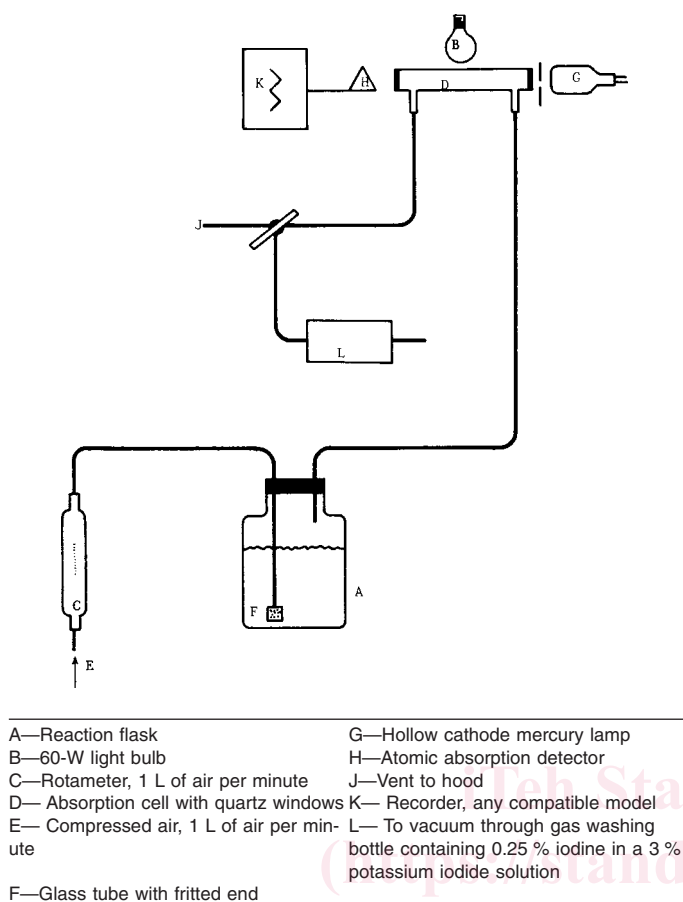
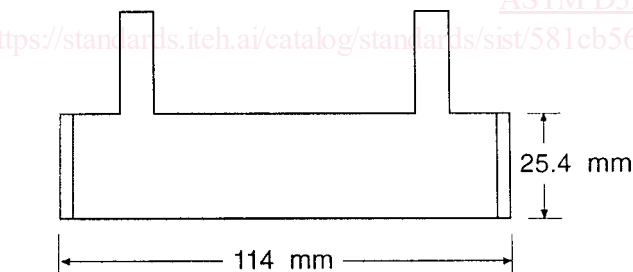


FIG. 2 Schematic Arrangement of Equipment for Mercury Measurement by Cold Vapor Atomic Absorption Technique Open One-Pass System



NOTE 1—The length and outside diameter of the cell are not critical. The body of the cell may be of any tubular material but the end windows must be of quartz because of the need for UV transparency. The length and diameter of the inlet and outlet tubes are not important, but their position may be a factor in eliminating recorder noise. There is some evidence that displacement of the air inlet tube away from the end of the cell results in smoother readings. A mild pressure in the cell can be tolerated, but too much pressure may cause the glued-on end windows to pop off. Cells of this type may be purchased from various supply houses.

FIG. 3 Cell for Mercury Measurement by Cold-Vapor Technique

7.7 Aeration Tubing—A straight glass frit having a coarse porosity is used in the reaction flask. Clear flexible vinyl plastic tubing is used for passage of the mercury vapor from the reaction flask to the absorption cell.

7.8 Lamp—A small reading lamp containing a 60-W bulb is used to prevent condensation of moisture inside the cell. The

lamp shall be positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient. Alternatively, a drying tube, 150 by 18 mm in diameter, containing 20 g of magnesium perchlorate, may be placed in the line to prevent moisture in the absorption cell. (**Warning**—If the presence of organic vapors is expected, the purity of the drying agent should be determined to establish the absence of traces of free perchloric acid in the salt. This is to prevent the formation of perchloric esters, some of which are known to be violently explosive compounds.)

7.9 Reaction Flask—A 250- to 300-mL glass container fitted with a rubber stopper may be used.

8. Reagents

8.1 Purity of Reagents—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society.⁵ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 Purity of Water—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D1193 Type I. Other reagent water types may be used, provided it is first ascertained that the water is of sufficiently high purity to permit its use without adversely affecting the bias and precision of the test method. Type II water was specified at the time of round-robin testing of this test method.

8.3 Mercury Solution, Stock (1 mL = 1 mg Hg)—Dissolve 0.1354 g of mercuric chloride (HgCl₂) in a mixture of 75 mL of water and 10 mL of HNO₃ (sp gr 1.42) and dilute to 100 mL with water.

8.4 Mercury Solution, Intermediate (1 mL = 10 µg Hg)—Pipet 10.0 mL of the stock mercury solution into a mixture of 500 mL of water and 2 mL of HNO₃ (sp gr 1.42) and dilute to 1 L with water. Prepare fresh daily.

8.5 Mercury Solution, Standard (1 mL = 0.1 µg Hg)—Pipet 10.0 mL of the intermediate mercury standard into a mixture of 500 mL of water and 2 mL of HNO₃ (sp gr 1.42) and dilute to 1 L with water. Prepare fresh daily.

8.6 Nitric Acid (sp gr 1.42)—Concentrated nitric acid (HNO₃).

NOTE 3—If the reagent blank concentration is greater than the method detection limit, distill the HNO₃ or use a spectrograde acid.

8.7 Potassium Permanganate Solution (50 g/L)—Dissolve 50 g of potassium permanganate (KMnO₄) in water and dilute to 1 L.

8.8 Potassium Persulfate Solution (50 g/L)—Dissolve 50 g of potassium persulfate (K₂S₂O₈) in water and dilute to 1 L.

⁵ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For Suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

8.9 *Sodium Chloride-Hydroxylamine Sulfate Solution* (120 g/L)—Dissolve 120 g of sodium chloride (NaCl) and 120 g of hydroxylamine sulfate [(NH₂OH)₂H₂SO₄] in water and dilute to 1 L.

NOTE 4—The analyst may wish to use hydroxylamine hydrochloride instead of hydroxylamine sulfate. The analyst should dissolve 12 g of hydroxylamine hydrochloride in 100 mL of Type I water.

8.10 *Stannous Sulfate Solution* (100 g/L)—Dissolve 100 g of stannous sulfate (SnSO₄) in water containing 14 mL of H₂SO₄ (sp gr 1.84) and dilute to 1 L. This mixture is a suspension and should be mixed continuously when being applied as a reagent.

NOTE 5—The analyst may wish to use stannous chloride instead of stannous sulfate. Stannous chloride crystal (100 g in 50 mL) should be dissolved in concentrated HCl. The solution is heated and cooled until dissolved and diluted to 1 L.

8.11 *Sulfuric Acid* (sp gr 1.84)—Concentrated sulfuric acid (H₂SO₄).

9. Sampling

9.1 Collect the samples in accordance with Practices **D3370**. The holding time for the samples can be calculated in accordance with Practice **D4841**.

9.2 Collect samples in acid-washed glass or high density-hard polyethylene bottles. Samples shall be analyzed within 38 days if collected in glass bottles, and within 13 days if collected in polyethylene bottles (**6**).

9.3 Samples shall be preserved with HNO₃ (sp gr 1.42) to a pH of 2 or less immediately at the time of collection, normally about 2 mL/L of HNO₃. If only dissolved mercury is to be determined, the sample, before acidification shall be filtered through a 0.45-μm membrane filter using an all-glass filtering apparatus.

10. Calibration

10.1 Transfer 0, 1.0, 2.0, 5.0, and 10.0 mL-aliquots of the standard mercury solution containing 0 to 1.0 μg of mercury to a series of reaction flasks. Add enough water to each flask to make a total volume of 100 mL.

10.2 Mix thoroughly and add cautiously 5 mL of H₂SO₄ (sp gr 1.84) and 2.5 mL of HNO₃ (sp gr 1.42) to each flask.

NOTE 6—Loss of mercury may occur at elevated temperatures. However, with the stated amounts of acid the temperature rise is only about 13°C (25–38°C) and no losses of mercury will occur (**2**).

10.3 Add 15 mL of KMnO₄ solution to each bottle and allow to stand at least 15 min.

10.4 Add 8 mL of K₂S₂O₈ solution to each flask, heat for 2 h in a water bath at 95°C, and cool to room temperature.

10.5 Turn on the circulating pump and adjust its rate to 1 L/min. The pump may be allowed to run continuously throughout the entire series of samples.

10.6 Add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate, as evident by loss of solution color. Refer to **Note 4**.

10.7 After waiting 30 s treat each flask individually by adding 5 mL of the SnSO₄ solution and immediately attach the bottle to the aeration apparatus forming a closed system. Refer to **Note 5**.

10.8 After the absorbance has reached a maximum and the recorder pen has leveled off, prepare the system for the next standard by one of the following procedures:

10.8.1 *Closed Recirculating System*—Open the bypass valve and continue aeration until the absorbance returns to its minimum value. Close the bypass valve, remove the stopper and frit from the reaction flask, and continue the aeration.

10.8.2 *Open One-Pass System*—Remove the stopper and frit from the reaction flask, open the valve, and evacuate the system with vacuum until the absorbance returns to its minimum value. Close the valve and continue aeration. (**Warning**—Because of the toxic nature of mercury vapor, precaution must be taken to avoid its inhalation. 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 KMnO₄ solution and 10 % H₂SO₄, or (b) 0.25 % iodine in 3 % KI solution.)

10.9 Proceed with the standards and construct a standard curve by plotting peak height versus micrograms of mercury.

11. Procedure

11.1 Transfer 100 mL or an aliquot diluted to 100 mL containing not more than 1.0 μg of mercury to a reaction flask.

11.2 Add cautiously 5 mL of H₂SO₄ (sp gr 1.84) and 2.5 mL of HNO₃ (sp sr 1.42) mixing after each addition (**10.8.2**).

11.3 Add 15 mL of KMnO₄ solution to each sample bottle. Shake and add additional portions of KMnO₄ solution until the purple color persists for at least 15 min.

11.4 Add 8 mL of K₂S₂O₈ solution to each flask and heat for 2 h in a water bath at 95°C and cool to room temperature.

11.5 Turn on the circulating system and adjust its rate to 1 L/min. The pump may be allowed to run continuously throughout the entire series of samples.

11.6 Add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate as evident by loss of solution color. Refer to **Note 4**.

11.7 Wait 30 s and add 5 mL of SnSO₄ solution to each flask individually and immediately attach it to the aeration apparatus. Refer to **Note 5**.

11.8 Continue as described in **10.8**.

12. Calculation

12.1 Determine the peak height of the unknown from the recorder chart and read the micrograms of mercury from the standard curve.

12.2 Calculate the mercury concentration in the sample as follows:

$$\text{Mercury (total), } \mu\text{g/L} = (W \times 1000)/S$$

where: