Designation: D3223 – 12

Standard Test Method for Total Mercury in Water[1]

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 U.S. Department of Defense.

1. Scope*

1.1 This test method[2] covers the determination of total mercury in water in the range from 0.5 to 10.0 µg 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 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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

1.6 *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 and .

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

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[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.

[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.

***A Summary of Changes section appears at the end of this standard**

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.

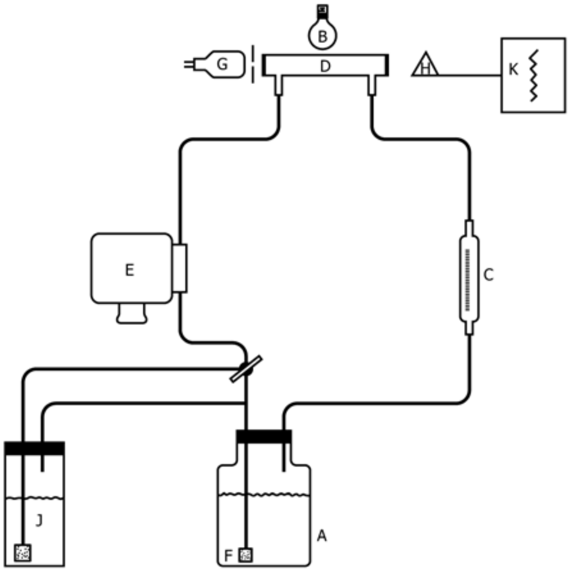
7. Apparatus

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 (HNO_3) (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 mercury using the cold vapor technique in the working range specified may be used. Direct reading instruments are also acceptable.

7.2.1 *Mercury Hollow Cathode Lamp.*



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

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

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.

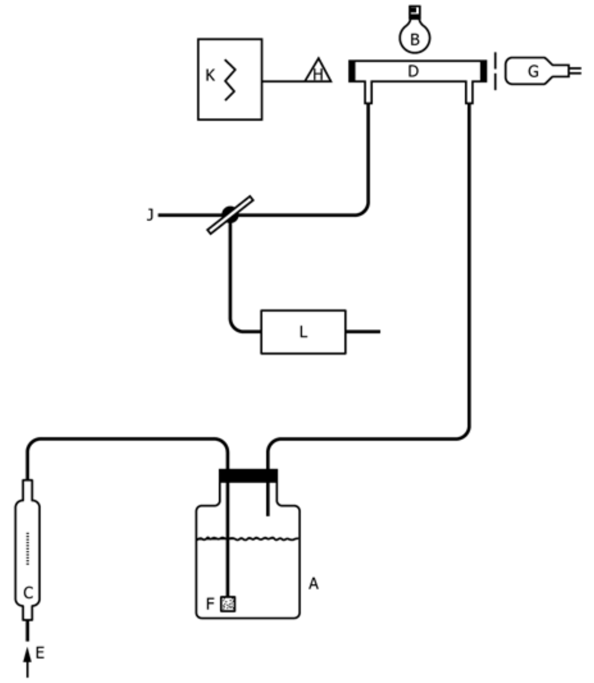
7.4 *Absorption Cell*—The cell (Fig. 3) is constructed from glass 25.4-mm outside diameter by 114 mm (Note 2). The ends are ground perpendicular to the longitudinal axis and quartz windows (25.4-mm diameter by 1.6 mm thickness) are cemented in place. Gas inlet and outlet ports (6.4-mm diameter) are attached 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.

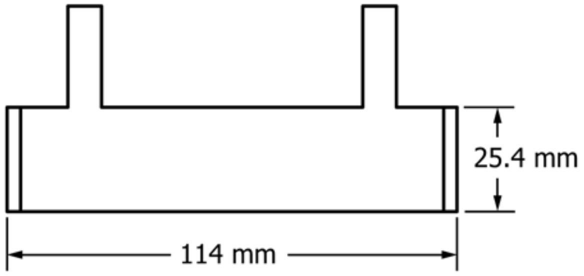
7.6 *Flowmeter,* capable of measuring an air flow of 1 L/min.

7.7 *Aeration Tubing*—A straight glass frit having a coarse porosity is used in the reaction flask. Clear flexible vinyl plastic



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

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

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 ($HgCl_2$) in a mixture of 75 mL of water and 10 mL of HNO_3 (sp gr 1.42) and dilute to 100 mL with water. A purchased mercury stock solution of appropriate known purity is also acceptable.

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 HNO_3 (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 HNO_3 (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 (HNO_3).

NOTE 3—If the reagent blank concentration is greater than the method detection limit, distill the HNO_3 or use a spectrograde acid.

8.7 *Potassium Permanganate Solution* (50 g/L)—Dissolve 50 g of potassium permanganate ($KMnO_4$) in water and dilute to 1 L.

8.8 *Potassium Persulfate Solution* (50 g/L)—Dissolve 50 g of potassium persulfate ($K_2S_2O_8$) in water and dilute to 1 L.

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[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 [$(NH_2OH)_2H_2SO_4$] 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 ($SnSO_4$) in water containing 14 mL of H_2SO_4 (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 (H_2SO_4).

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 **(8)**.

9.3 Samples shall be preserved with HNO_3 (sp gr 1.42) to a pH of 2 or less immediately at the time of collection, normally about 2 mL/L of HNO_3. 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.

NOTE 6—Alternatively, the pH may be adjusted in the laboratory if the sample is returned within 14 days. This could reduce hazards of working with acids in the field when appropriate.

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 H_2SO_4 (sp gr 1.84) and 2.5 mL of HNO_3 (sp gr 1.42) to each flask.

NOTE 7—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 $KMnO_4$ solution (8.7) to each bottle and allow to stand at least 15 min.

10.4 Add 8 mL of $K_2S_2O_8$ solution (8.8) 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 (8.9) 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 $SnSO_4$ solution (8.10) 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* $KMnO_4$ solution and 10 % H_2SO_4, 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 H_2SO_4 (sp gr 1.84) and 2.5 mL of HNO_3 (sp sr 1.42) mixing after each addition ().

11.3 Add 15 mL of $KMnO_4$ solution (8.7) to each sample bottle. Shake and add additional portions of $KMnO_4$ solution until the purple color persists for at least 15 min.

11.4 Add 8 mL of $K_2S_2O_8$ solution (8.8) to each flask and heat for 2 h in a water bath at 95°C and cool to room temperature.

NOTE 8—Many laboratories have found block digestion systems a useful way to digest samples for trace metals analysis. Systems typically consist of either a metal or graphite block with wells to hold digestion tubes. The block temperature controller must be able to maintain uniformity of temperature across all positions of the block. For trace metals analysis, the digestion tubes should be constructed of polypropylene and have a volume accuracy of at least 0.5%. All lots of tubes should come with a certificate of analysis to demonstrate suitability for their intended purpose.

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 (8.9) 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 $SnSO_4$ solution (8.10) 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:

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

where:

W = mercury in aliquot determined from calibration curve, μg, and

S = aliquot used for analysis, mL.

13. Precision and Bias (7,8)[6]

13.1 ASTM and the U. S. Environmental Protection Agency conducted a joint study of this test method in October 1972. One hundred and one laboratories from the United States and Canada, including federal, state and local agencies, universities and private and industrial groups, participated in the interlaboratory study.

NOTE 9—If the analyst uses hydroxylamine hydrochloride instead of hydroxylamine sulfate and stannous chloride instead of stannous sulfate, then it is the analyst's responsibility to determine the precision and bias of this test method.

13.2 Eight water sample concentrates were prepared in sealed glass ampules by dissolving weighed amounts of reagent grade chemicals in reagent water, Type II, to produce accurately known concentrations of inorganic and organic mercury. All eight samples contained the same ratio of inorganic to organic mercury, 40 to 60, as mercuric chloride and methyl mercury chloride, respectively.

13.3 Each laboratory was instructed to dilute a separate 5.0-mL aliquot of each concentrate to 1 L with reagent water and to 1L with a natural water or wastewater of their choice. Then, the laboratory was instructed to perform a single analysis on each of the resulting sixteen samples. The natural water was also analyzed without a spike to determine the background level of mercury.

13.4 The precision of this test method within the range from 0.2 to 10 μg/L mercury may be expressed as follows:

In reagent water, Type II:

$$S_t = 0.307X + 0.183$$

$$S_0 = 0.076X + 0.293$$

In natural waters:

$$S_t = 0.386X + 0.107$$

$$S_0 = 0.145X + 0.023$$

where:

S_t = overall precision,

S_0 = single-operator precision, and

X = determined concentration of mercury, μg/L.

13.5 *Bias*—Recoveries of known amounts of mercury are shown in Table 1.

13.6 These data apply to fresh water, saline waters, and some industrial and sewage effluents. It is the analyst's responsibility to ensure the validity of the test method to waters of other matrices or to a particular matrix.

13.7 Precision and bias for this test method conform to Practice D2777 – 77, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of Practice D2777 – 08, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

14. Quality Control

14.1 In order to be certain that analytical values obtained using these test methods are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when analyzing mercury.

14.2 *Calibration and Calibration Verification:*

14.2.1 Analyze at least three working standards containing concentrations of mercury that bracket the expected sample concentration prior to analysis of samples to calibrate the instrument.

14.2.2 Verify instrument calibration after standardization by analyzing a standard at the concentration of one of the calibration standards. The absorbance shall fall within 4 % of the absorbance from the calibration. Alternately, the concentration of a mid-range standard should fall within ±10% of the known concentration.

14.2.3 If calibration cannot be verified, recalibrate the instrument.

14.2.4 It is recommended to analyze a continuing calibration blank (CCB) and continuing calibration verification (CCV) at a 10% frequency.

TABLE 1 Determination of Precision and Bias

Amount Added, μg/L Hg	Amount Found, μg/L Hg	% Bias	Statistically Significant, 95 % Confidence Level	Overall Precision, S_t	Degrees of Freedom
		Reagent water, Type II			
0.21	0.418	+ 99.0	yes	0.226	71
0.27	0.450	+ 66.7	yes	0.213	70
0.51	0.653	+ 28.0	yes	0.377	75
0.60	0.744	+ 24.0	yes	0.344	71
3.4	3.49	+ 0.03	no	0.71	74
4.1	4.28	+ 3.9	no	0.80	73
8.8	8.48	–3.6	no	1.56	72
9.6	9.38	–2.3	no	1.67	72
		Natural water of choice			
0.21	0.349	+ 66.2	yes	0.174	56
0.27	0.414	+ 53.3	yes	0.262	59
0.51	0.674	+ 32.2	yes	0.381	64
0.60	0.709	+ 18.2	yes	0.359	61
3.4	3.41	+ 0.3	no	0.71	66
4.1	3.81	–7.1	yes	0.72	62
8.8	8.77	–0.34	no	1.68	63
9.6	9.10	–5.2	no	1.98	60

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[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1019. Contact ASTM Customer Service at service@astm.org.

14.3 *Initial Demonstration of Laboratory Capability:*

14.3.1 If a laboratory has not performed the test before, or if there has been a major change in the measurement system, for example, new analyst, new instrument, etc., a precision and bias study must be performed to demonstrate laboratory capability.

14.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material containing a mid-range concentration of mercury. The matrix and chemistry of the solution should be equivalent to the solution used in the collaborative study. Each replicate must be taken through the complete analytical test method including any sample preservation and pretreatment steps.

14.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in Table 1. This study should be repeated until the recoveries are within the limits given in Table 1. If a concentration other than the recommended concentration is used, refer to Test Method D5847 for information on applying the F test and t test in evaluating the acceptability of the mean and standard deviation.

14.4 *Laboratory Control Sample (LCS):*

14.4.1 To ensure that the test method is in control, analyze a LCS containing a mid-range concentration of mercury with each batch or 10 samples. If large numbers of samples are analyzed in the batch, analyze the LCS after every 10 samples. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The result obtained for the LCS shall fall within ±15 % of the known concentration.

14.4.2 If the result is not within these limits, analysis of samples is halted until the problem is corrected, and either all the samples in the batch must be reanalyzed, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

14.5 *Method Blank:*

14.5.1 Analyze a reagent water test blank with each batch. The concentration of mercury found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of mercury is found above this level, analysis of samples is halted until the contamination is eliminated, and a blank shows no contamination at or above this level, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

14.6 *Matrix Spike (MS):*

14.6.1 To check for interferences in the specific matrix being tested, perform a MS on at least one sample from each batch by spiking an aliquot of the sample with a known concentration of mercury and taking it through the analytical method.

14.6.2 The spike concentration plus the background concentration of mercury must not exceed the high calibration standard. The spike must produce a concentration in the spiked sample that is 2 to 5 times the analyte concentration in the unspiked sample, or 10 to 50 times the detection limit of the test method, whichever is greater.

14.6.3 Calculate the percent recovery of the spike (P) using the following formula:

$$P = 100\left[A\left(V_s + V\right) - B\ V_s\right] \over C\ V \tag{1}$$

where:

A = analyte known concentration (µg/L) in spiked sample
B = analyte known concentration (µg/L) in unspiked sample
C = known concentration (µg/L) of analyte in spiking solution
V_s = volume (mL) of sample used, and
V = volume (mL) of spiking solution added.

14.6.4 The percent recovery of the spike shall fall within the limits based on the analyte concentration, listed in Guide D5810, Table 1. If the percent recovery is not within these limits, a matrix interference may be present in the sample selected for spiking. Under these circumstances, one of the following remedies must be employed: the matrix interference must be removed, all samples in the batch must be analyzed by a test method not affected by the matrix interference, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method. Note: acceptable spike recoveries are dependent on the concentration of the component of interest. See Guide D5810 for additional information.

14.7 *Duplicate:*

14.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each batch. If the concentration of the analyte is less than five times the detection matrix spike duplicate (MSD) should be used.

14.7.2 Calculate the standard deviation of the duplicate values and compare to the precision in the collaborative study using an F test. Refer to 6.4.4 of Test Method D5847 for information on applying the F test.

14.7.3 If the result exceeds the precision limit, the batch must be reanalyzed or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

14.8 *Independent Reference Material (IRM):*

14.8.1 In order to verify the quantitative value produced by the test method, analyze an IRM submitted as a regular sample (if practical) to the laboratory at least once per quarter. The concentration of the reference material should be in the concentration mid-range for the method chosen. The value obtained must fall within the control limits established by the laboratory.

15. Keywords

15.1 atomic absorption; cold vapor technique; mercury; total mercury

APPENDIX

(Nonmandatory Information)

X1. DISPOSAL OF MERCURY-CONTAINING WASTES (5)

X1.1 Introduction

X1.1.1 The practices described in this Appendix may not be legal in some jurisdictions.

X1.1.2 Mercury salts are components of the wastes from the following ASTM determinations: Test Methods D1252, D1426, D512, and D1245. Also, mercuric chloride is often used to preserve water samples for nitrogen and phosphorus analysis.

X1.1.3 Mercury salts may be retained most safely in the sulfide form at high pH. Acidic solutions should be neutralized and combined with alkaline wastes and water samples containing mercury preservatives. To precipitate mercury, a convenient source of the sulfide ion is sodium thiosulfate. However, it should not be added to acidified wastes because of its rapid decomposition to elemental sulfur. The sulfur which precipitates increases the volume of sludge which must be processed and stored.

X1.1.4 Mercury sulfide is insoluble and is stable to most reagents except aqua regia and bromine. Bacterial conversions to methyl mercury is prevented by maintaining the pH above 10.

X1.2 Procedure

X1.2.1 Dilute all combined acidic wastes to about twice their original volume.

X1.2.2 Adjust the pH to greater than 7 by slowly adding sodium hydroxide solution (40 to 50 %, w/v) with stirring and combine this neutralized waste and any pooled alkaline wastes with stirring. At this point the combined wastes should have a pH of 10 or higher; if not, add sodium hydroxide until a pH of 10 to 11 is attained.

X1.2.3 Stir in small portions of sodium thiosulfate solution (40 to 50 %, w/v) while the combined alkaline wastes are still warm and until no further precipitation seems to occur.

X1.2.4 Allow the precipitate to settle and draw off a few millilitres of the clear supernatant liquid making sure the pH is still above 10, and then add an equal volume of sodium thiosulfate solution. If the supernatant still contains dissolved mercury, a precipitate will rapidly form, indicating that additional sodium thiosulfate shall be added to the waste slurry.

X1.2.5 Decant or siphon off the clear tested supernatant and discard it after the precipitate has settled.

X1.2.6 Wash the precipitate twice with water containing a trace of NaOH, allow to settle, and discard both of the clear washings.

X1.2.7 Dry the washed precipitate first in air, then in an oven at a temperature no higher than 110°C.

X1.2.8 Store the dry solids until a sufficient quantity has accumulated to justify shipment to a commercial reprocessor (**5**).[7] Metallic mercury and waste organomercurials should be stored in suitable airtight containers until a commercial reprocessor can be contacted for specific shipping instructions.[7]

NOTE X1.1—It is the responsibility of the analyst to ensure that the supernatant and the precipitate are disposed of properly, meeting disposal regulations.

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[7] Names of suitable reprocessors of mercury are available from ASTM International Headquarters.

REFERENCES

(1) Hatch, W. R. and Ott, W. L., “Determination of Sub-Microgram Quantities of Mercury by Atomic Absorption Spectrophotometry,” *Analytical Chemistry*, Vol 40, 1968, p. 2085.

(2) Kopp, J. F., Longbottom, M. C., and Lobring, L. B.,“ Cold Vapor Method for Determining Mercury,” Vol 64, 1972, p. 20.

(3) Uthe, J. F., Armstrong, F. A. J., and Stainton, M. P., “Mercury Determination in Fish Samples by Wet Digestion and Flameless Atomic Absorption Spectrophotometry,” *Journal of Fisheries Research Board of Canada*, Vol 27, 1970, p. 805.

(4) “Mercury Recovery Study,” Environmental Protection Agency, Region IV Surveillance and Analysis Division, Athens, GA (notpublished).

(5) Dean, R. B., Williams, R. T., and Wise, R. H.,“ Disposal of Mercury Wastes From Water Laboratories,” *Environmental Science and Technology*, Vol 5, 1971, p. 1044.

(6)

(7)

(8) “Mercury Preservation Study,” Environmental Protection Agency, Region IV, Surveillance and Analysis Division, Athens, GA (not published).

(9) “ASTM-EPA Method Study of Total Mercury in Water,” Environmental Protection Agency, Analytical Quality Control Laboratory, Cincinnati, OH, December 1972.

(10) *Water Quality Parameters, ASTM STP 573*, 1975, pp. 566–580.

SUMMARY OF CHANGES

Committee D19 has identified the location of selected changes to this standard since the last issue (D3223 – 02 (2007)$^{\varepsilon 1}$) that may impact the use of this standard. (Approved Sept. 1, 2012.)

(1) The SI statement was added to Section 1.
(2) Section 7 was modified to allow for direct reading instruments.
(3) Section 8.3 was modified to allow for commercial standards.
(4) Section 9 was modified to allow for pH of the samples in the laboratory.
(5) Reagent references were added to sections 10 and 11.
(6) Section 11 was modified to include note about the use of block digestion systems.
(7) Sections 14.2.4, 14.3.2 and 14.6.3 were modified.

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