Designation: D3697 − 17

Standard Test Method for Antimony in Water[1]

This standard is issued under the fixed designation D3697; 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.

1. Scope*

1.1 This test method covers the determination of dissolved and total recoverable antimony in water by atomic absorption spectroscopy.[2]

1.2 This test method is applicable in the range from 1 to 15 µg/L of antimony. The range may be extended by less scale expansion or by dilution of the sample.

1.3 The precision and bias data were obtained on reagent water, tap water, salt water, and two untreated wastewaters. The information on precision and bias may not apply to other waters.

1.4 The values stated in SI units are to be regarded as standard. The values given in parentheses are mathematical conversion to inch-pound units that are provided for information only and are not considered standard.

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.*

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D1129 Terminology Relating to Water
D1193 Specification for Reagent 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
D5673 Test Method for Elements in Water by Inductively Coupled Plasma—Mass Spectrometry
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:*

3.1.1 For definitions of terms used in this standard, refer to Terminology D1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *continuing calibration blank, n*—a solution containing no analytes (of interest) which is used to verify blank response and freedom from carryover.

3.2.2 *continuing calibration verification, n*—a solution (or set of solutions) of known concentration used to verify freedom from excessive instrumental drift; the concentration is to cover the range of calibration curve.

3.2.3 *laboratory control sample, n*—a solution with a certified concentration of the antimony.

3.2.4 *total recoverable antimony, n*—a descriptive term relating to forms of antimony that are determinable by the digestion method which is included in the procedure; some organic compounds may not be completely recovered.

4. Summary of Test Method

4.1 Organic antimony-containing compounds are decomposed by adding sulfuric and nitric acids and repeatedly evaporating the sample to fumes of sulfur trioxide. The antimony so produced, together with inorganic antimony originally present, is subsequently reacted with potassium iodide and stannous chloride, and finally with sodium borohydride to form stibine. The stibine is removed from solution by aeration and swept by a flow of nitrogen into a hydrogen flame where it is determined by atomic absorption at 217.6 nm.

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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] Platte, J. A., and Marcy, V. M., "A New Tool for the Water Chemist," *Industrial Water Engineering*, IWEGA, May 1965.

[3] 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**

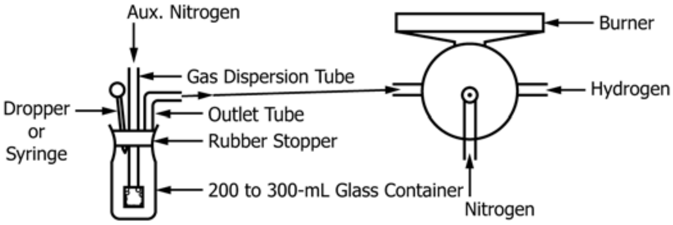

FIG. 1 Stibine Vapor Analyzer

5. Significance and Use

5.1 Because of the association with lead and arsenic in industry, it is often difficult to assess the toxicity of antimony and its compounds. In humans, complaints referable to the nervous system have been reported. In assessing human cases, however, the possibility of lead or arsenic poisoning must always be borne in mind. Locally, antimony compounds are irritating to the skin and mucous membranes.

5.2 ICP-MS may also be appropriate but at a higher instrument cost. See Test Method D5673.

6. Interference

6.1 Since the stibine is freed from the original sample matrix, interferences in the flame are minimized.

6.2 Selenium and arsenic, which also form hydrides, do not interfere at concentrations of 100 µg/L. Higher concentrations were not tested.

7. Apparatus

7.1 *Atomic Absorption Spectrophotometer,* for use at 217.6 nm with a scale expansion of approximately 3. A general guide for the use of flame atomic absorption applications is given in Practice D4691.

NOTE 1—The manufacturer's instructions should be followed for all instrumental parameters.

7.1.1 *Antimony Electrodeless Discharge Lamp.*

7.2 *Recorder or Digital Readout*—Any multirange variable speed recorder or digital readout accessory, or both, that is compatible with the atomic absorption spectrophotometer is suitable.

7.3 *Stibine Vapor Analyzer,* assembled as shown in Fig. 1.

NOTE 2—A static system, such as one using a balloon, has been found to be satisfactory. See McFarren (1979).[4]

8. Reagents and Materials

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 for the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[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, II, or III water. Type I is preferred and more commonly used. 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 precision and bias of the test method. Type II water was specified at the time of round robin testing of these test methods.

NOTE 3—The user must ensure the type of reagent water chosen is sufficiently free of interferences. The water should be analyzed using the test method.

8.3 *Antimony Solution, Stock* (1.00 mL = 100 µg Sb)—Dissolve 274.3 mg of antimony potassium tartrate, $KSbOC_4H_4O_6 \cdot 1/2H_2O$, in water and dilute to 1000 mL with water. A purchased antimony stock solution of appropriate known purity is also acceptable.

8.4 *Antimony Solution, Intermediate* (1.00 mL = 10 µg Sb)—Dilute 50.0 mL of antimony stock solution to 500.0 mL with water.

8.5 *Antimony Solution, Standard* (1.0 mL = 0.10 µg Sb)—Dilute 5.0 mL of antimony intermediate solution to 500.0 mL with water. Prepare fresh before each use, or as determined by Practice D4841. This standard is used to prepare working standards at the time of analysis, or as determined by Practice D4841.

8.6 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl).

8.7 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO_3).

8.8 *Nitric Acid* (1 + 1)—Add 250 mL of concentrated nitric acid (sp gr 1.42) to 250 mL of water.

8.9 *Potassium Iodide Solution* (15 g/100 mL)—Dissolve 15 g of potassium iodide (KI) in 100 mL of water. This solution is stable when stored in an amber bottle or in the dark.

8.10 *Sodium Borohydride Solution* (4 g/100 mL)—Dissolve 4 g of sodium borohydride ($NaBH_4$) and 2 g of sodium hydroxide (NaOH) in 100 mL water. Prepare weekly.

8.11 *Stannous Chloride Solution* (4.6 g/100 mL of concentrated HCl)—Dissolve 5 g of stannous chloride ($SnCl_2 \cdot H_2O$) in 100 mL of concentrated HCl (sp gr 1.19). This solution is stable if a few small pieces of mossy tin are added to prevent oxidation.

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[4] McFarren, E. F., "New, Simplified Method for Metal Analysis," *Journal of American Water Works Association*, JAWWA, Vol 64, 1972, p. 28.

[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.

8.12 *Sulfuric Acid* (1 + 1)—**Cautiously**, and with constant stirring and cooling, add 250 mL of concentrated sulfuric acid (H_2SO_4, sp gr 1.84) to 250 mL of water.

8.13 *Hydrogen,* commercially available. Set pressure on burner control box to 55 KPa (8 psi) and adjust flowmeter to approximately 6 L/min.

8.14 *Nitrogen,* commercially available. Set pressure on burner control box to 206.8 KPa (30 psi) and adjust flowmeter for maximum sensitivity by volatilizing standards. A flow of approximately 9 L/min has been found satisfactory. This will vary depending on the burner used.

8.15 *Filter Paper*—Purchase suitable filter paper. Typically the filter papers have a pore size of 0.45-µm membrane. Material such as fine-textured, acid-washed, ashless paper, or glass fiber paper are acceptable. The user must first ascertain that the filter paper is of sufficient purity to use without adversely affecting the bias and precision of the test method.

9. Sampling

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

9.2 Immediately preserve samples with HNO_3 (sp gr 1.42) to a pH of 2 or less at the time of collection; normally about 2 mL/L is required. If only dissolved antimony is to be determined, filter the sample through a (No. 325) 0.45-µm membrane filter before acidification.

NOTE 4—Alternatively, the pH may be adjusted in the laboratory within 14 days of collection. However, acid must be added at least 24 hours before analysis to dissolve any metals that adsorb to the container walls. This could reduce hazards of working with acids in the field when appropriate.

10. Standardization

10.1 An effective way to clean all glassware to be used for preparation of standard solutions or in the digestion step, or both, is by rinsing first with HNO_3 (1 + 1) (8.8) and then with water.

10.2 Prepare, in 200 to 300-mL wide-mouth glass containers, a blank and sufficient standards that contain from 0.0 to 1.5 µg of antimony by diluting 0.0 to 15.0-mL portions of the antimony standard solution to 100 mL with water.

10.3 Proceed as directed in 11.3 to 11.8.

10.4 Read directly in concentration if this capability is provided with the instrument or prepare an analytical curve by plotting recorder scale readings versus micrograms of antimony on linear graph paper or calculate a standard curve.

11. Procedure

11.1 An effective way to clean all glassware to be used for preparation of standard solutions or in the digestion step, or both, is by rinsing first with HNO_3 (1 + 1) (8.8) and then with reagent.

11.2 Pipet a volume of well-mixed acidified sample containing less than 1.5 µg of antimony (100-mL max) into a 200 to 300-mL wide-mouth glass container, and dilute to 100 mL with water (see Fig. 1).

NOTE 5—If only dissolved antimony is to be determined, use a filtered and acidified sample (9.2).

11.3 To each container, add 7 mL of H_2SO_4 (1 + 1) (8.12) and 5 mL of concentrated HNO_3 (8.7). Add a small boiling chip and carefully heat the samples (between 65°C to 95°C) on a steam bath or hot plate below boiling in a well-ventilated hood to evaporate to fumes of SO_3. Maintain an excess of HNO_3 until all organic matter is destroyed. This prevents darkening of the solution and possible reduction and loss of antimony. Cool, add 25 mL of water, and again evaporate to fumes of SO_3 to expel oxides to nitrogen.

NOTE 6—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. The digestion block must be capable of maintaining a consistent temperature between 65°C and 95°C. 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.

11.4 Cool, and adjust the volume of each container to approximately 100 mL with water.

11.5 To each container, add successively, with thorough mixing after each addition, 8 mL of concentrated HCl (8.6), 1 mL of KI solution (8.9), and 0.5 mL of $SnCl_2$ (8.11) solution. Allow about 15 min for reaction.

11.6 Attach one container at a time to the rubber stopper containing the gas dispersion tube.

11.7 Fill the medicine dropper or syringe with 1 mL of $NaBH_4$ (8.10) solution and insert into the hole in the rubber stopper.

11.8 Add the $NaBH_4$ solution (8.10) to the sample solution. After the recorder reading (scale reading) has reached a maximum and has returned to the baseline, remove the container. Rinse the gas dispersion tube in water before proceeding to the next sample. Treat each succeeding sample, blank, and standard in a like manner.

12. Calculation

12.1 If instrument readout is not in concentration, determine the weight or concentration of antimony in each sample by referring to 10.4. If the weight is determined from the analytical curve, calculate the concentration of antimony in the sample in micrograms per litre, as follows:

$$\text{Antimony, } \mu g/L = 1000 \times W/V \qquad (1)$$

where:

1000 = 1000 mL / L,
V = volume of sample, mL, and
W = weight of antimony in sample, µg.

13. Precision and Bias

13.1 The single operator and overall precision of this test method for four laboratories, which included a total of six operators analyzing each sample on three different days, within its designated range varies with the quantity being tested.