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Standard Test Method for Antimony in Water¹

This standard is issued under the fixed designation D 3697; 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 This test method is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water. Current edition approved ~~June 15, 1992~~, May 10, 2002. Published ~~October 1992~~, June 2002. Originally published as D 3697 – 78. Last previous edition D 3697 – ~~892~~ (1996).



1. Scope

1.1 This test method² covers the determination of dissolved and total recoverable antimony in water by atomic absorption spectroscopy.

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 *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 precautionary statements, see 5.1 and 8.12.*

2. Referenced Documents

2.1 ASTM Standards:

D 1129 Terminology Relating to Water³

D 1193 Specification for Reagent Water³

D 2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D-19 on Water³

D 3370 Practices for Sampling Water from Closed Conduits³

D 4691 Practice for Measuring Elements in Water by Flame Atomic Absorption Spectrophotometry³

D 4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents³

D 5847 Practice for the Writing Quality Control Specifications for Standard Test Methods for Water Analysis⁴

3. Terminology

3.1 *Definitions:* For definitions of terms used in this test method, refer to Terminology D 1129.

3.2 *Definition of Term Specific to This Standard:*

3.2.1 *total recoverable antimony*—an arbitrary analytical 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.

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

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.

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.

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 D 4691.

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

7.1.1 *Antimony Electrodeless Discharge Lamp.*

² Platte, J. A., and Marcy, V. M., "A New Tool for the Water Chemist," *Industrial Water Engineering*, IWEGA, May 1965.

³ *Annual Book of ASTM Standards*, Vol 11.01.

⁴ *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 *Analar ASTM 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: Vol 11.02.

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, E. F., “New, Simplified Method for Metal Analysis,” *Journal of American Water Works Assoc.*, JAWWA, Vol 64, 1972, p. 28.

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 D 1193, 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, $\text{KSbOC}_4\text{H}_4\text{O}_6 \cdot 1/2\text{H}_2\text{O}$, in water and dilute to 1000 mL with water.

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. This standard is used to prepare working standards at the time of analysis.

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 ($\text{SnCl}_2 \cdot \text{H}_2\text{O}$) 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.

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 8 psig (55 KPa) and adjust flowmeter to approximately 6 L/min.

8.14 *Nitrogen*, commercially available. Set pressure on burner control box to 30 psig (206.8 KPa) 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.

9. Sampling

9.1 Collect the sample in accordance with Practices D 3370. The holding time for the samples may be calculated in accordance with Practice D 4841.

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.

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 *Analar 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.

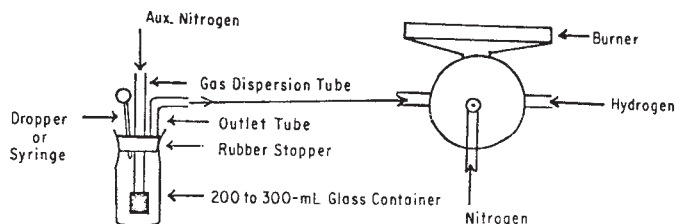


FIG. 1 Stibine Vapor Analyzer

10. Standardization

- 10.1 Clean all glassware before use by rinsing first with HNO₃ (1 + 1) 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 Prepare an analytical curve by plotting recorder scale readings versus micrograms of antimony on linear graph paper or calculate a standard curve. Alternatively, read directly in concentration if a concentration readout is provided with the instrument.

11. Procedure

- 11.1 Clean all glassware before use by rinsing first with HNO₃ (1 + 1) and then with water.
- 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 4—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 H₂SO₄ (1 + 1) and 5 mL of concentrated HNO₃. Add a small boiling chip and carefully evaporate to fumes of SO₃. Maintain an excess of HNO₃ 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 SO₃ to expel oxides to nitrogen.

- 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, 1 mL of KI solution, and 0.5 mL of SnCl₂ 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 NaBH₄ solution and insert into the hole in the rubber stopper.
- 11.8 Add the NaBH₄ solution 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 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:

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

where:

- 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.

13.2 Recoveries of known amounts of antimony (from antimony potassium tartrate) in a series of prepared standard for the same laboratories and operators are given in Table 1.

13.3 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.

~~13.4 This precision~~

~~13.4 Precision and bias statement for this test method conforms to the edition of Practice D 2777 that D 2777-77, which was in place at the time of round-robin collaborative testing. It does not meet Under the allowances made in 1.4 of D 2777-98, these precision and bias data do meet existing requirements for interlaboratory studies of the current edition of Practice D 2777-Committee D19 test methods.~~

TABLE 1 Recovery and Precision Data

Method	Test Solution	Number of Labs	True Value, µg/L	Mean Value, µg/L	S _T , µg/L	S _O , µg/L	Bias, %	Stated Range, µg/L	R ²	Precision Regression Equations
Hydride/ Flame AAS	RGW	4	3.0	3.15	0.92	0.70	+ 5.0	1-15	0.80	S _T = 0.451 + 0.104 \bar{x} S _O = 0.255 + 0.109 \bar{x}
			7.0	6.42	0.88	0.78	-8.3 %		0.89	
			12.0	11.16	1.71	1.54	-7.0			
	WOC	4	3.0	2.74	0.66	0.66	-8.7	0.98	S _T = 0.346 + 0.132 \bar{x} S _O = 0.386 + 0.0967 \bar{x}	
			7.0	6.00	1.22	0.95	-14.3 %	1.00		
			12.0	10.73	1.73	1.43	-10.6 %			

14. Quality Control (QC)

14.1 The following quality control information is recommended for the determination of antimony in water.

14.2 The instrument shall be calibrated using a minimum of four calibration standards and a calibration blank. The calibration correlation coefficient shall be equal to or greater than 0.990. In addition to the initial calibration blank, a calibration blank should be analyzed at the end of the batch run to ensure contamination was not a problem during the batch analysis.

14.3 An instrument check standard shall be analyzed at a minimum frequency of 10 % throughout the batch analysis. The value of the instrument check standard shall fall between 80 % and 120 % of the true value.

14.4 Two method blanks shall be prepared ensuring that an adequate method blank volume is present for a minimum of seven repetitive analysis. The standard deviation of the method blank is used to determine the minimum detectable concentration of each sample and control in the batch.

14.5 A Laboratory Control Sample shall be analyzed with each batch of sample at a minimum frequency of 10 %.

14.6 If the QC for the sample batch is not within the established control limits, reanalyze the samples or qualify the results with the appropriate flags, or both.

14.7 Blind control samples should be submitted by an outside agency in order to determine the laboratory performance capabilities.

15. Keywords

145.1 antimony; atomic absorption; vapor hydride generation; water

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