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.

[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.

Current edition approved June 1, 2017. Published June 2017. Originally approved in 1978. Last previous edition approved in 2012 as D3697 – 12. DOI: 10.1520/D3697-17.

[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**

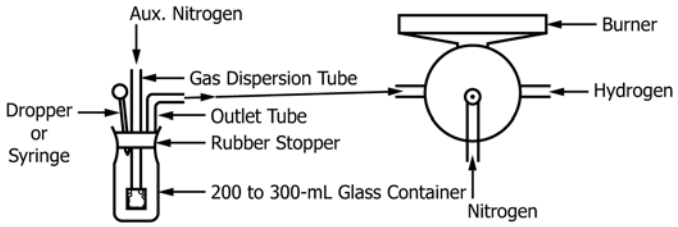

FIG. 1 Stibine Vapor Analyzer

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.

[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:

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

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.

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	$S_T = 0.451 + 0.104\ \bar{x}$
			7.0	6.42	0.88	0.78	–8.3 [y]		0.89	$S_o = 0.255 + 0.109\ \bar{x}$
			12.0	11.16	1.71	1.54	–7.0			
	WOC	4	3.0	2.74	0.66	0.66	–8.7		0.98	$S_T = 0.346 + 0.132\ \bar{x}$
			7.0	6.00	1.22	0.95	–14.3 [y]		1.00	$S_o = 0.386 + 0.0967\ \bar{x}$
			12.0	10.73	1.73	1.43	–10.6 [y]			

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 Precision and bias for this test method conforms to Practice D2777 – 77, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of D2777 – 13, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

14. Quality Control (QC)

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 antimony.

14.2 *Calibration and Calibration Verification:*

14.2.1 Analyze at least three working standards containing concentrations of antimony that bracket the expected sample concentration, prior to analysis of samples, to calibrate the instrument (see 10.4). The calibration correlation coefficient shall be equal to or greater than 0.990.

14.2.2 Verify instrument calibration after standardization by analyzing a standard at the concentration of one of the calibration standards. The concentration of a mid-range standard should fall within ±15 % of the known concentration. Analyze a calibration blank to verify system cleanliness. The blank result should be less than the method reporting limit.

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. The CCB result should be less than the method reporting limit. The CCV results should fall within the expected precision of the method or ±15 % of the known concentration.

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, and so forth, 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 midrange concentration of antimony. 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 Practice 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, prepare and analyze a LCS containing a known concentration of antimony with each batch (laboratory-defined or 20 samples). The laboratory control samples for a large batch should cover the analytical range when possible. It is recommended, but not required to use a second source, if possible and practical for the LCS. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The result obtained for a mid-range 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 laboratory-defined batch. The concentration of antimony found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of antimony 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 laboratory-defined batch by spiking an aliquot of the sample

with a known concentration of antimony and taking it through the analytical method.

14.6.2 The spike concentration plus the background concentration of antimony 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:

$$P = [A\ (V_s + V) - BV_s]/CV \quad (2)$$

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 7—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 laboratory-defined batch. If the concentration of the analyte is less than five times the detection limit for the analyte, a 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 Practice 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 Independent Reference Material (IRM) submitted as a regular sample (if practical) to the laboratory at least once per quarter. The concentration of the IRM 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 antimony; atomic absorption; vapor hydride generation; water

SUMMARY OF CHANGES

Committee D19 has identified the location of selected changes to this standard since the last issue (D3697 – 12) that may impact the use of this standard. (Approved June 1, 2017.)

(1) Revised 1.4 to update the units of measurement statement.
(2) Revised Section 2 to include D5673 and D5810.
(3) Revised Section 3 to update and add terms.
(4) Added 5.2 to include information on using ICP-MS.
(5) Revised Section 8 to allow for standard preparation and add information on filter paper.
(6) Revised Note 4 to allow for pH of the samples in the laboratory.
(7) Revised Section 10 to allow for direct reading instruments.
(8) Revised 10.1 and 11.1 with information on cleaning glassware.
(9) Revised Section 11 and Note 6 with information on the use of block digestion systems.
(10) Rewrote and expanded Section 14.