



## Standard Test Methods for Silver in Water<sup>1</sup>

This standard is issued under the fixed designation D3866; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

### 1. Scope\*

1.1 These test methods cover the atomic absorption determination of silver in water. Section 34 on Quality Control pertains to these test methods. Three test methods are given as follows:

	Concentration Range	Sections
Test Method A—Atomic Absorption—Chelation-Extraction <sup>A</sup>	1 to 10 $\mu\text{g/L}$	7 – 15
Test Method B—Atomic Absorption—Direct	0.1 to 10 $\text{mg/L}$	16 – 24
Test Method C—Atomic Absorption—Graphite Furnace	1 to 25 $\mu\text{g/L}$	25 – 33

<sup>A</sup> Similar to that in Brown, E., Skougstad, M. W., and Fishman, M. J., "Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases," *Techniques of Water-Resources Investigations of the U.S. Geological Survey*, Book 5, Chapter A1, 1970, p. 46.

1.2 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.

1.3 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in 11.5, 11.12.1, 13.8, and 22.1.

1.4 *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.*

<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee D19 on Water and are the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

Current edition approved Feb. 1, 2018. Published March 2018. Originally approved in 1979. Last previous edition approved in 2012 as D3866 – 12. DOI: 10.1520/D3866-18.

### 2. Referenced Documents

#### 2.1 ASTM Standards:<sup>2</sup>

- D1129 Terminology Relating to Water
- D1193 Specification for Reagent Water
- D1976 Test Method for Elements in Water by Inductively-Coupled Argon Plasma Atomic Emission Spectroscopy
- 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
- D3919 Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry
- 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 *laboratory control sample, n*—a solution with a certified concentration of silver.

3.2.2 *total recoverable silver, n*—a descriptive term relating to forms of silver that are determinable by the digestion method that is included in these test methods.

### 4. Significance and Use

4.1 The principal adverse effect of silver in the body is cosmetic. It causes argyria, a permanent, blue-gray discoloration of the skin, eyes, and mucous membranes.

<sup>2</sup> 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 Relatively small quantities of silver are bactericidal or bacteriostatic and find limited use in both disinfection of swimming pool waters and point-of-use water filters.

4.3 ICP-MS or ICP-AES may also be appropriate but at a higher instrument cost. See Test Methods [D5673](#) and [D1976](#).

## 5. Purity of Reagents

5.1 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, when such specifications are available.<sup>3</sup> 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.

5.2 *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 1—The user must ensure the type of reagent water chosen is sufficiently free of interferences. The water should be analyzed using these test methods.

## 6. Sampling

6.1 Collect the sample in accordance with Practices [D3370](#). The holding time for the samples may be calculated in accordance with Practice [D4841](#).

6.2 Preserve samples for Test Method A with HNO<sub>3</sub> (sp gr 1.42) to a pH of 2 or less immediately at the time of collection; normally about 2 mL/L is required. If only dissolved silver is to be determined, filter ([11.13](#)) the sample at time of collection through a 0.45- $\mu$ m membrane filter before acidification.

NOTE 2—Alternatively, the pH may be adjusted in the laboratory within 14 days of collection. This could reduce hazards of working with acids in the field when appropriate.

6.3 Do not preserve samples for Test Methods B and C at the time of collection. If only dissolved silver is to be determined, filter the sample through a 0.45- $\mu$ m membrane filter at time of collection. Add cyanogen iodide (CNI) solution to the samples in the laboratory prior to analysis. For total recoverable silver it is preferable to add the cyanogen iodide to the entire sample to avoid a nonhomogeneous solution; therefore, it is advisable to collect a discrete sample for silver.

<sup>3</sup> *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.

## TEST METHOD A—ATOMIC ABSORPTION—CHELATION EXTRACTION

### 7. Scope

7.1 This test method<sup>4</sup> covers the determination of dissolved and total recoverable silver in most water and wastewaters.

7.2 This test method is applicable in the range from 1 to 10  $\mu$ g/L of silver. The range may be extended by dilution of the original sample.

7.3 This test method has been used successfully with reagent water, natural surface water, and drinking water. The information on precision and bias may not apply to other waters. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

### 8. Summary of Test Method

8.1 Silver is determined by atomic absorption spectrometry. The element, either dissolved or total recoverable, is chelated with ammonium pyrrolidine dithiocarbamate (APDC) and extracted with methyl isobutyl ketone (MIBK). The extract is aspirated into an air-acetylene flame of the spectrophotometer. Total recoverable silver is determined following nitric acid digestion and filtration.

### 9. Interferences

9.1 Concentrations of iron greater than 25 mg/L interfere by suppressing the silver absorption.

### 10. Apparatus

10.1 *Atomic Absorption Spectrophotometer* for use at 328.1 nm. A general guide for the use of flame atomic absorption applications is given in Practice [D4691](#).

NOTE 3—The manufacturer's instructions should be followed for instrumental parameters. Wave-lengths other than 328.1 nm may be used if they have been determined to be equally suitable.

10.2 *Silver Hollow-Cathode Lamp*.

10.3 *Pressure-Reducing Valves*—The supplies of fuel and oxidant shall be maintained at pressures somewhat higher than the controlled operating pressure of the instrument by suitable pressure-reducing valves.

### 11. Reagents and Materials

11.1 *Ammonium Pyrrolidine Dithiocarbamate (APDC) Solution* (1 g/100 mL)—Dissolve 1.0 g of APDC in 100 mL of water. Prepare fresh before each use.

11.2 *Bromophenol Blue Indicator Solution* (0.1 g/100 mL)—Dissolve 0.1 g of bromophenol blue in 100 mL of 50 % ethanol or isopropanol.

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

<sup>4</sup> Similar to that in Brown, E., Skougstad, M. W., and Fishman, M. J., "Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases," *Techniques of Water-Resources Investigations of the U.S. Geological Survey*, Book 5, Chapter A1, 1970, p. 46.

11.4 *Hydrochloric Acid* (1 + 49)—Add 1 volume of hydrochloric acid (HCl, sp gr 1.19) to 49 volumes of water.

11.5 *Methyl Isobutyl Ketone (MIBK)*. (**Warning**—Avoid inhalation and conduct all manipulation in a well-ventilated hood.)

11.6 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO<sub>3</sub>).

NOTE 4—If a high reagent blank is obtained, distill the HNO<sub>3</sub> or use a spectrograde acid.

11.7 *Silver Solution, Stock* (1.0 mL = 100 µg Ag)—Crush approximately 2 g of silver nitrate (AgNO<sub>3</sub>) crystals and dry to constant mass at 40°C. Dissolve 0.1575 g of AgNO<sub>3</sub> in water containing 5 mL of concentrated HNO<sub>3</sub> and dilute to 1000 mL. Store in an amber glass bottle. A purchased silver stock solution of appropriate known purity is also acceptable.

11.8 *Silver Solution, Intermediate* (1.0 mL = 1.00 µg Ag)—Dilute 10.0 mL of silver stock solution and 5 mL of concentrated HNO<sub>3</sub> to 1000 mL with water. Store in an amber glass bottle. A purchased stock solution of adequate purity is also acceptable.

11.9 *Silver Solution, Standard* (1.0 mL = 0.100 µg Ag)—Dilute 100 mL of silver intermediate solution and 5 mL of concentrated HNO<sub>3</sub> to 1000 mL with water. Prepare fresh before use.

11.10 *Sodium Hydroxide Solution* (100 g/L)—Dissolve 100 g of NaOH in water and dilute to 1000 mL.

#### 11.11 *Oxidant:*

11.11.1 *Air*, that has been passed through a suitable filter to remove oil, water, and other foreign substances is the usual oxidant.

#### 11.12 *Fuel:*

11.12.1 *Acetylene-Standard*, commercially available acetylene is the usual fuel. Acetone, always present in acetylene cylinders, can affect analytical results. The cylinder should be replaced at 345 kPa (50 psi). (**Warning**—“Purified” grade acetylene containing a special proprietary solvent rather than acetone must not be used with poly(vinyl chloride) tubing as weakening of the tubing walls causes a potentially hazardous situation.)

11.13 *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.

## 12. Standardization

12.1 An effective way to clean all glassware to be used for preparation of standard solutions or in the digestion step, or both, is by soaking the glassware for 2 h first with HNO<sub>3</sub> (1 + 1) and then rinsing with reagent water.

12.2 Prepare a blank and sufficient standards containing from 0.0 to 1.0 µg of silver by diluting 0.0 to 10.0-mL portions of silver standard solution to approximately 100 mL.

**TABLE 1 Determination of Bias and Precision for Test Method A**

Amount Added, µg/L Ag	Amount Found, µg/L Ag	Bias, %	Statistically Significant, 95 % Confidence Level	Overall Precision, S <sub>t</sub>	Degrees of Freedom
Reagent Water, Type II					
2.0	2.18	+ 9.0	no	0.77	7
5.0	5.15	+ 3.0	no	1.34	7
8.0	8.08	+ 1.0	no	1.86	7
Natural Water of Choice					
2.0	2.37	+ 18.5	yes	0.74	7
5.0	4.99	-0.2	no	0.92	7
8.0	8.38	+ 4.8	no	2.21	7

12.3 To determine total recoverable silver, use 125-mL beakers or flasks, add 5.0 mL of HNO<sub>3</sub> (sp gr 1.42), and proceed as directed in 13.3 through 13.10. To determine dissolved silver use 200-mL volumetric flasks and proceed as directed in 13.5 through 13.10. Treat the blank and each standard in the same manner as the samples.

12.4 Read directly in concentration if this capability is provided with the instrument or measure the absorbance of the standards or construct an analytical curve by plotting the absorbances of standards versus micrograms of silver.

## 13. Procedure

13.1 Measure a volume of a well-mixed acidified sample containing less than 1.0 µg of silver (100-mL maximum) into a 125-mL beaker or flask and adjust the volume to 100 mL with water.

NOTE 5—If only dissolved silver is to be determined, measure a volume of filtered and acidified sample containing less than 1.0 µg of silver (100 mL maximum) into a 200-mL volumetric flask and adjust the volume to 100 mL and start with 13.5.

13.2 Add 5 mL of HNO<sub>3</sub> (sp gr 1.42) (11.6) to each sample.

13.3 Heat the samples (between 65°C and 95°C) on a steam bath or hot plate below boiling in a well-ventilated hood until the volume has been reduced to 15 to 20 mL making certain that the samples do not boil.

NOTE 6—For brines and samples with a high concentration of suspended matter, the amount of reduction in volume is left to the discretion of the analyst.

NOTE 7—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 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. If a block digestion system is used, reduced volumes of samples and reagents will be required. Make sure that the reagent volumes maintain the same proportions as in the macro method.

13.4 Cool and filter each sample through a filter (such as a fine-textured acid washed, ashless paper; 11.13) into a 200-mL volumetric flask. Wash the filter paper two or three times with water and adjust the filtrate to about 100 mL.

13.5 Add 2 drops of bromophenol blue indicator solution (11.2) and mix.

13.6 Adjust the pH by addition of NaOH solution (100 g/L) (11.10) until a blue color persists. Add HCl (1 + 49) (11.4) by drops until the blue color just disappears; then add 2.5 mL of HCl (1 + 49) (11.4) in excess. The pH at this point should be 2.3.

NOTE 8—The pH adjustment in 13.6 may be made with a pH meter instead of using indicator.

13.7 Add 2.5 mL of APDC solution (11.1) and mix. The pH should be approximately 2.8.

13.8 Add 10.0 mL of MIBK (11.5) and shake vigorously for 1 min. (**Warning**—Perform in a well ventilated hood (see 11.5).)

13.9 Allow the layers to separate and add, carefully down the side of the flask, water until the ketone layer is completely in the neck of the flask.

NOTE 9—MIBK is soluble to some extent in water; therefore avoid any undue agitation of the solution during and after addition of water which could result in a concentration of the metal chelate in the MIBK layer. To avoid this problem, MIBK-saturated water may be used to raise the MIBK layer into the neck of the flask.

13.10 Atomize the ketone layer and record the scale reading or concentration (Note 10). Aspirate water-saturated MIBK between each sample.

NOTE 10—It is necessary to reduce the acetylene flow when aspirating an organic solvent (MIBK) to obtain a nonluminous flame. Also allow the flame conditions to come to equilibrium before aspirating samples.

#### 14. Calculation

14.1 If instrument readout is not in concentration, determine the weight of silver in each sample by referring to 12.4. Calculate the concentration of silver in micrograms per litre as follows:

$$\text{Silver, } \mu\text{g/L} = (1000/A) \times B \quad (1)$$

where:

1000 = 1000 mL/L,

A = volume of original sample, mL, and

B = weight of silver in sample,  $\mu\text{g}$ .

#### 15. Precision and Bias<sup>5</sup>

15.1 The single-operator and overall precision of this test method within its designated range for four laboratories, which include a total of seven operators analyzing each sample on three different days varies with the quantity being tested, see Table 1.

15.2 Recoveries of known amounts of silver (from silver nitrate) in a series of prepared standards for the same laboratories and operators are shown in Table 1.

15.3 The collaborative test data were obtained on reagent water, natural surface water, and drinking water. This data may not apply to untested matrices. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

<sup>5</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1062. Contact ASTM Customer Service at service@astm.org.

15.4 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 Practice D2777 – 13, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

### TEST METHOD B—ATOMIC ABSORPTION—DIRECT

#### 16. Scope

16.1 This test method covers the determination of dissolved and total recoverable silver in most waters, and wastewaters.

16.2 This test method is applicable in the range from 0.1 to 10 mg/L of silver. The range may be extended by dilution of the original sample.

16.3 This test method has been used successfully with reagent water, natural surface water and ground waters, an industrial outfall, and a brine. The information on precision and bias may not apply to other waters. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

#### 17. Summary of Test Method

17.1 Silver is determined by atomic absorption spectrometry. Dissolved silver is determined after filtration (11.13) and addition of cyanogen iodide. Total recoverable silver is determined by aspirating the sample following addition of cyanogen iodide to solubilize the silver and, if necessary, the sample is filtered prior to aspiration.

#### 18. Interferences

18.1 Background correction by techniques such as a continuous source, nonabsorbing lines, or chelation-extraction (Test Method A) may be necessary to determine low levels of silver in some waters.

#### 19. Apparatus

19.1 See Section 10.

#### 20. Reagents and Materials

20.1 *Ammonium Hydroxide* (sp gr 0.90)—Concentrated ammonium hydroxide ( $\text{NH}_4\text{OH}$ ).

20.2 *Cyanogen Iodide Solution*—Dissolve 65 g of potassium cyanide (KCN) in 50 mL of iodine solution (see 20.3). Dissolve 2 g of sodium hydroxide in the solution, add 40 mL of concentrated ammonium hydroxide, and dilute to 1 L with water. The solution is stable for 1 week.

NOTE 11—Before discarding the unused solution, add 50 mL of 3 % hydrogen peroxide for each gram of potassium cyanide remaining in the unused solution.

20.3 *Iodine Solution* (127 g/L)—Dissolve 12.7 g of iodine and 40 g of potassium iodide (KI) in a minimum volume of water and dilute to 100 mL.

20.4 *Silver Solution, Stock* (1.0 mL = 0.100  $\mu\text{g}$  Ag)—See 11.7.