



Designation: D 3866 – 02

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

This standard is issued under the fixed designation D 3866; 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. Three test methods are given as follows:

	Concentration Range	Sections
Test Method A—Atomic Absorption—Chelation-Extraction <sup>4</sup>	1 to 10 $\mu\text{g/L}$	7 to 15
Test Method B—Atomic Absorption—Direct	0.1 to 10 $\text{mg/L}$	16 to 24
Test Method C—Atomic Absorption—Graphite Furnace	1 to 25 $\mu\text{g/L}$	25 to 33

<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.

1.2 *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.* Specific precautionary statements are given in [Note 3](#), [Note 5](#), [Note 9](#), and [Note 13](#).

### 2. Referenced Documents

#### 2.1 ASTM Standards:

- [D 1129](#) Terminology Relating to Water<sup>2</sup>
- [D 1193](#) Specification for Reagent Water<sup>2</sup>
- [D 2777](#) Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D-19 on Water<sup>2</sup>
- [D 3370](#) Practices for Sampling Water from Closed Conduits<sup>2</sup>
- [D 3919](#) Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry<sup>2</sup>
- [D 4691](#) Practice for Measuring Elements in Water by Flame Atomic Absorption Spectrophotometry<sup>2</sup>
- [D 4841](#) Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents<sup>2</sup>

<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.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 11.01.

[D 5810](#) Guide for Spiking into Aqueous Samples<sup>2</sup>

[D 5847](#) Practice for the Writing Quality Control Specifications for Standard Test Methods for Water Analysis<sup>3</sup>

### 3. Terminology

#### 3.1 Definition of Term Specific to These Test Methods:

3.1.1 *laboratory control sample, n*—a solution with a certified concentration of silver.

3.1.2 *total recoverable silver*—an arbitrary analytical term relating to forms of silver that are determinable by the digestion method that is included in the procedures.

3.2 *Definitions*—For definition of terms used in these test methods, refer to Terminology [D 1129](#).

### 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.

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.

### 5. Purity of Reagents

5.1 Reagent grade chemicals shall be used<sup>4</sup> 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>4</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 [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

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 11.02.

<sup>4</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 *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.

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 the test method.

## 6. Sampling

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

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 the sample at time of collection through a 0.45- $\mu$ m membrane filter before acidification.

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.

## TEST METHOD A—ATOMIC ABSORPTION— CHELATION EXTRACTION

### 7. Scope

7.1 This test method<sup>5</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 D 4691.

NOTE 2—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).

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)*.

NOTE 3—**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  $\mu$ g 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.

11.8 *Silver Solution, Intermediate (1.0 mL = 1.00  $\mu$ g 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.

11.9 *Silver Solution, Standard (1.0 mL = 0.100  $\mu$ g 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 50 psig (345 kPa). (**Warning**, see Note 5.)

NOTE 5—**Warning:** "Purified" grade acetylene containing a special

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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.

## 12. Standardization

12.1 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.

12.2 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.

12.3 Construct an analytical curve by plotting the absorbances of standards versus micrograms of silver. Alternatively, read directly in concentration if this capability is provided with the instrument.

## 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 6—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) to each sample.

13.3 Heat the samples on a steam bath or hot plate 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 7—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.

13.4 Cool and filter each sample through a filter (such as a fine-textured acid washed, ashless paper) 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 and mix.

13.6 Adjust the pH by addition of NaOH solution (100 g/L) until a blue color persists. Add HCl (1 + 49) by drops until the blue color just disappears; then add 2.5 mL of HCl (1 + 49) 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 and mix. The pH should be approximately 2.8.

13.8 Add 10.0 mL of MIBK and shake vigorously for 1 min.

NOTE 9—**Warning:** Perform in a well ventilated hood (see Note 3).

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 10—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 11). Aspirate water-saturated MIBK between each sample.

NOTE 11—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 Determine the weight of silver in each sample by referring to 12.3. Calculate the concentration of silver in micrograms per litre as follows:

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

where:

- A = volume of original sample, mL, and
- B = weight of silver in sample, µg.

## 15. Precision and Bias <sup>6</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.

15.4 Precision and bias for this test method conforms to Practice D 2777-77, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of D 2777-98, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

**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

<sup>6</sup> Supporting data are available from ASTM Headquarters. Request RR: D-19-1062.