



Designation: D3866 – 18 (Reapproved 2026)

Standard Test Methods for Silver in Water¹

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 (ε) 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 ^A	1 µg/L to 10 µg/L	7 – 15
Test Method B—Atomic Absorption—Direct	0.1 mg/L to 10 mg/L	16 – 24
Test Method C—Atomic Absorption—Graphite Furnace	1 µg/L to 25 µg/L	25 – 33

^A 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.*

¹ 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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2. Referenced Documents

- 2.1 *ASTM Standards:*²
D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
D1976 Test Method for Elements in Water by Inductively-Coupled 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 Flowing Process Streams
D3919 Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry (Withdrawn 2024)³
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.

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at www.astm.org/contact. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.
³ The last approved version of this historical standard is referenced on www.astm.org.

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.

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.⁴ 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 HNO₃ (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 µm 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 µm 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 method⁵ 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 µg/L to 10 µg/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.

⁴ ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials, 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.

⁵ 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.