



# 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.

Current edition approved Jan. 10, 2002. Published April 2002. Originally published as D 3866 – 79. Last previous edition D 3866 – 92 (1996).

<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 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

<sup>5</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.

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, <i>S<sub>t</sub></i>	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.

## 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 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 (NH<sub>4</sub>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 12—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 µg Ag)—See 11.7.

20.5 *Materials*— See Section 11.

### 21. Standardization

21.1 Prepare a blank and at least four standard solutions to bracket the expected silver concentration range of the samples to be analyzed by diluting the stock silver solution. Prepare the standards (100 mL) each time the test is to be performed and select so as to give zero, middle, and maximum points for an analytical curve.

21.2 Add 1.0 mL of cyanogen iodide solution to each standard, mix and let stand for 30 min.

21.3 Aspirate the blank and standards and record the instrument readings. Aspirate water between each standard.

21.4 Construct an analytical curve by plotting the absorbance of standards versus milligrams of silver per litre. Alternatively, read directly in concentration if this capability is provided with the instrument.

### 22. Procedure

22.1 Add cyanogen iodide solution to each bottle (1.0 mL/100-mL sample), mix and let stand for 30 min.

NOTE 13—**Warning:** If the sample collected is acidic, neutralize with ammonium hydroxide solution before adding cyanogen iodide to prevent hydrogen cyanide from being liberated.

NOTE 14—If only dissolved silver is to be determined, add 1.0 mL of cyanogen iodide per 100.0 mL of filtered sample and proceed to 22.3.

22.2 Filter portions of the samples if necessary through a suitable filter (such as a fine texture, acid-washed, ashless paper) into a clean 125-mL flask or beaker.

22.3 Aspirate each sample and determine its absorbance or concentration. Aspirate water between each sample.

### 23. Calculation

23.1 Calculate the concentration of silver in each sample in milligrams per litre, referring to 21.4.

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

24.1 The single-operator and overall precision of this method within its designated range for four laboratories, which include a total of eight operators (at 0.2, 0.6, and 1.0 mg/L), and six laboratories, which include a total of ten operators (at 2.0, 5.0, and 8.0 mg/L) analyzing each sample on three different days may be expressed as follows:

24.1.1 *In Reagent Water, Type II:*

$$S_O = 0.0119X + 0.0085$$

$$S_T = 0.0314X + 0.0068$$

24.1.2 *In Water of Choice:*

$$S_O = 0.0147X + 0.0057$$

$$S_T = 0.0425X + 0.0004$$

where:

$S_O$  = single-operator precision, mg/L,

$S_T$  = overall precision, mg/L, and

$X$  = determined concentration of silver, mg/L.

24.2 Recoveries of known amounts of silver (from silver nitrate) in a series of prepared standards for the same laboratories and operators were as shown in Table 2.

24.3 The collaborative test data were obtained on reagent water, natural surface and ground waters, an industrial outfall, and a brine. 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.

24.4 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

**TABLE 2 Determination of Bias and Precision for Test Method B**

Amount Added, mg/L Ag	Amount Found, mg/L Ag	Bias, %	Statistically Significant, 95 % Confidence Level	Overall Precision, $S_t$	Degrees of Freedom
Reagent Water, Type II					
0.20	0.197	-2.0	no	0.015	7
0.60	0.588	-2.0	no	0.029	7
1.0	0.99	-1.2	no	0.037	7
2.0	2.02	+ 1.0	no	0.068	7
5.0	5.06	+ 1.2	yes	0.157	7
8.0	7.98	-0.2	no	0.263	7
Natural Water of Choice					
0.20	0.195	-2.5	no	0.012	7
0.60	0.586	-2.3	yes	0.028	7
1.0	0.99	-1.2	no	0.034	7
2.0	1.99	-0.5	no	0.091	7
5.0	5.00	0.0	no	0.206	7
8.0	7.88	-1.5	no	0.399	7

2777-98, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

### TEST METHOD C—ATOMIC ABSORPTION—GRAPHITE FURNACE

#### 25. Scope

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

25.2 This test method is applicable in the range from 1 to 25  $\mu\text{g/L}$  of silver using a 20  $\mu\text{L}$  injection. The range can be increased or decreased by varying the volume of sample injected or the instrumental settings. High concentrations may be diluted but preferably should be analyzed by direct aspiration atomic absorption spectrometry (Test Method B).

25.3 This test method has been used successfully with reagent water, natural surface and ground waters, drinking waters, and storm runoff 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.

25.4 The analyst is encouraged to consult Practice D 3919 for a general discussion of interferences and sample analysis procedures for graphite furnace atomic absorption spectrophotometry.

#### 26. Summary of Test Method

26.1 Silver is determined by an atomic absorption spectrophotometer used in conjunction with a graphite furnace. A sample is placed in a graphite tube, evaporated to dryness, charred (pyrolyzed or ashed) and atomized. The absorption signal generated during atomization is recorded and compared to standards. A general guide for the application of the graphite furnace is given in Practice D 3919.

26.2 Dissolved silver is determined after filtration and addition of cyanogen iodide.

26.3 Total recoverable silver is determined following addition of cyanogen iodide to solubilize the silver and filtration.

**TABLE 3 Determination of Bias and Precision for Test Method C**

Amount Added, $\mu\text{g/L}$ Ag	Amount Found, $\mu\text{g/L}$ Ag	Bias, %	Statistically Significant, 95 % Confidence Level	Overall Precision, $S_t$	Degrees of Freedom
Reagent Water, Type II					
2.0	2.28	+ 14.0	yes	0.50	7
8.0	8.58	+ 7.2	yes	1.00	7
15.0	16.00	+ 6.7	yes	1.71	7
22.0	23.41	+ 6.4	yes	2.84	7
Natural Water of Choice					
2.0	1.97	-1.5	no	0.81	7
8.0	7.23	-9.6	yes	1.40	7
15.0	14.13	-5.8	no	3.25	7
22.0	19.95	-9.3	no	5.37	7

#### 27. Interferences

27.1 For a complete discussion on general interferences with furnace procedures, the analyst is referred to Practice D 3919.

#### 28. Apparatus

28.1 *Atomic Absorption Spectrophotometer*, for use at 328.1 nm with background correction.

NOTE 15—A wavelength other than 328.1 nm may be used if it has been determined to be suitable. Greater linearity may be obtained at high concentrations by using a less sensitive wavelength such as 338.3 nm.

NOTE 16—The manufacturer's instruction should be followed for all instrumental parameters.

28.2 *Silver Hollow-Cathode Lamp*.

28.3 *Graphite Furnace*, capable of reaching temperatures sufficient to atomize the element of interest.

28.4 *Graphite Tubes*, compatible with furnace device. Standard graphite tubes are preferred unless extreme sensitivity is required. In this instance and to eliminate the possible formation of carbides, pyrolytically coated graphite tubes are recommended.

28.5 *Pipets*, microlitre with disposable tips. Sizes may range from 1- $\mu\text{L}$  to 100- $\mu\text{L}$ , as required.

28.6 *Data Storage and Reduction Device*—Computer and microprocessor controlled devices, or a strip chart recorder, shall be utilized for data collection, reduction, storage, and problem recognition (drift, incomplete atomization, changes in sensitivity, etc.). Strip chart recorders shall have a full-scale deflection time of 0.2 s or less to ensure accuracy.

28.7 *Automatic Sampling* may be used if available.

#### 29. Reagents and Materials

29.1 *Cyanogen Iodide Solution*—See 20.2 and Note 12.

29.2 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid ( $\text{HNO}_3$ ). (See Note 3.)

29.3 *Silver Solution, Stock* (1.0 mL = 100  $\mu\text{g}$  Ag)—See 11.7.

29.4 *Silver Solution, Intermediate* (1.0 mL = 1.00  $\mu\text{g}$  Ag)—See 11.8.

29.5 *Silver Solution, Standard* (1.0 mL = 0.100  $\mu\text{g}$  Ag)—See 11.9.

29.6 *Argon*, standard, welders grade, commercially available. Nitrogen may also be used if recommended by the instrument manufacturer.

### 30. Standardization

30.1 Initially, set the instrument in accordance with the manufacturer's specifications. Follow the general instructions as provided in Practice D 3919.

30.2 Add 0.2-mL cyanogen iodide solution to 100 mL of each standard; mix and let stand for 30 min.

### 31. Procedure

31.1 Clean all glassware to be used for preparation of standard solutions or in the solubilization step, or both, by rinsing first with HNO<sub>3</sub> (1 + 1) and then rinsing with water. Alternatively, soaking the glassware overnight in HNO<sub>3</sub>(1 + 1) is useful for low levels.

31.2 Add cyanogen iodide solution to each sample bottle (0.2 mL per 100 mL sample), mix, and let stand for 30 min (See Note 17.)

NOTE 17—If only dissolved silver is to be determined, add 0.2-mL cyanogen iodide per 100.0-mL filtered sample and proceed to step 31.4.

31.3 Filter portions of the samples if necessary through a suitable filter (such as a fine-textured acid-washed, ashless paper) into a 125-mL flask or beaker.

31.4 Inject a measured aliquot of sample into the furnace device following the directions as provided by the particular instrument manufacturer. Refer to Practice D 3919.

### 32. Calculation

32.1 Determine the concentration of silver in each sample by referring to Practice D 3919.

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

33.1 The collaborative test data were obtained on reagent water, natural surface and ground waters, drinking waters, and storm runoff 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.

33.2 The single-operator and overall precision of this method within its designated range for six laboratories, which include a total of seven operators analyzing each sample on three different days varies with the quantity being tested (see Table 3).

33.3 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 3.

33.4 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 D-19 test methods.

### 34. Quality Control (QC)

34.1 The following quality control information is recommended for the determination of silver in water.

34.2 For each method 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 shall be analyzed at the end of the batch run to ensure contamination was not a problem during the batch analysis.

34.3 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.

34.4 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.

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

34.6 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.

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

### 35. Keywords

35.1 atomic absorption; chelation-extraction; graphite furnace; silver; water

*ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.*

*This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.*

*This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org).*