



Standard Test Methods for Fluoride Ion in Water¹

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This standard has been approved for use by agencies of the Department of Defense.

1. Scope

1.1 These test methods² cover the determination of fluoride ion in water. The following two test methods are given:

	Sections
Test Method A—Distillation	7 to 13
Test Method B—Ion Selective Electrode	14 to 22

1.2 Test Method A covers the accurate measurement of total fluoride in water through isolation of the fluoride by distillation and subsequent measurement in the distillate by use of the ion selective electrode (ISE) method. The procedure covers the range from 0.1 to 2.6 mg/L of fluoride.

1.3 Test Method B covers the accurate measurement of simple fluoride ion in water by means of an ion selective electrode. With this test method, distillation is eliminated because the electrode is not affected by the interferences common to colorimetric procedures. Concentrations of fluoride from 0.1 to 1000 mg/L may be measured.

1.4 *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.* For a specific precautionary statement, see 12.1.2.

1.5 Former Test Method A, SPADNS Photometric Procedure, was discontinued. Refer to Appendix X1 for historical information.

2. Referenced Documents

2.1 ASTM Standards:

- D 1066 Practice for Sampling Steam³
- D 1129 Terminology Relating to Water³
- D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits³
- D 1193 Specification for Reagent Water³

¹ These test methods are under the jurisdiction of ASTM Committee D-19 on Water and are the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

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² Bellack, E., "Simplified Fluoride Distillation Method," *Journal of the American Water Works Association*, Vol 50, 1958, p. 530.

³ *Annual Book of ASTM Standards*, Vol 11.01.

- D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water³
- D 3370 Practices for Sampling Water from Closed Conduits³

3. Terminology

3.1 Definitions—For definitions of terms used in these test methods, refer to Terminology D 1129.

4. Significance and Use

4.1 Simple and complex fluoride ions are found in natural waters. Fluoride forms complexing ions with silicon, aluminum, and boron. These complexes may originate from the use of fluorine compounds by industry.

4.2 Fluoridation of drinking water to prevent dental caries is practiced by a large number of communities in this country. Fluoride is monitored to assure that an optimum treatment level of 1.4 to 2.4 mg/L, depending on the corresponding range of ambient temperatures of 32 to 10°C, is maintained.

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, where 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 Type I reagent water conforming to Specification D 1193.

6. Sampling

6.1 Collect the sample in accordance with Practice D 1066, Specification D 1192, or Practices D 3370, as applicable.

⁴ *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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

TEST METHOD A—DISTILLATION

7. Scope

7.1 This test method is applicable to the accurate determination of fluoride ion in water, including most wastewaters. This test method may not be applicable to concentrated brines and oily wastes.

7.2 This test method was tested on reagent water and wastewater. 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 The fluoride is distilled as hydrofluosilicic acid and is determined by the ion selective electrode.

9. Interferences

9.1 In sample distillation, interferences may be experienced due to the following factors.

9.1.1 Aluminum in excess of 300 mg/L and silicon dioxide as colloidal silica in excess of 400 mg/L will hold up in the condenser to a certain extent, causing low results and acting as a positive interference for subsequent samples of lower fluoride content. In these cases, the condenser should be flushed with 300 to 400 mL of water and the washwater added to the distillate. The distillate may then be diluted to 1.0 L. If the analyst prefers, a smaller sample aliquot diluted to 300 mL may be selected for distillation.

9.1.2 Sea water, brines, and generally samples of dissolved solids in excess of 2500 mg/L will cause bumping in the distillation flask. Dilution of the sample with fluoride-free water to a lesser-dissolved solids concentration is an effective remedy to bumping.

9.1.3 Samples containing oily matter which may result in a two-phase distillate, an emulsion, or anything other than a clear distillate may prevent accurate measurement of fluoride. Such samples should be extracted initially with a suitable solvent (such as ether, chloroform, benzene, and similar solvents) to remove the oily material, and then warmed on a steam bath to remove traces of the added solvent.

10. Apparatus

10.1 *Distillation Assembly*—Glassware consisting of a 1-L, round bottom, borosilicate boiling flask, an adapter with a thermometer opening, a connecting tube, a condenser, and a thermometer reading to 200°C, assembled as shown in Fig. 1. Standard-taper or spherical ground glass joints shall be used throughout the apparatus.

11. Reagents

11.1 *Silver Sulfate* (Ag_2SO_4), powder.

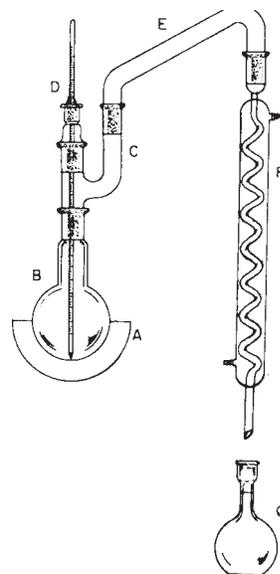
11.2 *Sodium Arsenite Solution* (2 g/L)—Dissolve 2 g of sodium arsenite ($NaAsO_2$) in water and dilute to 1 L.

11.3 *Sodium Fluoride Solution, Standard* (1.0 mL = 0.01 mg F)—Dissolve 0.2210 g of sodium fluoride (NaF) in water and dilute to 1.0 L. Dilute 100 mL of this solution to 1.0 L with water. Store in borosilicate glass or polyethylene.

11.4 *Sulfuric Acid* (H_2SO_4), Concentrated (sp gr 1.84).

12. Procedure

12.1 *Distillation*:



A—Heating mantle (quartz).
 B—Round-bottom flask, 1000 mL.
 C—Adapter with thermometer opening.
 D—Thermometer, 200°C.
 E—Connecting tube.
 F—Graham condenser, 300 mm.
 G—Vessel, calibrated at 300 mL.

FIG. 1 Distillation Assembly for Fluoride Isolation

12.1.1 Place 400 mL of water in the distilling flask and add 200 mL of concentrated H_2SO_4 (sp gr 1.84). Observe the usual precautions while mixing the H_2SO_4 by slow addition of the acid accompanied by constant swirling. Add sufficient boiling stones⁵ and assemble the apparatus as shown in Fig. 1. Heat the solution in the flask, preferably with an electric heating mantle, until the temperature of the contents reaches exactly 180°C. (A quartz heating mantle is preferred in order to reach the required 180°C in a minimum time.) While heating, the tip of the thermometer must extend below the level of the liquid in the flask. Discard the distillate. The procedure, to this step, serves to adjust the acid-water ratio for subsequent distillations.

12.1.2 **Caution**—Cool the acid-water mixture to below 100°C, slowly add 300 mL of sample, and mix thoroughly before heating. Distill as described in 12.1.1, until the temperature reaches 180°C. Do not allow the temperature to exceed 180°C; excessive carryover of sulfate occurs at temperatures of or above 180°C, resulting with interference in the subsequent fluoride measurement.

12.1.3 Collect the distillate in any suitably calibrated vessel. If a calibrated vessel is used, it is possible to dispense with thermometer readings and stop the distillation when the volume of distillate reaches 300 mL.

12.1.4 In the case of samples containing chlorides in concentrations which may interfere in the subsequent reaction, add Ag_2SO_4 to the distillation mixture at a rate of 5 mg/mg of chloride.

⁵ Glass beads must be of a soft glass (rather than borosilicate). Use about 12 beads. Soft beads will provide silica to the fluoride and protect the distillation flask.

TABLE 1 Determination of Precision—Final Statistics for Test Method A

NOTE 1—Precision of Test Method A was determined from round robin data using distillation with ion selective electrode finish.

Amount added, mg/L	0.150	0.560	0.840	2.600
Reagent Water				
Concentration, x	0.147	0.558	0.818 ^A	2.520
S _t	0.033	0.053	0.034 ^A	0.099
S _o	0.013	0.017	0.004 ^A	0.031
Wastewater				
Concentration, x ^A	0.126	0.505	0.771	2.454 ^A
S _t	0.048	0.068	0.092	0.070 ^A
S _o	0.018	0.013	0.017	0.030 ^A

^ACalculated with outlier point removed from data base.

12.1.5 The acid-water distilling solution may be used repeatedly until the buildup of interference materials equals the concentration given in Section 9.

12.2 Analysis:

12.2.1 Use Test Method B (Ion Selective Electrode) with the buffer solution described in 18.1.

13. Precision and Bias

13.1 The precision and bias for Test Method A, shown in Table 1 and Table 2 were determined using distillation followed by an ion selective electrode finish. Four concentrations and three replicates were provided by six laboratories for reagent water and wastewater.

TEST METHOD B—ION SELECTIVE ELECTRODE

14. Scope

14.1 This test method is applicable to the measurement of fluoride ion in finished waters, natural waters, and most industrial wastewaters. With this test method, distillation is eliminated and concentrations of fluoride from 0.1 to 1000 mg/L may be measured.

14.2 The test method is not applicable to samples containing more than 10 000 mg/L of dissolved solids.

14.3 This test method was tested on reagent water. It is the user’s responsibility to ensure the validity of this test method for waters of untested matrices.

TABLE 2 Determination of Bias for Test Method A

NOTE 1—Bias of Test Method A was determined from round robin data using distillation with ion selective electrode finish.

Amount added mg/L	Mean recovery mg/L	Bias	% Bias	Statistically significant at 5 % level
Reagent Water				
0.150	0.147	– 0.003	–2.0 %	no
0.560	0.558	–0.002	–0.4 %	no
0.840	0.818	– 0.022	–2.6 %	yes
2.600	2.520	– 0.080	–3.1 %	yes
Wastewater				
0.150	0.126	– 0.024	– 16.0 %	no
0.560	0.505	– 0.055	–9.8 %	yes
0.840	0.771	–0.069	–8.2 %	yes
2.600	2.454	– 0.146	–5.7 %	yes

TABLE 3 Allowable Interference Levels with Selective Ion Electrode and Buffer ^A

Interfering Ion	Maximum Allowable Concentration at 1.0 mg/L F [–]
Al ⁺³	0.5
Si ⁺⁴	50
Fe ⁺³	65

^ARefer to 16.2 for description of interfering cations.

15. Summary of Test Method

15.1 The fluoride is determined potentiometrically using an ion selective fluoride electrode in conjunction with a standard single junction, sleeve-type reference electrode, and a pH meter having an expanded millivolt scale, or an ISE meter having a direct concentration scale for fluoride.

15.2 The fluoride electrode consists of a lanthanum fluoride crystal across which a potential is developed by fluoride ions.^{6,7} The cell may be represented by Ag/AgCl, Cl (0.3), F (0.001) LaF₃/test solution/KCl/AgCl/Ag.

16. Interferences

16.1 Extremes of pH interfere; sample pH should be between 5.0 and 9.0.

16.2 Polyvalent cations of Si ⁺⁴, Fe ⁺³, and Al ⁺³ interfere by forming complexes with fluoride. The degree of interference depends upon the concentration of fluoride, and the pH of the sample (see Table 3). The addition of the buffer solution, 18.1, buffers the solution pH and will complex small amounts of aluminum, as well as silicon and iron. The use of one of the two selective buffers (see 18.2 and 18.3) is recommended when aluminum is present, because they are more effective over a greater range of aluminum concentrations.

16.3 Interferences usually encountered in other test methods, such as sulfate or phosphate, do not affect this test method.

17. Apparatus

17.1 pH Meter, with expanded millivolt scale or ISE meter.

17.2 Fluoride Ion Selective Electrode.

17.3 Reference Electrode, single-junction sleeve-type.

17.4 Mixer, magnetic, with a TFE-fluorocarbon coated stirring bar.

18. Reagents

18.1 Buffer Solution (pH from 5.0 to 5.5)—To approximately 500 mL of water, add 57 mL of glacial acetic acid (sp gr 1.06), 58 g of sodium chloride (NaCl), and 0.30 g of sodium citrate dihydrate in a 1000-mL beaker. Stir the solution to dissolve, and cool to room temperature. Adjust the pH of the solution to between 5.0 and 5.5 with 5 N sodium hydroxide (NaOH) (about 150 mL will be required). Transfer the solution to a 1000-mL volumetric flask and dilute to the mark with water.

⁶ Frant, M.S., and Ross, J.W., “Electrode for Sensing Fluoride Ion Activity in Solution,” *Science*, Vol 154, 1966, p. 1553.

⁷ Frant, M.S., and Ross, J.W., “Use of a Total Ionic Strength Adjustment Buffer for Electrode Determination of Fluoride in Water Supplies,” *Anal. Chem.*, Vol 40, 1968, p. 1169.

TABLE 4 Determination of Precision Without Distillation using Buffers

Concentration, mg/L	Buffer A		Buffer B	
	S _t	S _o	S _t	S _o
0.25	0.05	0.023	0.066	0.02
2.5	0.025	0.091	0.04	0.035
25	1.21	0.356	0.896	0.218
250	22.2	3.46	1.68	0.80

18.2 *Buffer A for Aluminum*—To approximately 500 mL of water, add 84 mL of reagent grade hydrochloric acid (sp gr 1.19), 242 g of tris-(hydroxymethyl)-aminomethane (THAM) (also known as 2-amino-2-(hydroxymethyl)-1,3-propanediol), and 230 g of sodium tartrate (Na₂C₄H₄O₆·2H₂O). Stir to dissolve, and cool to room temperature. Transfer the solution to a 1000-mL volumetric flask and dilute to the mark with water.

18.3 *Buffer B for Aluminum*—Dissolve 60 g of citric acid monohydrate, 210 g of sodium citrate dihydrate, and 53.5 g of ammonium chloride in 500 mL of water. Add 67 mL of ammonium hydroxide (sp gr 0.90). Transfer the solution to a 1000-mL volumetric flask and dilute to the mark with water.

18.4 *Sodium Fluoride Solution, Standard* (1.0 mL = 0.01 mg of F)—See 11.3.

19. Calibration

19.1 Prepare a series of three standards, 0.5, 1.0, and 2.0 mg/L, using the standard fluoride solution (see 18.4). Dilute the following volumes to 100 mL:

Fluoride Solution, Standard, mL (1.0 mL = 0.01 mg F)	Concentration, mg F/L
5.00	0.50
10.00	1.00
20.00	2.00

19.1.1 For unusual waters containing high concentrations of fluorides, the range of standards may be expanded up to 1000 mg/L, if necessary.

19.2 Pipet 50 mL of each standard into a 150-mL beaker. Using a pipet, add 50 mL of buffer. Mix each solution well using a magnetic stirrer.

19.3 *Calibration of pH Meter*—Immerse the pH electrodes in each standard solution, starting with the lowest concentration, and measure the developed potential while mixing. The electrodes must remain in the solution for at least 3 min, or until the reading has stabilized. Using semilogarithmic graph paper, plot the concentration of fluoride in milligrams per litre on the logarithmic axis versus the electrode potential developed in the standard on the linear axis, starting with the lowest concentration at the bottom of the scale.

19.4 *Calibration of ISE Meter*—Follow the directions of the manufacturer for the operation of the instrument. See 19.1 and 19.1.1 for selection of standards.

20. Procedure

20.1 Place 50.0 mL of the sample and 50.0 mL of buffer into a 150-mL beaker. Place the solution on a magnetic stirrer and mix at medium speed. Immerse the electrodes in the solution and observe the meter reading while mixing. The electrodes

TABLE 5 Determination of Bias Without Distillation (Buffer A)

Amount Added, mg/L	Amount Found, mg/L	± Bias	± % Bias
0.25	0.23	-0.02	-8
2.5	2.53	+ 0.07	+ 1.2
25	24.35	- 0.65	- 2.6
250	246.7	-3.3	- 1.32

TABLE 6 Determination of Bias Without Distillation (Buffer B)

Amount Added, mg/L	Amount Found, mg/L	± Bias	± % Bias
0.25	0.257	+ 0.007	+ 2.8
2.5	2.486	- 0.01	- 0.56
25	24.98	-0.02	- 0.08
250	245.75	- 4.25	-1.7

must remain in the solution for at least 3 min, or until the reading has stabilized. At concentrations less than 0.5 mg/L of fluoride, it may take as long as 5 min to reach a stable meter reading; higher concentrations stabilize more quickly. If a pH meter is used, record the potential measurement for each unknown sample and convert the potential reading to the fluoride ion concentration of the unknown, using the standard curve. If an ISE meter is used, read the fluoride level in the unknown sample directly in milligrams per litre on the fluoride scale.

NOTE 1—It is recommended that the solution samples are the same temperature as calibration standards. This recommendation was not in place during the original round robin.

21. Calculation

21.1 Calculate the concentration of fluoride ion, in milligrams per litre, in accordance with Eq 1

$$\text{Fluoride, mg/L} = 50A/V \quad (1)$$

where:

A = fluoride measured by using the Test Method B (Ion Selective Electrode) and the buffer solution described in 18.1, and

V = sample, mL.

22. Precision and Bias ⁸

22.1 The precision of this test method, using the buffer solution described in 18.1 (see Table 4), was tested by 111 laboratories doing single analysis and found to be 0.030 at a concentration of 0.85 mg/L of fluoride.⁸

22.2 The precision of this test method (Table 5), using the buffer solution A described in 18.2, was tested by seven operators in five laboratories doing three replicates of four concentrations. Each concentration was analyzed in the presence of 20 mg/L of aluminum. The results were from analysis in reagent waters. It is the responsibility of the user to test the application to other matrices.

22.3 The precision of this test method (Table 6), using the buffer solution B described in 18.3 was tested by six operators

⁸ Supporting data are available from ASTM Headquarters. Request RR:D19-161.

in four laboratories doing three replicates of four concentrations. Each concentration was analyzed in the presence of 20 mg/L of aluminum. The results were from the analysis of reagent water. It is the responsibility of the user to test the application to other matrices.

22.4 This precision and bias statement conforms to Practice D 2777 – 77, which was in place at the time of round robin testing. It does not meet the requirements of Practices D 2777 – 86.

23. Keywords

23.1 analysis; electrode; fluoride; water

APPENDIX

(Nonmandatory Information)

X1. RATIONALE FOR DISCONTINUATION OF TEST METHODS

X1.1 SPADNS Procedure, Photometric

X1.1.1 This test method was discontinued in 1988. The test method may be found in its entirety in the *1988 Annual Book of ASTM Standards*, Vol 11.01.

X1.1.2 This test method is applicable to the accurate determination of fluoride ion in water, including most wastewaters. This test method may not be applicable to certain exceptions, such as concentrated brines and oily wastes.

X1.1.3 The fluoride is distilled as hydrofluosilicic acid and is determined photometrically by its bleaching effect upon the SPADNS dye. Distillation may be omitted without loss of

precision only if it is known that the concentration of certain interfering substances will not cause a 0.1 mg/L error at 1.0 mg F/L.

X1.1.4 This test method was discontinued and replaced by a distillation method which determines fluoride content in water by the selective ion electrode. The SPADNS photometric procedure was discontinued because there were insufficient laboratories interested in participating in another collaborative study to obtain the necessary precision and bias as required by Practice D 2777.

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