



## Designation: D1179 – 16 (Reapproved 2021)<sup>e 1</sup>

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

This standard is issued under the fixed designation D1179; 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.

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

<sup>e 1</sup> NOTE—The WTO caveat was added editorially in December 2021.

## 1. Scope

1.1 These test methods<sup>2</sup> 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 21

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 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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

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

1.7 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the*

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

*Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>3</sup>

- D1066 Practice for Sampling Steam
- D1129 Terminology Relating to Water
- D1193 Specification for Reagent Water
- 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
- D4127 Terminology Used with Ion-Selective Electrodes
- 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 Terminologies D1129 and D4127.

## 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, usually near 1 mg/L, 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

<sup>3</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.

**TABLE 1 Allowable Interference Levels with Selective Ion Electrode and Buffer<sup>A</sup>**

Interfering Ion	Maximum Allowable Concentration at 1.0 mg/L F <sup>-</sup>
Al <sup>+3</sup>	0.5
Si <sup>+4</sup>	50
Fe <sup>+3</sup>	65

<sup>A</sup>Refer to 16.2 for description of interfering cations.

conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where 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 Type I reagent water conforming to Specification D1193. 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 this test method.

## 6. Sampling

6.1 Collect the sample in accordance with Practice D1066 or Practices D3370, as applicable.

### 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. Samples that may require distillation include high concentrations of fluoborate or fluoboric acid (such as electroplating wastes), and samples which contain aluminum, silica, or iron (see Table 1). Anions such as chloride, bromide, iodide, sulfate, bicarbonate, nitrate, phosphate and acetate do not interfere with ISE measurement unless present at greater than about 1 % and do not necessitate distillation. 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.

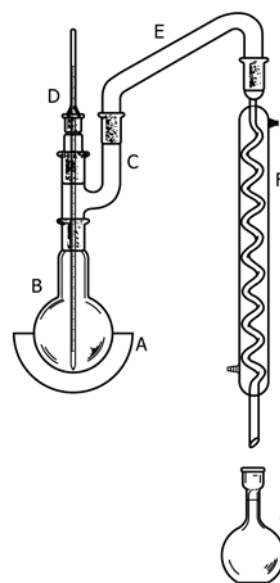
## 8. Summary of Test Method

8.1 The fluoride is distilled as hydrofluosilicic acid and is determined by the ion selective electrode method.

## 9. Interferences

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

<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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.



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**

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 *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. Alternately, commercially prepared fluoride standards of appropriate known purity may be used.

11.2 *Sulfuric Acid (H<sub>2</sub>SO<sub>4</sub>), Concentrated* (sp gr 1.84).

## 12. Procedure

### 12.1 Distillation:

12.1.1 Place 400 mL of water in the distilling flask and add 200 mL of concentrated H<sub>2</sub>SO<sub>4</sub> (sp gr 1.84). Observe the usual precautions while mixing the H<sub>2</sub>SO<sub>4</sub> by slow addition of the acid accompanied by constant swirling. Add sufficient boiling stones<sup>5</sup> 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.

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 Samples containing chlorides less than about 1 % do not interfere with ISE measurements.

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*—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 2 and Table 3 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.

13.2 Precision and bias for this test method conform 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.

<sup>5</sup> 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 2 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 <sup>A</sup>	2.520
S <sub>t</sub>	0.033	0.053	0.034 <sup>A</sup>	0.099
S <sub>o</sub>	0.013	0.017	0.004 <sup>A</sup>	0.031
Wastewater				
Concentration, x <sup>A</sup>	0.126	0.505	0.771	2.454 <sup>A</sup>
S <sub>t</sub>	0.048	0.068	0.092	0.070 <sup>A</sup>
S <sub>o</sub>	0.018	0.013	0.017	0.030 <sup>A</sup>

<sup>A</sup> Calculated with outlier point removed from data base.

**TABLE 3 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

## 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. Concentrated solutions of fluoborate or fluoboric acid, such as in electroplating wastes, should be distilled or tested using a fluoroborate ISE. Samples which contain aluminum, silica, or iron may require distillation (see Table 1). Anions such as chloride, bromide, iodide, sulfate, bicarbonate, nitrate, phosphate, and acetate typically do not interfere unless present at greater than about 1 % or more.

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.

### 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 or a combination fluoride electrode. Use the electrode(s) with a pH meter having an expanded millivolt scale, or an ISE meter having a direct concentration readout.

15.2 The fluoride electrode consists of a lanthanum fluoride crystal across which a potential is developed by fluoride ions.<sup>6,7</sup> The cell may be represented by Ag/AgCl, Cl (0.3), F (0.001) LaF<sub>3</sub>/test solution/KCl/AgCl/Ag.

15.3 The electrode(s) is calibrated in known fluoride solutions, and the concentrations of unknowns are determined in solutions with the same background. Samples and standards should be measured at the same temperature.

15.4 Standards and samples are diluted with an ionic strength adjustor that also minimizes possible interferences from hydroxide and low levels of aluminum and iron.

## 16. Interferences

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

16.2 Polyvalent cations of Si<sup>+4</sup>, Fe<sup>+3</sup>, and Al<sup>+3</sup> interfere by forming complexes with fluoride. The degree of interference depends upon the concentration of fluoride, and the pH of the sample (see Table 1). 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, chloride, or phosphate, do not affect this test method.

## 17. Apparatus

17.1 *pH Meter*, with expanded millivolt scale or selective-ion meter.

17.2 *Fluoride Ion Selective Electrode*, half-cell or combination electrode.

17.3 *Reference Electrode*, single-junction sleeve-type (when using fluoride half-cell).

17.4 *Mixer*, magnetic, with a TFE-fluorocarbon coated stirring bar or motorized stirrer.

## 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.

18.2 *Buffer A for Aluminum*—To approximately 500 mL of water, add 84 mL of reagent grade hydrochloric acid (sp gr

**TABLE 4 Determination of Precision Without Distillation using Buffers**

Concentration, mg/L	Buffer A		Buffer B	
	S <sub>t</sub>	S <sub>o</sub>	S <sub>t</sub>	S <sub>o</sub>
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

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 (Na<sub>2</sub>C<sub>4</sub>H<sub>4</sub>O<sub>6</sub> · 2H<sub>2</sub>O). 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 11.1.

## 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 electrode(s) 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 an electronic spreadsheet, plot the electrode potential on the x-axis and the log concentration of fluoride in milligrams per litre on the y-axis or use a direct reading selective-ion meter to get the concentration of the fluoride.

19.4 *Calibration of Selective-Ion 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. Use a motorized stirrer or 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 must remain in the solution for at least

<sup>6</sup> Frant, M. S., and Ross, J. W., "Electrode for Sensing Fluoride Ion Activity in Solution," *Science*, Vol 154, 1966, p. 1553.

<sup>7</sup> Frant, M. S., and Ross, J. W., "Use of a Total Ionic Strength Adjustment Buffer for Electrode Determination of Fluoride in Water Supplies," *Analytical Chemistry*, Vol 40, 1968, p. 1169.