Designation: D1179 – 16 (Reapproved 2021)ε1

Standard Test Methods for Fluoride Ion in Water[1]

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 (ε) 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.

ε[1] NOTE—The WTO caveat was added editorially in December 2021.

1. Scope

1.1 These test methods[2] 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 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:*[3]

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

[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.

Current edition approved Nov. 1, 2021. Published December 2021. Originally approved in 1951. Last previous edition approved in 2016 as D1179 – 16. DOI: 10.1520/D1179-16R21E01.

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

[3] 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 [A]

Interfering Ion	Maximum Allowable Concentration at 1.0 mg/L F^-
Al^{+3}	0.5
Si^{+4}	50
Fe^{+3}	65

[A]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.[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 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.

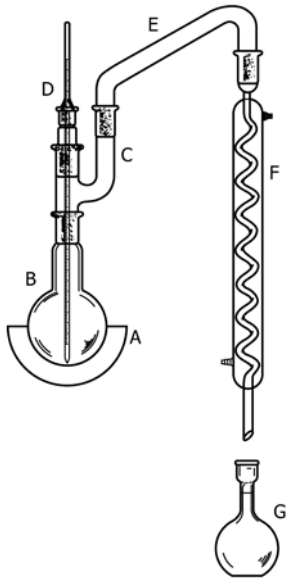
7.2 This test method was tested on reagent water and wastewater. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

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.



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.

[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.