



Standard Test Methods for Fluoride Ion in Water¹

This standard is issued under the fixed designation D 1179; 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 approval. 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 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:

Test Method A—Distillation	Sections 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.

Current edition approved Feb. 10, 1999. Published April 1999. Originally published as D 1179 – 51. Last previous edition D 1179 – 93.

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.

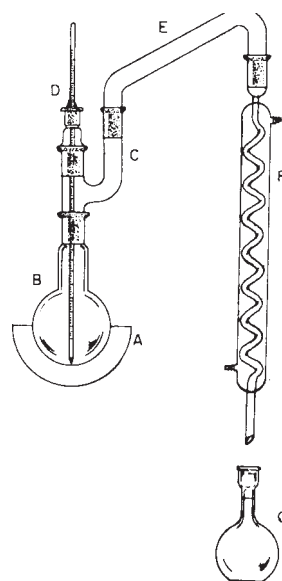
11.2 *Sodium Arsenite Solution* (2 g/L)—Dissolve 2 g of sodium arsenite ($NaAsO_2$) in water and dilute to 1 L.

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.