



Designation: D 3270 – 00

## Standard Test Methods for Analysis for Fluoride Content of the Atmosphere and Plant Tissues (Semiautomated Method)<sup>1</sup>

This standard is issued under the fixed designation D 3270; 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 describe the semiautomated procedure for the analyses of various types of samples for the purpose of determining total fluoride. Since the test methods incorporate microdistillation of the sample, they may be applied to any fluoride-containing solution where standards of identical composition have been carried through the same sample preparation procedures and have proven to provide quantitative recovery when analyzed by the semiautomated system. Conversely, the methods shall not be applied for analyses until the applicability has been demonstrated.

1.2 In normal use, the procedure can detect 0.1  $\mu\text{g/mL}$  of F. The normal range of analysis is from 0.1 to 1.6  $\mu\text{g/mL}$  of F. Higher concentrations can be analyzed by careful dilution of samples with reagent water. If digested samples routinely exceed 1.6  $\mu\text{g/mL}$  of F, the analytical portion of the pump manifold can be modified to reduce sensitivity. However, the best procedure is to analyze a smaller aliquot of the sample. Most accurate results are obtained when the fluoride concentration falls in the middle or upper part of the calibration curve.

1.3 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

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.* See 8.3, 10.2.4, and 10.2.5 for additional precautions.

### 2. Referenced Documents

#### 2.1 ASTM Standards:

D 1193 Specification for Reagent Water<sup>2</sup>

D 1356 Terminology Relating to Sampling and Analysis of Atmospheres<sup>3</sup>

D 3266 Test Method for Automated Separation and Collection of Particulate and Acidic Gaseous Fluoride in the Atmosphere (Double Paper Tape Sampler Method)<sup>3</sup>

D 3267 Test Method for Separation and Collection of Particulate and Water-Soluble Gaseous Fluorides in the Atmosphere (Filter and Impinger Method)<sup>3</sup>

D 3268 Test Method for Separation and Collection of Particulate and Gaseous Fluorides in the Atmosphere (Sodium Bicarbonate-Coated Glass Tube and Particulate Filter Method)<sup>3</sup>

D 3269 Test Methods for Analysis for Fluoride Content of the Atmosphere and Plant Tissues (Manual Procedures)<sup>3</sup>

D 3614 Guide for Laboratories Engaged in Sampling and Analysis of Atmospheres and Emissions<sup>3</sup>

### 3. Terminology

3.1 *Definitions*—For definitions of terms used in these methods, see Terminology D 1356.

### 4. Summary of Test Methods

4.1 These semiautomated methods are based on the distillation of hydrogen fluoride (HF) from the sample and subsequent reaction of the distillate with alizarin fluorine blue-lanthanum nitrate reagent, to form a blue complex which is measured colorimetrically at 624 nm (**1**)<sup>4</sup>, or the subsequent measurement with a specific ion probe.

#### 4.2 General, Plant Material:

4.2.1 The plant material including leaf samples, washed or unwashed, is dried, and ground, then dissolved with perchloric acid and diluted to 50 mL with water. In the case of leaf samples, an appreciable amount of fluoride may be deposited on the external leaf surfaces. This fluoride behaves differently physiologically from fluoride absorbed into the leaf and it is often desirable to wash it from the surface as a preliminary step in the analysis. Details of a leaf-washing process are described in 9.1.

#### 4.3 General, Atmospheric Samples:

4.3.1 Test Methods D 3269 contains acceptable procedures and also techniques for the proper preparation of atmospheric samples. Test Methods D 3266, D 3267, and D 3268 are

<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee D22 on Sampling and Analysis of Atmospheres and are the direct responsibility of Subcommittee D22.03 on Ambient Atmospheres and Source Emissions.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 11.03.

<sup>4</sup> The boldface numbers in parenthesis refer to the references at the end of this method.

sampling procedures for ambient air and each method contains specific instructions for sample preparation prior to analyses by the semiautomated method.

4.4 General, System Operation:

4.4.1 The dissolved digest is pumped into the polytetrafluoroethylene coil of a microdistillation device maintained at 170°C (2-6). A stream of air carries the acidified sample through a coil of TFE-fluorocarbon tubing to a fractionation column. The fluoride and water vapor distilled from the sample are swept up the fractionation column into a condenser, and the condensate passed into a small collector. Acid and solid material pass through the bottom of the fractionation column and are collected for disposal. Acid and solid material pass through the bottom of the fractionation column and are collected for disposal. In the colorimetric method, the distillate is mixed continuously with alizarin fluorine blue-lanthanum reagent, the colored stream passes through a 15-mm tubular flow cell of a colorimeter, and the absorbance measured at 624 nm. In the potentiometric method, the distillate is mixed continually with a buffer, the mixed streams pass through a flow-through fluoride ion electrode, and the differential millivoltage is measured with an electrometer. The impulse is transmitted to a recorder.

4.4.2 All pieces of apparatus are commercially available, or may be adapted from commercially available equipment. The test method can also be run on most commercially available robot chemical analyzers. Details of construction of the microdistillation device are described in 7.10. Earlier versions of this test method have been published (3,5,6).

4.5 Principle of Operation:

4.5.1 Colorimetric System—The absorbance of an alizarin fluorine blue-lanthanum reagent is changed by very small amounts of inorganic fluoride.

4.5.2 Potentiometric System—Since the sample system is the same for this procedure as for the colorimetric procedure, the distillation step removes all of the interfering cations. The volatile acids that remain can be buffered by mixing with the Total Ionic Strength Adjustment Buffer (TISAB).

4.5.3 Distillation System—Since HF has a high vapor pressure, it is more efficiently distilled than the other acids previously mentioned (4.5). The factors controlling efficiency of distillation are temperature, concentration of acid in the distillation coil, and vacuum in the system. Large amounts of solid matter, particularly silicates, will also retard distillation. Accordingly, the smallest sample of vegetation consistent with obtaining a suitable amount of fluoride should be analyzed. The aforementioned conditions must be carefully controlled, since accurate results depend on obtaining the same degree of efficiency of distillation from samples as from the standard fluoride solutions used for calibration.

4.5.4 Temperature control is maintained within ± 2°C by the thermoregulator and by efficient stirring of the oil bath. Acid concentration during distillation is regulated by taking plant samples in the range from 0.1 to 2.0 g and by using 100 ± 10 mg of CaO and 3.0 ± 0.1 g of NaOH for ashing and fusion of each sample. Vacuum in the system is controlled with flowmeters and a vacuum gage. Any marked change in vacuum (greater than 0.7 kPa or 0.2 in. Hg) over a short time period

indicates either a leak or a block in the system. Distillation should take place at the same vacuum each day unless some other change in the system has been made. It is also essential to maintain the proper ratio between air flow on the line drawing liquid and solid wastes from the distillation coil and on the line drawing HF and water vapor (Fig. 1) from the distillation unit. Occasional adjustments on the two flowmeters should be made to keep this ratio constant and to maintain higher vacuum on the line drawing HF vapor so that little or no HF is diverted into the liquid and solid waste line. (See 10.3.4 for description of air flow system.)

5. Significance and Use

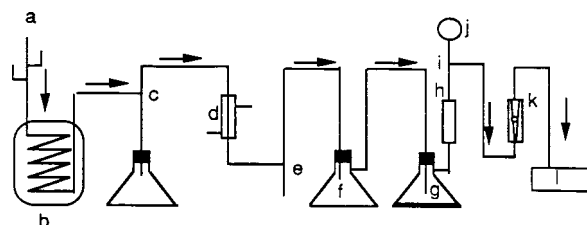
5.1 These test methods may be used for determining the fluoride content of particulate matter and gases collected from the atmosphere by passive and active means, including plant tissues. The user is warned that the fluoride content of passive collectors (including plants) give only qualitative or semiquantitative measurement of atmospheric fluoride content.

6. Interferences

6.1 Since the air that is swept through the microdistillation unit is taken from the ambient atmosphere, airborne contaminants in the laboratory may contaminate samples. If this is a problem, a small drying bulb filled with calcium carbonate granules can be attached to the air inlet tube of the microdistillation unit.

6.2 If the polytetrafluoroethylene distillation coil is not cleaned periodically, particulate matter will accumulate and will reduce sensitivity.

6.3 Silicate, chloride, nitrate, and sulfate ions in high concentration can be distilled with fluoride ion and will interfere with the analysis by bleaching the alizarin fluorine blue-lanthanum reagent. Phosphate ion is not distilled, and therefore does not interfere. Metals such as iron and aluminum are not distilled and will not interfere with the analysis (most materials distilled over do not interfere with the potentiometric method). Maximum concentrations of several common anions at which there was no detectable interference are given in Table 1. The sulfate concentration shown is the amount tolerated above the normal amount of sulfuric acid used in microdistillation. A number of materials cause changes in absorbance at



- |   |                          |   |  |
|---|--------------------------|---|--|
| a | Air Inlet                | g | Waste Bottle with H <sub>2</sub> SO <sub>4</sub> |
| b | Microdistillation Coil   | h | Gas-Drying Tower                                 |
| c | Fractionation Column     | i | T-Tube   |
| d | Water-Jacketed Condenser | j | Vacuum Gauge                                     |
| e | Sample Trap              | k | Flowmeter  |
| f | Waste Bottle             | l | Vacuum Pump                                      |

FIG. 1 Schematic Drawing of Air Flow System for Semiautomated Analysis of Fluorides

**TABLE 1 Maximum Detectable Concentration of Several Anions Present in Samples at Which There is No Detectable Analytical Interference**

Compound Tested	Interfering Anion	Molarity Tolerated
Na <sub>2</sub> SO <sub>4</sub>	SO <sub>4</sub> (-2)	2 E-2
Na <sub>2</sub> SiO <sub>3</sub>	SiO <sub>3</sub> (-2)	5 E-3
NaCl	Cl(-1)	1 E-3
NaH <sub>2</sub> PO <sub>4</sub>	PO <sub>4</sub> (-3)	3.8
NaNO <sub>3</sub>	NO <sub>3</sub> (-1)	5 E-3

624 nm. Potential interfering substances commonly found in plant tissues are metal cations such as iron and aluminum, inorganic anions such as phosphate, chloride, nitrate, and sulfate, and organic anions such as formate and oxalate. Fortunately, metal cations and inorganic phosphate are not distilled in this system, and organic substances are destroyed by preliminary ashing. The remaining volatile inorganic anions may interfere if present in a sufficiently high concentration because they are distilled as acids. Hydrogen ions bleach the reagent which, in addition to being an excellent complexing agent, is also an acid-base indicator. To reduce acidic interferences, a relatively high concentration of acetate buffer is used in the reagent solution despite some reduction in sensitivity.

**7. Apparatus**

7.1 *Multichannel Proportioning Pump*, with assorted pump tubes, nipple connectors, glass connectors, and manifold platter.

7.2 *Pulse Suppressors*, for the sample and alizarin fluorine blue-lanthanum reagent streams are each made from 3.05 m lengths of 0.89-mm inside diameter polytetra fluoroethylene standard wall tubing. They are both an effective reagent filter and a pulse suppressor. Discard them after one month of use. The outlet ends of the suppressor tubes are forced into short lengths of (0.081-in.) inside diameter silicone rubber tubing, that is then connected to the reagent pump tube, and the other end then slipped over the *h* fitting which joins the sample and reagent streams.

7.3 *Automatic Sampler*, with 8.5 mL plastic sample cups.

7.4 *Voltage Stabilizer*.

7.5 *Colorimeter* (for colorimetric method), with 15-mm tubular flow cell and 624-nm interference filters.

7.6 *Ion Selective Electrode Detector*, (for potentiometric method) with flow-through electrodes.

7.7 *Rotary Vacuum and Pressure Pump*, with continuous oiler.

7.8 *Recorder*.

7.9 *Range Expander*.

7.10 *Microdistillation Apparatus*—A schematic drawing is shown in Fig. 2. Major components of microdistillation apparatus include the following:

7.10.1 *Reaction Flask*, 1000-mL, with a conical flange and cover (Fig. 2 A).

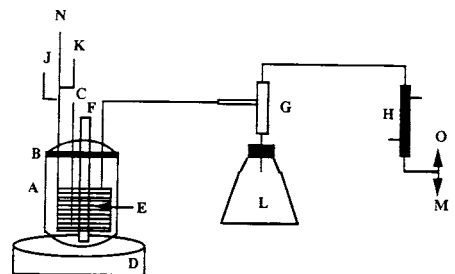
7.10.2 *Reaction Flask Flange Clamp* (Fig. 2B).

7.10.3 *Variable Speed Magnetic Stirrer* (Fig. 2D).

7.10.4 *Thermometer-Thermoregulator*, range 0 to 200°C (Fig. 2 C).

7.10.5 *Electronic Relay Control Box*.

7.10.6 *Immersion Heater*, 500 W (Fig. 2F).



- A Reaction Flask, Flange, Cover
- B Flange Clamp
- C Thermometer-Thermoregulator
- D Variable Speed Magnetic Stirrer
- E Flexible TFE Tubing
- F Immersion Heater
- G Fractionation Column
- H Water-Jacketed Condenser
- I Sample Trap
- J Sample Inlet
- K Acid Inlet
- L Waste Trap
- M Tubing
- N Air Inlet
- O Sample Trap Top

**FIG. 2 Schematic Drawing of Semiautomated Microdistillation Apparatus**

7.10.7 *Flexible Polytetrafluoroethylene, TFE tubing*, 4.8-mm outside diameter, 0.8-mm wall. A9.14-m length is coiled on a rigid support of such a diameter that the completed coil shall fit into the resin reaction flask (7.10.1). Care must be taken to prevent kinking of the tubing.

7.10.8 *Flowmeter*, with ranges from 0 to 5 L/min, with needle valve control.

7.10.9 *Vacuum Gage*, with a range from 0 to 34 kPa (254 torr).

7.10.10 *Microdistillation Column*, (Fig. 2G, also see Fig. 3).

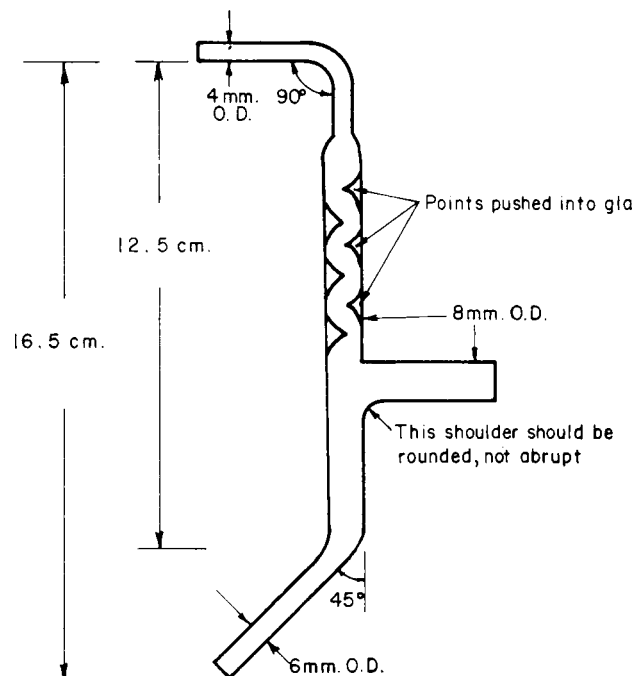
7.10.11 *Distillate Collector* (Fig. 2I and Fig. 3).

7.10.12 *Water-Jacketed Condenser* (Fig. 2H).

7.10.13 *Heat Exchange Fluid*, for reaction flask (7.10.1).

7.11 *Mechanical Convection Oven*.

7.12 *Wiley Cutting Mill*.



**FIG. 3 Microdistillation Column**

7.13 *Crucibles*, 40 mL, nickel, platinum or inconel.

7.14 *Muffle Furnace*.

7.15 *pH Meter*.

## 8. Reagents and Materials

8.1 *Purity of Reagents*—All reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>5</sup>

8.2 *Purity of Water*—Water shall be Type II reagent water conforming to Specification D 1193

8.3 *Reagents for Automated Fluoride Determination*:

8.3.1 *Acetate Buffer (pH 4.0)*—Dissolve 60 g of sodium acetate trihydrate (8.3.14) in 500 mL of reagent water. Add 100 mL of acetic acid (8.3.2) and dilute to approximately 900 mL with water. Measure the pH and adjust it to pH 4.0 with NaOH (8.3.16.1) or acetic acid (8.3.2). Dilute to 1 L with water.

8.3.2 *Acetic Acid, Glacial*, (sp gr 1.06).

8.3.3 *Acetone*.

8.3.4 *Alizarin Fluorine Blue (alizarin complexone, 3-amino-ethylalizarin-*N,N*-diacetic acid) Stock Solution, 0.01 M*—Suspend 0.9634 g of alizarin fluorine blue in about 100 mL of reagent water in a 250-mL volumetric flask. Add 2 mL of NH<sub>4</sub>OH (8.3.5) and shake until dye has completely dissolved. Add 2 mL of glacial acetic acid (8.3.2). Dilute the solution to 250-mL volume with reagent water and store at 4°C.

8.3.5 *Ammonium Hydroxide*, (NH<sub>4</sub>OH, sp gr 0.80).

8.3.6 *Wetting Agent*—Dissolve 50 g in 100 mL of reagent water by heating on a hot plate.

8.3.7 **t*-Butanol*.

8.3.8 *CDTA*, (1,2-cyclohexylenedinitrilo)-tetraacetic acid.

8.3.9 *Diluent Solution*—Mix 3.0 mL of 100 ppm standard fluoride solution (8.4.1), 0.5 mL wetting agent (8.3.6) and dilute to 1 L with reagent water.

8.3.10 *ISA Reagent*—Add 2.0 mL wetting agent (8.3.6) to 4.0 L of TISAB (8.3.19) and mix.

8.3.11 *Lanthanum Nitrate Stock Solution (0.01 M)*—Dissolve 2.1652 g of lanthanum nitrate hexahydrate [La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O] in reagent water in a 250-mL volumetric flask and dilute to volume with reagent water.

8.3.12 *Reference Electrode Reagent*—Add 1.0 mL of 100 ppm standard fluoride solution (8.4.1) and 0.5 mL Brij 35 (8.3.6) to a 1-L flask. Dilute to mark with TISAB (8.3.19).

8.3.13 *Silica Gel, Indicating*.

8.3.14 *Sodium Acetate Trihydrate*.

8.3.15 *Sodium Chloride* (NaCl).

8.3.16 *Sodium Hydroxide Pellets* (NaOH).

8.3.16.1 *Sodium Hydroxide Solution, (5 N)*—Dissolve 220 g NaOH in reagent water, and dilute to 1 L.

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

8.3.18 *Sulfuric Acid, Analytical Grade, (50 %, volume per volume)*—Mix 500 mL of H<sub>2</sub>SO<sub>4</sub> (8.3.17) with 500 mL of reagent water. Cool before use. (**Warning**—This mixture can react violently. Use eye protection and prepare in safety hood.)

8.3.19 *TISAB Buffer*—Add 57 mL glacial acetic acid (8.3.2), 58 g NaCl (8.3.15), and 4.0 g CDTA (8.3.8) to 500 mL of reagent water. Stir to dissolve and add 5 N NaOH (8.3.16.1) until pH is between 5.0 and 5.5. Cool and dilute to 1 L.

8.3.20 *Alizarin Fluoride Blue-Lanthanum Reagent*—The reagent is a modification of that reported by Yamamura, et al (7). Mix the following quantities of solutions in the order listed to make 1 L of alizarin blue-lanthanum reagent: 300 mL of acetate buffer (8.3.1), 244 mL of reagent water, 300 mL of acetone (8.3.3), 100 mL *t*-butanol (8.3.7), 36 mL of alizarin fluorine blue (8.3.4), 20 mL of La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (8.3.11), and 40 drops of wetting agent (8.3.8). Just prior to using reagent, place under vacuum for about 10 min to remove dissolved air. Unused working reagent is stable at 4°C for at least 7 days.

8.4 *Standards*.

8.4.1 *Standard Fluoride Solutions*—Dissolve 0.2207 g of dry reagent grade NaF (that had been stored in a desiccator prior to use) in reagent water and dilute to 1 L. The stock solution will contain 100 µg F/mL (100 ppm).

8.4.1.1 *Sodium Fluoride Solution (10 ppm)*—Dilute 100 mL of the 100 ppm NaF solution (8.4.1) to 1 L.

8.4.2 *Working Standards*—Prepare working standards by taking suitable aliquots to eight final concentrations of 0.2, 0.4, 0.8, 1.0, 1.6, 2.4, 3.2, and 4.0 µg F/mL. Plant analysis shall contain 6 g NaOH (8.3.16) and 20 mL HClO<sub>4</sub> (8.4.3) for each 100 mL of solution in order to compensate for the amounts of these substances used in alkali fusion of the ashed plant samples. Standard solutions for fluoride analysis of water samples or of air samples absorbed in water are made up in reagent water. Store stock solutions in clean polyethylene bottles in the cold. Since, as will be seen later, plant tissue samples are diluted to a 50-mL volume before analysis, the standard containing 0.20 µg/mL of fluoride is equivalent to a sample of plant material containing 10.0 µg of fluoride (0.20 µg/mL × 50 mL).

8.4.3 *Perchloric Acid, concentrated, (70 %)* (HClO<sub>4</sub>, sp gr 1.66).

8.4.3.1 *Perchloric Acid, (1 + 1 Solution)*—Dilute 250 mL of concentrated HClO<sub>4</sub> (8.4.3) to 500 mL with reagent water.

8.5 *Tetrasodium Ethylenediamine Tetraacetate (Na<sub>4</sub>EDTA), 1 % (weight per volume)*—Dissolve 1 g of Na<sub>4</sub>EDTA in 99 mL of reagent water.

8.6 *Plant Tissue Solution*—Dissolve 0.5 g of detergent and 0.5 g Na<sub>4</sub>EDTA in reagent water to make 1 L.

8.7 *Reagents for Ashing and Alkali Fusion of Plant Samples*:

8.7.1 *Calcium Oxide* (CaO), with a known, low fluoride content.

8.7.2 *Cheesecloth*.

8.7.3 *Ethanol or Propanol*.

8.7.4 *Hydrochloric Acid, (4 N)*—Dilute 342 mL of concentrated hydrochloric acid (HCl, sp gr 1.19) to 1 L.

8.7.5 *Kraft Paper Bags*.

<sup>5</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.