Designation: D3270 – 13 (Reapproved 2021)

Standard Test Methods for Analysis for Fluoride Content of the Atmosphere and Plant Tissues (Semiautomated Method)[1]

This standard is issued under the fixed designation D3270; 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.

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 µg/mL of F. The normal range of analysis is from 0.1 to 1.6 µg/mL of F. Higher concentrations can be analyzed by careful dilution of samples with reagent water. If digested samples routinely exceed 1.6 µg/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 standard. The values given in parentheses after SI units are provided for information only and are not considered standard.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* See 8.3, 10.2.4, and 10.2.5 for additional precautions.

1.5 *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:*[2]

D1193 Specification for Reagent Water

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

D3266 Test Method for Automated Separation and Collection of Particulate and Acidic Gaseous Fluoride in the Atmosphere (Double Paper Tape Sampler Method)

D3267 Test Method for Separation and Collection of Particulate and Water-Soluble Gaseous Fluorides in the Atmosphere (Filter and Impinger Method)

D3268 Test Method for Separation and Collection of Particulate and Gaseous Fluorides in the Atmosphere (Sodium Bicarbonate-Coated Glass Tube and Particulate Filter Method)

D3269 Test Methods for Analysis for Fluoride Content of the Atmosphere and Plant Tissues (Manual Procedures) (Withdrawn 2010)[3]

D3614 Guide for Laboratories Engaged in Sampling and Analysis of Atmospheres and Emissions

3. Terminology

3.1 *Definitions*—For definitions of terms used in these methods, see Terminology D1356.

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**),[4] or the subsequent measurement with a specific ion probe.

[1] These test methods are under the jurisdiction of ASTM Committee D22 on Air Quality and are the direct responsibility of Subcommittee D22.03 on Ambient Atmospheres and Source Emissions.

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[2] 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.

[3] The last approved version of this historical standard is referenced on www.astm.org.

[4] The boldface numbers in parentheses refer to the references at the end of this method.

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 D3269 contains acceptable procedures and also techniques for the proper preparation of atmospheric samples. Test Methods D3266, D3267, and D3268 are 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.

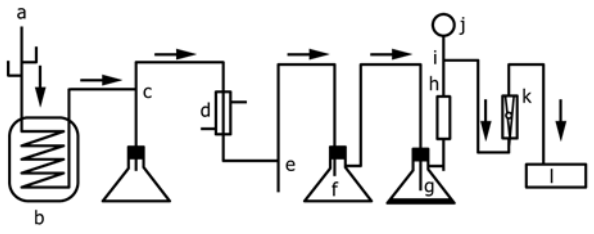
4.5.4 Temperature control is maintained within ±2°C by the thermoregulator and by efficient stirring of the oil bath. Acid concentration during distillation is regulated by taking plant samples in the range from 0.1 to 2.0 g and by using 100 ± 10 mg of CaO and 3.0 ± 0.1 g of NaOH for ashing and fusion 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



a	Air Inlet	g	Waste Bottle with H_2SO_4
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