# Standard Test Method for Separation and Collection of Particulate and Water-Soluble Gaseous Fluorides in the Atmosphere (Filter and Impinger Method)[1]

This standard is issued under the fixed designation D3267; 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 This test method provides a procedure for separation and collection on a chemically treated filter and in an impinger of particulate and water-soluble gaseous fluoride in the atmosphere. The sampling rate may vary from 30 L/min (1.0 $ft^3$/min) to 15 L/min (0.5 $ft^3$/min) for longer sampling periods depending on the atmospheric fluoride concentration. This test method is not intended to be applied to gaseous fluorine compounds that are not water-soluble

1.2 There are several limitations of the test method:

1.2.1 Although the acid-treated, medium retentive, prefilter has been shown to allow passage of HF, it will restrict passage of particulate matter only as small as about 1 µm. Thus, smaller particulate matter may pass through the filter and be collected in or pass through the impingers.

1.2.2 The maximum sample volume to be taken using this test method prior to changing the acid-treated prefilter is recommended as 12 $m^3$. This recommendation is made to minimize any effects due to particulate matter build-up.

1.3 The values stated in SI units are to be regarded as the standard. The inch-pound units 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.*For specific precautionary statements, see 7.2 and 7.4.6.

## 2. Referenced Documents

2.1 *ASTM Standards:*[2]
D1071 Test Methods for Volumetric Measurement of Gaseous Fuel Samples
D1193 Specification for Reagent Water
D1356 Terminology Relating to Sampling and Analysis of Atmospheres
D1357 Practice for Planning the Sampling of the Ambient Atmosphere
D2009 Practice for Collection by Filtration and Determination of Mass, Number, and Optical Sizing of Atmospheric Particulates (Withdrawn 1995)[3]
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]
D3270 Test Methods for Analysis for Fluoride Content of the Atmosphere and Plant Tissues (Semiautomated Method)
E337 Test Method for Measuring Humidity with a Psychrometer (the Measurement of Wet- and Dry-Bulb Temperatures)

## 3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D1356.

## 4. Summary of Test Method

4.1 Air is drawn through an air inlet tube (see Practice D1357) and is first passed through an acid-treated prefilter to remove particulate matter that may contain fluoride and then through an impinger to remove water-soluble fluorides.

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[1] This test method is under the jurisdiction of ASTM Committee D22 on Air Quality and is 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.

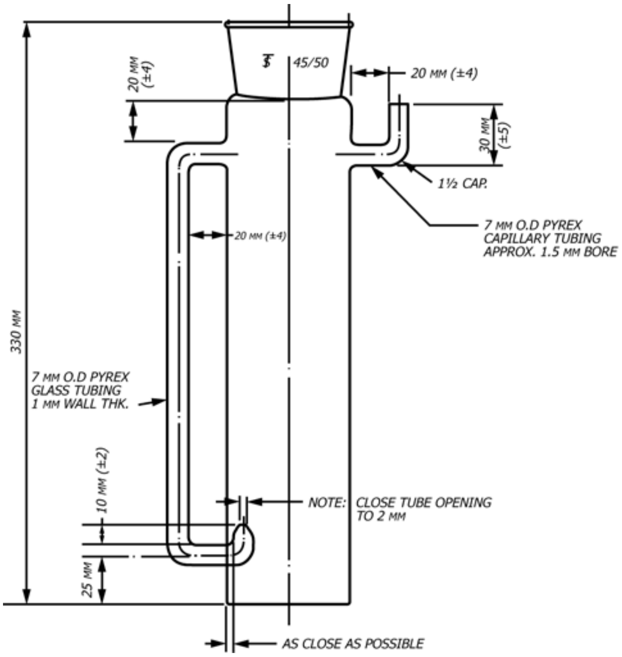

**FIG. 1 Modified Standard Impinger**

4.2 The prefilter and impinger solution are removed from the sampling system at the end of the selected sampling period and taken to an analytical work area and analyzed by either a potentiometric or photometric method (**1-4**).[4] See Test Methods D3269 and D3270.

## 5. Significance and Use

5.1 This test method provides a means of separation and collection of particulate and water soluble gaseous fluoride and provides samples that are convenient to analyze.

## 6. Interferences

6.1 Particulate metallic salts, such as those of aluminum, iron, calcium, magnesium or rare-earth elements, may react with and remove some or all of the water-soluble gaseous fluoride on the prefilter. If interfering quantities of such particulate metallic salts are present, the use of Test Method D3268 is recommended because the acidic fluoride gases are collected prior to the filter.

6.2 Aluminum or certain other metals or phosphates can interfere with subsequent analyses by photometric or electrometric methods. These potential interferences are discussed in Test Methods D3269 and D3270.

## 7. Apparatus

7.1 *Standard Impinger,* (Fig. 2C) for sampling covering periods up to 3 h. When sampling is initiated, the collecting impinger shall contain 75 to 150 mL of reagent water (see 8.2).

7.2 *Impinger, Modified, Standard,* Smith-Greenburg (Fig. 1). For sampling periods from 3 to 72 h, see Fig. 1 and Fig. 3C. (**Warning—**If a different size impinger is used, the recovery of the sample should be determined.)

7.3 *Water Level Control Device,* for use with long-term sampling train (Fig. 3).

7.3.1 *Liquid Level Controller.* (See Fig. 3G and H.)

7.3.2 *Control Valve,* solenoid-activated. (See Fig. 3D.)

7.3.3 *Water Reservoir,* equipped with a guard tube containing an alkaline reagent to prevent fluoride contamination. (See Fig. 3E and F.)

7.4 *Sampling Equipment* (see Fig. 1, Fig. 2, and Fig. 3 for dimensions and details).

7.4.1 *Sampling Tube* (see Fig. 2A), constructed of a 1225-mm (4-ft) length of a material that is inert to the atmosphere being sampled. (See Note 1.)

Note 1—Stainless steel coated with plastic material is preferred because of its rigidity and permanence. Plastic materials which have been shown to have a low absorbance for gaseous fluorides are polytetrafluoroethylene, polyethylene, polypropylene and polychlorotrifluoroethylene.

However, high air velocities through some types of plastic tubing may create a static charge and cause deposition of particulate matter. Consequently, if plastic is selected for use, it should be tested to demonstrate that this effect does not occur to a significant degree.

7.4.2 *Filter Holder,* stainless steel or polypropylene, (Fig. 2B), to hold the acid-treated prefilter. (See Note 2.)

Note 2—Note that filter changes are recommended after 12 $m^3$ are sampled.

7.4.3 *Mercury Manometer* (Fig. 2E), for the determination of pressure in the metered sampling line. A calibrated vacuum gage is also satisfactory.

7.4.4 *Dry Test Meter* (Fig. 2F), for measuring the total volume sampled.

7.4.5 *Thermometer*—Temperature measuring devices such as RTDs (Resistance Temperature Devices), thermistors and organic liquid-in-glass thermometers meeting the requirements of specific applications may be used.

7.4.6 *Control Valve* (Fig. 2H), to adjust the sample rate through a dry test meter. (See 7.4.4.) (**Warning—**Exercise care to see that all sampling apparatus is clean and free of contamination. Clean with a detergent low in fluoride and phosphate, followed by thorough rinsing with water (see 8.2.)

7.4.7 *Vacuum Pump* (see Fig. 2J), capable of a 30 L/min (1 $ft^3$/min) sampling rate and capable of continuous operation

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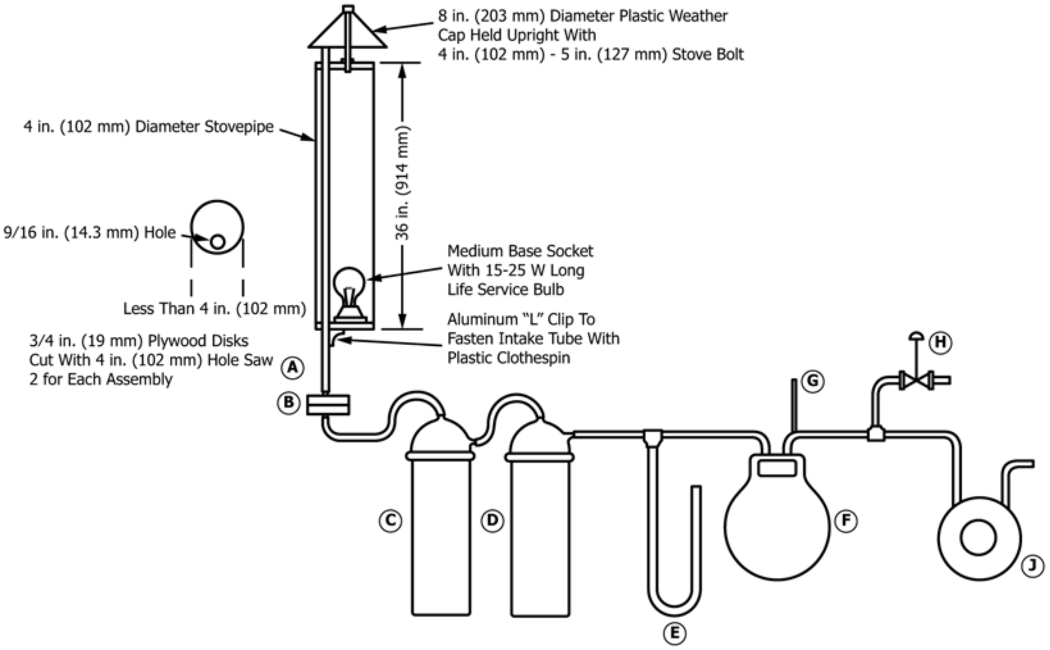
[4] The boldface numbers in parentheses refer to the references at the end of this standard.



A Sampling tube
B Filter holder
C Standard impinger
D Deminster (dry-impinger)
E Manometer
F Meter
G Thermometer
H Metering valve
J Vacuum pump

**SI Equivalents**

| in. | 9⁄16 | 3⁄4 | 4 | 5 | 8 | 36 |
|---|---|---|---|---|---|---|
| mm | 14 | 19 | 102 | 127 | 203 | 914 |

FIG. 2 Diagram of a Sample Train for Short-Term Sampling of Atmospheric Fluorides

over the maximum sample period selected under the environmental conditions imposed by the sampling location.

## 8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. All reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[5]

8.2 *Purity of Water*—Water shall be Type II reagent water conforming to Specification D1193. Additionally, test the water with a specific ion electrode or by concentration and photometric analysis to demonstrate that it contains less than 0.005 µg/mL of fluoride.

8.3 *Alcoholic Citric Acid Solution* (0.1 *N*)—Dissolve 4.203 g of citric acid monohydrate in 200 mL of 95 % ethyl alcohol.

8.4 Chemically treated filters are used as the prefilter. (See 10.1.)

8.5 *Sodium Hydroxide Solution (5N)*—Dissolve 200 g of sodium hydroxide (NaOH) in 250 mL of water in a 1-L volumetric flask, swirl to mix, cool and dilute to 1000 mL with water. Mix thoroughly.

8.6 *Sodium Hydroxide Solution (1.0 N)*—Dissolve 40.0 g of NaOH in 250 mL of reagent water in a 1000-mL volumetric flask. Swirl to mix, cool, and dilute to 1000 mL with reagent water. Mix thoroughly.

8.7 *Sulfuric Acid (1.0 N)*—Add 28.0 mL of concentrated $H_2SO_4$ (sp gr 1.84) to 250 mL of reagent water in a 1000-mL volumetric flask. Swirl to mix, cool, and dilute to 1000 mL with reagent water. Mix thoroughly.

8.8 *Total Ionic Strength Adjustment Buffer* (TISAB)—Add 57 mL of glacial acetic acid, 58 g of sodium chloride (NaCl) and 4.0 g of CDTA ((1,2-cyclohexylene-dinitrilo)tetraacetic acid) to 500 mL of distilled water. Stir and add 5 *N*NaOH solution (see 8.5) slowly until the pH is between 5.0 and 5.5. Cool and dilute to 1 L.

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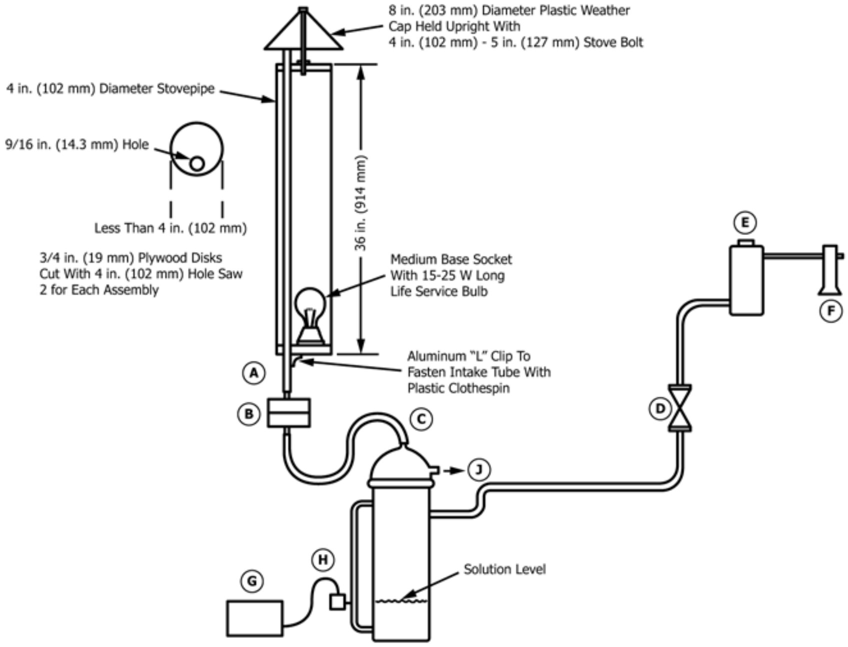
[5] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.



A Sampling tube
B Filter holder
C Modified standard impinger
D Control valve
E Water-reservoir
F Guard tube
G Water level controller
H Water level sensor
J Refer to Fig. 2 for Remainder of Sampling train following impinger C

**SI Equivalents**

| in. | 9⁄16 | ¾ | 4 | 5 | 8 | 36 |
|---|---|---|---|---|---|---|
| mm | 14 | 19 | 102 | 127 | 203 | 914 |

FIG. 3 Diagram of a Modified Standard Impinger for Long-Term Sampling of Atmospheric Fluorides

8.9 *TISAB* (1:1)—Dilute the full strength TISAB (see 8.8) 1:1 with an equal amount of water.

## 9. Calibration

9.1 Calibrate the dry test meter (see 7.4.4) in accordance with Test Methods D1071.

## 10. Procedure

10.1 *Treatment of Prefilter:*

10.1.1 Immerse medium retentive prefilter (**Warning—**Exercise care to see that all sampling apparatus is clean and free of contamination. Clean with a detergent low in fluoride and phosphate, followed by thorough rinsing with water (see 8.2.)) in the alcoholic citric acid solution (0.1 *N*) (see 8.3) and place under an infrared lamp to dry. After drying and prior to use, store the treated filter in a sealed container to prevent contamination.

NOTE 3—If the person using this test method demonstrates a requirement for prefilter of higher retentivity, other filters may be used. Membrane filters, if used, require reduction of the alcohol content of the alcoholic citric acid solution to 65 % to prevent deformation of the pores.

10.2 *Sampling:*

10.2.1 *Test the System for Leaks:*

10.2.1.1 Fill the impinger with the required volume of reagent water (see 8.2) that will be utilized during sampling.

10.2.1.2 Turn on the vacuum pump (see 7.4.7) and develop a vacuum slightly greater than that required for the desired sampling rate.

NOTE 4—For short term sampling (3 h or less), utilize a flow rate of 30 L/min (1 ft$^3$/min). For long-term sampling (24 to 72 h), a flow rate of 15 L/min (0.5 ft$^3$/min) shall be used with the modified standard impinger (see 7.2) and the water level controller (see 7.3) to compensate for solution evaporation.

10.2.2 During the sampling period, record the time, vacuum, and meter reading at the beginning and end of the sampling period. Also record barometric pressure in accordance with Test Method D3270 and the ambient temperature at intervals during the sampling period.

10.2.3 Use field blanks with each sample. (See Note 4.)

NOTE 5—Take two filters to the field and use one for sampling. Use the second filter as a field blank. Carry an impinger containing 150 mL of deionized water to the sampling site and treat in the same manner as the sample impingers except do not connect into a sample train. Use this impinger as a field blank.

10.2.4 At the end of the sampling period, transfer the filter and impinger contents to suitable containers for transporting to the work area where analyses are to be performed.

10.3 See Practice D1357 for guidance on sampling.

## 11. Preparation of Samples for Fluoride Analysis

11.1 Carry out the analysis in a work area with an atmosphere free of contamination by fluorides.

11.2 *Preparation of Impinger Solutions for Fluoride Analysis:*

11.2.1 Measure the volume of liquid in the impinger by weight if a tare weight is available on the impinger or by transferring to a tared polyethylene bottle and weighing the total contents after transfer. Record the weight of the liquid contents. Mix the contents thoroughly.

11.2.2 *For Potentiometric Analysis:* (Note 5 and Note 6).

11.2.2.1 Transfer 10.0 mL of the sample into a clean polyethylene (or polypropylene or TFE-fluorocarbon) beaker and dilute an equal amount with TISAB buffer. (8.9)

11.2.2.2 Analyze the aliquot using the potentiometric Test Method D3269.

NOTE 6—If the fluoride levels in the impinger solutions are lower than the sensitivities of the prescribed methods, then the solutions may be concentrated for analysis as described in Test Methods D3269 or analyzed as described in Note 6.

NOTE 7—In the potentiometric method, the sample may be spiked with an exactly measured amount of fluoride (for example: 0.4-mL of 0.01 mg $F^-$/mL standard NaF solution in 40 mL of final volume). This addition would be used if required to raise the concentration to a more favorable part of the response curve of the fluoride specific ion electrode. The concentration added will be deducted from the concentration determined.

11.2.3 *For Semiautomated Analyses:*

11.2.3.1 Transfer the solution to an 8.5-mL sample cup.

11.2.3.2 Analyze the sample using Method D3270.

11.3 *Preparation of the Prefilter Used to Collect Particulate for Fluoride Analysis:*

11.3.1 *For Potentiometric Analysis:*

11.3.1.1 Place the filter in a clean polyethylene (or polypropylene or TFE-fluorocarbon) beaker. Add 10.0 mL of 1 *N* $H_2SO_4$ (see 8.7), mix for a minimum of 5 min with a magnetic stirrer, and allow to stand for 5 min.

11.3.1.2 Add an equal volume of 1 *N*NaOH solution (see 8.6) and mix. (See Note 7.)

NOTE 8—In any specific sampling program, confirm the quantitative recovery of the fluoride content of the filter extraction with 1 *N* $H_2SO_4$ (see 8.7) (see Test Methods D3269.)

11.3.1.3 Add 20 mL of TISAB, (8.9) mix, and analyze by the potentiometric method in Test Methods D3269. Modification of the method as given in Note 6 may be used.

11.3.2 *For Semiautomated Analysis:*

11.3.2.1 Place the filters in clean 15 by 150-mm test tubes. Add 5.0 mL of 1 *N* $H_2SO_4$, (8.6) mix for several seconds with a vortex mixer, and allow to stand for 5 min. Filter samples (to remove cellulose filters) into 8.5-mL sample cups by a semimicro filtration method.

11.3.2.2 Analyze the sample using the semiautomated method given in Test Methods D3269.

## 12. Calculation

12.1 Calculate the volume of air sampled in standard cubic metres as follows:

$$C = (V_m \times 10^{-3})\,[(P_b - V_a - V_p)/P_s][(T_s + 273)/(T_m + 273)] \quad (1)$$

where:

$C$ = sample volume at 25°C (77°F) and 101.3 kPa (760 mm Hg)
$V_m \times 10^{-3}$ = meter reading at meter conditions, L (if the meter reads in cubic feet, $0.0283 \times ft^3 = V_m$),
$P_b$ = average barometric pressure during the sampling period, kPa, (mm Hg),
$P_s$ = standard pressure, 101.3 kPa (760 mm Hg),
$V_a$ = sample vacuum, kPa (mm Hg),
$V_p$ = water vapor pressure at metered air temperature, kPa, (mm Hg) See Test Method E337, Table X2.1. See Note 8.
$T_s$ = standard temperature, 25°C, and
$T_m$ = metered sample temperature, °C.

NOTE 9—Vapor pressure values in Table X2.1 of Test Method E337, are in Pa. Convert to kPa or mm Hg before using in equation in 12.1.

12.2 Calculate the fluoride concentration in the atmosphere as follows:

$$\text{Fluoride, } \mu g/m^3 = (A - B)/C \quad (2)$$

where:

$A$ = mass of fluoride in the sample, and
$B$ = mass of fluoride in the blank, µg.

## 13. Precision and Bias

13.1 *Precision:*

13.1.1 *Particulate Fluorides*—Nineteen pairs of duplicate samples collected near an industrial fluoride source (**5**) showed a standard deviation of a single determination of 0.034 for samples containing less than 0.5 µg $F^-/m^3$ and 0.208 for samples containing 0.5 to 4 µg $F^-/m^3$. Samples were analyzed by the potentiometric method in Test Methods D3269.

13.1.2 *Gaseous Fluorides*—Twenty-two pairs of duplicate samples collected and analyzed showed a standard deviation of a single determination of 0.069 for samples containing less than 0.5 µg $F^-/m^3$ and 0.168 for samples containing 0.5 to 3 µg $F^-/m^3$.

13.2 *Bias:*

13.2.1 *Particulate Fluorides*—The bias of collection of particulate fluorides has not been assessed. However, filters that have been certified by the manufacturer to collect particles greater than a stated size can be used with the assurance that quantitative recovery of the particulate matter of this size can be attained provided that proper attention is given to such precautions as the proper seating of the filter in the holder and checking for holes in the filter. See Practice D2009.

13.2.2 *Gaseous Fluorides*—Recovery of a known amount of HF in air which was passed through a standard Greenburg-Smith impinger containing water has been determined (**5**). Average recovery for 40 tests was 99.8 %. The regression equation was $Y = 1.0014X - 1.0957$ where $X$ is the mass of F delivered and $Y$ is the mass of F found.

## 14. Keywords

14.1 ambient atmospheres; fluorides; gaseous fluorides; particulate fluorides; sampling

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