Designation: D3266 – 91 (Reapproved 2011)

Standard Test Method for Automated Separation and Collection of Particulate and Acidic Gaseous Fluoride in the Atmosphere (Double Paper Tape Sampler Method)[1]

This standard is issued under the fixed designation D3266; 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.

1. Scope

1.1 This test method describes the automatic separation and collection on chemically treated paper tapes of particulate and gaseous forms of acidic fluorides in the atmosphere by means of a double paper tape sampler. The sampler may be programmed to collect and store individual air samples obtained over time periods from several minutes to 3 h. A 30.5-m (100-ft) tape will allow unattended operation for the automatic collection of up to 600 samples.

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

1.3 *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.*

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
D3195 Practice for Rotameter Calibration
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D3269 Test Methods for Analysis for Fluoride Content of the Atmosphere and Plant Tissues (Manual Procedures) (Withdrawn 2010)[3]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)
D3609 Practice for Calibration Techniques Using Permeation Tubes
D3614 Guide for Laboratories Engaged in Sampling and Analysis of Atmospheres and Emissions

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 paper tape to remove particulate matter which may contain fluoride and then through an alkali-treated paper tape to remove acidic fluoride gases.

4.2 The exhaust air is filtered through soda lime-glass wool, and the cleaned air is used to pressurize the front compartment to prevent fluoride contamination of the paper tapes from the ambient air.

4.3 Automatically, at the end of the preset sampling period, the vacuum pump is turned off, the tapes are indexed, and after indexing the vacuum pump is turned on. Indexing results in a "dead time" of several seconds.

4.4 The paper tapes are removed from the sampler after a selected period of operation and taken to an analytical work

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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.

area where the individual sample spots are cut out, treated to dissolve the fluoride, and analyzed by potentiometric or photometric methods.[4,5,6]

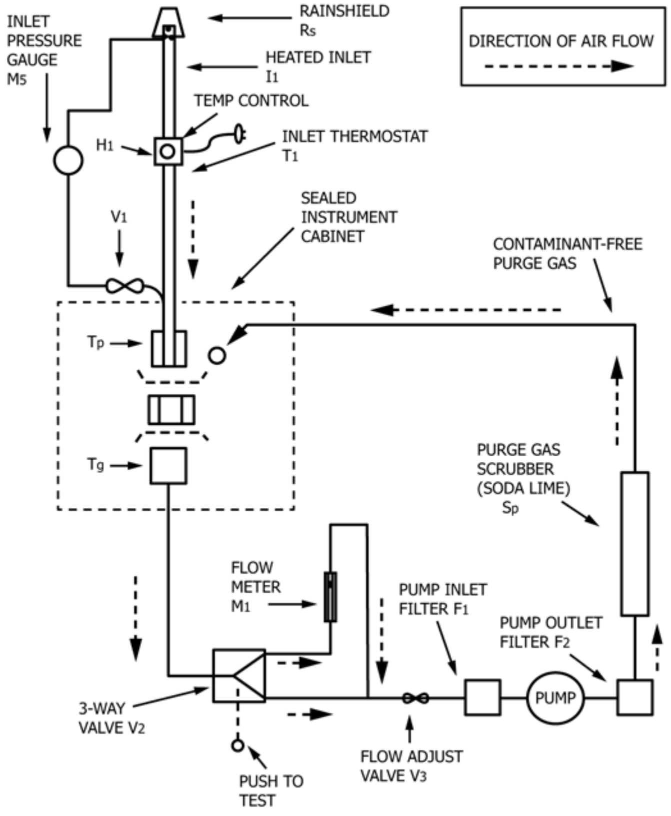

FIG. 1 Dual Tape Sampler Flow Schematic

5. Significance and Use

5.1 This test method provides a means of automatically separating and collecting atmospheric particulate and acidic gaseous fluoride samples.

5.2 Since the samples are collected on dry tapes, the samples are in a form which allows elution of the fluoride content with a small volume of eluent. Consequently, the method allows analyses of air samples taken for a time period as short as several minutes.

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 acidic gaseous fluoride on the prefilter. If interfering quantities of such particulate metallic salts are present, the use of Test Methods D3268 is recommended because the acidic fluoride gases are collected prior to the filter.

6.2 Acid aerosols or gases might neutralize or acidify the alkali-treated tape and prevent quantitative uptake of the acidic fluoride gases from the atmosphere. If this potential interference is present the decreased alkalinity of the water extract (13.2.2.1) may provide relevant information.

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

6.4 There are several limitations of the test method that could possibly occur:

6.4.1 Although the acid-treated medium retentive prefilter has been shown to allow passage of hydrofluoric acid, it will restrict passage of particulate matter only as small as about 1 µm. Thus, smaller particulate matter may pass through the filter and impinge on or pass through the alkali-treated second tape.

6.4.2 The maximum sampling time recommended in the method is 3 h. This time is limited to minimize the possible effect of particulate matter sorbing the acidic fluoride gases or reducing the sampling rate.

7. Apparatus[7]

7.1 The double paper tape sampler is a modification of and utilizes the basic principles of the sequential paper tape sampler used for dust collection. The commercially available apparatus requires modification, as described in this test method, prior to use.[8] It consists of the following:

7.1.1 *Heated Inlet*—I$_1$, TFE-fluorocarbon, 1 m (3.3 ft) in length, 9.5 mm ($\frac{3}{8}$ in.) (outside diameter), encased in a 9.5 mm ($\frac{3}{8}$ in.) (inside diameter) aluminum tube. See Fig. 1. The aluminum jacket is wrapped in a constant wattage heating wire of 25 W/m (8 W/ft). The tube is connected to the instrument with a TFE-fluorocarbon fitting.

7.1.1.1 *Rainshield, R$_s$*—Constructed of TFE-fluorocarbon.

7.1.1.2 *Proportional Temperature Controller*—H$_1$, with thermocouple reference point located at the bottom of the sample chamber.

7.1.1.3 *Inlet Thermostat*—T$_1$.

7.1.1.4 *Inlet Pressure Gauge*—M$_5$ with shutoff valve, V$_1$. One side of the gauge is connected to a TFE-fluorocarbon run tee placed between the intake tube and the sample block, and the other side is connected to a TFE-fluorocarbon run tee placed at the entrance to the intake tubing.

7.1.2 *Sampler*—See Figs. 1 and 2.

7.1.2.1 The upper part of the sampling block and sample inlet tube (Note 1) are constructed of polytetrafluoroethylene to minimize reactivity with acidic fluoride gases. The upper part of the sampling block (T$_p$) has a cylindrical cavity 25.4 mm (1 in.) in diameter with the inlet tube to the cavity perpendicular to the paper tapes. The lower part of the sampling block (T$_g$)

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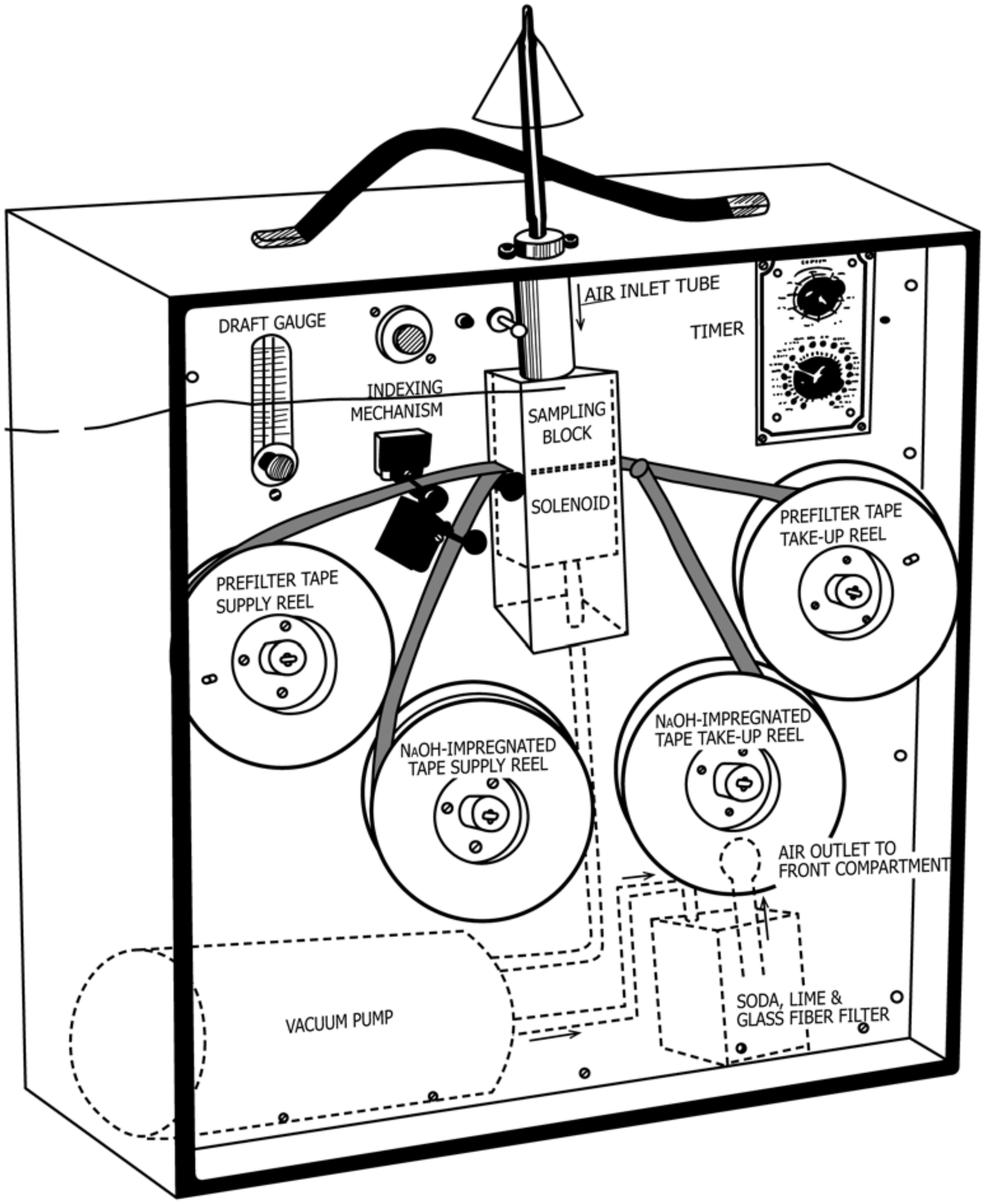
[4] Mandl, R. H., Weinstein, L. H., Weiskopf, G. J., and Major, J. L., "The Separation and Collection of Gaseous and Particulate Fluorides," *Paper CP-25A*, 2D International Clean Air Congress, Washington, DC, 1970.

[5] Weinstein, L. H., and Mandl, R. H., "The Separation and Collection of Gaseous and Particulate Fluorides," *VDI Berichte Nr.*, Vol 164, 1971, pp. 53–63.

[6] Lodge, James P. Jr., ed., "Methods of Air Sampling and Analysis," *Intersociety Committee*, 3rd ed., Lewis Publishers, Inc., 1988, pp. 352–356.

[7] The sole source of supply of the apparatus known to the committee at this time is Anderson Samplers, Atlanta, GA. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

[8] Zankel, K. L., McGirr, R., Romm, M. Campbell, Miller, R. "Measurement of Ambient Ground-Level Concentrations of Hydrogen Fluoride," *Journal of The Air Pollution Control Association*, Vol 37, 1987, pp. 1191–1196.



Double Paper Tape Sampler

FIG. 2 Schematic Drawing of Double Paper Tape Sampler

shall be constructed of stainless steel with a 25.4 mm (1-in.) cylindrical cavity. The outlet tube from the cylindrical cavity passes at a right angle into the pump compartment. The lower block shall be spring-loaded with a total force of 1.36 kg (3 lb) against the lower surface of the upper block. The surfaces of the two blocks shall be machined flat to ensure a tight seal. The lower block shall be lowered by means of an electric solenoid which counteracts the spring pressure.

7.1.2.2 *Capstans,* positioned to guide the paper tapes through the sampling block and to the take-up reel.

7.1.2.3 The paper tapes shall be drawn through the sample block and wound on the take-up reels by 1⁄30 Hz (2 rpm) synchronous motors. Indexing is accomplished either by mechanical or photoelectric means to provide even spacing between samples. Provision is made by the use of tape perforated at regular intervals, or by some other means, to locate the collected sample spots for subsequent analysis. A relay is wired in series with the indexing mechanism to turn off the vacuum pump during tape transport.

7.1.2.4 *Interval Timer,* used to provide desired sampling times.

7.1.2.5 *Carbon-Vane Vacuum Pump,* to sample air, of nominal 30 L/min (1 ft^3/min) free-air capacity. This provides a sampling rate through two tapes of about 15 L/min (0.5 ft^3/min). Exhaust air from the pump is passed through a soda lime-glass wool filter (S_p) and the filtered air is used to pressurize the front compartment and prevent contamination by fluorides from the ambient air.

7.1.2.6 *Sample Flow Adjustment Valve*—An inline needle valve, V_3.

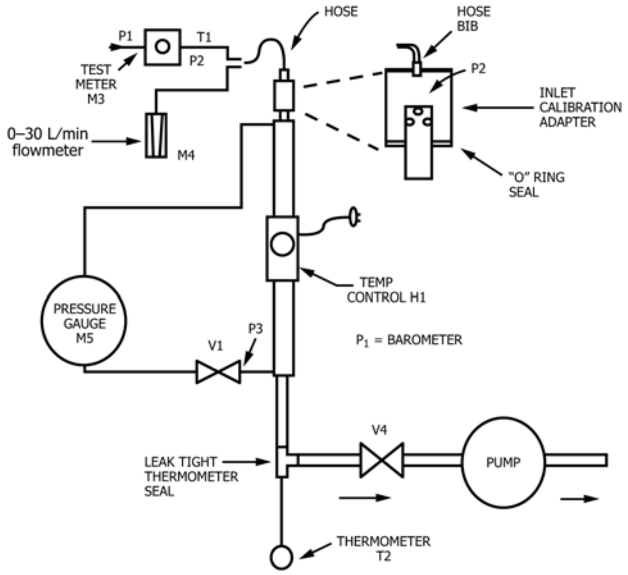


FIG. 3 Inlet Flow Calibration Schematic

7.1.2.7 *Flow Indicator*—0–30 L/min (0–1 ft^3/min) M$_1$.

7.1.2.8 *Paper Tape*—38-mm (1.5-in.) wide, appropriately treated chemically (10.1).

7.1.2.9 Provision shall be made for manual override of the tape transport mechanism.

7.1.2.10 All fittings shall be constructed of TFE-fluorocarbon.

7.2 *Calibration Equipment*—See Fig. 3.

7.2.1 *Inlet Calibration Adapter*—To connect hose from flow calibration equipment to sampler inlet.

7.2.2 *Flow Meter*—M$_4$, 0–30 L/min (0–1 ft^3/min), calibrated in accordance with Practice D3195.

7.2.3 *Wet Testmeter*—M$_3$, calibrated in accordance with Test Methods D1071.

7.3 *HF Permeation Tube Calibrator*—A permeation tube device, modified as described in Footnote 10. See also Practice D3609. All components of the calibrator that come into contact with HF shall be constructed of TFE-fluorocarbon.

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.[9]

8.2 *Purity of Water*—Water shall be Grade II Reagent conforming to Specification D1193. Additionally, the water used in the sampling and analytical procedures shall be demonstrated by testing with a specific ion electrode or by concentration and photometric analysis to contain less than 0.005 µg/mm of fluoride.

8.3 Chemically treated medium retentive filter paper tape 38-mm (1.5-in.) wide shall be used as the prefilter.

8.4 Chemically treated soft open filter paper 38-mm (1.5-in.) wide shall be used to remove acidic gaseous fluorides.

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

8.6 *Sodium Hydroxide, Alcoholic Glycerin Solution (0.5 N)*—Dissolve 4.000 g of NaOH pellets in 200 mL of 95 % ethyl alcohol containing 5 % glycerol.

8.7 *Total Ionic Strength Adjustment Buffer (TISAB)*—Add 57 mL of glacial acetic acid, 58 g of NaCl and 4.0 g of CDTA ((1,2-cyclohexylenedinitrilo)tetraacetic acid) to 500 mL of distilled water. Stir and add 5 *N* NaOH solution (8.11) slowly until pH is between 5.0 and 5.5. Cool and dilute to 1 L.

8.8 *TISAB* (1 + 1) —Dilute the full strength TISAB (8.7) 1 + 1 with an equal amount of reagent water.

8.9 *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 1-L volumetric flask. Swirl to mix, cool, and dilute to 1 L with reagent water. Mix thoroughly.

8.10 *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.

8.11 *Sodium Hydroxide Solution*(5.0 *N*)Dissolve 200.0 g of NaOH in a 1-L volumetric flask. Swirl to mix, cool, and dilute to 1 L with water. Mix thoroughly.

8.12 *Hydrogen Fluoride Permeation Tube*—200 ng/min at 35°C is satisfactory.[8]

9. Sampling

9.1 See Practice D1357 for general sampling guidelines.

9.2 Carefully align the sample block assembly to minimize leakage.

9.3 Adjust temperature controller for a temperature of 54°C (130°F).

9.4 Adjust flow rate to 15 L/min (0.5 ft^3/min).

9.5 Adjust timer to required sample time.

9.6 When temperature of inlet is stable at 54°C, at a flow rate of 15 L/min, advance tape, and commence sampling.

9.7 Record the reading of the inlet pressure gauge, M$_5$, for measurement of the air flow through the inlet tube. The air flow should remain reasonably constant over the sampling period selected.

9.8 Prior to removing the tapes, the reading of the static pressure meter should again be recorded to provide an average air flow measurement over the total operational period.

9.9 Remove the paper tapes at convenient intervals and place each in separate clean containers.

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[9] *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.

9.10 Analyze the individual samples by photometric or electrometric methods as referenced below and described in Test Methods D3269 and D3270.

10. Preparation of Apparatus

10.1 *Treatment of Paper Tapes*—Treat the paper tapes by passing the tapes through the appropriate impregnating solution and under a dryer and then rewinding. This is preferably done with a continuous motor-driven system.

10.1.1 *Treatment of the Medium Retentive Prefilter*—Treat this tape with the alcoholic citric acid solution, 0.1 M (8.5).

10.1.2 *Treatment of the Soft Open Prefilter*—Treat this tape with the alcoholic NaOH glycerol solution, 0.5 N (8.6).

10.2 Place the prefilter tape on the upper supply reel and the acidic gaseous fluoride tape on the lower supply reel. Thread the tapes through the sampling block and to their respective take-up reels.

11. Flow Calibration

11.1 Remove the inlet from the calibration system, and set up calibration equipment in accordance with Fig. 3.

11.2 Open valve V_1.

11.3 Adjust temperature controller for a temperature of 54°C (130°F) at T_2, when 30 L/min (1.0 ft^3/min) is flowing through the system.

11.4 Connect tubing from inlet calibration adapter to flow meter M_4, and adjust the flow rate to 30 L/min.

11.5 Without changing the valve setting, connect inlet hose to the test meter (M_3). Allow the system to establish equilibrium, and record the pressure at P_3, with pressure gauge M_5.

11.6 Measure the flow through the system, using the wet test meter and stopwatch.

11.7 Repeat at 6 other flowrates, such as 1.5, 6, 12, 18, and 24 L/min, adjusting the outlet temperature at T_2 to 54°C each time.

11.8 Draw a calibration curve of corrected flow into the instrument versus indicating gauge scale (M_5).

11.9 Reinstall the inlet on the instrument after removing the thermometer T_2 and the inlet calibration adapter. Close valve V_1 when flow is not being monitored. See Note 1.

NOTE 1—If other inlet temperatures are used within the limits of the control, prepare a new calibration curve for each temperature selected. An empirical calibration of this type is more accurate than a calculated correction based on the gas laws.

12. Procedure for Obtaining Tape "Blank Values"

12.1 *Blank on Reagents*—About 50 % of the treated tapes should be checked for fluoride levels by preparing and analyzing the unused tape as outlined in Section 13.

12.2 *Field Blanks on Tapes*—Cut the equivalent of four spots from the section of tape following the last sample after removing and discarding the last few inches of the tape which may have been handled during removal of the tape from the tape sampler. Analyze these four spots as one sample. The total fluoride content of these field blanks should rarely exceed 0.3 µg of fluoride.

13. Preparation of Samples for Fluoride Analysis

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

13.2 Preparation of the tapes used to collect acidic gaseous fluoride for fluoride analysis.

13.2.1 *For Potentiometric Analysis:*

13.2.1.1 Cut out individual sample spots and place in clean 15 by 150-mm test tubes. Add 5 mL of 1 + 1 TISAB solution (8.8) and mix for several seconds with a vortex mixer. Decant into a clean high-pressure linear polyethylene (or polypropylene or TFE-fluorocarbon) beaker.

13.2.1.2 Analyze using the potentiometric method given in Test Methods D3269.

13.2.2 *For Semiautomated Analysis:*

13.2.2.1 Cut out individual sample spots and place in clean 15 by 150-mm test tubes. Add 5.0 mL of deionized water and mix for several seconds with a vortex mixer. Filter samples (to remove cellulose fibers) into 8.5-mL sample cups by a semimicro filtration method.

13.2.2.2 Analyze using the semiautomated method given in Test Methods D3270.

13.3 *Preparation of the Prefilter Tapes Used to Collect Particulate Matter for Fluoride Analysis:*

13.3.1 *For Potentiometric Analysis:*

13.3.1.1 Cut out individual sample spots and place in 15 by 150-mm test tubes. Add 5.0 mL of 1 N H_2SO_4 (8.9), mix for several seconds with a vortex mixer, and allow to stand for 5 min.

13.3.1.2 Add an equal volume of 1 N NaOH solution (8.10). Decant into a clean high-pressure linear polyethylene (or polypropylene or TFE-fluorocarbon) beaker and add 10.0 mL of TISAB solution (8.8). See Note 2.

NOTE 2—In any specific sampling program, the quantitative recovery of the fluoride content of the tape by 1 N H_2SO_4 extraction shall be confirmed. (See Test Methods D3269).

13.3.1.3 Analyze using the potentiometric method given in Test Methods D3269.

13.3.2 *For Semiautomated Analysis:*

13.3.2.1 Cut out individual sample spots and place in clean 15 by 150-mm test tubes. Add 5.0 mL of 1 N H_2SO_4 (8.9), mix for several seconds with a vortex mixer, and allow to stand for 5 min. Filter samples (to remove cellulose fibers) into 8.5-mL sample cups by a semimicro filtration method.

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

13.4 *Calibration and Standards*—None required.

14. Calculation

14.1 Calculate the volume of air sampled as follows:

$$C = (R \times 10^{-3})(t_s)(n_s) \quad (1)$$

where:

C = sample volume at 25°C (77°F) and 101.3 kPa (760 mm Hg), m^3

R = sampling rate at 25°C (77°F) and 101.3 kPa (760 mm Hg), L/min obtained from the calibration curve prepared for the draft gauge,

t_s = minutes sampled per spot, and

n_s = number of spots used for one analytical sample.

14.2 Calculate the results for either the prefilter tape or the acidic gaseous fluoride tape.

$$S = (A - B)/C \quad (2)$$

where:

S = concentration of fluoride, μg/m^3,

A = mass of fluoride in the spots, n_s, μg, and

B = mass of fluoride in the blank of n_s spots, μg.

15. Quality Assurance

15.1 Establish a Quality Assurance Program for ambient HF measurement systems in accordance with Guide D3614. It shall include the use of the HF calibrator and HF permeation tube to determine the efficiency of sample collection, at a frequency determined by the results of the QA program.

16. Precision and Bias[10]

16.1 *Precision:*

16.1.1 With 1-h samples, the relative standard deviation of the fluoride measurements (including collection efficiency) was found to be 5 % in the range of 1 to 3 μg/m^3, and <1 % at higher concentrations (10 to 20 μg/m^3). With a probe heated at 70°C, relative humidities of 45 to 90 % had no effect on precision in the range of 1 to 20 μg/m^3.

16.1.2 For potentiometric measurements of concentrations in air less than 3 μg/m^3, the temperature of eluted samples must be maintained to ±1°C during the measurement. Each degree Celsius differential results in a 2 to 3 % error.

16.2 *Bias*—Fluoride recovery was >95 % for known amounts of fluoride in the range 2 to 20 μg/m^3 and sampling times of 20 to 120 min. Negligible amounts of gaseous fluoride were removed by the prefilter at relative humidities of 45 to 95 % when the sample air passing through the inlet tube was heated to 54°C. Since the studies showed that dust can effect bias significantly, the inlet probe must be cleaned regularly under dusty conditions.

17. Keywords

17.1 acidic gaseous fluoride; ambient atmospheres; double paper tape sampler; fluoride; particulate fluoride; tape sampler

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[10] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D22-1020. Contact ASTM Customer Service at service@astm.org.