



Designation: D 4765 – 9803

Standard Test Method for Fluorides in Workplace Atmospheres¹

This standard is issued under the fixed designation D 4765; 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 covers the simultaneous collection and separate measurements of gaseous and particulate fluoride found in certain industrial workplaces. The gaseous inorganic fluorides collected are reported in terms of fluoride; the procedure is not applicable to the collection or analysis of other fluoride-bearing gases (for example, fluorocarbon or fluorosulfur compounds). This test method covers sample collection, preparation, and fluoride measurement.

1.2 *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:

D 1193 Specification for Reagent Water²

¹ This test method is under the jurisdiction of ASTM Committee D-22 on Sampling and Analysis of Atmospheres and is the direct responsibility of Subcommittee D22.04 on Workplace Atmospheres.

Current edition approved ~~May~~ April 10, 1998; 2003. Published ~~July~~ 1998; June 2003. Originally published as D 4765—88; approved in 1988. Last previous edition approved in 1998 as D 4765 – 938.

- D 1356 Terminology Relating to Sampling and Analysis of Atmospheres³
D 1357 Practice for Planning the Sampling of the Ambient Atmosphere³
D 5337 Practice for Flow Rate for Calibration of Personal Sampling Pumps³

3. Terminology

3.1 *Definitions*— For definitions of terms used in this test method, refer to Terminology D 1356.

4. Summary of Test Method

4.1 Particulate material from a measured volume of air is collected by means of a membrane filter. Gaseous fluoride, from the sample of air, is absorbed by an alkali-impregnated cellulose pad placed immediately behind the membrane filter. The membrane filter and collected solids are made alkaline, ashed, and the residue fused with additional alkali. Finally, the fluoride is determined in a solution of the melt by use of a fluoride ion-selective electrode. Gaseous fluoride is determined in an aqueous extract of the cellulose pad, also by means of the fluoride ion-selective electrode.

5. Significance and Use

5.1 The capability of this test method to collect and quantitate both particulate and gaseous fluorides over the ranges normally encountered in industrial atmospheres makes it applicable for industrial hygiene evaluation and control purposes. The recommended range of this test method is from 0.005 to 5 mg F⁻/m³ air.

6. Interferences

6.1 Because an ion-selective electrode responds to ionic activity, insoluble and complex forms of fluoride must be released by appropriate combinations of fusion, adjustment of pH, and addition of complexing agents.

6.2 Acidity (pH) and ionic strengths of fluoride standard solutions must be matched to those of samples.

6.3 Temperature of sample and standard solutions must be controlled within $\pm 2^{\circ}\text{C}$.

7. Apparatus

7.1 *Personal Sampling Pump*, Equipped with a flow-monitoring device (rotameter, critical orifice) or a constant-flow device capable of drawing 2 L/min of air through the 0.8- μm membrane filter and pad for a period of 8 h.

7.2 *Filter Holder*— Plastic holders of the preloaded personal monitor type, that accept filters of 37-mm diameter, are preferred. The holder is to be numbered for identification.

7.3 *Membrane Filter*, of mixed-cellulose esters, 0.8- μm pore size, and of diameter to fit the filter holder (see 7.2).

7.4 *Cellulose Pad*, of size to fit the filter holder (see 7.2). The pad is commercially available as a plain, unpregnated pad or as an alkali-impregnated pad.

7.5 *Crucibles*, 20-mL, nickel, Inconel,⁴ or platinum.

7.6 *Fluoride Ion-Selective Electrode*.

7.7 *Reference Electrode*, calomel type, preferably combined with the fluoride ion-selective electrode.

7.8 *Electrometer or Expanded Scale pH Meter*, with a millivolt scale for measurement of potentials.

7.9 *Magnetic Stirrer*.

7.10 *Plastic Beakers*, 50 and 100-mL capacities.

7.11 *Beakers*, 250-mL capacity.

7.12 *Volumetric Flasks*, 100-mL capacity.

8. Reagents

8.1 *Purity of Reagents*— 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.⁵

8.2 *Purity of Water*— Unless otherwise indicated, references to water shall be understood to mean Type I Reagent Water conforming to Specification D 1193.

8.3 *Alkaline Fixative Solution*— Dissolve 25 g of sodium carbonate (Na_2CO_3) in water, add 20 mL glycerol, and dilute to 1 L.

8.4 *Buffer Solution (ALCOA)*— Dissolve 60 g of citric acid monohydrate ($\text{C}_2\text{H}_8\text{O}_7\cdot\text{H}_2\text{O}$), 210 g of sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7\cdot 2\text{H}_2\text{O}$) and 53.5 g of ammonium chloride (NH_4Cl) in 500 mL water. Add 67 mL of ammonium hydroxide (NH_4OH) (sp gr = 0.90) and dilute to 1 L with water.

² Annual Book of ASTM Standards, Vol 11.01.

³ Annual Book of ASTM Standards, Vol 11.03.

⁴ Inconel is a trademark for a group of corrosion-resistant alloys of nickel and chromium.

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.

8.5 *Fluoride Solution, Standard* (100 µg/mL)—Dissolve 0.2211 g sodium fluoride (NaF, dried at 105°C for 2 h) in water and dilute to volume in a 1-L volumetric flask.

8.6 *Ethanol, Denatured*—Formula 30 denatured alcohol is satisfactory.

8.7 *Borate-Carbonate Fusion Mixture*—Intimately mix a 1+2 (w/w) combination of sodium tetraborate (Na₂B₄O₇) and sodium carbonate (Na₂CO₃).

8.8 *Hydrochloric Acid* (1+1)—Mix one part hydrochloric acid to one part distilled water as a solution.

9. Sampling

9.1 For general information on sampling, refer to Practice D 1357.

9.2 Equip the worker whose exposure is to be evaluated with a personal monitor connected by a 75-cm length of hose to a belt-supported sampling pump. Attach the monitor to the worker's collar and remove the plug for closed-face sampling. Air is drawn through the filter at the calibrated rate of approximately 2.0 L/min and maintained at that rate by occasional checking and adjustment. On termination of sampling, note the duration of sampling, reseal the monitor and return the monitor to the laboratory. Filter a minimum air sample of 250 L.

9.3 Total particulate loading may be determined, if required, by pre- and post-weighing of the membrane filter.

10. Preparation of Monitors

10.1 Disassemble the personal monitor (see 7.2), removing the membrane filter and cellulose pads. Moisten the pad with a measured volume of alkaline fixative solution (see 8.3); 0.8 mL is required for a pad of 37-mm diameter. Dry the pad at 105°C for 30 to 45 min.

NOTE 1—Preparation of alkali-impregnated pads must be carried out in a low-fluoride environment with minimum exposure.

10.2 Reassemble the filter monitor, inserting an impregnated pad and membrane filter, and closing with the filter retaining ring and front cover. Seal the assembly against air leakage by a wrap of masking tape or cellulose shrink bands, covering the crevice between the retaining ring and back cover. Close the inlet and outlet openings of the monitor with plastic plugs.

11. Calibration of the Personal Monitoring Pump

11.1 Refer to Practice 5337.

11.2 Select several of the prepared monitors at random for calibration of air flow rate with the personal sampling pump (see 7.1). Connect the monitor exit to the sampling pump by means of a 75-cm length of hose. Connect the flowmeter (preferably a bubble flowmeter, magnehelic flowmeter, or wet test meter) to the inlet port of the monitor. Start the pump and adjust its rate, noting the position of the rotameter ball when a sampling rate of about 2.0 L/min is indicated by use of the calibration flowmeter and a timer.

NOTE 2—Calibration of pumps with monitors in both in-line and open-face modes showed no significant difference.

12. Calibration

12.1 *Fluoride Standards, Particulate*—Add 1.0 g borate-carbonate fusion mixture to each of four 250-mL beakers containing 10 mL of water and 50 mL of buffer solution (8.4). Add a few drops of (1 + 1) hydrochloric acid (see 8.8) and add various size aliquots (1, 5, 10, and 25 mL) of 100 µg/mL standard fluoride solution (see 8.5) to produce a series of working standards (1, 5, 10, and 25 µg/F⁻/mL). Transfer to a 100-mL volumetric flask, and dilute to volume with water.

NOTE 3—These standards may be stored for several months in tightly capped polyethylene bottles, under refrigeration.

12.2 For calibration of the electrode, pour about 20 mL of the working standard solution into a plastic beaker containing a TFE-fluorocarbon-coated stirring bar. Adjust solution to within ± 2°C of an arbitrarily selected standard temperature. Insert the fluoride and reference electrodes into the constantly stirred solution and measure the potential after 2 min. Repeat for each of the working standards.

12.3 Prepare a calibration graph, on three-cycle semilog paper, relating potential, in mV (linear scale), to concentration of fluoride in µm/mL (log scale). Reproducibility of each point should be ± 1 mV. A linear calibration graph is obtained in the 0.5 to 25 µg/mL range, with a slope of between 57 and 59 mV per tenfold change in fluoride concentration.

NOTE 4—If solutions containing less than 0.5 µg/mL are measured, additional standards must be prepared since the calibration graph is not linear at low fluoride concentrations.

12.4 *Fluoride Standards, Gaseous*—Into each of four 100-mL volumetric flasks, place 10 mL of water and 50 mL of buffer solution (see 8.4). Add various size aliquots (1, 5, 10, and 25 mL) of 100 µg/mL standard fluoride solution (see 8.5) to produce a series of working standards (1, 5, 10, and 25 µg F⁻/mL). Dilute to volume with water.

12.5 A separate calibration graph for gaseous fluoride is prepared from potential measurements of these standards (see 12.4), by the same procedure as used for particulate fluorides (see 12.2 and 12.3).

NOTE 5—The analysis of control standards and blanks is recommended to determine recovery levels.

13. Procedure

13.1 *Particulate Fluoride*—Carefully remove the membrane filter from the filter holder and place it in a nickel, Inconel, or

TABLE 1 Recoveries of Known Amounts of Standard Particulate Fluoride

Amount Added mg F	Mean Recovery (\bar{x}) mg F	+Bias	+% Bias	% Recovery	Statistically Significant (95 % Confidence Level)
0.742	0.575	-0.167	-22.5	77.5	Yes
1.48	1.15	-0.33	-22.3	77.7	Yes
2.41	1.91	-0.50	-20.7	79.3	Yes

platinum crucible containing 0.5 g borate-carbonate fusion mixture. Transfer any dust from inside the filter cover and retaining ring to the crucible. Drench the filter with ethanol and ignite with a small gas flame. Heat the residue to fusion temperature for 1 to 2 min, then cool and dissolve in a few mL of water. Transfer the same solution into a plastic beaker by means of 25 mL of buffer solution (see 8.4) followed by a rinse of the crucible with a few drops of (1+1) hydrochloric acid (see 8.8). Dilute to 50 mL in a volumetric flask, mix and bring to standard temperature. Pour about 20 mL of the solution into a plastic beaker and measure the potential while the electrodes are immersed in the gently stirred solution. Convert potential (mV) to fluoride concentration ($\mu\text{g/mL}$) by means of the calibration graph determined from the standard fluoride series containing borate-carbonate flux (see 12.3).

NOTE 6—During the fusion procedure, do not overheat crucible. Fluoride can be lost due to volatilization. The crucible should be heated to a dull, red glow until all of the sample is consumed.

13.2 *Gaseous Fluoride*— Transfer the impregnated cellulose pad to a 100-mL plastic beaker containing 25 mL water and 25 mL buffer solution (see 8.4). Allow the pad to soak for about 30 min with sufficient stirring to reduce it to a pulp. Bring the solution to standard temperature, insert the electrodes, and measure potential of the gently stirred mixture after 2 min. Convert potential (mV) to fluoride concentration ($\mu\text{g/mL}$) by means of the calibration graph determined from the standard fluoride series (see 12.5).

14. Calculations

14.1 The concentration of particulate fluorides in air, integrated over the sampling period, is calculated as follows:

$$C_p = 0.05 \times \frac{C_1}{V} \quad (1)$$

where:

- C_p = concentration of particulate fluoride, in mg/m^3 ,
- 0.05 = conversion factor for a 50-mL sample size and the conversion of micrograms to milligrams,
- C_1 = concentration of fluoride in particulate sample solution in $\mu\text{g/mL}$, and
- V = volume of air sample in m^3 , corrected to 25°C and 760 torr.

14.2 The concentration of gaseous fluoride in air, integrated over the sampling period, is calculated as follows:

$$C_g = 0.05 \times \frac{C_2}{V} \quad (2)$$

where:

- C_g = concentration of gaseous fluoride in mg/m^3 ,
- 0.05 = conversion factor for a 50-mL sample size and the conversion of micrograms to milligrams,
- C_2 = concentration of fluoride in gaseous sample solution in $\mu\text{g/mL}$,
- V = volume of air sample in m^3 , corrected to 25°C and 760 torr.

14.3 If desired, gaseous fluoride concentration in air, in mg/m^3 , may be converted to equivalent concentration expressed as parts per million as follows:

$$C_g, \text{mg/m}^3 \times 1.29 = C_g, \text{ppm} \quad (3)$$

15. Precision and Bias

15.1 *Precision*—Repeatability (Both single-analyst and overall):

15.1.1 Four levels of gaseous fluoride were generated and collected on a treated filter: 0.030, 0.295, 1.49, and 2.90 mg fluoride/sample. Each concentration was analyzed in triplicate by eight participating laboratories. The single operator relative standard deviation (RSD) varied from 10.3 % to 2.8 % with a pooled relative standard deviation of 7.5 %. The overall relative standard deviation for the eight laboratories varied from 24.8 % to 7.6 % with a pooled relative standard deviation of 16.0 %.⁶

15.1.2 Three levels of particulate fluoride were generated by weighing a standard sample and encapsulating the sample onto a filter: 0.742, 1.48, and 2.41 mg fluoride/sample. Each concentration was analyzed in triplicate by eight participating laboratories.

⁶ Supporting data are available from ASTM Headquarters. Request RR D22-1015.

The single operator relative standard deviation (RSD) varied from 13.9 % to 4.4 % with a pooled relative standard deviation of 9.2 %. The overall relative standard deviation for the eight laboratories varied from 31.5 % to 21.2 % with a pooled relative standard deviation of 27.2 %.⁶

15.2 *Bias:*

15.2.1 *Gaseous Standards*—Recoveries of known amounts of standard generated gaseous fluoride adsorbed on a filter are shown in Table 2. The overall percent recovery of the gaseous fluoride samples was 99.1 % over a concentration range from 0.03 to 2.9 mg of fluoride.⁶

15.2.2 *Particulate Standards*—Recoveries of known amounts of standard particulate fluoride are shown in Table 1. The overall percent recovery of the particulate fluoride sample was 78.2 % over a concentration range from 0.74 to 2.41 mg of fluoride per filter.⁶

16. Keywords

16.1 air monitoring; fluoride; gaseous fluoride; hydrogen fluoride; particulate fluoride; sampling and analysis; workplace atmospheres

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TABLE 2 Recoveries of Known Amounts of Standard Generated Gaseous Fluoride Adsorbed on a Filter

Amount Generated mg F	Mean Recovery (\bar{x}) mg F	+Bias	+% Bias	% Recovery	Statistically Significant (95 % Confidence Level)
0.030	0.032	+0.002	+6.7	106.7	No
0.295	0.278	-0.017	-5.8	94.2	Yes
1.49	1.44	-0.05	-3.4	96.6	Yes
2.90	2.87	-0.03	-1.0	99.0	No