Designation: D4765 – 13

Standard Test Method for Measurement of Fluorides in Workplace Atmospheres by Ion-Selective Electrodes[1]

This standard is issued under the fixed designation D4765; 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 fluoride (for example, hydrogen fluoride) and particulate fluoride found in certain industrial workplaces. The gaseous fluorides and particulate fluorides collected are reported in terms of fluoride. The method covers sample collection, preparation, and fluoride measurement.

1.2 The procedure is not applicable to the collection or analysis of gaseous fluoro compounds (for example, fluorocarbon or fluorosulfur compounds).

1.3 The values stated in SI units are to be regarded as the 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 and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

D4840 Guide for Sample Chain-of-Custody Procedures

D5337 Practice for Flow Rate Adjustment of Personal Sampling Pumps

E1370 Guide for Air Sampling Strategies for Worker and Workplace Protection

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 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 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^-/m^3 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 *Filter Materials*—Not all filter materials can be used effectively for sampling particulate fluorides in workplace air. Cellulosic membrane filters are the most suitable filter types for sampling of fluorides. Several manufacturers offer mixed-cellulose ester filters commercially; nevertheless it is essential to check the quality of each filter batch used for sampling.

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

6.4 Temperature of sample and standard solutions must be controlled within ±2°C.

7. Apparatus

7.1 *Personal Sampling Pump,* capable of maintaining constant air flow (±5 %) in the range 1–5 L/min through a filter holder (7.2) containing a 0.8-µm pore size cellulosic membrane filter (7.3) and cellulose pad (7.4) for a period of up to 8 hours.

[1] This test method is under the jurisdiction of ASTM Committee D22 on Air Quality and is the direct responsibility of Subcommittee D22.04 on Workplace Air Quality.

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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.

7.2 *Filter Holder*—For sampling of inhalable fraction of aerosols, of suitable diameter for the filters (for example, 37-mm; see 7.3). The holder shall be numbered for identification.

7.3 *Membrane Filter,* of mixed-cellulose esters (MCE), 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, unimpregnated pad or impregnated with alkali (8.3).

7.5 *Crucibles,* 20-mL, nickel, platinum, or suitable alloys of nickel and chromium.

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.

NOTE 1—Commercial potentiometers for fluoride sensitive electrodes are equipped with internal calibration modes.

7.9 *Magnetic Stirring Bar,* fluorocarbon-coated.

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

7.11 *Beakers,* borosilicate glass, 250-mL capacity.

7.12 *Volumetric Flasks,* 50 and 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.[3]

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type I Reagent Water conforming to Specification D1193.

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 with water.

8.4 *Buffer Solution*—Dissolve 60 g of citric acid monohydrate ($C_2H_8O_7{\cdot}H_2O$), 210 g of sodium citrate ($Na_3C_6H_5O_7{\cdot}2H_2O$) 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.

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,* analytical grade.

8.7 *Borate-Carbonate Fusion Mixture*—Thoroughly mix a 1+2 (w/w) combination of sodium tetraborate ($Na_2B_4O_7$) and sodium carbonate (Na_2CO_3).

8.8 *Hydrochloric Acid* (1+1)—Mix one part hydrochloric acid to one part water (8.2) as a homogeneous solution.

9. Sampling

9.1 *Cellulose Pad Impregnation*—Moisten the cellulose pad (7.4) 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, or allow to dry overnight at room temperature in a dessicator.

NOTE 2—Preparation of alkali-impregnated pads must be carried out in a low-fluoride environment with minimum potential for contamination.

9.2 *Sampler Assembly*—Assemble the filter holder, inserting an impregnated pad with membrane filter atop it, and seal the assembly against air leakage. Close the inlet and outlet openings of the filter holder.

9.3 *Personal Sampling Pump*—Use personal sampling pumps at their design flow rate (1-5 L/min) and calibrated in accordance with Practice D5337.

9.4 *Sample Collection*—For general information on sampling strategies, refer to Guide E1370.

9.4.1 Equip the worker whose exposure is to be evaluated with a sampler (9.2) connected by a ca. 75-cm length of flexible tubing to a belt-supported personal sampling pump (9.3). Attach the sampler to place it within the worker's personal breathing zone for sampling. Draw air through the sampler at a calibrated rate of 1-5 L/min; a sampling rate of 2 L/min is common. On termination of sampling, record the duration of sampling. Obtain a minimum air sample of 250 L.

9.5 *Sample Transport*—Transport the samplers to the laboratory so as to prevent contamination or damage. Follow chain-of-custody procedures to document sample traceability in accordance with Guide D4840.

10. Analysis

10.1 *Fluoride Calibration Standards:*

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

10.1.1 *Particulate Fluoride*—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.

10.1.2 *Gaseous Fluoride*—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.

[3] *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.

10.2 *Calibration:*

10.2.1 For calibration of the electrode, pour about 20 mL of the working standard solution into a plastic beaker containing a fluorocarbon-coated stirring bar (7.9). Adjust solution to within ±2°C of a selected standard temperature, for example, 25°C. Insert the fluoride and reference electrodes into the constantly stirred solution and measure the potential after two minutes. Repeat for each of the working standards (10.1).

10.2.2 Prepare a calibration graph, on semilog scale, 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.

10.2.3 Prepare separate calibration graphs for particulate and gaseous fluoride from potential measurements of these standards (see 10.1). If solutions containing less than 0.5 µg/mL are measured, additional standards must be prepared since the calibration graph might not be linear at low fluoride concentrations.

10.3 *Sample Preparation and Measurement Procedure:*

10.3.1 *Particulate Fluoride*—Carefully remove the membrane filter from the filter holder and place it in a nickel, Inconel, or 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 (as evidenced by a dull, red glow until all of the sample is consumed) for 1 to 2 min. During the fusion procedure, do not overheat crucible, as fluoride can be lost due to volatilization. Cool to room temperature and dissolve the crucible contents 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, for example, 25°C. 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 (µg/mL) by means of the calibration graph determined from the standard fluoride series containing borate-carbonate flux (see 10.2).

10.4 *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 (for example, 25°C), insert the electrodes, and measure the potential of the gently stirred mixture after 2 min. Convert potential (mV) to fluoride concentration (µg/mL) by means of the calibration graph determined from the standard fluoride series (see 10.2).

11. Calculations

11.1 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 volume and the conversion of micrograms to milligrams,
C_1 = concentration of fluoride in particulate sample solution in µg/mL, and
V = volume of air sample in m^3, corrected to 25°C and 1 atm.

11.2 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 voume and the conversion of micrograms to milligrams,
C_2 = concentration of fluoride in gaseous sample solution in µg/mL,
V = volume of air sample in m^3, corrected to 25°C and 1 atm.

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

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

12. Precision and Bias

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

12.1.1 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 %.[4]

12.1.2 To prepare performance evaluation samples, three levels of particulate fluoride were produced by weighing a standard sample and placing sample aliquots onto filters at levels of 0.742, 1.48, and 2.41 mg fluoride/sample. Each loading level was analyzed in triplicate by eight participating laboratories. 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 %.[4]

12.2 *Bias:*

12.2.1 *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.[4]

[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D22-1015. Contact ASTM Customer Service at service@astm.org.

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

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

12.2.2 *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.[4]

13. Keywords

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