



Designation: D4765 – 13

Standard Test Method for Measurement of Fluorides in Workplace Atmospheres by Ion-Selective Electrodes¹

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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](#).

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.

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 quantify 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 *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 $\pm 2^{\circ}\text{C}$.

7. Apparatus

7.1 *Personal Sampling Pump*, capable of maintaining constant air flow ($\pm 5\%$) 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.

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 ($\text{C}_2\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$), 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.

8.5 *Fluoride Solution, Standard* (100 $\mu\text{g}/\text{mL}$)—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.

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.

8.7 *Borate-Carbonate Fusion Mixture*—Thoroughly mix a 1+2 (w/w) combination of sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$) 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 desiccator.

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 $\mu\text{g}/\text{mL}$ standard fluoride solution (see 8.5) to produce a series of working standards (1, 5, 10, and 25 $\mu\text{g}/\text{F}^-/\text{mL}$). 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 $\mu\text{g}/\text{mL}$ standard fluoride solution (see 8.5) to produce a series of working standards (1, 5, 10, and 25 $\mu\text{g}/\text{F}^-/\text{mL}$). Dilute to volume with water.