



Designation: **D4765 – 03 (Reapproved 2008) D4765 – 13**

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

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 inorganic fluorides and particulate 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 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

D4357/D4840 Practice for Planning the Sampling of the Ambient Atmosphere

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 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.

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.

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*, Equipped with a flow-monitoring device (rotameter, critical orifice) or a constant-flow device capable of drawing 2 L/min of air through the capable of maintaining constant air flow ($\pm 5\%$) in the range 1–5 L/min through a filter holder (7.20.8- μm membrane filter) containing a 0.8- μm pore size cellulosic membrane filter (7.3) and cellulose pad (7.4) for a period of up to 8 h hours.

7.2 *Filter Holder*—Plastic holders of the preloaded personal monitor type, that accept filters of 37-mm diameter, are For sampling of inhalable fraction of aerosols, of suitable diameter for the filters (for example, 37-mm; see 7.3 preferred). The holder is to shall be numbered for identification.

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

7.5 *Crucibles*, 20-mL, nickel, Inconel, platinum, or platinum-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 Stirrer-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. [ASTM D4765-13](https://standards.iteh.ai/catalog/standards/sist/39164fb5-3cea-49d1-9076-7db8f65acf7/astm-d4765-13)

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 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.

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, Denatured*—Formula 30 denatured alcohol is satisfactory analytical grade.

8.7 *Borate-Carbonate Fusion Mixture*—Intimately 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 distilled water (8.2) as a homogeneous solution.

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.

9. Sampling

9.1 For general information on sampling, refer to Practice [D1357](#).

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.

9. Preparation of Monitors Sampling

9.1 Cellulose Pad Impregnation—Disassemble the personal monitor (see Moisten the cellulose pad (7.27.4), 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, 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 exposure potential for contamination.

9.2 Sampler Assembly—Reassemble the filter monitor, inserting an impregnated pad and membrane filter, and closing with the filter retaining ring and front cover. Seal with membrane filter atop it, and 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.

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](#).

11. Calibration of the Personal Monitoring Pump

11.1 Refer to Practice [D5337](#).

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.

10. Calibration Analysis

10.1 Fluoride Standards, Particulate—Calibration Standards: 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.

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.