

METHOD 13B  
DETERMINATION OF TOTAL FLUORIDE EMISSIONS FROM STATIONARY SOURCES  
SOURCES - SPECIFIC ION ELECTRODE METHOD

**NOTE:** This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, and Method 13A.

1.0 Scope and Application.

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Total fluorides as Fluorine	7782-41-4	Not determined

1.2 Applicability. This method is applicable for the determination of fluoride ( $F^-$ ) emissions from sources as specified in the regulations. It does not measure fluorocarbons, such as Freons.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary.

Gaseous and particulate  $F^-$  are withdrawn isokinetically from the source and collected in water and on a filter. The total  $F^-$  is then determined by the specific ion electrode method.

3.0 Definitions. [Reserved]

4.0 Interferences.

Grease on sample-exposed surfaces may cause low  $F^-$  results because of adsorption.

5.0 Safety.

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burn as thermal burn.

5.2.1 Sodium Hydroxide (NaOH). Causes severe damage to eye tissues and to skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.2 Sulfuric Acid ( $H_2SO_4$ ). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema.  $1\text{ mg}/\text{m}^3$  for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

## 6.0 Equipment and Supplies.

6.1 Sample Collection and Sample Recovery. Same as Method 13A, Sections 6.1 and 6.2, respectively.

6.2 Sample Preparation and Analysis. The following items are required for sample preparation and analysis:

6.2.1 Distillation Apparatus, Bunsen Burner, Electric Muffle Furnace, Crucibles, Beakers, Volumetric Flasks, Erlenmeyer Flasks or Plastic Bottles, Constant Temperature Bath, and Balance. Same as Method 13A, Sections 6.3.1 to 6.3.9, respectively.

6.2.2 Fluoride Ion Activity Sensing Electrode.

6.2.3 Reference Electrode. Single junction, sleeve type.

6.2.4 Electrometer. A pH meter with millivolt-scale capable of  $\pm 0.1$ -mv resolution, or a specific ion meter made specifically for specific ion electrode use.

6.2.5 Magnetic Stirrer and Tetrafluoroethylene (TFE) Fluorocarbon-Coated Stirring Bars.

6.2.6 Beakers. Polyethylene, 100-ml.

## 7.0 Reagents and Standards.

Unless otherwise indicated, all reagents are to conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise, use the best available grade.

7.1 Sample Collection and Sample Recovery. Same as Method 13A, Sections 7.1 and 7.2, respectively.

7.2 Sample Preparation and Analysis. The following reagents and standards are required for sample analysis:

7.2.1 Calcium Oxide (CaO). Certified grade containing 0.005 percent  $F^-$  or less.

7.2.2 Phenolphthalein Indicator. Dissolve 0.1 g phenolphthalein in a mixture of 50 ml of 90 percent ethanol and 50 ml water.

7.2.3 Sodium Hydroxide (NaOH), Pellets.

7.2.4 Sulfuric Acid ( $H_2SO_4$ ), Concentrated.

7.2.5 Filters. Whatman No. 541, or equivalent.

7.2.6 Water. Same as Section 7.1.2 of Method 13A.

7.2.7 Sodium Hydroxide, 5 M. Dissolve 20 g of NaOH in 100 ml of water.

7.2.8 Sulfuric Acid, 25 Percent (v/v). Mix 1 part of concentrated H<sub>2</sub>SO<sub>4</sub> with 3 parts of water.

7.2.9 Total Ionic Strength Adjustment Buffer (TISAB). Place approximately 500 ml of water in a 1-liter beaker. Add 57 ml of glacial acetic acid, 58 g of sodium chloride, and 4 g of cyclohexylene dinitrilo tetraacetic acid. Stir to dissolve. Place the beaker in a water bath and cool to 20 °C (68 °F). Slowly add 5 M NaOH to the solution, measuring the pH continuously with a calibrated pH/reference electrode pair, until the pH is 5.3. Pour into a 1-liter volumetric flask, and dilute to volume with deionized, distilled water. Commercially prepared TISAB may be substituted for the above.

7.2.10 Fluoride Standard Solution, 0.1 M. Oven dry approximately 10 g of sodium fluoride (NaF) for a minimum of 2 hours at 110 °C (230 °F), and store in a desiccator. Then add 4.2 g of NaF to a 1-liter volumetric flask, and add enough water to dissolve. Dilute to volume with water.

8.0 Sample Collection, Preservation, Storage, and Transport.

Same as Method 13A, Section 8.0.

9.0 Quality Control.

9.1 Miscellaneous Quality Control Measures.

Section	Quality Control Measure	Effect
8.0, 10.1	Sampling equipment leak-check and calibration	Ensure accurate measurement of stack gas flow rate and sample volume
10.2	Fluoride electrode	Evaluate analytical technique, preparation of standards
11.1	Interference/recovery efficiency-check during distillation	Minimize negative effects of used acid

9.2 Volume Metering System Checks. Same as Method 5, Section 9.2.

10.0 Calibration and Standardizations.

**NOTE:** Maintain a laboratory log of all calibrations.

10.1 Sampling Equipment. Same as Method 13A, Section 10.1.

10.2 Fluoride Electrode. Prepare fluoride standardizing solutions by serial dilution of the 0.1 M fluoride standard solution. Pipet 10 ml of 0.1 M fluoride standard solution into a 100-ml volumetric flask, and make up to the mark with water for a 10<sup>-2</sup> M standard solution. Use 10 ml of 10<sup>-2</sup> M solution to make a 10<sup>-3</sup> M solution in the same manner. Repeat the dilution procedure, and make 10<sup>-4</sup> and 10<sup>-5</sup> M solutions.

10.2.1 Pipet 50 ml of each standard into a separate beaker. Add 50 ml of TISAB to each beaker. Place the electrode in the most dilute standard solution. When a steady millivolt reading is obtained, plot the value on the linear axis of semilog graph paper versus concentration on the log axis. Plot the nominal value for concentration of the standard on the log axis, (e.g., when 50 ml of 10<sup>-2</sup> M standard is diluted with 50 ml of TISAB, the concentration is still designated "10<sup>-2</sup> M").

10.2.2 Between measurements, soak the fluoride sensing electrode in water for 30 seconds, and then

remove and blot dry. Analyze the standards going from dilute to concentrated standards. A straight-line calibration curve will be obtained, with nominal concentrations of  $10^{-4}$ ,  $10^{-3}$ ,  $10^{-2}$ ,  $10^{-1}$  fluoride molarity on the log axis plotted versus electrode potential (in mv) on the linear scale. Some electrodes may be slightly nonlinear between  $10^{-5}$  and  $10^{-4}$  M. If this occurs, use additional standards between these two concentrations.

10.2.3 Calibrate the fluoride electrode daily, and check it hourly. Prepare fresh fluoride standardizing solutions daily ( $10^{-2}$  M or less). Store fluoride standardizing solutions in polyethylene or polypropylene containers.

**NOTE:** Certain specific ion meters have been designed specifically for fluoride electrode use and give a direct readout of fluoride ion concentration. These meters may be used in lieu of calibration curves for fluoride measurements over a narrow concentration ranges. Calibrate the meter according to the manufacturer's instructions.

## 11.0 Analytical Procedures.

11.1 Sample Loss Check, Sample Preparation, and Distillation. Same as Method 13A, Sections 11.1 through 11.3, except that the **NOTE** following Section 11.3.1 is not applicable.

### 11.2 Analysis.

11.2.1 Containers No. 1 and No. 2. Distill suitable aliquots from Containers No. 1 and No. 2. Dilute the distillate in the volumetric flasks to exactly 250 ml with water, and mix thoroughly. Pipet a 25-ml aliquot from each of the distillate into separate beakers. Add an equal volume of TISAB, and mix. The sample should be at the same temperature as the calibration standards when measurements are made. If ambient laboratory temperature fluctuates more than  $\pm 2$  °C from the temperature at which the calibration standards were measured, condition samples and standards in a constant-temperature bath before measurement. Stir the sample with a magnetic stirrer during measurement to minimize electrode response time. If the stirrer generates enough heat to change solution temperature, place a piece of temperature insulating material, such as cork, between the stirrer and the beaker. Hold dilute samples (below  $10^{-4}$  M fluoride ion content) in polyethylene beakers during measurement.

11.2.2 Insert the fluoride and reference electrodes into the solution. When a steady millivolt reading is obtained, record it. This may take several minutes. Determine concentration from the calibration curve. Between electrode measurements, rinse the electrode with water.

11.2.3 Container No. 3 (Silica Gel). Same as in Method 13A, Section 11.4.2.

## 12.0 Data Analysis and Calculations.

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

12.1 Nomenclature. Same as Method 13A, Section 12.1, with the addition of the following:

M =  $F^-$  concentration from calibration curve, molarity.

12.2 Average DGM Temperature and Average Orifice Pressure Drop, Dry Gas Volume, Volume of Water Vapor and Moisture Content, Fluoride Concentration in Stack Gas, and Isokinetic Variation. Same as Method 13A, Sections 12.2 to 12.4, 12.6, and 12.7, respectively.

12.3 Total Fluoride in Sample. Calculate the amount of  $F^-$  in the sample using Equation 13B-1:

$$F_t = \frac{K V_t V_d M}{A_t}$$

where:

K = 19 [(mg·l)/(mole·ml)] (metric units)  
= 0.292 [(gr·l)/(mole·ml)] (English units)

### 13.0 Method Performance.

The following estimates are based on a collaborative test done at a primary aluminum smelter. In the test, six laboratories each sampled the stack simultaneously using two sampling trains for a total of 12 samples per sampling run. Fluoride concentrations encountered during the test ranged from 0.1 to 1.4 mg F<sup>-</sup>/m<sup>3</sup>.

13.1 Precision. The intra-laboratory and inter-laboratory standard deviations, which include sampling and analysis errors, are 0.037 mg F<sup>-</sup>/m<sup>3</sup> with 60 degrees of freedom and 0.056 mg F<sup>-</sup>/m<sup>3</sup> with five degrees of freedom, respectively.

13.2 Bias. The collaborative test did not find any bias in the analytical method.

13.3 Range. The range of this method is 0.02 to 2,000 µg F<sup>-</sup>/ml; however, measurements of less than 0.1 µg F<sup>-</sup>/ml require extra care.

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

16.0 Alternative Procedures.

16.1 Compliance with ASTM D 3270-73T, 91, 95 "Analysis for Fluoride Content of the Atmosphere and Plant Tissues (Semiautomated Method)" is an acceptable alternative for the distillation and analysis requirements specified in Sections 11.1 and 11.2 when applied to suitable aliquots of Containers 1 and 2 samples.

17.0 References.

Same as Method 13A, Section 16.0, References 1 and 2, with the following addition:

1. MacLeod, Kathryn E., and Howard L. Crist. Comparison of the SPADNS- Zirconium Lake and Specific Ion Electrode Methods of Fluoride Determination in Stack Emission Samples. Analytical Chemistry. 45:1272-1273. 1973.

18.0 Tables, Diagrams, Flowcharts, and Validation Data. [Reserved]