

**State of California
Air Resources Board**

Method 13B

Determination of Total Fluoride Emissions from Stationary Sources - Specific Ion Electrode Method

**Adopted: March 28, 1986
Amended: July 1, 1999**

Method 13B - Determination of Total Fluoride Emissions from Stationary Sources (Specific Ion Electrode Method)

1. APPLICABILITY AND PRINCIPLE

1.1 Applicability. This method applies to the determination of fluoride (F) emissions from stationary sources as specified in the regulations. It does not measure fluorocarbons, such as Freons.

1.2 Principle. Gaseous and particulate F are withdrawn isokinetically from the source and collected in water and on a filter.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.

Any modification of this method beyond those expressly permitted shall be considered a major modification subject to the approval of the Executive Officer. The term Executive Officer as used in this document shall mean the Executive Officer of the Air Resources Board (ARB), or his or her authorized representative.

2. RANGE AND SENSITIVITY

The range of this method is 0.02 to 2,000 $\mu\text{g F/ml}$; however, measurements of less than 0.1 $\mu\text{g F/ml}$ require extra care. Sensitivity has not been determined.

3. INTERFERENCES

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

4. PRECISION AND ACCURACY

4.1 Precision. 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/m^3 . The within-laboratory and between-laboratory standard deviations, which include sampling and analysis errors, are 0.037 mg F/m^3 with 60 degrees of freedom and 0.056 mg F/m^3 with five degrees of freedom, respectively.

4.2 Accuracy. The collaborative test did not find any bias in the analytical method.

5. APPARATUS

NOTE: Mention of any trade name or specific product does not constitute endorsement by the Air Resources Board.

5.1 Sampling Train and Sample Recovery. Same as Method 13A, Sections 5.1 and 5.2, respectively.

5.2 Analysis. The following items are needed:

5.2.1 Distillation Apparatus, Bunsen Burner, Electric Muffle Furnace, Crucibles, Beakers, Volumetric Flasks, Erlenmeyer Flasks or Plastic Bottles, Constant Temperature Bath, and Balance. Same as in Method 13A, Sections 5.3.1 to 5.3.9, respectively, except include also 100-ml polyethylene beakers.

5.2.2 Fluoride Ion Activity Sensing Electrode.

5.2.3 Reference Electrode. Single junction, sleeve type.

5.2.4 Electrometer. A pH meter with millivolt-scale capable of ± 0.1 -mv resolution, or a specific ion meter made specifically for specific ion use.

5.2.5 Magnetic Stirrer and TFE Fluorocarbon-Coated Stirring Bars.

6. REAGENTS

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

6.2 Analysis. Use ACS reagent grade chemicals (or equivalent), unless otherwise specified. The reagents needed for analysis are as follows:

6.2.1 Calcium Oxide (CaO). Certified grade containing 0.005 percent F or less.

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

6.2.3 Sodium Hydroxide (NaOH), Pellets.

6.2.4 Sulfuric Acid (H₂SO₄), Concentrated.

6.2.5 Filters. Whatman No. 541, or equivalent.

6.2.6 Water. Same as Section 6.1.2 of Method 13A.

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

6.2.8 Sulfuric Acid, 25 Percent (v/v). Mix 1 part of concentrated H₂SO₄ with 3 parts of water.

6.2.9 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 to cool it. 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. Cool to room temperature. Pour into a 1-liter volumetric flask, and dilute to volume with water. Commercially prepared TISAB may be substituted for the above.

6.2.10 Fluoride Standard Solution, 0.1 M. Oven dry some sodium fluoride (NaF) for a minimum of 2 hours at 110°C, 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.

7. PROCEDURE

7.1 Sampling, Sample Recovery, and Sample Preparation and Distillation. Same as in Method 13A, Sections 7.1, 7.2, and 7.3, respectively, except the notes concerning chloride and sulfate interferences are not applicable.

7.2 Analysis.

7.2.1 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 distillates 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 $\pm 2^\circ\text{C}$ 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.

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.

7.2.2 Container No. 3 (Silica Gel). Same as in Method 13A, Section 7.4.2.

8. CALIBRATION

Maintain a laboratory log of all calibrations.

8.1 Sampling Train. Same as Method 13A.

8.2 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^{-2} M standard solution. Use 10 ml of 10^{-2} M solution to make a 10^{-3} M solution in the same manner. Repeat the dilution procedure, and make 10^{-4} and 10^{-5} solutions.

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^{-2} M standard is diluted with 50 ml of TISAB, the concentration is still designated " 10^{-2} M."

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.

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 narrow concentration ranges. Calibrate the meter according to the manufacturer's instructions.

9. CALCULATIONS

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

9.1 Nomenclature. Same as Section 9.1 of Method 13A. In addition:

M = F concentration from calibration curve, molarity.

9.2 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 and Acceptable Results. Same as Method 13A, Sections 9.2 to 9.4, 9.5.2, and 9.6, respectively.

9.3 Fluoride in Sample. Calculate the amount of F in the sample using the following:

$$F_t = K \frac{V_t V_d}{A_t M} \quad \text{Eq. 13B-1}$$

where:

K = 19 mg/millimole.

10. BIBLIOGRAPHY

1. EPA Method 13B, Determination of Total Fluoride Emissions from Stationary Sources (Specific Ion Electrode Method), CFR40, Part 60, Appendix A

2. ARB Method 13A, Determination of Total Fluoride Emissions from Stationary Sources - SPADNS Zirconium Lake Method