

FLUORIDES, aerosol and gas by ISE

7902

F⁻ MW: 18.998 CAS: (HF) 7664-39-3 RTECS: (HF) MW7875000

METHOD: 7902, Issue 2

EVALUATION: PARTIAL

Issue 1: 15 February 1984

Issue 2: 15 August 1994

OSHA : 2.5 mg/m³ (fluorides); 3 ppm (HF)
NIOSH: 2.5 mg/m³ (fluorides); 3 ppm (HF);
 STEL 6 ppm (HF)
ACGIH: 2.5 mg/m³ (fluorides); C3 ppm (HF)
 (1 ppm HF=0.818 mg/m³ @ NTP)

PROPERTIES: HF: liquid; BP 19.5 °C; fluoride salts liberate HF in presence of acids

SYNONYMS: sodium fluoride (CAS #7681-49-4); hydrogen fluoride; hydrofluoric acid; cryolite; sodium hexafluoroaluminate (CAS #13775-53-6).

SAMPLING	MEASUREMENT
<p>SAMPLER: FILTER + TREATED PAD (0.8 µm cellulose ester membrane + Na₂CO₃-treated cellulose pad)</p> <p>FLOW RATE: 1 to 2 L/min</p> <p>VOL-MIN: 12 L @ 2.5 mg/m³ -MAX: 800 L</p> <p>SHIPMENT: routine</p> <p>SAMPLE STABILITY: stable</p> <p>BLANKS: 2 to 10 field blanks per set</p>	<p>TECHNIQUE: ION-SPECIFIC ELECTRODE</p> <p>ANALYTE: fluoride ion (F⁻)</p> <p>FILTER (particulate F⁻): fuse in NaOH, dissolve in 50 mL water + TISAB</p> <p>TREATED FILTER (gaseous F⁻): extract in 50 mL water + TISAB</p> <p>CALIBRATION: standard F⁻ solutions in TISAB</p> <p>RANGE: 0.03 to 1.2 mg F⁻ per sample</p> <p>ESTIMATED LOD: 3 µg F⁻ per sample [1]</p> <p>PRECISION (\bar{S}_r): 0.017 @ 55 to 220 µg per sample [2]</p>
ACCURACY	
<p>RANGE STUDIED: not studied</p> <p>BIAS: not determined</p> <p>OVERALL PRECISION (\hat{S}_{rt}): not determined</p> <p>ACCURACY: not determined</p>	

APPLICABILITY: The working range is 0.12 to 8 mg/m³ for a 250-L air sample. The method applies to mining samples, and samples from the aluminum reduction, ceramic, glass etching, electroplating, semi-conductor, and fluorocemical industries if other aerosols are present, gaseous fluoride may be underestimated owing to sorption on collected particles, with concurrent overestimation of particulate/gaseous fluoride ratio [3-8].

INTERFERENCES: In samples containing cryolite, aluminum is sufficiently concentrated to give erroneous fluoride concentrations [3]. Hydroxide ion greater than 1/10 of the fluoride level will interfere positively. Fe³⁺, Si⁴⁺, and Al³⁺ give a negative interference. Concentrations >8 µg/mL of these elements cannot be suppressed [9]. The TISAB suppresses up to 500 µg/mL Fe³⁺ and up to 90 µg/mL Si⁴⁺.

OTHER METHODS: This revises method 7902 [10] which was withdrawn on 5/15/89. The method was originally based on a method by Elfers and Decker [11], and NIOSH method S176 for HF [2]. Method 7903 (Acids, Inorganic) is an alternative method for HF. Method 7906 (Fluorides by IC) employs the same sampling procedure, but uses ion chromatography for measurement.

REAGENTS:

1. Sodium carbonate (Na_2CO_3).
2. Glycerol.
3. Potassium chloride(KCl).
4. Sodium acetate ($\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$).
5. Cyclohexylene diamine tetraacetic acid (CDTA).
6. Hydrochloric acid, 1:1 (v/v).
7. Sodium fluoride(NaF).*
8. Deionized water.
9. Fixative solution. Dissolve 25 g Na_2CO_3 in deionized water. Add 20 mL glycerol. Dilute to 1 L.
10. Total ionic strength activity buffer (TISAB), pH 5.5. Dissolve 37 g KCl, 68 g sodium acetate and 36 g CDTA in H_2O . Adjust to pH 5.5 ± 0.2 with 1:1 HCl. Dilute to 1L.
11. Calibration stock solution, 100 $\mu\text{g}/\text{mL}$: Dissolve 0.2211 g NaF (dried at 105°C for 2 h) in deionized water; dilute to 1 L.
12. Sodium hydroxide, 20% (w/v). Dissolve 200 g NaOH in deionized water to make 1 L solution.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 37- mm, 0.8- μm pore size, with porous plastic backup pad (Nuclepore #220800, or equivalent), treated cellulose pad (Moisten with 0.8 mL fixative solution and dry at 105°C for 30 to 45 minutes. Discard if charred.) in a 3-piece cassette with a $\frac{1}{2}$ " extension. Assembly of sampler: Place treated pad in rear (outlet) piece of cassette, insert $\frac{1}{2}$ -inch extension, place porous plastic pad and membrane filter in upper part of extension, and insert top piece (inlet) of cassette. Press tightly together and seal with shrink band or tape. NOTE: Leak test with hand vacuum pump.
2. Personal sampling pump, 1 to 2 L/min, with flexible connecting tubing.
3. Crucibles, nickel, zirconium, or Inconel, 20- or 30-mL.
4. Bunsen or Meaker burner.
5. Tripod.
6. Triangle, ceramic-covered.
7. Volumetric flasks, 50- and 100-mL, and 1-L.
8. Pipets, appropriated sizes for standards.
9. Beakers, plastic, 100-mL or 150-mL.
10. Magnetic stirrer.
11. PTFE-coated stirring bars.
12. Fluoride ion selective electrode (ISE), NaF combination or with calomel-type reference electrode.
13. pH/ion meter with millivolt readout and pH electrode.
14. Hand vacuum pump.

SPECIAL PRECAUTIONS: Fluorides are extremely corrosive to skin, eyes and mucous membranes [12]. Perform all fusions in fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 2 L/min for a total sample size of 12 to 800 L. Do not exceed 2 mg total dust loading on the filter.
3. Pack securely for shipment.

SAMPLE PREPARATION:

4. **Cellulose ester membrane filter** (particulate fluoride).
NOTE: Water-soluble particulate fluorides may be extracted by the procedure for gaseous fluorides. Insoluble particles require fusion.
 - a. Transfer the membrane filter to a crucible containing 5 mL 20% NaOH.
 - b. Evaporate to dryness.
 - c. Heat residue to fusion temperature, 1 to 2 min, cool and dissolve in ca. 5 mL deionized water.
 - d. Transfer sample into 100-mL plastic beakers.
 - e. Rinse crucible with 25 mL of TISAB then with a few drops of 1:1 HCl.
 - f. Adjust to pH 5.5 ± 0.2 using 1:1 HCl.
 - g. Transfer to 50 mL volumetric flask; dilute to volume with deionized water.
5. **Treated pad** (gaseous fluoride).
 - a. Transfer treated pads to 100-mL plastic beakers.
 - b. Add 25 mL TISAB and 25 mL deionized water.
 - c. Soak pad for 30 min with sufficient stirring to reduce it to pulp.

CALIBRATION AND QUALITY CONTROL:

6. Calibrate daily with at least six working standards over the range 3 to 1200 $\mu\text{g F}^-$ per sample.
 - a. Add known amounts of calibration stock solution to 25 mL TISAB and 5 mL 20% NaOH (particulate fluoride) or 25 mL TISAB (gaseous fluoride) in 100-mL beakers.
 - b. Adjust pH to 5.5 ± 0.2 with 1:1 HCl.
 - c. Transfer to 50-mL volumetric flasks. Dilute to the mark with deionized water.
NOTE: Working standards are stable at least one month in polyethylene bottles at 4 °C.
 - d. Analyze together with samples and blanks (steps 7 through 10).
 - e. Prepare separate calibration graphs (mV vs. $\log \text{F}^-$ concentration) for particulate and
NOTE: Calibration curve is not linear below 0.1 $\mu\text{g/mL}$ or above 25 $\mu\text{g/mL}$.

MEASUREMENT:

7. Bring sample and standard solutions to room temperature.
NOTE: Samples and standards must be at same temperature (within ± 2 °C) for accurate results.
8. Pour ca. 20 mL of each solution into plastic beakers.
9. Add magnetic stir bar, insert electrodes and gently stir on magnetic stirrer.
10. Record potential (mV) after 2 min.
NOTE: If measured concentration of F^- is $>25 \mu\text{g/mL}$, dilute with appropriate matrix (step 6), reanalyze and apply dilution factor in calculations.

CALCULATIONS:

11. Using the proper calibration graph (particulate or gaseous), convert potential (mV) to solution fluoride concentration, C_s ($\mu\text{g/mL}$), in the sample solution volume, V_s (mL), and the average media blank, C_b , in the blank solution volume, V_b (mL).

12. Calculate the concentration of fluoride, C (mg/m³), in the air volume sampled, V (L):

$$C = \frac{C_s V_s - C_b V_b}{V}, \text{mg} / \text{m}^3$$

EVALUATION OF METHOD:

Measurement precision, \bar{S}_r , in the range 0.055 to 0.22 mg HF per sample averaged 0.017 with average recovery 100.0% [2]. Analytical results on field samples report detection limits of 3 µg per sample for both gaseous and particulate fluorides [1]. Reported collection ranges for gaseous fluoride and particulate fluorides were 4 to 61 µg per sample and 4 to 410 µg per sample, respectively [10].

REFERENCES:

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- [12] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services Publ. (NIOSH) 81-123 (1981), available as GPO Stock #17-033-00337-8 from Superintendent of Documents, Washington, DC 20402.

METHOD WRITTEN (REVISED) BY:

Charles Lorberau, NIOSH/DPSE.