

FLUORIDES aerosol and gas, by IC

7906

F⁻ MW: 18.998

CAS: (HF) 7664-39-3

RTECS: (HF) MW7875000

METHOD: 7906, Issue 1

EVALUATION: PARTIAL

Issue 1: 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); C 3 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	
SAMPLER:	FILTER + TREATED PAD (0.8-µm cellulose ester membrane + Na ₂ CO ₃ -treated cellulose pad)	TECHNIQUE:	ION CHROMATOGRAPHY/ CONDUCTIVITY
FLOW RATE:	1 to 2 L/min	ANALYTE:	fluoride ion (F ⁻)
VOL-MIN:	1 L @ 3 ppm (HF) 120 L @ 2.5 mg/m ³ (water-insoluble particulate)	FILTER (particulate F):	fuse in NaOH, dissolve in 100 mL water, dilute 1:40 with water
-MAX:	800 L	TREATED FILTER (gaseous F):	extract in 100 mL water
SHIPMENT:	routine	INJECTION VOLUME:	50 µL
SAMPLE STABILITY:	stable	ELUENT:	1.25 mM Na ₂ B ₄ O ₇ , 2 mL/min
BLANKS:	2 to 10 field blanks per set	COLUMNS:	IonPac-AS4A separator, IonPac-AG4A guard, anion micromembrane suppressor
		CONDUCTIVITY SETTING:	10 µS full scale
		CALIBRATION:	standard F ⁻ solutions in water
		RANGE:	0.01 to 0.25 mg F ⁻ per sample (gas) [1] 0.30 to 10 mg F ⁻ per sample (particulate) [1]
		ESTIMATED LOD:	3 µg F ⁻ per sample (gas) [1] 120 µg F ⁻ per sample (particulate) [1]
		PRECISION (S_r):	0.019 (gas) [1] 0.066 (particulate) [1]
ACCURACY			
RANGE STUDIED:	not studied		
BIAS:	not determined		
OVERALL PRECISION (S_{r,T}):	not determined		
ACCURACY:	not determined		

APPLICABILITY: The working ranges are 0.05 to 10 ppm HF (0.04 to 8 mg/m³) and 1.2 to 8 mg/m³ water-insoluble fluorides for a 250-L air sample. Water soluble particulate fluorides may be extracted by the procedure for gaseous fluoride. Insoluble particles require fusion. The method applies to mining samples; aluminum reduction, ceramic, glass etching, electroplating, semi-conductor, and fluorochemical industries. The method is applicable to ceiling limit and short-term exposure limit (STEL) monitoring.

INTERFERENCES: If other aerosols are present, gaseous fluoride may be slightly underestimated owing to adsorption onto or reaction with particles, with concurrent overestimation of particulate/gaseous fluoride ratio [2-6].

OTHER METHODS: Method 7902 (Fluorides by ISE) employs the same sampling procedure, but uses ion selective electrode for measurement. Method 7903 (Acids, Inorganic) is an alternative method for HF.

REAGENTS:

1. Sodium carbonate (Na_2CO_3).
2. Glycerol.
3. Sodium fluoride (NaF)*.
4. Sodium acetate ($\text{NaC}_2\text{H}_3\text{O}_2$).
5. Sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$).
6. Alkaline Fixative Solution: Dissolve 25 g Na_2CO_3 in deionized water. Add 20 mL glycerol. Dilute to 1 L.
7. 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.
8. Sodium Hydroxide, 20% (w/v): Dissolve 200 g NaOH in deionized water. Dilute to 1 L.
9. Acetate Stock Solution: Dissolve 0.1389 g sodium acetate in deionized water. Dilute to 100 mL.
10. Mixed Anion Solution: Add 0.10 mL of fluoride stock solution and 0.10 mL acetate stock solution to deionized water. Dilute to 50 mL.
11. Eluent, 1.25 mM sodium tetraborate: dissolve 1.9079 g $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ in deionized water. Dilute to 4 L.

* 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 1/2" extension.
Assembly of sampler: Place treated pad in rear (outlet) piece of cassette, insert 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. Ion chromatograph, conductivity detector, set to conditions on p. 7906-1.
4. Crucibles, nickel, zirconium, or Inconel, 20- or 30-mL.
5. Bunsen or Meeker burner.
6. Tripod.
7. Triangle, ceramic-covered.
8. Volumetric flasks, 50- and 100-mL, and 1-L.
9. Pipets, appropriate sizes for standards.
10. Specimen containers, screw caps, plastic, 150-mL.
11. Syringes, plastic, 10-mL
12. Syringe filters, 25-mm
13. Ultrasonic bath
14. Hot plate
15. Hand vacuum pump

SPECIAL PRECAUTIONS: Fluorides are extremely corrosive to skin, eyes and mucous membranes. 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 1 L (gas) or 120 L (particulate) 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 particulates require fusion, which decreases sensitivity in the measurement.
 - a. Transfer the membrane filter to a crucible containing 5 mL of 20% NaOH .
 - b. Evaporate to dryness on hot plate.
 - c. Heat residue to fusion temperature over Bunsen or Meeker burner, 1 to 2 min, and let cool.
 - d. Transfer crucible with sample to specimen container, add 100 mL of deionized water with a

- volumetric pipet, and seal with screw cap.
 - e. Place in an ultrasonic bath for 15 to 20 min.
 - f. Dilute 1:40 with deionized water and transfer by syringe fitted with filter into appropriate vial for IC analysis.
5. **Alkaline-impregnated backup pad** (gaseous fluoride).
- a. Transfer impregnated pad to specimen container, add 100 mL of deionized water with a volumetric pipet, and seal with screw cap.
 - b. Place in an ultrasonic bath for 15 to 20 min.
 - c. Filter into appropriate vial for IC analysis.

CALIBRATION AND QUALITY CONTROL:

- 6. Calibrate daily with at least six working standards over the range of the samples.
 - a. Add known amounts of mixed-anion calibration stock solution to deionized water in 50-mL volumetric flasks. Dilute to the mark with deionized water.
 - b. Prepare fresh standards weekly.
 - c. Analyze together with samples and blanks (steps 8 through 10).
 - NOTE: Insure fluoride and acetate ion peaks are resolved. Baseline resolution is not required when using peak height for determination.
 - d. Prepare a calibration graph (peak height, μS or mm, vs. $\mu\text{g/mL}$ of F^-).
- 7. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph is in control.

MEASUREMENT:

- 8. Set ion chromatograph according to manufacturer's instructions and to conditions on p. 7906-1.
- 9. Inject a 50- μL sample aliquot.
 - NOTE: All samples and standards must be filtered to avoid plugging the system valves or columns.
- 10. Measure peak height.
 - NOTE: If peak height exceeds the linear calibration range, dilute, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

- 11. Determine the mass, μg , of fluoride found on the particulate filter, W_p and the treated pad, W_g , and the corresponding average media blanks, B_p and B_g , using the solution volumes of the samples, V_p and V_g , and blanks, V_{pb} and V_{gb} .
- 12. Calculate the concentration of particulate fluoride, C_p (mg/m^3), and gaseous fluoride, C_g (mg/m^3), in the volume of air sampled, V (L):

$$C_p = \frac{W_p V_p - B_p V_{pb}}{V}, \text{ mg/m}^3 \qquad C_g = \frac{W_g V_g - B_g V_{gb}}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

With ion chromatographic analysis the following performance criteria were determined [1]. The LOD for gaseous fluoride (rear treated pad) was estimated at 3 μg fluoride per sample, with a range of 0.01 to 0.25 mg fluoride per sample. The precision (\bar{S}_r) was determined to be 0.019 over the range 13 to 250 μg per sample for the rear treated pad. Because the high ionic strength resulting from the fusion of the particulate sample in NaOH required a further 1:40 dilution, the limit of detection (LOD) for particulate fluoride (front section) was estimated at 120 μg fluoride per sample, with a range of 0.30 to 10 mg fluoride per sample. The precision (\bar{S}_r) for the particulate filter was estimated at 0.066 at 250 μg per sample. The overall precision and bias were not determined.

REFERENCES:

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- [7] 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, D.C. 20402.

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