PARTICULATE FLUORIDES and HYDROFLUORIC ACID by Ion Chromatography

7906

MW: F^-, 18.998 (HF, 20.01) CAS (HF): 7664-39-3 RTECS: (HF) MW7875000

METHOD: 7906, Issue 2 **EVALUATION: FULL** **Issue 2: 20 May 2014**
Issue 1: 15 August 1994

U. S. OELs
OSHA : 2.5 mg/m^3 (fluorides); 3 ppm (HF)
NIOSH: 2.5 mg/m^3 (fluorides);
3 ppm (HF), STEL (HF): 6 ppm
Other OELs: **[1,2]**

PROPERTIES: HF: gas; mp = -83.1 °C; bp = 19.5 °C; sp. gr. 0.987; VP = 783 mm Hg (104.4 kPa).
Fluoride salts liberate HF vapor in the presence of acids.

SYNONYMS: Hydrogen fluoride; hydrofluoric acid; Sodium fluoride (CAS #7681-49-4)

SAMPLING

SAMPLER: PRE-FILTER, cellulose nitrate, 0.8 µm pore size, 37-mm diameter, + TREATED FILTER, cellulose nitrate impregnated with Na_2CO_3, 0.8 µm pore size, 37-mm diameter, separated by a chemically inert spacer

FLOW RATE: 1 to 2 L/min

VOL-MIN: 15 L
-MAX: 1000 L

SHIPMENT: 4 °C

SAMPLE STABILITY: Stable for at least 14 days (fluorides) / 28 days (HF) if stored at @ 20 °C for 7 days and 4 °C thereafter [1]

BLANKS: 3 minimum field blanks per set

ACCURACY*

RANGE STUDIED: 0.04 to 5.9 mg/m^3 (fluorides);
0.30 to 6 ppm (HF)

BIAS*: Negligible [3]

OVERALL PRECISION*($\hat{S}_{rT}$): Fluorides, 0.074; HF, 0.125 [5,6]

EXPANDED UNCERTAINTY*: less than 20% for F^-;
less than 22% for HF [4,5]

*Accuracy calculations were determined using reference 4 rather than the traditional NIOSH accuracy criterion.

MEASUREMENT

TECHNIQUE: ION CHROMATOGRAPHY (IC) with conductivity detection

ANALYTE: Fluoride ion (F^-)

EXTRACTION: Aqueous solution of sodium carbonate / sodium hydrogen carbonate

INJECTION VOLUME: 50 µL

ELUENT: 8 mM Na_2CO_3 / 1 mM $NaHCO_3$
flow rate 1.0 mL/min

COLUMNS: Pre-column, anion-exchange column and suppressor column

CALIBRATION RANGE: F^-; 0.4 to 8.0 mg/L [3,5]

ESTIMATED LOD: 0.1 mg/L / 0.009 mg/m^3 (120 L air volume; as F^-) [3]

PRECISION ($\bar{S}_r$): Fluorides, 0.033; HF, 0.056 [3]

APPLICABILITY: The working range is (at least) 0.1 to 8 mg/sample for a 250 Liter air sample.

INTERFERENCES: Co-sampled formate and acetate compounds in the work environment can cause a positive interference; thus detection by ion selective electrodes is a suitable alternative if airborne formate and acetate are expected. Cations that form insoluble fluorides, such as Ca^{2+}, Fe^{3+}, and Al^{3+} can cause negative interferences. Recovery of gaseous HF is reduced at high humidity.

OTHER METHODS: This method updates NIOSH 7906 [7] by providing full method accuracy information, and specifies the use of an impregnated filter instead of a treated cellulose pad. The procedure, which is consistent with ISO 21438-3 [6], replaces NIOSH 7903 [8] for the determination of particulate fluorides and gaseous HF in workplace air samples. The advantages of this method are that it can allow for the collection of the inhalable fraction of particulate fluorides by means of the pre-filter (housed within an optional inhalable sampler) and it can provide for lower limits of detection and quantitation for gaseous HF due to higher sampling flow rates. NIOSH 7902 [9] and ASTM D4765 [10] are alternative methods that are recommended for insoluble fluorides, which rely on detection of F- by ion-selective electrode.

REAGENTS:

1. Water, deionized (DI), ≥18 MΩ-cm resistivity
2. Sodium carbonate (Na_2CO_3), anhydrous, American Chemical Society (ACS) analytical grade
3. Sodium hydrogen carbonate ($NaHCO_3$), ACS analytical grade
4. Filter impregnation solution (0.75 M Na_2CO_3); Dissolve 7.95 g Na_2CO_3 in deionized water and swirl to mix. Then bring to 100 mL in a volumetric flask, stopper and mix thoroughly.
5. Eluent stock solution: 0.8 M Na_2CO_3 / 0.1 M $NaHCO_3$; Dissolve 16.96 g Na_2CO_3 and 1.68 g $NaHCO_3$ in deionized water and swirl to mix. Then bring to 200 mL in a volumetric flask, stopper and mix thoroughly.
6. Eluent solution: 8 mM Na_2CO_3 / 1 mM $NaHCO_3$; Transfer 10 mL of 0.8 M Na_2CO_3 / 0.1 M $NaHCO_3$stock solution to a 1 Liter volumetric flask, dilute to the mark with deionized water, stopper and mix thoroughly. Prepare fresh eluent solution weekly.
7. Fluoride (F^-) standard solution, 1000 mg/L
8. Calibration stock solution, 100 mg/mL (as the anion): Place a 10 mL aliquot of fluoride standard solution into a 100 mL volumetric flask, dilute to the mark and mix thoroughly. The solution is stable for at least 4 weeks at room temperature.
9. To prepare the impregnated filter, evenly distribute 120 µL 0.75 M Na_2CO_3 over the surface of the filter and allow to dry at room temperature for several hours.

*See Special Precautions

EQUIPMENT:

1. Sampler: 37-mm diameter cellulose nitrate pre-filter, 0.8 µm pore size, 37-mm impregnated cellulose nitrate filter. The untreated filter collects particulate fluorides, while the impregnated filter collects HF vapor. Arrange the filters serially (with the pre-filter upstream of the impregnated filter) in a 37-mm diameter 3-piece chemically inert cassette filter holder.
2. Personal sampling pump, 1 to 2 L/min, with flexible connecting tubing
3. Ion chromatograph (IC), with pre-column (50 mm by 4.0 mm), anion-exchange column (200 mm by 4.0 mm), suppressor column (4 mm) and conductivity detector; and connected to data processing unit
4. Ultrasonic bath
5. Vessels, 10-mL, inert plastic, with screw caps
6. Volumetric flasks, 25- to 1000 mL
7. Pipets, 50- to 10000 µL
8. Beakers, 25- to 100 mL
9. Filtration apparatus, with filter funnel
10. Disposable filters, cellulosic, 0.45 µm pore size
11. Styrene-based sulfonic acid resin cartridges
12. Water purification system, to prepare greater than or equal to 18 MΩ-cm resistivity deionized water
13. Bottles, polyethylene, 100 mL
14. Syringes, plastic, 5 mL and/or 10 mL
15. Syringe filter cartridges, with 0.8-µm pore size polytetrafluoroethylene (PTFE) membrane filters
16. Micro-syringes, 50 µL, with 60 mm x 0.6 mm needles
17. Auto-sampler vials, polypropylene, 0.75 mL capacity.

SPECIAL PRECAUTIONS: Acids, particularly HF, are extremely corrosive to skin, eyes, and mucous membranes. HF will attack glass. Plastic labware is recommended. Wear gloves, lab coat, and safety glasses while handling acids. All work should be performed with adequate ventilation for personnel and equipment. It is imperative that acid be added to water in order to avoid a violent exothermic reaction [11,12].

SAMPLING, SAMPLE TRANSPORT AND STORAGE:

1. Prior to sampling, load each clean sampler, first with a sampling (impregnated) filter, then with a pre-filter, separating the filters with a spacer. Ensure that the configuration in which the filters are loaded leads to the sampled air passing first through the pre-filter and then through the sampling filter.
2. Calibrate each personal sampling pump with a representative sampler in the line.
3. Sample at an accurately known flow rate between 1 to 2 mL/min for a total sample size of 15 to 1000 L. Avoid sampler overloading.
4. After sampling, remove the filters from the cassette and place them in screw-cap plastic vessels. For the pre-filter portion: With approximately 2 mL eluent(extraction) solution, rinse material from the inside surfaces of the pre-filter portion of the cassette into the vessel. Add eluent solution into the vessels until a final volume of 10 mL is reached.
5. Submit at least three blank untreated filters and three blank impregnated filters as field blanks for each set of samples collected per day. Handle these in the same way as the field samples; i.e., place each filter into a vessel, add 10 mL of eluent solution and ship it to the lab along with the remaining samples.
6. Refrigerate all samples that are to be stored overnight (or longer) prior to shipment to the laboratory. Ship all samples to the laboratory in accordance with established chain-of-custody procedures [13].
7. Refrigerate the samples immediately upon receipt at the lab until ready for analysis.
8. Analyze samples within 2 weeks of receipt. The samples can be stored at room temperature for one week; for longer storage, refrigerate the samples (4 °C).

SAMPLE PREPARATION AND MEASUREMENT:

9. Remove sample vessels from storage and bring them to room temperature.
10. Sonicate the samples in an ultrasonic bath for at least 15 minutes and allow to cool for at least 30 minutes.
11. Using 5- or 10-mL syringes, filter each sample extract solution through a PTFE filter and a styrene-based sulfonic acid resin cartridge (follow the manufacturer's instructions), discard the first two milliliters and place the remaining solution in clean plastic vessels.

CALIBRATION AND QUALITY CONTROL:

12. With dilution of the calibration stock solution in eluent solution, prepare calibration working standard solutions covering the range of approximately 0.4 to 8 µg/mL of fluoride. Store working standards in tightly sealed polyethylene bottles. Prepare fresh working standards biweekly.
13. Calibrate the ion chromatograph with at least six working standards covering the range of (at least) 0.4 to 8 µg/mL of fluoride per sample by preparing a calibration graph of anion peak height (mm or µS) vs. concentration (µg/mL).
14. Analyze working standards together with samples, reagent blanks and field blanks at a frequency of at least 1 per 20 samples (3 minimum of each). Cellulose nitrate filters demonstrate variable batch-dependent blank values, thus media blank correction is essential.

MEASUREMENT

15. Set the ion chromatograph to recommended eluent flow rate, (e.g. 1.0 mL/min or approximately 13 MPa pressure), and other conditions as specified by the instrument manufacturer.
16. Inject a sample aliquot (e.g. 50 µL) into the chromatograph and measure the peak height of the fluoride peak. If the peak height exceeds the linear calibration range, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.

CALCULATIONS:

17. Calculate the mass concentration of fluoride, C (mg/m^3), in the air volume sampled, V (L):

$$C=\left\{\frac{(C_1 * V_1 * F_d)-(C_0 * V_0)}{V * \eta}\right\} * F_c$$

where:
C_0 = mean concentration, in µg/mL, of fluoride in the field blank test solutions;
C_1 = concentration, in µg/mL, of fluoride in the sample test solution;
V = volume, in liters, of the air sample;
V_0 = volume, in mL, of the field blank test solutions;
V_1 = volume, in mL, of the sample test solutions;
F_d = dilution factor for each sample test solution;
F_c = 1.053 = conversion factor to convert from fluoride to HF concentration (if applicable);
η = recovery.

EVALUATION OF METHOD:

This updates Issue 1, NIOSH 7906 [7], by providing full method accuracy information, and specifies the use of an impregnated filter instead of a treated cellulose pad. The procedure described in issue 2 of NIOSH 7906, which is consistent with ISO 21438-3 [6], also replaces NIOSH 7903 [8] for the determination of particulate fluorides and gaseous HF in workplace air samples.
Recovery of 100% ± 2% was found after sample collection for both F^- and HF [3,5,6], and no breakthrough of HF was observed from impregnated filters for up to 5 mg fluoride [6,14]. The component of the coefficient of variation of the method that arises from analytical variability, determined from the analysis of spiked filters, was 2.4% to 5.6% for HF and 1.7% to 3.3% for fluorides [3,6]. Laboratory testing with test atmospheres of HF (0.5 to 5 mg/m^3) demonstrated quantitative sampling efficiencies (greater than 95%) at relative humidity (RH) of 20% to 60%, but recovery was around 60% at relative humidity of 80%.
The recovery of HF as an effect of relative humidity (RH) greater than 60 percent can be calculated as follows (see also Figure 1):

$$\eta=\frac{[226.5-(2.0914 * RH)]}{100}$$

No effect of humidity (RH from 20% to 80%) was observed on recovery of particulate fluoride over the concentration range of 0.3 to 5 mg/m^3. Results for repeatability and reproducibility of the method for test atmospheres of hydrogen fluoride and fluoride aerosol (Relative humidity was approximately 50%) are shown in Table I. The method has been successfully applied in independent investigations [14] and has been promulgated as an International Standard [6]. The back-up data and user check reports are references 3 and 14 respectively.

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FIGURE 1. HF recovery as function of relative humidity

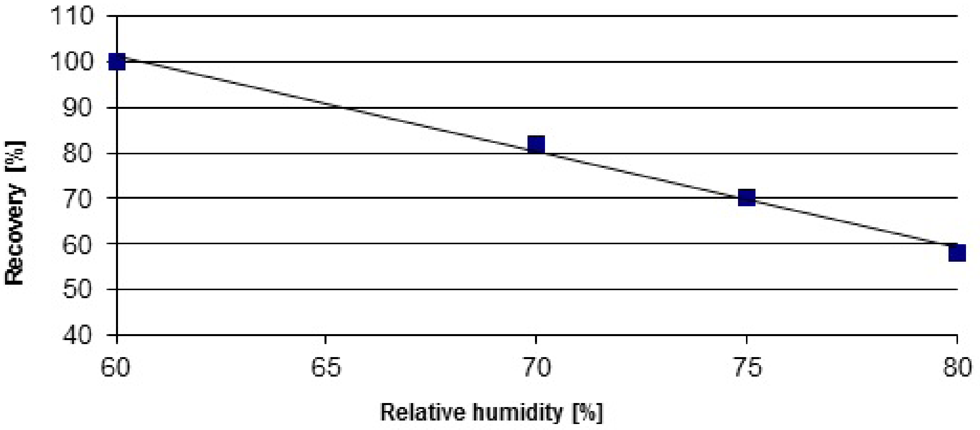

TABLE 1. Performance evaluation for HF and F⁻ ion measurements from test atmospheres [5]

Analyte	Concentration (mg/m^3)	S_r[1] (n = 6)	RSD[2](%)	U[3]
HF	0.25	0.007	3.1	0.22
HF	1.2	0.044	2.8	0.21
HF	2.3	0.026	1.1	0.20
HF	5.0	0.099	2.0	0.11
Fluoride	0.04	0.002	3.8	0.19
Fluoride	0.52	0.006	1.3	0.12
Fluoride	2.95	0.009	0.3	0.11
Fluoride	5.9	0.065	1.1	0.11

1 Standard deviation for 6 test samples
2 Relative standard deviation
3 Expanded measurement uncertainty; k = 2 (calculated in accordance with EN 482 [15])