(1) HF; (2) HCl; (3) H_3PO_4; (4) HBr; (5) HNO_3; (6) H_2SO_4 MW: Table 1 CAS: Table 1 RTECS: Table 1

METHOD: 7903, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : Table 1
NIOSH: Table 1
ACGIH: Table 1

PROPERTIES: Table 1

SYNONYMS: (1) hydrofluoric acid; hydrogen fluoride
(2) hydrochloric acid; hydrogen chloride
(3) phosphoric acid; ortho-phosphoric acid; meta-phosphoric acid
(4) hydrobromic acid; hydrogen bromide
(5) nitric acid; aqua fortis
(6) sulfuric acid; oil of vitriol

SAMPLING

SAMPLER: SOLID SORBENT TUBE (washed silica gel, 400 mg/200 mg with glass fiber filter plug)

FLOW RATE: 0.2 to 0.5 L/min

VOL-MIN: 3 L
-MAX: 100 L

SHIPMENT: routine

SAMPLE STABILITY: stable at least 21 days @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: see EVALUATION OF METHOD

BIAS: see EVALUATION OF METHOD

OVERALL PRECISION ($\hat{S}_{rT}$): see EVALUATION OF METHOD

ACCURACY: ± 12 to ± 23%

MEASUREMENT

TECHNIQUE: ION CHROMATOGRAPHY

ANALYTE: F^-, Cl^-, PO_4^{3-}, Br^-, NO_3^-, SO_4^{2-}

DESORPTION: 10 mL 1.7 mM $NaHCO_3$/1.8 mM Na_2CO_3

INJECTION LOOP VOLUME: 50 µL

ELUENT: 1.7 mM $NaHCO_3$/1.8 mM Na_2CO_3; 3 mL/min

COLUMNS: HPIC-AS4A anion separator, HPIC-AG4A guard, anion micro membrane suppressor [2]

CONDUCTIVITY SETTING: 10 µS full scale

RANGE: see EVALUATION OF METHOD

ESTIMATED LOD: see EVALUATION OF METHOD

PRECISION ($\bar{S}_r$): see EVALUATION OF METHOD

APPLICABILITY: The working range is ca. 0.01 to 5 mg/m^3 for a 50-L air sample (see EVALUATION OF METHOD). This method measures the total concentration of six airborne anions. The corresponding acids may be collected on a single sam pler and determined simultaneously. Formic acid has been determined by this method [3].

INTERFERENCES: Particulate salts of all the acids will give a positive interference. Chlorine or hypochlorite ion interfere with chloride determination and bromine interferes with bromide. Silica gel will collect ca. 30% of the free Cl_2 and Br_2 in an atmosphere [4]. Acetate, formate and propionate have elution times similar to F^- and Cl^-. If these anions are present, use a weak eluent (e.g., 5 mM $Na_2B_4O_7$) for greater resolution.

OTHER METHODS: This is P&CAM 339 in a revised format [5]. Alternate methods are 7902 for fluoride and P&CAM 268 for sulfate [6].

REAGENTS:

1. $NaHCO_3$, reagent grade.
2. Na_2CO_3, reagent grade.
3. Distilled, deionized water, filtered through 0.45-µm membrane filter.
4. Eluent: bicarbonate/carbonate buffer solution (1.7 mM $NaHCO_3$/1.8 mM Na_2CO_3). Dissolve 0.5712 g $NaHCO_3$ and 0.7631 g Na_2CO_3 in 4 L filtered deionized water.
5. Calibration stock solutions, 1 mg/mL (as the anion). Dissolve salt in filtered deionized water.
   a. Fluoride: 0.2210 g NaF/100 mL.
   b. Chloride: 0.2103 g KCl/100 mL.
   c. Phosphate: 0.1433 g KH_2PO_4/100 mL.
   d. Bromide: 0.1288 g NaBr/100 mL.
   e. Nitrate: 0.1371 g $NaNO_3$/100 mL.
   f. Sulfate: 0.1814 g K_2SO_4/100 mL.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 11 cm x 7-mm OD, containing a 400-mg front section and 200-mg backup section of washed silica gel, flame-sealed ends with plastic caps. Front section is retained with a glass fiber filter plug. Urethane plugs separate and retain the backup section. Tubes are commercially available (Supelco ORBO 53 or equivalent) or may be prepared according to APPENDIX.
2. Personal sampling pump, 0.2 to 0.5 L/min, with flexible connecting tubing.
3. Ion chromatograph, HPIC-AG4A anion separator and HPIC-AG4A anion micro membrane suppressor, conductivity detector, integrator and strip chart recorder.
4. Waterbath: hotplate with beaker of boiling water.
5. Centrifuge tubes, 15-mL, graduated, plastic, with caps.*
6. Syringes, 10-mL, polyethylene with luer tip.
7. Filters, luer tip, with membrane filter, 13-mm, 0.8-µm pore size.
8. Micropipettes, disposable tips.
9. Volumetric flasks, 50- and 100-mL.*
10. Laboratory timer.
11. Bottles, polyethylene, 100-mL.
12. Auto sampler vials (optional).

* Thoroughly clean glassware with mild detergent, rinse thoroughly with deionized water, to minimize anion blank values.

SPECIAL PRECAUTIONS: Acids, particularly HF, are extremely corrosive to skin, eyes, and mucous membranes. HF will attack glass. Plastic labware is recommended.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.2 and 0.5 L/min for a total sample size of 3 to 100 L.
   NOTE: Do not exceed 0.3 L/min when sampling for HF.

SAMPLE PREPARATION:

4. Score sampler with a file in front of primary sorbent section.
5. Break sampler at score line. Transfer glass fiber filter plug and front sorbent section to a 15-mL graduated centrifuge tube.

NOTE: Particulate salts of the volatile acids (HCl, HB, HF, and HNO_3), if present in the air sample, will collect on the glass fiber filter plug. To estimate the concentration these salts, analyze the plug separately from the front sorbent section.

6. Place backup sorbent section in separate centrifuge tube. Discard urethane plugs.
7. Add 6 to 8 mL eluent to each centrifuge tube. Heat in boiling waterbath for 10 min.
   NOTE: Eluent used for desorption should be from same batch as the eluent used in the chromatograph to avoid carbonate/bicarbonate peaks near F^- and Cl^-.
8. Allow to cool, dilute to 10.0-mL volume with eluent.
9. Cap the centrifuge tube and shake vigorously.
10. Pour sample into 10-mL plastic syringe fitted with in-line filter.

CALIBRATION AND QUALITY CONTROL:

11. Calibrate daily with at least six working standards covering the range 0.001 to 0.3 mg of each anion per sample.
    a. Add known aliquots of calibration stock solution to eluent in 50-mL volumetric flasks and dilute to the mark.
    b. Store working standards in tightly-capped polyethylene bottles. Prepare fresh working standards weekly.
    c. Analyze working standards together with samples and blanks (steps 12 through 14).
    d. Prepare a calibration graph for each anion [peak height (mm or µS) vs. concentration (µg per sample)].

MEASUREMENT:

12. Set ion chromatograph to conditions given on page 7903-1, according to manufacturer's instructions.
13. Inject 50-µL sample aliquot. For manual operation, inject 2 to 3 mL of sample from filter/syringe to ensure complete rinse of sample loop.
    NOTE: All samples, eluents and water flowing through the IC must be filtered to avoid plugging system valves or columns.
14. Measure peak height.
    NOTE: If sample peak height exceeds linear calibration range, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.

CALCULATIONS:

15. Determine the mass, µg, of anion found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
16. Calculate concentration, C, of acid in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot F}{V}, \text{ mg/m}^3.$$

where: F (conversion factor from anion to acid) = 1.053 for HF; 1.028 for HCl; 1.032 for H_3PO_4; 1.012 for HBr; 1.016 for HNO_3; and 1.021 for H_2SO_4.

EVALUATION OF METHOD:

The method was evaluated for hydrochloric, hydrobromic, nitric, phosphoric and sulfuric acids by laboratory generation of mixed acids [1]. Data for the individual analytes are:

Acid	Range Studied (mg/m^3)	(µg/sample)	(%)	Measurement Precision ($\bar{S}_r$)	Overall Precision ($\hat{S}_{rT}$)	Accuracy (%)	Estimated LOD [2] (µg per sample)
HF [7]	0.35 - 6	0.5 - 200	0.7	0.053	0.116	±23.4	0.7
HCl [8]	0.14 - 14	0.5 - 200	0.3	0.025	0.059	±11.9	0.6
H_3PO_4 [1]	0.5 - 2	3 - 100	-0.9	0.029	0.096	±19.7	2.0
HBr [1]	2 - 20	3 - 960	2.0	0.056	0.074	±16.5	0.9
HNO_3 [1]	1 - 10	3 - 500	2.0	0.018	0.085	±18.7	0.7
H_2SO_4 [1]	0.5 - 2	3 - 100	2.4	0.028	0.087	±19.4	0.9

The method was field-evaluated at two electroplating facilities using side-by-side silica gel tubes and bubblers. The method was evaluated for hydrofluoric acid in 1983 using the silica gel tubes and impingers [7]. Recovery based on impinger collection was 106% with $\hat{S}_{rT}$ of 0.116. The capacity of the silica gel sampler for HF was 820 µg. This is equivalent to an 8-h sample at two to three times the OSHA PEL. Samples were stable for at least 21 days at 25 °C. Updated analytical columns have been used by NIOSH for analytical sequences [2].

REFERENCES:

[1] Cassinelli, M. E. and D. G. Taylor. Airborne Inorganic Acids, ACS Symposium Series 149, 137-152 (1981).
[2] DataChem, Inc. NIOSH Analytical Sequences #7546, #7357, and #7594 (unpublished, 1992).
[3] DataChem Laboratories, NIOSH Sequence #7923-C,D (unpublished, Jan. 25, 1994).
[4] Cassinelli, M.E. "Development of a Solid Sorbent Monitoring Method for Chlorine and Bromine in Air with Determination by Ion Chromatography." Appl. Occup. Environ. Hyg. 6:215-226 (1991)
[5] NIOSH Manual of Analytical Methods, 2nd. ed., V. 7, P&CAM 339, U.S. Department of Health and Human Services, (NIOSH) Publication No. 82-100 (1982).
[6] NIOSH Manual of Analytical Methods, 2nd. ed., V. 5, P&CAM 268, U.S. Department of Health and Human Services, (NIOSH) Publication No. 82-100 (1982).
[7] Cassinelli, M. E. "Laboratory Evaluation of Silica Gel Sorbent Tubes for Sampling Hydrogen Fluoride," Am. Ind. Hyg. Assoc. J., 47(4):219-224 (1986).
[8] Cassinelli, M. E. and P. M. Eller. Ion Chromatographic Determination of Hydrogen Chloride, Abstract No. 150, American Industrial Hygiene Conference, Chicago, IL (1979).

METHOD WRITTEN BY:

Mary Ellen Cassinelli, NIOSH/DPSE.

APPENDIX: SAMPLING TUBE PREPARATION

Silica gel cleaning procedure: Add 500 to 600 mL deionized water, slowly and with stirring, to ca. 200 mL volume of silica gel in 1-L beaker. When exothermal reaction has subsided, heat in boiling waterbath for ca. 30 min with occasional stirring. Decant and rinse four to five times with deionized water. Repeat cleaning procedure and dry overnight in 100 °C oven until free flowing. If blank of silica gel shows impurities upon analysis by ion chromatography, repeat cleaning procedure.

Silica gel tubes: Pack glass tubes, 7-mm OD, 4.8-mm ID, 11 cm long, with 400 mg of 20/40 mesh washed silica gel in front section and 200 mg backup section. Use urethane foam plugs between sorbent sections and at back end. Hold front section in place with 6-mm diameter, 1-mm thick glass fiber filter plug (Gelman 66088).

TABLE 1. GENERAL INFORMATION.

Acid	PROPERTIES		EXPOSURE LIMITS				
and BP M.W. (°C)	CAS Sp. Gr. RTECS (liq.)	VP @ 20 °C OSHA kPa (mm Hg)	NIOSH	ACGIH	mg/m^3 = 1 ppm @ NTP	Physical State	MP (°C)
HF 19.5 (20.01)	7664-39-3 0.987 MW7875000	3 ppm >101 (>760)	3 ppm; 6 ppm STEL	C 3 ppm;	0.818	gas	-83.1
HCl -114.8 (36.46)	7647-01-0 -85.0 MW4025000	C 5 ppm 1.194	C 5 ppm >101 (760)	C 5 ppm	1.491	gas	
H_3PO_4 260 (97.99)	7664-38-2 1.7 TB6300000	1 mg/m^3 0.0038 (0.03)	1 mg/m^3;* STEL 3 mg/m^3	1 mg/m^3; STEL 3 mg/m^3	(aerosol)	liquid	21.0
HBr -66.8 (80.92)	10035-10-6 2.16 MW3850000	3 ppm >101 (>760)	C 3 ppm	C 3 ppm	3.31	gas	-88.5
HNO_3 -42.0 (63.01)	7697-37-2 83 QU5775000	2 ppm 1.50	2 ppm; 0.39 (2.9) STEL 4 ppm	2 ppm; STEL 4 ppm	2.58	liquid	
H_2SO_4 290 (98.08)	7664-93-9 1.84 W55600000	1 mg/m^3 <0.0001 (<0.001)	1 mg/m^3*	1 mg/m^3 STEL 3 mg/m^3	(aerosol)	liquid	3.0

*Group I Pesticide