

# SULFURYL FLUORIDE

6012



MW: 102.06

CAS: 2699-79-8

RTECS: WT5075000

METHOD: 6012, Issue 1

EVALUATION: FULL

Issue 1: 15 August 1994

**OSHA :** 5 ppm  
**NIOSH:** 5 ppm; STEL 10 ppm; Group I Pesticide  
**ACGIH:** 5 ppm; STEL 10 ppm  
 (1 ppm = 4.17 mg/m<sup>3</sup> @ NTP)

**PROPERTIES:** gas; BP -55 °C; vapor density (air = 1)  
 3.5; nonflammable, colorless, odorless

**SYNONYMS:** sulfur difluoride, sulfuric oxyfluoride, Vikane

SAMPLING		MEASUREMENT	
<b>SAMPLER:</b>	SOLID SORBENT TUBE (coconut shell charcoal, 800 mg/200 mg)	<b>TECHNIQUE:</b>	ION CHROMATOGRAPHY CONDUCTIVITY DETECTION
<b>FLOW RATE:</b>	0.05 to 0.1 L/min	<b>ANALYTE:</b>	fluoride ion (F <sup>-</sup> )
<b>VOL-MIN:</b>	1.3 L @ 5 ppm	<b>EXTRACTION:</b>	20 mL 40 mN NaOH; sonicate 60 min
<b>-MAX:</b>	10 L	<b>INJECTION VOLUME:</b>	50 µL
<b>SHIPMENT:</b>	ship at 0 °C	<b>ELUENT:</b>	40 mN NaOH, 1.0 mL/min
<b>SAMPLE STABILITY:</b>	at least 12 days @ 0 °C	<b>COLUMN:</b>	Dionex IonPac-AG4A guard, IonPac-AS4A anion separator column; Dionex micromembrane-suppressor
<b>BLANKS:</b>	2 to 10 field blanks per set	<b>DETECTOR:</b>	conductivity, 30 µS full scale
<b>ACCURACY</b>		<b>CALIBRATION:</b>	standard solutions of fluoride ion spiked onto sample media
<b>RANGE STUDIED:</b>	20 to 420 mg/m <sup>3</sup> (0.2- to 6-L samples)	<b>RANGE:</b>	10 to 80 µg fluoride per sample [2]
<b>BIAS:</b>	-3.0%	<b>ESTIMATED LOD:</b>	7 µg SO <sub>2</sub> F <sub>2</sub> per sample [2]
<b>OVERALL PRECISION (<math>\hat{S}_{r,T}</math>):</b>	0.070 [1]	<b>PRECISION (<math>\hat{S}_r</math>):</b>	0.052 (9 to 140 mg/m <sup>3</sup> SO <sub>2</sub> F <sub>2</sub> per sample) [1]
<b>ACCURACY:</b>	±16.7%		

**APPLICABILITY:** The working range is 2.2 to 17 ppm (9 to 75 mg/m<sup>3</sup>) for a 3-L air sample. This method is applicable to STEL measurements using a 1.5 L sample. The method has been used to sample for suluryl fluoride at dwelling fumigation sites [2,3].

**INTERFERENCES:** Other fluoride compounds may interfere.

**OTHER METHODS:** This method is based on the method of Bouyoucos, et al. [4]. NIOSH Method #S245 uses gas bag samples, gas chromatography/FPD [5].

**REAGENTS:**

1. Sodium hydroxide\*, ACS reagent grade.
2. Water, high purity.
3. Desorbing/extracting solution and eluent: 40 mN NaOH. Dissolve 3.2 g NaOH in 2 L of degassed high purity water.
4. Suppressor regenerant, 25 m N H<sub>2</sub>SO<sub>4</sub>\*.
5. Calibration stock solution, 1 mg fluoride anion per mL. Dissolve 0.2210 g NaF in 100 mL deionized water.
6. Sulfuryl fluoride\*, gas. Calibrated gas standards may be obtained from Scott-Marrin, Inc., Riverside, CA 92507.

\* See SPECIAL PRECAUTIONS.

**EQUIPMENT:**

1. Sampler: glass tube, 11 cm long, 10-mm OD, 7-mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 800 mg, back = 200 mg), separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.05 to 0.10 L/min, with flexible polyethylene or PTFE tubing.
3. Refrigerant, bagged ("Blue Ice," or equivalent).
4. Filter, membrane, 0.45- $\mu$ m pore size, 13-mm, with luer fitting.
5. Ion chromatograph, with a conductivity detector, chart recorder, integrator and columns (p. 6012-1).
6. Vials, glass, 20-mL, with plastic caps.
7. Vials, polyethylene, 20-mL, with plastic caps.
8. Micropipettes, with disposable plastic tips.
9. Volumetric flasks, 100-mL
10. Pipet, 10-mL, graduated in 0.1-mL intervals.
11. Pipet, volumetric, 20-mL.
12. Syringes, 10-mL, plastic, with luer tip.

**SPECIAL PRECAUTIONS:** Sulfuryl fluoride is a restricted use pesticide owing to its inhalation toxicity. It is extremely hazardous as vapor or liquid. Inhalation of vapors may be fatal. Read and follow all label precautions [6].

Sulfuric acid and sodium hydroxide are corrosive to skin, eyes, and mucous membranes. Handle all hazardous chemicals in a fume hood.

**SAMPLING:**

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach a sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.05 and 0.1 L/min for a total sample volume of 1.3 to 10 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment, at 0 °C.

**SAMPLE PREPARATION:**

5. Place the front and back sorbent sections of the sampler tube in separate 20-mL plastic vials. Discard the glass wool and foam plugs.
6. Add 20 mL 40 m N NaOH eluent to each plastic vial. Cap. Sonicate for 60 minutes.
7. Transfer a 5 to 7 mL aliquot to a tare weighted 20-mL glass vial using a plastic syringe fitted with a 0.45  $\mu$ m membrane filter.
8. Re-weigh each glass vial and contents so that the net weight of the aliquot can be calculated.
9. Take each sample to complete dryness in an uncapped glass vial on a hot plate. Cool, then re-constitute to the original net weight with high-purity water.

**CALIBRATION AND QUALITY CONTROL:**

10. Calibrate daily with at least six working standards.  
NOTE: Standards should be spiked onto charcoal tubes as follows to avoid high recoveries seen with liquid standards [3].
  - a. Add known amounts of calibration stock solution onto charcoal tubes (5.0 to 80 µg F<sup>-</sup>) and desorb in the same manner as field samples (steps 5 through 9).
  - b. Analyze working standards together with samples and blanks (steps 12 through 14).
  - c. Prepare a calibration graph of peak height vs. amount (µg) of fluoride per 20 mL of sample.
11. (Optional). Determine recovery (R) for each lot of tubes used for sampling in the concentration range of interest. Prepare four tubes at each of five levels plus three media blanks.
  - a. Collect a known amount of SO<sub>2</sub>F<sub>2</sub> gas onto each charcoal tube (steps 1 through 9).
  - b. Analyze samples in the same manner as field samples (steps 12 through 14).
  - c. Prepare graph of recovery vs. µg sulfonyl fluoride.

**MEASUREMENT:**

12. Set ion chromatograph to conditions given on page 6012-1.
13. Re-filter sample if necessary, then inject a sample aliquot into the ion chromatograph.
14. Measure peak height.

**CALCULATIONS:**

15. Determine mass (µg) of fluoride found on the front (W<sub>f</sub>) and back (W<sub>b</sub>) sections, and in the average media blank front (B<sub>f</sub>) and back (B<sub>b</sub>) sorbent section.
16. Calculate concentration C of sulfonyl fluoride (mg/m<sup>3</sup>) in the actual air volume, V(L), applying the conversion factor 2.686 (MW SO<sub>2</sub>F<sub>2</sub>/MW F<sup>-</sup>; the reaction is SO<sub>2</sub>F<sub>2</sub> + 4NaOH → 2NaF + Na<sub>2</sub>SO<sub>4</sub> + 2H<sub>2</sub>O):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 2.686}{V}, \text{ mg/m}^3.$$

**EVALUATION OF METHOD:**

This method was evaluated over the range 20 to 420 mg/m<sup>3</sup>. Overall sampling and measurement precision,  $\hat{S}_{\text{PT}}$ , was 0.070 [1]. The average recovery of SO<sub>2</sub>F<sub>2</sub> from charcoal was 99% when sampling atmospheres prepared in aluminized gas bags (Calibrated Instruments, Inc., Hawthorne, NY 10532). Recovery of fluoride from sampling media was 97% in the range 10 to 160 µg F<sup>-</sup> per sample. Sample stability during storage was evaluated at 417 mg/m<sup>3</sup> SO<sub>2</sub>F<sub>2</sub> per sample. Samples showed 101% recovery after twelve days of storage at 0-5 °C compared to one-day old samples.

**REFERENCES:**

- [1] Williamson, G.Y. Backup Data Report for Sulfonyl Fluoride. NIOSH/MRSB Internal Report (unpublished) (1991).
- [2] Analysis of NIOSH Samples for Sulfonyl Fluoride, NIOSH/MRSB Sequence #7161-A, (unpublished, May 13, 1991).
- [3] Analysis of NIOSH Samples for Sulfonyl Fluoride, NIOSH/MRSB Sequence #7691-D (unpublished, January 27, 1993).
- [4] Bouyoucos, S.A., Melcher, R.G., and Vaccaro, J.R., Collection and Determination of Sulfonyl Fluoride in Air by Ion Chromatography, *Am. Ind. Hyg. J.*, **44**, 57-61 (1983).
- [5] NIOSH Manual of Analytical Methods, 2nd. ed., V. 6, S245, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 80-125 (1980).

- [6] NIOSH/OSHA Occupational Health Guidelines for Occupational Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.

**METHOD WRITTEN BY:**

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