# SULFURYL FLUORIDE 6012

$SO_2F_2$ MW: 102.06 CAS: 2699-79-8 RTECS: WT5075000

**METHOD: 6012, Issue 2** **EVALUATION: FULL** **Issue 1: 15 August 1994**
**Issue 2: 12 January 2016**

**OSHA:** 5 ppm
**NIOSH:** 5 ppm; STEL 10 ppm
(1 ppm = 4.17 mg/m$^3$ @ NTP)

**PROPERTIES:** Gas; BP −55 °C; vapor density (air = 1) 3.5; VP 1.7 × 10$^3$ kPa; nonflammable, colorless, odorless [1]

**SYNONYMS:** Sulfonyl difluoride, sulfur difluoride dioxide, sulfuric oxyfluoride

## SAMPLING

**SAMPLER:** SOLID SORBENT TUBE
(coconut shell charcoal, 800 mg/200 mg)

**FLOW RATE:** 0.05 L/min to 0.1 L/min

**VOL-MIN:** 1.3 L @ 5 ppm
**-MAX:** 10 L

**SHIPMENT:** Ship at 0 °C

**SAMPLE STABILITY:** At least 12 d @ 0 °C

**BLANKS:** 2 to 10 field blanks per set

## ACCURACY

**RANGE STUDIED:** 20 mg/m$^3$ to 420 mg/m$^3$ (0.2 L to 6 L samples)

**BIAS:** −3.0%

**OVERALL PRECISION ($\hat{S}_{rT}$):** 0.070 [2]

**ACCURACY:** ±16.7%

## MEASUREMENT

**TECHNIQUE:** ION CHROMATOGRAPHY
CONDUCTIVITY DETECTION

**ANALYTE:** Fluoride ion

**EXTRACTION:** 20 mL 40 mmol/L sodium hydroxide; sonicate 60 min

**INJECTION:** 50 µL

**ELUENT:** 40 mmol/L sodium hydroxide, 1.0 mL/min

**COLUMN:** US Pharmacopeia (USP) L12 separator column, manufacturer's compatible anion guard column, and micromembrane suppressor as recommended by the manufacturer. See OTHER METHODS.

**DETECTOR:** Conductivity, 30 µS full scale

**CALIBRATION:** Standard solutions of fluoride ion spiked onto sample media

**RANGE:** 10 µg to 80 µg fluoride per sample [3]

**ESTIMATED LOD:** 7 µg sulfuryl fluoride per sample [3]

**PRECISION ($\bar{S}_r$):** 0.052 (27 µg to 420 µg sulfuryl fluoride per sample) [2]

**APPLICABILITY:** The working range is 2.2 ppm to 17 ppm (9 mg/m$^3$ to 75 mg/m$^3$) 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 sulfuryl fluoride at dwelling fumigation sites [3,4].

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

**OTHER METHODS:** This method is based on the method of Bouyoucos, et al. [5]. NIOSH method S245 uses gas bag samples, gas chromatography-flame photometric detector (GC-FPD) [6].

**REAGENTS:**

1. Sodium hydroxide,* ACS reagent grade.
2. Sulfuric acid,* concentrated, ACS reagent grade.
3. Water, high-purity.
4. Desorbing/extracting solution and eluent: 40 mmol/L sodium hydroxide. Dissolve 3.2 g sodium hydroxide in 2 L of degassed high-purity water.
5. Suppressor regenerant, 12.5 mmol/L sulfuric acid. Add 0.70 mL concentrated sulfuric acid to 1 L of high-purity water.
6. Calibration stock solution, 1 mg/mL fluoride anion. Dissolve 0.2210 g sodium fluoride in high-purity water and dilute to the mark in a 100 mL volumetric flask.
7. Sulfuryl fluoride* calibration gas standard(s) (optional).

*See SPECIAL PRECAUTIONS.

**EQUIPMENT:**

1. Sampler: Activated coconut shell charcoal sampling tube; 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.
2. Personal sampling pump, 0.05 L/min to 0.10 L/min, with flexible polyethylene or PTFE tubing.
3. Refrigerant, water solution, sealed, refreezable, reusable.
4. Filter, membrane, 0.45 µm pore size, 13 mm, with Luer fitting.
5. Ion chromatograph, with a conductivity detector, chart recorder, integrator, and columns (page 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.
13. Sonicator.
14. Analytical balance, to ±0.0001 g.

**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 [7]. Sulfuric acid and sodium hydroxide are corrosive to skin, eyes, and mucous membranes. Use proper protective clothing including gloves, safety glasses, and laboratory coat. 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 L/min and 0.1 L/min for a total sample volume of 1.3 L 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 mmol/L sodium hydroxide eluent to each plastic vial. Cap. Sonicate for 60 min.
7. Transfer a 5 mL to 7 mL aliquot to a tare weighted 20 mL glass vial using a plastic syringe fitted with a 0.45 µm membrane filter.
8. Reweigh 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 reconstitute 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 [4].
    a. Add known amounts of calibration stock solution onto charcoal tubes (5.0 µg to 80 µg fluoride) and desorb in the same manner as field samples (steps 5, 6, 7, 8, and 9).
    b. Analyze working standards together with samples and blanks (steps 12, 13, and 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 sulfuryl fluoride gas onto each charcoal tube (steps 1, 2, 3, 4, 5, 6, 7, 8, and 9).
    b. Analyze samples in the same manner as field samples (steps 12, 13, and 14).
    c. Prepare graph of recovery vs. µg sulfuryl fluoride.

**MEASUREMENT:**

12. Set ion chromatograph to conditions given on page 6012-1.
13. Refilter 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 ($W_f$) and back ($W_b$) sections, and in the average media blank front ($B_f$) and back ($B_b$) sorbent section.
    NOTE: If $W_f > W_b / 10$, report breakthrough and possible sample loss.
16. Calculate concentration, *C*, of sulfuryl fluoride in the actual air volume, *V* (L), applying the conversion factor 2.686 (molecular weight of sulfuryl fluoride divided by the atomic weight of 2 fluoride anions; the reaction is $SO_2F_2 + 4\ NaOH \rightarrow 2\ NaF + Na_2SO_4 + 2\ H_2O$):

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

**EVALUATION OF METHOD:**

This method was evaluated over the range 20 mg/m$^3$ to 420 mg/m$^3$. Overall sampling and measurement precision, $\hat{S}_{rT}$, was 0.070 [2]. The average recovery of sulfuryl fluoride 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 µg to 160 µg fluoride per sample. Sample stability during storage was evaluated at an air concentration of 417 mg/m$^3$ sulfuryl fluoride. Samples showed 101% recovery after 12 d of storage at 0 °C to 5 °C compared to one-day-old samples.

**REFERENCES:**

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**METHOD WRITTEN BY:**

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