

# SULFUR HEXAFLUORIDE by portable GC

6602

SF<sub>6</sub>

MW: 146.06

CAS: 2551-62-4

RTECS: WS4900000

**METHOD:** 6602

**EVALUATION:** FULL

**Issue 1:** 15 August 1994

**OSHA :** 1000 ppm  
**NIOSH:** 1000 ppm  
**ACGIH:** 1000 ppm  
 (1 ppm = 5.97 mg/m<sup>3</sup> @ NTP)

**PROPERTIES:** colorless, odorless gas; MP -50.8 °C;  
 sublimes -63.8 °C; d = 5.0 (air = 1)

**SYNONYMS:** (none)

**APPLICABILITY:** The working range of this method is 0.1 to 10,000 ppb in relatively non-complex atmospheres where sulfur hexafluoride is known to be present, such as indoor environments where ventilation testing is being conducted by the release of SF<sub>6</sub>.

**INTERFERENCES:** Any compound having the same or nearly the same retention time as sulfur hexafluoride on the column may cause a positive interference. Carbon dioxide, another common substance monitored to evaluate ventilation systems in indoor air quality studies, will not interfere.

**OTHER METHODS:** Method S244 [1] describes the determination of SF<sub>6</sub> by thermal conductivity detection after collection in bags, with a lower limit of 500 ppm, i.e., not sensitive enough for ventilation studies.

**REAGENTS:**

1. Sulfur hexafluoride in air at known concentration(s) for use in field calibration. Prepared in the field by filling sample bag (see "Equipment") with verified commercial standard compressed gas\*, or by injecting known amount of pure (or high concentration) SF<sub>6</sub>\* into sample bag containing a metered volume of clean air.
2. Compressed argon or other gas\* at approximately 30 psi for use as carrier gas.

\* See SPECIAL PRECAUTIONS.

**EQUIPMENT:**

1. Portable gas chromatograph (GC), with electron capture detector, gas sampling loop if desired (use of loop will limit variability of injection volume and therefore restrict range of method), and strip chart recorder if appropriate.
2. Personal sampling pump, 0.02 to 1 L/min or other rate suitable for filling sample bags, with flexible connecting tubing.  
NOTE: Pumps lubricated with petroleum products should not be used.
3. Sample bags, 1 to 20 L or other appropriate sizes. Sources include: Calibrated Instruments, Inc., 200 Saw Mill River Rd., Hawthorne, NY 10532; SKC, Inc., 334 Valley View Rd., Eighty-Four, PA 15330-9614.
4. Syringes, gas-tight, of various sizes appropriate to the GC.  
NOTE: To reduce the possibility of contamination, use separate, previously unused syringes for working standards and samples. Test syringes for contamination occasionally by filling them with clean air and analyzing the contents.
5. Label tape and marking pen for labeling bags.

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**SPECIAL PRECAUTIONS:** Shipment of radioisotopes, calibration materials, and compressed gases must comply with 49CFR171-177 regulations regarding shipment of hazardous materials. Appropriate safety precautions should be followed when working with compressed gases.

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**SAMPLING AND MEASUREMENT:**

1. Start GC and recorder and allow to warm up according to manufacturer's instructions.  
NOTE: A stable standing current and stable baseline should be attained at the highest sensitivity likely to be used.
2. Select either or both of the following sampling modes:
  - a. **Spot sample** - Draw air sample into gas sampling loop of the GC with the on-board sampling pump, if supplied. Alternatively, inject an aliquot of air to be sampled into the GC with a gas-tight syringe.  
NOTE: A potential source of random error in the method is imprecision of replicate injections. To reduce this error: i) use a gas sampling loop for injections; ii) make at least three replicate determinations per sample; iii) use an injection volume precisely readable, and consistent with that used in calibration.
  - b. **Integrated air sample for time weighted average (TWA) determination** Attach a clean sample bag to the outlet port of a personal sampling pump with a minimum length of flexible tubing.  
NOTE 1: To reduce memory effects and contamination, sample bags should be purged with clean air between samples. Ideally the bags should be filled with clean air prior to use, and an aliquot of that air from the bag injected into the GC to demonstrate that the bag is indeed clean prior to use. Pump the air sample into the bag at a rate calculated to fill <80% of the bag capacity over the desired

sampling period.

NOTE 2: While it is not necessary to know precisely the sample flow rate, it is important that the flow rate be constant over the duration of the sample. Within eight hours after completion of sampling, introduce an aliquot of the sample into the GC (as in step 2a above).

NOTE 3: Bag samples may be stored for longer periods if integrity has been demonstrated in the bag being used.

- c. Obtain the peak height or area for the injected sample of sulfur hexafluoride.

#### CALIBRATION AND QUALITY CONTROL:

4. Perform the following in the laboratory before field work begins:
  - a. Establish a laboratory calibration graph by at least three replicate determinations of at least five analyte volumes. Plot peak height (or area) vs. volume of sulfur hexafluoride.
  - b. Determine detector drift, averaged over the time period expected to be used in the field.
  - c. Determine the ability of the GC column to separate the sulfur hexafluoride from other substances known or predicted to be present in the field samples.
5. Establish a daily field calibration graph of peak height (or area) vs. volume of sulfur hexafluoride by triplicate determinations of working standards under the same conditions as for samples (step 2a). Alternate analyses of samples and working standards, if possible.

#### CALCULATIONS:

6. Calculate volume of analyte in the sample,  $V_a$  (expressed in picoliters), by comparison of sample peak height or area with the daily calibration graph (step 5). Determine sulfur hexafluoride concentration,  $C$  (ppb) in the sample by dividing  $V_a$  by the volume of the injection,  $V_i$  (mL):

$$C = \frac{V_a}{V_i}, \text{ ppb.}$$

NOTE 1: Some GCs will perform some or all calculations electronically.]

NOTE 2: Determination of sulfur hexafluoride concentration expressed in pg/mL (i.e.,  $\text{mg/m}^3$ ) can be accomplished by establishing lab and field calibration graphs (Steps 4 and 5) of peak height or area vs mass of analyte in mg. " $V_a$ " in Step 6 would then become " $M_a$ ", mass of analyte.]

#### EVALUATION OF METHOD:

This method was evaluated over the range 0.1 to 200 ppb ( $0.0006$  to  $1.2 \text{ pg/m}^3$ ) sulfur hexafluoride using an Ion Track Instruments (ITI) Model 505 portable  $\text{SF}_6$  detector chromatograph modified by the addition of an injection port to allow syringe injections of samples. Mixtures of  $\text{SF}_6$  in air were obtained from Scott Specialty Gases, Inc. at concentrations certified ( $\pm 5\%$ ) of 1.02, 10.5, 36.6, 77.6, 105, 155, and 203 ppb. (The 10.5 ppb standard was diluted 1:100 to obtain a 0.105 ppb standard.) Calibration standards were prepared by dilution of sulfur hexafluoride (99.8% minimum purity, Union Carbide) with air from the laboratory compressed air supply. This dilution air was passed through activated charcoal to remove traces of hydrocarbons, but was tested prior to use since trace amounts of  $\text{SF}_6$  may not be removed by the charcoal. The  $\text{SF}_6$  was measured with the same type of gastight syringe used for sample injection, but the syringes used for the preparation of standards were not used for injections into the GC since they were shown to retain traces of  $\text{SF}_6$  which would show up in such injections. The

dilution air was metered into the same type of inert bags that were used for samples using a 2-L Hamilton syringe.

Packed column, ambient temperature isothermal gas chromatography provides rapid analysis of samples with little sample preparation, but at the expense of providing limited separation of the analyte of interest from potential interferences. The column used in the evaluation of this method was 38 cm x 0.6-cm (OD) stainless steel, packed with 100-120 mesh activated aluminum oxide, using an Argon carrier gas flow of approximately 30 mL/min. These conditions provided a retention time of approximately 1.4 minutes for SF<sub>6</sub>, allowing replicate analyses of multiple samples and calibration standards during a work shift. Increasing the carrier gas flow provided a somewhat faster analysis, but resulted in a loss of sensitivity. Decreasing the carrier gas flow lengthened the retention time, but did not result in an increase in sensitivity. Baseline drift was typically less than 10% per hour. Relative standard deviations for replicate analyses ranged from 0.90 to 5.64%, with a mean of 2.2%. Analysis of certified commercial standards ranged from 97.6 to 102.8%, with a mean of 99.6%.

Samples in multi-layer 5.5-mil bags (Calibrated Instruments, Inc.) showed no detectable change in concentration over a 28-hr period. Samples in 4 mil Tedlar bags (SKC, Inc.) showed no detectable change in concentration after 28 hrs.

**REFERENCES:**

- [1] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 5, U.S. Department of Health, Education, and Welfare (NIOSH) Publ. 79-141 (1979).

**METHOD WRITTEN BY:**

G.E. Burroughs, NIOSH/DPSE.