FLUOROTRICHLOROMETHANE 1006

CCl_3F MW: 137.37 CAS: 75-69-4 RTECS: PB6125000

METHOD: 1006, Issue 2 **EVALUATION: FULL** **Issue 1: 15 August 1987**
Issue 2: 15 August 1994

OSHA : C 1000 ppm
NIOSH: C 1000 ppm
ACGIH: C 1000 ppm
(1 ppm = 5.62 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.53 g/mL @ 0 °C; BP 23.8 °C; MP -111 °C; VP 92 kPa (690 mm Hg; 91% v/v) @ 20 °C; not combustible

SYNONYMS: Freon 11; trichlorofluoromethane; monofluorotrichloromethane

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 400 mg/200 mg)

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 0.3 L
-MAX: 7 L

SHIPMENT: refrigerate

SAMPLE STABILITY: quantitative recovery after 8 days @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 2390 to 10500 mg/m^3 [1] (4-L samples)

BIAS: - 2.66%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.072 [1]

ACCURACY: ± 16.08%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: fluorotrichloromethane

DESORPTION: 5 mL CS_2; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTOR: 175 °C
-DETECTOR: 220 °C
-COLUMN: 65 °C

CARRIER GAS: nitrogen, 30 mL/min

COLUMN: 6 m x 3-mm OD stainless steel packed with 10 % FFAP on 100/120 Chromosorb WHP.

CALIBRATION: standard solutions of analyte in CS_2

RANGE: 2 to 40 mg per sample

ESTIMATED LOD: 0.01 mg per sample

PRECISION ($\bar{S}_r$): 0.063 @ 11 to 32 mg per sample [1]

APPLICABILITY: The working range is 90 to 1800 ppm (500 to 10000 mg/m^3) for a 4-L air sample.

INTERFERENCES: None identified. The chromatographic column or separation conditions may be changed to circumvent interference problems.

OTHER METHODS: This revises Method S102 [2].

REAGENTS:

1. Eluent: carbon disulfide,* chromatographic quality, containing 0.1% (v/v) nonane as internal standard.
2. Fluorotrichloromethane, 99%.
3. Nitrogen, purified.
4. Hydrogen, prepurified.
5. Air, filtered, compressed.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 10 cm long, 8-mm OD, 6-mm ID, flame-sealed ends with plastic caps, containing two sections of 20/40 mesh activated (600 °C) coconut shell charcoal (front = 400 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, 0.01 to 0.05 L/min, with flexible connecting tubing.
3. Refrigerant, bagged.
4. Gas chromatograph, flame ionization detector, integrator, and column (see page 1006-1).
5. Vials, glass, 10-mL, PTFE-lined septum crimp caps.
6. Syringes, 10-µL, readable to 0.1 µL.
7. Syringes, gas-tight, 10-µL to 10-mL.
8. Syringe needle, 22-gauge.
9. Volumetric flasks, 10-mL.
10. Pipet, TD, 5-mL.
11. Balance, 0.1-mg sensitivity.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and a serious fire and explosion hazard (flash point = -30 °C). Work with it only in a hood and away from spark sources.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.05 L/min for a total sample size of 0.3 to 7 L.
4. Cap the sampler. Pack securely for shipment in an insulated container with bagged refrigerant.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler in separate vials. Discard the glass wool and foam plugs. Seal each vial with a septum and crimp seal.
6. Insert a syringe needle through the septum to serve as a vent.
7. Add 5.0 mL eluent to each vial with a syringe. Remove the vent from the septum.
8. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least five working standards over the range 0.01 to 40 mg fluorotrichloromethane per sample. Use serial dilutions for the smallest concentrations.
   a. Add 5.0 mL eluent to each of a series of vials. Attach septum with crimp seal to each vial.
   b. Weigh each vial.
   c. Inject amounts (2 to 30 µL) of neat liquid fluorotrichloromethane (or of a standard solution in CS_2) into the vials.
   d. Reweigh the vials. Calculate the mass of fluorotrichloromethane added.
   e. Analyze with samples and blanks (steps 12 and 13).
   f. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. mg fluorotrichloromethane).
10. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the range of interest. Prepare three tubes at each of five levels plus three media blanks.
   a. Add 400 mg charcoal (e.g., an unused front section) to each of a series of vials.
   b. Seal each vial with a septum and crimp seal.
   c. Weigh each vial.
   d. Inject amounts (2 to 30 µL) of neat fluorotrichloromethane (or of a standard solution in CS_2) into the vials.
   e. Reweigh each vial. Calculate the mass of fluorotrichloromethane added. Allow to stand overnight.
   f. Desorb (steps 6 through 8) and analyze with freshly prepared working standards (steps 12 and 13).
   g. Prepare a graph of DE vs. mg fluorotrichloromethane recovered.
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

12. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1006-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
   NOTE 1: t_r = 3 min for fluorotrichloromethane and 4.5 min for nonane under these conditions.
   NOTE 2: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with eluent, reanalyze, and apply the appropriate dilution factor in calculations.
13. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

14. Determine the mass, mg (corrected for DE), of fluorotrichloromethane found in the sample front (W_f) and back (W_b) sorbent tubes, and in the average media blank front (B_f) and back (B_b) sorbent tubes.
   NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
15. Calculate concentration, C, of fluorotrichloromethane in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S102 was issued on October 29, 1976 [2], and validated with atmospheres generated by a cooled, calibrated syringe drive [1]. Average recovery was 0.98 with $\bar{S}_r = 0.046$ (17 samples) in the range 2388 to 10520 mg/m ^{3} for 4-L samples. No significant difference in recovery was seen between samples (with or without backup sections) stored one or seven days at room temperature. In a separate experiment to check for migration, no significant difference in recovery was seen in samples stored for seven days, with and without backup sections, and no analyte was detectable in any of the backup sections.

Results of breakthrough (effluent concentration = 5% of test concentration) experiments were:

	Breakthrough		Test			
Charcoal, mg	Volume, L	Capacity, mg	Concentration, mg/m^3	Rate L/min	Humidity, % RH	Ref.
100	2	25	12502	0.05	0	[3]
400	10.5	112	10660	0.187	0	[1]
400	6.2	63	10170	0.187	90	[1]

Desorption efficiency for seventeen 400-mg samples of SKC Lot 105 charcoal spiked with 10.5 to 32 mg fluorotrichloromethane averaged 1.04 with $\bar{S}_r = 0.063$.

REFERENCES:

[1] Backup Data Report for Fluorotrichloromethane, prepared under NIOSH Contract 210-76-0123, available as "Ten NIOSH Analytical Methods, Set 1," Order No. PB-271-712 from NTIS, Springfield, VA 22161.
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 2, S102, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[3] Failure Report S102, prepared under Contract No. CDC (NIOSH) 99-74-45 (NIOSH, unpublished, 1977).

METHOD REVISED BY:

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