

(1) 1,1,1,2-TETRACHLORO-2,2-DIFLUOROETHANE and
(2) 1,1,2,2-TETRACHLORO-1,2-DIFLUOROETHANE

1016

(1): CCl₃CClF₂
(2): CCl₂FCCl₂F

MW: 203.83

CAS: (1) 76-11-9
(2) 76-12-0

RTECS: (1) KI1425000
(2) KI1420000

METHOD: 1016, Issue 2

EVALUATION: PARTIAL

Issue 1: 15 May 1989

Issue 2: 15 August 1994

OSHA : 500 ppm
NIOSH: 500 ppm
ACGIH: 500 ppm
(1 ppm = 8.34 mg/m³ @ NTP)

PROPERTIES: solids; MP (1) 40.6 °C; (2) 25 °C;
BP (1) 91.5 °C, (2) 93 °C;
VP 5.3 kPa (40 mm Hg; 5.2% v/v)
@ 20 °C; not combustible

SYNONYMS: (1): Refrigerant 112a.
(2): Refrigerant 112.

SAMPLING		MEASUREMENT	
SAMPLER:	SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)	TECHNIQUE:	GAS CHROMATOGRAPHY, FID
FLOW RATE:	0.01 to 0.035 L/min	ANALYTE:	1,1,1,2-tetrachloro-2,2-difluoroethane; 1,1,2,2-tetrachloro-1,2-difluoroethane
VOL-MIN:	0.5 L @ 500 ppm	DESORPTION:	1 mL CS ₂ ; stand 30 min
-MAX:	2 L	INJECTION	
SHIPMENT:	routine	VOLUME:	5 µL
SAMPLE STABILITY:	not tested	TEMPERATURE-INJECTION:	(1) 185 °C (2) 50 °C
BLANKS:	2 to 10 field blanks per set	-DETECTOR:	250 °C 240 °C
		-COLUMN:	50 °C 50 °C
		CARRIER GAS:	nitrogen, 30 mL/min
		COLUMN:	3 m x 3-mm OD stainless steel packed with 10% FFAP on 80/100 mesh Chromosorb WHP
		CALIBRATION:	standard solutions in CS ₂
		RANGE:	2 to 20 mg per sample
		ESTIMATED LOD:	0.3 mg per sample
		PRECISION (\hat{S}_p):	(1): 0.27 @ 4 to 17 mg per sample [1]; Ø 0.005 @ 4 to 17 mg per sample [1]
ACCURACY			
RANGE STUDIED:	(1): 2160 to 9020 mg/m ³ [1] (2): 1880 to 8060 mg/m ³ [1]		
BIAS:	(1) 0.17% (2) 2.0%		
OVERALL PRECISION (\hat{S}_{RT}):	(1): 0.069; (2): 0.054 [1]		
ACCURACY:	(1) ± 32.4% (2) ± 11.4%		

APPLICABILITY: The working range for either analyte is 120 to 1400 ppm (1000 to 12,000 mg/m³) for a 2-L air sample. These compounds are used as degreasing solvents, refrigerants, foaming agents and corrosion inhibitors. Capillary columns may be used (DB-Wax or Nukol on fused silica, 3 m x 0.32-mm, 0.5 µm film) with appropriate changes in instrumental conditions.

INTERFERENCES: None reported.

OTHER METHODS: This combines and revises Methods S131 and S132 [2].

REAGENTS:

1. Carbon disulfide (CS₂), chromatographic quality.*
2. 1,1,1,2-Tetrachloro-2,2-difluoroethane and 1,1,2-tetrachloro-1,2-difluoroethane, reagent grade.*
3. Hexane, chromatographic quality.
4. Calibration stock solution, 0.2 mg/μL. Dissolve 2 g analyte in CS₂ to prepare 10 mL solution. Prepare in duplicate.
5. DE stock solution, 1 mg/μL. Dissolve 10 g analyte in hexane to prepare 10 mL solution. Prepare in duplicate.
6. Nitrogen, purified.
7. Hydrogen, prepurified.
8. Air, filtered, compressed

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 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 0.035 L/min, with flexible connecting tubing.
3. File, triangular.
4. Gas chromatograph, flame ionization detector, integrator and column (page 1016-1).
5. Vials, 2-mL, PTFE-lined caps.
6. Syringes, 10-μL, readable to 0.1 μL.
7. Volumetric flasks, 10-mL.
8. Pipets, 10- to 1000-μL.

SPECIAL PRECAUTIONS: Tetrachloro-1,2-difluoroethane has been determined to be a carcinogen [3]. Both analytes react with chemically-active metals such as sodium, potassium and beryllium or with powdered magnesium, aluminum and zinc.

Hazardous products such as hydrogen chloride, hydrogen fluoride and carbon monoxide may be released when either analyte decomposes. Both analytes will attack some forms of plastics, rubber and coatings.

Carbon disulfide is toxic and flammable; work with it only in a 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 sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.035 L/min for a total sample size of 0.5 to 2 L.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL CS₂ to each vial. Cap each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards.
 - a. Add known amounts of calibration stock solution to CS₂ in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain analyte concentrations in the range 0.3 to 20 mg/mL.
 - b. Analyze with samples and blanks (steps 11 and 12).
 - c. Prepare calibration graph (peak area vs. mg analyte).
9. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interests. Prepare three tubes at each of five levels plus three media blanks.
 - a. Remove and discard back sorbent section of a media blank sampler.
 - b. Inject a known amount (2 to 20 µL) of DE stock solution, or a serial dilution thereof, directly onto front sorbent section with a microliter syringe.
 - c. Cap the tube. Allow to stand overnight.
 - d. Desorb (steps 5 through 7) and analyze with working standards (steps 11 and 12).
 - e. Prepare a graph of DE vs. mg analyte recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1016-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
NOTE: If peaks area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with CS₂, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and the average media blank front (B_f) and back (B_b) sorbent sections.
NOTE: If W_b > W_f/10, report breakthrough and possible sample loss.
14. Calculate concentration, C, of analyte 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:

1,1,1,2-Tetrachloro-2,2-difluoroethane: Method S131 was issued on May 9, 1975 [2], and was validated at 2.08, 4.17 and 8.35 mg/m³ [1]. The generated concentrations were confirmed by gas chromatographic analysis and comparison to bag standards. The average desorption efficiency was 103.6% over the range 4 to 17 mg per sample. The breakthrough volume was 2.7 L when sampling 14,300 mg/m³ at 0.035 L/min.

1,1,2,2-Tetrachloro-1,2-difluoroethane: Method S132 was issued on May 9, 1975 [2], and was validated at 20.05, 4.15 and 8.35 mg/m³ [1]. The generated concentrations were confirmed by gas chromatographic analysis and comparison to bag standards. The average desorption efficiency was 105% over the range 4 to 17 mg per sample. Breakthrough had not occurred after 3 h sampling 6990

mg/m³ at 0.041 L/min. The test was stopped after 3 h.

REFERENCES:

- [1] Documentation for the NIOSH Validation Tests, S131 and S132, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as Stock No. PB 274-248 from NTIS, Springfield, VA 22161.
- [2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 2, S131 and S132, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
- [3] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as Stock #PB83-154609 from NTIS, Springfield, VA 22161.

METHOD REVISED BY:

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