

1,1,2,2-TETRACHLOROETHANE

1019

Cl₂CHCHCl₂ M.W.: 167.85

CAS: 79-34-5

RTECS: KI8575000

METHOD: 1019, Issue 2

EVALUATION: PARTIAL

Issue 1: 15 May 1989

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OSHA : 5 ppm (skin)
NIOSH: 1 ppm; carcinogen; Group I Pesticide
ACGIH: 1 ppm (skin)
 (1 ppm = 6.86 mg/m³ @ NTP)

PROPERTIES: liquid; d 1.5866 g/mL @ 25 °C;
 BP 146.5 °C; MP -44 °C;
 VP 0.8 kPa (6 mm Hg; 0.8% v/v)
 @ 25 °C; nonflammable

SYNONYMS: acetylene tetrachloride; bonoform; 1,1-dichloro-2,2-dichloroethane

SAMPLING		MEASUREMENT	
SAMPLER:	SOLID SORBENT TUBE (petroleum charcoal, 100 mg/50 mg)	TECHNIQUE:	GAS CHROMATOGRAPHY, FID
FLOW RATE:	0.01 to 0.2 L/min	ANALYTE:	1,1,2,2-tetrachloroethane
VOL-MIN:	3 L @ 5 ppm	DESORPTION:	1 mL CS ₂ ; stand 30 min
-MAX:	30 L	INJECTION VOLUME:	5 µL
SHIPMENT:	routine	TEMPERATURE-INJECTOR:	175 °C
SAMPLE STABILITY:	not determined	-DETECTOR:	230 °C
BLANKS:	2 to 10 field blanks per set	-COLUMN:	160 °C
ACCURACY		CARRIER GAS:	N ₂ , 25 mL/min
RANGE STUDIED:	18 to 74 mg/m ³ [1] (10-L samples)	COLUMN:	stainless steel, 3 m x 3-mm OD, packed with 10% FFAP on 80/100 mesh Chromosorb WHP
BIAS:	6.6%	CALIBRATION:	standard solutions of analyte in CS ₂
OVERALL PRECISION ($\hat{S}_{r,T}$):	0.057 [1]	RANGE:	0.1 to 1 mg per sample
ACCURACY:	± 16.7%	ESTIMATED LOD:	0.01 mg per sample [2]
		PRECISION (\hat{S}_r):	0.016 @ 0.16 to 0.64 mg per sample [1]

APPLICABILITY: The working range is 1.5 to 15 ppm (10 to 100 mg/m³) for a 10-L air sample. Capillary columns may be substituted for the packed column, with appropriate changes in instrumental conditions.

INTERFERENCES: None known.

OTHER METHODS: This revises Method S124 [3] and the method which appears in the criteria document [4].

REAGENTS:

1. Carbon disulfide (CS₂), chromatographic quality.*
2. 1,1,2,2-Tetrachloroethane, reagent grade.*
3. DE stock solution, 50 mg/mL. Dilute 0.5 g 1,1,2,2-tetrachloroethane to 10 mL with CS₂.
4. Nitrogen, purified.
5. Hydrogen, prepurified.
6. Air, filtered, compressed.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps, containing two sections of 20/40 mesh activated petroleum-based 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 (SKC 226-38, or equivalent).
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator, and column (see page 1019-1).
4. Vials, 2-mL, PTFE-lined caps.
5. Syringes, 10- μ L, readable to 0.1 μ L.
6. Volumetric flasks, 10-mL.
7. Pipet, TD, 1-mL.

SPECIAL PRECAUTIONS: 1,1,2,2-Tetrachloroethane is a powerful narcotic, liver poison, and suspected carcinogen, and can be absorbed through the skin [4-6]. Carbon disulfide is toxic and a serious fire and explosion hazard (flash point = -30 °C). Work with these substances 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 0.2 L/min for a total sample size of 3 to 30 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 1,1,2,2-tetrachloroethane to CS₂ in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain 1,1,2,2-tetrachloroethane concentrations in the range 0.01 to 1 mg/mL.
 - b. Analyze with samples and blanks (steps 11 and 12).
 - c. Prepare calibration graph (peak area vs. mg 1,1,2,2-tetrachloroethane).

9. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interest. Prepare three tubes at each of five concentrations 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 1,1,2,2-tetrachloroethane 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 1019-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
NOTE: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with CS_2 , reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of 1,1,2,2-tetrachloroethane found in the sample front (W_f) and back (W_b) sorbent sections and in 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 1,1,2,2-tetrachloroethane 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 S124 was issued on May 9, 1975 [3], and validated with generated atmospheres which were calibrated by gas chromatography [1]. Average recovery was 106% at 5 ppm. Breakthrough did not occur after sampling 4 h at 0.185 L/min from an atmosphere containing 101 mg/m^3 in dry air. Desorption efficiency for SKC Lot 104 petroleum-based charcoal was 0.83, 0.87, and 0.88 at 0.16, 0.32, and 0.64 mg 1,1,2,2-tetrachloroethane per sample, respectively. Lower recoveries were observed for coconut shell charcoal (SKC Lot 105). In subsequent work, 1,1,2,2-tetrachloroethane was observed to degrade rapidly into trichloroethylene during storage on Pittsburgh activated carbon; 19% converted during one day and 63% converted during eight days at ambient conditions [7]. Therefore, the analyte is sensitive to the sorbent type; only the recommended sorbent should be used. Breakthrough at high relative humidity was not tested, nor was sample stability.

REFERENCES:

- [1] Documentation of the NIOSH Validation Tests, S124, 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] UBTL Report for Sequence 1977 (NIOSH, unpublished, September 7, 1979).

- [3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 2, S124, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
- [4] Criteria for a Recommended Standard...Occupational Exposure to 1,1,2,2-Tetrachloroethane, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-121 (1976), available as PB 273-802 from NTIS, Springfield, VA 22161.
- [5] NIOSH Current Intelligence Bulletin 27, Chloroethanes: Review of Toxicity, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-181 (1978).
- [6] 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.
- [7] Arnold, J. Internal memo (NIOSH, unpublished, May 8, 1984).

METHOD REVISED BY:

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