

1,2-DICHLOROTETRAFLUOROETHANE
See DICHLORODIFLUOROMETHANE (METHOD 1018) for procedure

CCIF₂CCIF₂

MW: 170.92

CAS: 76-14-2

RTECS: KI1101000

METHOD: 1018, Issue 2

EVALUATION: FULL

Issue 1: 15 August 1987

Issue 2: 15 August 1994

OSHA : 1000 ppm
NIOSH: 1000 ppm
ACGIH: 1000 ppm
 (1 ppm = 6.99 mg/m³ @ NTP)

PROPERTIES: gas; BP 3.8 °C; MP -94 °C

SYNONYMS: cryofluorane, Refrigerant 114

SAMPLING	MEASUREMENT
<p>SAMPLER: SOLID SORBENT TUBES (two coconut shell charcoal tubes in series, 400/200 mg and 100/50 mg)</p> <p>FLOW RATE: 0.01 to 0.05 L/min</p> <p>VOL-MIN: 1 L @ 1000 ppm -MAX: 4 L</p> <p>SHIPMENT: refrigerated</p> <p>SAMPLE STABILITY: at least 7 days @ -10 °C</p> <p>BLANKS: 2 to 10 field blanks per set</p>	<p>TECHNIQUE: GAS CHROMATOGRAPHY, FID</p> <p>ANALYTE: 1,2-dichlorotetrafluoroethane</p> <p>DESORPTION: 20 mL methylene chloride</p> <p>INJECTION VOLUME: 1 µL</p> <p>TEMPERATURE-INJECTOR: 200 °C -DETECTOR: 260 °C -COLUMN: 35 °C for 3 min, 15 °C/min to 75 °C, hold 6 min</p> <p>CARRIER GAS: He, 1.5 mL/min</p> <p>COLUMN: DB-1 fused silica capillary, 30 m x 0.32-mm ID, 1-µm film thickness or equivalent</p> <p>CALIBRATION: standard solutions of analyte in methylene chloride</p> <p>RANGE: 5 to 40 mg per sample [1]</p> <p>ESTIMATED LOD: 0.03 mg per sample [1]</p> <p>PRECISION (\hat{S}_p): 0.038 @ 10-40 mg per sample [1]</p>
ACCURACY	
<p>RANGE STUDIED: 1800 to 6970 mg/m³ [3]</p> <p>BIAS: 0%</p> <p>OVERALL PRECISION (\hat{S}_{RT}): 0.074 [3]</p> <p>ACCURACY: ± 14.5%</p>	

APPLICABILITY: The working range is 700 to 5700 ppm 1,2-dichlorotetrafluoroethane (5000 to 40,000 mg/m³) for a 1-L air sample. This method was first evaluated for dichlorodifluoromethane and 1,2-dichlorotetrafluoroethane with packed column gas chromatography [1].

INTERFERENCES: None identified.

OTHER METHODS: This combines and revises Methods S111 and S108 [2].

REAGENTS:

1. Chlorodifluoromethane, 99%
2. Dichlorodifluoromethane, 99%
3. 1,2-Dichlorotetrafluoroethane, 99%
4. Methylene chloride^{*}, distilled in glass.
5. Nitrogen, purified.
6. Hydrogen, prepurified
7. Air, filtered, compressed.
8. Helium, purified

^{*} See Special Precautions

EQUIPMENT:

1. Sampler: two glass tubes (9 cm long, 8-mm OD, 6-mm ID, followed by 7 cm long, 6-mm OD, 4-mm ID) connected in series with a short piece of tubing, flame-sealed ends with plastic caps, containing two sections of activated (600 °C) coconut shell charcoal (1st 400 mg/200 mg; 2nd 100 mg/50 mg), front and back sections 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 25 mm/Hg. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.05 mL/min, with flexible connecting tubing.
3. Gas chromatograph with a FID detector, recorder, integrator and column (page 1018-1).
4. Bottles, 22-mL, PTFE-lined septum screw caps.
5. Syringes, gas-tight, 10-mL and other sizes as needed.
6. Pipet, TD, 20-mL, with pipet bulbs.
7. DE apparatus. Glass or plastic T equipped with septum in one arm to allow introduction of analyte to a flowing stream of nitrogen.

SPECIAL PRECAUTIONS: Methylene chloride is an irritant, can be absorbed through the skin, and is a suspect carcinogen [4]. Prepare samples 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 0.5 L/min for a total sample size of 1 to 4 L.
4. Separate and cap the tubes. Pack securely for shipment in an insulated container with bagged refrigerant.

SAMPLE PREPARATION:

NOTE: Refrigerate samples at -10 °C if not analyzed immediately.

5. Pipet 20.0 mL methylene chloride into a series of bottles.
6. Place both sections of the front sampler tube into a bottle containing solvent, discarding the glass wool and foam plugs. Immediately cap and gently shake the bottle. Analyze within 6 hrs.
7. Perform step 6 for the back sampler tube.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards.
 - a. Pipet 20.0 mL methylene chloride into each of a series of bottles. Cap the bottles.
 - b. Using a gas-tight syringe, add known amounts of analyte, e.g., 0.01 to 6 mL (0.034 to 21.2 mg @ NTP) chlorodifluoromethane, or 0.01 to 6 mL (0.094 to 29.6 mg @ NTP) dichlorodifluoromethane, or 0.01 to 6 mL (0.0699 to 41.9 mg @ NTP) 1,2-dichlorotetrafluoroethane by bubbling the gas slowly through the methylene chloride. Gently shake the bottles.
 - c. Analyze with samples and blanks (steps 11 and 12).
 - d. Prepare calibration graph (area vs. mg analyte).
9. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interest (step 8). Prepare three tubes at each of five levels plus three media blanks.
 - a. Using a gas-tight syringe, inject a known amount of analyte (0.01 to 6 mL) through the septum of the DE apparatus unto a stream of nitrogen (ca. 20 mL/min) which carries the analyte into a large (400/200 mg) sorbent tube. Allow the nitrogen to flow an additional 30.
 - b. Cap the tube. Allow to stand overnight.
 - c. Desorb (steps 5 through 7) and analyze with working standards (steps 11 and 12)
 - d. 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 1018-1. 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 methylene chloride, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

NOTE: The order of elution is chlorodifluoromethane, dichlorodifluoromethane, 1,2-tetrafluoroethane. If analyzing for two or more of the compounds, a temperature rate of 5 °C/min is required.

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 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 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:

Validation this method for dichlorodifluoromethane and 1,2-dichlorotetrafluoroethane was done using packed column gas chromatographic techniques. The column was stainless steel 1.2 m x 6-mm OD, packed with 80/100 mesh Chromosorb 102. Chlorodifluoromethane was evaluated using the capillary chromatographic conditions listed on p.1018-1. The use of capillary gas chromatographic analysis was

determined to be appropriate for all three compounds.

Dichlorodifluoromethane: Method S111 was issued September 30, 1976 [2], and validated using test atmospheres generated in air and monitored with a calibrated total hydrocarbon analyzer [1,5]. Average recovery for 18 samples was 98.2%. In breakthrough tests at 12 and 94% relative humidity (RH), the capacity of the sampler was 61 and 44 mg of dichlorodifluoromethane, respectively, when sampling at ca. 0.045 L/min from atmospheres containing ca. 10,000 mg/m³. Desorption efficiency averaged 0.97 in the range 7.4 to 30 mg per sample.

Dichlorotetrafluoroethane: Method S108 was issued October 29, 1976 [2], and validated using test atmospheres generated in air and monitored with a calibrated total hydrocarbon analyzer [1,4]. The average recovery for 18 samples was 99.8%. Breakthrough (effluent concentration = 5% of test concentration) occurred after 158 min when sampling 14,600 mg/m³ at 90% RH at 0.046 L/min. Desorption efficiency averaged 0.99 in the range 10.7 to 42.8 mg per sample.

The precision and accuracy of the method for chlorodifluoromethane were determined using test gas bag atmospheres generated and monitored with a halide meter. Average recovery for 18 samples over the range of 1780 to 6970 mg/m³ was 100 %. In breakthrough tests at 80% relative humidity, the sampler retained 15.4 mg of chlorodifluoromethane when sampling at 0.025 L/min from atmospheres containing 7000 mg/m³. The desorption efficiency of chlorodifluoromethane from activated charcoal averaged 0.96 in the range of 0.53 to 10.4 mg per sample.

REFERENCES:

- [1] Backup Data Reports S111 (Dichlorodifluoromethane) and S108 (Dichlorotetrafluoroethane), 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, S111 and S108, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
- [3] Seymour, M.J., M.F. Lucas. Evaluation of Sampling and Analytical Methods for the Determination of Chlorodifluoromethane in Air, *Am. Ind. Hyg. Assoc. J.*, (accepted for publication July 1992)
- [4] NIOSH Current Intelligence Bulletin 46, U.S. Department of Health and Human Services, Publ. (NIOSH) 86-114 (1986).
- [5] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

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