$Cl_2C:CClCCl:CCl_2$ MW: 260.74 CAS: 87-68-3 RTECS: EJ0700000

METHOD: 2543, Issue 2 **EVALUATION: FULL** **Issue 1: 28 June 1979**
Issue 2: 15 August 1994

OSHA : no PEL
NIOSH: 0.02 ppm (skin); carcinogen
ACGIH: 0.02 ppm (skin); carcinogen
(1 ppm = 10.67 mg/m^3 @ NTP)

PROPERTIES: clear, colorless liquid with a mild odor; d = 1.675 (15.5 °C); VP 2.9 kPa (22 mm Hg) @ 100 C°; B.P. 220 °C

SYNONYMS: 1,3-hexachlorobutadiene; HCBD; perchlorobutadiene; DOLEN-PUR

SAMPLING

SAMPLER: SOLID SORBENT TUBE (XAD-2; 100 mg/50 mg)

FLOW RATE: 0.05 to 0.2 L/min

VOL-MIN: 1 L
-MAX: 100 L @ 0.2 L/min

SHIPMENT: routine, but store in dark

SAMPLE STABILITY: 7 days @ 25 °C; 28 days @ 0 °C in dark

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.01 to 2 mg/m^3 [1] (100-L samples)

BIAS: + 0.5%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.09 [1]

ACCURACY: ± 18.1%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY/ECD

ANALYTE: hexachlorobutadiene (HCBD)

EXTRACTION: 2 mL hexane; ultrasonic bath 1 h

INJECTION VOLUME: 1 µL

TEMPERATURE-INJECTOR: 150 °C
-DETECTOR: 250 °C
-COLUMN: 135 °C

COLUMN: Nukol or Stabilwax-DA

CARRIER GAS: Ar, 30 mL/min

DETECTOR: ECD

PURGE GAS: He or N_2, 80 mL/min

CALIBRATION: standard solutions of hexachlorobutadiene in hexane

RANGE: 0.06 µg to 6 µg per sample [1]

ESTIMATED LOD: 0.02 µg per sample [1]

PRECISION ($\hat{S}_r$): 0.03 [1]

APPLICABILITY: The working range is 0.01 to 2.0 mg/m^3 for a 100-L sample [1]. An alternate column, DB-210, may be used with appropriate changes in instrumental conditions.

INTERFERENCES: Conditions of high humidity (>90%) may reduce capacity. Any compound with overlapping or similar retention times, or any sample containing chloroform may interfere[2].

OTHER METHODS: This revises method P&CAM 307 [1].

REAGENTS:

1. Hexane (spectrographic grade).
2. Hexachlorobutadiene, 98+ purity.
3. Argon, high purity.
4. Methane, high purity.
5. Hexachlorobutadiene calibration stock solution (16.7 mg/mL): Dilute 1 mL (1.67 g) hexachlorobutadiene to 100 mL with hexane.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 8-mm OD, 6-mm ID, with plastic caps, containing two sections of 20/50 mesh XAD-2 (front = 150 mg; back = 75 mg) separated and held in place by plugs of silylated glass wool. Pressure drop across the tube must be <3.4 kPa (2.5 cm Hg) at 1 L/min airflow.
2. Personal sampling pump, 0.05 to 0.2 L/min, with flexible tubing.
3. Gas chromatograph with 63 Ni ECD.
4. Capillary column (Nukol, or equivalent)
5. Vials, glass, 4 mL, with PTFE-lined caps.
6. Microliter syringes (10-µL, 25-µL, etc.)
7. Pipettes (1-mL, 2-mL, etc.)
8. Ultrasonic bath.

SPECIAL PRECAUTIONS: Hexachlorobutadiene is a toxic material. Exercise all appropriate safety precautions.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break open the ends of sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurate flow rate between 0.05 and 0.2 L/min for a total sample size of 1 to 100 L.
4. Cap the samplers with plastic caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sections of the sorbent tube in separate 4 mL vials. Discard glass wool plugs.
6. Add 2.0 mL hexane to the vials containing the front sections and 1.0 mL hexane to vials containing the backup sections. Desorb each vial for 1 h in an ultrasonic bath.
7. Transfer 1 mL aliquots to 13-mm autosampler vials for analysis.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range of 0.02 µg to 6 µg per sample.
   a. Add appropriate aliquots of calibration stock solution to hexane in 10-mL volumetric flasks and dilute to mark.
   b. Analyze working standards together with samples and blanks (steps 11 and 12).
   c. Prepare a calibration graph of peak area vs. µg of hexachlorobutadiene per sample.
9. Determine desorption efficiency (DE) at least once for each lot of XAD-2 used for sampling in the concentration range of interest. Prepare three tubes at each of five levels, plus three media blanks.
   a. Remove and discard the back sorbent section of a sampler.
   b. Inject a known amount (e.g., 1 to 20 µL) of calibration stock solution, or a dilution thereof in hexane, directly onto the front 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 graphs of DE vs. µg hexachlorobutadiene recovered.

10. Analyze three quality control blind spikes and three analyst spikes with each subsequent set from the same lot to ensure that the calibration graph and DE graph are in control

MEASUREMENT:

11. Set gas chromatograph to conditions given on p. 2543-1. Inject a 1 µL sample aliquot.
12. Measure and record peak area.
    NOTE: If peak area is above linear range of the working standards, dilute, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE) of HCBD 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 the concentration of HCBD in the actual air volume, V (L), at the sampling site:

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

EVALUATION OF METHOD:

This method was validated over the range 0.01 to 2 mg/m^3 at 25 °C to 28 °C at a relative humidity of 90% or greater using a 3-L sample [1]. Generation samples at four concentration levels gave an average mean recovery of 100.5% with an overall precision, $\hat{S}_{rT}$, of 0.09 [3]. Desorption efficiency (DE) of HCBD from XAD-2 tubes was 100% at a loading of 0.0167 µg per sample [3]. Samples showed good storage stability for 28 days if stored @ 0 °C after the seventh day [3].

REFERENCES:

[1] Hexachlorobutadiene, NIOSH Method P&CAM 307, 1979.
[2] Imagawa, T. and Miyazaki, A., Formation of hexachlorobutadiene and related compounds from chloroform in a flame ionization detector, Bunski Kagaku, 36(2), 118-120, 1987.
[3] Backup Data Report for Hexachlorobutadiene, NIOSH Contract 210-78-0012.

METHOD REVISED BY:

S.M. Pendergrass, NIOSH/DPSE/MRSB; P&CAM 307 originally validated under NIOSH Contract 210-78-0012.