ETHYLENE DIBROMIDE

BrH_2CCH_2Br MW: 187.88 CAS: 106-93-4 RTECS: KH9275000

METHOD: 1008, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 February 1984**
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OSHA : 20 ppm; C 30 ppm; PEAK 50 ppm/5 min
NIOSH: 0.045 ppm; C 0.13 ppm/15 min; Group I Pesticide
ACGIH: carcinogen (skin)
(1 ppm = 7.68 mg/m^3 @ NTP)

PROPERTIES: liquid; d 2.169 g/mL @ 25 °C;
BP 131 °C; MP 10 °C;
VP 1.5 kPa (11 mm Hg; 1.4% v/v) @ 25 °C

SYNONYMS: EDB, 1,2-dibromoethane

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.02 to 0.2 L/min

VOL-MIN: 0.1 L @ 0.1 ppm
-MAX: 25 L

SHIPMENT: insulated container, dry ice

SAMPLE STABILITY: 2 weeks at -25 °C or below [1,2].

FIELD BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: see EVALUATION OF METHOD [1]

BIAS: not significant

OVERALL PRECISION ($\hat{S}_{rT}$): not determined

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, ^{63}Ni ECD

ANALYTE: ethylene dibromide

DESORPTION: 10 mL 99:1 benzene:methanol (v/v); stand 1 h

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 175 °C
-DETECTOR: 315 °C
-COLUMN: 50 °C

CARRIER GAS: N_2, 35 mL/min

COLUMN: 1.8 m x 4-mm ID, borosilicate glass packed with 3% OV-210 on 80/100 Gas Chrom Q

CALIBRATION: ethylene dibromide in 99:1 benzene:methanol (v/v) with internal standard

RANGE: 0.1 to 0.5 µg per sample [1]

ESTIMATED LOD: 0.01 µg per sample [1,2]

PRECISION ($\hat{S}_r$): 0.044 [3]

APPLICABILITY: The working range is 0.0003 to 1 ppm (0.002 to 8 mg/m^3) for a 25-L air sample. The range of an ECD most useful for quantitation depends on the type of detector and chromatograph used. For reliable quantitation, the ECD must be optimized for the smallest possible amount of analyte.

INTERFERENCES: None identified. The chromatographic column or separation conditions may be changed to circumvent interference problems. An alternate chromatographic column packing is GP 20% SP-2100/0.1% Carbowax 1500 on 100/120 Chromosorb WHP [2].

OTHER METHODS: This revises P&CAM 260 [1] and Method 1008 (dated 2/15/84). Method S104 [4], which has not been revised, can also be used but uses the less sensitive flame ionization detector.

REAGENTS:

1. Benzene, pesticide quality.*
2. Methanol, pesticide quality.*
3. Ethylene dibromide, high purity (density=2.169 g/mL @ 25 °C).*
4. An appropriate internal standard such as 1,1,2,2-tetrachloroethane (density = 1.587 g/mL @ 25 °C) or 1,2-dibromopropane (density = 1.923 g/mL @ 25 °C).
5. 99:1 benzene:methanol (v/v).
6. Eluent*: 99:1 benzene:methanol (v/v) containing 0.1 µg internal standard/mL.
7. Calibration stock solution, 10 ng/µL. Dissolve 50 mg ethylene dibromide in benzene to make 25 mL solution. Dilute 50 µL of this solution to 10 mL with benzene. Stable 3 weeks if refrigerated.

* 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 (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, 0.02 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, ^{63}Ni electron-capture detector, integrator and column (page 1008-1).
4. Syringe*, 10-µL, readable to 0.1 µL, and 50-µL, readable to 1 µL.
5. Volumetric flasks, 10-mL, 25-mL, and 500 mL.
6. Pipet, 10-mL with pipet bulb.

SPECIAL PRECAUTIONS: Benzene and ethylene dibromide [1] are carcinogens and can be absorbed through the skin. Benzene and methanol are flammable. All work with these should be performed in a hood, while wearing gloves.

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 0.02 and 0.2 L/min for a total sample size of 0.1 to 25 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely in an insulated container with dry ice for shipment.

SAMPLE PREPARATION:

NOTE: Store the samplers at -25 °C or below until preparation begins.

5. Place the front and back sorbent sections of the sampler tube in separate 10-mL volumetric flasks. Discard the glass wool and foam plugs.
6. Add 10.0 mL eluent to each flask.
7. Allow to stand 60 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.01 to 0.5 µg ethylene dibromide per sample.
   a. Add known amounts of calibration stock solution to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. µg ethylene dibromide).

9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard the back sorbent section of a media blank sampler.
   b. Inject a known amount of calibration stock solution 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 together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. µg ethylene dibromide recovered.
10. Analyze three quality control blind spikes and five 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 1008-1. Inject sample aliquot manually using solvent flush technique or with autosampler. Retention times under these conditions are: ethylene dibromide, 2.2 min; 1,2-dibromo propane, 2.9 min; and 1,1,2,2-tetrachloroethane, 4.1 min.
    NOTE: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid, reanalyze, and apply the appropriate dilution factor in the calculations.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE) of ethylene chlorohydrin 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 ethylene dibromide in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

P&CAM 260 [1] was evaluated with coconut shell charcoal (SKC Lot 106 and MSA Lot 6) fortified with solutions of ethylene dibromide. Average recoveries ranged from 0.85 to 0.93; overall precision (s_r) was 0.044 (31 samples, pooled) [3]. Samples based on 0.2- and 2-µg quantities of ethylene dibromide were stable on charcoal during storage below -20 °C for 13 and 12 days, respectively. Gasoline samples which contained ethylene dibromide were placed into U-tubes; ethylene dibromide vapor was collected with charcoal tubes (flow rate of air was 0.6 L/min). Recoveries were 0.91 and 0.93 for 0.2- and 2.4-µg quantities of ethylene dibromide, respectively. No significant breakthrough from front sections of charcoal occurred with 200-µg quantities of ethylene dibromide in the vapor phase (flow rate of air was 0.6 L/min); quantities of ethylene dibromide (if any) on the back sections of charcoal were less than 0.04 µg (<0.02%).

Breakthrough was determined for SKC Lot 105 charcoal [5]. At an ethylene dibromide concentration of 446 mg/m^3 in dry air, the effluent concentration was 2% of the test concentration after 4 h of sampling (48 L air). Thus, the capacity of the charcoal was at least 21 mg ethylene dibromide under these conditions. In the analysis of a large set of field samples over a period of seven days, DE was found to vary day-to-day in the range of 0.76 to 0.87 at 0.1 µg ethylene dibromide per sample [6]. Overall precision ($\hat{S}_{rT}$) and bias were not determined.

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2nd ed., V. 4, P&CAM 260, U.S. Dept. Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[2] User check, UBTL, Inc., NIOSH Seq. #4585-R (unpublished, May 21, 1985)
[3] Tucker, S. P., J. J. Sweeney and A. W. Teass. "A Charcoal Tube Method for Determining 1,2-Dibromoethane in Air," NIOSH (unpublished, 1979).
[4] NIOSH Manual of Analytical Methods, 2nd. ed., V. 2, S104, U.S. Dept. Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[5] Documentation of the NIOSH Validation Tests, S104, U.S. Dept. Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[6] Report of NIOSH Seq. #5332-A (unpublished, May 5, 1986).

METHOD REVISED BY:

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