DIFLUORODIBROMOMETHANE 1012

CBr_2F_2 MW: 209.83 CAS: 75-61-6 RTECS: PA7525000

METHOD: 1012, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA: 100 ppm
NIOSH: 100 ppm
ACGIH: 100 ppm
(1 ppm = 8.58 mg/m^3 @ NTP)

PROPERTIES: liquid; d 2.35 g/mL @ 0 °C; BP 24.5 °C; FP −141 °C; VP 83 kPa (620 mm Hg; 82% v/v) @ 20 °C; non-flammable

SYNONYMS: dibromodifluoromethane; Freon 12B2

SAMPLING

SAMPLER: SOLID SORBENT TUBES (2 tubes in tandem, each with 150 mg coconut shell charcoal)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 2.5 L
-MAX: 10 L

SHIPMENT: routine

SAMPLE STABILITY: not determined

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 470 to 1875 mg/m^3 [1] (10-L samples)

BIAS: 2.5%

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

ACCURACY: ±18.8%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: difluorodibromomethane

DESORPTION: 1.0 mL 2-propanol; stand overnight

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 200 °C
-DETECTOR: 300 °C
-COLUMN: 60 °C

CARRIER GAS: N_2, 30 mL/min

COLUMN: 3 m × 6 mm OD stainless steel, packed with 10% FFAP on 100/120 Chromosorb WHP or equivalent

CALIBRATION: difluorodibromomethane in 2-propanol

RANGE: 2 to 20 mg per sample

ESTIMATED LOD: 0.4 mg per sample

PRECISION ($\bar{S}_r$): 0.067 @ 4 to 19 mg per sample [1]

APPLICABILITY: The working range is 200 to 2000 mg/m^3 (23 to 230 ppm) for a 10-L air sample. Difluorodibromomethane is used in the synthesis of dyes, pharmaceuticals, and quaternary ammonium compounds, and as a fire extinguishing agent.

INTERFERENCES: Carbon disulfide has about the same GC retention volume as difluorodibromomethane [1].

OTHER METHODS: This is Method S107 in a revised format [2].

REAGENTS:

1. 2-Propanol, chromatographic grade.
2. Difluorodibromomethane.*
3. Nitrogen, purified.
4. Hydrogen, prepurified.
5. Air, filtered, compressed.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: two glass tubes in series, each with both ends flame sealed, 7 cm long, 6-mm OD, 4-mm ID, each containing 150 mg of 20/40 mesh activated (600 °C) coconut shell charcoal; four plastic caps for sealing after use. A silylated glass wool plug precedes the charcoal beds and a 3-mm urethane foam plug follows the charcoal beds.
   NOTE: A pair of two-section (100 mg/50 mg) tubes may be used.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator, and column (page 1012-1).
4. Vials, 2-mL, glass, with PTFE-lined septa and crimp seals.
5. Syringe, 10-µL, readable to 0.1 µL.
6. Volumetric flask, 10-mL.
7. Pipets, 1.0-mL.
8. Cold room or cold box for preparing standards at 0 °C or lower.
9. Syringes, gas-tight, 10- and 100-µL.

SPECIAL PRECAUTIONS: Difluorodibromomethane does not have adequate warning properties [3].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the front and back sorbent tubes immediately before sampling. Connect the tubes with a short piece of plastic tubing and 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 2.5 to 10 L.
4. Separate the two sorbent tubes. Cap the ends of each tube with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the charcoal from the front and back sorbent tubes in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL 2-propanol to each vial. Attach crimp cap to each vial.
7. Allow to stand overnight with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.4 to 20 mg dibromodifluoromethane per sample.
   NOTE: Prepare the working standards in a cold room or cold box.
   a. Add known amounts of cold (<0 °C) difluorodibromomethane to 2-propanol in 10-mL volumetric flasks and stopper.

b. Allow standards to come to room temperature, and dilute to the mark.
c. Analyze together with samples and blanks (steps 11 and 12).
d. Prepare calibration graph (peak area vs. mg difluorodibromomethane).

9. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the calibration range (step 8). 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 of cold (<0 °C) difluorodibromomethane directly onto front sorbent section with a microliter syringe.
      NOTE 1: Perform this step in a cold room or cold box.
      NOTE 2: For small quantities (0.4 to 4 mg), use 2 to 20 µL of a 200 mg/mL standard solution of difluorodibromomethane in pentane.
   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. mg dibromodifluoromethane 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 1012-1. 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 2-propanol, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of difluorodibromomethane 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 difluorodibromomethane in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \times 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S107 was issued on April 11, 1975, and evaluated at 470, 932, and 1876 mg/m^3 [1]. Spiking of samples and standards preparation were done in a cold room (0 °C). Samples of difluorodibromomethane in air were generated and collected on activated coconut charcoal (SKC Lot 105). The air concentration was independently determined by gas chromatographic analysis using a 5-mL sampling loop and comparison to gas bag samples. The mean desorption efficiency over the range 4.4 to 18.5 mg difluorodibromomethane per sampler was 99.5%. The breakthrough volume for 100-mg charcoal beds was 15.6 L at 1875 mg/m^3, low relative humidity, and a flow rate of 0.2 L/min. No storage stability study was done.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S107, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as GPO Stock #017-033-00231-2 from Superintendent of Documents, Washington, DC 20402.
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 2, S107, 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 GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.

METHOD REVISED BY:

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