

METHYL BROMIDE

CH₃Br

MW: 94.94

CAS: 74-83-9

RTECS: PA4900000

METHOD: 2520, Issue 2

EVALUATION:

Issue 1: 15 May 1985

Issue 2: 15 August 1993

OSHA : 5 ppm (skin)
NIOSH: lowest feasible; suspect carcinogen;
Group I Pesticide
ACGIH: 5 ppm (skin)
(1 ppm = 3.88 mg/m³ @ NTP)

PROPERTIES: gas; BP 3.6 °C; MP -94 °C; vapor density
(air = 1) 3.3; explosive range 13.5 to 14.5%
v/v in air

SYNONYMS: bromomethane.

SAMPLING		MEASUREMENT	
SAMPLER: SOLID SORBENT TUBES (two petroleum charcoal tubes, 400 mg and 200 mg)		TECHNIQUE: GAS CHROMATOGRAPHY, FID	
FLOW RATE: 0.01 to 1 L/min		ANALYTE: methyl bromide	
VOL-MIN: 2.5 L @ 20 ppm -MAX: 11 L		DESORPTION: 2 MI CS ₂ ; stand 60 min	
SHIPMENT: routine		INJECTION VOLUME: 5 µL	
SAMPLE STABILITY: >7 days @ 20 °C		TEMPERATURE-INJECTION: 155 °C -DETECTOR: 200 °C -COLUMN: 65 °C	
BLANKS: 2 to 10 field blanks per set		CARRIER GAS: N ₂ , 30 MI/min	
		COLUMN: 6 m x 3 mm stainless steel packed with 10% FFAP on 100/200 mesh Chromosorb WHP	
		CALIBRATION: methyl bromide in CS ₂ ; internal standard	
		RANGE: 0.2 to 2 mg per sample	
		ESTIMATED LOD: 0.01 mg per sample [1]	
		PRECISION (\hat{S}_r): 0.053 @ 0.4 to 1.6 mg per sample [1]	
ACCURACY			
RANGE STUDIED: 35 to 150 mg/m ³ [1] (11-L samples)			
BIAS: not significant @ 71 to 160 mg/m ³ ; -13% at 30 mg/m ³ [1]			
OVERALL PRECISION (\hat{S}_{rt}): 0.013 [1]			
ACCURACY:			

APPLICABILITY: The working range is 40 to 400 mg/m³ (10 to 100 ppm) for a 5-L air sample. NIOSH has sampled for methyl bromide at grain elevators [2,3].

INTERFERENCES: None known. A 2 m x 3 mm ID glass column packed with 1% SP-1000 also has been used [2].

OTHER METHODS: This revises Method S372 [4].

REAGENTS:

1. Eluent: carbon disulfide,* chromatographic quality, containing 0.1% v/v n-decane, n-pentane or other suitable internal standard.
2. Methyl bromide, 99.5%.*
3. Calibration stock solution, ca. 200 mg/ML. Bubble methyl bromide gas slowly into eluent into a fitted glass bubbler. Determine the methyl bromide concentration by comparison with gas standards.
4. Nitrogen, purified.
5. Hydrogen, prepurified.
6. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: two glass tubes connected in series with a short piece of plastic tubing; each tube 10 cm long, 8-mm OD, 6-mm ID, containing 20/40 mesh activated (600 °C) petroleum charcoal (front = 400 mg; back = 200 mg). A plug of silylated glass wool is placed at each end of each tube. Pressure drop across sampler <3.4 kPa (2.5 cm Hg) at 1 L/min airflow. Four plastic caps are used to seal the tubes after sampling.
2. Personal sampling pump, 0.01 to 1 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 2520-1).
4. Vials, 5-ML, glass, with PTFE-lined caps.
5. Syringe, gas-tight, 10-ML.
6. Microliter syringes, 10- μ L.
7. Pipets, 2-ML, graduated in 0.1-ML increments.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an extreme fire and explosion hazard (flash point = -30 °C).

Methyl bromide has poor warning properties and can produce fatal pulmonary edema at high concentrations; chronic exposure can cause CNS depression and kidney injury [5,6]. Contact between methyl bromide and aluminum or strong oxidizers may cause fire or explosion.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler tubes immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 1 L/min for a total sample size of 2.5 to 11 L.
4. Separate the front and back tubes immediately after sampling. Cap the tubes. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections in separate vials. Discard the glass wool and foam plugs.
6. Add 2.0 ML eluent to each vial. Immediately cap each vial.
7. Allow to stand 60 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.01 to 2 mg methyl bromide per sample.
 - a. Add known amounts of calibration stock solution, or a serial dilution thereof, to known volumes of eluent in vials. Immediately cap each vial.
 - 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. mg methyl bromide).
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 levels plus three media blanks.
 - a. Inject a known amount (1 to 10 μL) of calibration stock solution, or a serial dilution thereof, directly onto front sorbent section of a media blank sampler with a microliter syringe.
 - b. Cap the tube. Allow to stand overnight.
 - c. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
 - d. Prepare a graph of DE vs. mg methyl bromide 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 2520-1. 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 eluent, reanalyze, and apply the appropriate dilution factor in 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, mg (corrected for DE) of methyl bromide found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blanks for the 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 methyl bromide 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 S372 was issued on June 6, 1975 [4], and validated at 35, 75, and 150 mg/m^3 [1]. Test atmospheres were generated by delivering methyl bromide gas from a cylinder via an orifice and needle valve to a dry airstream flowing at a rate of 0.1 m^3/min . The concentration was confirmed with a total hydrocarbon analyzer calibrated with known amounts of methyl bromide gas. Six samples at each level were collected (11-L sample volume) on SKC Lot 104 petroleum-based charcoal and stored seven days prior to analysis. Recoveries were 87, 96, and 107% at 30, 75, and 150 mg/m^3 , respectively, for 11-L air samples. The average recovery was 96.5% with a $s_r = 10.3\%$. Desorption efficiency was 0.72, 0.81, and 0.82 at 0.4, 0.8, and 1.6 mg methyl bromide per sample, respectively.

A test determined that 10 to 20% of the methyl bromide collected on the front section migrated to the back section after storage for seven days prior to analysis. For this reason, separate tubes for the front and back sections are specified.

Breakthrough (5%) occurred after sampling 18 L of an atmosphere containing 161 mg/m^3 methyl bromide at 0.19 L/min; the front sorbent section held 2.9 mg methyl bromide.

REFERENCES:

- [1] Documentation of the NIOSH Validation Tests, S372, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as PB 274-248 from NTIS, Springfield, VA 22161.
- [2] UBTL, Inc., NIOSH Sequence #3709-N (NIOSH, unpublished, November 19, 1982).
- [3] Arthur D. Little, Inc., NIOSH Sequence #4264 (NIOSH, unpublished, February 29, 1984).
- [4] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 3, S372, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
- [5] 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 #017-033-0037-8 from Superintendent of Documents, Washington, DC 20402.
- [6] The Merck Index, 9th ed., Merck & Co., Inc., Rahway, NJ (1976).

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