

ETHYL BROMIDE

1011

CH₃CH₂Br

MW: 108.97

CAS: 74-96-4

RTECS: KH6475000

METHOD: 1011, Issue 2

EVALUATION: PARTIAL

Issue 1: 15 May 1985

Issue 2: 15 August 1994

OSHA : 200 ppm
 NIOSH: no REL
 ACGIH: 5 ppm (skin); suspected carcinogen
 (1 ppm = 4.46 mg/m³ @ NTP)

PROPERTIES: liquid; d 1.461 g/mL @ 20 °C;
 BP 38 °C; MP -119 °C;
 VP 51 kPa (380 mm Hg; 50% v/v)
 @ 20 °C; explosive range 6.8 to
 11% v/v in air

SYNONYMS: bromoethane

SAMPLING		MEASUREMENT	
SAMPLER:	SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)	TECHNIQUE:	GAS CHROMATOGRAPHY, FID
FLOW RATE:	0.01 to 0.2 L/min	ANALYTE:	ethyl bromide
VOL-MIN:	0.5 L @ 200 ppm	DESORPTION:	1 mL 2-propanol; overnight
-MAX:	4 L	INJECTION VOLUME:	5 µL
SAMPLE STABILITY:	not known	TEMPERATURE-INJECTION:	200 °C
FIELD BLANKS:	2 to 10 field blanks per set	-DETECTOR:	300 °C
		-COLUMN:	60 °C
		CARRIER GAS:	N ₂ or He, 30 mL/min
		COLUMN:	3 m x 3-mm OD stainless steel; 10% FFAP; on 80/100 mesh Chromosorb W-AW
		CALIBRATION:	standard solutions of ethyl bromide in 2-propanol
		RANGE:	0.4 to 10 mg per sample
		ESTIMATED LOD:	0.02 mg per sample [2]
		PRECISION (\hat{S}_r):	0.025 @ 1.8 to 8.5 mg per sample [1]
ACCURACY			
RANGE STUDIED:	550 to 2200 mg/m ³ [1] (4-L samples)		
BIAS:	- 6.4%		
OVERALL PRECISION (\hat{S}_{rT}):	0.054 [1]		
ACCURACY:	± 15.0%		

APPLICABILITY: The working range is 22 to 560 ppm (100 to 2500 mg/m³) for a 4-L air sample. Ethyl bromide is used in organic synthesis as a solvent and as a refrigerant, anesthetic, and grain and fruit fumigant.

INTERFERENCES: None reported. An alternate GC column is 30 m x 0.32-mm fused silica capillary coated with 0.5-µm DBWAX at 50 °C isothermal [2].

OTHER METHODS: This revises Method S106 [3].

REAGENTS:

1. 2-Propanol, chromatographic grade.*
2. Ethyl bromide, reagent grade.*
3. Calibration stock solution, 0.073 mg/ μ L. Dilute 0.5 mL ethyl bromide to 10 mL with 2-propanol.
4. Nitrogen or helium, purified.
5. Hydrogen, prepurified.
6. Air, filtered, compressed.

* 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 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, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1011-1).
4. Vials, glass, 2-mL, PTFE-lined caps.
5. Syringes, 10- μ L and other convenient sizes for preparing standards, readable to 0.1 μ L.
6. Volumetric flasks, 10-mL.
7. Pipets, 1- and 5-mL, with pipet bulb.

SPECIAL PRECAUTIONS: Ethyl bromide is flammable, a dangerous fire hazard (flash point = 26 °C), respiratory irritant, narcotic, and a hepato- and renal toxin [4].

2-Propanol is flammable and a dangerous fire risk with a flash point of 11 °C.

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 0.2 L/min for a total sample size of 0.5 to 4 L.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube 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 six working standards over the range 0.02 to 10 mg ethyl bromide per sample.
 - a. Add known amounts of ethyl bromide or calibration stock solution to 2-propanol in 10-mL volumetric flasks and dilute to the mark. Make serial dilutions as necessary to obtain solutions in the range 0.02 to 10 mg ethyl bromide/mL.

- b. Analyze together with samples and blanks (steps 11 and 12).
- c. Prepare calibration graph (peak area vs. mg ethyl 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. Remove and discard back sorbent section of a media blank sampler.
 - b. Inject a known amount (1 to 20 μL) of ethyl bromide or 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. mg ethyl 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 1011-1. 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 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 ethyl bromide 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 ethyl 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 S106 was issued on April 11, 1975 [3], and validated over the range 550 to 2200 mg/m^3 using 4-L air samples [1]. The concentrations of ethyl bromide were independently determined by gas chromatographic analysis of the synthetic atmospheres using a 5-mL sampling loop. The average recovery of generated samples was 93.8% with a relative standard deviation of 6.3%. No storage stability study was done. The breakthrough volume was 6.4 L when dry air containing 2213 mg/m^3 of ethyl bromide was sampled at 0.2 L/min. Desorption efficiencies averaged 0.84 over the range 1.8 to 7.1 mg per sample. At 0.03 mg per sample, a desorption efficiency of 0.63 was found [2].

REFERENCES:

- [1] Documentation of the NIOSH Validation Tests, 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] User check, UBTL, Inc., NIOSH Sequence #4585-K (NIOSH, unpublished, October 31, 1984).
- [3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 2, S106, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

- [4] 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:

Y. T. Gagnon, NIOSH/DPSE; S106 originally validated under NIOSH Contract CDC-99-74-45.