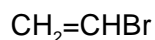


VINYL BROMIDE

1009



MW: 106.95

CAS: 593-60-2

RTECS: KU8400000

METHOD: 1009, Issue 2

EVALUATION: FULL

Issue 1: 15 February 1984

Issue 2: 15 August 1994

OSHA : 1 ppm; C 5 ppm
NIOSH: suspect carcinogen; lowest feasible conc.
 (0.2 ppm LOQ)
ACGIH: 5 ppm; suspect carcinogen
 (1 ppm = 4.37 mg/m³ @ NTP)

PROPERTIES: d 1.493 g/mL @ 20 °C; BP 15.8 °C;
 MP -137.8 °C; VP 141 kPa (1054 mm Hg)
 @ 20 °C; explosive range 9 to 15% v/v in air

SYNONYMS: bromoethene; bromoethylene.

| SAMPLING | | MEASUREMENT | |
|---|--|--|--|
| SAMPLER: | SOLID SORBENT TUBE (coconut shell charcoal, 400 mg/200 mg) | TECHNIQUE: | GAS CHROMATOGRAPHY, FID |
| FLOW RATE: | 0.01 to 0.2 L/min | ANALYTE: | vinyl bromide |
| VOL-MIN: | 2 L @ 1 ppm | DESORPTION: | 15 mL ethanol, 30 min ultrasonic agitation |
| -MAX: | 10 L | INJECTION VOLUME: | 5 µL |
| SHIPMENT: | no special precautions | TEMPERATURE-INJECTION: | 140 °C |
| SAMPLE STABILITY: | at least 14 days @ 25 °C | -DETECTOR: | 240 °C |
| BLANKS: | 2 to 10 field blanks per set | -PROGRAM: | 3 min @ 50 °C, 40 °C/min to 225 °C, 5 min hold |
| ACCURACY | | CARRIER GAS: | N ₂ , 25 mL/min |
| RANGE STUDIED: | 1.32 to 56.5 mg/m ³ [1] (6-L samples) | COLUMN: | nickel, 6 m x 2-mm ID, 10% FFAP on 80/100 mesh Chromosorb W AW DMCS |
| BIAS: | 0.021 [2] | CALIBRATION: | vinyl bromide in ethanol |
| OVERALL PRECISION (\hat{S}_{rT}): | 0.090 (1.3 to 6.4 mg/m ³) [1]; 0.063 (6.4 to 56 mg/m ³) | RANGE: | 8 to 355 µg per sample |
| ACCURACY: | ± 17.1% | ESTIMATED LOD: | 3 µg per sample |
| | | PRECISION (\hat{S}_r): | 0.040 [1] |

APPLICABILITY: The working range is 0.3 to 33 ppm (1.3 to 145 mg/m³) for a 6-L air sample.

INTERFERENCES: Presence of other volatile compounds may interfere with collection of vinyl bromide or reduce capacity of sorbent tube. Under stated chromatographic conditions, ethylene, acetylene, and ethylene dibromide are separated from vinyl bromide; bromine is not separated.

OTHER METHODS: This is Method P&CAM 349 [1] in a revised format. OSHA Method 08 uses a smaller (100 mg/50 mg coconut charcoal) sorbent tube and desorption by CS₂, recommends a 5-L sample, and was evaluated for a 1-ppm target level.

REAGENTS:

1. Ethanol, absolute.*
2. Vinyl bromide (liquid), $\geq 98\%$ purity.*
3. Calibration stock solution, ca. 30 $\mu\text{g}/\mu\text{L}$.
 - a. Accurately weigh ca. 5 mL ethanol in a stoppered 10-mL volumetric flask.
 - b. Chill (0 °C) the flask, vinyl bromide and a 1-mL gas-tight syringe.
 - c. Transfer 0.2 mL vinyl bromide to the volumetric flask with the gas-tight syringe.
 - d. Allow flask to return to room temperature. Reweigh flask to determine mass of vinyl bromide transferred.
 - e. Fill flask to mark with ethanol and calculate solution concentration.
4. Nitrogen, purified.
5. Hydrogen, prepurified.
6. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 10 cm long, 8-mm OD, 6-mm ID, with flame-sealed ends containing two sections of 20/40 mesh activated (600 °C) coconut shell charcoal; (front = 400 mg; back = 200 mg) separated by a urethane foam plug. A silyated glass wool plug precedes the front section and a urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less 3.4 kPa. Tubes are commercially available (Supelco ORBO-32; SKC ST 226-09).
2. Personal sampling pumps, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Ultrasonic bath.
4. Gas chromatograph, FID, integrator and column (page 1009-1).
5. Vials, glass, 25-mL, crimp seals or caps with FTFE-lined silicone rubber septa.
6. Pipet, 15-mL, with pipet bulb.
7. Syringes, 10- μL , readable to 0.1 μL ; 1-mL, gas-tight, with valve.
8. Balance, readable to 1 mg.
9. Flasks, volumetric, 2-, 5-, 10- and 25-mL.
10. File, triangular.
11. Ice.

SPECIAL PRECAUTIONS: Ethanol (flash point = 12 °C) is a fire hazard. Vinyl bromide is suspect carcinogen. Prepare samples and standards in a well-ventilated hood.

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 know flow rate between 0.01 and 0.2 L/min for at total sample size of 2 to 10 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the glass wool and front sorbent section in one vial. Place the back sorbent section and foam plugs into another vial.
6. Add 15.0 mL ethanol to each vial. Attach crimp cap to each vial.
7. Place vials in an ultrasonic bath for 30 min.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 1 to 750 µg vinyl bromide per sample.
 - a. Add known amounts of calibration stock solution to ethanol 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 (peak area vs. µg vinyl bromide per 15 mL).
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 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 vinyl bromide recovered per sample.
10. Analyze three quality control blind spikes and three analyst spikes to insure 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 1009-1. Inject sample aliquot manually using solvent flush technique or with autosampler. Under given conditions, retention time is about 3.0 min.
NOTE: If peak area is above the linear range of the working standards, dilute with ethanol, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE) of vinyl 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 vinyl bromide 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:

Analytical precision was determined by analyzing spiked sampling media. Average desorption efficiency was 0.910. Breakthrough volume was 10 L for a concentration of 130 mg/m³ at 40 °C and >80% RH. Overall precision, bias, and storage stability were determined by sampling and analyzing generated atmospheres. Generated concentrations were independently verified. Reference [2] provides more specific information.

REFERENCES:

- [1] NIOSH Manual of Analytical Methods, 2nd. ed., V. 7, P&CAM 349, U.S. Department of Health and Human Services, Publ. (NIOSH) 82-100 (1982).
- [2] Spafford, R. B. and H. K. Dillon. Analytical Methods Evaluation and Validation for Vinylidene Fluoride, Vinyl Bromide, Vinyl Fluoride, Benzenethiol, and n-Octanethiol: Research Report for Vinyl Bromide, NIOSH Contract No. 210-79-0100, Southern Research Institute, Birmingham, AL, available from NTIS (PB 83-133447), Springfield, VA (1981).

METHOD REVISED BY:

R. Alan Lunsford, Ph.D., NIOSH/DPSE; data obtained under NIOSH Contract 210-79-0100.