METHYL BROMIDE 2520

CH_3Br MW: 94.94 CAS: 74-83-9 RTECS: PA4900000

METHOD: 2520, Issue 3 **EVALUATION: FULL** **Issue 1: 15 May 1985**
Issue 3: 20 January 2016

OSHA: C 20 ppm (skin)
NIOSH: Lowest feasible; carcinogen
(1 ppm = 3.95 mg/m^3 @ NTP)

PROPERTIES: Gas; d 1.73 g/mL @ 0 °C; BP 4 °C; VP 189.34 kPa (1420 mmHg) @ 20 °C

SYNONYMS: Monobromomethane; bromomethane

SAMPLING

SAMPLER: SOLID SORBENT TUBES (two petroleum charcoal tubes, 400 mg and 200 mg; drying tube, 9 g sodium sulfate, necessary at humidity >50%)

FLOW RATE: 0.01 L/min to 0.1 L/min

VOL-MIN: 1 L @ 5 ppm
-MAX: 5 L with drying tube, 1 L without drying tube [1]

SHIPMENT: Ship on dry ice at −10 °C [1]

SAMPLE STABILITY: Six d at −10 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.84 ppm to 32.0 ppm (5 L samples)

BIAS: −5.2%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.089

ACCURACY: ±19.4%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, ATOMIC EMISSION DETECTION (GC-AED) monitoring bromine, carbon, and hydrogen channels

ANALYTE: Methyl bromide

DESORPTION: 400 mg tube: 3 mL methylene chloride; 200 mg tube: 2 mL methylene chloride

INJECTION: 1 µL

TEMPERATURE-INJECTOR: 250 °C
-TRANSFER LINE/ CAVITY BLOCK: 250 °C
-COLUMN: 30 °C, 3.5 min; 12 °C /min to 130 °C; hold 1 min

CARRIER GAS: Helium

COLUMN: US Pharmacopeia (USP) G2 capillary, 30 m × 0.32 mm ID, 1.0 µm film thickness; 1 m × 0.53 mm deactivated fused silica pre-column

CALIBRATION: Brominated compounds in methylene chloride

RANGE: 33.0 µg to 2687 µg bromine per sample

ESTIMATED LOD: 16.6 µg per sample [1]

PRECISION ($\bar{S}_r$): 0.066 [1]

APPLICABILITY: The working range is 0.84 ppm to 32.0 ppm (3.3 mg/m^3 to 126 mg/m^3) for a 5 L sample. Ceiling measurement samples may require dilution when analyzed.

INTERFERENCES: Water vapor interferes with collection at relative humidities (RH) >50%. To eliminate the interference, precede the sampling train with a drying tube, and limit the sample volume to 5 L. If drying tubes are not available, limit the sample volume to 1 L under humid conditions.

OTHER METHODS: This is NIOSH method 2520 [2] revised to account for humidity effects, as well as instability of standards and samples. Other researchers [3] have prepared methyl bromide standards gravimetrically and used GC-ECD for analysis. The gravimetric calibration procedure did not give consistent results when compared with the procedure used in this revision of NIOSH method 2520. GC-ECD with a US Pharmacopeia (USP) S3 capillary column may be an alternative technique to GC-AED if other bromine standards are used to confirm the concentration of methyl bromide standards.

REAGENTS:

1. Eluant: methylene chloride,* chromatographic grade.
2. Methyl bromide,* 99.5%.
3. Calibration stock solution: To 4 mL of methylene chloride, add 12 µL dibromomethane.
   NOTE: Other brominated compounds may be used if liquid at room temperature.
4. Desorption stock solution: Bubble methyl bromide gas slowly into chilled eluant. Determine the methyl bromide concentration by comparison with calibration standards.
5. Helium,* prepurified, 99.995%.
6. Oxygen,* ultra purified, as reagent gas for plasma, 207 kPa (30 psi).
7. Air, filtered.
8. Dry ice, flaked, for chilling solvent.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: petroleum charcoal sampling tubes; two glass tubes, each tube, 10 cm long, 8 mm OD, 6 mm ID, containing 20/40 mesh activated (600 °C) petroleum charcoal, first tube 400 mg, second tube 200 mg, held in place with silylated glass wool plugs; drying tube, glass, 9 g sodium sulfate. Tubes are connected in series with short pieces of plastic tubing. Pressure drop across sampler <3.4 kPa (25 mmHg) at 1.0 L/min airflow. Tubes are commercially available.
   NOTE: If RH ≥50%, precede sampling train with drying tube.
2. Personal sampling pump, 0.01 to 0.1 L/min, with flexible connecting tubing.
3. Gas chromatograph, atomic emission detector (helium plasma), integrator or computer, and column (page 2520-1).
4. Vials, 4 mL and 10 mL, glass, with PTFE-lined caps.
5. Syringe, gas-tight, 10 mL.
6. Microliter syringes, 10 µL, 50 µL, 100 µL, 250 µL, 500 µL for preparing standard solutions.
7. Pipettes, 2 mL, graduated in 0.1 mL increments.

SPECIAL PRECAUTIONS: Methylene chloride is a suspect carcinogen. Methyl bromide is a suspect carcinogen and is toxic by ingestion, inhalation, and skin absorption [4]. Users must be familiar with the proper use of flammable and nonflammable gases, cylinders, and regulators.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampling tubes immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
   NOTE: Place drying tube in front of the sorbent train.
3. Sample at an accurately known flow rate between 0.01 L/min and 0.1 L/min for a total sample size of 1.0 L to 5.0 L.
   NOTE: Limit sample volume to 1.0 L if RH ≥ 50% and no drying tube is used.
4. Separate the front and back tubes immediately after sampling. Cap the tubes. Pack securely in dry ice for shipment. Store at −10 °C until analysis.

SAMPLE PREPARATION:

5. Place the sorbent sections from each sampling tube in separate vials. Discard the glass wool plugs.
6. Add 3.0 mL chilled eluant (methylene chloride) to each 400 mg section, and 2.0 mL chilled eluant to each 200 mg section. Immediately cap each vial.
7. Allow to stand at least 30 min at room temperature with occasional agitation. Rechill before transferring to autosampler vials or diluting.
   NOTE: Because of the volatility of the analyte, it is suggested that any dilutions be prepared at the

time of transfer to autosampler vials. Dilutions can be stored in the freezer until determined that they are needed.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.14 µg to 272 µg methyl bromide per sample from calibration stock solution.
   NOTE: 0.085 µmol/µL bromine is equivalent to a methyl bromide concentration of 8.07 µg/µL.
   a. Add known aliquots (2.0 µL, 20 µL, 45 µL, and 120 µL) of calibration stock solution to methylene chloride in 10 mL vials with PTFE-lined caps. Take 1 mL of lowest standard and dilute to 10 mL with methylene chloride. Transfer standards to autosampler vials and immediately cap each vial.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. concentration).
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 µL to 10 µL) of methyl bromide desorption stock solution (concentration determined against other brominated compounds), or a serial dilution thereof, directly onto media blank samplers with a microliter syringe.
   b. Cap the tubes. Allow to stand overnight at 0 °C.
   c. Desorb (steps 5, 6, and 7) and analyze together with working standards (steps 11 and 12).
   d. Prepare a graph of DE vs. µg bromine 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-atomic emission detector to manufacturer's recommendations and to conditions given on page 2520-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE 1: Methyl bromide elutes before the methylene chloride solvent peak. Vent the solvent peak to avoid extinguishing the helium plasma. Vent time ranges from 3.2 min to 5.9 min; this may need to be adjusted for each system.
    NOTE 2: If peak area is above the linear range of the working standards, dilute with eluant, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE) of methyl bromide found in the 400 mg sample tube (W_f) and 200 mg sample tube (W_b), and in the average media blanks for the 400 mg (B_f) and 200 mg (B_b) sorbent tubes.
    NOTE: If $W_f > W_b / 10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of methyl bromide in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

NIOSH method 2520 for methyl bromide, issued in May 1985 [2], was based on NIOSH method S372 [5]. Issue 2 (dated 5/15/96) of NIOSH method 2520 was further revised to account for the effect of humidity and to address the instability of standards and samples [1]. The addition of a drying tube to the sampling train helped reduce the effects of >50% RH. The analytical technique was changed to GC with atomic emission detection (GC-AED). The atomic emission detector monitors individual elements, in this case bromine, independent of the source compound. Calibration can be done with brominated compounds that are liquid at room temperature, thereby eliminating the need for methyl bromide standards. Methylene chloride replaced carbon disulfide as desorption solvent.

The revised NIOSH method 2520 (issued 5/15/96) for methyl bromide was evaluated at 7.8 mg/m^3, 20.0 mg/m^3, and 125.0 mg/m^3 (2 ppm, 5 ppm, and 32 ppm, respectively) [1]. Test atmospheres were generated by delivering methyl bromide gas from two diffusion tubes kept at −12 °C into an airstream flowing at 12 L/min. Humidity was added downstream when needed, and airflow passed through two mixing chambers before reaching a sampling manifold. The concentration was monitored with a total hydrocarbon analyzer and confirmed by calibrating against other brominated standards by GC-AED. Three compounds used as calibration standards (dibromomethane, 1-bromopropane, and 1-bromobutane) were chosen as closest in chemical structure to methyl bromide, although a compound-independent response was assumed [6]. A three-compound calibration was used during the development of the GC-AED analytical procedure. Since there was good agreement between the three compounds, the method was written with only one brominated standard, dibromomethane.

When challenged with methyl bromide at a calculated concentration of 27 ppm, the capacity of the sampler (a 400 mg petroleum charcoal tube plus a 200 mg petroleum charcoal tube) at 40% RH and 20 °C was 1386.5 µg regardless of flow rate (10.5 mL/min, 40 mL/min, or 100 mL/min). However, at 100% RH and 39 °C, the average capacity fell to 298.6 µg. With a 9 g sodium sulfate drying tube in line, the capacity was increased to 651.8 µg; concentration averaged 130 mg/m^3 (33 ppm). Even with a drying tube in line, severe breakthrough occurred at the 10 L sample volume (50% was found on the back tube). Without the use of a drying tube, a 1 L sample volume is recommended, based on a 170.6 µg capacity (1.6 L) found at the 40 mL/min rate multiplied by a 0.67 caution factor.

Recovery fell below 70% for sample loadings less than 58 µg when carbon disulfide was used for desorption (Figure 1). This would not allow accurate sampling at 7.8 mg/m^3 (2 ppm), the exposure level most frequently encountered. Therefore, alternate desorption solvents were tested. Desorption with methylene chloride improved recovery at the 15 µg level to 76.7%. However, sample stability still fell below 70% after storage for six days at −10 °C regardless of sample level. This stability limitation remains a concern and rapid sample analysis is required.

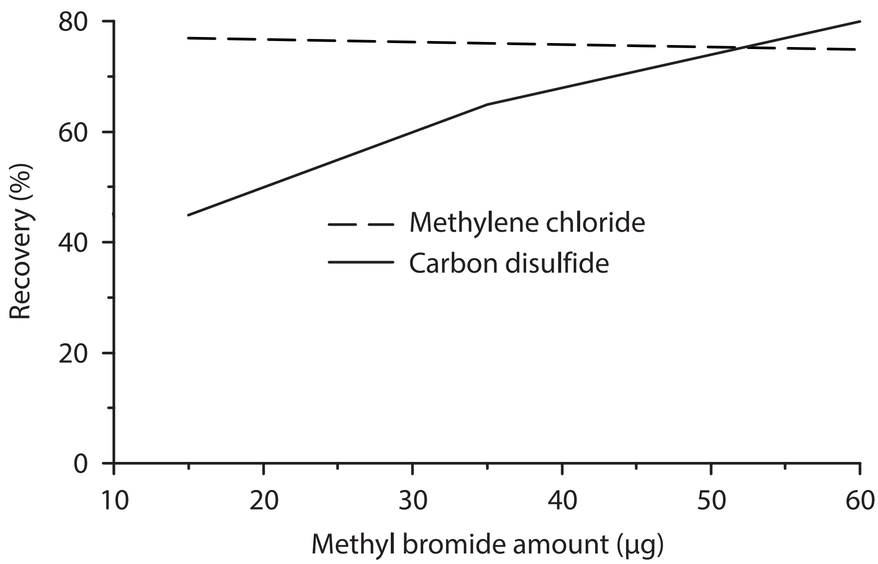

Figure 1. Comparison of desorption solvents.

REFERENCES:

[1] NIOSH [1995]. Research into problems with NIOSH method 2520 for methyl bromide. By Gagnon YT, Ringenburg VL, Fajen JM. Cincinnati, OH: U.S. Department of Health and Human Services, Centers

for Disease Control and Prevention, National Institute for Occupational Safety and Health, available as accession No. PB95-179842 from NTIS [www.ntis.gov]. Unpublished.

[2] NIOSH [1984]. Methyl bromide: Method 2520 (supplement issued 5/15/85). In: Eller PM, ed. NIOSH manual of analytical methods. 3rd ed. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 84-100, available as accession No. PB86-116266 from NTIS [www.ntis.gov].

[3] Woodrow JE, McChesney MM, Sieber JN [1988]. Determination of methyl bromide in air samples by headspace gas chromatography. Anal Chem *60*:509–512.

[4] NIOSH [1984]. Current intelligence bulletin 43—monohalomethanes: methyl chloride, methyl bromide, methyl iodide. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 84-117, available as accession No. PB85-178549 from NTIS [www.ntis.gov].

[5] NIOSH [1977]. Methyl bromide: Method S372. In: Taylor DG, ed. NIOSH manual of analytical methods. 2nd ed. Vol. 3. Cincinnati, OH: U.S. Department of Health, Education, and Welfare, Center for Disease Control, National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No. 77-157-C, available as accession No. PB276838 from NTIS [www.ntis.gov].

[6] Weile Y, Yieru H, Qingyu O [1992]. Quantitative characteristics of gas chromatography with microwave-induced plasma detection. In: Uden PC, ed. Element-specific chromatographic detection by atomic emission spectroscopy. Washington DC: American Chemical Society, ACS Symposium Series No. 479, pp. 44–61.

METHOD REVISED BY:

Yvonne T. Gagnon, MRB/DPSE/NIOSH

DISCLAIMER: Mention of any company or product does not constitute endorsement by NIOSH. In addition, citations to websites external to NIOSH do not constitute NIOSH endorsement of the sponsoring organizations or their programs or products. Furthermore, NIOSH is not responsible for the content of these websites. All web addresses referenced in this document were accessible as of the publication date.