

METHYL BROMIDE

2520

CH₃Br

MW: 94.94

CAS: 74-83-9

RTECS: PA4900000

METHOD: 2520, Issue 2

EVALUATION: FULL

Issue 1: 15 August 1990

Issue 2: 15 May 1996

OSHA : C 20 ppm (skin)
NIOSH: lowest feasible; carcinogen; Group I Pesticide
ACGIH: 5 ppm (skin)
 (1 ppm = 3.95 mg/m³ @ NTP)

PROPERTIES: gas; d 1.73 g/mL @ 0 EC; BP 4 EC;
 vp 189.34 kPa (1420 mm Hg) @ 20 EC

SYNONYMS: monobromomethane; bromomethane

SAMPLING		MEASUREMENT	
SAMPLER:	SOLID SORBENT TUBES (two petroleum charcoal tubes, 400 mg and 200 mg; drying tube, 9-g Na ₂ SO ₄ , necessary at humidity >50%)	TECHNIQUE:	GAS CHROMATOGRAPHY, ATOMIC EMISSION DETECTION (GC-AED) monitoring Br, C and H channels
FLOW RATE:	0.01 to 0.1 L/min	ANALYTE:	methyl bromide
VOL-MIN:	1 L @ 5 ppm	DESORPTION:	400 mg tube: 3 mL methylene chloride; 200 mg tube: 2 mL methylene chloride
-MAX:	5 L with drying tube, 1 L w/o drying tube [1]	INJECTION VOLUME:	1 µL
SHIPMENT:	ship on dry ice at -10 EC [1]	TEMPERATURE	-INJECTION: 250 EC
SAMPLE STABILITY:	six days at -10 EC [1]	-TRANSFER LINE/CAVITY BLOCK:	250 EC
BLANKS:	2 to 10 field blanks per set	-COLUMN:	30 EC, 3.5 min; 12 EC/min to 130 EC; hold 1 min.
ACCURACY		CARRIER GAS:	Helium
RANGE STUDIED:	0.84 to 32.0 ppm (5-L samples)	COLUMN:	DB-1 capillary, 30 m x 0.32-mm ID, 1.0-µm film thickness; 1 m x 0.53-mm deactivated fused silica pre-column
BIAS:	! 5.2%	CALIBRATION:	brominated compounds in methylene chloride
OVERALL PRECISION (Ö_r):	0.089	RANGE:	33.0 to 2687 µg bromine per sample
ACCURACY:	± 19.4%	ESTIMATED LOD:	16.6 µg per sample [1]
		PRECISION (p_r):	0.066 [1]

APPLICABILITY: The working range is 0.84 to 32.0 ppm (3.3 to 126 mg/m³) 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 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 Method 2520. GC-ECD with a Porapak Q 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 μ L 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, 30 psi.
7. Air, filtered.
8. Dry ice, flaked, for chilling solvent.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: two glass tubes, each tube, 10-cm long, 8-mm OD, 6-mm ID, containing 20/40 activated (60 EC) 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 (2.5 cm Hg) at 1.0 L/min airflow. Tubes are commercially available (SKC, Inc.#226-38-02, or equivalent).
NOTE: If RH \geq 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-, and 10-mL, glass, with PTFE-lined caps.
5. Syringe, gas-tight, 10-mL.
6. Microliter syringes, 10- μ L, 50- μ L, 100- μ L, 250- μ L, 500- μ L 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].

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 and 0.1 L/min for a total sample size of 1.0 to 5.0 L.
NOTE: Limit sample volume to 1.0 L if RH \geq 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 EC 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 minutes 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 to 272 µg methyl bromide per sample from calibration stock solution.
NOTE: 0.085 µmoles bromine per µL is equivalent to a methyl bromide concentration of 8.07 µg/µL.
 - a. Add known aliquots (2.0-, 20-, 45-, 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 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 EC.
 - c. Desorb (steps 5 through 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 to 5.9 mins; 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.
14. Calculate concentration, C, of methyl bromide in the air volume sampled, V (L):

$$C = \frac{W_f \% W_b \& B_f \& B_b}{V}, \text{ mg/m}^3$$

EVALUATION OF METHOD:

Method 2520 for methyl bromide, issued in August 1990 [2], was based on method S372 [5]. This issue (Issue 2, dated 1/15/96) of 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.

This revised Method 2520 (issued 1/15/96) for methyl bromide was evaluated at 7.8, 20.0, and 125.0 mg/m³ (2, 5, and 32 ppm) [1]. Test atmospheres were generated by delivering methyl bromide gas from two diffusion tubes kept at -12 EC 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 20EC was 1386.5 μg regardless of flow rate (10.5, 40, or 100 mL/min). However, at 100% RH and 39EC, 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 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 the 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 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 -10EC regardless of sample level. This stability limitation remains a concern and rapid sample analysis is required.

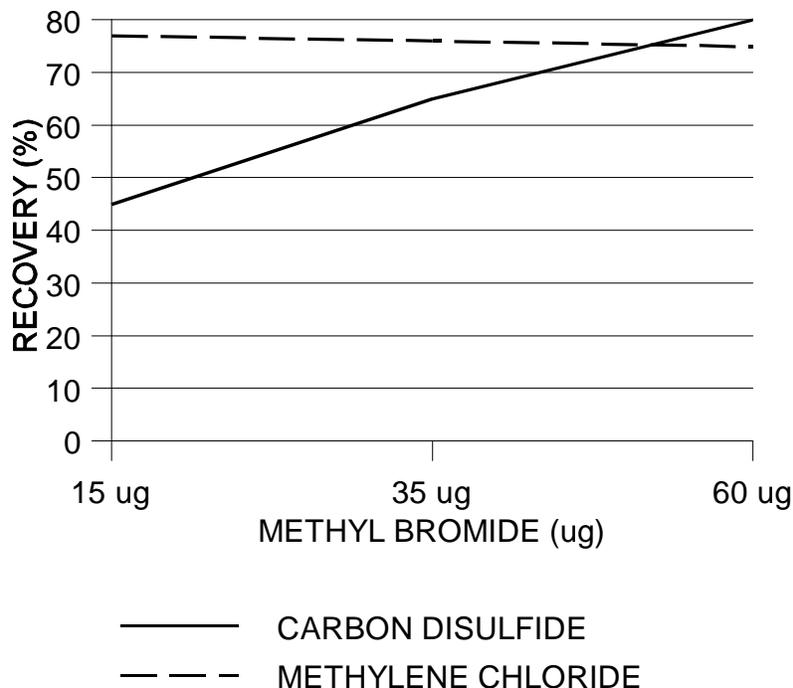


FIGURE 1. COMPARISON OF DESORPTION SOLVENTS

REFERENCES:

- [1] NIOSH [1995]. Research into problems with NIOSH method 2520 for methyl bromide. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) NTIS Pub. No. PB95-179842.
- [2] NIOSH [1984]. Methyl Bromide: Method 2520. In: Eller PM, Ed. NIOSH Manual of Analytical Methods, 3rd ed. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 84-100.
- [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; evidence of carcinogenicity. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 84-117.
- [5] NIOSH [1977]. Methyl bromide: Method S372. In: Taylor DG, Ed. NIOSH manual of analytical methods, 2nd. Ed., Vol. 2. Cincinnati, OH: National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No. 77-157-C.
- [6] Yu W, Haung Y, Ou O [1992]. Quantitative characteristics of gas chromatography with microwave-induced plasma detection. In Uden PC, Ed. Element-specific chromatographic detection by atomic emission spectroscopy, ACS Symposium Series 479, American Chemical Society, pp. 44-61.

METHOD REVISED BY:

Yvonne T. Gagnon, MRB/DPSE/NIOSH