

1,1,2,2-TETRABROMOETHANE

2003



MW: 345.70

CAS: 79-27-6

RTECS: KI8225000

METHOD: 2003, Issue 2

EVALUATION: PARTIAL

Issue 1: 15 May 1985

Issue 2: 15 August 1994

OSHA : 1 ppm
 NIOSH: no REL
 ACGIH: 1 ppm
 (1 ppm = 14.14 mg/m³ @ NTP)

PROPERTIES: liquid; d 2.964 g/mL @ 20 °C;
 BP 243.5 °C; MP 0 °C; VP 13 Pa
 (0.1 mm Hg) @ 20 °C

SYNONYMS: acetylene tetrabromide; Muthmann's liquid; sym-tetrabromoethane

APPLICABILITY: The working range is 0.5 to 2.8 ppm (7 to 40 mg/m³) for a 100-L air sample. High humidity during sampling will reduce breakthrough volume.

INTERFERENCES: None identified.

OTHER METHODS: This is Method S117 [2] in a revised format.

REAGENTS:

1. Tetrahydrofuran (THF), chromatographic quality and free from peroxides.*
2. 1,1,2,2-Tetrabromoethane, $\geq 98\%$ pure.*
3. Hexane, chromatographic quality.*
4. Calibration stock solution, 89 mg/mL. Dissolve 0.89 g (300 μL at 20 °C) 1,1,2,2-tetrabromoethane in tetrahydrofuran to make 10 mL of solution. Prepare fresh daily.
5. Desorption efficiency (DE) stock solution, 237 $\mu\text{g}/\mu\text{L}$. Dissolve 2.37 g (800 μL at 20 °C) 1,1,2,2-tetrabromoethane in hexane to make 10 mL of solution.
6. Nitrogen, purified.
7. Hydrogen, purified.
8. Air, filtered.

* 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 20/40 mesh silica gel (front = 150 mg; back = 75 mg) separated by a 2-mm plug of urethane foam. A plug of silylated glass wool precedes the front section. A 3-mm plug of urethane foam follows the backup section. Pressure drop across tube must be < 3.4 kPa at 1 L/min airflow. Tubes are commercially available.
2. Personal sampling pump, 0.2 to 1 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator and column (page 2003-1).
4. Vials, 2-mL, with PTFE-lined caps.
5. Pipet, 1-mL, with pipet bulb.
6. Volumetric flasks, 10-mL.
7. Syringes, 500- μL , readable to 10 μL .
8. Syringes, 10- μL , readable to 0.1 μL .
9. U-tube, 25 cm x 15-mm ID, with glass stopcocks.
10. Temperature bath, 75 °C.

SPECIAL PRECAUTIONS: THF is a serious fire risk [flash point (open cup) = -15 °C]. Explosive peroxides can form in THF during exposure to air in the absence of an inhibitor. THF vapor irritates the eyes and respiratory tract and cause headache, dizziness and narcosis. THF liquid can irritate the skin. If THF is distilled, distill in the presence of ferrous sulfate or other reducing agent. Store THF under nitrogen in a dark glass or metal container.

1,1,2,2-Tetrabromoethane is toxic, narcotic and can irritate the eyes and skin [3].

n-Hexane is a serious fire risk [flash point (closed cup) = -30 °C]. Inhalation of n-hexane vapor can irritate the upper respiratory tract and cause depression of the central nervous system. n-Hexane as a liquid can cause dermatitis and irritate the eyes.

Work in a well-ventilated fume cabinet, wear gloves, avoid inhalation of vapors and protect solvents from sparks and open flame.

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 0.2 and 1 L/min for a total sample size of 50 to 100 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 THF to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.1 to 4 mg 1,1,2,2-tetrabromoethane per sample. Working standard should be prepared fresh daily.
 - a. Add known amounts of calibration stock solution to THF 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 or height vs. mg 1,1,2,2-tetrabromoethane).
9. Determine desorption efficiency (DE) at least once for each batch of silica gel used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
 - a. Place aliquots of DE stock solution into a U-tube partly immersed in a temperature bath at about 75 °C, and draw air through the U-tube into media blank samplers with a pump at 0.2 to 1 L/min.

NOTE: Although values of DE for the original method [2] are based on liquid spikes, values of DE should be determined for vapor spikes. Values of DE for liquid and vapor spikes may be different [4].
 - b. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).

NOTE: If breakthrough occurs with the vapor spikes, determine DE using liquid spikes.
 - c. Prepare a graph of DE vs. mg 1,1,2,2-tetrabromoethane recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph is in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2003-1. 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 THF, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area or peak height.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of 1,1,2,2-tetrabromoethane 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 1,1,2,2-tetrabromoethane 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 S117 [2] was evaluated with controlled atmospheres of 1,1,2,2-tetrabromoethane [1]. Overall precision (\hat{S}_{rT}) was 0.096 for 98-L samples (18 samples, pooled) at 6.5 to 23 mg/m³. Concentrations found by this method, 6.5, 14 and 23 mg/m³, were 7, 4 and 17% lower than the corresponding concentrations based on the delivery rate of the syringe pump and flow rates of dilution air in the generation system. The discrepancies were attributed to difficulties in generating the atmospheres. Breakthrough from front sections of sorbent was not observed during passage of 220 L of dry air at 0.9 L/min when the concentration was 23 mg/m³. Breakthrough at high relative humidity was not tested. Portions of silica gel were fortified with solutions of 1,1,2,2-tetrabromoethane in hexane. Average values of desorption efficiency were 0.79, 0.92 and 0.98 after applications of 0.70-, 1.4- and 2.8-mg quantities of 1,1,2,2-tetrabromoethane; precision (\hat{S}_r) was 0.041 (18 samples, pooled). A storage study to determine the stability of 1,1,2,2-tetrabromoethane on silica gel was not performed. Peroxides in tetrahydrofuran may cause rapid deterioration of standard solutions of 1,1,2,2-tetrabromoethane; thus, standards should be prepared daily.

REFERENCES:

- [1] Documentation of the NIOSH Validation Tests, S117, 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] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 2, S117, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
- [3] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, Acetylene Tetrabromide, 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.
- [4] Tucker, S. P., and G. J. Deye. *Anal. Lett.*, **14** (A12), 959-976 (1981).

METHOD REVISED BY:

Samuel P. Tucker, Ph.D., NIOSH/DPSE; S117 originally validated under NIOSH Contract CDC-99-74-45.