

METHYL CHLORIDE

1001

CH₃Cl

MW: 50.49

CAS: 74-87-3

RTECS: PA6300000

METHOD: 1001, Issue 2

EVALUATION: FULL

Issue 1: 15 August 1987

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OSHA : 100 ppm; C 200 ppm; P 300 ppm
 NIOSH: lowest feasible; carcinogen
 ACGIH: 50 ppm; STEL 100 ppm (skin)
 (1 ppm = 2.06 mg/m³ @ NTP)

PROPERTIES: gas; vapor density 1.8 (air = 1);
 BP -24.2 °C; MP -97.7 °C;
 explosive range 7.6 to 19% v/v air

SYNONYMS: chloromethane.

SAMPLING		MEASUREMENT	
SAMPLER:	SOLID SORBENT TUBES (two coconut shell charcoal tubes in series, 400 mg/200 mg and 100 mg/50 mg)	TECHNIQUE:	GAS CHROMATOGRAPHY, FID
FLOW RATE:	0.01 to 0.1 L/min	ANALYTE:	methyl chloride
VOL-MIN:	0.4 L @ 100 ppm	DESORPTION:	3 mL CH ₂ Cl ₂
-MAX:	3 L	INJECTION VOLUME:	5 µL
SHIPMENT:	refrigerated	TEMPERATURE-INJECTOR:	200 °C
SAMPLE STABILITY:	95% recovery after 7 days @ 25 °C [1]	-DETECTOR:	260 °C
BLANKS:	2 to 10 field blanks per set	-COLUMN:	100 °C
ACCURACY		CARRIER GAS:	N ₂ , 30 mL/min
RANGE STUDIED:	110 to 460 mg/m ³ (1.5-L air samples); 300 to 1200 mg/m ³ (0.5-L air samples) [1]	COLUMN:	stainless steel, 1.2 m x 6-mm OD, packed with 80/100 mesh Chromosorb 102
BIAS:	1.04%	CALIBRATION:	standard solutions of methyl chloride in CH ₂ Cl ₂
OVERALL PRECISION (S_{r,T}):	0.052 [1]	RANGE:	0.1 to 1 mg per sample
ACCURACY:	± 12.41%	ESTIMATED LOD:	0.01 mg per sample [2]
		PRECISION (S_p):	0.017 @ 0.16 to 0.62 mg per sample [1]

APPLICABILITY: The working range is 31 to 320 ppm (66 to 670 mg/m³) for a 1.5-L air sample. The method is applicable to STEL determinations.

INTERFERENCES: None reported. An alternate GC column is fused silica capillary, 30 m x 0.315-mm, coated with 0.25-µm Durawax DX-4 at 45 °C [2].

OTHER METHODS: This combines and revises Methods S99 [3] and P&CAM 201 [4].

REAGENTS:

1. Methylene chloride (CH_2Cl_2), chromatographic quality, methyl chloride-free.*
2. Methyl chloride, 99.5%.*
3. Nitrogen, purified.
4. Hydrogen, prepurified.
5. Air, filtered, compressed.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: two glass tubes (9 cm long, 8-mm OD, 6-mm ID, followed by 7 cm long, 6-mm OD, 4-mm ID) connected in series with a short piece of tubing, flame-sealed ends and plastic end caps. Each tube contains two sections of 20/40 mesh activated (600 °C) coconut shell charcoal (front tube = 400 mg + 200 mg; back tube = 100 mg + 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes each front section and a 3-mm urethane foam plug follows each back section. Pressure drop across the tubes at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.1 L/min, with flexible connecting tubing.
3. Refrigerant, bagged (e.g., "Blue Ice") and insulated shipping container.
4. Gas chromatograph, flame ionization detector, integrator, and column (see page 1001-1).
5. Bottles, glass, 15-mL, with PTFE-lined septum crimp caps.
6. Syringes, gas-tight, 10- μL , and 0.1- to 1-mL.
7. Pipet, TD, 3-mL.
8. DE apparatus. Glass tubing, through which nitrogen flows at ca. 30 mL/min, with T-connection and septum.

SPECIAL PRECAUTIONS: Methyl chloride has poor warning properties, is a narcotic and a suspect carcinogen and teratogen [5,6]. Methylene chloride is a suspect carcinogen [6,7].

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, with the smaller tube nearer the sampling pump.
3. Sample at an accurately known flow rate between 0.01 and 0.1 L/min for a total sample size of 0.4 to 3 L (e.g., at 0.1 L/min for 15 min for STEL measurement and 0.01 L/min for 50 to 300 min for TWA measurement).
4. Separate and cap the tubes. Pack securely for shipment in an insulated container with bagged refrigerant.

SAMPLE PREPARATION:

5. Pipet 3.0 mL CH_2Cl_2 into each of several bottles.
6. Place, in order, the back and front sorbent sections of the front sampler tube into a bottle, discarding the glass wool and foam plugs. Immediately cap and gently shake the bottle. Analyze within 6 h.

7. Place, in order, the back and front sorbent sections of the back sampler tube into a second bottle, discarding the glass wool and foam plugs. Immediately cap and gently shake the bottle. Analyze within 6 h.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards.
 - a. Pipet 3.0 mL CH₂Cl₂ into each of a series of bottles. Cap the bottles.
 - b. Using a gas-tight syringe, add known amounts of methyl chloride (0.005 to 0.5 mL; 0.01 to 1 mg at NTP) by bubbling the gas slowly through the CH₂Cl₂. Gently shake the bottles.
 - c. Analyze with samples and blanks (steps 10 and 11).
 - d. Prepare calibration graph (peak area vs. mg methyl chloride).
9. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interest. Prepare three tubes at each of five levels plus three media blanks.
 - a. Using a gas-tight syringe, slowly inject a known amount of methyl chloride (0.005 to 0.5 mL) through the septum of the DE apparatus into a stream of nitrogen which carries the analyte into a large (400 mg/200 mg) sorbent tube. Allow the nitrogen to flow an additional 1 min.
 - b. Cap the tube. Allow to stand overnight.
 - c. Desorb (steps 5 through 7) and analyze with working standards (steps 10 and 11).
 - d. Prepare a graph of DE vs. mg methyl chloride recovered.

MEASUREMENT:

10. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1001-1. 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 an aliquot of the desorbed liquid with CH₂Cl₂, reanalyze and apply the appropriate dilution factor in calculations.
11. Measure peak area.
NOTE: Methyl chloride elutes before CH₂Cl₂ under these conditions.

CALCULATIONS:

12. Determine the mass, mg (corrected for DE) of methyl chloride 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.
13. Calculate concentration, C, of methyl chloride in the air volume sample, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S99 was issued on March 18, 1977 [3], and validated with generated atmospheres monitored by total hydrocarbon analyzer [1,8]. Average recovery was 105% with $\bar{S}_r = 0.05$ for eighteen 1.5-L samples in the range 110 to 460 mg/m³ and 101% with $\bar{S}_r = 0.05$ for eighteen 0.5-L samples in the range 300 to 1200 mg/m³. Breakthrough (effluent = 5% of test concentration) occurred after sampling for 135 min at 0.0235 L/min from an atmosphere containing 410 mg/m³ methyl chloride in air at 80% RH, and at 24.4

min when sampling at 0.105 L/min from an atmosphere containing 1425 mg/m³ at 84% RH. Desorption efficiency for 18 samples in the range 0.16 to 0.62 mg methyl chloride averaged 0.99 with $s_r = 0.02$. Desorption with carbon disulfide, chloroform, or ethanol as eluent gave lower recoveries. Samples stored in the laboratory for seven days gave a mean recovery of 95% relative to samples analyzed immediately after collection.

REFERENCES:

- [1] Backup Data Report S99, available as "Ten NIOSH Analytical Methods, Set 2," Order No. PB 271-464, from NTIS, Springfield VA 22161.
- [2] UBTL report for Sequence #4131-L,M (NIOSH, unpublished, November 28, 1983).
- [3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 4, S99, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
- [4] Ibid., Vol. 1, P&CAM 201, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
- [5] NIOSH Current Intelligence Bulletin 43, Monohalomethanes, U.S. Department of Health and Human Services, Publ. (NIOSH) 84-117 (September 27, 1984).
- [6] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as Stock #PB83-154609 from NTIS, Springfield, VA 22161.
- [7] NIOSH Current Intelligence Bulletin 46, U.S. Department of Health and Human Services, Publ. (NIOSH) 86-114 (1986).
- [8] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY:

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