

METHYLAL

1611



MW: 76.10

CAS: 109-87-5

RTECS: PA8750000

METHOD: 1611, Issue 2

EVALUATION: FULL

Issue 1: 15 May 1985

Issue 2: 15 August 1994

OSHA : 1000 ppm
NIOSH: 1000 ppm
ACGIH: 1000 ppm
 (1 ppm = 3.11 mg/m³ @ NTP)

PROPERTIES: liquid; d 0.8593 g/mL @ 20 °C;
 BP 42 °C; MP -105 °C;
 VP 44 kPa (330 mm Hg; 43% v/v)
 @ 20 °C; explosive range 1.6 to
 17.6% v/v in air

SYNONYMS: dimethoxymethane; formal; formaldehyde dimethyl acetal

SAMPLING		MEASUREMENT	
SAMPLER:	SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)	TECHNIQUE:	GAS CHROMATOGRAPHY, FID
FLOW RATE:	0.01 to 0.2 L/min	ANALYTE:	methylal
VOL-MIN:	1 L @ 1000 ppm	DESORPTION:	1 mL hexane; stand 30 min
-MAX:	3 L	INJECTION	
SHIPMENT:	routine	VOLUME:	5 µL
SAMPLE		TEMPERATURE-INJECTION:	190 °C
STABILITY:	unknown	-DETECTOR:	250 °C
FIELD BLANKS:	2 to 10 field blanks per set	-COLUMN:	195 °C
ACCURACY		CARRIER GAS:	N ₂ , 30 mL/min
RANGE STUDIED:	1684 to 6670 mg/m ³ [1] (2-L samples)	COLUMN:	stainless steel, 1.2 m x 6-mm OD, packed with 50/80 mesh Porapak Q or equivalent
BIAS:	+ 4.8%	CALIBRATION:	standard solutions of methylal in hexane
OVERALL PRECISION ($\hat{S}_{r,T}$):	0.060 [1]	RANGE:	3 to 12 mg per sample
ACCURACY:	± 15.1%	ESTIMATED LOD:	0.1 mg per sample
		PRECISION (\hat{S}_p):	0.017 [1]

APPLICABILITY: The working range is 480 to 1930 ppm (1500 to 6000 mg/m³) for a 2-L air sample. Samples containing smaller quantities of methylal may have low desorption efficiency. Breakthrough capacity at high humidity is not known.

INTERFERENCES: None identified.

OTHER METHODS: This revises Method S71 [2].

REAGENTS:

1. Hexane, chromatographic quality.*
2. Methylal, reagent grade.*
3. Nitrogen, purified.
4. Hydrogen, prepurified.
5. 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 activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1611-1).
4. Vials, glass, 2-mL, PTFE-lined caps.
5. Syringe, 20- μ L, readable to 0.1 μ L.
6. Volumetric flasks, 10-mL.
7. Pipet, volumetric, 1.0-mL, with pipet bulb.

SPECIAL PRECAUTIONS: n-Hexane is extremely flammable (flash point = -22 °C). Methylal is also very flammable (flash point = -18 °C) and will attack some forms of plastics and rubber. Work with these only in a 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 known flow rate between 0.01 and 0.2 L/min for a total sample size of 1 to 3 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 hexane to each vial. Attach 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 12 mg methylal per sample.
 - a. Add known amounts of pure methylal to hexane in 10-mL volumetric flasks and dilute to the mark. Prepare solutions in the range 0.1 to 12 mg methylal/mL.
 - b. Analyze together with samples and blanks (steps 11 and 12).
 - c. Prepare calibration graph (peak area vs. mg methylal).
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. Remove and discard back sorbent section of a media blank sampler.
 - b. Inject a known amount (1 to 20 μL) of pure methylal or a standard solution of methylal in hexane 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. mg methylal 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 according to manufacturer's recommendations and to conditions given on page 1611-1. 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 hexane, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of methylal 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 methylal 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 S71 [2] was issued on February 14, 1975, and validated over the range 1684 to 6670 mg/m^3 at 22 $^\circ\text{C}$ using 2-L air samples [1]. Samples of methylal in dry air were generated using a three-neck round-bottom generator flask containing the liquid methylal. An accurately measured flow of nitrogen gas was used to sweep the vapors out of the flask. Overall precision, s_r , was 0.060 with average recovery of 104%. Desorption efficiency was 78, 81, and 88%, respectively, at 3.1, 6.2, and 12.3 mg methylal taken per sample. Breakthrough (5% on back section) occurred at 20 min when sampling an atmosphere containing 6250 mg/m^3 methylal at 0.183 L/min at 0% RH. Breakthrough at high humidity was not tested, nor was sample stability.

REFERENCES:

- [1] Documentation of the NIOSH Validation Tests, 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, S71, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

METHOD REVISED BY:

Ardith A. Grote, NIOSH/DPSE; S71 originally validated under NIOSH Contract CDC-99-74-45.