METHANOL 2000

CH_3OH MW: 32.04 CAS: 67-56-1 RTECS: PC1400000

METHOD: 2000, Issue 3 **EVALUATION: FULL** **Issue 1: 15 August 1984**
Issue 3: 15 January 1998

OSHA : 200 ppm
NIOSH: 200 ppm (skin); STEL 250 ppm (skin)
ACGIH: 200 ppm (skin); STEL 250 ppm (skin)
(1 ppm = 1.310 mg/m³ @ NTP)

PROPERTIES: liquid; d = 0.792 g/ml @ 20 C; BP = 64.5 C; VP = 15.3 kPa (115 mm Hg; 15.1% v/v) @ 20 C; explosive range is 6 to 36% (v/v) in air

SYNONYMS: Methyl alcohol, wood alcohol, carbinol, wood naphtha, wood spirit

SAMPLING

SAMPLER: SOLID SORBENT TUBE (silica gel, 100/50 mg)

FLOW RATE: 0.02 to 0.2 L/min

VOL-MIN: 1 L @ 200 ppm
-MAX: 5 L

SHIPMENT: pack securely for shipment; store at 5°C.

SAMPLE STABILITY : at least 30 days at 5°C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 140 to 540 mg/m³ [2]

BIAS: -4.4%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.074 [1, 2]

ACCURACY: ±16.2%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: methanol

DESORPTION: 1 mL water/isopropanol (95:5) [1]

INJECTION VOLUME: 1 µL

TEMPERATURE- INJECTION: 250 °C
-DETECTOR: 300 °C
-COLUMN: 50 to 90 °C (8 °C/min) [1] (Split Ratio 10:1)

CARRIER GAS: He, 2.6 mL/min

COLUMN: capillary, 30 m x 0.53-mm ID; 3-µm film 35% diphenyl-65% dimethyl polysilozane, Rtx™-35 or equivalent [1]

CALIBRATION: standard solutions of methanol in water/isopropanol (95:5)

RANGE: 2.2 to 6000 µg per sample [1,2]

ESTIMATED LOD: 0.7 µg per sample [1]

PRECISION ($\hat{S}_r$): 0.030 [1]

APPLICABILITY: Under the GC parameters stated in the method, methanol may be identified based upon retention time and quantified. The working range is 0.4 to 1200 mg/m³ (0.3 to 916.0 ppm) for a 5-L air sample [1]. At high concentrations of methanol or under conditions of high relative humidity, a large silica gel tube (700 mg) is required [2].

INTERFERENCES: No specific interferences were identified. However, any compound with a similiar retention time may interfere. Positive identification can be confirmed by dual column chromatography with a 100% PEG capillary column. Mass spectrometry can also be used as a confirmation aid.

OTHER METHODS: This method updates and replaces NMAM 2000 (August 15, 1994), which combined and replaced Method S59 [3] and P&CAM 247 [4].

REAGENTS:

1. Methanol, chromatographic grade. *
2. Water, distilled and prepurified.
3. Isopropanol (IPA), chromatographic grade.*
4. Helium, purified.
5. Hydrogen, prepurified.
6. Air, filtered.
7. Desorbing solution, 5% isopropanol in 95% distilled water.
8. Calibration stock solution, 2µg/µL. Add 25.3µL Methanol to 10 mL of desorbing solution.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: silica gel tube, 7 cm long, 4-mm ID, containing two sections of 20/40 mesh silica gel (front = 100 mg, back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section. A 4-mm foam plug follows the back section. Samplers are commercially available.
   NOTE: At high relative humidity or high methanol concentrations, use a larger tube: 15 cm long, 8-mm ID, with three sections of silica gel (700 mg, 150 mg, 150 mg).
2. Personal sampling pump, 0.02 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detection, integrator, and Rtx-35 capillary column, or equivalent (page 2000-1).
4. Utrasonic bath.
5 Vials, autosampler, with PTFE-lined caps.
6. Microliter syringes, 10-µL and other sizes as needed, readable to 0.1 µL.
7. Flasks, volumetric, various sizes.
8. Pipets, various sizes.

SPECIAL PRECAUTIONS: Methanol is flammable and a dangerous fire and explosion risk. It is moderately toxic by ingestion and inhalation. Isopropanol is flammable and a fire risk. Wear appropriate protective clothing and work with these compounds in a well ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.02 and 0.2 L/min for a total sample size of 1 to 5 L.
4. Cap the samplers with plastic caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place front (include glass wool plug) and back sorbent sections of the sampler tube in separate vials. Discard foam plugs.
6. Add 1 mL of water/IPA (95/5) to each vial and attach crimp caps.
7. Place vials in an ultrasonic bath for 30 to 60 min to aid desorption.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range of interest. Three standards (in duplicate) should cover the range from LOD to LOQ.
   a. Add known amounts of calibration stock solution to water/isopropanol (95/5) 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. µg methanol).
9. Determine desorption efficiency (DE) at least once for each lot of silica gel tubes used for sampling

in the calibration range (step 8). Prepare three samplers at each of six levels plus three media blanks.

a. Remove and discard back sorbent sections of samplers and media blanks.
b. Inject a known amount of calibration stock solution directly onto the front sorbent bed of each silica gel tube.
c. Allow the tubes to air equilibrate for several minutes, then cap the ends of the tubes and allow to stand overnight.
d. Desorb the samples (steps 5 through 7) and analyze together with working standards and blanks (steps 11 and 12).
e. Prepare a graph of DE vs. µg analyte recovered.

10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graphs are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2000-1. Inject a 1-µL sample aliquot manually using solvent flush technique or with an autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with water/IPA (95/5), reanalyze and apply the appropriate dilution factor in the calculations.
12. Measure peak areas.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE), for methanol 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 methanol in the air volume sampled, V (L).

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

NOTE: µg/L = mg/m^3

EVALUATION OF METHOD:

The method was reevaluated and revised. Improvements were made to enhance the recovery of methanol from silica gel, to improve baseline resolution, and to improve the precision of the method. Desorption efficiency (DE) was determined for three levels using the improved analytical parameters stated on page 2000-1. The average DE for methanol was determined at 20 µg (0.942), 40 µg (0.945), and 79 µg (0.942) [1]. The LOD was determined to be 0.7 µg/sample [1]. The precision, as determined from the pooled relative standard deviation ($\bar{S}_r$) was determined to be 0.030 [1].

The original method S59 [3] was issued on January 17, 1975 and was validated over the range of 140 to 540 mg/m^3 at 25 °C and 758 mm Hg with 5-L sample volumes [2]. The estimated LOD determined for a user check was 0.010 mg/sample [5]. Overall precision ($\hat{S}_{rT}$) was determined to be 0.063 with an average recovery for 18 samples of 94.2%, representing non-significant bias. The atmospheres were generated by calibrated syringe pump. Desorption efficiency (DE) was determined to be 0.92 at 1.3 mg methanol and 0.84 at 0.65 mg methanol per sample. The breakthrough volume was 10.4 L (5% on back section) when sampling a methanol atmosphere containing 541 mg/m^3 in dry air at 0.2 L/min for 52 min.

Data gathered using larger silica gel tubes (700 mg front section) under conditions of high humidity were published in P&CAM 247 [4]. The data are consistent with a recommended maximum sample volume of 5 L.

REFERENCES:

[1] Pendergrass, SM [1996]. Backup data report for methanol method development. Cincinnati, OH: National Institute for Occupational Safety and Health, DPSE/NIOSH (unpublished May).
[2] NIOSH [1977]. Documentation of the NIOSH validation tests. Cincinnati, OH: National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No. 77-185.
[3] NIOSH [1977]. NIOSH Manual of Analytical Methods (NMAM), V. 2, S59. Cincinnati, OH: National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No. 77-157-B.
[4] NIOSH [1977]. NIOSH Manual of Analytical Methods (NMAM), V. 1, P&CAM 247. Cincinnati, OH: National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No. 77-157-A (1977).
[5] NIOSH [1983]. User Check, UBTL, NIOSH Sequence # 4121-K (unpublished November 3).

METHOD WRITTEN BY:

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