METHYL ACETATE

CH_3COOCH_3 MW: 74.08 CAS: 79-20-9 RTECS: AI9100000

METHOD: 1458, Issue 2 **EVALUATION: FULL** **Issue 1: 16 December 1974**
Issue 2: 15 August 1994

OSHA : 200 ppm
NIOSH: 200 ppm; STEL 250 ppm
ACGIH: 200 ppm; STEL 250 ppm
(1 ppm = 3.03 mg/m^3)

PROPERTIES: liquid; d = 0.9244 g/mL @ 25 °C; BP = 54.05 °C; VP 23 kPa (173 mm Hg) @ 20 °C; vapor density (air = 1) 2.8

SYNONYMS: acetic acid methyl ester; methyl acetic ester; methyl ethanoate

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/minute

VOL-MIN: 0.2 L @ 200 ppm
-MAX: 10 L

SHIPMENT: refrigerated

SAMPLE STABILITY: at least 6 days @ 5 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 343 to 1130 mg/m^3 [1] (7-L samples)

BIAS: 7.2%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.0547 [1]

ACCURACY: ± 16.8%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: methyl acetate

EXTRACTION: 1 mL CS_2

INJECTION VOLUME: 1 µL

TEMPERATURE-INJECTOR: 250 °C
-DETECTOR: 300 °C
-COLUMN: 35 °C (2 min) to 150 °C (10 °C/min)

COLUMN: DB-wax; 30 m, 0.32-mm ID, 1-µm film thickness

CARRIER GAS: He, 1 mL/min;

MAKEUP GAS: N_2, 30 mL/min

CALIBRATION: solutions of methyl acetate in CS_2

RANGE: 7 µg to 1000 µg [2]

ESTIMATED LOD: 2 µg [2]

PRECISION ($\hat{S}_r$): 0.036 @ 20 to 876 µg per sample [2]

APPLICABILITY: The working range is 0.3 to 1330 ppm (1 to 440 mg/m^3) for a 7-L air sample [1]. The method may be adapted for other esters with appropriate changes in chromatographic conditions.

INTERFERENCES: Any compounds with similar retention times.

OTHER METHODS: This revises Method S42 [1]. Improved recovery of analyte may be achieved with the addition of 5% butyl carbitol to the CS_2 desorption procedure [3,4].

REAGENTS:

1. Methyl acetate (reagent grade).
2. Carbon disulfide (chrom. grade).
3. Prepurified helium.
4. Hydrogen, prepurified.
5. Decane, reagent grade, or other suitable internal standard.
6. Air, filtered, compressed.

* 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 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 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. Refrigerant, bagged ("Blue Ice," or equivalent).
4. Gas chromatograph equipped with FID, integrator and column (page 1458-1).
5. Vials, 2-mL, glass, PTFE-lined crimp caps.
6. Syringe, 10-µL, readable to 0.1 µL, and other convenient sizes.
7. Pipet, 1-mL, readable to 0.1 mL.
8. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (F.P. = -30°C). Use 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 accurate flow rate between 0.01 and 0.2 L/min for a total sample size of 0.2 to 10 L.
4. Cap the samplers with plastic caps and pack securely for shipment with bagged refrigerant.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials.
6. Add 1.0 mL to CS_2 to each vial and attach a crimp cap to each vial.
7. Allow to stand 30 minutes with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 2 to 2000 µg analyte per sample.
   a. Add known amounts of analyte to CS_2 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 vs. µg methyl acetate).
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 concentrations plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.

b. Inject a known amount of analyte or of a standard solution of analyte in CS_2 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. µg analyte recovered.

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

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations to conditions given on page 1458-1. 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, reanalyze, and apply appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE), of methyl acetate 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.
14. Calculate concentration, C, of analyte 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:

This method was validated over the range 343 to 1330 mg/m^3 at 24 °C and 761 mm Hg using 7-liter samples [1]. Breakthrough capacity was 14 mg when sampling dry air containing 1330 mg/m^3. Overall sampling and measurement precision, $\hat{S}_{rT}$, was 0.0547. Desorption efficiency (DE) of methyl acetate from charcoal tubes was 85.7% in the range of 87 to 342 µg per sample [2]. Sample storage stability was evaluated at 203 µg per sample [2]. Samples stored at ambient temperature in the dark had a 91.8% recovery after three days when compared to day 1 samples. Samples stored at 5 °C gave recoveries of 96.4% on day 6 and 90.4% on day 9. Therefore, methyl acetate is stable on charcoal for at least 6 days and up to 9 days, when refrigerated at 5 °C.

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 2, S42, U.S. Dept. of Health, Education, and Welfare, Publ. (NIOSH) 77-157B (1977).
[2] Pendergrass, S.M., Methyl Acetate Method Development (Unpublished report), NIOSH/MRSB, 1990.
[3] Analysis of NIOSH Samples for Methyl Acetate, NIOSH/MRSB/MDS, Sequence #7034, Cincinnati, Ohio (unpublished, 1990).
[4] Beck, S, T. Stock, and L. Whitehead, Improved Efficiency of Desorption of Oxygenated Solvents from Activated Charcoal Using a New Polar Additive to Carbon Disulfide, Appl. Occup. Environ. Hyg. 5(3), 171-177, 1990.

METHOD REVISED BY:

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