KETONES II 1301

TABLE 1 MW: TABLE 1 CAS: Table 1 RTECS: Table 1

METHOD: 1301, Issue 2 **EVALUATION: FULL**
COMPOUNDS (3) and (5): PARTIAL

Issue 1: 15 February 1984
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OSHA/NIOSH/ACGIH: Table 1 **PROPERTIES:** Table 1

COMPOUNDS: (Synonyms in Table 1)	(1) camphor (2) mesityl oxide	(3) 5-methyl-3-heptanone (4) methyl-(n-amyl)-ketone	(5) ethyl butyl ketone

SAMPLING

SAMPLER:	SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)
FLOW RATE:	0.01 to 0.2 L/min
VOL-MIN:	1 L
-MAX:	25 L
SHIPMENT:	routine
SAMPLE STABILITY:	unknown
FIELD BLANKS:	2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	see EVALUATION OF METHOD
BIAS:	see EVALUATION OF METHOD
OVERALL PRECISION ($\hat{S}_{rT}$):	see EVALUATION OF METHOD
ACCURACY:	see EVALUATION OF METHOD

MEASUREMENT

TECHNIQUE:	GAS CHROMATOGRAPHY, FID
ANALYTE:	compounds above
DESORPTION:	1 mL 1% methanol in CS_2; stand in 30 min
INJECTION VOLUME:	5 µL
COLUMN:	stainless steel (3 m x 3-mm ID), 10% FFAP on 80/100 Chromosorb W-AW
TEMPERATURE-INJECTOR:	200 °C
-DETECTOR:	300 °C
-COLUMN:	100 to 200 °C @ 10 °C/min
CARRIER GAS:	N_2 or He, 30 mL/min
CALIBRATION:	standard solutions of analyte in elution solvent
RANGE AND PRECISION:	see EVALUATION OF METHOD
ESTIMATED LOD:	0.05 mg per sample

APPLICABILITY: This method was developed to give better desorption than obtainable with carbon disulfide extraction of the charcoal. This method can be used in paint and resin manufacturing plants.

INTERFERENCES: None reported. Alternate columns, e.g., 4 m 10% SP-2100/0.1% Carbowax 1500 on Supelcoport 100/120 or DB-1 fused silica capillary may be used.

OTHER METHODS: This method combines and replaces Methods S10, S12, S13, S15 and S16 [1].

REAGENTS:

1. Eluent: Carbon disulfide* (chromatographic grade) with 1% (v/v) methanol (chromatographic grade).
2. Analytes, reagent grade.
3. Nitrogen, prepurified.
4. Hydrogen, dry.
5. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, 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 must be less than 3.4 kPa at the sampling flow rate. Tubes are commercially available.
2. Personal sampling pump, 0.02 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1301-1).
4. Vials, 2-mL glass, PTFE-lined crimp caps.
5. Syringe, 10-µL, readable to 0.1 µL.
6. Pipet, 1-mL, with pipet bulb.
7. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = -30 °C); all work done with it must be performed in a fume 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 25 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent 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 five working standards over the range 0.01 to 0.5 mg camphor; and 0.05 to 5 mg of the other analytes per sample.
   a. Add known amounts of analyte to eluent 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. mg analyte).
9. Determine desorption efficiency (DE) at least once for each batch 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 of analyte 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 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 and to conditions given on page 1301-1. 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 CS_2, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of analyte 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 analyte 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:

Laboratory testing with spiked samples and samples collected from atmospheres generated by syringe pump/air dilution and verified by FID continuous monitor [2]. Results were:

Compound	Method [1,2]	Range (mg per sample)	DE[2]-	$\hat{S}_r$	S/A Range (mg/m^3)	S/A Breakthrough[1] (L)	S/A Overall Precision $\hat{S}_rT$	Bias (%)	Accuracy (±%)
Camphor	S10	0.02 to 0.40	0.97	0.018	6 to 25	>48	0.074	0.9	10.5
Mesityl oxide	S12	0.10 to 3.0	0.81	0.014	45 to 210	>48	0.071	7.0	22.8
5-Methyl-3-heptanone	S13	0.15 to 4.0	0.90	0.014	60 to 270	>36	0.10	13.1	31.0
Methyl-(n-amyl)-ketone	S15	0.5 to 10.0	0.82	0.012	200 to 925	>36	0.066	4.9	15.0
Ethyl butyl ketone	S16	0.25 to 7.0	0.94	0.022	100 to 460	>24	0.086	-3.1	26.3

[1] 5% breakthrough, 0.2 L/min at high end of concentration range in dry air.
[2] Averaged over mass range shown.

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2nd. ed., V. 2, S10, S12, S13 and S15, S16, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

[2] Documentation of the NIOSH Validation Tests, S10, S12, S13 and S15, S16, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).

METHOD REVISED BY:

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

TABLE 1. GENERAL INFORMATION

		Exposure Limits, ppm				
Compound (Synonyms) CAS RTECS	Formula (M.W.)	OSHA	NIOSH	ACGIH TLV STEL	mg/m^3/ppm @NTP	
Camphor (CAS #76-22-2) RTECS EX1225000	$C_{10}H_{16}O$ (152.24)	2	2	2 3	6.22	[illegible]
Mesityl oxide (4-methyl-3-penten-2-one) (CAS #141-79-7) RTECS SB4200000	$CH_3COCH=C(CH_3)_2$; $C_6H_{10}O$ (98.15)	25	10	15 25	4.01	[illegible]
5-Methyl-3-heptanone (Ethyl amyl ketone) (CAS #541-85-5) RTECS MJ7350000	$CH_3CH_2COCH_2CH(CH_3)$-CH_2CH_3; $C_8H_{16}O$ (122.22)	25	25	25 --	5.00	[illegible]
Methyl-(n-amyl)-ketone (2-Heptanone) (CAS #110-43-0) RTECS MJ5075000	$CH_3CO(CH_2)_4CH_3$; $C_7H_{14}O$ (114.19)	100	100	50	4.67	[illegible]
Ethyl butyl ketone (3-heptanone) (CAS #106-35-4) RTECS MJ5250000	$CH_3CH_2CO(CH_2)_3CH_3$; $C_7H_{14}O$ (114.19)	50	50	50	4.67	[illegible]

*NOTE: All densities and vapor pressures are at 20 °C unless stated otherwise.