KETONES II 2553

FORMULAS: TABLE 1 MW: TABLE 1 CAS: TABLE 1 RTECS: TABLE 1

METHOD: 2553, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

OSHA : Table 1
NIOSH: Table 1
ACGIH: Table 1

PROPERTIES: Table 1

COMPOUNDS/ SYNONYMS:
(1) 2-Heptanone: Methyl-n-amyl ketone
(2) 3-Heptanone: Ethyl butyl ketone
(3) Mesityl oxide: 4-Methyl-3-penten-2-one
(4) 5-Methyl-3-heptanone: Ethyl amyl ketone
(5) Camphor: 2-Camphanone, Gum Camphor

SAMPLING

SAMPLER: SOLID SORBENT TUBE (Anasorb CMS, 150/75 mg) [1]

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 1 L
-MAX: 25 L

SHIPMENT: Routine

SAMPLE STABILITY: 30 days @ 5°C [1]

BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: Not Determined.

BIAS: Not Determined.

OVERALL PRECISION ($\hat{S}_{r_T}$): Not Determined.

ACCURACY: Not Determined.

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: Table 1

DESORPTION: 1 mL of 2% isopropanol in CS_2 with agitation [1]

INJECTION VOLUME: 1 µL

TEMPERATURE
-INJECTION: 225°C [1]
-DETECTOR: 300°C [1]
-COLUMN: 55°C (3 min hold) to 190°C (8°C/min) [1]

CARRIER GAS: Helium (4.8 mL/min) [1]

COLUMN: Capillary, fused silica, 30-m x 0.32-mm ID; 1.00 µm film crossbond trifluoro-propylmethyl polysiloxane or equivalent [1]

CALIBRATION: Solutions of analytes in desorption solvent

RANGE: See Table 2 [1]

ESTIMATED LOD: See Table 2 [1]

PRECISION ($\hat{S}_r$): See Table 2 [1]

APPLICABILITY: For a 10-L air sample, the working range for 2-heptanone is 0.86 to 24.8 ppm (4.0 to 121 mg/m^3); for 3-heptanone is 0.43 to 12.9 ppm (2.0 to 60.3 mg/m^3); for mesityl oxide is 0.22 to 6.89 ppm (0.9 to 22.6 mg/m^3); for 5-methyl-3-heptanone is 0.21 to 6.29 ppm (1.1 to 33.0 mg/m^3); and for camphor is 0.14 to 4.84 ppm (0.9 to 30.2 mg/m^3) [1].

INTERFERENCES: Any compound having the same retention times as the analytes of interest.

OTHER METHODS: This method was developed as part of an update of NIOSH Method 1301 (Issue 2, 15 August 1994) [2] which combined the NIOSH Methods: S10, S12, S13, S15, and S16 from the 2nd edition of the NIOSH Manual of Analytical Methods [3,4]. Improvements included: lower LOD/LOQ values, improved DE recovery results (at lower levels) by using Anasorb CMS and 2% IPA in CS_2, a 30 day storage stability study, and the replacement of the packed column with a Rtx-200 fused silica capillary column.

REAGENTS:

1. 2-Heptanone, reagent grade (98%).
2. 3-Heptanone, reagent grade (98%).
3. Mesityl oxide, reagent grade (98%).
4. 5-Methyl-3-heptanone, reagent grade (97%).
5. Camphor, reagent grade (99%).
6. Carbon disulfide, low benzene grade.*
7. Isopropanol.
8. Helium, prepurified and filtered.
9. Hydrogen, prepurified and filtered.
10. Air, compressed and filtered.
11. Desorption solvent: 2% isopropanol in carbon disulfide (v/v).
12. DE stock solution: Add known amount of analyte to desorption solvent in 10-mL volumetric flask.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of Anasorb CMS (front = 150 mg; back = 75 mg) separated by a 2-mm urethane plug. A silylated glass wool plug precedes the front section and a 3-mm urethane plug follows the back section. Tubes are commercially available (SKC # 226-121).
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator, and Rtx-200 fused silica capillary column.
4. GC autosampler vials, 2-mL glass, with PTFE-lined crimp caps.
5. Syringes, 10-µL, 25-µL, and 1-mL.
6. Pipets, 3-mL and 5-mL, with pipet bulb.
7. Volumetric flasks, 250-mL and 10-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and a fire/explosion hazard (flash point = -30°C). Isopropanol is flammable. All work should be performed in a ventilated fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately prior to sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at a 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 and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front (include the initial glass wool plug) and back sorbent sections of the sampler in separate vials. Discard the foam plugs.
6. Add 1.0 mL of the 2% isopropanol/carbon disulfide desorption solvent to each vial. Securely attach crimp caps to each vial.
7. Allow to desorb for 30 minutes with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards to cover the analytical range. If necessary, additional standards may be added to extend the calibration curve.
   a. Add known amounts of each analyte to the desorption solvent solution in 10-mL volumetric flasks and dilute to the mark. Mix well.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area versus µg analyte).
9. Determine desorption efficiency (DE) at least once for each lot of Anasorb CMS used for sampling in the calibration range (step 8).
   a. Prepare three tubes at each of five levels plus three media blanks.

b. Inject a known amount of DE stock solution directly onto the front sorbent section of each Anasorb CMS with a microliter syringe.
c. Allow the tubes to air equilibrate for several minutes, then cap the ends of each tube and allow to stand overnight.
d. Desorb (steps 5-7) and analyze together with standards and blanks (steps 11 and 12).
e. Prepare a graph of DE versus µg analyte 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 2553-1. Inject a 1-µL sample aliquot manually using the solvent flush technique or with an autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with solvent, reanalyze and apply the appropriate dilution factor in the calculations.
12. Measure peak areas.

CALCULATIONS:

13. Determine the mass, µg (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):

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

NOTE: µg/L= mg/m^3

EVALUATION OF METHOD:

This method updates NMAM 1301, which was identified as a problematic gas chromatographic method from a survey of external users of the NIOSH Manual of Analytical Methods. This new method, by use of capillary column chromatography coupled with an improved solid sorbent sampler and modified desorption solvent, resulted in improvements in LOD/LOQ, sample recovery and storage stability compared to NMAM 1301. The average DE recovery was improved for all analytes at levels lower than those reported in NMAM 1301, ranging from 95% for mesityl oxide to 100% for 3-heptanone. All samples were stable for 30 days with recoveries ranging from 94% for camphor to 99% for 2-heptanone. The complete summary of results is in Table 2.

REFERENCES:

[1] Pendergrass SM [1999]. Ketones II Method Development Backup Data Report, unpublished data, NIOSH/DART.
[2] NIOSH [1994]. Ketones II: Method 1301. In: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods, 4th ed. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.

[3] NIOSH [1977]. Methods S10, S12, S13, S15, and S16. NIOSH Manual of Analytical Methods, 2nd, ed., V. 2. Cincinnati, OH: National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No. 77-157-B.

[4] NIOSH [1977]. Documentation of NIOSH Validation Tests, S10, S12, S13, S15, and S16. Cincinnati, OH: National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No. 77-185.

METHOD WRITTEN BY:

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TABLE 1. GENERAL INFORMATION

Compound/ (Synonyms) CAS # RTECS	Formula (M.W.)	Exposure Limits			mg/m^3= 1 ppm	Properties
		NIOSH REL (ppm)	OSHA PEL (ppm)	ACGIH TLV (ppm)	@ NTP	
Methyl-n-amyl-ketone (2-Heptanone) (CAS # 110-43-0) RTECS MJ5075000	$C_7H_{14}O$ (114.19)	100	100	50	4.67	liquid; d 0.820 g/mL; BP 151 °C; VP 0.27 kPa (2 mm Hg)
Ethyl butyl ketone (3-Heptanone) (CAS # 106-35-4) RTECS MJ5250000	$C_7H_{14}O$ (114.19)	50	50	50	4.67	liquid; d 0.818 g/mL; BP 148 °C; VP 0.53 kPa (4 mm Hg)
Mesityl oxide (4-methyl-3-penten-2-one) (CAS # 141-79-7) RTECS SB4200000	$C_6H_{10}O$ (98.15)	10	25	15	4.01	liquid; d 0.822 g/mL; BP 129 °C; VP 1.1 kPa (8 mm Hg)
5-Methyl-3-heptanone (Ethyl amyl ketone) (CAS # 541-85-5) RTECS MJ7350000	$C_8H_{16}O$ (128.21)	25	25	25	5.00	liquid; d 0.822 g/mL; BP 159 °C; VP 0.27 kPa (2 mm Hg)
Camphor (CAS # 76-22-2) RTECS EX1225000	$C_{10}H_{16}O$ (152.24)	2	2	2	6.22	solid; spec. gr. 0.992 @ 25 °C; MP 174 °C; VP 0.024 kPa (0.18 mm Hg, 1470 mg/m3); sublimes

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

TABLE 2. ANALYTICAL RESULTS [1]

Analyte	LOD (µg)	Precision (S_r)	Range (µg)	DE (Avg)	Storage Stability (at 5 °C after 30 Days)
2-heptanone	0.5	0.025	40-1206	0.970	0.994
3-heptanone	0.7	0.031	20-603	1.004	0.984
mesityl oxide	0.3	0.014	9-276	0.950	0.993
5-methyl-3-heptanone	0.7	0.032	11-330	0.987	0.990
camphor	0.7	0.043	9-302	0.970	0.939