Formula: Table 1   MW: Table 1   CAS: Table 1   RTECS: Table 1

METHOD: 2027, Issue 1   **EVALUATION:** FULL   **Issue 1:** 19 July 2016

OSHA: Table 2
NIOSH: Table 2
Other OELs: Refs [1,2}

                                                PROPERTIES: Table 1

SYNONYMS: See individual compounds in Table 1

SAMPLING	MEASUREMENT
SAMPLER: SOLID SORBENT TUBE (silica gel, 500 mg/1000 mg); min. of 2 field blanks per set	**TECHNIQUE:** gas chromatography, FID
FLOW RATE: 0.05 – 0.1 l/min	**ANALYTE:** see Table 1
VOL-MIN: 2 L **-MAX:** 10 L	**DESORPTION:** ternary mixture of CH_2Cl_2/methanol/water (65:33:2)
SHIPMENT: routine	**INJECTION VOLUME:** 1 µL
SAMPLE STABILITY: Stable at least 28 days @ 20 °C [3,4]	**COLUMNS (IN PARALLEL):** 60 m low-polarity fused silica, ID 0.25 mm and film thickness 0.25 µm; and 60 m high-polarity polyethylene glycol, ID 0.25 mm and film thickness 0.25 µm.

ACCURACY	**TEMPERATURE:**
	  INJECTION: 250 °C
	  DETECTOR: 250 °C
	  COLUMN: 50 °C (11 min) to 150 °C (4 °C/min)

RANGE STUDIED: Table 3	
BIAS: Negligible	**CALIBRATION:** solution of analytes in desorption solvent
OVERALL PRECISION ($\widehat{S}_{rT}$): Table 3	**RANGE:** Table 3
UNCERTAINTY: Table 3	**ESTIMATED LOD:** Table 3
	PRECISION ($\bar{S}_r$): Table 3

APPLICABILITY: 2-2400 mg/m^3 for air sample vol. up to 10 L.

INTERFERENCES: Organic compounds with similar retention times as the analytes of interest may interfere.

OTHER METHODS: NIOSH 2553 and 2555 [5] are partially validated methods for the determination of ketones using CS_2 for desorption.   OSHA methods based on sorbent tube sampling, solvent desorption and GC/FID analysis have been promulgated for several ketones [6].

REAGENTS:

1. Acetone, >99.8%, analytical grade.
2. 2-Butanone, >99.8%, analytical grade.
3. Cyclohexanone, >99.5%, analytical grade.
4. Cyclopentanone, >99.0% purity.
5. 2-Hexanone, >98 % purity.
6. 4-Methyl -2-pentanone, >99.0%, analytical grade.
7. 2,6-Dimethyl-4-heptanone, ≥99%, analytical grade.*
8. Methanol, >99.9 %, analytical grade.
9. Dichloromethane, analytical grade.
10. Water, ultrapure, ≥18.2 MΩ-cm resistivity.
11. 2-Methylheptane, chromatographic quality.
12. n-Undecane, chromatographic quality.
13. Air, prepurified and filtered.
14. Hydrogen, prepurified and filtered.
15. Helium, prepurified and filtered.
16. Nitrogen, prepurified and filtered.
17. Internal standard solution: Mix 500 μL of n-undecane and 500 μL 2-methylheptane.
18. Ternary mixture: Mix 650 mL dichloromethane, 330 mL methanol and 20 mL water in a 1000-mL- volumetric flask.

    *NOTE: Each new bottle must be analyzed immediately after opening to accurately measure the concentration.

EQUIPMENT

1. Sampler: glass tube, length 125 mm, 7-mm OD, 5-mm ID, flame sealed ends, containing two sections of silica gel (front 500 mg, back 1000 mg) separated by a 2-mm ceramic plug. The ceramic plug is in front and a silylated glass wool plug follows the back section. Tubes are commercially available.
2. Personal sampling pump capable of producing flow rates between 0.05 to 0.1 L/min, with flexible connecting tubing.
3. Gas chromatograph, equipped with split injector (capillary flow split), two separation columns with separate FIDs, and data processing unit.
4. Fused silica capillary columns (for parallel separation): 60 m low-polarity fused silica, 0.25 mm ID and film thickness 0.25 μm. 60 m high-polarity polyethylene glycol, 0.25 mm ID and film thickness 0.25 μm.
5. Vessels, 15-mL, glass, with screw caps and PTFE septum.
6. Volumetric flasks, 5, 50 and 1000 mL.
7. Syringes, glass, 10 to 500 μL.
8. Pipettes, glass, 5 and 10 mL.
9. Bottles, polyethylene, 100 mL.
10. Syringes, polypropylene, 2 mL.
11. Syringe filter cartridges, with 0.45-μm pore size polytetrafluoroethylene (PTFE) membrane filters.
12. Micro-syringes, 50 μL, with 60 mm x 0.6 mm needles.
13. Auto-sampler vials, with PTFE septum, 1.5 mL capacity.

SPECIAL PRECAUTIONS: Analytes should be handled in a fume hood. Wear protective clothing and eyewear. Dichloromethane is a potential occupational carcinogen [12].

SAMPLING, SAMPLE TRANSPORT AND STORAGE

1. Calibrate each personal sampling pump with a representative sampler in the line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to the personal sampling pump with flexible tubing.
3. Sample at an accurate known flow rate between 0.05 and 0.1 L/min for a total sample size of not more than 10 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.
5. Analyze samples within 28 days of receipt.

SAMPLE PREPARATION

6. Place the entire contents of the sorbent tube in a 15-mL screw-cap-vessel.
7. Add 5 mL ternary mixture and securely cap the vessel immediately.
8. Allow to stand at least 18 hours with occasional agitation.
9. Add 2.5 µl of internal standard solution.
10. Take sample solution with a 2-ml-polypropylene syringe and filter through a PTFE filter into an auto sampler vial.

CALIBRATION AND QUALITY CONTROL

11. Calibrate with at least six standards for each substance in the range given in Table 3.
    a. Place the contents of a sorbent tube in a 15-mL screw-cap-vessel and add 5 mL ternary mixture solvent.
    b. Add known amount of analyte.
    c. Store at room temperature for 18 hours and then add 2.5 µL of internal standard solution.
       Note: Internal standards are used to aid in identification of retention times of unknowns.
    d. Analyze and prepare a calibration graph for the two columns separately (peak areas of analyte and internal standard (nonpolar column:2-methylheptane; polar column: n-undecane) vs concentration).
12. Prepare each day at least three quality control solutions in the same manner and range and analyze together with samples and blanks.
13. Determine desorption efficiency (DE) at least once for each batch of sorbent used for sampling in the calibration range.
    a. Prepare three tubes at each of five levels plus three media blanks.
    b. Inject a known amount of analyte solution directly onto the front sorbent section while drawing purified air through the tube.
    c. Draw approximately 10 L air through the sorbent tube, then cap the ends of each tube and allow to stand overnight.
    d. Desorb (steps 6 to 9) and analyze together with quality control samples and blanks (steps 14 to 15).
14. Analyze a minimum of three quality control spikes and three analyst spikes to insure that the calibration graph and the DE graph are in control.

MEASUREMENT

15. Set gas chromatograph parameters to manufacturer's recommendations and to conditions give on Page 1. Inject a 1-µL sample aliquot into the gas chromatograph.
    NOTE: If the peak area exceeds the linear calibration range, dilute with desorption solvent, reanalyze and apply the appropriate dilution factor in calculations.
16. Measure analyte peak areas at applicable retention times (Table 4).

CALCULATIONS:

17. Calculate the mass concentration of each analyte, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{(C_1 \cdot V_1 \cdot F_d) - (C_0 \cdot V_0)}{V \cdot \eta}$$

where:

C_0 = mean concentration, in mg/L, of analyte in the field blank test solutions;

C_1 = concentration, in mg/L, of analyte in the sample test solution;

V = volume, in liters, of the air sample;

V_0 = volume, in mL, of the field blank test solutions;

V_1 = volume, in mL, of the sample test solutions;

F_d = dilution factor for each sample test solution;

η = desorption efficiency.

EVALUATION OF METHOD:

The method recovery, at levels from the LOQ to at least 2 times the REL, was determined for each analyte by carrying out sampling and analytical experiments at a dynamic test gas facility [3,4]. Experiments were conducted at four concentration levels of each analyte and for relative humidities of 20%, 50% and 80% at 20 °C. All analytes exhibited method recovery >95 % at the levels evaluated (see Table 3). At low relative humidity (<30%) the recoveries of cyclohexanone, cyclopentanone and 2-hexanone were reduced without water in the extraction solution. Use of a small content of water (2%) during extraction avoids losses based on low humidity during sampling. Each analyte, at levels below and above the REL, was evaluated for its storage stability [3,4]. The samples were prepared by sampling at a dynamic test gas device at a relative humidity of 50% (20 °C). The samples were then stored at room temperature for four weeks. All analytes demonstrated acceptable recoveries (>90%) after 28 days of storage [3]. The performance of the method was separately verified in independent laboratories [4,13].

REFERENCES:

[1]   American Conference of Governmental Industrial Hygienists (ACGIH), Threshold Limit Values for Chemical Substances and Physical Agents & Biological Exposure Indices. ACGIH: Cincinnati (2014); updated annually.

[2]   Institut für Arbeitsschutz der Deutschen Gesetzlichen Unfallversicherung (IFA), GESTIS – Database on International Limit Values for Hazardous Substances (German Social Accident Insurances). IFA: Sankt Augustin, Germany (2014); http://www.dguv.de/dguv/ifa/Gefahrstoffdatenbanken/GESTIS-Internationale-Grenzwerte-für-chemische-Substanzen-limit-values-for-chemical-agents/index-2.jsp.

[3]   Breuer, D.: Ketones, IFA Working Folder, Sheet No. 7708; Institute for Occupational Safety and Health of the German Social Accident Insurances. Erich Schmidt Verlag: Bielefeld, Germany (2005).

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[6]   Occupational Safety and Health Administration (OSHA), Sampling and Analytical Methods (Method nos. 1, 16, 69, PV2031). OSHA Salt Lake Technical Center, Sandy, UT; www.osha.gov/dts/sltc/methods/index.html (accessed May 2015).

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[9]   NIOSH Pocket Guide to Chemical Hazards, DHHS (NIOSH), Cincinnati; www.cdc.gov/niosh/npg; (accessed June 2015).

[10]   EN 482: Workplace exposure – General requirements for the performance of procedures for the measurement of chemical agents. CEN: Brussels (2012).

[11]   EN 1076: Workplace exposure – Procedures for measuring gases and vapours using pumped samplers – Requirements and test methods. CEN: Brussels (2009).

[12]   NIOSH [1986]. Current intelligence bulletin 46: Methylene Chloride, U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 86-114.

[13]   Bureau Veritas North America [2016]. Ketones User Check Sequence 11762-CA (unpublished report). BVNA: Novi, MI, 3 Feb. 2016.

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Table 1. Synonyms, Formulae, Molecular weights, Properties, CAS#, RTECS

Compound/ synonyms CAS# RTECS	Empirical formula	Molecular weight	Boiling point[a] (°C)	Melting point[a] (°C)	Vapor pressure @ 20°C (kPa)[a]	Vapor pressure @ 20°C (mm Hg)[a]	Density @ 20 °C[a] (g/mL)
Acetone / 2-Propanone 67-64-1 AL3150000	C_3H_6O	58.08	56.2	-95	24.6	184	0.79
2-Butanone Methylethyl ketone 78-93-3 EL6475000	C_4H_8O	72.11	79.6	-86	10.5	78.8	0.81
Cyclohexanone / Cyclohexyl ketone 108-94-1 GW1050000	$C_6H_{10}O$	98.14	155.6	-26	0.455	3.41	0.95
Cyclopentanone / Ketocyclopentane 120-92-3 GY4725000	C_5H_8O	84.12	130.6	-58.2	1.14	8.55	0.95
2-Hexanone / Butyl methyl ketone 591-78-6 MP1400000	$C_6H_{12}O$	100.16	127.2	-56	1.28	9.60	0.81
4-Methyl-2-pentanone / MIBK/Methyl isobutyl ketone 108-10-1 SA9275000	$C_6H_{12}O$	100.16	116.8	-80.3	1.88	14.1	0.80
2,6-Dimethyl-4-heptanone/ Diisobutyl ketone 108-83-8 MJ5775000	$C_9H_{18}O$	142.24	168	-46	0.23[b]	1.7[b]	0.81

[a] Physical and chemical property data from GESTIS substance database, except where noted otherwise [7]

[b] Vapor pressure for 2,6-dimethyl-4-heptanone [8]

Table 2. Occupational exposure limits, ppm [9]

Substance	OSHA PELs	NIOSH RELs		
	TWA	TWA	STEL	mg/m³ per ppm
Acetone	1000	250		2.41
2-Butanone	200	200	300	2.95
Cyclohexanone	50	25		4.08
Cyclopentanone				3.50
2-Hexanone	100	1		4.16
4-Methyl-2-pentanone	100	50	75	4.16
2,6-Dimethyl4-heptanone	50	25		5.91

Table 3. Measurement range, precision, uncertainty and recovery (N=6)

Substance	LOD (mg/sample)	LOQ (mg/sample)	Measurement Range (mg/sample)	Precision (S_r)	U^a (%)	Mean Recovery (DE)
Acetone	0.006	0.02	0.02 – 26	0.0083-0.024	11 – 12	0.97
2-Butanone	0.006	0.02	0.02 – 14	0.0078-0.024	11 – 12	0.98
Cyclohexanone	0.006	0.02	0.02 – 12	0.010-0.022	12 – 13	0.97
Cyclopentanone	0.006	0.02	0.02 – 2	0.008-0.023	11 – 12	0.95
2-Hexanone	0.006	0.02	0.02 – 0.47	0.018-0.022	11 – 12	0.98
4-Methyl2-pentanone	0.006	0.02	0.02 – 2	0.011-0.023	11 – 12	0.99
2,6-Dimethyl-4-heptanone	0.005	0.02	0.02 – 5	0.006-0.023	11 – 12	1.01

[a] Expanded uncertainty calculated in accordance with EN 482 [10] and EN 1076 [11]

Table 4. Approximate retention times on polar and nonpolar separation columns

Substance	Approximate retention time non-polar column (min)	Approximate retention time polar column (min)
Acetone	6.5	7.1
2-Butanone	9.2	[a]
Cyclohexanone	25.5	25.9
Cyclopentanone	20.3	21.2
2-Hexanone	20.0	17.3
4-Methyl-2-pentanone	17.2	13.8
2,6-Dimethyl4-heptanone	28.4	22.0

[a] The retention time of butanone is equal to that of the solvent on the polar column.