KETONES I 2555

Formulas: See Table 1 MW: Table 1 CAS: Table 1 RTECS: Table 1

METHOD: 2555, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

OSHA : See Table 2
NIOSH: See Table 2
ACGIH: See Table 2

PROPERTIES: See Table 3

SYNONYMS: (1) Acetone: dimethyl ketone, ketone propane, 2-propanone.
(2) Methyl ethyl ketone: methyl acetone, 2-butanone, MEK.
(3) 2-Pentanone: ethyl acetone, methyl propyl ketone, MPK.
(4) Methyl isobutyl ketone: hexone, 4-methyl-2-pentanone, MIBK.
(5) 2-Hexanone: methyl n-butyl ketone, methyl butyl ketone, MBK.
(6) Di-isobutyl ketone: sym-diisopropyl acetone, 2,6-dimethyl-4-heptanone, isovalerone, valerone, DIBK.
(7) Cyclohexanone: anone, cyclohexyl ketone, pimelic ketone.

SAMPLING

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

FLOW RATE: 0.01 to 0.2 L/min

	Acetone	Others
VOL-MIN:	0.5 L	1 L
-MAX:	3.0 L	10 L

SHIPMENT: Refrigerate samples.

SAMPLE STABILITY: All analytes 30 days @ 5°C

BLANKS: 2 to 10 field blanks per set.

ACCURACY

RANGE STUDIED: Not studied.

BIAS: Not determined.

OVERALL PRECISION ($\hat{S}_{r,T}$): Not determined.

ACCURACY: Not determined.

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: See Table 1

DESORPTION: 1 mL CS_2 for 30 minutes

INJECTION VOLUME: 1 µL

TEMPERATURE
-INJECTION: 250°C
-DETECTOR: 300°C
-COLUMN: 40°C (1 min) to 200°C (8°C/min)

CARRIER GAS: Helium, 1mL/min

COLUMN: Capillary, fused silica, 30 m x 0.53-mm ID, 3.00-µm film crossbonded® 35% diphenyl - 65% dimethyl polysiloxane

CALIBRATION: Standard solutions of analytes in CS_2

RANGE: See Table 4.

ESTIMATED LOD: See Table 4.

PRECISION ($\hat{S}_r$): See Table 4.

APPLICABILITY: For three-liter sample, the working range for acetone was 0.378 to 41.4 ppm (0.92 to 100.2 mg/m^3). For a 10-L sample the working range for methyl ethyl ketone was 0.092 to 10.2 ppm (0.275 to 30.5 mg/m^3), for 2-pentanone was 0.077 to 8.67 ppm (0.276 to 31.1 mg/m^3), for methyl isobutyl ketone was 0.066 to 6.83 ppm (0.275 to 28.5 mg/m^3), for 2-hexanone was 0.066 to 7.45 ppm (0.275 to 31.1 mg/m^3), for diisobutyl ketone was 0.052 to 5.07 ppm (0.308 to 30.1 mg/m^3), and for cyclohexanone was 0.075 to 9.79 ppm (0.300 to 39.2 mg/m^3).

INTERFERENCES: Any compounds with similar retention times as the analytes of interest. Alternate columns include Rtx-1 and Rtx-5 or equivalent capillary columns.

OTHER METHODS: This method was developed as part of an update for NMAM 1300, issue 2 (dated 15 August 1994) [1]. NMAM 1300, issue 2 was based on NIOSH Manual of Analytical Methods, 2nd edition methods S1, S18, S19, S20, S178, and S358. This method includes: lower LOD/LOQ values for each analyte, improved DE recovery results for each analyte (at lower levels), inclusion of methyl ethyl ketone and methyl isobutyl ketone in the method by the use of a different sorbent tube (Anasorb CMS), a 30-day storage stability study, and replacement of the packed column with a Rtx-35 fused silica capillary column.

REAGENTS:

1. Carbon disulfide (GC grade).*
2. Analytes, reagent grade.*
3. Helium, prepurified and filtered.
4. Hydrogen, prepurified and filtered.
5. Air, compressed, purified, filtered.
6. Calibration stock solution: Add known amounts of analytes to carbon disulfide 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 with plastic caps, containing two sections of Anasorb CMS (150 mg/ 75 mg) separated by a 2-mm urethane plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, connected with flexible tubing.
3. Gas chromatograph equipped with FID, integrator and capillary column (page 2555-1).
4. Autosampler vials, 2-mL, glass, with PTFE-lined crimp caps.
5. Syringes, 10-µL, 25-µL, and 1-mL.
6. Pipettes, 3-mL and 5-mL.
7. Volumetric flasks, 10-mL.
8. Bagged refrigerant, Blue-ice or equivalent.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic, explosive, and a fire hazard (FP = -30°C). Work with carbon disulfide in a well ventilated hood. Analytes should be handled in a fume hood. Use protective clothing and eyewear.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampling tube immediately before sampling. Attach sampling tube 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 3 L for acetone and 10 L for all other analytes.
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 tube in separate vials. Place the glass wool preceding the front section into the vial containing the front sorbent section. Discard the urethane foam plugs.
6. Add 1.0 mL of carbon disulfide into each vial. Attach crimp caps to each vial.
7. Allow to stand for 30 minutes with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards from below the LOD to 10 times the LOQ. If necessary, additional standards may be added to extend the calibration curve.
   a. Add known amounts of analytes to carbon disulfide solvent in a 10-mL volumetric flask and dilute to the mark. Prepare additional standards by serial dilution in 10-mL volumetric flasks.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs µg analyte).
9. Determine desorption efficiency (DE) at least once for each lot of Anasorb CMS used for sampling in the calibration ranges (step 8).
   a. Prepare three tubes at each of five levels plus three media blanks.

b. Inject a known amount (5 to 25 µL) of DE stock solution directly onto the front sorbent section of each Anasorb CMS tube 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 vs µg analyte recovered.

10. Analyze a minimum of 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 2555-1. 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 development was based upon a prioritized list of problematic gas chromatographic methods identified in a survey of external users of the NIOSH Manual of Analytical Methods. Method improvements include the use of capillary column chromatography, lower LOD/LOQ values, improved desorption efficiency (DE) at lower quantitative levels, and a storage stability study conducted at 7, 14, and 30 days. The method also incorporates the use of an improved solid sorbent tube sampler (Anasorb CMS) resulting in improved sample recovery and allowing methyl ethyl ketone and methyl isobutyl ketone to be included in the method without loss of sample recovered from the sorbent tube. Table 4 lists the method evaluation data, the LOD/LOQ values, the range of measurements, and the precisions for each analyte. [2]

The average DE determined for acetone was 98.2% (RSD = 0.019), for methyl ethyl ketone was 98.6% (RSD = 0.017), for 2-pentanone was 99.3% (RSD = 0.011), for methyl isobutyl ketone was 96.4% (RSD = 0.011), for 2-hexanone was 100.6% (RSD = 0.013), for diisobutyl ketone was 102.4% (RSD = 0.013), and for cyclohexanone was 95.4% (RSD = 0.015).

The average 30-day storage stability recovery for acetone was 100.7% (RSD = 0.017), for methyl ethyl ketone was 101.7% (RSD = 0.018), for 2-pentanone was 101.5% (RSD = 0.028), for methyl isobutyl ketone was 103.8% (RSD = 0.018), for 2-hexanone was 101.4% (RSD = 0.029), for diisobutyl ketone was 103.5% (RSD = 0.019), and for cyclohexanone was 87.4% (RSD = 0.009).

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 4th ed., V. 2, U.S. Dept. of Health and Human Services, Publ. (NIOSH) 94-113 (1994).
[2] Pendergrass SM [1998]. Backup data for Ketones I, NIOSH Method 2555, Issue 1. Cincinnati, Oh: Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, (unpublished, February).

METHOD WRITTEN BY:

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TABLE 1. GENERAL INFORMATION

Analyte	Formula	MW	CAS #	RTECS #
Acetone	$(CH_3)_2CO$	58.1	67-64-1	AL3150000
MEK	$CH_3COCH_2CH_3$	72.1	78-93-3	EL6475000
2-Pentanone	$CH_3CO(CH_2)_2CH_3$	86.1	107-87-9	SA7875000
MIBK	$CH_3COCH_2CH(CH_3)_2$	100.2	108-10-1	SA9275000
2-Hexanone	$CH_3CO(CH_2)_3CH_3$	100.2	591-78-6	MP1400000
Diisobutyl ketone	$[(CH_3)_2CHCH_2]_2CO$	142.3	108-83-8	MJ5775000
Cyclohexanone	$C_6H_{10}O$	98.2	108-94-1	GW1050000

TABLE 2. ANALYTE EXPOSURE LIMITS

Analyte	OSHA PEL (ppm)	NIOSH REL (ppm)	ACGIH TLV (ppm)	Conversion ppm to mg/m^3
Acetone	1000	250	500	1 ppm = 2.42 mg/m^3
MEK	200	200	200	1 ppm = 3.00 mg/m^3
2-Pentanone	200	150	200	1 ppm = 3.58 mg/m^3
MIBK	100	50	50	1 ppm = 4.17 mg/m^3
2-Hexanone	100	1	5	1 ppm = 4.17 mg/m^3
Diisobutyl ketone	50	25	25	1 ppm = 5.92 mg/m^3
Cyclohexanone	50	25	25 (A3 - unclassified carcinogen)	1 ppm = 4.00 mg/m^3

TABLE 3. PHYSICAL PROPERTIES.

Analyte	State	Density @ 20°C (g/mL)	BP (°C)	Vapor Pressure (@ 20°C) kPa(mm Hg)
Acetone	liquid	0.7915	56.2	35.5 (266)
MEK	liquid	0.8050	79.6	13.0 (100)
2-Pentanone	liquid	0.8120	101.7	3.6 (27)
MIBK	liquid	0.8042	115.8	2.0 (15)
2-Hexanone	liquid	0.8120	127.2	0.4 (3)
Diisobutyl ketone	liquid	0.8089	168.2	0.23 (1.7)
Cyclohexanone	liquid	0.9470	156.7	0.3 (2)

TABLE 4. METHOD EVALUATION

Analyte	LOD (µg/sample)	LOQ (µg/sample)	Range (µg/sample)	Precision (S_r)
Acetone	0.9	2.7	2.7 - 295.0	0.021
Methyl Ethyl Ketone	0.9	2.7	2.7 - 300.0	0.008
2-Pentanone	0.9	2.7	2.7 - 305.0	0.009
Methyl Isobutyl Ketone	0.9	2.7	2.7 - 280.0	0.013
2-Hexanone	0.9	2.7	2.7 - 305.0	0.010
Diisobutyl Ketone	1.0	3.0	3.0 - 295.0	0.010
Cyclohexanone	1.0	3.0	3.0 - 273.0	0.006