$CH_3C_6H_9(=0)$ (3 isomers) MW: 112.17 CAS: 1331-22-2 RTECS: GW1575000

METHOD: 2521, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : 100 ppm (skin) (2-methyl isomer)
NIOSH: 50 ppm (skin); STEL 75 ppm (2-methyl isomer)
(1 ppm = 4.59 mg/m^3 @ NTP)
ACGIH: 50 ppm (skin); STEL 75 ppm (2-methyl isomer)
(1 ppm = 4.59 mg/m^3 @ NTP)

PROPERTIES:

Isomer	BP, °C	d, g/mL @ 20 °C
2-$CH_3C_6H_9O$	165	0.925
3-$CH_3C_6H_9O$	169	0.914
4-$CH_3C_6H_9O$	170	0.914

SYNONYMS: Isomers: 2-methylcyclohexanone; CAS #583-60-8.
3-methylcyclohexanone; CAS #591-24-2.
4-methylcyclohexanone; CAS #589-92-4.
Mixture of isomers: CAS #1331-22-2.

SAMPLING

SAMPLER: SOLID SORBENT TUBE (Porapak Q, 150 mg/75 mg)

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 1 L @ 460 mg/m^3
-MAX: 6 L

SHIPMENT: routine

SAMPLE STABILITY: ≥ 7 days @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 213 to 852 mg/m^3 [1] (3-L samples)

BIAS: 0.69%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.057 [1]

ACCURACY: ± 11.35%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: 3- and 4-methylcyclohexanone

DESORPTION: 1 mL acetone; stand 15 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 200 °C
-DETECTOR: 260 °C
-COLUMN: 190 °C

CARRIER GAS: N_2, 30 mL/min

COLUMN: stainless steel, 1.2 m x 3-mm OD, packed with 50/80 mesh Porapak Q

CALIBRATION: standard solutions of 3- and 4- methylcyclohexanone isomers in acetone

RANGE: 0.5 to 4 mg per sample

ESTIMATED LOD: 0.09 mg [1]

PRECISION ($\hat{S}_r$): 0.041 @ 0.7 to 2.9 mg per sample [1]

APPLICABILITY: The working range is 100 to 800 mg/m^3 (20 to 170 ppm) for a 5-L air sample. This method was developed for the 3- and 4-methylcyclohexanones. 2-Methylcyclohexanone is not of major commercial importance and has not been test ed with this method. The use of a capillary column would give better sensitivity; however, all the isomers may not elute as a single peak.

INTERFERENCES: None reported.

OTHER METHODS: This revises Method S375 [2].

REAGENTS:

1. Acetone, reagent grade.*
2. Analytes: 3-methylcyclohexanone* and 4-methylcyclohexanone*, reagent grade.
3. n-Hexane, chromatographic quality.*
4. Calibration stock solution, 45.7 mg/mL. Dilute 457 mg (0.5 mL at 20 °C) of a 50/50 mixture of 3- and 4-methylcyclohexanone to 10 mL with acetone.
5. Desorption efficiency (DE) stock solution, 274 mg/mL. Dilute 2.74 g (3.0 mL at 20 °C) of a 50/50 mixture of 3- and 4-methylcyclohexanone to 10 mL with hexane.
6. Nitrogen, purified.
7. Hydrogen, prepurified.
8. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 8.5 cm long, 6-mm OD, 4-mm ID; containing two sections of 50/80 mesh Porapak Q (front = 150 mg; back = 75 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and follows the back section. Flame-sealed ends with plastic caps. Pressure drop across the tube at 0.05 L/min airflow must be less than 1.4 kPa. Tubes are commercially available (e.g. SKC Inc. Cat No. ST 226-115).
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 2521-1).
4. Vials, glass, 2-mL, PTFE-lined caps.
5. Syringes, 10-µL, readable to 0.1 µL, and 25-, 100-, 300-, and 500-µL.
6. Pipet, 1.0-mL, with pipet bulb.
7. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Acetone, methylcyclohexanone, and n-hexane are highly flammable. All work should be performed in a well-ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Remove the end caps from 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 to 0.05 L/min for a total sample size of 1 to 6 L.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL acetone to each vial. Attach cap to each vial and shake vigorously.
7. Allow to stand 15 min. Analyze within one day after desorption.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.1 to 4 mg methylcyclohexanone per sample.
   a. Add known amounts of calibration stock solution to acetone 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 methylcyclohexanone).

9. Determine desorption efficiency (DE) at least once for each lot of Porapak Q 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 (1 to 20 µL) of DE stock solution 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 methylcyclohexanone 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 2521-1. Inject a 5-µL sample aliquot manually using solvent flush technique. Do not use an autosampler because of possible plugging of the syringe needle with Porapak Q.
    NOTE: If peak area is above the linear range of the working standards, dilute with acetone, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area. A retention time of ca. 9 min is expected under these conditions. Acetone elutes before the single peak observed for the methylcyclohexanone isomers.

CALCULATIONS:

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

Method S375 was issued on February 18, 1977 [2]. The precision and accuracy were determined by analyzing generated atmospheres of 50/50 mixtures of 3- and 4-methylcyclohexanone containing 213, 426, and 852 mg/m^3 at 22 °C and 759 mm Hg using 3-L samples [1,3]. The concentration of methylcyclohexanone was determined using the rate of delivery of a syringe drive system and the flow rates of the dilution air. The stability of the concentrations was monitored with a total hydrocarbon analyzer; no bias was found. Storage stability was determined to be at least seven days at room temperature. Breakthrough of the front section of the Porapak Q tube was not observed after sampling 8.1 L of a test atmosphere containing 852 mg/m^3 at ≥ 80% RH for 185 min at 0.044 L/min. Desorption efficiencies for samples spiked with methylcyclohexanone in the range 0.73 to 2.93 mg per sample were 0.91 to 0.94.

REFERENCES:

[1] Backup Data Report for Methylcyclohexanone, S375, available as "Ten NIOSH Analytical Methods, Set 2," Order No. PB 271-464 from NTIS, Springfield, VA 22161.

[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 4, S375, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-157 (1978).
[3] NIOSH Research Report - Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY:

Julie R. Okenfuss, NIOSH/DPSE: S375 originally validated under NIOSH Contract 210-76-0123.