

ALCOHOL AND KETONE MIXTURES BY GC

UOP Method 537-91

SCOPE

This gas chromatographic method is for determining the composition of overhead stream samples from the production of UOP inhibitors. These samples typically consist of a ketone, the corresponding alcohol and other impurities. The ketone and alcohol pairs separated by this method are: methyl hexyl ketone-methyl hexyl carbinol (MHK-MHC), methyl isoamyl ketone-methyl isoamyl carbinol (MIAK-MIAC), ethyl amyl ketone-ethyl amyl carbinol (EAK-EAC), methyl ethyl ketone-methyl ethyl carbinol (MEK-MEC), and methyl isobutyl ketone-methyl isobutyl carbinol (MIBK-MIBC). Other sample components or group classifications may include light ends, unknowns, water, xylenes and low boiling intermediates. The lower limit of detection for a compound or group is 0.1 mass-%.

OUTLINE OF METHOD

All of the alcohol-ketone pairs referred to in this method cannot be separated on a single chromatographic column and, therefore, 2 different columns are required. Column 1 is capable of separating MHK-MHC, MIAK-MIAC and EAK-EAC; Column 2 separates MEK-MEC and MIBK-MIBC. The column chosen for an analysis depends on the specific ketone-alcohol in the sample.

For convenience, the 2 wide-bore fused silica capillary columns are installed in a dual column chromatograph and connected to each side of a thermal conductivity detector (see *NOTE*). The sample to be analyzed is injected into the appropriate column and the chromatographic separation is made. The mass-% composition of the sample is obtained by the internal normalization technique, wherein the peak areas are first corrected for differences in response and then normalized to 100%.

APPARATUS

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Balance, readability 0.1-mg

Chromatographic columns

Column 1: 30 m of 0.53-mm ID fused silica capillary, internally coated to a film thickness of 1.0 μm with cross-linked Carbowax 20M, Restek, Cat. No. 10655

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UOP Methods are available through ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken PA 19428-2959, United States. The Methods may be obtained through the ASTM website, www.astm.org, or by contacting Customer Service at service@astm.org, 610.832.9555 FAX, or 610.832.9585 PHONE.

Column 2: 30 m of 0.53-mm ID fused silica capillary, internally coated to a film thickness of 3.0 μm with 14% cyanopropylphenyl-86% methyl polysiloxane (RTx-1701), Restek, Cat. No. 12085 (see NOTE)

Gas chromatograph, temperature programmable, built for dual wide-bore capillary column chromatography, dual injection ports with glass liners, a capillary makeup adapter fitted into the detector column inlet, and equipped with a thermal conductivity detector suitable for the wide-bore capillary column that will give a minimum peak height response of 140- μV for 0.1 mass-% MEK when operated at the stated conditions. Background noise at these conditions is not to exceed 15- μV .

Integrator, electronic, for obtaining peak areas. This device must integrate areas at a sufficiently fast rate so that narrow peaks typically obtained from a capillary column can be accurately measured.

Oxygen remover, Oxy-Trap, Alltech Associates, Cat. No. 4001

Recorder, 1-mv full scale, 1-sec or less full-scale response

Regulator, helium, two-stage, high purity, Matheson, Model 3104-580

Sample injector, any syringe or injector capable of introducing a 0.4- μL volume of sample, such as a Hamilton 7101, available from Alltech Associates, Cat. No. 86200

REAGENTS AND MATERIALS

All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, when such specifications are available, unless otherwise specified.

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used. Only those reagents required for the specific ketone-alcohol mixtures to be analyzed (see *Calibration*) need to be obtained.

Ethyl amyl carbinol (5-methyl-3-heptanol), 99 mass-% minimum purity, Pfaltz & Bauer, Cat. No. M19060

Ethyl amyl ketone (5-methyl-3-heptanone), 99 mass-% minimum purity, Aldrich Chemical, Cat. No. 10,940-1

Helium, Chromographic grade, typically 99.995% purity

Methyl ethyl carbinol (2-butanol), 99 mass-% minimum purity, Aldrich Chemical, Cat. No. 24,056-7

Methyl ethyl ketone (2-butanone), 99 mass-% minimum purity, Aldrich Chemical, Cat. No. 11,026-4

Methyl hexyl carbinol (2-octanol), 98 mass-% minimum purity, Aldrich Chemical, Cat. No. 0-450-4

Methyl hexyl ketone (2-octanone), 98 mass-% minimum purity, Aldrich Chemical, Cat. No. 0-470-9

Methyl isoamyl carbinol (5-methyl-2-hexanol), 98 mass-% minimum purity, Aldrich Chemical, Cat. No. 18,973-1

Methyl isoamyl ketone (5-methyl-2-hexanone), 99 mass-% minimum purity, Aldrich Chemical, Cat. No. 11,025-6

Methyl isobutyl carbinol (4-methyl-2-pentanol), 99 mass-% minimum purity, Aldrich Chemical, Cat. No. 10,991-6

Methyl isobutyl ketone (4-methyl-2-pentanone), 99.5 mass-% minimum purity, Aldrich Chemical, Cat. No. 24, 289-6

Water, deionized or distilled

Xylenes, mixed, Aldrich Chemical, Cat. No. 24,764-2

PROCEDURE

Chromatographic Technique

1. Install the oxygen remover in the supply line between the carrier gas source and the carrier gas inlets on the gas chromatograph.
 - Column life is significantly reduced if an oxygen remover is not used.
2. Install one or both of the fused silica capillary columns in the dual column gas chromatograph depending on the specific mixtures to be analyzed (see *NOTE*).
 - Follow column manufacturer's recommendations for conditioning the column if it is new.
3. Establish the operating conditions given in Tables 1 and 2.
 - Other operating conditions may be used provided they produce the required sensitivity and chromatographic separations equivalent to those in the Typical Chromatograms (Figs. 1 through 5).
4. Program the column oven to 200 C and maintain the temperature until a stable baseline has been obtained at the required sensitivity.
5. Cool the column oven to the recommended starting temperature.
6. Allow the starting temperature to equilibrate and the baseline to stabilize.
7. Inject nominally 0.4 μL of the sample into the appropriate column in the gas chromatograph (see Table 2) and start the recorder, integrator, and column temperature programming sequence.
 - Column 1 is used to separate mixtures of MHK-MHC, MIAK-MIAC and EAK-EAC.
 - Column 2 is used to separate mixtures of MEK-MEC and MIBK-MIBC.
8. Identify the components of interest by comparing the chromatogram obtained to Figs. 1 through 5.
 - Components eluting before the ketone are commonly grouped and classified as light ends. Components eluting between the ketone and alcohol are commonly grouped and classified as unknowns. Components eluting after the alcohol are grouped and classified as low boiling intermediates.
 - Water is identified in MEK-MEC mixtures.
 - Xylenes are identified in MIBK-MIBC mixtures.

Table 1**General Conditions**

Carrier and makeup gas	helium
Carrier gas flow rate	5 mL/min
Makeup gas flow rate	25 mL/min
Detector	thermal conductivity, suitable for wide-bore capillary columns
Detector temperature	250 C
Injection port temperature	250 C
Chart speed	1 cm/min
Sample size	0.4 μ L (splitless)

Table 2**Specific Conditions**

	Sample Types		
	MHK-MHC MIAK-MIAC EAK-EAC	MEK-MEC- H ₂ O	MIBK-MIBC- Xylenes
Column	Carbowax 20M (Column 1)	RTx-1701 (Column 2)	RTx-1701 (Column 2)
Column temperature program:			
Initial temperature, C	70	40	70
Time at initial temperature, min	0	6	0
Programming rate, C/min	10	10	10
Final temperature, C	200	200	200
Time at final temperature, min	6	7.5	7.5

Calibration

Response factors are required to relate instrument response for each sample component to mass-%.

1. Prepare calibration blends as described in ASTM Method D 4307, to approximate the composition of the ketone-alcohol mixtures to be analyzed. Include water in MEK-MEC mixtures and mixed xylenes in MIBK-MIBC mixtures.
2. Analyze the blends as described under Steps 6, 7 and 8 of the *Chromatographic Technique* section.
3. Based on three replicate analyses of each blend, determine the average relative response factors (RRF) for each component in each blend using the ketone as a reference and the following formula:

$$F = \frac{AB}{CD} \quad (1)$$

where:

- A** = component of interest, mass-% as blended
- B** = peak area of ketone peak
- C** = ketone, mass-% as blended
- D** = peak area of component of interest
- F** = relative response factor

Apply a RRF of 1.0000 to light ends, unknowns and low boiling intermediate component groups.

CALCULATIONS

Using the peak areas for each sample component, calculate the composition of the sample to the nearest 0.1 mass-% using the following formula:

$$\text{Component, mass-\%} = \frac{100PF}{T} \quad (2)$$

where:

- F** = previously defined, Eq. 1
- P** = peak area of individual component
- T** = sum of the products PF, of all recorded peaks
- 100** = factor to convert to mass-%

NOTE

If the ketone-alcohol mixtures requiring analysis can all be separated on a single column, only that one column needs to be installed.

PRECISION

Repeatability

Based on 2 tests performed by each of 2 analysts on each of 2 different days (8 tests), the within-laboratory estimated standard deviations (esd) were calculated for components at specific concentrations in typical process streams and are listed in Table 3. Two tests performed in one laboratory by different analysts on different days should not differ by more than the allowable differences in Table 3 at the concentrations listed (95% probability).

Reproducibility

There is insufficient data to calculate reproducibility of the test at this time.

Table 3

Component	Concentration, mass-%	Repeatability	
		Within-Lab esd, mass-%	Allowable Difference, mass-%
Ethyl amyl ketone	10.6	0.0575	0.23
Ethyl amyl ketone	60.1	0.1485	0.58
Ethyl amyl ketone	82.7	0.0958	0.38
Ethyl amyl carbinol	82.8	0.2832	0.95
Ethyl amyl carbinol	35.6	0.1217	0.48
Ethyl amyl carbinol	10.3	0.0228	0.09
Methyl isoamyl ketone	17.5	0.0487	0.16
Methyl isoamyl ketone	56.8	0.1076	0.42
Methyl isoamyl ketone	57.9	0.0600	0.21
Methyl isoamyl carbinol	79.2	0.0536	0.21
Methyl isoamyl carbinol	41.2	0.0550	0.22
Methyl isoamyl carbinol	35.0	0.0591	0.23
Methyl hexyl ketone	0.3	0.0146	0.05
Methyl hexyl ketone	76.2	0.2176	0.85
Methyl hexyl ketone	66.6	0.1403	0.55
Methyl hexyl carbinol	96.5	0.1207	0.47
Methyl hexyl carbinol	21.5	0.0565	0.19
Methyl hexyl carbinol	26.7	0.0777	0.26
Methyl isobutyl ketone	7.7	0.0238	0.09
Methyl isobutyl ketone	66.6	0.0896	0.35
Methyl isobutyl ketone	50.8	0.1388	0.54
Methyl isobutyl carbinol	83.2	0.1241	0.49
Methyl isobutyl carbinol	30.0	0.0457	0.15
Methyl isobutyl carbinol	24.1	0.0622	0.24
Xylenes	5.8	0.0264	0.10
Xylenes	2.4	0.0134	0.05
Xylenes	11.6	0.0648	0.25
Methyl ethyl ketone	0.6	0.0160	0.05
Methyl ethyl ketone	63.8	0.0833	0.29
Methyl ethyl ketone	52.4	0.1052	0.41
Methyl ethyl carbinol	85.5	0.1081	0.42
Methyl ethyl carbinol	31.9	0.0907	0.36
Methyl ethyl carbinol	30.0	0.0541	0.18
Water	0.4	0.0261	0.10
Water	0.9	0.0783	0.27
Water	1.1	0.0684	0.23

TIME FOR ANALYSIS

The elapsed time for one analysis is 0.5 hour. The labor requirement is 0.25 hour.

REFERENCE

ASTM Method D 4307, www.astm.org

SUGGESTED SUPPLIERS

Alltech Associates, 2051 Waukegan Rd., Deerfield, IL 60015

Aldrich Chemical Co., 940 W. Saint Paul Ave., Milwaukee, WI 53233

Matheson, P.O. Box 96, Joliet, IL 60434

Pfaltz & Bauer, 172 E. Aurora St., Waterbury, CT 06708

Restek Corp., 110 Benner Circle, Bellefonte, PA 16823

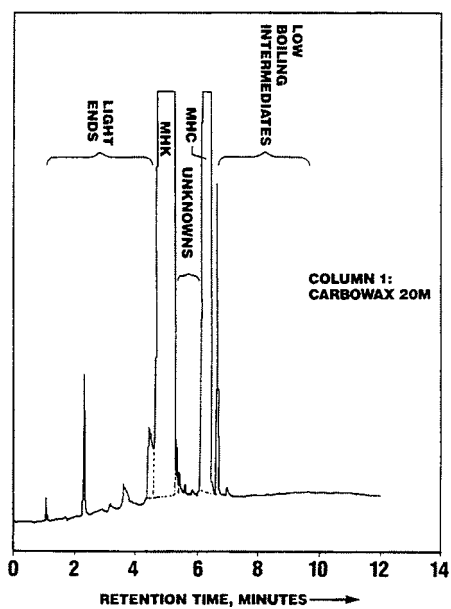


Figure 1

Typical Chromatogram, MHK-MHC

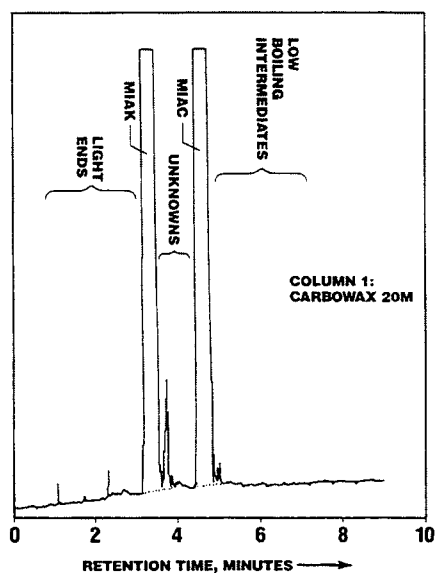


Figure 2

Typical Chromatogram, MIAK-MIAC

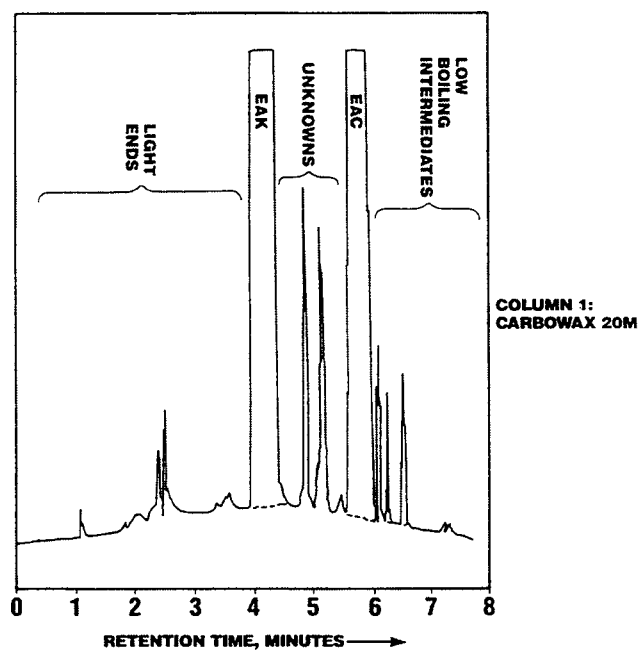


Figure 3

Typical Chromatogram, EAK-EAC

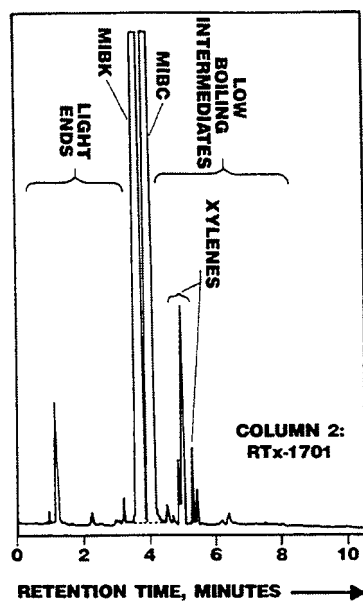


Figure 4

Typical Chromatogram, MIBK-MIBC

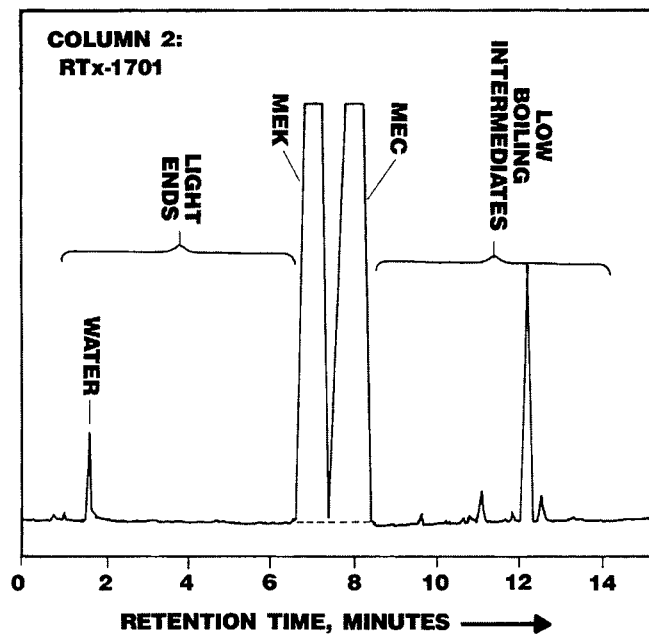


Figure 5

Typical Chromatograph, MEK-MEC