

TRACE ALCOHOLS IN LPG BY GC

UOP Method 845-90

SCOPE

This method is for determining trace amounts of C₄ and lower molecular weight alcohols in C₃ and C₄ olefin/paraffin hydrocarbon streams for the UOP Oleflex® or similar processes. Methanol and *tert*-butanol are reported as a composite. The lower limit of detection is 2 mass-ppm for any alcohol or composite. Aromatics and/or hydrocarbons containing eight or more carbon atoms cannot be present in the stream. If MTBE or ETBE are present in the samples, their reaction products may interfere with the determination of methanol, ethanol and *tert*-butanol.

OUTLINE OF METHOD

A repeatable volume of liquefied sample is removed from the sampling cylinder using a cylinder adapter and a high pressure valved syringe. The sample is injected into a gas chromatograph that is equipped with a fused silica capillary column and a flame ionization detector. The external standard method of quantitation is used.

APPARATUS

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

Chromatographic column, 30 m of 0.53-mm ID fused silica capillary, internally coated to a film thickness of 0.5 µm with Nukol, Supelco, Cat. No. 2-5327

Cylinder, for quantitative blend, one-liter LPG piston, Alpha Gaz.

Cylinder, for sample collection, type 304 stainless steel, high pressure, 12,400 kPa gauge maximum working pressure, 500-mL capacity, Whitey, Cat. No. 304L-HDF4-500. Equip the cylinder with 2 stainless steel valves, Whitey, Cat. No. 16DKM4-F4

Cylinder adapter, Dynatech Precision Sampling, Cat. No. 230250

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).
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Gas chromatograph, temperature programmable, built for capillary column chromatography and equipped with a flame ionization detector that will give a minimum peak height response of 10 times the background noise for 2 mass-ppm of isopropanol when operated at the recommended conditions

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

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

Regulator, air, two-stage, high purity, Matheson, Model 3104-590

Regulator, hydrogen, two-stage, high purity, Matheson, Model 3104-350

Regulator, nitrogen, single-stage, high pressure, Matheson, Model 2-580

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

Syringe, capable of injecting a 5- μ L volume, such as a Hamilton 701-NWG syringe, Alltech Associates, Cat. No. 80307

Syringe, high-pressure, valved, 0.5- to 5- μ L variable volume, Dynatech, Cat. No. 230051

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.

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Air, zero gas, total hydrocarbons less than 2.0 ppm as methane

Blend, quantitative, containing nominally 5 mass-ppm of each of the following alcohols in either propane or butane depending on the stream to be analyzed: methanol, ethanol, isopropanol, isobutanol, *n*-propanol, *sec*-butanol, *tert*-butanol, and *n*-butanol, Alpha Gaz

Hydrogen, zero gas, 99.95% minimum purity, total hydrocarbons less than 0.5 ppm as methane

Methylene chloride, 99.6% minimum purity, Aldrich Chemical, Cat. No. D6,510-0

Nitrogen, zero gas, 99.99% minimum purity, total hydrocarbons less than 0.5 ppm as methane

PROCEDURE

Operating Conditions

The recommended operating conditions for this analysis are given in Table 1. Other conditions may be used provided they produce the required sensitivity and chromatographic separations equivalent to those shown in the Typical Chromatogram.

Table 1

Carrier gas	hydrogen
Carrier gas flow rate	5 mL/min
Detector	flame ionization
Detector temperature	150 C
Injection port temperature	150 C
Hydrogen flow rate*	30 mL/min
Air flow rate*	350 mL/min
Makeup gas	nitrogen
Makeup gas flow rate*	30 mL/min
Column temperature program	
Initial temperature	30 C
Initial hold time	4 min
Programming rate	5 C/min
Final temperature	80 C
Sample size	2 μL repeatable
Chart speed	1 cm/min

***Consult the manufacturer's instrument manual for suggested flow rates.**

Chromatographic Technique

Install the fused silica capillary column in the gas chromatograph and establish the recommended operating conditions. Verify the carrier gas flow and establish a stable baseline at the required sensitivity. Pressurize the cylinder containing the sample to approximately 1700-2050 kPa (250-300 psi) with nitrogen.

Attach the cylinder adapter to the sample cylinder and open the valve between the adapter and cylinder. In a hood or well ventilated area, open the valve at the end of the adapter and purge the sample chamber until it is liquid full (approximately 15 seconds). Close the valve. Insert the high pressure valved syringe into the yoke assembly, and push the yoke forward to open the internal valve thereby exposing the sample to the syringe. Draw 2 μ L of sample into the syringe and pull back on the syringe to lock. Push the yoke back to the original position to close the internal valve. Remove the syringe from the adapter. Draw the plunger of the syringe back to allow partial expansion of the sample in the syringe.

Promptly inject the sample by inserting the needle into the injection port and pushing down on the barrel and plunger at the same time. Immediately start the temperature programmer, the integrator and recorder. A typical chromatogram is shown in the attached Figure. The exact retention times for the alconol components of interest should be verified on each chromatographic column by reference to the chromatogram of the blend used for calibration (see *Calibration*). If it is found that the hydrocarbon or alcohol peaks tail so severely as to interfere with the separation of the components of interest, modify the column by making approximately 10 successive 5- μ L injections of methylene chloride with the temperature of the column at 125 C.

Calibration

The external standard technique is used for calibration. Quantitative results are based on the injection of a repeatable volume of sample and the use of a response factor to relate the peak areas obtained to mass-ppm. A calibration blend that represents, as closely as possible, the samples to be analyzed is used to determine the response factors.

Attach the cylinder adapter to the piston cylinder containing the blend and analyze the blend in triplicate as described under *Chromatographic Technique*. Determine the average peak area for each alcohol component. Calculate the response factor for each alcohol using the following formula:

$$R = \frac{A}{B}$$

where:

A = concentration of alcohol component/composite in the blend, mass-ppm

B = average peak area of alcohol component/composite

R = response factor for alcohol component/composite, mass-ppm/unit area

Determine the response factors daily for each instrument used.

CALCULATIONS

Calculate the concentration of each alcohol component/composite in the sample to the nearest mass-ppm using the following equation:

$$\text{Component/Composite, mass-ppm} = ER$$

where:

E = component/composite peak area

R = response factor for the component/composite, previously defined

PRECISION

Repeatability

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

Table 2

Component	Concentration, mass-ppm	Repeatability	
		Within-lab esd, mass-ppm	Allowable Difference, mass-ppm
Methanol	34	0.3	1
Isopropanol	22	0.2	1
Ethanol	20	0.3	1
2-Butanol	24	0.3	1
<i>n</i>-Propanol	23	0.4	1
Isobutanol	26	0.3	1
<i>n</i>-Butanol	25	0.6	2

Reproducibility

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

TIME FOR ANALYSIS

The elapsed time for one analysis is 0.25 hour. The labor requirement is 0.15 hour.

SUGGESTED SUPPLIERS

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

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

Alpha Gaz, P.O. Box 1026, 11426 Fairmont Pkwy., La Porte, TX 77571

Dynatech Precision Sampling Corp., P.O. Box 15886, Baton Rouge, LA 70895

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

Supelco, Inc., Supelco Park, Bellefonte, PA 16823-0048

Whitey Co., 318 Bishop Rd., Highland Heights, OH 44143

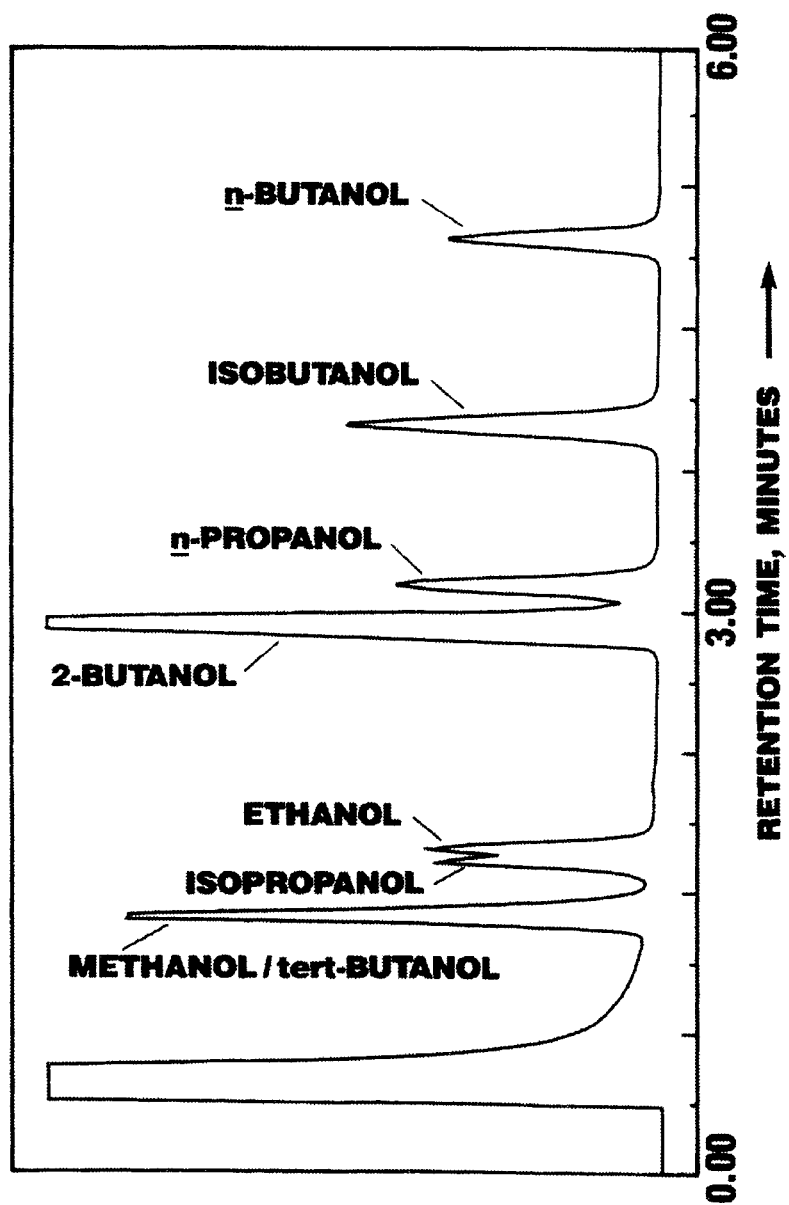


Figure
Typical Chromatogram