

COMPOSITION OF C₄ OLEX EFFLUENT BY GAS CHROMATOGRAPHY

UOP Method 846-83

SCOPE

This method is for determining individual C₄ components and total C₆ components in liquefied hydrocarbon mixtures typically found in C₄ Olex[®] process streams. All C₄ olefins including 1-butene and isobutylene are separated while C₆'s, along with any C₅ and/or C₇+ hydrocarbons that may be present, are determined as a composite. The lower limit of detection for a single component is 0.05 mass-%.

OUTLINE OF METHOD

A pressurized liquid sample is injected into a gas chromatographic column comprised of two sections, the first packed with Carbowax 1540 on Porasil C and the second with bis(2-ethoxyethyl) adipate on Chromosorb. After the C₄ components have eluted, the column is backflushed to elute the remaining heavier components as a single group. Internal normalization of peak areas after correction for differences in thermal response is used to obtain a distribution of the components.

APPARATUS

Chromatographic column, 3 m of 2.5-mm ID (1/8-inch OD) stainless steel tubing packed with 2.7% Carbowax 1540 on 80/100 mesh Porasil C, followed by 5 m of 2.5-mm ID (1/8-inch OD) stainless steel packed with 27.5% bis(2-ethoxyethyl)adipate on 45/60 mesh Chromosorb P AW, Carle Instruments, Column 2A & 2B of Application 196A, or equivalent

Gas chromatograph, capable of isothermal operation, equipped with a thermal conductivity detector and provision for a high pressure liquid sampling valve. The column oven must provide space for internally mounting a 4-port rotary backflush valve. The thermal conductivity detector must be capable of producing a minimum peak height response of 30 μ V for 0.1% of isobutane when operated at the stated conditions. Background noise at these conditions is not to exceed 3 μ V.

Integrator, electronic, or equivalent equipment for obtaining peak areas

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

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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Regulator, two stage, high purity. Matheson Model 3104-580 (helium) or Model 3104-350 (hydrogen), or equivalent. The appropriate regulator is dependent upon the carrier gas chosen, see *NOTE*.

Valve, column backflush, 4-port rotary, Carle Instruments, Cat. No. 2011, or equivalent

Valve, high pressure liquid sampling, 2- μ L sample volume, Bendix Part No. 3526749-1-2-1-02-1, or equivalent

Valve, fine metering valve, Nupro Company, Cat. No. SS-2MG, or equivalent

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 exist, unless otherwise specified.

Blends, calibration, see *CALIBRATION*. These blends may be prepared in house or may be obtained from Matheson (Certified Standard, accurate to 2% of the component concentration), or equivalent.

Helium or Hydrogen, purified chromatographic grade, typically 99.995% purity, see *NOTE*.

PROCEDURE

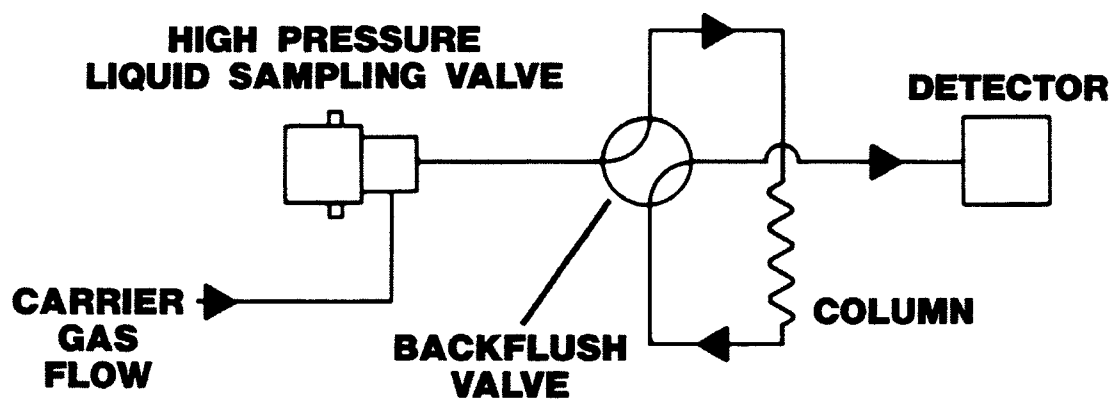
Operating Conditions

The operating conditions for this analysis are given in Table 1.

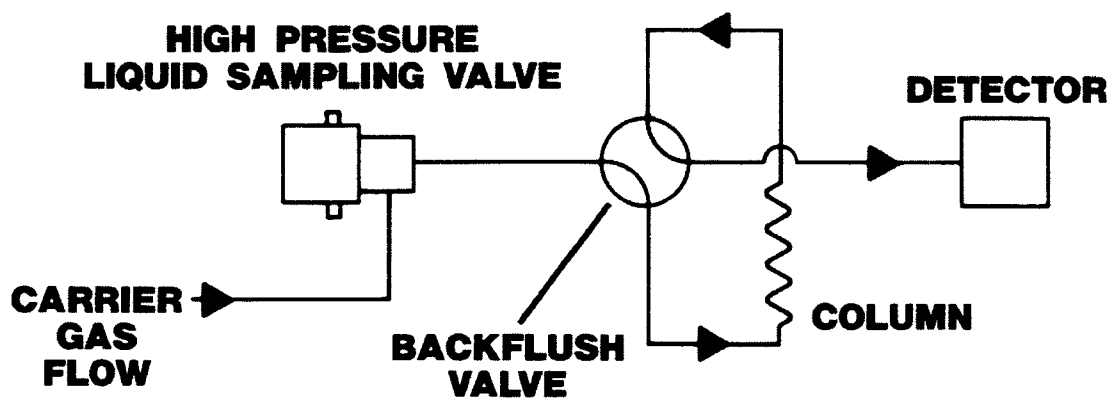
Table 1	
Carrier gas	helium or hydrogen (see <i>NOTE</i>)
Carrier gas flow rate	20 mL/min
Detector type	thermal conductivity
Detector temperature	150 C
Column temperature	38 C
Sample valve temperature	
Sample Zone	ambient
Vaporization Zone	150 C
Recorder chart speed	0.5 cm/min
Sample size	2 μL

Chromatographic Technique

Install the high pressure liquid sampling valve and the chromatographic column with backflush valve as in Fig. 1. Establish the flow rate and operating temperature specified under *Operating Conditions*. Condition the column until a stable recorder baseline is established at the required sensitivity.



ANALYSIS POSITION



BACKFLUSH POSITION

Figure 1
Flow Diagram

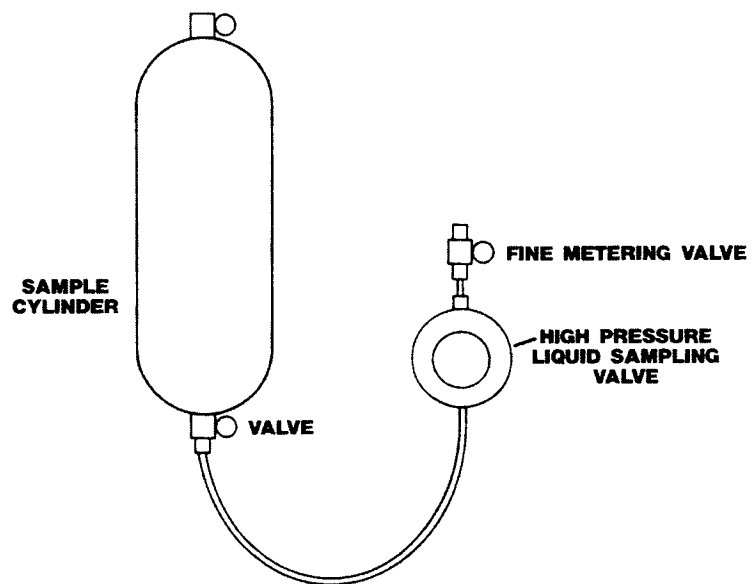


Figure 2

Sample Cylinder Connection

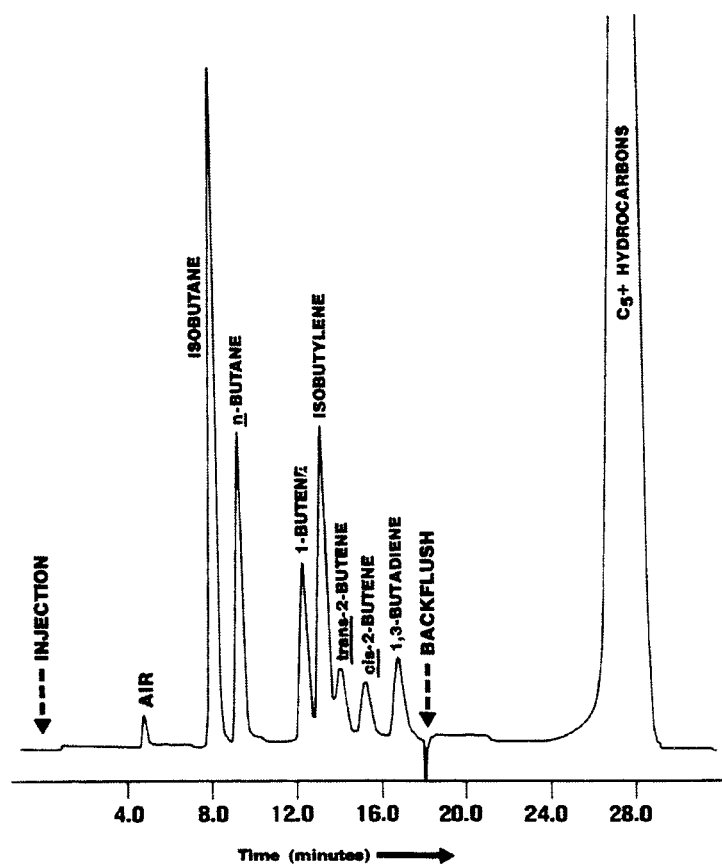


Figure 3

Sample Chromatogram

The sample must be in the liquid state, without bubbles, in the liquid sampling valve during injection to assure a representative sample. To obtain a bubble-free sample use the following procedure. Connect the cylinder containing the sample to the liquid sampling valve as shown in Fig. 2. With the fine metering valve closed, open fully the bottom cylinder valve. Slightly open the fine metering valve until liquid can be seen venting from it. Close the fine metering valve and inject the sample with the liquid sampling valve. Immediately start the integrator and recorder. Vent the sampling system by closing the bottom cylinder valve and opening the fine metering valve. Switch the rotary backflush valve after 1,3-butadiene has eluted from the column, thereby backflushing the C₅+ hydrocarbons out of the column. A typical chromatogram is shown in Fig. 3. The exact retention times should be checked on each individual instrument by running a calibration blend. If the determination of vinylacetylene is required, delay the backflush time until after the vinylacetylene has eluted. Its retention time relative to 1,3-butadiene is 1.6. Several C₅ hydrocarbons, if present, will elute between 1,3-butadiene and vinylacetylene. Add the areas of these peaks to the area of the peaks resulting from the backflush to obtain an area for the total C₅+ hydrocarbons.

Calibration

Calibration blends are required to relate the thermal response of the various components to each other. Prepare or purchase one or more blends containing the components of interest at approximately the concentrations expected in the samples. Analyze each blend in duplicate as described under *Chromatographic Technique* and determine the average area for each peak.

Calculate the mass response factor for each component relative to isobutane as follows:

$$F = \frac{AB}{CD}$$

where:

- A** = component in blend, mass-%
- B** = area of isobutane peak
- C** = isobutane in blend, mass-%
- D** = area of the component peak, units consistent with B, above
- F** = relative response factor for component (other than isobutane)

Determine relative response factors as directed above for each instrument used. The factors shown in Table 2 are examples, and will not be valid for all instruments. A deviation of more than 10% from the values shown in Table 2 is sufficient reason to suspect a problem with the apparatus and/or the calibration blend.

Table 2
Typical Response Factors

<u>Component</u>	<u>Response Factor</u>
Isobutane	1.00
<i>n</i>-Butane	0.95
1-Butene	1.01
Isobutylene	0.95
<i>trans</i>-2-Butene	0.89
<i>cis</i>-2-Butene	0.87
1,3-Butadiene	0.96
C₆ Mixture	1.12

CALCULATIONS

Calculate the concentration of each hydrocarbon to the nearest 0.1 mass-%, using the following equation:

$$\text{Hydrocarbon, mass-\%} = \frac{100 \text{ EF}}{\text{S}}$$

where:

E = component peak area

F = relative response factor, previously defined

S = sum of the products EF of all the recorded peaks

NOTE

Helium is the carrier gas of choice, however, in locations where helium is not readily available, hydrogen may be used as the carrier gas. *CAUTION:* If hydrogen is used, leakage into the confined volume of the column compartment can cause a violent explosion. It is, therefore, mandatory to test for leaks each time a connection is made, and periodically thereafter.

PRECISION

Based on six replicate determinations, the estimated standard deviation (esd) was calculated for the components listed below. Duplicate results by the same operator should not differ by more than the allowable difference indicated (95% probability).

<u>Component</u>	<u>Concentration, mass-%</u>	<u>esd, mass-%</u>	<u>Allowable Difference, mass-%</u>
Isobutane	3.6	0.026	0.09
<i>n</i> -Butane	7.3	0.024	0.08
1-Butene	26.0	0.082	0.28
C ₆ Mixture	50.1	0.242	0.84

TIME FOR ANALYSIS

The elapsed time for one analysis is 0.5 hour. The labor requirement is 0.2 hour.

SUGGESTED SUPPLIERS

Bendix, Environmental and Process Instruments Division, P.O. Box 831, Lewisburg, WV 24901

Carle Instruments, 1200 Knollwood Circle, Anaheim, CA 92801

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

Nupro Co., 4800 E. 345th Street, Willoughby, OH 44094