

## **TRACE HYDROCARBONS IN HYDROGEN OR LPG BY GAS CHROMATOGRAPHY**

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### **UOP Method 899-97**

#### **SCOPE**

This method is for determining individual trace C<sub>5</sub> minus hydrocarbon impurities in hydrogen or liquefied petroleum gas (LPG), where the specific trace components are sufficiently resolved from the major components, typically propane/propylene or ethane/ethylene. Components eluting after ethyl acetylene are grouped and reported as heavies. The range of quantitation for each component is 2 to 3000 mol-ppm; however, the lower limit of quantitation increases when major components interfere with the resolution of the impurities.

#### **OUTLINE OF METHOD**

A reproducible volume of gas sample is injected into a gas chromatograph equipped with an alumina PLOT capillary column, capillary injection port, a flame ionization detector (FID), and a gas sampling valve. The concentrations of the hydrocarbon impurities are determined by the external standard method of quantitation, wherein peak areas are compared to the area of a calibration blend containing a known concentration of isobutane.

#### **APPARATUS**

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

*Chromatographic column*, 50 m of 0.53-mm ID PLOT fused silica capillary, internally coated to a film thickness of 9- $\mu$ m with alumina (GS-Alumina), J&W Scientific, Cat. No. 93872. Columns from other suppliers, commonly called Al<sub>2</sub>O<sub>3</sub>/Na<sub>2</sub>SO<sub>4</sub>, provide similar separation but may not be quantitative for diolefins and acetylenes, and their use is not recommended when analysis of these components is necessary.

**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*, capable of temperature ramping, equipped with electronic pressure control, built for capillary column chromatography utilizing a split injection system, having a glass injection port insert, a heated valve box, and a FID that will give a minimum peak height response of 10 times the background noise for 2 mol-ppm of isobutane when operated at the recommended conditions, Hewlett Packard, Model 6890

*Gas purifier*, helium, used to remove oxygen and moisture from carrier gas, UOP Mat/Sen, Cat. No. P-100-1

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

*LPG expansion apparatus*, for quantitative expansion of LPG from a liquid to a gas phase:

*Fitting*, male connector, stainless steel, 0.25-inch tube fitting to 0.25-inch male NPT, Swagelok, Dearborn Valve & Fitting, Cat. No. SS-400-1-4. Sample cylinders having an outlet fitting other than 0.25-inch female NPT will require a different fitting.

*Fitting*, port connector, stainless steel, 0.25-inch tube fitting, Swagelok, Dearborn Valve & Fitting, Cat. No. SS-401-PC, 2 required

*Fitting*, union tee, stainless steel, 0.25-inch, Swagelok, Dearborn Valve & Fitting, Cat. No. 400-3

*Tubing*, stainless steel, Type 304, 0.25-inch OD x 0.210-inch ID, 83-mm (9-inches) long, Alltech Associates, Cat. No. 30301

*Vacuum pump*, capable of achieving a vacuum of 0.1-mm Hg, Fisher Scientific, Cat. No. 01-115-2

*Valve*, stainless steel, 0.25-inch Swagelok, Whitey, Dearborn Valve & Fitting, Cat. No. SS-1RS4

*LPG expansion cylinder*, sample cylinder for containing expanded LPG sample:

*Cylinder*, 4- x 6-inch, 316 stainless steel, 200 psi (1380 kPa) internal pressure, double connection, 0.25-inch pipe hex bored through, Arthur Harris, Cat. No. B-270

*Fitting*, hex nipple, stainless steel, 0.25-inch NPT, Cajon, Dearborn Valve & Fitting, Cat. No. SS-4-HN, 3 required

*Fitting*, tee, stainless steel, 0.25-inch NPT, Cajon, Dearborn Valve & Fitting, Cat. No. SS-4-T

*Gauge*, stainless steel, vacuum-pressure, -100 to +200 kPa gauge (-14.5 to +29.0 psig) range, Matheson Gas Products, Cat. No. 63-2204

*Valve*, stainless steel, 0.25-inch NPT inlet, 0.25-inch tube fitting outlet, Whitey, Dearborn Valve & Fitting, Cat. No. SS-1RM4-S4, 2 required

*Recorder* (optional), used to supplement integrator plot

*Regulator*, air, two-stage, high purity, Matheson Gas Products, Model 3122-590

*Regulator*, helium, two-stage, high purity, Matheson Gas Products, Model 3122-580

*Regulator*, hydrogen, two-stage, high purity, Matheson Gas Products, Model 3122-350

*Regulator*, nitrogen, two-stage, high purity, Matheson Gas Products, Model 3122-580

*Valve*, 6-port, stainless steel, 1.59-mm (0.0625-inch) fittings, manual with standoff, Valco Instruments, Cat. No. C6UWE

*Sample loop*, stainless steel, 100- $\mu$ L, Valco Instruments, Cat. No. SL100CUW

*Tubing*, stainless steel, 1.59-mm (0.0625-inch) OD, Alltech Associates, Cat. No. 300010

## 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.

*Air*, zero-gas, total hydrocarbons less than 2 ppm as methane

*Calibration blend*, quantitative, primary standard, to contain from 250 to 500 mol-ppm isobutane in helium, Matheson Gas Products

*Helium*, zero-gas, total hydrocarbons less than 0.5 ppm as methane

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

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

## PROCEDURE

### Chromatographic Technique

Quantitative results are based on the injection of a reproducible volume of both sample and calibration blend.

1. Install the gas purifier in the supply line between the carrier gas source and the carrier gas inlet on the gas chromatograph.
  - Column life is significantly reduced if the gas purifier is not used.
2. Install the 6-port gas sampling valve in the valve box of the instrument and the fused silica capillary column as shown in Fig. 1.
3. Establish the recommended operating conditions as 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, Fig. 2.

4. Condition the column according to the manufacturer's instructions.
5. Cool the column oven to a stabilized initial temperature of 35°C.
6. Proceed to Step 7 if the sample is in the gas phase. If not, LPG must be carefully expanded into the gas phase to ensure that a representative sample is analyzed. Proceed to *LPG Sampling*.
7. Set the gas sampling valve in the sample purge position. Purge the sample loop with the sample to be analyzed for approximately one minute. Turn off the sample purge, allow several seconds for the pressure to equilibrate and inject the sample by rotating the gas sampling valve to the inject position.
8. Start the integrator and the column temperature programming sequence.
9. Identify the components of interest by comparing the chromatogram obtained to the Typical Chromatograms (Figs. 2 and 4).
  - The PLOT columns will overload easily which causes retention times to shift and, depending on component concentrations, some very large components will mask smaller ones. Care should be taken when identifying these components. A typical chromatogram of an expanded LPG sample containing some high concentration level components is included for reference (Fig. 4).
10. Sum the peak areas of the unidentified components eluting after ethyl acetylene to obtain the peak area of the heavies composite.

### **LPG Sampling**

Liquefied petroleum gas (LPG) must be carefully expanded to ensure that a representative sample is analyzed. Various procedures are used to quantitatively expand LPG from a liquid phase into a representative gas phase prior to analysis. The following is the recommended procedure that has been proved to be satisfactory.

1. Assemble the LPG Expansion Cylinder consisting of a small stainless steel expansion cylinder, a stainless steel gauge with a reading range from vacuum to 200 kPa gauge and two stainless steel shut-off valves (see Fig. 3).
  - Some expansion cylinders have two valves (C and D) as shown in Fig. 3, some have only one (Valve C). The version shown in Fig. 3 is easier to clean, but either may be used.
2. Connect the apparatus to the vacuum system and evacuate the cylinder assembly to 0.013 kPa (0.1-mm Hg).
3. Connect two small pieces of clean stainless steel tubing, a tee and Valve B to the evacuated cylinder as shown in Fig. 3 (LPG Expansion Apparatus).

Table 1

| <b><u>Recommended Operating Conditions</u></b>             |                         |
|------------------------------------------------------------|-------------------------|
| <b>Carrier gas</b>                                         | <b>helium</b>           |
| <b>Column head pressure @ 35°C,<br/>constant flow mode</b> | <b>70 kPa (10 psig)</b> |
| <b>Equivalent flow</b>                                     | <b>10 mL/min</b>        |
| <b>Equivalent linear velocity</b>                          | <b>59 cm/sec</b>        |
| <b>Split flow rate</b>                                     | <b>150 mL/min</b>       |
| <b>Injection port temperature</b>                          | <b>200°C</b>            |
| <b>Valve box temperature</b>                               | <b>100°C</b>            |
| <b>Electronic pressure control</b>                         | <b>constant flow on</b> |
| <b>Column temperature program</b>                          |                         |
| <b>Initial temperature</b>                                 | <b>35°C</b>             |
| <b>Initial time</b>                                        | <b>2 min</b>            |
| <b>Programming rate</b>                                    | <b>10°C/min</b>         |
| <b>Final temperature</b>                                   | <b>190°C</b>            |
| <b>Final time</b>                                          | <b>10 min</b>           |
| <b>Detector</b>                                            | <b>FID</b>              |
| <b>Detector temperature</b>                                | <b>200°C</b>            |
| <b>Hydrogen flow rate*</b>                                 | <b>30 mL/min</b>        |
| <b>Air flow rate*</b>                                      | <b>350 mL/min</b>       |
| <b>Makeup gas</b>                                          | <b>nitrogen</b>         |
| <b>Makeup gas flow rate*</b>                               | <b>30 mL/min</b>        |
| <b>Sample size</b>                                         | <b>100µL repeatable</b> |

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

4. Determine if the LPG sample cylinder contains a dip tube. If not, place the LPG sample cylinder in a vertical position in a hood or well-vented area. Briefly open the bottom valve (A) to check that no water or sediment is present in the LPG. If the sample cylinder contains a dip tube, invert the cylinder (both valves on the bottom) and briefly open the valve not connected to the dip tube to check that no water or sediment is present. If water or sediment is determined to be present, discontinue the analysis and obtain a clean sample.
  - LPG samples are usually contained in a cylinder having valves on both ends or, in some cases, a cylinder where one of the valves is connected to a dip tube.
5. Connect the bottom valve or the valve connected to the dip tube of the LPG sample cylinder with a short stainless steel connector to the expansion apparatus. Fully open Valve B in Fig. 3.
6. Open (about 1/4 turn) Valve A, rapidly, on the sample cylinder until only liquid comes out of Valve B. *Important:* The valve must be opened wide enough so that a portion of liquid sample enters the stainless steel tubing before it vaporizes. Fractionation must not take place at the valve, or the composition of the sample will change.

7. Close Valve B and then Valve A and open Valve C (Fig. 3).
8. Close Valve C on the apparatus and disconnect the apparatus from the sample vessel. A positive pressure of 10 to 15 psig (69 to 103 kPa gauge) should be displayed on the expansion cylinder gauge. If not, repeat Steps 1 through 8 with a longer or shorter piece of stainless steel tubing in the expansion apparatus. The cylinder now contains a gas phase sample that is representative of the LPG sample in the original pressurized cylinder.
9. Inject the expanded sample following Steps 7 through 10 under *Chromatographic Technique*.

### Calibration

Since it may be difficult to purchase and maintain a calibration blend that contains all components of interest, a blend containing a known concentration (250 to 500 mol-ppm) of isobutane in helium is used as a quantitative standard.

1. Analyze the quantitative standard, in triplicate, as described under *Chromatographic Technique* each time samples are analyzed.
2. Identify the isobutane peak and average the peak area from the triplicate runs.
  - Peak areas from each of the triplicate runs should not deviate from the average by more than 5% of the value. If greater deviations occur, make certain that there are no problems with the equipment, then make additional runs until the required repeatability is obtained on three consecutive runs.
3. Determine the response factor relating the mol-ppm concentration of isobutane in the calibration blend to unit peak area using Eq. 1.

$$K = \frac{P}{A} \quad (1)$$

where:

**A** = average peak area of isobutane  
**K** = response factor for isobutane  
**P** = isobutane concentration in blend, mol-ppm

4. Determine the response factors relative to isobutane to relate the peak areas of the other hydrocarbon components to mol-ppm using Eq. 2.

$$F = \frac{C}{D} \quad (2)$$

where:

**C** = molecular weight of isobutane, g/mole  
**D** = molecular weight of the component of interest, g/mole  
**F** = relative response factor for the component of interest

The molecular weight of *n*-hexane is used when calculating the factor for the heavies component. See Table 2 for examples of the calculated relative response factors.

Table 2

**Typical Response Factors Relative to Isobutane**

|                  |      |                        |      |
|------------------|------|------------------------|------|
| Methane          | 3.62 | Propadiene             | 1.45 |
| Ethane           | 1.93 | <i>trans</i> -2-Butene | 1.04 |
| Ethylene         | 2.07 | 1-Butene               | 1.04 |
| Propane          | 1.32 | Isobutylene            | 1.04 |
| Cyclopropane     | 1.38 | <i>cis</i> -2-Butene   | 1.04 |
| Propylene        | 1.38 | Isopentane             | 0.81 |
| Isobutane        | 1.00 | <i>n</i> -Pentane      | 0.81 |
| Methyl acetylene | 1.45 | <i>n</i> -Butane       | 1.00 |
| Vinyl acetylene  | 1.12 | Ethyl acetylene        | 1.07 |
| <i>n</i> -Hexane | 0.67 | 1,2-Butadiene          | 1.07 |
| Acetylene        | 2.23 | 1,3-Butadiene          | 1.07 |

**CALCULATIONS**

Calculate the mol-ppm of any component or composite of interest in the sample to the nearest mol-ppm below 100 mol-ppm, or to the nearest 10 mol-ppm at or above 100 mol-ppm, using Eq. 3.

$$\text{Component, mol-ppm} = \text{BFK} \quad (3)$$

where:

**B** = peak area of the component or composite of interest

**F** = relative response factor, previously defined (Eq. 2)

**K** = response factor of isobutane, previously defined (Eq. 1)

**PRECISION****Repeatability**

Based on two tests performed by each of two analysts on each of two different days (8 tests), the within-laboratory estimated standard deviations (esd) were calculated for components at specific concentrations 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).

When the method is run routinely in the field, use of control charts is recommended to establish estimates of long-term repeatability. The data in Table 3 are an estimate of short-term repeatability.

**Reproducibility**

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

**Table 3**  
**Repeatability**

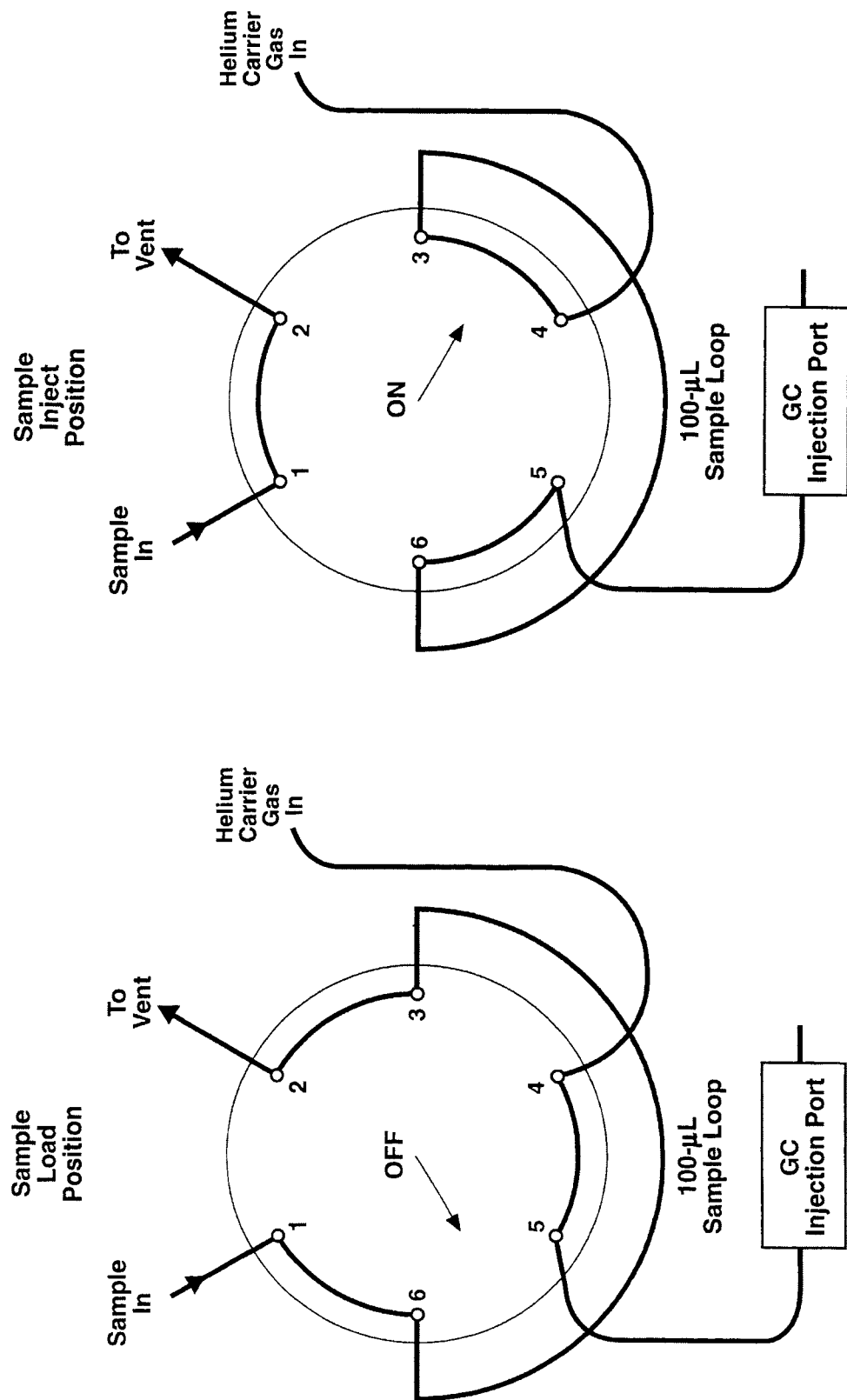
| <b>Source<br/>Component</b>           | <b>Concentration,<br/>mol ppm</b> | <b>Within-Lab<br/>esd, mol ppm</b> | <b>Allowable<br/>Difference,<br/>mol ppm</b> |
|---------------------------------------|-----------------------------------|------------------------------------|----------------------------------------------|
| <b>Propylene Feed,<br/>Gas Sample</b> |                                   |                                    |                                              |
| <b>Methane</b>                        | <b>33</b>                         | <b>0.5</b>                         | <b>2</b>                                     |
| <b>Ethane</b>                         | <b>730</b>                        | <b>10.5</b>                        | <b>40</b>                                    |
| <b>Cyclopropane</b>                   | <b>1170</b>                       | <b>15.1</b>                        | <b>50</b>                                    |
| <b>Isobutane</b>                      | <b>200</b>                        | <b>5.6</b>                         | <b>20</b>                                    |
| <b><i>n</i>-Butane</b>                | <b>34</b>                         | <b>0.9</b>                         | <b>3</b>                                     |
| <b>Propylene Feed,<br/>LPG Sample</b> |                                   |                                    |                                              |
| <b>Cyclopropane</b>                   | <b>61</b>                         | <b>2.1</b>                         | <b>7</b>                                     |
| <b>Isobutane</b>                      | <b>780</b>                        | <b>40.</b>                         | <b>140</b>                                   |
| <b><i>n</i>-Butane</b>                | <b>4</b>                          | <b>0.8</b>                         | <b>3</b>                                     |
| <b>1-Butene</b>                       | <b>34</b>                         | <b>1.1</b>                         | <b>4</b>                                     |
| <b>Methyl acetylene</b>               | <b>6</b>                          | <b>0.5</b>                         | <b>2</b>                                     |

## TIME FOR ANALYSIS

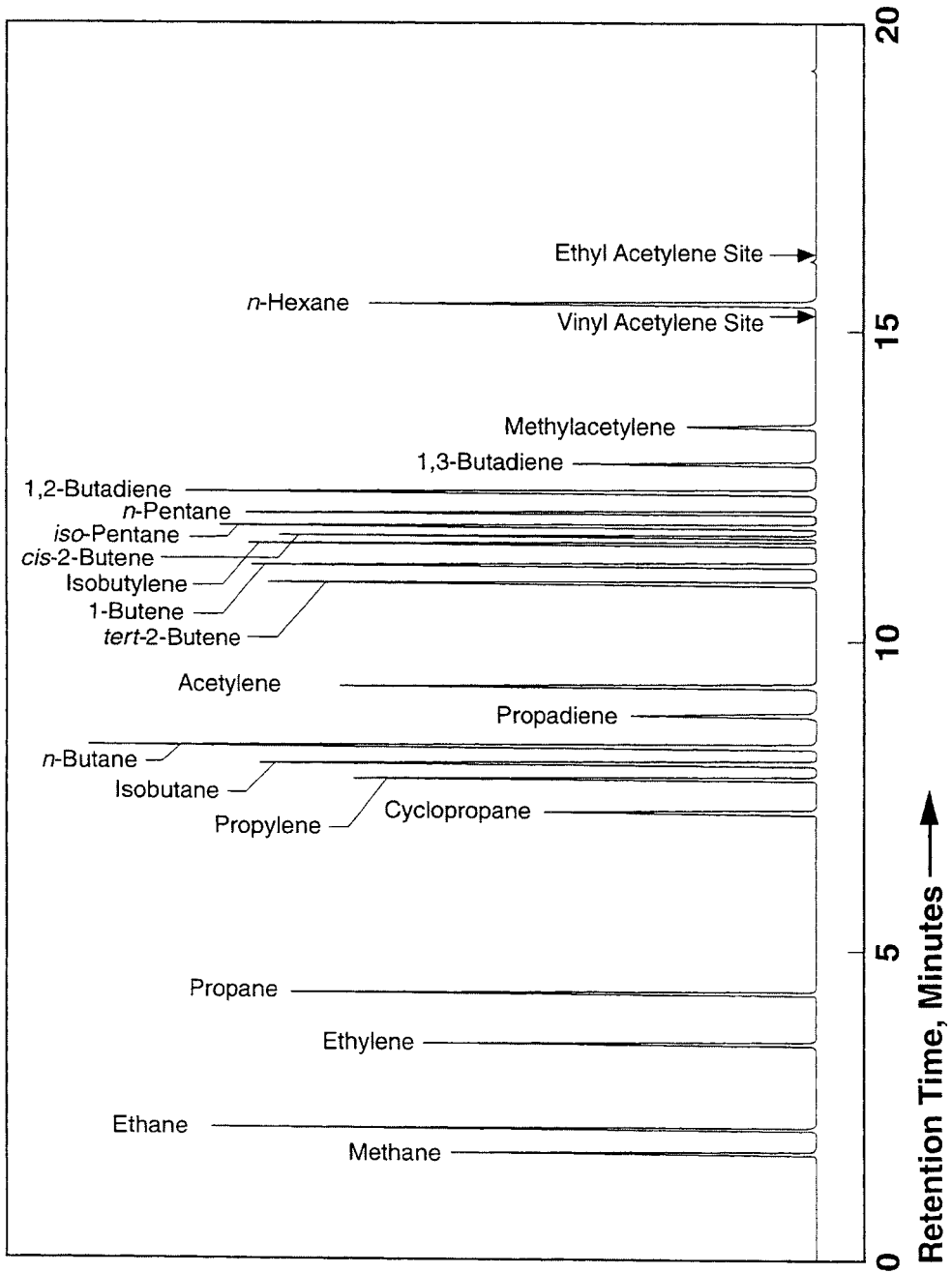
The elapsed time for one analysis (or calibration) is 0.60 hour. The labor requirement is 0.25 hour.

## SUGGESTED SUPPLIERS

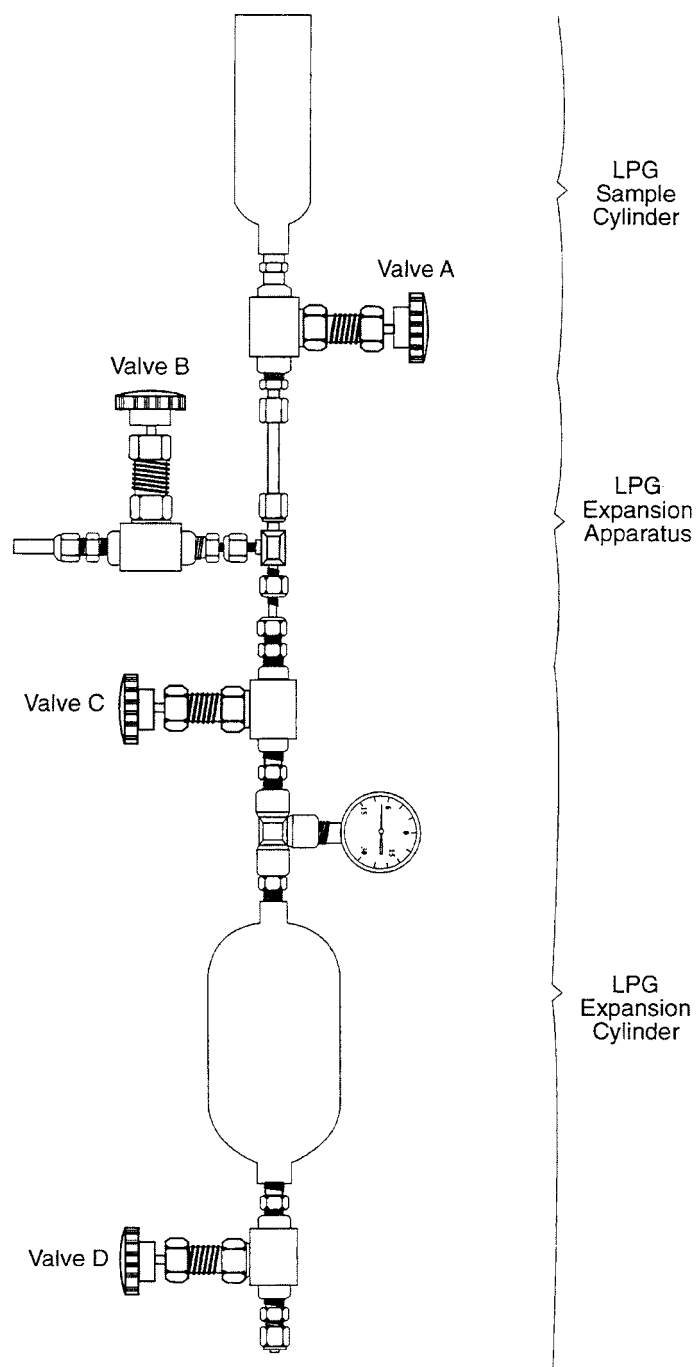
Alltech Associates, 2051 Waukegan Rd., Deerfield, IL 60015 (847-948-8600)  
 Arthur Harris and Co., 210 N. Aberdeen St., Chicago, IL 60607 (773-666-6832)  
 Dearborn Valve & Fitting Co., 1540 N. Old Rand Rd., Wauconda, IL 60084-0847 (847-526-6900)  
 Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219-4785 (412-562-8300)  
 Hewlett Packard Co., 2850 Centerville Rd., Wilmington, DE 19808-1610 (302-633-8000)  
 J&W Scientific, 91 Blue Ravine Rd., Folsom, CA 95630-4717 (916-985-7888)  
 Matheson Gas Products, Inc., P.O. Box 96, Joliet, IL 60434 (815-727-4848)  
 UOP Mat/Sen, 4509 Golden Foothill Pkwy., El Dorado Hills, CA 95762 (916-939-8800)  
 Valco Instrument Co., Inc., P.O. Box 55603, Houston, TX 77255 (713-688-9345)



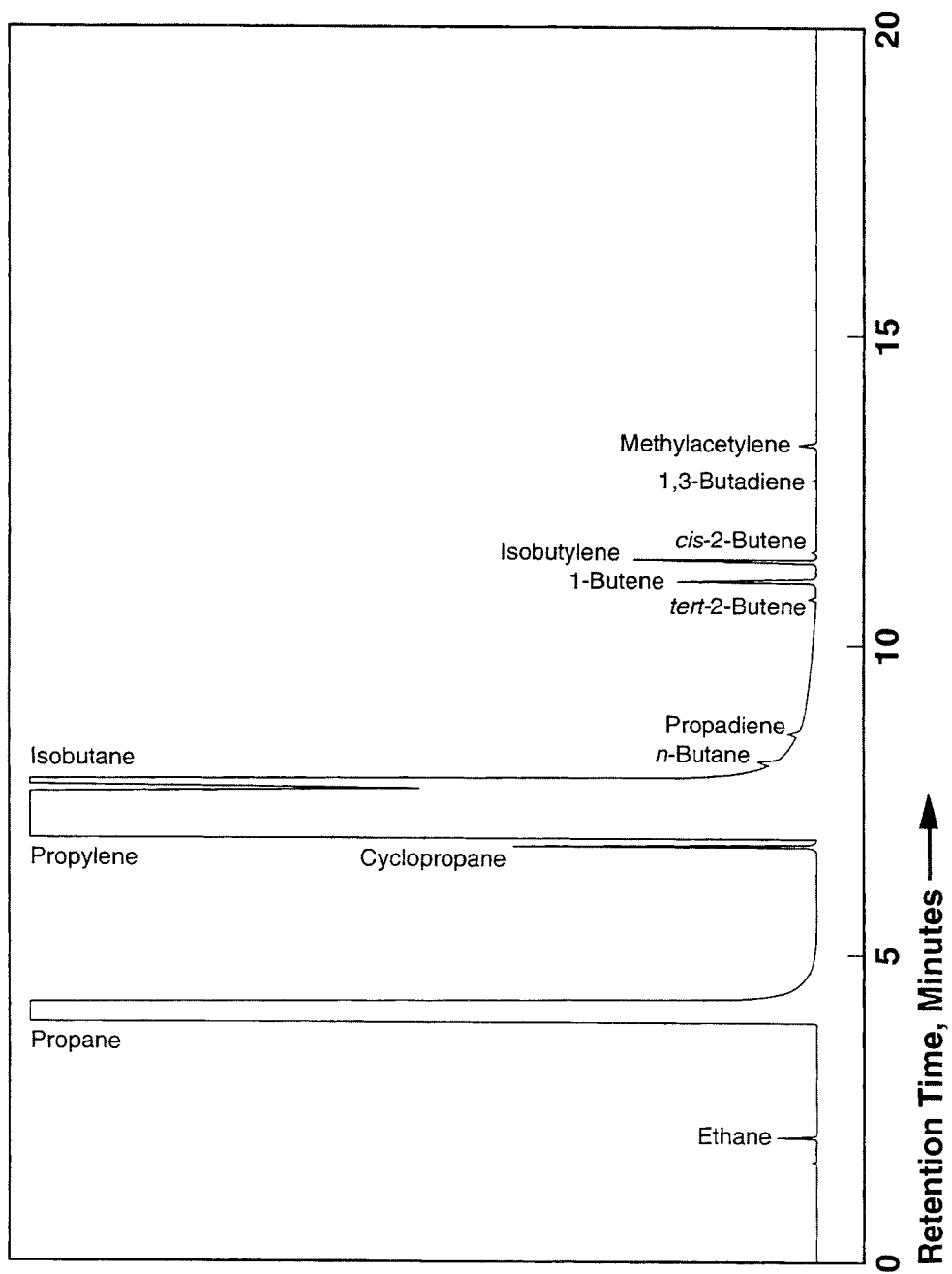
**Figure 1**  
Sample Valve Flow Diagram



**Figure 2**  
Typical Chromatogram



**Figure 3**  
Sample Expansion  
Setup



**Figure 4**  
Propylene Feed  
Typical Chromatogram