



A Honeywell Company

Composition of C₂ through C₅ Hydrocarbon Mixtures by GC

UOP Method 373-08

Scope

This method is for determining individual components in C₂ through C₅ hydrocarbon mixtures. The lower limit of detection for a single component is 0.01 mass-%. C₆ and heavier components, if present, may not be fully quantitated. Trace concentrations of these components can be determined using U899.

References

- ASTM Practice D1265, "Sampling Liquefied Petroleum (LP) Gases (Manual Method)," www.astm.org
- Scanlon, J. T. and Willis, D. E., *Journal of Chromatographic Science*, 23, 333-340 (1985)
- UOP Method 516, "Sampling and Handling of Gasolines, Distillate Fuels, and C₃-C₄ Fractions," www.astm.org
- UOP Method 899, "Trace Hydrocarbons in Hydrogen or LPG by Gas Chromatography," www.astm.org
- UOP Method 999, "Precision Statements in UOP Methods," www.astm.org

Outline of Method

The sample to be analyzed is injected into a gas chromatograph that is equipped with a liquid phase sampling valve, a porous layer open tubular (PLOT) column, and a flame ionization detector (FID). The mass-% or mol-% 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.

Chromatographic column, 50m x 0.32mm x 5µm (length, ID, layer thickness) Al₂O₃/KCl, Varian, Cat. No. CP-7515

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Gas chromatograph, temperature programmable, built for capillary column chromatography, utilizing a split injection system, equipped with a glass injection port insert, provision for both gas and liquid sampling valves and a flame ionization detector that will give a minimum peak height response of five times the background noise for 0.01 mass-% *n*-butane when operated at the recommended conditions, Agilent Technologies, Model 7890.

Integrator, or data system, 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. The integrator must have programmable parameters for controlling baseline events, and have graphics capabilities. ChemStation, Agilent Technologies.

Reducer, Swagelok, Cat. No. SS-200-R-1

Regulator, air, two-stage, high purity, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Model 3122-590

Regulator, hydrogen, two-stage, high purity, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Model 3122-350

Regulator, nitrogen, two-stage, high purity, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Model 3122-580

Regulator, nitrogen or helium, two-stage, high purity, delivery pressure range 70-1700 kPa (10-250 psi), Matheson Tri-Gas, Model 3126-580

Stainless Steel tubing, 1/16" OD x 0.04" ID, Alltech Associates, Cat. No. 30033

Tubing, translucent, FEP Teflon, 3.2-mm (1/8-inch) OD, 1.6-mm (1/16-inch) ID, 3450 kPa (500 psi), Alltech Associates, Cat. No. 45740

Valve, liquid sampling valve, 4-port rotary, with 0.5- μ l internal groove, Valco, Cat. No. DCI4UWE.5

Vent Shut-off valve, Swagelok, Cat. No. SS-ORS2 (Shut-off valve for LPG sampling)

Reagents and Materials

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 2.0 ppm as methane

Hydrocarbon Blends, for calibration, Matheson Tri-Gas

Hydrogen gas purifier, Valco, Cat. No. P-200

Hydrogen, purified chromatographic grade, typically 99.995% purity

Nitrogen, make-up gas, total hydrocarbons less than 0.5 ppm as methane

Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of gas chromatography, and the equipment being used.

Sampling

Obtain the sample by following the procedures described in ASTM Practice D 1265, "Sampling Liquefied Petroleum (LP) Gases (Manual Methods)," UOP Method 516, "Sampling and Handling of

Gasolines, Distillate Fuels, and C3-C4 Fractions,” or other reliable technique. The specially coated cylinders described in UOP Method 516 may be used but are not required for this application.

Chromatographic Technique

1. Install the gas purifier in the supply line between the carrier gas source and the carrier gas inlets on the gas chromatograph.
 - Column life is significantly reduced if the gas purifier is not used.
2. Install the LPG sampling valve (see Figure 1).
 - The injection valve should be mounted so that it maintains ambient temperature at the start of the run to keep liquid from bubbling in the valve or injection lines prior to injection.
 - If it is desired to make gas injections, replace the liquid injection valve on the GC with a gas injection valve and refer to the appendix of this method for how to inject a gas sample.
3. Install the fused silica capillary column in the gas chromatograph, according to the column and gas chromatograph manufacturer’s instructions.
4. Establish the flow rate and operating temperature specified under Operating Conditions (see Table 1).
 - Caution: Hydrogen 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.
5. Program the column oven to 200°C. Maintain this temperature until a stable baseline has been obtained at the required sensitivity.
6. If the sample may contain water or sediment, or is of unknown origin, it must be checked for these contaminants before analysis by releasing a small amount of the sample from the bottom of the cylinder. Place the LPG sample cylinder in a vertical position in a hood or well vented area. If the cylinder has an outage tube, the outage tube must be at the top. Briefly open the bottom valve onto the floor of a hood to check that no water or sediment is present in the LPG. If water or sediment is determined to be present, discontinue the analysis and obtain a clean sample.
7. Pressurize the LPG cylinder containing the sample (or blend) to approximately 1400 to 2000 kPA gauge (200- to 300-psig) with nitrogen or helium.
8. Mount the cylinder in a vertical position.
 - The LPG sample is delivered to the lab at elevated pressure. Make sure to connect the sample vessel securely so LPG flows into the GC sampling valve prior to opening valves on the sample vessel.
 - If the cylinder has an outage tube, the outage tube fitting must be at the top. Connect the bottom valve to the sample injector valve inlet tubing.
 - If the cylinder is fitted with an eductor tube, connect the eductor tube outlet to the sample injection inlet tubing in such a manner that the eductor tube is sampling liquid LPG.
 - The connecting tubing between the cylinder and the injector valve must be as short as possible.
9. Place the injection valve in the fill position.
10. Ensure that the vent shut-off valve is closed.
11. Fully open the bottom valve, or eductor valve of the sample cylinder.
12. Partially open the vent shut-off valve to permit LPG flow through the sampling system.

Table 1**Recommended Operating Conditions**

Carrier gas	hydrogen
Mode	constant pressure
Head pressure	75 kPa gauge (11 psig)
Linear velocity @ 85°C	45 cm/sec
Equivalent flow @ 85°C	2.4 mL/min
Split flow	300 mL/min
Injection port temperature	210°C
Column temperature program^a	
Initial temperature	85°C
Initial hold time	2.5 min
Programming rate A	2°C/min
Intermediate 1 temperature	100°C
Intermediate 1 hold time	0 min
Programming rate B	5.3C/min
Intermediate 2 temperature	135°C
Intermediate 2 hold time	0 min
Programming rate C	14°C/min
Final hold temperature	200°C
Final hold time	24.25 min
Detector	flame ionization
Detector temperature	250°C
Hydrogen flow rate^b	35 mL/min
Air flow rate^b	350 mL/min
Makeup gas	nitrogen
Makeup gas flow rate^b	30 mL/min
Sample size	0.5 µl for LPG

^a The column used for this analysis has an upper limit of 200°C; do not exceed.

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

13. Purge the sample valve with sample, watching the translucent tubing to ensure it is liquid full. Continue the flow until entrained bubbles are no longer observed in the translucent tubing, and inlet lines are adequately flushed of previous sample residuals.
 - CAUTION: Inspect the translucent tubing regularly. Replace at first signs of wear or kinking. Pressure on the translucent tubing must never exceed 2000 kPa (300 psig).
14. Stop the sample flow by closing the vent shut-off valve.
15. Inject the sample immediately by switching the injection valve to the inject position, and start the integrator and the column temperature programming sequence.
 - The injection valve remains in the inject position for the duration of the sample run.
16. Close the LPG cylinder valve and immediately open the vent shut-off valve to vent the sampling system.
17. Identify each component and calculate their concentrations as described in *Calculations*.
 - The C2 through C5 hydrocarbon separation is complete in less than 18 minutes. Additional time is required for heavier components to elute if present.

Calibration

It has been found that using effective carbon number factors, sometimes called theoretical factors, provides accurate quantitation. The theoretical relative response factors were calculated using the effective carbon number (ECN) concept as described by Scanlon and Willis. These factors are listed in Table 2 and are used in the Calculations portion of this method.

Table 2
Theoretical Response Factors

<u>Component</u>	<u>Response Factor, mass-%, F</u>	<u>Response Factor, mol-%, G</u>
Ethane	1.050	1.960
Ethylene	1.031	2.063
Propane	1.027	1.307
Cyclopropane	1.014	1.352
Propylene	1.014	1.352
Isobutane	1.015	0.980
<i>n</i>-Butane	1.015	0.980
Cyclobutane	1.005	1.005
<i>trans</i>-2-Butene	1.005	1.005
1-Butene	1.005	1.005
Isobutene	1.005	1.005
<i>cis</i>-2-Butene	1.005	1.005
Neopentane	1.008	0.784
Isopentane	1.008	0.784
<i>n</i>-Pentane	1.008	0.784
1,3-Butadiene	0.994	1.031
3-Methyl-1-butene	1.000	0.800
<i>trans</i>-2-Pentene	1.000	0.800
2-Methyl-2-butene	1.000	0.800
1-Pentene	1.000	0.800
2-Methyl-1-butene	1.000	0.800
<i>cis</i>-2-Pentene	1.000	0.800

Purchase a hydrocarbon calibration blend whose composition is similar to the samples to be analyzed. Analyze the blend as a sample to verify instrument calibration. If the results differ by more than 10% relative, check the apparatus, operating conditions, and the blend composition.

Calculations

When LPG injections are made, data is typically reported in mass-%, but may be reported in mol-%. Calculate the concentration of each hydrocarbon to the nearest 0.01 mass- or mol-%, using Equation 1 for mass-% or Equation 2 for mol-%:

$$\text{Hydrocarbon, mass-\%} = \frac{100EF}{S} \quad (1)$$

where:

E = component peak area
F = relative response factor, for mass-%, Table 2
S = sum of the products **EF** for all the recorded peaks
100 = factor to convert to mass-%

$$\text{Hydrocarbon, mol-\%} = \frac{100EG}{T} \quad (2)$$

where:

E = component peak area
G = relative response factor, for mol-%, Table 2
T = sum of the products **EG** of all the recorded peaks
100 = factor to convert to mol-%

Precision

The precision statement was determined using UOP Method 999. The LPG sample loop was purged and filled. The start button was pushed and the GC automatically injected the sample using the installed injection valve.

Repeatability and Site Precision

A nested design was carried out for determining components in one LPG hydrocarbon sample-with four analysts in one laboratory. Each analyst carried out two tests on two separate days. The total number of tests for each component was 16. The precision data are summarized in Table 3. Two tests performed by the same analyst on the same day should not differ by more than the repeatability allowable difference with 95% confidence. Two tests performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable difference with 95% confidence.

Table 3
Repeatability and Site Precision, mass-%

Component	Mean Conc.	Repeatability		Site Precision	
		Within- Day esd	Allowable Difference	Within- Lab esd	Allowable Difference
Propane	14.05	0.03	0.10	0.04	0.14
Propylene	25.69	0.09	0.30	0.13	0.42
Isobutane	16.28	0.03	0.10	0.04	0.14
<i>n</i>-Butane	9.53	0.06	0.20	0.06	0.21
<i>trans</i>-2-Butene	9.01	0.03	0.09	0.04	0.12
1-Butene	8.25	0.06	0.18	0.04	0.14
Isobutene	9.34	0.02	0.06	0.02	0.08
<i>cis</i>-2-Butene	6.47	0.02	0.06	0.02	0.08
Isopentane	0.75	0.01	0.03	0.01	0.03
1,3-Butadiene	0.24	0.01	0.02	0.01	0.02
3-Methyl-1-butene	0.30	0.01	0.02	0.01	0.01
2-Methyl-1-butene	0.09	0.01	0.01	0.01	0.01

The data in Table 3 are a short-term estimate of repeatability. When the test is run routinely, a control standard and chart should be used to develop a better estimate of the long-term repeatability.

Reproducibility

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

Time for Analysis

The elapsed time for one analysis is 0.8 hour. The labor requirement is 0.4 hour.

Suggested Suppliers

Agilent Technologies, 2850 Centerville Road, Wilmington, DE 19808-1610 (302-633-8000)
www.agilent.com

Alltech Associates, 2051 Waukegan Road, Deerfield, IL 60015-1899 (847-948-8600)
www.alltechweb.com

Chicago Fluid Systems Technologies, 360 Windy Point Drive, Glendale Heights, IL 60139 (630 545 0003) www.swagelok.com

Cole Parmer Instrument Company, 625 East Bunker Court, Vernon Hills, IL 60061-9872 (847 549 7600) www.coleparmer.com

Matheson Tri-Gas, Inc., 166 Keystone Drive, Montgomery, PA 18936 (215-641-2700)
www.matheson.com

Varian, Inc., (Chrompack columns), 2700 Mitchell Drive, Walnut Creek, CA 94598 (925 945 2360)
www.varianinc.com

VICI Valco Instruments Co. Inc., P.O. Box 55603, Houston, TX 77255 (713-688-8106)
www.vici.com

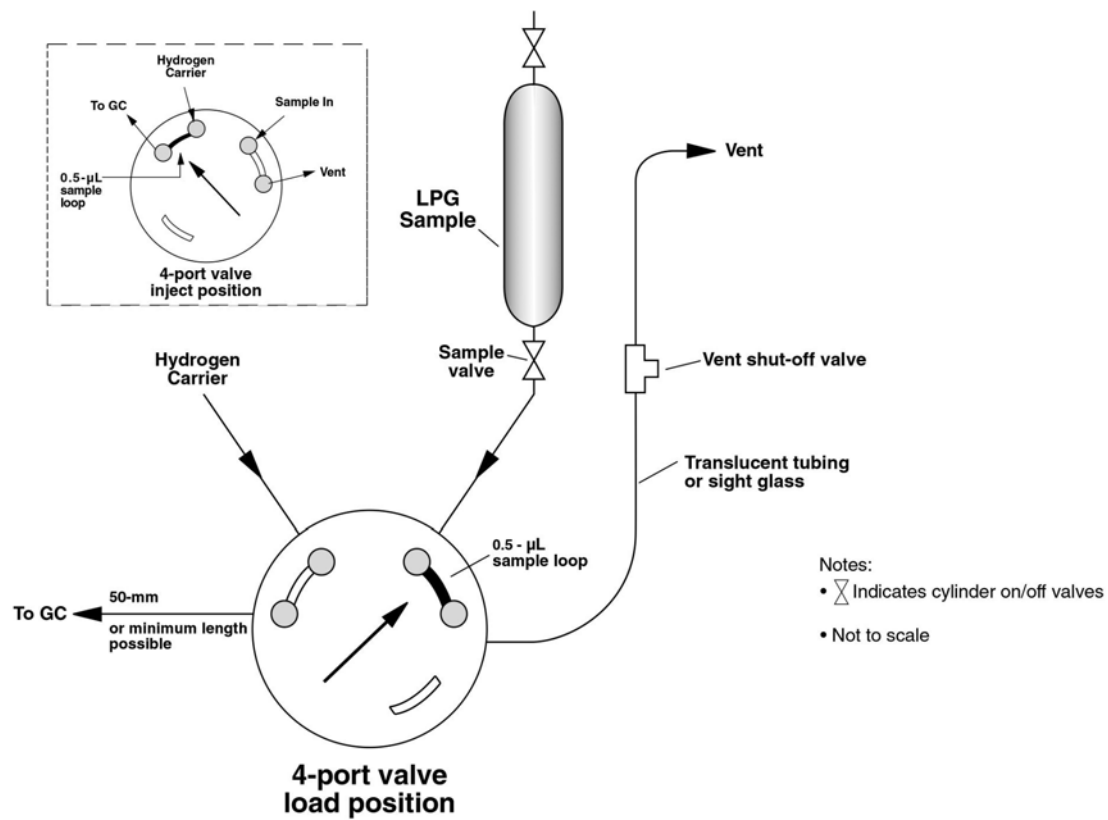


Figure 1
LPG Sampling System

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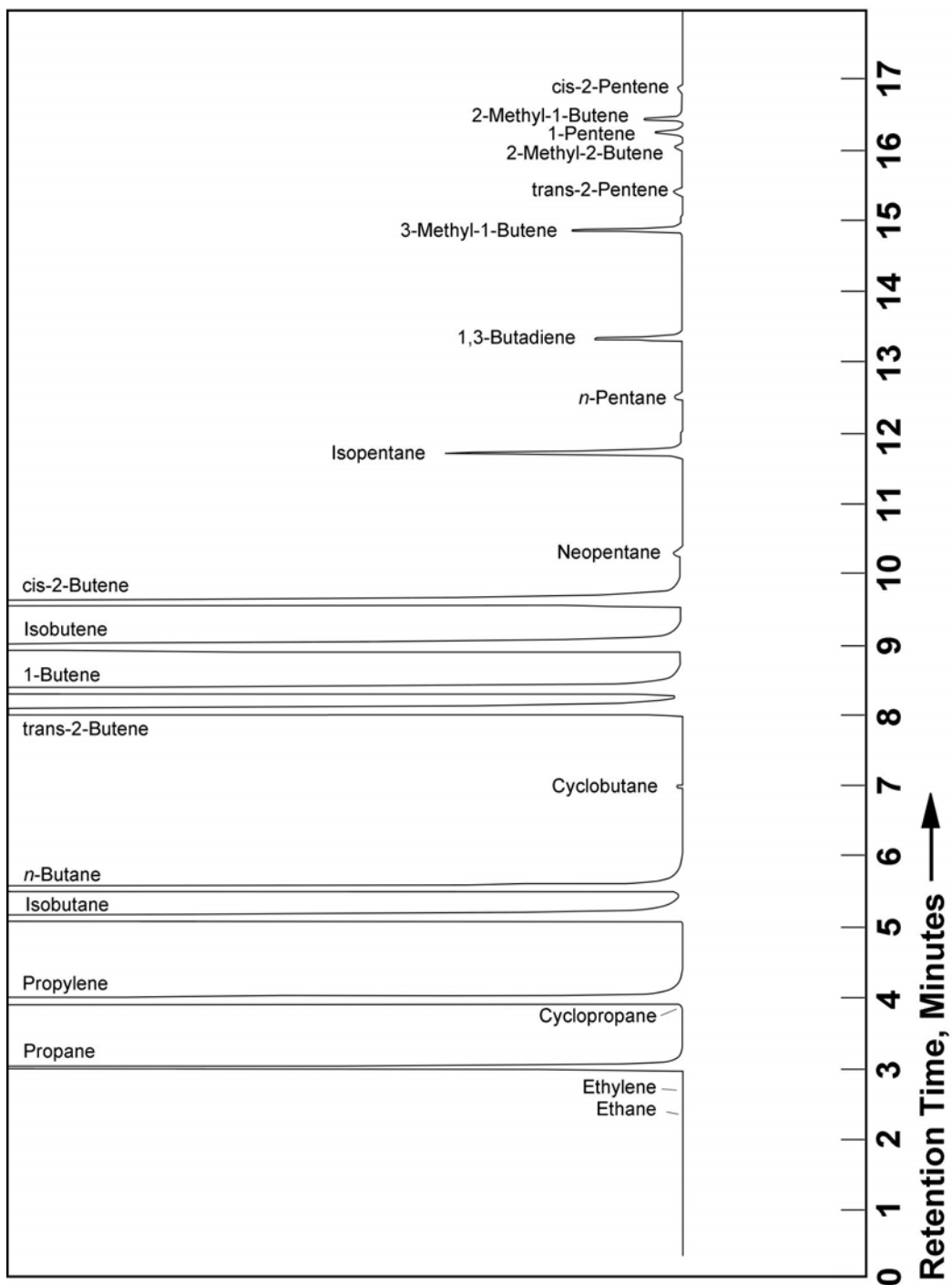


Figure 2
Typical Chromatogram

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Appendix

Scope

This appendix describes how to inject a gaseous sample.

Apparatus

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

Valve, gas sampling, 6-port valve, with a 100- μ l sample loop, Valco, Cat. No. DC6UWE

Procedure

Chromatographic Technique

1. Connect the sample or calibration blend cylinder to the sample inlet (Figure A1) and purge the sample loops with the gas to be analyzed.
2. Stop the flow, allow 5 to 10 seconds for the pressure to equilibrate, and start the analysis.
3. Identify each component and calculate their concentrations as described in *Procedure*, Step 15, and *Calculations* in the body of the method.

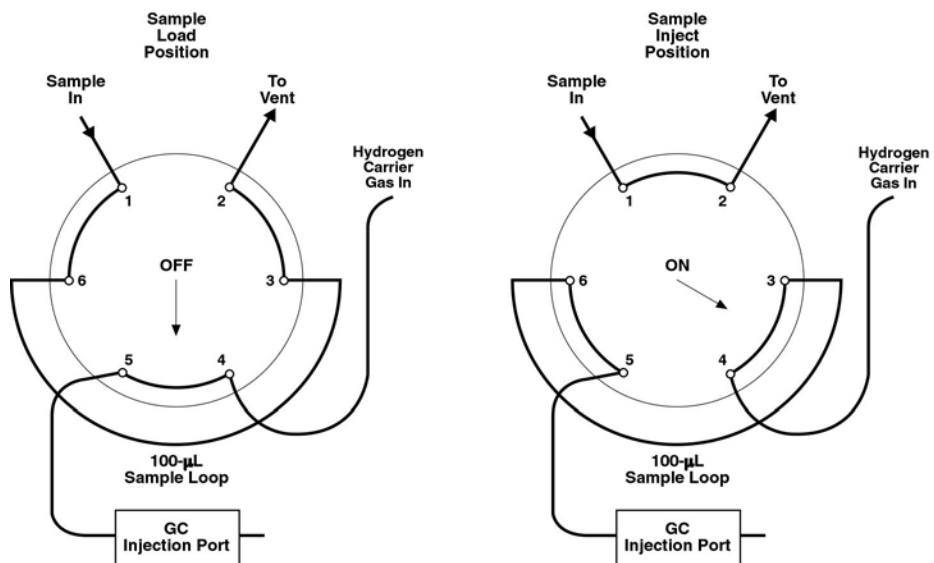


Figure A1
Sample Valve Flow Diagram

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