

ACETYLENES IN 1,3-BUTADIENE BY GC

UOP™ Method 983-04

SCOPE

This method is for determining low percent levels of acetylenes in crude butadiene feedstock and product, and is specifically applicable to KLP™ process streams. The following components and group classifications may be reported: methane, ethane, ethylene, propane, cyclopropane, propylene, isobutane, acetylene, *n*-butane, propadiene, *trans*-2-butene, 1-butene, isobutylene, *cis*-2-butene, isopentane, *n*-pentane, 1,2-butadiene, methyl acetylene, 1,3-butadiene, 3-methyl-1-butene, *trans*-2-pentene, 2-methyl-1-butene, vinyl acetylene, ethyl acetylene, 2-methyl-2-butene, and total heavies. Components that do not elute from the chromatographic system under the specified conditions are not determined. The range of quantitation for any compound is 0.01 to 99.9 mass-%. The analysis is applicable to laboratory or on-line use.

REFERENCES

ASTM Practice D 1265, "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 999, "Precision Statements in UOP Methods," www.astm.org

OUTLINE OF METHOD

The sample to be analyzed is injected as a liquefied petroleum gas (LPG) into a gas chromatograph equipped with an alumina PLOT (porous layer open tubular) capillary column, a capillary injection port, a flame ionization detector (FID), an LPG sampling valve, and a backflush valve. The PLOT column elutes individually measured components through 2-methyl-2-butene, after which the remainder of the sample is back-flushed to elute any remaining heavy materials. The composition of

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the sample is obtained by the normalization technique, wherein the peak areas of the entire sample are first corrected for differences in response and then normalized to 100%.

Because of the toxicity of 1,3-butadiene, follow safe venting and environmental practices.

APPARATUS

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used if equivalent performance can be obtained.

Fittings and connectors are listed to connect to the specified apparatus. Additional fittings will be required for the specific sample cylinders, for instrument gases, for on-line connections, and to conform to good laboratory procedures and local safety regulations.

Chromatographic column, 50 m of 0.32-mm ID fused silica capillary, internally coated to a film thickness of 5- μ m with potassium chloride washed aluminum oxide ($\text{Al}_2\text{O}_3/\text{KCl}$), Chrompack Cat. No. 7515, Varian Inc.

Fittings, bulkhead, 1.6-mm (1/16-inch) zero dead volume union with internal bore of 0.25 mm used as connection between fused silica and stainless steel tubing. Valco Instruments, Cat. No. ZBU1C. See Figure 1.

Gas chromatograph, temperature programmable, capable of constant flow, built for capillary column chromatography, utilizing a split injection system, having a glass injection port insert, a heated valve box with valve actuators, and equipped with an FID that will give a minimum peak height response of five times the background noise for 0.01 mass-% of 1-butene when operated at the recommended conditions, Agilent Technologies, Model 6890

Injection apparatus, LPG, for injection of LPG samples in the liquid phase. See Figure 1.

Fitting, internal union, for connecting injection port to 4-port sampling valve, Valco Instruments, Cat. No. ZU1T

Fitting, reducing union, 3.2-mm (1/8-inch) to 1.6-mm (1/16-inch), Swagelok, Cat. No. SS-200-6-1

Tubing, stainless steel, for connecting the sample cylinder to the 4-port sampling valve, 1.6-mm (1/16-inch) OD, 0.76-mm (0.30-inch) ID, Alltech Associates, Cat. No. 300010

Tubing, translucent, for connecting the 4-port sampling valve to the vent shut-off valve, FEP Teflon, 3.2-mm (1/8-inch) OD, 1.6-mm (0.062-inch) ID, 3450 kPa (500 psig), Alltech Associates, Cat. No. 45740

Valve, sample injection, 4-port, stainless steel, 0.5- μ L internal sample volume, 1.6-mm (1/16-inch) fittings, Valco Instruments, Cat. No. CI4UWE.5, with air actuator, Valco Instruments, Cat. No. A-904, controlled by GC

Valve, vent shut-off, Swagelok, Cat. No. SS-ORS2

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 graphic capabilities. ChemStation, Agilent Technologies

Leak detector, gas, Alltech Associates, Cat. No. 21-250

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

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

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

Tubing, fused silica, 5-m x 0.32-mm ID or smaller, deactivated fused silica tubing. If deactivated tubing is not available, a thin film poly-dimethyl siloxane column may be substituted.

Tubing, stainless steel, 6-m (20-ft) x 1.6-mm (1/16-inch) OD, with internal diameter 0.5-mm (0.02-inch) or smaller, used as connection between bulkhead unions and backflush valve, and between GC and remote injection valve.

Valve, backflush, Valco Instruments, Cat. No. C4UWE

REAGENTS AND MATERIALS

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

Air, for valve actuation

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

Gas purifier, helium, Mat/Sen, Cat. No. P100-1

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

Sampling

Obtain the sample by following the procedures described in ASTM Practice D 1265, "Sampling Liquified Petroleum (LP) Gases (Manual Method)," UOP Method 516, "Sampling and Handling of Gasolines, Distillate Fuels, and C₃-C₄ Fractions," or other reliable technique.

Instrument Set-up

For health and safety reasons, set up the GC so that the sample vent, split vent and septum purge streams are vented out of the lab, or into a hood or other well ventilated area. The backflush valve is mounted in the valve box. The LPG sample injection valve must not be heated, and should be mounted on the GC, but away from heat sources. A bracket holding the valve near but not touching the injection port is best. If safety practices demand, the LPG injection valve may be mounted up to 2 m from the GC, with only a small degradation in peak shape. For on-line applications, connect the sample stream to the sample valve as shown in the process flow diagrams.

Chromatographic Technique

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

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 4-port LPG sampling valve external to the GC near the split injection system. Connect the related apparatus as shown in Figure 1.

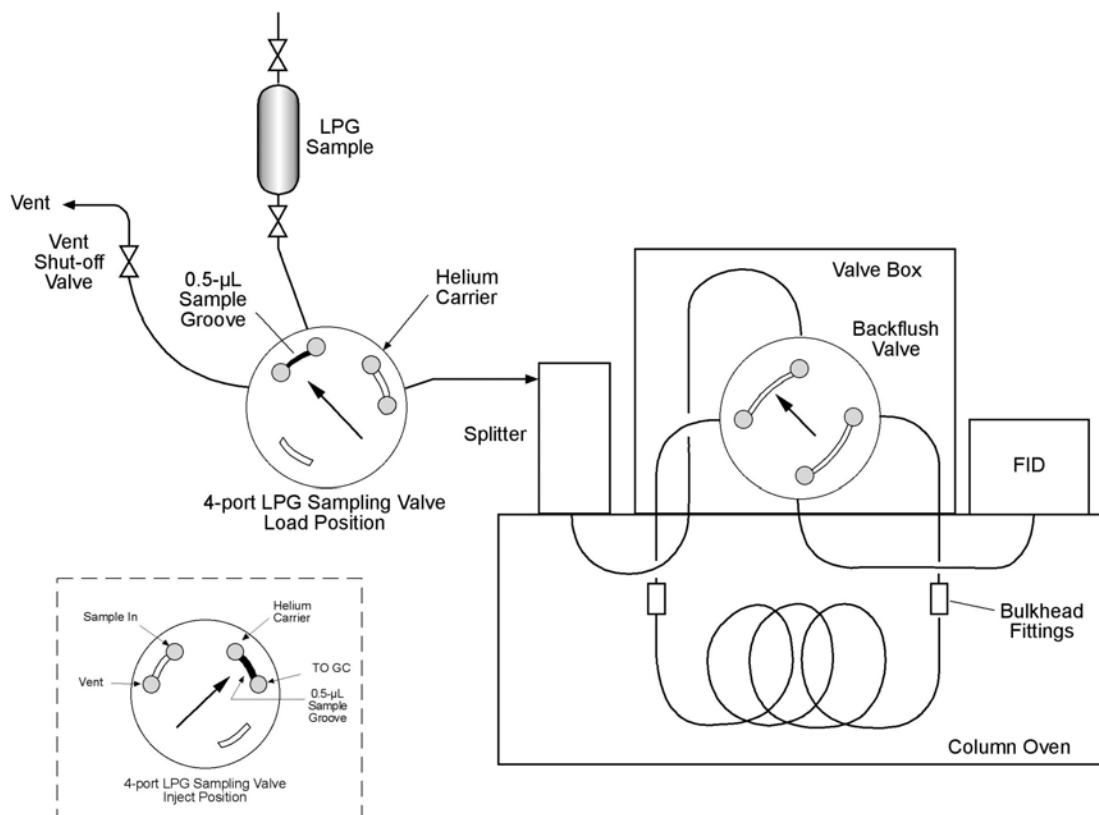


Figure 1
Sampling and Gas Chromatograph Flow Diagram

3. Establish the recommended operating conditions as given in Table 1.

Table 1
Recommended Operating Conditions

Carrier gas	helium
Column head pressure @ 80°C, constant flow mode	160 kPa (23.2 psig)
Equivalent flow	10 mL/min
Equivalent linear velocity	43.5 cm/sec
Split flow rate	290 mL/min
Injection port temperature	225°C
Valve box temperature	100°C
Electronic pressure control	constant flow on
Column temperature program	
Initial temperature	35°C
Initial time	3.1 min
Programming rate A	4°C/min
Intermediate temperature A	125°C
Intermediate time A	0 min
Programming rate B	8°C/min
Intermediate temperature B	169°C
Intermediate time B	0 min
Programming rate C	20°C/min
Final temperature	200°C
Final time	36 min
Detector	FID
Detector temperature	250°C
Hydrogen flow rate*	30 mL/min
Air flow rate*	400 mL/min
Makeup gas	nitrogen
Makeup gas flow rate*	30 mL/min
Sample size	0.5µL

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

4. Condition the column according to the manufacturer's instructions.
5. Cool the column oven to a stabilized 35°C.
6. 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 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.
- 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 an eductor tube. If the sample cylinder contains an eductor tube, invert the cylinder (both valves on the bottom) and briefly open the valve not connected to the eductor tube to check that no water or sediment is present.

7. Pressurize the LPG cylinder containing the sample to approximately 1400- to 2000-kPa gauge (200- to 300-psig) with nitrogen or helium.
8. Mount the cylinder in a vertical position. If the cylinder has an outage tube, the outage tube 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.
13. Continue the flow until no entrained bubbles are observed through the translucent tubing.
 - **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. Backflush the GC column immediately after the elution of 2-methyl-2-butene (approximately 23 minutes for the conditions listed). If no 2-methyl-2-butene is present in the sample, follow the pattern of the peaks shown in Figure 2, and backflush at the appropriate time.
18. Identify the components of interest by comparing the chromatogram obtained to the Typical Chromatogram (Figure 2) and Table 2.
 - If there is a question about the identification of any peak, prepare or purchase a qualitative blend containing the components of interest, analyze it, and compare its chromatogram to the sample chromatogram.

Calibration

Since it may be difficult to purchase and maintain a calibration blend that contains all components of interest, calculated response factors are used. These were calculated using the effective carbon number (ECN) concept as described by Scanlon and Willis, and are listed in Table 2.

Table 2
Retention Order of Identified Components and
Calculated Mass Response Factors Relative to 1,3-Butadiene

<u>Peak No.</u>	<u>Component</u>	<u>Response Factor</u>
1	Methane	1.12
2	Ethane	1.05
3	Ethylene	1.11
4	Propane	1.03
5	Cyclopropane	0.99
6	Propylene	1.02
7	Isobutane	1.02
8	Acetylene	0.71
9	<i>n</i> -Butane	1.02
10	Propadiene	0.99
11	<i>trans</i> -2-Butene	1.01
12	1-Butene	1.01
13	Isobutylene	1.01
14	<i>cis</i> -2-Butene	1.01
15	Isopentane	1.01
16	<i>n</i> -Pentane	1.01
17	1,2-Butadiene	1.00
18	Methyl acetylene	0.78
19	1,3-Butadiene	1.00
20	3-Methyl-1-butene	1.00
21	<i>trans</i> -2-Pentene	1.00
22	2-Methyl-1-butene	1.00
23	Vinyl acetylene	0.81
24	Ethyl acetylene	0.83
25	2-Methyl-2-butene	1.00
26	Heavies	0.99

CALCULATIONS

Obtain the peak area for each individual component or group of components and calculate the concentration of each to the nearest 0.01 mass-%, using Equation 1.

$$\text{Component, mass-\%} = 100 \frac{PF}{T} \quad (1)$$

where:

F = relative response factor, from Table 2

P = area of individual component or group of components

T = the sum of the products, **PF**, of all the recorded components or groups of components

100 = factor to convert to mass-%

PRECISION

Precision statements were determined using UOP Method 999.

Repeatability and Intermediate Precision

The same feed sample was injected into an on-line GC a total of 16 times on four separate days over a period of 2½ weeks. The precision data are summarized in Table 3. Two tests performed on the same instrument on the same day should not differ by more than the repeatability allowable difference with 95% confidence. Two tests performed by the same instrument on different days should not differ by more than the intermediate precision allowable difference with 95% confidence.

Reproducibility

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

Table 3
Repeatability and Intermediate Precision, mass-%

<u>Component</u>	<u>Concentration</u>	<u>Repeatability</u>		<u>Intermediate Precision</u>	
		<u>Within-Day esd</u>	<u>Allowable Difference</u>	<u>Within-Lab esd</u>	<u>Allowable Difference</u>
Propane	0.07	0.0085	0.028	0.0093	0.031
Acetylene	0.02	0.0008	0.003	0.0008	0.003
Propadiene	0.02	0.0010	0.003	0.0010	0.003
<i>trans</i>-2-Butene	2.82	0.0068	0.022	0.0068	0.022
1-Butene	7.21	0.0371	0.121	0.0783	0.255
1,2-Butadiene	0.48	0.0065	0.021	0.0097	0.032
1,3-Butadiene	75.19	0.0439	0.143	0.0671	0.219
Vinyl acetylene	1.85	0.0061	0.020	0.0129	0.042
Ethyl acetylene	0.02	0.0019	0.006	0.0031	0.011
Heavies	0.35	0.0173	0.057	0.0210	0.068

TIME FOR ANALYSIS

The elapsed time for one analysis is 1.3 hours. The labor requirement is 0.5 hour.

SUGGESTED SUPPLIERS

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

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

Chrompack, 1130 Route 202, Raritan, NJ 08869 (980-722-8930) www.varianinc.com

Matheson Tri-Gas, 166 Keystone Drive, Montgomeryville, PA 18936 (215-641-2700)
www.mathesontrigas.com

Mat/Sen, 26272 Twelve Trees #C, Poulsbo, WA 98370 (360-697-9199) www.vici.com

Swagelok Company, 29500 Solon Rd., Solon, OH 44139 (440-248-4600) www.swagelok.com

Valco Instrument Co., Inc. (VICI), P. O. Box 55603, Houston, TX 77255 (713-688-9345)
www.vici.com

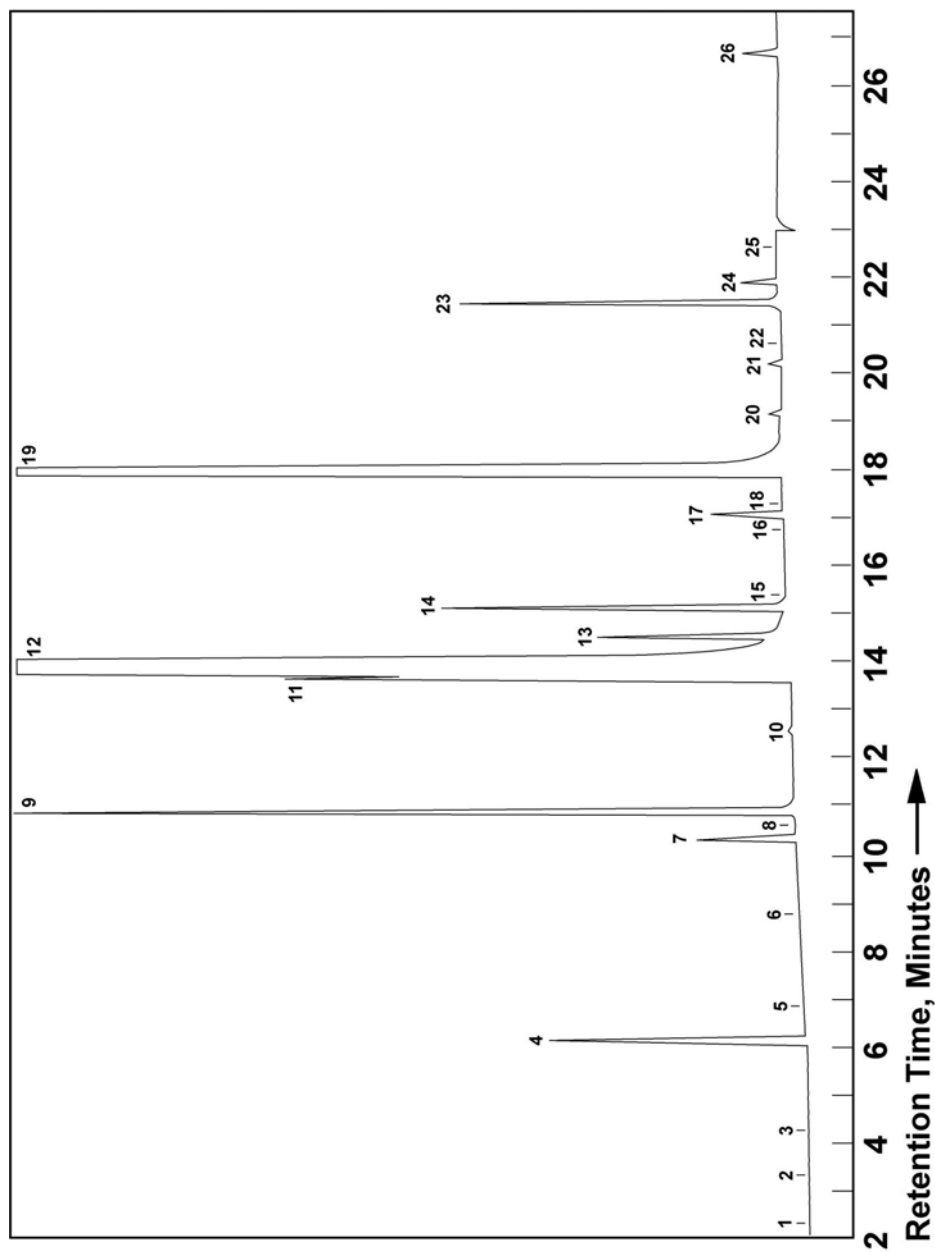


Figure 2
Typical Chromatogram

UOP Method 983-04