



Standard Test Method for Determination of Hydrocarbons in Liquefied Petroleum (LP) Gases and Propane/Propene Mixtures by Gas Chromatography¹

This standard is issued under the fixed designation D2163; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the quantitative determination of individual hydrocarbons in liquefied petroleum (LP) gases and mixtures of propane and propene, excluding high-purity propene in the range of C₁ to C₅. Component concentrations are determined in the range of 0.01 to 100 volume percent.

1.2 This test method does not fully determine hydrocarbons heavier than C₅ and non-hydrocarbon materials, and additional tests may be necessary to fully characterize an LPG sample.

1.3 The values stated in SI units are to be regarded as standard. The values given in parentheses are for information only.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:²

[D1265 Practice for Sampling Liquefied Petroleum \(LP\) Gases, Manual Method](#)

[D1835 Specification for Liquefied Petroleum \(LP\) Gases](#)

[D2421 Practice for Interconversion of Analysis of C₅ and Lighter Hydrocarbons to Gas-Volume, Liquid-Volume, or Mass Basis](#)

[D2598 Practice for Calculation of Certain Physical Properties of Liquefied Petroleum \(LP\) Gases from Compositional Analysis](#)

[D3700 Practice for Obtaining LPG Samples Using a Floating Piston Cylinder](#)

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.D0.03 on Propylene.

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[D6729 Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 100 Metre Capillary High Resolution Gas Chromatography](#)

[E355 Practice for Gas Chromatography Terms and Relationships](#)

[E594 Practice for Testing Flame Ionization Detectors Used in Gas or Supercritical Fluid Chromatography](#)

[E1510 Practice for Installing Fused Silica Open Tubular Capillary Columns in Gas Chromatographs](#)

2.2 *Canadian General Standards Board Publications:*³

[CAN/CGSB 3.0 No. 14.3 Standard Test Method for the Identification of Hydrocarbon Components in Automotive Gasoline Using Gas Chromatography](#)

2.3 *Gas Processors Association:*⁴

[GPA Std 2145-03](#) for hexane

3. Terminology

3.1 Definitions:

3.1.1 Additional terminology related to the practice of gas chromatography can be found in Practice [E355](#).

3.1.2 *liquefied petroleum gas (LPG), n*—hydrocarbon gases that can be stored or handled in the liquid phase through compression or refrigeration, or both.

3.1.2.1 *Discussion*—LPG's generally consist of C₃ and C₄ alkanes and alkenes or mixtures thereof and containing less than 10 volume percent of higher carbon number material. Vapor pressure does not normally exceed 2000 kPa at 40°C.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *propane/propene mixtures, n*—mixtures primarily composed of propane and propene where one of these components is usually in the concentration range of 30 to 85 mass % with the other comprising the majority of the remainder. "Commercial Propane in Specification [D1835](#) is typically this sort of product mixture.

3.2.1.1 *Discussion*—Other components may be present, usually at less than 10 mass %.

³ Available from CGSB, Canadian General Standards Board, Gatineau, Canada K1A 1G6. Visit the CGSB website, www.pwgsc.gc.ca/cgsb/

⁴ Available from Gas Processors Association (GPA), 6526 E. 60th St., Tulsa, OK 74145, <http://www.gasprocessors.com>.

4. Summary of Test Method

4.1 An LPG sample is analyzed via either liquid or gas sampling valves by gas chromatography and compared to corresponding components separated under identical operating conditions from a reference standard mixture of known composition or from use of pure hydrocarbons. The chromatogram of the sample is interpreted by comparing peak retention times and areas with those obtained for the reference standard mixture or pure hydrocarbons.

5. Significance and Use

5.1 The hydrocarbon component distribution of liquefied petroleum gases and propene mixtures is often required for end-use sale of this material. Applications such as chemical feed stocks or fuel require precise compositional data to ensure uniform quality. Trace amounts of some hydrocarbon impurities in these materials can have adverse effects on their use and processing.

5.2 The component distribution data of liquefied petroleum gases and propene mixtures can be used to calculate physical properties such as relative density, vapor pressure, and motor octane (see Practice D2598). Precision and accuracy of compositional data are extremely important when these data are used to calculate various properties of these petroleum products.

6. Apparatus

6.1 *Gas Chromatograph (GC)*—Any gas chromatographic instrument provided with a linear temperature programmable column oven. The temperature control must be capable of obtaining a retention time repeatability of 0.05 min (3 s) throughout the scope of this analysis.

6.2 *Detector*—A flame ionization detector (FID) having a sensitivity of 0.5 ppm (mole) or less for the compounds listed in Table 1 is strongly recommended (see Practice E594).

6.2.1 Other detectors may be used (alone or in series) provided that they have sufficient response, linearity, and sensitivity to measure the components of interest at the concentration levels required.

6.3 *Data Acquisition*—Any commercial integrator or computerized data acquisition system may be used for display of the chromatographic detector signal and peak area integration. The device should be capable of calibration and reporting of the final response corrected results.

6.4 *Sample Introduction*—Whether liquid or vapor sampling, the combination of valve injection size and split ratio must be selected such that the required sensitivity is achieved and also that no component concentration in a sample is greater than the detector upper linearity limit.

6.4.1 If capillary columns will be used, then the GC must include a heated splitting type injector that is operated isothermally. Split ratios in the range of 5:1 to 200:1, with a typical value of 100:1, will be used dependent upon the sample injection volume and sensitivity required. If packed columns will be used, then a splitting type injector is not required and a suitable packed inlet port may be used.

6.4.2 *Liquid Sampling (recommended)*—The GC should be equipped with a liquid sampling valve for introduction of the sample aliquot to the splitting injector. Liquid sampling valves with an internal fixed sample volume between 0.2 to 0.5 μL or a size to provide the minimum detection limits given in 1.1 have been used satisfactorily. The valve shall be rated for at least 1380 kPa (200 psi) above the vapor pressure of the sample at the valve operating temperature. A shut-off valve shall be provided at the exit of the sampling valve waste port. A 2 to 7 μm packed-screen type filter should be provided at the sample inlet port of the sampling valve to remove possible particulate material from the sample. The valve shall provide for a repeatability of at least 2% relative sample volume introduction. The sampling valve shall be located at the GC such that

TABLE 1 Expected Retention Order and Times

Component	Estimated Retention Time (min)	Estimated Retention Time (min)	FID	TCD
	(using typical Al_2O_3 PLOT operating conditions)	(using typical 100 m Dimethylpolysiloxane column operating conditions)		
C_5 Olefin/ C_6^+ Composite (backflush)	NA ^A	...	x	x
Air Composite (O_2 , Ar, N_2 , Co)	NA ^A	x
Methane	1.9	6.5	x	x
Ethane	2.1	6.7	x	x
Propane	2.7	7.3	x	x
Cyclopropane	3.4	...	x	x
Propene	3.5	7.2	x	x
2-Methyl Propane (Isobutane)	4.0	8.4	x	x
Butane	4.2	9.5	x	x
Propadiene	4.7	...	x	x
Ethyne (Acetylene)	5.0	...	x	x
Trans-2-Butene	5.5	9.9	x	x
1-Butene	5.6	9.2	x	x
2-Methyl Propene (Isobutene)	5.7	9.1	x	x
2,2-Dimethylpropane (Neopentane)	5.9	10.1	x	x
Cis-2-Butene	6.2	10.6	x	x
Cyclopentane	6.7	25.8	x	x
2-Methyl Butane (Isopentane)	6.8	14.0	x	x
Pentane	7.2	16.9	x	x
1,3-Butadiene	7.5	9.3	x	x
Propyne (Methyl Acetylene)	7.9	...	x	x
> nC_5 (Sum C_5 Olefins and Heavier) ^B	8.1 until end of run	...	x	x

^A Not applicable.

^B > nC_5 components may be speciated and reported individually.

it can be operated at ambient temperature. The use of floating piston sample cylinders is encouraged to minimize or eliminate the volatilization of lighter components into the headspace. Common 80% filled LPG storage cylinders should be pressurized with an inert gas such as helium to facilitate liquid transfer and accurate liquid injections. A minimum pressure of 200 psi above sample vapor pressure is recommended. A pressure gauge may be used to make this determination. Before pressurization, verify that the sample cylinder, transfer lines and valves are rated to safely contain the pressurized sample. It is customary to add a check valve between the helium cylinder and the sample cylinder to prevent contamination in the event the sample cylinder is higher in pressure than the pressurizing cylinder.

6.4.3 *Vapor Sampling (optional)*—A six-port gas sampling valve or a ten-port sampling/column switching valve with 1.6 mm (1/16 in.) fittings and a 200 µL fixed sampling loop may be provided. This valve shall be contained in a heated enclosure and operated at a temperature above the boiling point of the highest boiling component in the sample. The use of a 2 to 7 µm frit or packed-screen type filter ahead of the sample introduction port is recommended. The valve shall provide for a repeatability of at least 2% relative sample volume introduction.

6.5 *Gas Controls*—The GC shall be provided with suitable facilities for delivery and control of carrier gas and the detector gases. This will consist of the appropriate tank and downstream regulators and supply tubing as well as the mass or pressure controls for the precise regulation of the instrument operation.

NOTE 1—Most GC suppliers will provide these devices or recommend the proper supplies.

6.6 *Column Series/Reversal Switching Valve*—If desired, a multi-port valve mentioned may be used to provide the C₅ olefin/C₆+ determination for this analysis. The back-flush configuration should be configured according to the manufacturer's recommendations.

6.7 *Columns*—Condition all columns used according to the manufacturers' suggestions prior to use.

6.7.1 *Analytical Column*—The recommended analytical column is a 50 m by 0.53 mm (I.D.) Na₂SO₄ deactivated Al₂O₃ porous layer open tubular (PLOT) column. Relative retention order is dependent upon the deactivation method for the column. (**Warning**—Specifically test the column to ensure that the column does not adsorb propadiene and butadienes. This condition can exist depending upon the degree of column deactivation.)

6.7.1.1 Routine re-conditioning of the column may be required to maintain column performance.

6.7.1.2 Alternatively, any column(s) that provides the appropriate component separations may be used. Columns (100 m by 0.25 mm (ID) by 0.5 µm film thickness) employed in standard methods Test Method D6729 and CGSB 3.0 No. 14.3 have been successfully used.

6.7.2 *Pre-column (optional)*—If an initial back flush of the C₅ olefins or hexane plus (C₆+) components, or both, through the use of the sequence reversal/back flush valve is desired, a second column is required. Any pre-column that provides

separation between the components of interest and the composite heavier components may be used. Choices may include lengths of column such as a 10 to 30 m section of 0.53 mm (I.D.) 1 µm film thickness dimethylpolysiloxane or polyethylene glycol capillary column or a 9 to 15 cm section of the same column material as the analytical column or any pre-column that provides the desired retention of C₅ olefins, hexanes, and heavier components. This pre-column acts to keep the heavier components away from the analytical column and to back flush the heavier components as a composite peak to the detector for quantitation. A pre-column that also has the ability to retain water and oxygenated hydrocarbon compounds is recommended to keep those materials from entering the analytical column.

7. Reagents and Materials

7.1 *Carrier Gases*—For carrier gases, it is recommended to install commercial active oxygen scrubbers and water dryers, such as molecular sieves, ahead of the instrument to protect the system's chromatographic columns. Follow supplier instructions in the use of such gas purifiers and replace as necessary.

7.1.1 *Hydrogen*, 99.995% minimum purity, <0.1 ppm H₂O. (**Warning**—Hydrogen is a flammable gas under high pressure.)

7.1.2 *Helium*, 99.995 % minimum purity, <0.1 ppm H₂O. (**Warning**—These materials are flammable and may be harmful or fatal if ingested or inhaled.)

7.2 *Detector Gases:*

7.2.1 *Hydrogen*, 99.99 % minimum purity. (**Warning**—Hydrogen is a flammable gas under high pressure.)

7.2.2 *Air*, less than 10 ppm each of total hydrocarbons and water. (**Warning**—These materials are flammable and may be harmful or fatal if ingested or inhaled.)

7.3 *Reference Standards:*

7.3.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, all reagents should conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.⁵ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.3.2 *Reference Gas Mixture*—Individual and mixed component reference materials are commercially available and may be used to establish qualitative and quantitative calibration. The calibration standard mixture should be gravimetrically prepared, supplied with both gravimetric and calculated volumetric concentrations, and certified. Due to the high partial pressure exerted by methane and ethylene, it is recommended that these components be limited to no greater than 0.2 vol% of the mixture composition. It is strongly recommended that the calibration standards be contained in floating piston cylinders

⁵ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For Suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

pressurized to at least 1380 kPa (200 psi) above the vapor pressure of the mixture at all times (a constant pressure source is suggested). Common LPG storage cylinders may also be used provided they can be maintained at the required pressure. Liquid mixtures containing levels of each of the analytes listed in [Table 1](#) in a balance of the type of LPG that is being analyzed should be used to calibrate the instrumentation. (**Warning**—These materials are flammable and may be harmful or fatal if ingested or inhaled.)

7.3.3 Calibration Gas Mixture—A mixture of known composition similar in concentration to the samples being analyzed may be used to monitor precision and accuracy. For liquid sampling, it is strongly recommended that the mixture be contained in floating piston or other cylinders pressurized to at least 1380 kPa (200 psi) above the vapor pressure of the mixture at all times (a constant pressure source is suggested).

8. Preparation of Apparatus

8.1 Set up the instrumentation in accordance with the manufacturer’s instructions or as specified herein.

8.2 Install and condition the column according to manufacturer’s instructions. See Practice [E1510](#) for recommended installation and conditioning procedures.

8.3 Set the GC instrument to the operating parameters. Allow the instrument to stabilize before proceeding with calibration and sample injections. Typical operating conditions for both PLOT and 100% dimethylpolysiloxane columns are provided in [Table 2](#). The conditions provided for the dimethylpolysiloxane column are equivalent to those described in Test Method [D6729](#).

8.4 Obtain duplicate chromatograms of the standard or sample, or both. Ensure that none of the peaks obtained have exceeded the upper range limit of the data handling device (at full scale on the data handling device, all peaks are on scale and display symmetrical, Gaussian shapes as opposed to flat peak tops). Peak areas of like components shall agree within

2%. Use the same sample size (split ratio) and range for all runs. Example chromatograms are provided in [Figs. 1 and 2](#).

8.5 *Liquid Sampling Valve (recommended)*—Set valve on and off times to comply with manufacturer’s instructions.

8.6 *Gas Sampling Valve (optional)*—Set valve on and off times to comply with manufacturer’s instructions.

8.7 *Switching (Backflush) Valve (optional)*—The valve rests in the “off” state, allowing a continuous back flush flow through the pre-column. Before or upon injection of the sample, the valve should be rotated to the “on” position so that the pre-column is placed at the head of the flow path from the sample valve. At a time which must be empirically determined and which is dependant upon the length and type of pre-column used, the valve must be returned to the “off” position, causing the flow to back flush through the pre-column and flush to the detector ahead of components eluting from the analytical column. Determining this switch time may require iterative attempts and interpolation. However, once the time has been determined, it should remain repeatable for all samples of similar composition.

9. Calibration and Standardization

9.1 *Qualitative*—Determine the retention times of components by analyzing known reference mixtures in the same manner as the samples (Section [10](#)). Typical retention times are given in [Table 1](#).

9.2 *Quantitative, Hydrocarbons*—Use response factors for correction of the detector response of hydrocarbons determined by this test method. Experimental or theoretical response factors may be used.

9.2.1 *Experimental Response Factors*—Determine the experimental response factor of components by analyzing known calibration mixtures under the same conditions of pressure and temperature as the samples (Section [10](#)). For each component present in the calibration standard, calculate the response factor according to Eq 1. (Note that some integrators or computer

TABLE 2 Typical Operating Conditions

Column Type	100% Dimethylpolysiloxane	Al ₂ O ₃ PLOT - Na ₂ SO ₄ deactivated
Column Dimensions	100 m by 0.25 mm by 0.5 μm	50 m by 0.53 mm by 15 μm
Backflush	No	No
Initial Temperature	0°C	80°C
Initial Hold Time	15 min	1 min
Program Rate 1	1°C/min	10°C/min
Final Temperature	50°C	200°C
Program Rate 2	2°C/min	...
Final Temperature	130°C	...
Program Rate 3	4°C/min	...
Final Temperature	270°C	...
Final Hold Time	0 min	12 min
Injector Temperature	250°C	250°C
Sample Size	0.2 to 0.5 μL	0.2 μL
Split Ratio	175:1 to 275:1	100:1
Detector Temperature	300 to 350°C	250°C
Fuel Gas Hydrogen Flow	30 to 40 mL/min	40 mL/min
Oxidizing Gas Air Flow	300 to 450 mL/min	400 mL/min
Make-up Gas Type	N ₂ or He	He
Make-up Gas Flow	30 mL/min	35 mL/min
Carrier Gas	He @ 2 mL/min (H ₂ optional)	Helium at 6 mL/min
Average Linear Velocity	25 cm/s	45 cm/s
Data Rate	10 to 20 Hz	5 Hz
Approximate Run Time	140 min	25 min

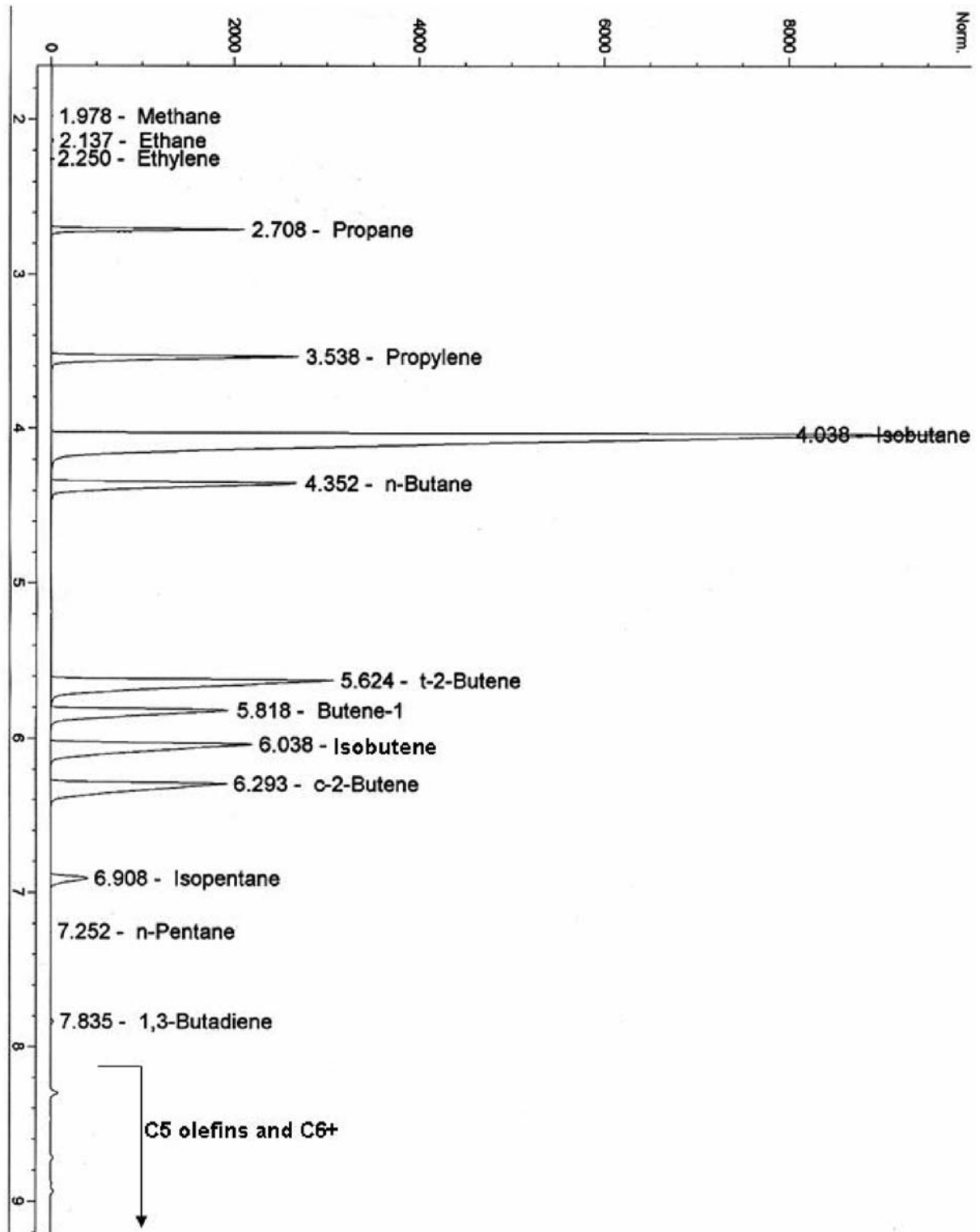


FIG. 1 Example Chromatogram Using the PLOT Column (without back-flush)

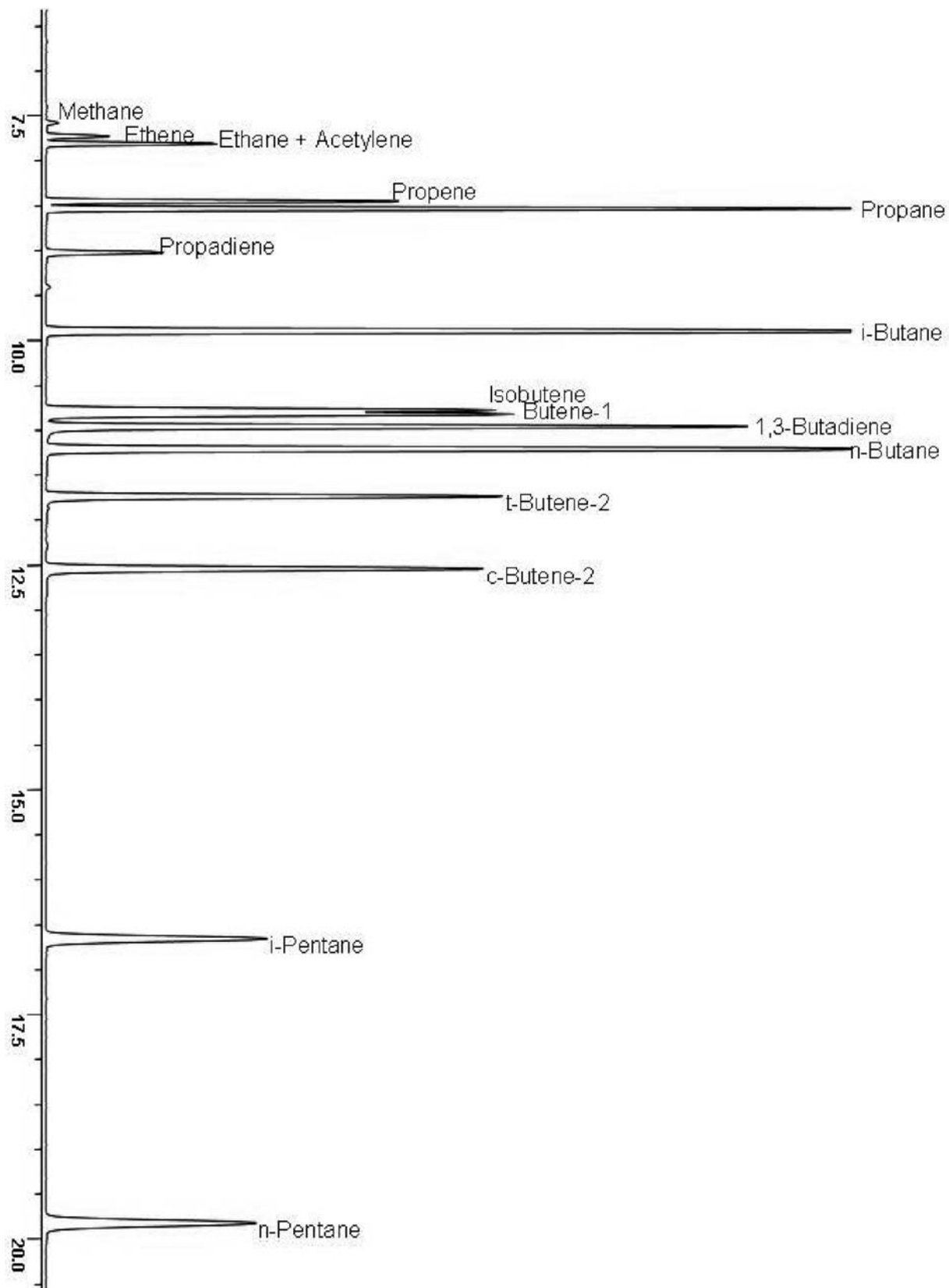


FIG. 2 Example Chromatogram Using the Dimethylpolysiloxane Column

data systems may use another formula (inverse of the formula given, in some cases) for calculating response factors.) After determining the response factors for each component, analyze a secondary standard as a sample and verify that the concentrations agree with the values for the standard within the precision and bias for this test method as determined by interlaboratory testing.

$$RF_i = C_i/A_i \quad (1)$$

where:

RF_i = the response factor for component i ,

C_i = the known concentration of i , and

A_i = the integrated area of peak i .

9.2.2 Theoretical Response Factors—If the samples to be assayed contain only hydrocarbons and a FID is employed for the determination of those components, then theoretical response factors may be applied. The results shall then be normalized to 100%.

9.2.2.1 Table 3 provides theoretical mass response factors relative to methane (RRF). Use of these response factors will produce results in mass percent units, which may be converted to other units (liquid volume percent or mole percent) by the user as needed. Alternately, the theoretical response factors may be converted to other units prior to quantification. Individually eluting C_5 olefins or hexane-plus components, or both, may be quantified using the same RRF as the $C_5=C_6+$ composite peak.

9.2.2.2 It is necessary to compare calculated results to the certified values for a known standard before adopting the calibration. The standard should contain all of the components typically observed in the samples. Results should agree within 5% of the certified value. Failure to compare may result from lack of injection split linearity or use of a standard that has not been maintained under pressure.

9.3 Quality Monitoring—The primary or secondary standard should be analyzed at least once a week to verify system accuracy, when the test method is in regular use. If the test method is used only occasionally, analyze a primary or secondary standard before each set of analyses.

10. Procedure

10.1 Sampling—Sampling at the sample source and at the chromatograph shall always be done in a manner that ensures that a representative sample is being analyzed. Lack of precision and accuracy in using this test method can most often be attributed to improper sampling procedures. (See Practice **D3700** and Practice **D1265**.)

10.2 Liquid Sample Valve Injection—For propene concentrations, butane samples, or other LPG samples, the sample may be introduced as a liquid by means of a liquid sample valve. It is strongly suggested that the use of a floating piston type sample cylinder be used and that the sample be pressurized to 1380 kPa (200 psi) above the vapor pressure of the sample prior to sampling.

10.2.1 In a hood, prior to connecting the cylinder, invert the cylinder and purge a small aliquot of the sample through the valve on the sample cylinder to remove any moisture or particulate matter which might be present.

10.2.2 Connect the pressurized liquid standard to the “sample in” port of the liquid sampling valve and close the waste vent shut-off valve. Open the outlet valve on the standard cylinder and open the waste shut-off valve for 10 to 15 s to allow sample to flow through the sampling valve. Flushing the valve several times prior to injection provides some local cooling, and it provides for more repeatable liquid injections. When liquid is flowing through the valve, quickly close the waste shut-off valve, then rotate the liquid sampling valve to inject the sample.

10.2.3 If the back flush option is being used, switch the back flush valve at the pre-determined time to elute the $C_5=C_6+$ composite to the detector.

10.3 Gas Sample Valve Injection (optional)—Vaporize the liquid sample according to the procedure given in **10.3.1** through **10.3.5**, or using an on-line heated vaporizing device that is heat-traced to the gas sampling valve, as described in **10.3.6**. Flush a gas sample loop with 5 to 10 mL of sample,

TABLE 3 Theoretical Mass Relative Response Factors^A

Component	RRF _i	Component	RRF _i
Methane	1.0	1-butene	0.874
Ethane	0.937	2-methylpropene (isobutene)	0.874
Ethene (Ethylene)	0.874	cis-2-butene	0.874
Propane	0.916	2,2-dimethyl propane (neopentane)	0.895
Propene (Propylene)	0.874	2-methyl butane (isopentane)	0.899
Cyclopropane	0.874	propyne (methyl acetylene)	0.834
2-Methylpropane (Isobutane)	0.906	cyclopentane	0.849
Ethyne (Acetylene)	0.813	n-pentane	0.899
Propadiene	0.834	1,3-butadiene	0.843
Butane	0.906	$C_5=C_6+$ composite (backflush only)	0.885
Trans-2-Butene	0.874	>nC ₅ (C ₅ and heavier)	0.885

^A RRF values obtained from Test Method **D6729**.

All response factors are relative to that of methane according to the following equation:

$$RRF_i = (MW_i / NC_i) \times (1 / MW_{\text{methane}})$$

where:

RRF_i = relative response factor of each component with respect to methane,

MW_i = the molecular weight of the component,

NC_i = the number of carbon atoms in the component molecule, and

MW_{methane} = the molecular weight of methane.

close cylinder valve, and allow the sample pressure to equilibrate to atmospheric pressure (stopped flow) before introducing the sample into the carrier gas stream.

10.3.1 In a hood, prior to connecting the cylinder, invert the cylinder and purge a small aliquot of the sample through the valve on the sample cylinder to remove any moisture or particulate matter which might be present.

10.3.2 Attach a secondary sampling vessel, consisting of two ball valves joined together and having an internal volume of approximately one mL to the liquid outlet on the sample vessel.

10.3.3 Evacuate the secondary vessel to approximately 0.13 kPa (1 mm Hg), including the connection to the liquid outlet of the sample vessel. Close all valves.

10.3.4 Slowly open the sample outlet valve of the sample cylinder to fill the connection with liquid. Open the inlet ball valve of the secondary vessel and fill the vessel with liquid. Holding the liquid sample vessel vertically with the secondary vessel on the bottom, open the outlet ball valve and allow a portion of the liquid to purge through the secondary vessel. Shut the outlet ball valve, followed by the inlet ball valve and the sample cylinder outlet valve, in that order. Disconnect the secondary vessel.

10.3.5 Connect the secondary vessel to a container with an approximate volume of 100 mL which is fitted with needle valves or shut-off valves. Open the container valves and evacuate the container and connecting pipe work. Close the container outlet valve and slowly open the secondary vessel outlet valve to allow the liquid sample to vaporize into the evacuated vessel. Close all valves. The 100 mL container will contain a vapor that is representative of the liquid sample and have a gauge pressure of 69 to 138 kPa (10 to 20 psi). This gas may be used to purge the sample loop of the gas sampling valve as described in 11.1.

10.3.6 Alternatively, an on-line heated vaporizing device, which is heat-traced to the gas sampling valve, may be used.

The device should consist of a volume of tubing of approximately 10 mL that is encased in a heated block (the block should be a high-mass block heated to approximately 60°C). The outlet of the tubing should be heat-traced and connected to the gas sampling valve. Connect the liquid sample cylinder to the inlet of the heated tubing. Using the sample cylinder outlet valve, pulse several small aliquots of the liquid sample through the tubing successively. Allow the sample loop of the gas sampling valve to equilibrate to ambient pressure, and then rotate the gas sampling valve to inject the vaporized sample.

11. Calculation

11.1 *External Standard Calibration Calculation (recommended)*—Calculate the concentration of each component according to Eq 2. Determine the total amount of hydrocarbons by summing the component concentrations. If the sample is known to contain only hydrocarbons, then the results shall be normalized to 100.00%. Occasionally, normalized results will not equal precisely 100.00% due to rounding. In this case, small differences are typically added to the largest component. As stated in 1.2, this test method does not fully determine non-hydrocarbon materials and normalization could cause skewed data.

$$SC_i = RF_i \times SA_i \quad (2)$$

where:

SC_i = concentration of component i in the sample,

RF_i = response factor for component i , and

SA_i = integrated area for peak i .

11.2 *Theoretical Relative Response Calibration Calculation*—If a FID is being employed for the determination of those components, then theoretical response factors, as listed in Table 3, may be applied in place of RF_i . The results shall then be normalized to 100%. Use of these response factors will produce results in mass percent units, which may be converted to other units (liquid volume percent or mole percent) by the user as needed. Alternately, the theoretical response factors may be converted to other units prior to quantitation. Quantitation using theoretical response factors does not account for the presence of non-hydrocarbon components. Example unit conversion calculations are found in Practice D2421. If non-hydrocarbon components are present, the results using this calculation method will not be representative or valid.

12. Report

12.1 Report the concentration of each component as liquid volume percent (vol%) to the nearest 0.01%.

12.2 Individually eluted C₅ olefins and hexanes-plus components may be speciated and reported separately or summed together into groups.

13. Precision and Bias

13.1 The precision of this test method (Table 4) was determined by statistical examination of limited interlaboratory results. The precision data are provisional, and further data are to be developed in a interlaboratory cooperative test program before the five-year reapproval required by the society.

13.2 No information can be presented on the bias of this test method at present, since no reference material is available.

TABLE 4 Repeatability Standard Deviation

Component	Repeatability Standard Deviation Vol. %
Methane	0.0014
Ethane	0.0009
Ethylene	0.0018
Propane	0.0731
Propylene	0.0854
Isobutane	0.0043
n-butane	0.0071
Propadiene	0.0004
Acetylene	0.0004
t2-butene	0.0036
1-butene	0.0057
Isobutylene	0.0025
c2-butene	0.0195
Cyclopentane	0.0132
Isopentane	0.0023
n-pentane	0.0048
1,3 butadiene	0.0006
Methyl acetylene	0.0001
3m 1-butene	0.0014
t2-pentene	0.0018
2m 2-butene	0.0008
1-pentene	0.0013
2m 1-butene	0.0010
c2-pentene	0.0007

14. Keywords

14.1 floating piston cylinder; gas chromatography; gas sampling valve; liquid sampling valve; liquefied petroleum gases; LP gases; propane; propene

APPENDIX

(Nonmandatory Information)

X1. THEORETICAL RESPONSE FACTORS

X1.1 *Conversion of From Mass to Volume Basis*—Example conversion of theoretical mass response factors to volume response factors are provided in [Table X1.1](#). Since methane is difficult to maintain reliably in an LPG standard, these response factors are presented relative to n-butane.

X1.2 *Comparison of Experimental and Theoretical Response Factors*—Whether employing experimental or theoretical response factors for quantitation, an initial evaluation of experimental response factors is recommended. The experimental values should compare to theoretical within 5%. Failure

to meet this criterion is typically attributed to a standard that no longer has sufficient pressure to keep the lighter components in the liquid phase. If this is the case, calibrating with the standard would result in inaccurate sample analyses. If the standard is confirmed to be good, the results may differ due to hardware problems. In this case, the hardware problems should be corrected before continuing with the calibration.

X1.2.1 If LPG standards are reported in liquid volume percent, the following conversion may be helpful to determine the theoretical relative mass response factors. See [Table X1.2](#).

TABLE X1.1 Conversion of Theoretical Mass RRF to Theoretical Volume RRF Relative to n-Butane

Component	Theoretical Mass RRF _i	Relative Density 15.6/15.6°C (60/60°F) ^A	Theoretical Vol. RRF (Mass RRF/Density)	Theoretical Vol. RRF _i (relative to butane)
Methane	1.000	0.3000	3.3333	2.149
Ethane	0.937	0.3564	2.6291	1.695
Ethene (Ethylene)	0.874	0.3700 ^B	2.3622	1.523
Propane	0.916	0.5074	1.8053	1.164
Propene (Propylene)	0.874	0.5226	1.6724	1.078
2-Methyl Propane (Isobutane)	0.906	0.5629	1.6095	1.038
Ethyne (Acetylene)	0.811	0.4180	1.9402	1.251
Propadiene	0.831	0.6000	1.3850	0.893
n-Butane	0.906	0.5841	1.5511	1.000
Trans-2-Butene	0.874	0.6112	1.4300	0.922
1-Butene	0.874	0.6004	1.4557	0.938
2-Methyl Propene (Isobutene)	0.874	0.6015	1.4530	0.937
Cis-2-Butene	0.874	0.6286	1.3904	0.896
2,2-Dimethyl Propane (Neopentane)	0.899	0.5967	1.5066	0.971
2-Methyl Butane (Isopentane)	0.899	0.6246	1.4393	0.928
Propyne (Methyl Acetylene)	0.843	0.6210	1.3575	0.875
n-Pentane	0.899	0.6311	1.4245	0.918
1,3-Butadiene	0.843	0.6272	1.3441	0.867
C ₅ ⁼ /C ₆ ⁺ Composite	0.885	0.6641 ^C	1.3326	0.859

^A See DS4B, *Physical Constants of Hydrocarbon and Non-Hydrocarbon Compounds*, ASTM International, 1991.

^B See Practice [D2421–95](#).

^C See [GPA Std 2145-03](#) for hexane. Note that the value has been rounded to four decimals from the five decimal value in the GPA standard.

TABLE X1.2 Theoretical Mass Response Factor Evaluation for Liquefied Petroleum Gas

Conversion from Volume Percent to Mass Percent								
#	Component	Certified Vol. %	Relative Density 15.6/15.6 °C (60/60 °F) ⁴		Certified Vol.% x Relative Density	Normalization factor	Mass %	
			x	=				x
1	Ethane	1.800	x	0.3564	=	0.64	1.13	
2	Propane	13.000		0.5074		6.60	=100/total 11.62	
3	Propylene	10.300		0.5226		5.38	= 1.762 9.49	
4	Isobutane	25.800		0.5629		14.52	25.59	
5	n-Butane	10.600		0.5841		6.19	10.91	
6	trans-2-Butene	7.000		0.6112		4.28	7.54	
7	Butene-1	9.930		0.6004		5.96	10.50	
8	Isobutylene	14.500		0.6015		8.72	15.37	
9	cis-2-Butene	2.880		0.6286		1.81	3.19	
10	Isopentane	2.470		0.6246		1.54	2.72	
11	n-Pentane	0.024		0.6311		0.02	0.03	
12	1,3-butadiene	1.150		0.6272		0.72	1.27	
13	Hexane	0.550		0.6641		0.37	0.64	
	Total	100.00				56.75	100.0	
Calculation of Experimental Mass Response Factors (Relative to n-Butane)								
#	Component	Mass %	Peak Area	Mass RF (MRF)		RF n-Butane	Experimental Mass RF relative to n-Butane	
				/	=			/
1	Ethane	1.13	/	2102	=	5.38E-04	/	1.074
2	Propane	11.62		22007		5.28E-04		1.055
3	Propylene	9.49		19931		4.76E-04		0.950
4	Isobutane	25.59		50050		5.11E-04		1.021
5	n-Butane	10.91		21787		5.01E-04	5.01E-04	1.000
6	trans-2-Butene	7.54		15056		5.01E-04		1.000
7	Butene-1	10.50		21042		4.99E-04		0.997
8	Isobutylene	15.37		31409		4.89E-04		0.977
9	cis-2-Butene	3.19		6458		4.94E-04		0.986
10	Isopentane	2.72		5434		5.00E-04		0.999
11	n-Pentane	0.03		55		4.91E-04		0.981
12	1,3-butadiene	1.27		2686		4.73E-04		0.945
13	Hexane	0.64		1306		4.93E-04		0.984
Comparison of Experimental and Theoretical Mass Response Factors								
#	Component	Experimental Mass RF relative to n-Butane	Theoretical Mass RF relative to n-Butane		Delta	Verify (+/- 0.05)		
			-	=			:	
1	Ethane	1.074	-	1.034	=	0.040	:	yes
2	Propane	1.055		1.011		0.044		yes
3	Propylene	0.950		0.965		-0.014		yes
4	Isobutane	1.021		1.000		0.021		yes
5	n-Butane	1.000		1.000		0.000		yes
6	trans-2-Butene	1.000		0.965		0.035		yes
7	Butene-1	0.997		0.965		0.032		yes
8	Isobutene	0.977		0.965		0.013		yes
9	cis-2-Butene	0.986		0.965		0.022		yes
10	Isopentane	0.999		0.992		0.007		yes
11	n-Pentane	0.981		0.992		-0.011		yes
12	1,3-butadiene	0.945		0.930		0.015		yes
13	Hexane	0.984		0.977		0.007		yes

⁴ See DS4B, *Physical Constants of Hydrocarbon and Non-Hydrocarbon Compounds*, ASTM International, 1991.

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