Designation: D2163 – 23[ε1]

Standard Test Method for
Determination of Hydrocarbons in Liquefied Petroleum (LP) Gases and Propane/Propene Mixtures by Gas Chromatography[1]

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 C_1 to C_5. Component concentrations are determined in the range of 0.01 % to 100 % by volume.

1.2 This test method does not fully determine hydrocarbons heavier than C_5 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.4.1 *The user is advised to obtain LPG safety training for the safe operation of this test method procedure and related activities.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

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 C_5 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

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

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*A Summary of Changes section appears at the end of this standard

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*—LPGs generally consist of C_3 and C_4 alkanes and alkenes or mixtures thereof and containing less than 10 % by volume 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 % by 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 % by mass.

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

TABLE 1 Expected Retention Order and Times

Component	Estimated Retention Time (min) (using typical Al_2O_3 PLOT operating conditions)	Estimated Retention Time (min) (using typical 100 m Dimethylpolysiloxane column operating conditions)	FID	TCD
C_5 Olefin/C_6^+ Composite (back-flush)	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.

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 µL 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 µm 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 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 µm 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 C_5 olefin/C_6+ 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 (ID) Na_2SO_4 deactivated Al_2O_3 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 C_5 olefins or hexane plus (C_6+) 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 m to 30 m section of 0.53 mm (ID) 1 µm film thickness dimethylpolysiloxane or polyethylene glycol capillary column or a 9 cm to 15 cm section of the same column material as the analytical column or any pre-column that provides the desired retention of C_5 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 H_2O. (**Warning**—Hydrogen is a flammable gas under high pressure.)

7.1.2 *Helium,* 99.995 % minimum purity, <0.1 ppm H_2O. (**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 % by volume of the mixture composition. It is strongly recommended that the calibration standards be contained in floating piston 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). 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 (Back-Flush) 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

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[5] *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar 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.

TABLE 2 Typical Operating Conditions

Column Type	100 % Dimethylpolysiloxane	Al₂O₃ PLOT - Na₂SO₄ deactivated
Column Dimensions	100 m by 0.25 mm by 0.5 µm	50 m by 0.53 mm by 15 µm
Back-flush	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 µL to 0.5 µL	0.2 µL
Split Ratio	175:1 to 275:1	100:1
Detector Temperature	300 °C to 350 °C	250 °C
Fuel Gas Hydrogen Flow	30 mL/min to 40 mL/min	40 mL/min
Oxidizing Gas Air Flow	300 mL/min to 450 mL/min	400 mL/min
Make-up Gas Type	N₂ or He	He
Make-up Gas Flow	30 mL/min	35 mL/min
Carrier Gas	He @ 2 mL/min (H₂ optional)	Helium at 6 mL/min
Average Linear Velocity	25 cm/s	45 cm/s
Data Rate	10 Hz to 20 Hz	5 Hz
Approximate Run Time	140 min	25 min

Norm.

2000

4000

6000

8000

0

1.978 - Methane
2.137 - Ethane
2.250 - Ethylene

2.708 - Propane

3.538 - Propylene

4.038 - Isobutane

4.352 - n-Butane

5.624 - t-2-Butene

5.818 - Butene-1

6.038 - Isobutene

6.293 - c-2-Butene

6.908 - Isopentane

7.252 - n-Pentane

7.835 - 1,3-Butadiene

C5 olefins and C6+
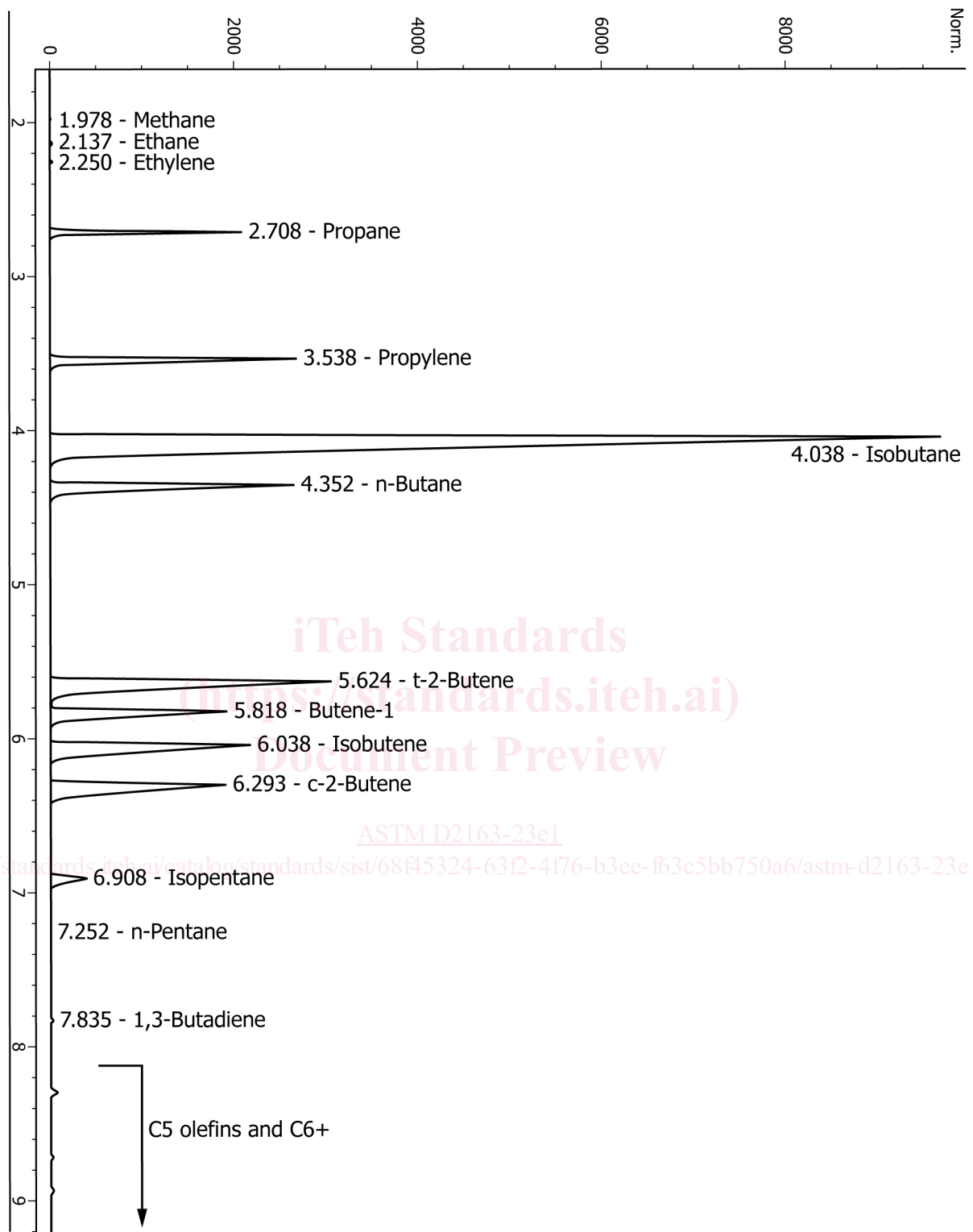
FIG. 1 Example Chromatogram Using the PLOT Column (without back-flush)
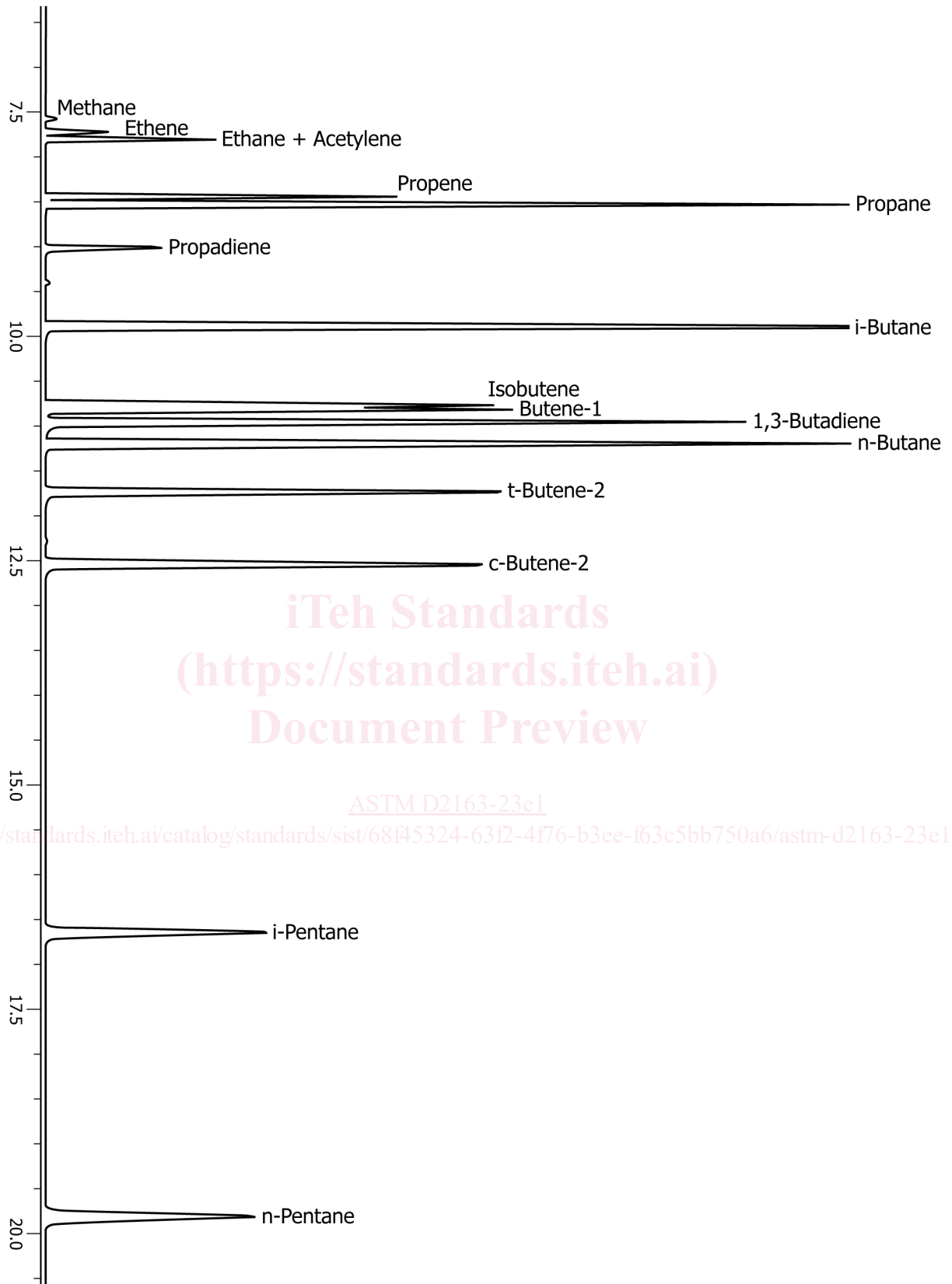
FIG. 2 Example Chromatogram Using the Dimethylpolysiloxane Column

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 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.

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

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 concentrates, 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

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 (back-flush only)	0.885
Trans-2-Butene	0.874	>nC$_5$ (C$_5^=$ and heavier)	0.885

[A]RF values obtained from Test Method D6729.

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

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

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.