



Designation: D2163 – 07

# Standard Test Method for Determination of Hydrocarbons in Liquefied Petroleum (LP) Gases and Propane/Propene Mixtures by Gas Chromatography<sup>1</sup>

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 ( $\epsilon$ ) 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 C<sub>1</sub> to C<sub>5</sub>. 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 C<sub>5</sub> 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:*<sup>2</sup>
- 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<sub>5</sub> 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

<sup>1</sup> 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.

Current edition approved Dec. 1, 2007. Published February 2008. Originally approved in 1963. Last previous edition approved in 1996 as D2163-91(1996) which was withdrawn December 2004 and reinstated in December 2007. DOI: 10.1520/D2163-07.

<sup>2</sup> 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.

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:*<sup>3</sup>

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:*<sup>4</sup>

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 C<sub>3</sub> and C<sub>4</sub> 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.

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

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

3.2.1.1 *Discussion*—Other components may be present, usually at less than 10 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 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  $\mu\text{L}$  or a size to provide the minimum detection limits given in 1.1 have been used satisfactorily. The valve shall be rated for at

**TABLE 1 Expected Retention Order and Times**

Component	Estimated Retention Time (min)	Estimated Retention Time (min)	FID	TCD
	(using typical $\text{Al}_2\text{O}_3$ PLOT operating conditions)	(using typical 100 m Dimethylpolysiloxane column operating conditions)		
$\text{C}_5$ Olefin/ $\text{C}_6^+$ Composite (backflush)	NA <sup>A</sup>	...	x	x
Air Composite ( $\text{O}_2$ , Ar, $\text{N}_2$ , Co)	NA <sup>A</sup>	...	...	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
> $\text{nC}_5$ (Sum $\text{C}_5$ Olefins and Heavier) <sup>B</sup>	8.1 until end of run	...	x	x

<sup>A</sup> Not applicable.

<sup>B</sup> > $\text{nC}_5$  components may be speciated and reported individually.

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  $\mu\text{m}$  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  $\mu\text{L}$  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  $\mu\text{m}$  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  $\text{C}_5$  olefin/ $\text{C}_6+$  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 (I.D.)  $\text{Na}_2\text{SO}_4$  deactivated  $\text{Al}_2\text{O}_3$  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  $\mu\text{m}$  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  $\text{C}_5$  olefins or hexane plus ( $\text{C}_6+$ ) 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 to 30 m section of 0.53 mm (I.D.) 1  $\mu\text{m}$  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  $\text{C}_5$  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  $\text{H}_2\text{O}$ . (**Warning**—Hydrogen is a flammable gas under high pressure.)

7.1.2 *Helium*, 99.995 % minimum purity, <0.1 ppm  $\text{H}_2\text{O}$ . (**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.<sup>5</sup> 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.

<sup>5</sup> *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.

**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 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**.

**TABLE 2 Typical Operating Conditions**

Column Type	100% Dimethylpolysiloxane	Al <sub>2</sub> O <sub>3</sub> PLOT - Na <sub>2</sub> SO <sub>4</sub> 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 <sub>2</sub> or He	He
Make-up Gas Flow	30 mL/min	35 mL/min
Carrier Gas	He @ 2 mL/min (H <sub>2</sub> 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

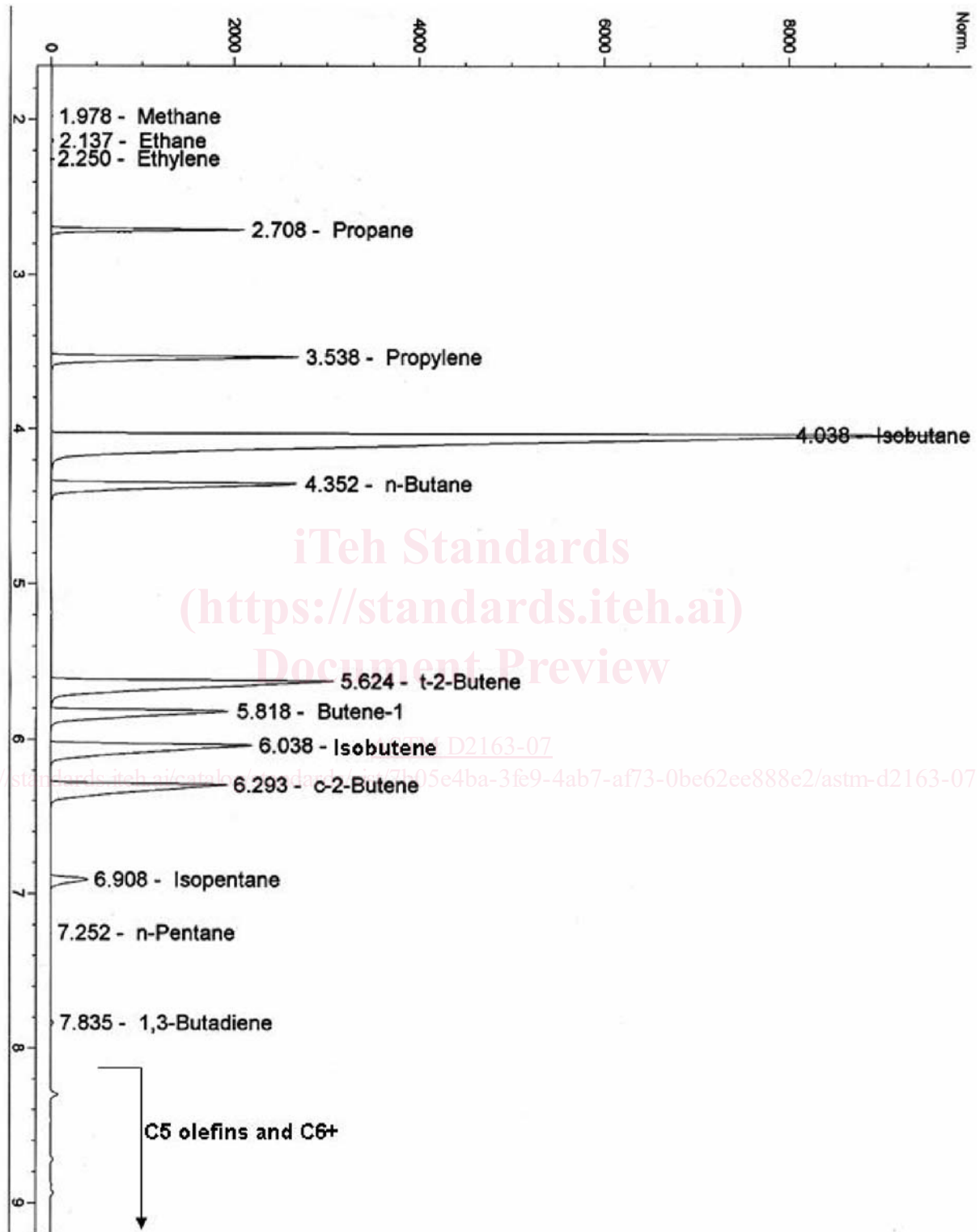
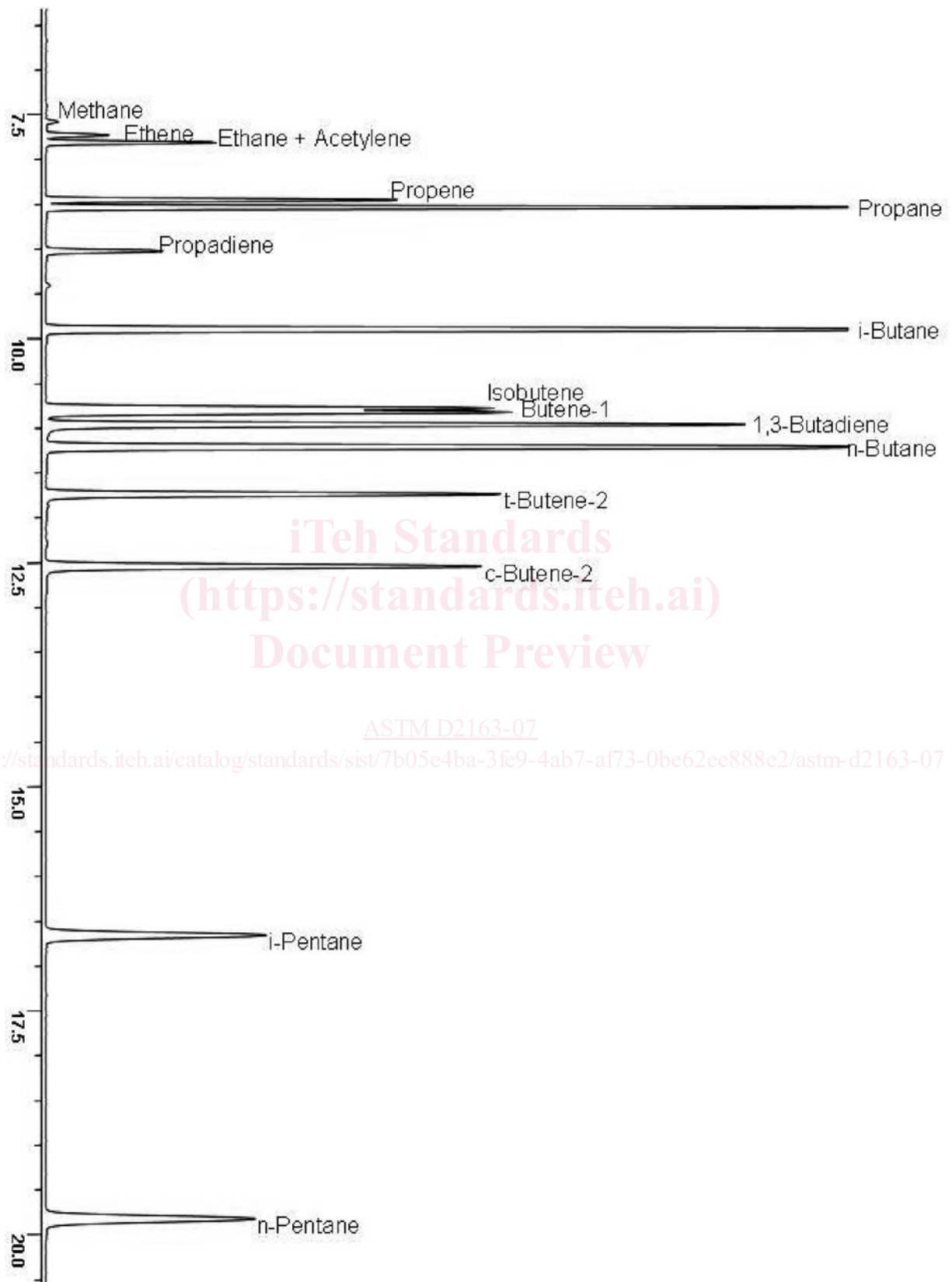


FIG. 1 Example Chromatogram Using the PLOT Column (without back-flush)



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ASTM D2163-07

<https://standards.itteh.ai/catalog/standards/sist/7b05e4ba-3fe9-4ab7-af73-0be62ee888e2/astm-d2163-07>

FIG. 2 Example Chromatogram Using the Dimethylpolysiloxane Column