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

This standard is issued under the fixed designation D 2163; 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 determination of the composition of liquefied petroleum (LP) gases. It is applicable to analysis of propane, propene, and butane in all concentration ranges 0.1% and above.~~

~~1.2~~

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 the 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.*

~~1.3 The values stated in SI units are to be regarded as standard.~~

2. Referenced Documents

2.1 *ASTM Standards:*²

D 1265 Practice for Sampling Liquefied Petroleum (LP) Gases, Manual Method

D 1835 Specification for Liquefied Petroleum (LP) Gases

D 2421 Practice for Interconversion of Analysis of C₅ and Lighter Hydrocarbons to Gas-Volume, Liquid-Volume, or Weight-Mass Basis

D 2598 Practice for Calculation of Certain Physical Properties of Liquefied Liquefied Petroleum (LP) Gases from Compositional Analysis

~~D 3700 Practice for Containing Hydrocarbon Fluid Samples Using a Floating Piston Cylinder~~ Practice for Obtaining LPG Samples Using a Floating Piston Cylinder

D 6729 Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 100 Metre Capillary High Resolution Gas Chromatography

E 355 Practice for Gas Chromatography Terms and Relationships

E 594 Practice for Testing Flame Ionization Detectors Used in Gas or Supercritical Fluid Chromatography

E 1510 Practice for Installing Fused Silica Open Tubular Capillary Columns in Gas Chromatographs

¹ This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.D0.03 on C4 Test Methods-Liquefied Petroleum Gas.

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² 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 D 2163-91(1996) which was withdrawn December 2004 and reinstated in December 2007.

³ 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*, Vol 05.01, volume information, refer to the standard's Document Summary page on the ASTM website.

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 propene concentrate—concentrate containing more than 50% propene. Definitions:

3.1.1 Additional terminology related to the practice of gas chromatography can be found in Practice E 355.

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 D 1835 is typically this sort of product mixture.

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

4. Summary of Test Method

4.1 Components in a 4.1 An LPG sample of LP gas are physically separated 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 heights or retention times and areas with those obtained on for the reference standard mixture or for pure hydrocarbons.

5. Significance and Use

5.1 The hydrocarbon component distribution of liquefied petroleum gases and propene concentrates mixtures is often required as a specification analysis for end-use sale of this material. Its wide use Applications such as chemical feed stocks or as fuel, fuel require precise compositional data to ensure uniform quality. Trace amounts of the desired reaction products. 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 concentrates mixtures can be used to calculate physical properties such as relative density, vapor pressure, and motor octane (see Practice D 2598). Precision and accuracy of compositional data are extremely important when these data are used to calculate various properties of these petroleum products.

6. Gas Chromatograph System Apparatus

6.1 Detector—The detector shall be a thermal conductivity type or its equivalent in sensitivity and stability. The system shall be capable of detecting 0.1% concentration of any component of interest. For calculation techniques utilizing a recorder, the signal for the concentration shall be at least 5 chart divisions above the noise level on a 0 to 100 scale chart. Noise level must be restricted to a maximum of 1 chart division. When electronic integration is employed the signal for 0.1% concentration must be at least twice the noise level. 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 Recorder—A strip chart recorder and integrator with a full-scale range of 10 mV or less shall be required. A maximum full-scale balance time of 2 s and a minimum chart speed of ½ in. (12.7 mm)/min shall be required. 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 E 594).

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 Attenuator—A multistep attenuator for the detector output signal shall be necessary to maintain maximum peaks within the recorder chart range. The attenuator system must be accurate to 0.5% in any position. 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.

³ Annual Book of ASTM Standards, Vol 05.02.

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

⁴ Suitable reference standard mixtures of pure hydrocarbons are available from Scott Specialty Gases, Inc., Plumsteadville, PA.

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

TABLE 1 Reference Standard Mixtures, Liquid Volume Percent⁴

Component	PropEstimated Retention Time (min) w(using th Neotypical Al ₂ O ₃ UnsaturoPLOT operateing conditions)	PropEstimated Retention Time (min) w(using typical 100 m Dimeth-Lypowylsiloxane Prcolumn operateing conditions)	Propene with-High PropeneFID	ButaTCD
C ₅ -Olefine	Propene- Butane Mixtures	Propene with-Low Propene	Propene with-High Propanex	x
C ₅ Olefin/C ₆ ⁺ Composite (backflush)	NA ⁴	...	x	x
— Ethane	4	4	3	x
Air Composite (O ₂ , Ar, N ₂ , Co)	NA ⁴	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	...	-2	0.2x
Cyclopropane	3.4	...	x	x
Propene	-0.15	7.2	x	x
Propene	3.5	7.2	x	x
— Propene	93	87	57	3x
2-Methyl Propane (Isobutane)	4.0	8.4	x	x
Butane	4.5	4.8	22.6x	x
Butane	4.2	9.5	x	x
— Propene	4.7	...	4	35x
Propadiene	4.7	...	x	x
Ethyne (Acetylene)	5.0	...	-6	94.9x
Ethyne (Acetylene)	5.0	...	x	x
Trans-2-Butene	76.65	9.9	x	x
Trans-2-Butene	5.5	9.9	x	x
— n-Butane	4	4	4	64x
1-Butene	5.6	9.2	x	x
2-Methyl Propene (Isobutene)	30	0.4	-0.5x	x
2-Methyl Propene (Isobutene)	5.7	9.1	x	x
— Isobutane	4	3	3	x
2,2-Dimethylpropane (Neopentane)	5.9	10.1	x	x
Cis-25	46	x
Cis-2-Butene	6.2	10.6	x	x
— Butene	-6x
Cyclopentane	6.7	25.8	x	x
2-Methyl Butane (Isopentane)	-0.2x	x
2-Methyl Butane (Isopentane)	6.8	14.0	x	x
— Isopentane	4	4	4	-2x
Pentane	7.2	16.9	x	x
1,3-Butadiene	2	9.3	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

⁴The e Nomposition v applues recorded in this table are.

^B>nC₅ offered as a guide to laboratories preparing their own mixtures from pure hydrocarbon or to commercial suppliers of standard reference materials. In either case, an accurate composition of the standard must be known to analyst.

6.4 *Sample Inlet System*—Provision shall be made to introduce up to 0.50 mL of the sample. The sample volume must be repeatable such that successive runs agree within 1 mm or 1% (whichever is larger) on each component peak height. *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 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 ($\frac{1}{16}$ 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 Temperature Control—The analyzer columns shall be maintained at a temperature constant to 0.3°C during the course of the sample and corresponding reference standard runs. 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 down-stream 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 Carrier Gas—The instrument shall be equipped with suitable facilities to provide a flow of carrier gas through the analyzer column at a flow rate that is constant to 1.0% throughout the analysis.

6.7 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—Any column may be used provided all component peaks for compounds present in concentration of more than 5% are resolved so that the ratio A/B shall not be less than 0.8, Fig. 1

where:

A = depth of the valley on either side of peak B , and

B = height above the baseline of the smaller of any two adjacent peaks (see Fig. 1).

For compounds present in concentrations of 5% or less, the ratio of A/B shall not be less than 0.4. In case the small-component peak is adjacent to a large one, it may be necessary to construct the baseline of the small peak tangent to the curve as shown in Fig. 2.—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.) 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 D 6729 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 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 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. Calibration Standard

7.1 Pure components or calibration standard mixtures may be used for calibration. If pure components are used, identical volumes of each component are injected into the chromatograph and relative area response factors are determined. These factors are valid for a given instrument and operating conditions and should be redetermined periodically. If pure components are used for calibration, the calculation should be made in mole percent and converted to liquid volume percent (Note 1). Factors repeatable to within 1% are required. The concentration of each component in the calibration standard mixtures shall be known to within 0.1%. The concentration of the major component in the calibration standard mixture shall not differ from that of the like component in the sample to be analyzed by more than 10% if the peak height method of calculation is used. On propene concentrates, the calibration standard mixtures shall not differ from that of like component in the sample to be analyzed by more than 5%. Typical composition ranges of suitable calibration standard mixtures are given in 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.)

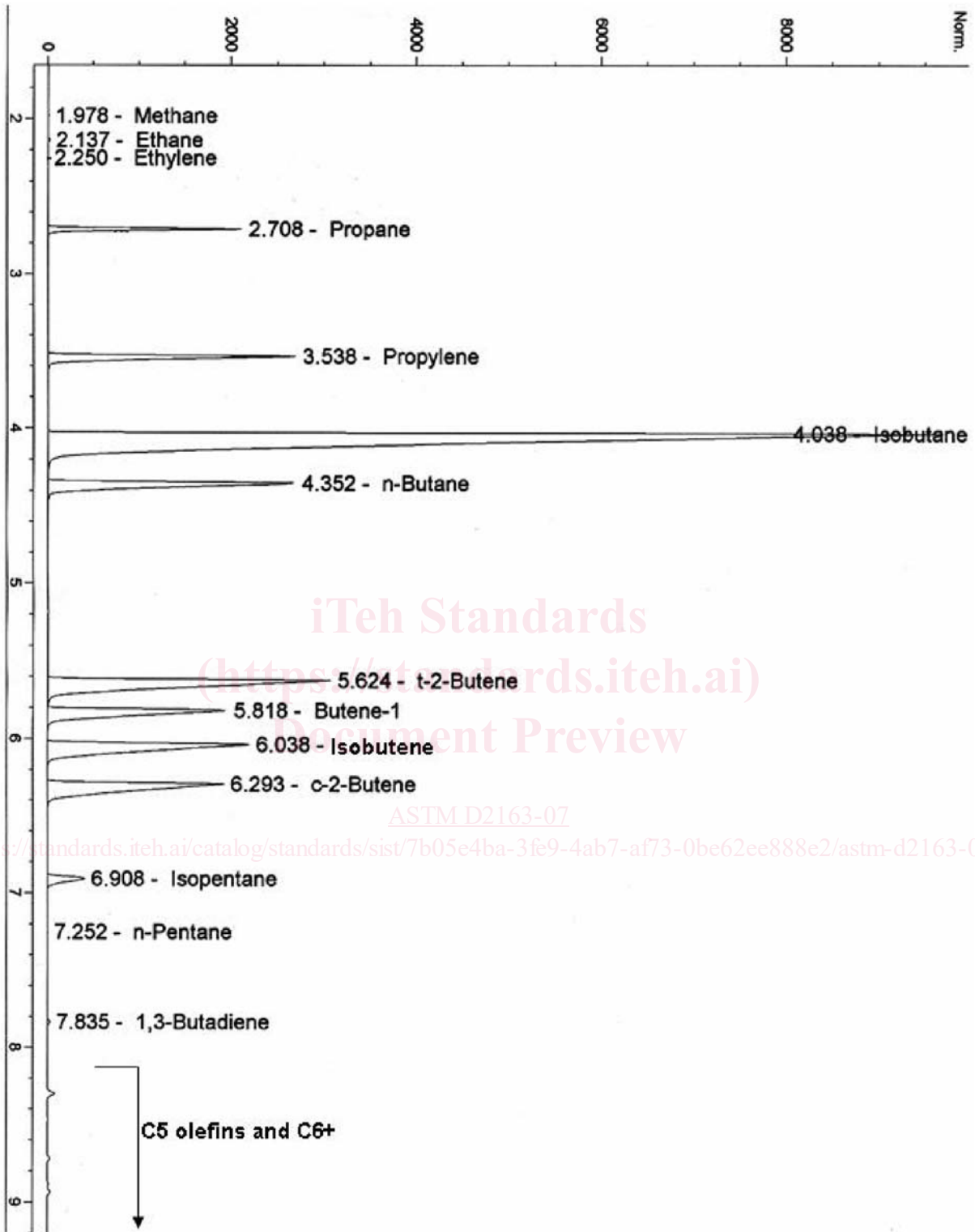


FIG. 1 Example Chromatogram Using the PLOT Column (without back-flush)

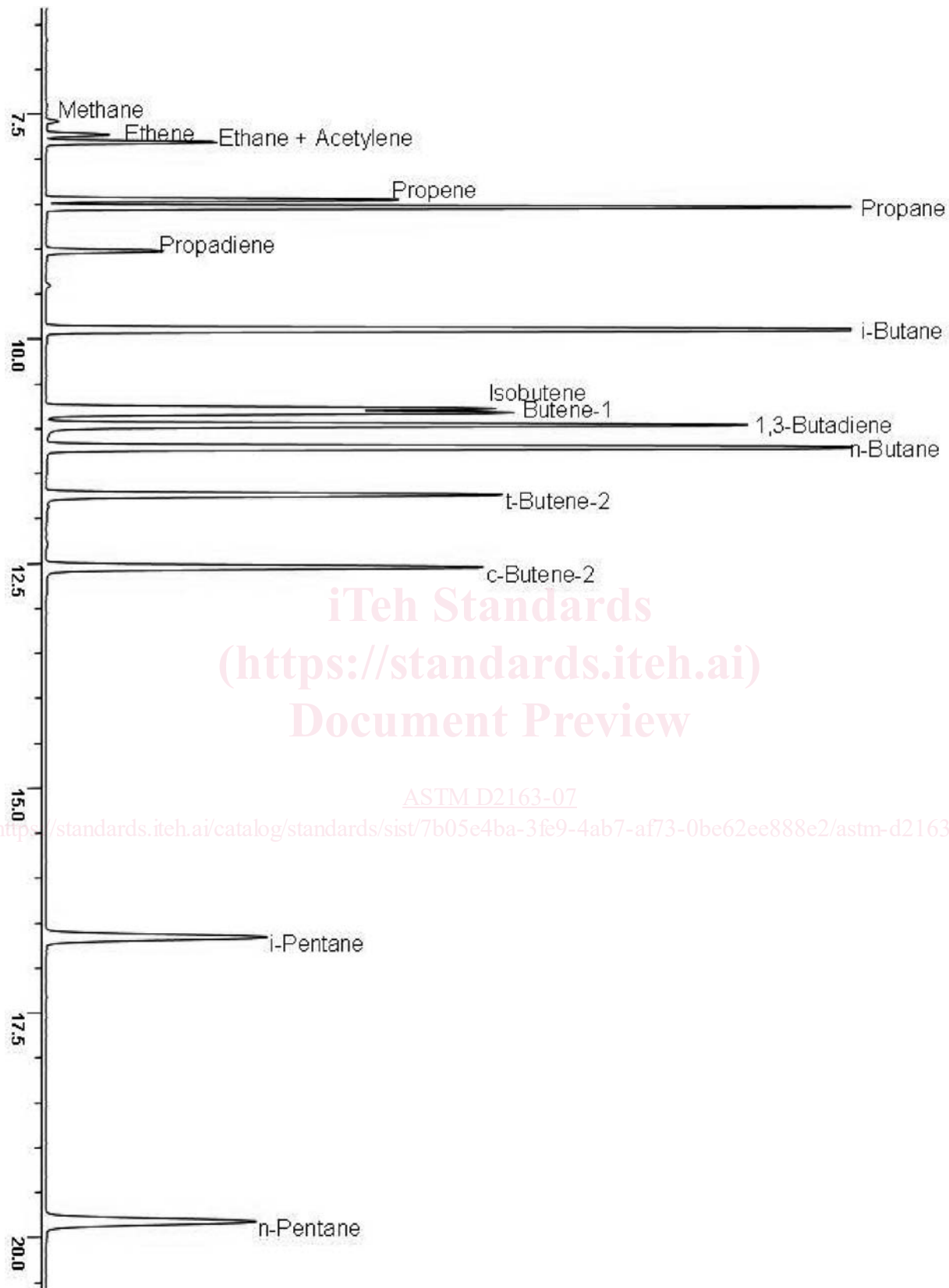


FIG. 2 Example Chromatogram Using the Dimethylpolysiloxane Column