



# Standard Test Method for Analysis of Demethanized Hydrocarbon Liquid Mixtures Containing Nitrogen and Carbon Dioxide by Gas Chromatography<sup>1</sup>

This standard is issued under the fixed designation D2597; 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 analysis of demethanized liquid hydrocarbon streams containing nitrogen/air and carbon dioxide, and purity products, such as an ethane/propane mix that fall within the compositional ranges listed in [Table 1](#). This test method is limited to mixtures containing less than 5 mol % of heptanes and heavier fractions.

1.2 The heptanes and heavier fractions, when present in the sample, are analyzed by either (1) reverse flow of carrier gas after *n*-hexane and peak grouping or (2) precut column to elute heptanes and heavier first as a single peak. For purity mixes without heptanes and heavier, no reverse of carrier flow is required. (**Caution**—In the case of samples with a relatively large C<sub>6+</sub> or C<sub>7+</sub> fraction and where precise results are important, it is desirable to determine the molecular weight (or other pertinent physical properties) of these fractions. Since this test method makes no provision for determining physical properties, the physical properties needed can be determined by an extended analysis or agreed to by the contracting parties.)

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

NOTE 1—[Annex A2](#) states values in manometric units, which are to be regarded as the standard in that section. Approximate SI units (from conversion) are given in parentheses.

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.* For specific hazard statements see [Annex A3](#).

<sup>1</sup> This test method is under the jurisdiction of Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.H0 on Liquefied Petroleum Gas.

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## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>2</sup>

D1265 Practice for Sampling Liquefied Petroleum (LP) Gases, Manual Method

D2163 Test Method for Determination of Hydrocarbons in Liquefied Petroleum (LP) Gases and Propane/Propene Mixtures by Gas Chromatography

D3700 Practice for Obtaining LPG Samples Using a Floating Piston Cylinder

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

D6849 Practice for Storage and Use of Liquefied Petroleum Gases (LPG) in Sample Cylinders for LPG Test Methods

### 2.2 GPA Standard:<sup>3</sup>

GPA 2177 Analysis of Demethanized Hydrocarbon Liquid Mixtures Containing Nitrogen and Carbon Dioxide by Gas Chromatography

## 3. Summary of Test Method

3.1 Components to be determined in a demethanized hydrocarbon liquid mixture are physically separated by gas chromatography and compared with calibration data obtained under identical operating conditions. A fixed volume of sample in the liquid phase is isolated in a suitable sample inlet system and entered onto the chromatographic column.

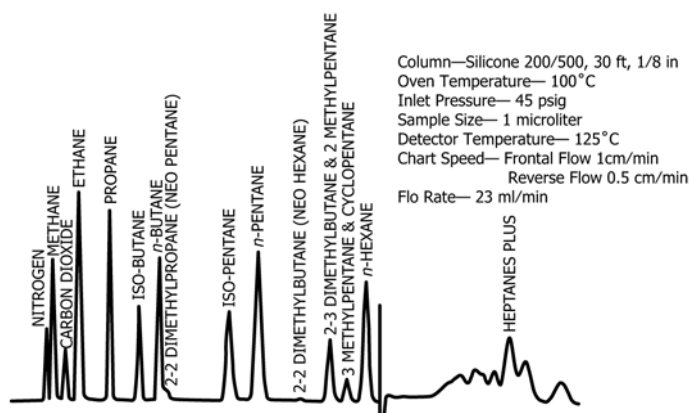
3.1.1 Components nitrogen/air through *n*-hexane are individually separated with the carrier flow in the forward direction. The numerous heavy end components are grouped into an irregularly shaped peak by reversing direction of carrier gas through the column by means of a switching valve immediately following the elution of normal hexane. (See [Fig. 1](#).) Samples that contain no heptanes–plus fraction are analyzed until the final component has eluted with no reverse of carrier flow.

<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

<sup>3</sup> Available from Gas Processors Association (GPA), 6526 E. 60th St., Tulsa, OK 74145, <http://gpaglobal.org/>.

TABLE 1 Components and Compositional Ranges Allowed

Components	Concentration Range, Mol %
Nitrogen	0.01–5.0
Carbon Dioxide	0.01–5.0
Methane	0.01–5.0
Ethane	0.01–95.0
Propane	0.01–100.0
Isobutane	0.01–100.0
<i>n</i> -Butane and 2,2-Dimethylpropane	0.01–100.0
Isopentane	0.01–15.0
<i>n</i> -Pentane	0.01–15.0
2,2-Dimethylbutane	0.01–0.5
2,3-Dimethylbutane and 2-Methylpentane	
3-Methylpentane and Cyclopentane	0.01–15.0
<i>n</i> -Hexane	
Heptanes and Heavier	0.01–5.0



NOTE 1—Reproduced with permission from GPA 2177.

FIG. 1 Chromatogram of Demethanized Hydrocarbon Liquid Mixture (Frontal Carrier Gas Flow Through *n*-Hexane, Reverse Grouping Heptanes-Plus)

3.1.2 An alternate procedure to the single column backflush method is the use of a precut column which is backflushed to obtain the heptanes-plus as a single peak at the beginning of the chromatogram.

NOTE 2—Two advantages of the alternate procedure are as follows: (1) better precision in measuring the C<sub>7+</sub> portion of the sample and (2) reduction in analysis time over the single column approach by approximately 40 %.

3.2 The chromatogram is interpreted by comparing the areas of component peaks obtained from the sample with corresponding areas obtained from a run of a selected reference standard. Any component in the sample suspected to be outside the linearity range of the detector, with reference to the known amount of that component in the reference standard, shall be determined by a response curve. Peak height method of integration can be used only if the chromatograph is operating in the linear range for all components analyzed. Linearity shall be proved by peak height for all components when using peak height method. (See Section 6 for further explanation of instrument linearity check procedures.)

#### 4. Significance and Use

4.1 The component distribution of hydrocarbon liquid mixtures is often required as a specification analysis for these

materials. Wide use of these hydrocarbon mixtures as chemical feedstocks or as fuel require precise compositional data to ensure uniform quality of the reaction product. In addition, custody transfer of these products is often made on the basis of component analyses of liquid mixtures.

4.2 The component distribution data of hydrocarbon mixtures can be used to calculate physical properties, such as specific gravity, vapor pressure, molecular weight, and other important properties. Precision and accuracy of compositional data are extremely important when these data are used to calculate physical properties of these products.

NOTE 3—Specifications for some hydrocarbon liquid mixtures, such as LPG, may be based on composition measured by Test Method D2163. Nitrogen and carbon dioxide determinations are not within the scope of Test Method D2163.

#### 5. Apparatus

5.1 Any gas chromatograph may be used that meets the following requirements.

5.1.1 *Detector*—The detector shall be a thermal-conductivity type. It shall be sufficiently sensitive to produce a deflection of at least 0.5 mv for 1 mol % of *n*-butane in a 1.0-μL sample.

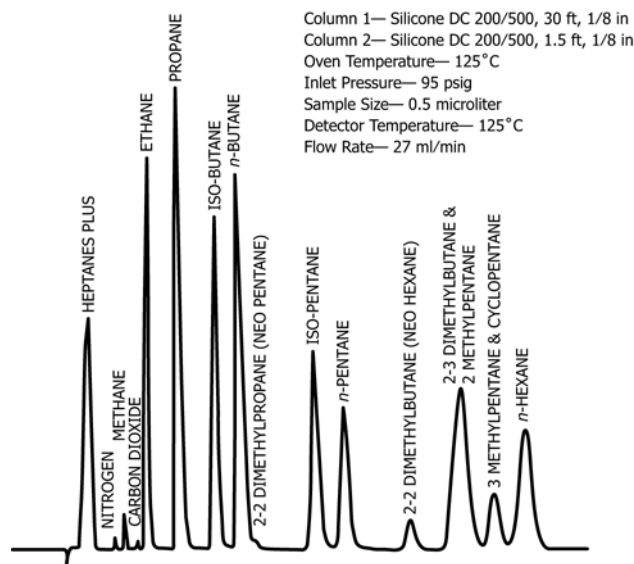
5.1.2 *Sample Inlet System, Liquid*—A liquid sampling valve shall be provided, capable of entrapping a fixed volume of sample at a pressure at least 1400 kPa (200 psi) above the vapor pressure of the sample at valve temperature, and introducing this fixed volume into the carrier gas stream ahead of the analyzing column. The fixed sample volume should not exceed 1.0 μL and should be reproducible such that successive runs agree within ±2 % on each component peak area. The liquid sampling valve is mounted exterior of any type heated compartment and thus can operate at laboratory ambient conditions.

5.1.3 *Sample Inlet System, Gas (Instrument Linearity)*—Provision shall be made to introduce a gas phase sample into the carrier gas stream ahead of the chromatographic column so that linearity of the instrument may be determined from response curves. The fixed volume loop in the gas sample valve shall be sized to deliver a total molar volume approximately equal to that delivered by the liquid sample valve in accordance with 5.1.2. (See Section 6 for further explanation of instrument linearity check procedures.)

##### 5.1.4 Chromatographic Columns:

5.1.4.1 *Column No. 1*—A partition column shall be provided capable of separating nitrogen/air, carbon dioxide, and the hydrocarbons methane through normal hexane. (See Fig. 1 and Fig. 2.) Separation of carbon dioxide shall be sufficient so that a 1-μL sample containing 0.01 mol % carbon dioxide will produce a measurable peak on the chromatogram. (The silicone 200/500 column, containing a 27 to 30 weight % liquid phase load, has proven satisfactory for this type of analysis.)

5.1.4.2 *Column No. 2*—A partition column similar to Column No. 1. It shall be of the same diameter as Column No. 1. The column shall be of an appropriate length to clearly separate the heptanes-plus fraction from the hexanes and lighter components.



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FIG. 2 Chromatogram of Demethanized Hydrocarbon Liquid Mixture (Precut Column Grouping Heptanes-Plus, Frontal Carrier Gas Flow Remaining Components)

5.1.5 *Temperature Control*—The chromatographic column(s) and the detector shall be maintained at their respective temperatures, constant to  $\pm 0.3^\circ\text{C}$  during the course of the sample and corresponding reference standard runs.

5.2 *Carrier Gas*—Pressure-reducing and control devices to give repeatable flow rates.

5.3 *Integration System:*

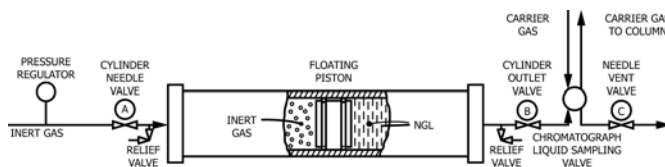
5.3.1 *Computerized Data System*—A computer-based chromatography data system capable of accurately and repeatedly measuring the retention time and areas of eluting peaks is preferred and recommended.

5.3.2 *Electronic Digital Integrator*—As an alternative, an electronic integrator may be used to record and measure peak retention times and areas. (**Caution**—Electronic digital integrators are able to integrate peak areas by means of several different methods employing various correction adjustments. The operator should be well versed in integrator operation, preventing improper handling and manipulation of data—ultimately resulting in false information.)

5.4 *Pressure Measuring Device*—Electronic pressure transducer or other device, covering the range from 0–120 kPa (0–900 mm Hg). This device is required in order to charge partial pressure samples of pure hydrocarbons when determining response curves for linearity checks when using the gas sampling valve.

5.5 *Vacuum Pump*—Shall have the capability of producing a vacuum of 0.01 kPa (0.1 mm Hg absolute) or less. Required for linearity checks when using the gas sampling valve.

5.6 *Sample Filter*—An optional device to protect the liquid sampling valve from scoring due to the presence of foreign contaminants, such as metal shavings or dirt in a liquid hydrocarbon sample. The filter may be of a small total volume, or an in-line type design and contain a replaceable/disposable



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FIG. 3 Repressuring System and Chromatographic Valving with Floating Piston Cylinder

element. (**Caution**—A filter can introduce error if not handled properly. The filter should be clean and free of any residual product from previous samples so that a buildup of heavy end hydrocarbon components does not result. (This can be accomplished by a heating/cooling process or inert gas purge, etc.) The filter element should be 15- $\mu\text{m}$  size or larger so that during the purging process, the sample is not flashed, preventing fractionation and bubble formation.)

5.7 *Sample Containers:*

5.7.1 *Floating Piston Cylinder*—A strongly preferred and recommended device suitable for securing, containing, and transferring samples into a liquid sample valve and that preserves the integrity of the sample. (See Fig. 3 and Test Method D3700.)

5.7.2 *Double-Valve Displacement Cylinder*—An alternate device used in the absence of a floating piston cylinder suitable for securing, containing, and transferring samples into a liquid sample valve. (See Fig. 4 and Fig. 5.) (**Caution**—This container is acceptable when the displacement liquid does not appreciably affect the composition of the sample of interest. Specifically, components such as  $\text{CO}_2$  or aromatic hydrocarbons are partially soluble in many displacement liquids and thus can compromise the final analysis. This caution is of the utmost importance and should be investigated prior to utilizing this technique.)

5.7.3 *High Pressure Sample Cylinder*—An alternate device that is suitable for obtaining representative samples for all routine tests for LPG and NGL products that are normally single phase. See Practice D1265.

6. Calibration

6.1 In conjunction with a calibration on any specific chromatography, the linear range of the components of interest shall be determined. The linearity is established for any new chromatograph and reestablished whenever the instrument has undergone a major change (that is, replaced detectors, increased sample size, switched column size, or dramatically modified run parameters).

6.1.1 The preferred and more exacting procedure is to prepare response curves. The procedure for developing the data necessary to construct these response curves for all components nitrogen through n-pentane is set forth in Annex A2.

6.1.2 A second procedure utilizes gravimetrically constructed standards of a higher concentration than is contained in the sample. Sets of response factors are first determined for all components by means of a blend mix. (See 6.3.) A second (or third) gravimetrically determined standard (either purity or blend) may then be run, using the originally obtained response