



# 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](#).

## 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>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.

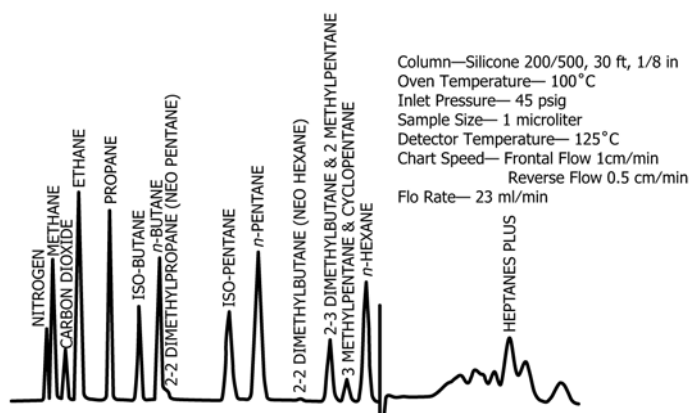
Current edition approved May 1, 2010. Published July 2010. Originally approved in 1967. Last previous edition approved in 2004 as D2597–94(2004). DOI: 10.1520/D2597-10.

<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



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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.

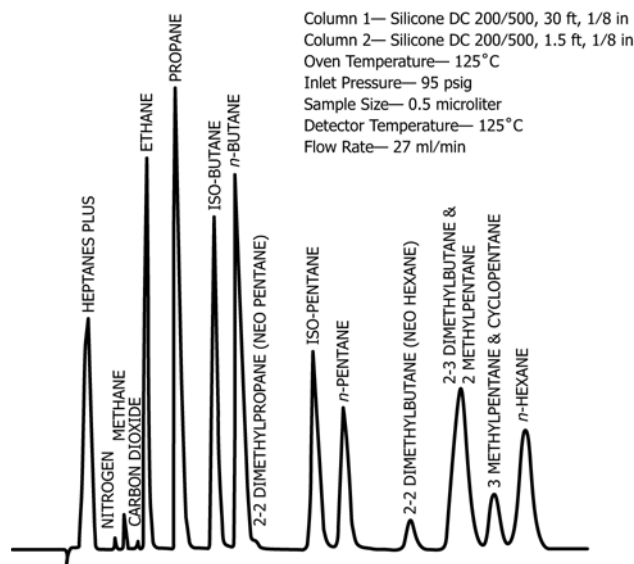
5.1.2 *Sample Inlet System, Liquid*—A liquid sampling valve shall be provided, capable of entrapping a fixed volume of sample at a pressure at least 1400 kPa (200 psi) above the vapor pressure of the sample at valve temperature, and introducing this fixed volume into the carrier gas stream ahead of the 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:*

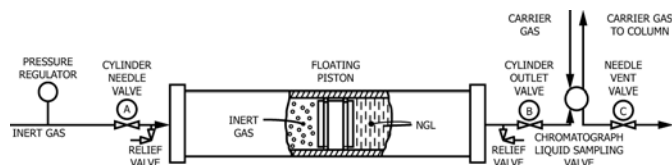
5.3.1 *Computerized Data System*—A computer-based chromatography data system capable of accurately and repeatedly measuring the retention time and areas of eluting peaks is preferred and recommended.

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.)

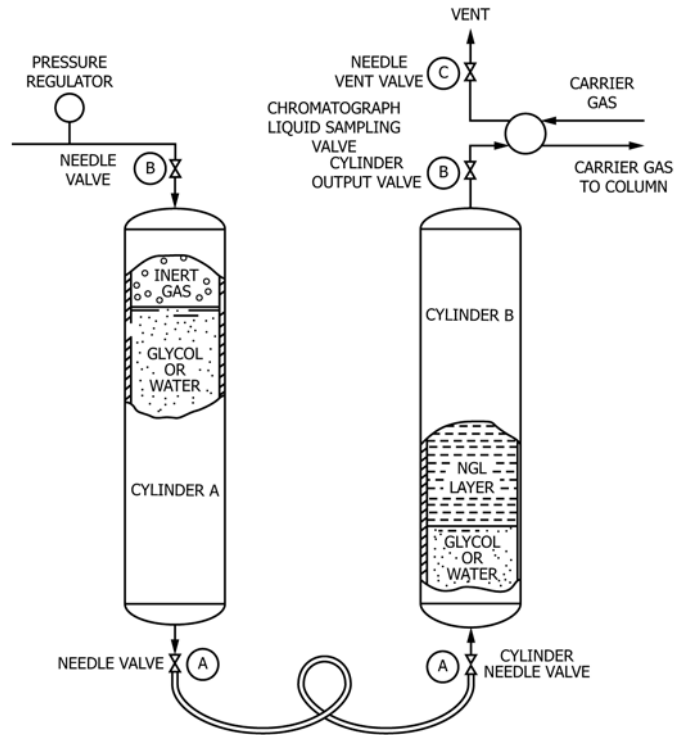
5.7.3 *High Pressure Sample Cylinder*—An alternate device that is suitable for obtaining representative samples for all routine tests for LPG and NGL products that are normally single phase. See Practice D1265.

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).

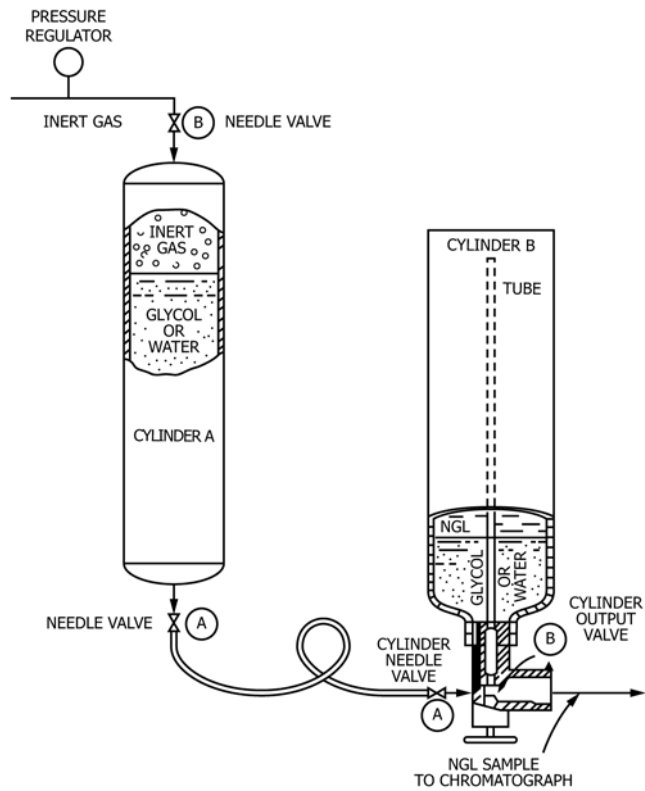
6.1.1 The preferred and more exacting procedure is to prepare response curves. The procedure for developing the data necessary to construct these response curves for all components nitrogen through *n*-pentane is set forth in Annex A2.

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



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**FIG. 4** Repressuring System and Chromatographic Valving with Double-Valve Displacement Cylinder



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**FIG. 5** Alternate Repressuring System with Double-Valve Displacement Cylinder

**TABLE 2 Example of Response Factors Determined from Reference Standard**

Component	Mol % in Referenced Standard	Peak Area Referenced Standard Run	Mol % Response Factors (×10 000)	Relative Response Factor (C <sub>3</sub> Reference Peak)
Nitrogen/air	0.10	311	$\frac{0.10}{311} = 3.2154$	$\frac{0.10}{311} \times \frac{122\,825}{28.05} = 1.4080$
Methane	1.49	3 552	$\frac{1.49}{3\,552} = 4.1948$	$\frac{1.49}{3\,552} \times \frac{122\,825}{28.05} = 1.8368$
Carbon dioxide	0.50	1 568	$\frac{0.50}{1\,568} = 3.1888$	$\frac{0.50}{1\,568} \times \frac{122\,825}{28.05} = 1.3963$
Ethane	53.90	182 108	$\frac{53.90}{182\,108} = 2.9598$	$\frac{53.90}{182\,108} \times \frac{122\,825}{28.05} = 1.2960$
Propane	28.05	122 825	$\frac{28.05}{122\,825} = 2.2837$	$\frac{28.05}{122\,825} \times \frac{122\,825}{28.05} = 1.0000$
Isobutane	3.05	15 306	$\frac{3.05}{15\,306} = 1.9927$	$\frac{3.05}{15\,306} \times \frac{122\,825}{28.05} = 0.8726$
<i>n</i> -Butane 2,2-Dimethylpropane	6.01	30 834	$\frac{6.01}{30\,834} = 1.9491$	$\frac{6.01}{30\,834} \times \frac{122\,825}{28.05} = 0.8535$
Isopentane	1.00	5 856	$\frac{1.00}{5\,856} = 1.7077$	$\frac{1.00}{5\,856} \times \frac{122\,825}{28.05} = 0.7478$
<i>n</i> -Pentane	2.00	12 280	$\frac{2.00}{12\,280} = 1.6287$	$\frac{2.00}{12\,280} \times \frac{122\,825}{28.05} = 0.7132$
2,2-Dimethylbutane	0.02	132	$\frac{0.02}{132} = 1.5152$	$\frac{0.02}{132} \times \frac{122\,825}{28.05} = 0.6635$
2,3-Dimethylbutane 2-Methylbutane	0.64	4 513	$\frac{0.64}{4\,513} = 1.4181$	$\frac{0.64}{4\,513} \times \frac{122\,825}{28.05} = 0.6210$
3-Methylpentane Cyclopentane	0.41	2 401	$\frac{0.41}{2\,401} = 1.7076$	$\frac{0.41}{2\,401} \times \frac{122\,825}{28.05} = 0.7477$
<i>N</i> -Hexane	0.74	5 064	$\frac{0.74}{5\,064} = 1.4613$	$\frac{0.74}{5\,064} \times \frac{122\,825}{28.05} = 0.6399$
Heptanes–Plus	2.09	14 851	$\frac{2.09}{14\,851} = 1.4073$	$\frac{2.09}{14\,851} \times \frac{122\,825}{28.05} = 0.6162$

factors, which contain a concentration of individual components exceeding the expected amounts in the samples. When both (or all three) runs match their respective standards within the precision guidelines allowed in Section 11, then the instrument may be considered linear within that range.

NOTE 4—This test method omits the need of a gas sample valve on the chromatographic instrument. However, several accurate primary standards are required and the exact point at which nonlinearity occurs is not determined.

6.2 For routine analysis using this procedure, it is intended that calibration be accomplished by use of a selected reference standard containing known amounts of all components of interest. It is recommended that the reference standard composition be similar to the one shown in Table 2, or closely

resemble the composition of expected samples. This approach is valid for all components that lie within the proven linear range for a specific gas chromatograph.

NOTE 5—Check the reference standard for validity when received and periodically thereafter. Annex A1 details one procedure for making the validity check.

6.3 Using the selected liquid reference standard, obtain a chromatogram as outlined in Section 7.

6.3.1 Determine peak areas (or peak heights) from the chromatogram for all components. These data shall be used to calculate response factors in accordance with 9.1.

6.3.2 Repeat 6.3 and 6.3.1 until a satisfactory check is obtained. Usually two runs will suffice.

6.4 *Test Method Quality Control Monitoring*—Primary or secondary standards should be analyzed on a regular basis to monitor test accuracy and precision relative to the uncertainty of the standard value and the established long-term precision of the test using statistical quality control techniques. If the test method is in regular use, the primary or secondary standards should be analyzed at least once a week; if used only occasionally, analyze a primary or secondary standard before each set of analyses. Practice D6849 provides guidance on storage and usage of LPG samples as quality control reference materials for LPG test methods. Practice D6299 provides guidance on test method statistical quality control monitoring techniques.

## 7. Procedure

7.1 *General*—In the routine analysis of samples described in the scope of this procedure, it is possible to obtain all components of interest from a single run. Response factors, determined in duplicate runs on a selected reference standard, are used to convert peak areas (or peak heights) of the sample to mol percent.

7.2 *Apparatus Preparation*—With the proper column(s) and liquid sample valve in place, adjust operating conditions to optimize the resultant chromatogram. Using the reference standard, introduce the sample in the following manner.

### 7.3 Introduction of Sample:

7.3.1 *Floating Piston Cylinders*—For floating piston cylinders, refer to Fig. 3 and proceed as follows: connect a source of inert gas to Valve A so that pressure can be applied to the sample by means of the floating piston. Apply a pressure not less than approximately 1400 kPa (200 psi) above the vapor pressure of the sample at the temperature of the sample injection valve.

7.3.2 Thoroughly mix the sample.

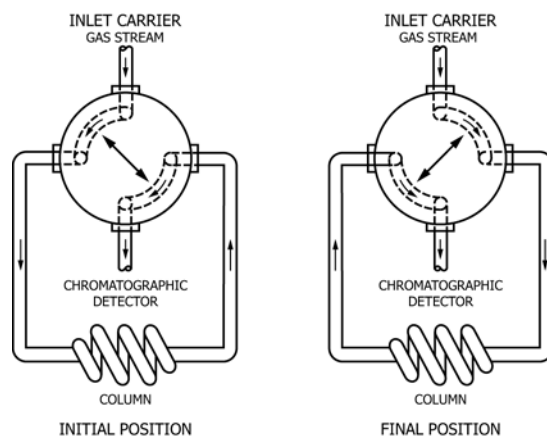
7.3.3 Connect the sample end of the cylinder, Valve B, to the inlet of the chromatograph liquid sample valve. All connections and tubing are to be made of material impervious to the sample composition and of as small diameter and shortest length of plumbing as is practical, thereby minimizing dead space. All tubing between sample cylinder and liquid sampling valve shall be the same diameter.

7.3.4 With Valve C closed, open Valve B to fill the sample valve and associated lines.

7.3.5 Slowly open Valve C to purge the sample valve. When the purge is complete, close Valve C. **Caution**—Use extreme care to ensure that no flashing of sample occurs in the inlet sampling line and valve system. Always meter at sample purge Valve C, never at sample Valve B. The sample line and valve system should remain at approximately 1400 kPa (200 psi) above the vapor pressure of the product.

7.3.6 Operate the liquid sample valve either manually or automatically to inject the liquid sample into the carrier gas flow immediately ahead of the chromatographic column. Actuate the sample valve quickly and smoothly to place the sample on the column all at once and to ensure continuous carrier gas flow through the column.

7.3.7 *Double-Valve Displacement Cylinders*—For double-valve displacement cylinders, refer to Fig. 4 and Fig. 5 and



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FIG. 6 Backflush Valve Configuration

proceed as follows: Connect the sample Cylinder B to Cylinder A so repressurizing fluid can be entered into the bottom of Cylinder B. With this configuration, the hydrocarbon sample is taken from the upper portion of the cylinder. Pressurize Cylinder A with an inert gas and maintain a pressure at least 1400 kPa (200 psi) above the vapor pressure of the hydrocarbon sample at operating conditions. Open the necessary valves to admit pressurizing fluid into the sample Cylinder B.

7.3.8 Mix the sample thoroughly by gently inverting Cylinder B several times. Fix the cylinder in a vertical position by means of a ringstand, or similar device.

7.3.9 Connect the sample outlet Valve B on Cylinder B to the inlet of the chromatograph liquid sample valve. All connections and tubing are to be made of material impervious to the sample composition and of as small diameter and shortest length of plumbing as is practical, thereby minimizing “dead space.” All tubing between sample cylinder and liquid valve should be the same diameter.

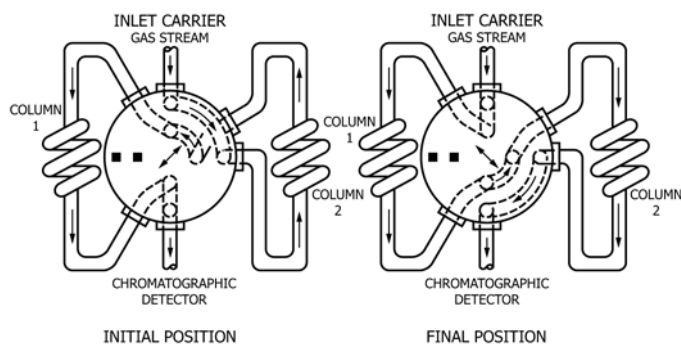
7.3.10 With Valve C closed, open Valve B to fill the sample valve and associated lines.

7.3.11 Slowly open Valve C to purge the sample valve. When the purge is complete, close Valve C. **Caution**—Use extreme care to ensure that no flashing of sample occurs in the inlet sampling line and valve system. Always meter at sample purge Valve C, never at sample Valve B. The sample line and valve system should remain at approximately 1400 kPa (200 psi) above the vapor pressure of the product.

7.3.12 Operate the liquid sample valve either manually or automatically to inject the liquid sample into the carrier gas flow immediately ahead of the chromatographic column. The liquid sample valve should be actuated quickly and smoothly to place the sample on the column all at once and to ensure continuous carrier gas flow through the column.

### 7.4 Valve Switching:

7.4.1 After the elution of *n*-hexane, the carrier gas flow is reversed by means of a backflush valve operated manually or automatically. (An acceptable backflush valve configuration is shown in Fig. 6.) Reversing carrier flow causes severe baseline deviations (see Fig. 1). When using electronic digital integrators, exercise care to ensure integration does not occur



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FIG. 7 Precut Valve Configuration

until baseline is adequately reestablished. The resulting irregular shaped  $C_{7+}$  peak is eluted over a period of time equivalent to time on forward flow minus the retention time for the air peak. Terminate the run only after the carrier gas flow has been returned to the original direction and the baseline has been reestablished.

7.4.2 An alternate procedure to backflushing after normal hexane is the use of a precut column to group the  $C_{7+}$  fraction at the beginning of the chromatogram as a single peak. (An acceptable valve configuration for the precut method is illustrated in Fig. 7.) The valve position is switched when normal hexane and lighter components have traveled through Column 2 and are in Column 1. At this point, heptanes and heavier components are retained in Column 2. When the valve is reversed, the heptanes-plus fraction will elute from Column 2 first. The baseline shall be clearly and distinctly established before elution of the  $C_{7+}$  peak so an accurate measurement of this peak may be obtained. After the elution of  $n$ -hexane, terminate the run and return the valve to the initial position.

## 8. Sample Analysis

8.1 Obtain a chromatogram of the sample in accordance with instructions outlined in Section 7.

8.1.1 Determine peak areas (or peak heights) from the chromatogram for all components. These data shall be used to calculate composition of the sample in accordance with instructions outlined in 9.2.

## 9. Calculation

9.1 Calculation of Response Factors Using a Known Reference Standard:

9.1.1 Determine the peak area (or peak height) of each component nitrogen/air through heptanes-plus (if applicable) from the chromatogram of the known reference standard.

NOTE 6—The backflush peak (where applicable) for heptanes-plus is considered to be a single component for the purpose of this calculation. In addition, the peak area method shall be used in calculating the heptanes-plus fraction.

9.1.2 Calculate a response factor for each of the preceding components in accordance with the following equation (see Table 2):

$$K = \frac{M}{P} \quad (1)$$

where:

- $K$  = response factor,
- $M$  = mol percent of component in reference standard, and
- $P$  = peak area or peak height in arbitrary units (millimetres, square inches, counts, and so forth) corrected to maximum sensitivity.

9.1.3 An alternative method of determining response factors is the use of a single reference component in the standard. Calculate a relative response factor for each component in accordance with the following equation (see Table 2):

$$KF_i = \frac{M_i}{P_i} \times \frac{P_{RP}}{M_{RP}} \quad (2)$$

where:

- $KF_i$  = relative response factor for component  $i$ ,
- $M_i$  = mol percent of component  $i$  in reference standard,
- $P_i$  = peak area (or peak height) in arbitrary units corrected to maximum sensitivity for component  $i$ ,
- $P_{RP}$  = peak area (or peak height) of the component selected as the reference peak, and
- $M_{RP}$  = mol percent of the component in reference standard as the reference peak.

From the equation defining the relative response factor, the component chosen as the reference peak always has a response factor of 1.000.

### 9.2 Calculation of Mol Percent of Components in Sample:

9.2.1 Determine peak area (or peak height) of each component nitrogen/air through heptanes-plus from the chromatogram of the sample using the same arbitrary units as in 9.1.

9.2.2 Calculate the concentration in mol percent of each of these components in accordance with the following equation (see Table 3):

$$M = P \times K \quad (3)$$

where:

- $M$  = mol percent of component in sample,
- $P$  = peak area (or peak height) of each component in sample, and
- $K$  = response factor as determined in 9.1.

9.2.2.1 Total the mol percent values and normalize to 100 %.

9.2.3 Using the relative response factors, calculate the concentration in mol percent of each of these components in accordance with the following equation (see Table 3):

$$M_i = \frac{KF_i \times P_i}{\sum_{i=1}^n (KF_i \times P_i)} \times 100 \quad (4)$$

where:

- $M_i$  = mol percent of component  $i$  in sample,
- $KF_i$  = relative response factor for component  $i$ ,
- $P_i$  = peak area (or peak height) of component  $i$  in sample, and
- $\sum_{i=1}^n (KF_i \times P_i)$  = summation of all relative response areas in the chromatogram.

9.2.3.1 Total mol percent values and normalize to 100 %.

**TABLE 3 Calculation of Sample Using Response Factors from Table 2**

Component	Peak Area	Mol % Response Factor (×10 000)	Unnormalized Mol %	Normalized Mol %	Relative Response Factor (C <sub>3</sub> Reference Peak)	Unnormalized Area × RRF	Normalized Mol %
Nitrogen/Air	91	3.2154	0.02926	0.04	1.4080	128	0.04
Methane	4 720	4.1948	1.97995	2.85	1.8368	8 670	2.85
Carbon Dioxide	2 615	3.1888	0.83387	1.20	1.3963	3 651	1.20
Ethane	64 090	2.9598	18.96936	27.27	1.2960	83 061	27.27
Propane	113 346	2.2837	25.88483	37.21	1.0000	113 346	37.21
Isobutane	31 590	1.9927	6.29494	9.05	0.8726	27 565	9.05
<i>n</i> -Butane	33 672	1.9491	6.56301	9.44	0.8535	28 739	9.44
2,2-Dimethylpropane							
Isopentane	16 368	1.7077	2.79516	4.02	0.7478	12 240	4.02
<i>n</i> -Pentane	17 235	1.6287	2.80706	4.04	0.7132	12 292	4.04
2,2-Dimethylbutane	75	1.5152	0.01136	0.02	0.6635	50	0.02
2,3-Dimethylbutane	4 027	1.4181	0.57107	0.82	0.6210	2 501	0.82
2-Methylpentane							
3-Methylpentane	1 584	1.7076	0.27048	0.39	0.7477	1 184	0.39
Cyclopentane							
<i>n</i> -Hexane	4 521	1.4613	0.66065	0.95	0.6399	2 893	0.95
Heptanes-Plus	13 335	1.4073	1.87663	2.70	0.6162	8 217	2.70
			69.54763	100.00		304 537	100.00

## 10. Report

10.1 Report the concentration of each component in mol % to the nearest 0.1 %, and reference this test method.

## 11. Precision and Bias

11.1 The precision of this test method as determined by statistical examination of interlaboratory results is as follows:

11.1.1 *Repeatability*—The difference between two test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

Component	Mol % Range	Percent Relative Repeatability
Nitrogen	0.01–.89	9
Carbon Dioxide	0.01–2.3	4
Methane	1.6–4.5	4
Ethane	27.–54.	.5
Propane	28.–34.	.5
Isobutane	3.0–8.8	1
<i>n</i> -Butane	6.0–9.3	1
Isopentane	1.0–3.9	2
<i>n</i> -Pentane	2.0–3.8	2
C <sub>6+</sub>	3.6–5.7	2

11.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators work-

ing in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

Component	Mol % Range	Percent Relative Reproducibility
Nitrogen	0.01–89	60
Carbon Dioxide	0.01–2.3	30
Methane	1.6–4.5	10
Ethane	27.–54.	2
Propane	38.–34.	2
Isobutane	3.0–8.8	4
<i>n</i> -Butane	6.0–9.3	4
Isopentane	1.0–3.9	6
<i>n</i> -Pentane	2.0–3.8	6
C <sub>6+</sub>	3.6–5.7	10

NOTE 7—The repeatability and reproducibility statements for this procedure are from the statistical data obtained in a GPA cooperative test program completed in 1986. The testing program included six samples analyzed in a round robin by eight laboratories. See also GPA 2177.

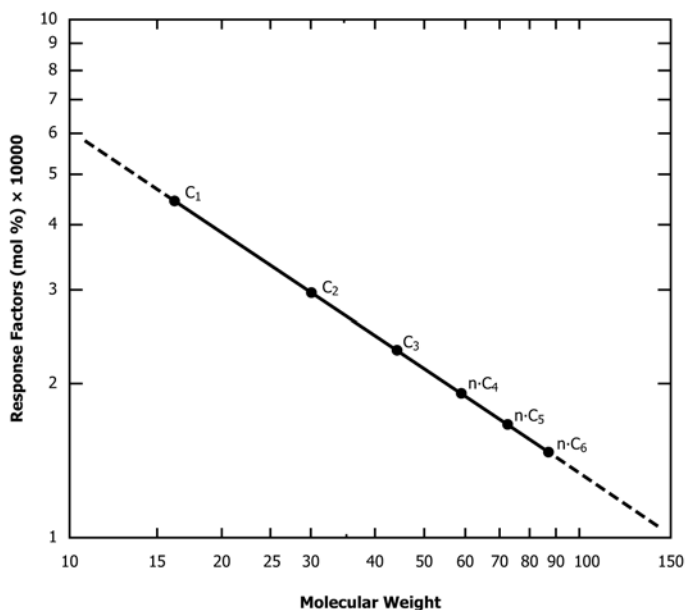
11.2 *Bias*—The bias of the procedure in this test method has not been determined.

## 12. Keywords

12.1 carbon dioxide; chromatography; demethanized hydrocarbons; hydrocarbon composition; liquefied petroleum gases; natural gas liquids; nitrogen



A1. FIDELITY OF SELECTED REFERENCE STANDARDS



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FIG. A1.1 Response Factors (mol %) Versus Molecular Weight

A1.1 Referring to Section 3 on Summary of Test Method, it is noted that the test method is based on response factors calculated from a selected reference standard using peak area measurements. Liquid reference standards are difficult to prepare and are subject to change in composition during use. Hence it is virtually mandatory that the reference standard be authenticated in some manner when received and periodically during use. One simple approach is described as follows:

A1.1.1 Determine mol percent response factors for normal hydrocarbons using area measurements of peaks recorded on the chromatogram of reference standard run (see 9.1.2).

A1.1.2 Determine molecular weight corresponding to each component hydrocarbon in A1.1.1.

A1.1.3 Using log/log paper, plot the response factor on the vertical scale versus molecular weights on the horizontal scale (see Fig. A1.1).

A1.1.4 If all is in order, the resultant plot will be essentially a straight line with a negative slope. For a specific instrument,

TABLE A1.1 Response Factors and Mol Weights Normal Hydrocarbon Components<sup>A</sup>

Component	Response Factor × 10 <sup>-4</sup>	Mol Weight
Methane	4.195	16.043
Ethane	2.960	30.070
Propane	2.284	44.097
n-Butane	1.949	58.123
n-Pentane	1.629	72.150
n-Hexane	1.461	86.177

<sup>A</sup>Initially with a new system and a new blend this check should be performed often, say once a day for the first week to satisfy the operator that the component analysis furnished with the blend is essentially correct. After this time, the check should be performed each time a calibration run is made to verify the continued fidelity of the selected reference blend.

the slope of the plot should remain essentially constant. A change in the angle usually indicates a change in blend composition.

A1.1.5 An example follows using data from Table 2 in this test method (see Table A1.1).

A1.2 It should be noted that the relationship described in A1.1.1 – A1.1.5 is valid for reference blends in the vapor state as well as the liquid state, so long as the following conditions are met.

A1.2.1 Chromatogram is obtained using a thermal conductivity detector.

A1.2.2 Peak areas in arbitrary units are used for peak measurements.

A1.2.3 Known concentrations of hydrocarbon components in the known reference blend are expressed in mol %.

A1.3 In addition to authentication of reported composition of a new blend and periodically verifying its validity, this plot can be used to:

A1.3.1 Reduce the frequency of calibrations required.

A1.3.2 Reveal calculation and interpretation errors in calibration runs.

A1.3.3 Pick off factors for components not in the standard by extrapolating the plot. A factor for the back flush peak can be picked off if the molecular weight can be satisfactorily estimated.

## A2. DETERMINATION OF RESPONSE FACTORS

### A2.1 Linearity Check

A2.1.1 In order to establish linearity of response for the thermal conductivity detector, it is necessary to carry out the procedure outlined as follows:

A2.1.2 The major component of interest (methane for natural gas) is charged to the chromatograph by means of the fixed-size sample loop at partial pressure of 100 to 700 mm Hg in increments of 100 mm. The peak area of the methane is plotted versus partial pressure. Any deviation from linearity indicates the fixed volume sample loop is too large. The sample size should be reduced until the pure major component is linear over the concentration range expected in the samples.

A2.1.2.1 Connect the pure component source to the sample entry system. Evacuate the sample entry system and observe the manometer for any leaks. (See Fig. A2.1 for a suggested manifold arrangement.) The sample entry system shall be vacuum tight.

A2.1.2.2 Carefully open the needle valve to admit the pure component up to 100 mm of partial pressure.

A2.1.2.3 Record exact partial pressure and actuate sample valve to place sample onto column. Record peak area of pure component.

A2.1.2.4 Repeat A2.1.2 for 200, 300, 400, 500, 600, and 700 mm Hg. Record peak area obtained at each pressure.

A2.1.2.5 Plot the area data versus partial pressure on the x and y axes of linear graph paper as shown in Fig. A2.2.

NOTE A2.1—Experience has shown that if the major component is linear over the expected concentration range in the sample, the lesser components will also be linear. Methane and ethane exhibit less than 1 % compressibility at 760 mm Hg and are therefore the components of choice for linearity checks.

NOTE A2.2—**Caution:** *n*-Butane at atmospheric pressure exhibits 3.5 % compressibility, which, if the detector response is linear, will produce a nonlinear response opposite to detector non-linearity.

### A2.2 Calibration Procedure

A2.2.1 Response factors of the components of interest can be established in two ways. The routine method is to use a gas reference standard of known composition to determine response factors, provided all components in the reference

standard and in the samples lie within the proven linear range for a specific chromatography instrument. An acceptable non-routine method of determining response factors is to charge the pure components to the chromatograph. The latter method is described in Annex A1.

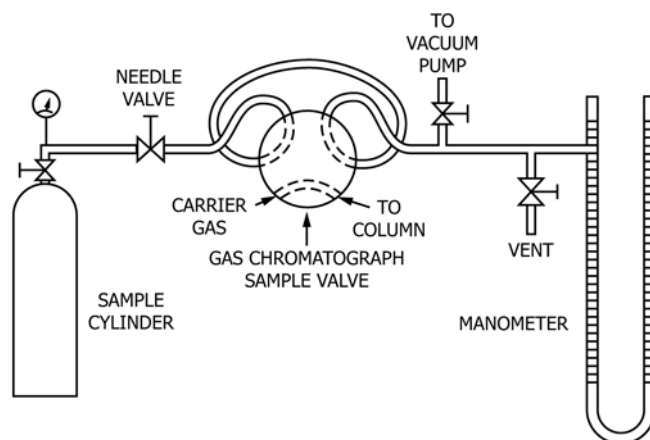
A2.2.1.1 Connect the reference standard gas to the sample entry system. Evacuate the sample entry system and observe the manometer for any leaks.

A2.2.1.2 Carefully open the needle valve to admit reference standard gas up to some predetermined partial pressure.

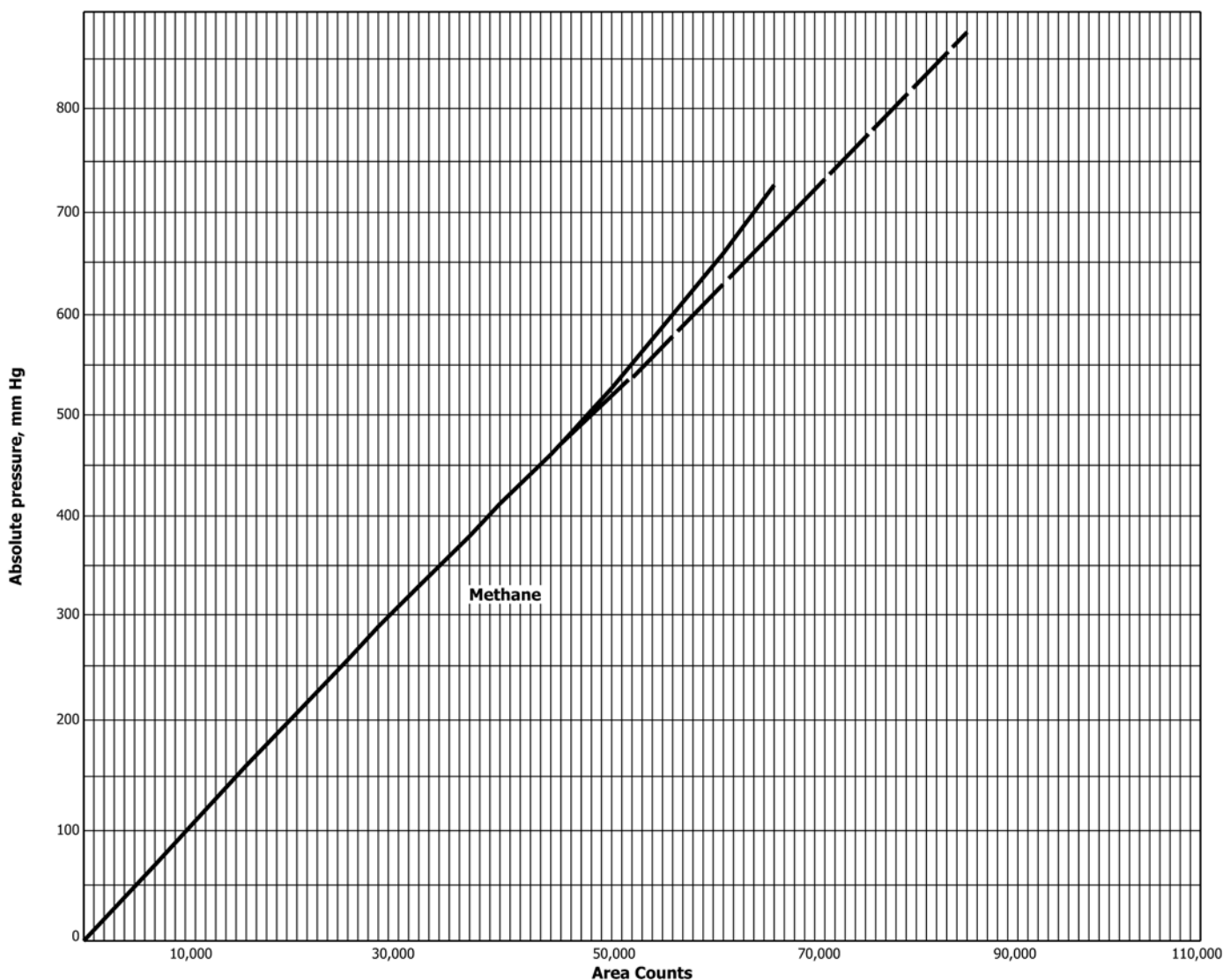
NOTE A2.3—The use of some constant partial pressure below atmospheric pressure avoids variations in sample size due to changes in barometric pressure.

A2.2.1.3 Record the partial pressure and operate the gas sampling valve to place the sample onto the column. Record the chromatogram, integrator/computer peak areas, and peak retention times.

NOTE A2.4—It is recommended that the integrator/computer has the capability to print out retention times of peak maxima to aid in peak identification and to monitor instrument conditions for unknown changes.



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**FIG. A2.1 Suggested Manifold Arrangement for Entering Vacuum Samples**



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FIG. A2.2 Linearity of Detector Response

### A3. HAZARD STATEMENTS

#### A3.1 Flammable Liquefied Gases

- A3.1.1 Keep away from sparks and open flame.
- A3.1.2 Keep container closed.
- A3.1.3 Use with adequate ventilation.
- A3.1.4 Avoid buildup of vapors and eliminate all sources of ignition, especially nonexplosive electrical devices and heaters.
- A3.1.5 Avoid prolonged breathing of vapor or spray mist.
- A3.1.6 Avoid prolonged or repeated skin contact.

#### A3.2 Compressed Gases (Helium, Nitrogen)

- A3.2.1 Keep container closed.
- A3.2.2 Use adequate ventilation.
- A3.2.3 Do not enter storage areas unless adequately ventilated.

- A3.2.4 Always use a pressure regulator.
- A3.2.5 Release regulator tension before opening cylinder.
- A3.2.6 Do not transfer to cylinder other than one in which gas is received.
- A3.2.7 Do not mix gases in cylinders.
- A3.2.8 Do not drop cylinders.
- A3.2.9 Make sure cylinder is supported at all times.
- A3.2.10 Stand away from cylinder outlet when opening cylinder valve.
- A3.2.11 Keep cylinder out of sun and away from heat.
- A3.2.12 Keep cylinder from corrosive environment.
- A3.2.13 Do not use cylinder without label.

A3.2.14 Do not use dented or damaged cylinder.

A3.2.15 For technical use only. Do not use for inhalation purposes.

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