Designation: D 2597 – 94 (Reapproved 1999)

An American National Standard

Standard Test Method for Analysis of Demethanized Hydrocarbon Liquid Mixtures Containing Nitrogen and Carbon Dioxide by Gas Chromatography[1]

This standard is issued under the fixed designation D 2597; 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 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 fraction, when present in the sample, is 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.

NOTE 1—**Caution:** In the case of unknown samples with a relatively large C_6 plus or C_7 plus 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.

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:*

D 3700 Practice for Containing Hydrocarbon Fluid Samples Using a Floating Piston Cylinder[2]

2.2 *Other Standard:*

GPA Standard 2177 Analysis of Demethanized Hydrocarbon Liquid Mixtures Containing Nitrogen and Carbon Dioxide by Gas Chromatography[3]

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
n-Butane and 2,2-Dimethylpropane	0.01–100.0
Isopentane	0.01–15.0
n-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
n-Hexane	
Heptanes and Heavier	0.01–5.0

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 to 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 irregular shape 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.

3.1.2 An alternative 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. Two advantages of the alternate method are as follows: (*1*) better precision in measuring the C_7 plus portion of

[1] This test method is under the jurisdiction of Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.H on Liquefied Petroleum Gas.

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[2] *Annual Book of ASTM Standards*, Vol 05.02.

[3] Available from Gas Processors Assn., 6526 E. 60th St., Tulsa, OK 74145.

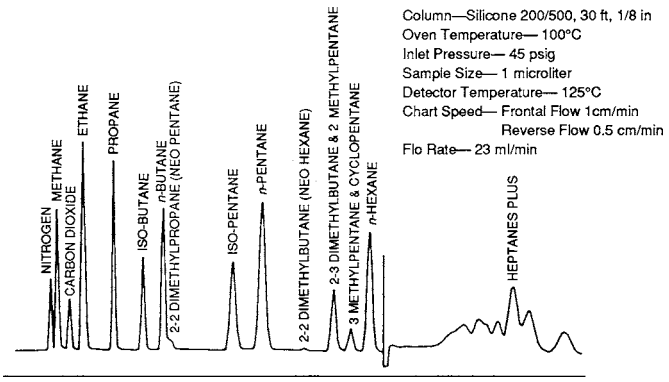

FIG. 1 Chromatogram of Demethanized Hydrocarbon Liquid Mixture (Frontal Carrier Gas Flow Through *N*-Hexane, Reverse Grouping Heptanes Plus)

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 unknown sample with corresponding areas obtained from a run of a selected reference standard. Any component in the unknown suspected to be outside the linearity range of the detector, with reference to the known amount of that component in the reference standard, must 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 must 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.

5. Apparatus

5.1 Any gas chromatograph can be used that meets the following specifications.

5.1.1 *Detector*—The detector shall be a thermal-conductivity type. It must 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 200 psi (1379 kPa) 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 is to be made to introduce a gas phase sample into the carrier gas stream ahead of the chromatographic column so that linearity of the instrument can be estimated 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.

5.1.5 *Attenuator*—A multistep device shall be included in the detector output circuitry to attenuate the signal from the detector to the recorder when using manual calculation methods. The attenuation between steps shall be accurate to ±0.5 %.

5.1.6 *Temperature Control*—The chromatographic column(s) and the detector shall be maintained at their respective

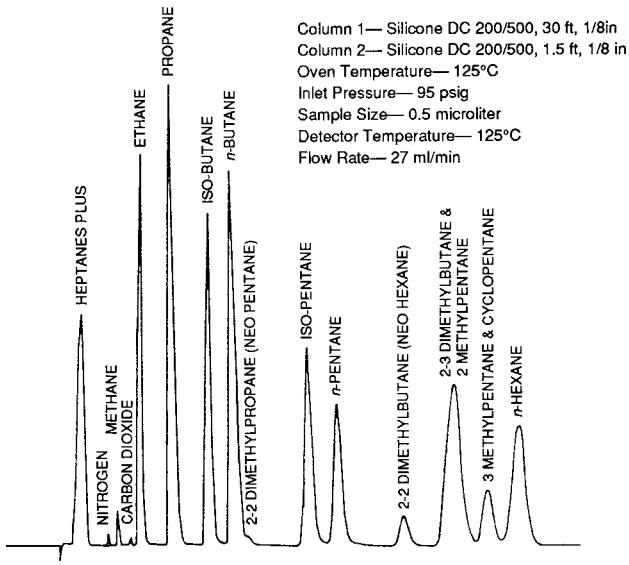

FIG. 2 Chromatogram of Demethanized Hydrocarbon Liquid Mixture (Precut Column Grouping Heptanes Plus, Frontal Carrier Gas Flow Remaining Components)

temperatures, constant to ±0.3°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 *Recorder*—A strip chart recorder with a full-scale range of 1 mv shall be required when using manual calculation methods. A maximum pen response time of 1 s and a minimum chart speed of 1 cm/min (0.5 in./min accepted) shall be required. Faster speeds up to 10 cm/min (3 in./min accepted) are required if the chromatogram is to be interpreted using manual methods to obtain areas.

NOTE 2—A strip chart recorder is recommended for monitoring the progress of the analysis if an electronic digital integrator without plotting capability is in service.

5.4 *Electronic Digital Integrator*—A strongly preferred and recommended device for determining peak areas. This device offers the highest degree of precision and operator convenience.

NOTE 3—**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.

5.5 *Ball and Disk Integrator*—An alternative device in the absence of an electronic digital integrator for determining peak areas. This device gives more precise areas than manual methods and saves operator time in interpreting the chromatogram.

5.6 *Manometer*—Well type, equipped with an accurately graduated and easily readable scale covering the range from 0 to 900 mm of mercury. The manometer 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.

5.7 *Vacuum Pump*—Shall have the capability of producing a vacuum of 0.1 mm of mercury absolute or less. Required for linearity checks when using the gas sampling valve.

5.8 *Sample Filter*—An optional device to protect the liquid sampling valve from scoring due to the presence of foreign contaminates such as metal shavings, dirt, and so forth, in a natural gas liquid (NGL) sample. The filter can be of a small total volume, or an in-line type design and contain a replaceable/disposable element.

NOTE 4—**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. (Can be accomplished by a heating/cooling process or inert gas purge, etc.) The filter element should be 15-µm size or larger so that during the purging process NGL is not flashed, preventing fractionation and bubble formation.

5.9 *Sample Containers*:

5.9.1 *Floating Piston Cylinder*—A strongly preferred and recommended device suitable for securing, containing, and transferring samples into a liquid sample valve and which preserves the integrity of the sample. (See Fig. 3 and Test Method D 3700.)

5.9.2 *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.)

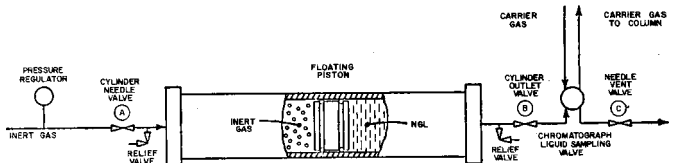

FIG. 3 Repressuring System and Chromatographic Valving with Floating Piston Cylinder

NOTE 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 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.

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

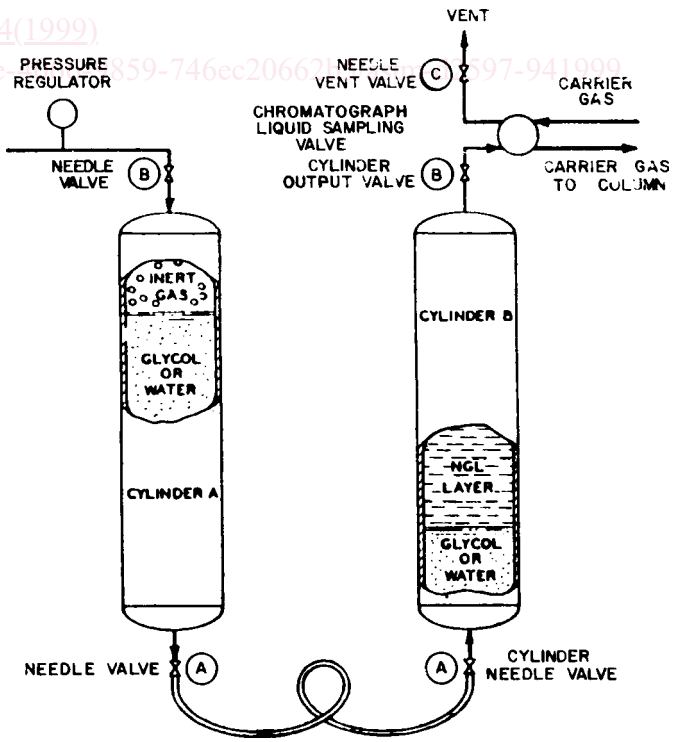

FIG. 4 Repressuring System and Chromatographic Valving with Double-Valve Displacement Cylinder

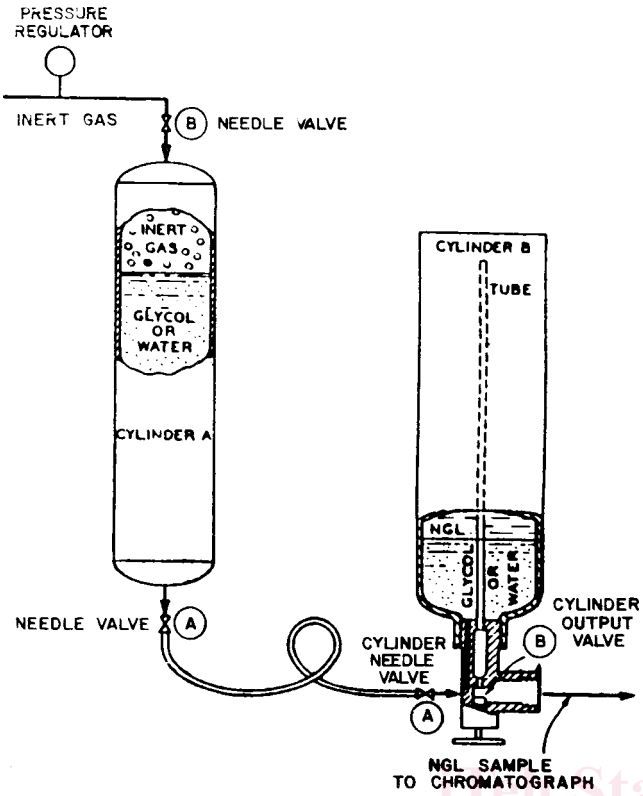

FIG. 5 Alternate Repressuring System with Double-Valve Displacement Cylinder

in the unknown. A set 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) can then be run, using the originally obtained response factors, which contain a concentration of individual components exceeding the expected amounts in the unknowns. When both (or all three) runs match their respective standards within the precision guidelines allowed in Section 10, then the instrument can be considered linear within that range.

NOTE 6—This test method omits the need of a gas sample valve on the chromatographic instrument. However, several accurate primary NGL 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 unknowns. This approach is valid for all components that lie within the proven linear range for a specific gas chromatograph.

NOTE 7—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 through 6.3.1 until a satisfactory check is obtained. Usually two runs will suffice.

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_3 Reference Peak)
Nitrogen/air	0.10	311	$\frac{0.10}{311} = 3.2154$	$\frac{0.10}{311} \times \frac{122825}{28.05} = 1.4080$
Methane	1.49	3552	$\frac{1.49}{3552} = 4.1948$	$\frac{1.49}{3552} \times \frac{122825}{28.05} = 1.8368$
Carbon dioxide	0.50	1568	$\frac{0.50}{1568} = 3.1888$	$\frac{0.50}{1568} \times \frac{122825}{28.05} = 1.3963$
Ethane	53.90	182108	$\frac{53.90}{182108} = 2.9598$	$\frac{53.90}{182108} \times \frac{122825}{28.05} = 1.2960$
Propane	28.05	122825	$\frac{28,05}{122825} = 2.2837$	$\frac{28.05}{122825} \times \frac{122825}{28.05} = 1.0000$
Isobutane	3.05	15306	$\frac{3.05}{15306} = 1.9927$	$\frac{3.05}{15306} \times \frac{122825}{28.05} = 0.8726$
n-Butane 2,2-Dimethylpropane	6.01	30834	$\frac{6.01}{30834} = 1.9491$	$\frac{6.01}{30834} \times \frac{122825}{28.05} = 0.8535$
Isopentane	1.00	5856	$\frac{1.00}{5856} = 1.7077$	$\frac{1.00}{5856} \times \frac{122825}{28.05} = 0.7478$
n-Pentane	2.00	12280	$\frac{2.00}{12280} = 1.6287$	$\frac{2.00}{12280} \times \frac{122825}{28.05} = 0.7132$
2,2-Dimethylbutane	0.02	132	$\frac{0.02}{132} = 1.5152$	$\frac{0.02}{132} \times \frac{122825}{28.05} = 0.6635$
2,3-Dimethylbutane 2-Methylbutane	0.64	4513	$\frac{0.64}{4513} = 1.4181$	$\frac{0.64}{4513} \times \frac{122825}{28.05} = 0.6210$
3-Methylpentane Cyclopentane	0.41	2401	$\frac{0.41}{2401} = 1.7076$	$\frac{0.41}{2401} \times \frac{122825}{28.05} = 0.7477$
N-Hexane	0.74	5064	$\frac{0.74}{5064} = 1.4613$	$\frac{0.74}{5064} \times \frac{122825}{28.05} = 0.6399$
Heptanes Plus	2.09	14851	$\frac{2.09}{14851} = 1.4073$	$\frac{2.09}{14851} \times \frac{122825}{28.05} = 0.6162$

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 unknown 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 200 psi (1379 kPa) 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 crack 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 1379 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 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 200 psi (1379 kPa) 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 crack 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 1379 kPa (200 psi) above the vapor pressure or 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 until baseline is adequately reestablished. The resulting irregular shaped C_7 plus peak is eluted over a period of time equivalent to time on forward flow minus the retention time for the air peak. Only after baseline is reestablished should the run be terminated and carrier flow returned to original direction.

7.4.2 An alternative to backflushing after normal hexane is the use of a precut column to group the C_7 plus 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. Baseline must be clearly and distinctly established before elution of the C_7 plus peak so an accurate measurement of this peak can be obtained. After the elution of *n*-hexane, terminate the run and return the valve to the initial position.

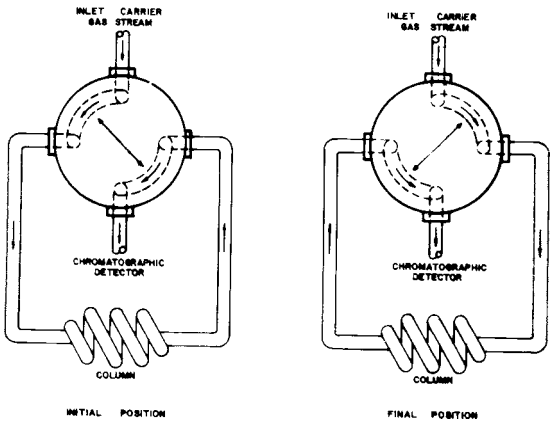

FIG. 6 Backflush Valve Configuration

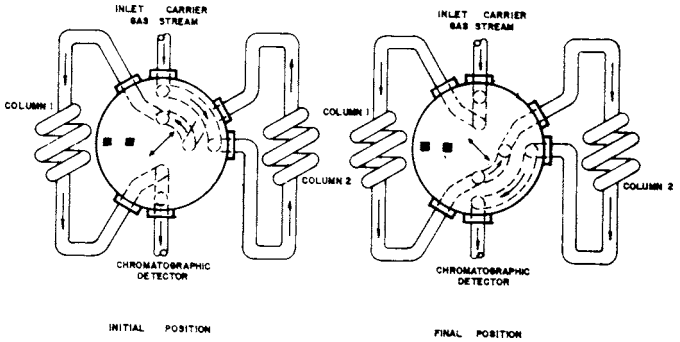

FIG. 7 Precut Valve Configuration

8. Unknown Sample Run

8.1 Obtain a chromatogram of the unknown 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 unknown 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 8—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):

$$K = \frac{M}{P} \tag{1}$$

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):

$$KF_i = \frac{M_i}{P_i} \times \frac{P_{RP}}{M_{RP}} \tag{2}$$

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 Unknown Sample*:

9.2.1 Determine peak area (or peak height) of each component nitrogen/air through heptanes plus from the chromatogram of the unknown 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):

$$M = P \times K \tag{3}$$

where:

M = mol percent of component in unknown,
P = peak area (or peak height) of each component in unknown sample, and

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

Component	Peak Area	Mol % Response Factor (×10 000)	Unnormalized Mol %	Normalized Mol %	Relative Response Factor (C_3 Reference Peak)	Unnormalized Area × RRF	Normalized Mol %
Nitrogen/Air	91	3.2154	0.02926	0.04	1.4080	128	0.04
Methane	4720	4.1948	1.97995	2.85	1.8368	8670	2.85
Carbon Dioxide	2615	3.1888	0.83387	1.20	1.3963	3651	1.20
Ethane	64090	2.9598	18.96936	27.27	1.2960	83061	27.27
Propane	113346	2.2837	25.88483	37.21	1.0000	113346	37.21
Isobutane	31590	1.9927	6.29494	9.05	0.8726	27565	9.05
n-Butane	33672	1.9491	6.56301	9.44	0.8535	28739	9.44
2,2-Dimethylpropane							
Isopentane	16368	1.7077	2.79516	4.02	0.7478	12240	4.02
N-Pentane	17235	1.6287	2.80706	4.04	0.7132	12292	4.04
2,2-Dimethylbutane	75	1.5152	0.01136	0.02	0.6635	50	0.02
2,3-Dimethylbutane	4027	1.4181	0.57107	0.82	0.6210	2501	0.82
2-Methylpentane							
3-Methylpentane	1584	1.7076	0.27048	0.39	0.7477	1184	0.39
Cyclopentane							
n-Hexane	4521	1.4613	0.66065	0.95	0.6399	2893	0.95
Heptanes Plus	13335	1.4073	1.87663	2.70	0.6162	8217	2.70
			69.54763	100.00		304537	100.00