Designation: D1945 – 03

Standard Test Method for
Analysis of Natural Gas by Gas Chromatography[1]

1. Scope*

1.1 This test method covers the determination of the chemical composition of natural gases and similar gaseous mixtures within the range of composition shown in Table 1. This test method may be abbreviated for the analysis of lean natural gases containing negligible amounts of hexanes and higher hydrocarbons, or for the determination of one or more components, as required.

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

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:* [2]

D2597 Test Method for Analysis of Demethanized Hydrocarbon Liquid Mixtures Containing Nitrogen and Carbon Dioxide by Gas Chromatography [3]

D3588 Practice for Calculating Heat Value, Compressibility Factor, and Relative Density of Gaseous Fuels [4]

E260 Practice for Packed Column Gas Chromatography

3. Summary of Test Method

3.1 Components in a representative sample are physically separated by gas chromatography (GC) and compared to calibration data obtained under identical operating conditions from a reference standard mixture of known composition. The numerous heavy-end components of a sample can be grouped into irregular peaks by reversing the direction of the carrier gas through the column at such time as to group the heavy ends either as C_5 and heavier, C_6 and heavier, or C_7 and heavier. The composition of the sample is calculated by comparing either the peak heights, or the peak areas, or both, with the corresponding values obtained with the reference standard.

TABLE 1 Natural Gas Components and Range of Composition Covered

Component	Mol %
Helium	0.01 to 10
Hydrogen	0.01 to 10
Oxygen	0.01 to 20
Nitrogen	0.01 to 100
Carbon dioxide	0.01 to 20
Methane	0.01 to 100
Ethane	0.01 to 100
Hydrogen sulfide	0.3 to 30
Propane	0.01 to 100
Isobutane	0.01 to 10
n-Butane	0.01 to 10
Neopentane	0.01 to 2
Isopentane	0.01 to 2
n-Pentane	0.01 to 2
Hexane isomers	0.01 to 2
Heptanes+	0.01 to 1

4. Significance and Use

4.1 This test method is of significance for providing data for calculating physical properties of the sample, such as heating value and relative density, or for monitoring the concentrations of one or more of the components in a mixture.

5. Apparatus

5.1 *Detector*—The detector shall be a thermal-conductivity type, or its equivalent in sensitivity and stability. The thermal conductivity detector must be sufficiently sensitive to produce a signal of at least 0.5 mV for 1 mol % *n*-butane in a 0.25-mL sample.

5.2 *Recording Instruments*—Either strip-chart recorders or electronic integrators, or both, are used to display the separated components. Although a strip-chart recorder is not required when using electronic integration, it is highly desirable for evaluation of instrument performance.

5.2.1 The recorder shall be a strip-chart recorder with a full-range scale of 5 mV or less (1 mV preferred). The width of the chart shall be not less than 150 mm. A maximum pen response time of 2 s (1 s preferred) and a minimum chart speed of 10 mm/min shall be required. Faster speeds up to 100 mm/min are desirable if the chromatogram is to be interpreted using manual methods to obtain areas.

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*A Summary of Changes section appears at the end of this standard.

5.2.2 *Electronic or Computing Integrators*—Proof of separation and response equivalent to that for a recorder is required for displays other than by chart recorder. Baseline tracking with tangent skim peak detection is recommended.

5.3 *Attenuator*—If the chromatogram is to be interpreted using manual methods, an attenuator must be used with the detector output signal to maintain maximum peaks within the recorder chart range. The attenuator must be accurate to within 0.5 % between the attenuator range steps.

5.4 *Sample Inlet System*:

5.4.1 The sample inlet system shall be constructed of materials that are inert and nonadsorptive with respect to the components in the sample. The preferred material of construction is stainless steel. Copper, brass, and other copper-bearing alloys are unacceptable. The sample inlet system from the cylinder valve to the GC column inlet must be maintained at a temperature constant to $\pm 1°C$.

5.4.2 Provision must be made to introduce into the carrier gas ahead of the analyzing column a gas-phase sample that has been entrapped in a fixed volume loop or tubular section. The fixed loop or section shall be so constructed that the total volume, including dead space, shall not normally exceed 0.5 mL at 1 atm. If increased accuracy of the hexanes and heavier portions of the analysis is required, a larger sample size may be used (see Test Method D2597). The sample volume must be reproducible such that successive runs agree within 1 % on each component. A flowing sample inlet system is acceptable as long as viscosity effects are accounted for.

Note 1—The sample size limitation of 0.5 mL or smaller is selected relative to linearity of detector response, and efficiency of column separation. Larger samples may be used to determine low-quantity components to increase measurement accuracy.

5.4.3 An optional manifold arrangement for entering vacuum samples is shown in Fig. 1.

5.5 *Column Temperature Control*:

5.5.1 *Isothermal*—When isothermal operation is used, maintain the analyzer columns at a temperature constant to 0.3°C during the course of the sample run and corresponding reference run.

5.5.2 *Temperature Programming*—Temperature programming may be used, as feasible. The oven temperature shall not exceed the recommended temperature limit for the materials in the column.

5.6 *Detector Temperature Control*—Maintain the detector temperature at a temperature constant to 0.3°C during the course of the sample run and the corresponding reference run. The detector temperature shall be equal to or greater than the maximum column temperature.

5.7 *Carrier Gas Controls*—The instrument shall be equipped with suitable facilities to provide a flow of carrier gas through the analyzer and detector at a flow rate that is constant to 1 % throughout the analysis of the sample and the reference standard. The purity of the carrier gas may be improved by flowing the carrier gas through selective filters prior to its entry into the chromatograph.

5.8 *Columns*:

5.8.1 The columns shall be constructed of materials that are inert and nonadsorptive with respect to the components in the sample. The preferred material of construction is stainless steel. Copper and copper-bearing alloys are unacceptable.

5.8.2 An adsorption-type column and a partition-type column may be used to make the analysis.

Note 2—See Practice E260.

5.8.2.1 *Adsorption Column*—This column must completely separate oxygen, nitrogen, and methane. A 13X molecular sieve 80/100 mesh is recommended for direct injection. A 5A column can be used if a pre-cut column is present to remove interfering hydrocarbons. If a recorder is used, the recorder pen must return to the baseline between each successive peak. The resolution (R) must be 1.5 or greater as calculated in the following equation:

$$R(1,2) = \frac{x_2 - x_1}{y_2 + y_1} \times 2, \tag{1}$$

where x_1, x_2 are the retention times and y_1, y_2 are the peak widths. Fig. 2 illustrates the calculation for resolution. Fig. 3 is a chromatogram obtained with an adsorption column.
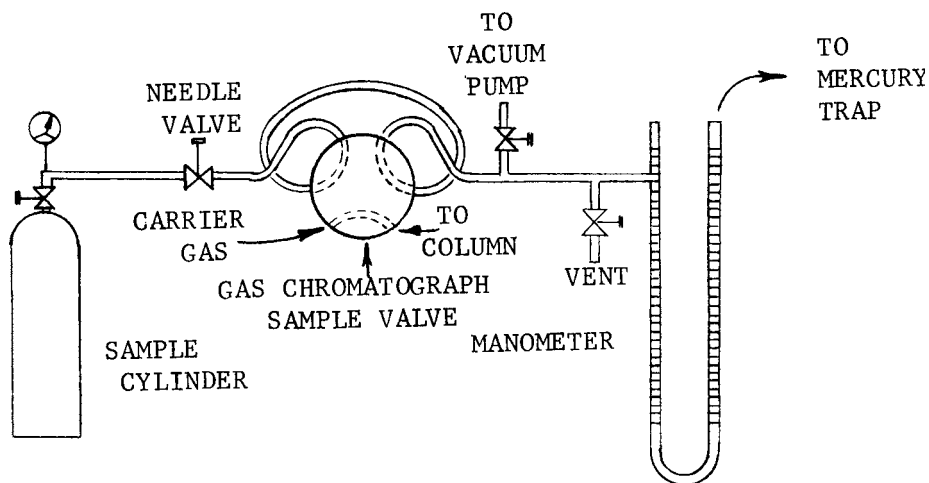

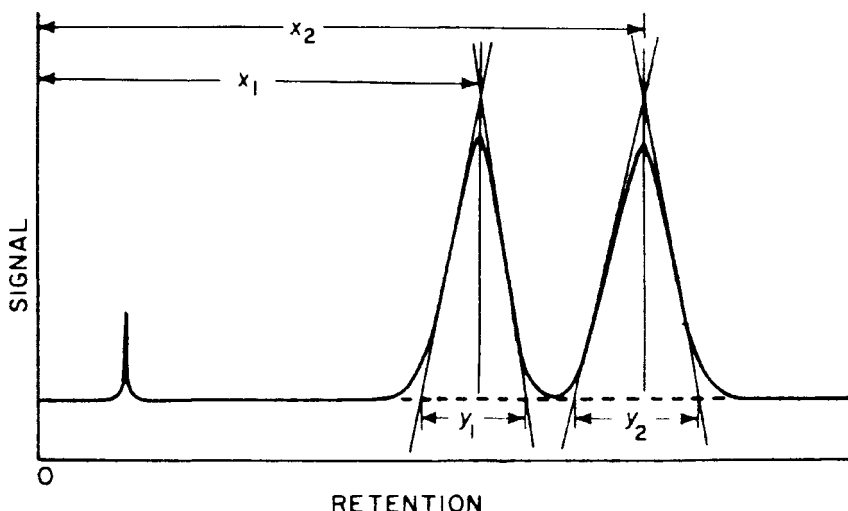**FIG. 1 Suggested Manifold Arrangement for Entering Vacuum Samples**

FIG. 2 Calculation for Resolution

COLUMN: 2 meter Type 13X molecular
        sieve, 80-100 mesh

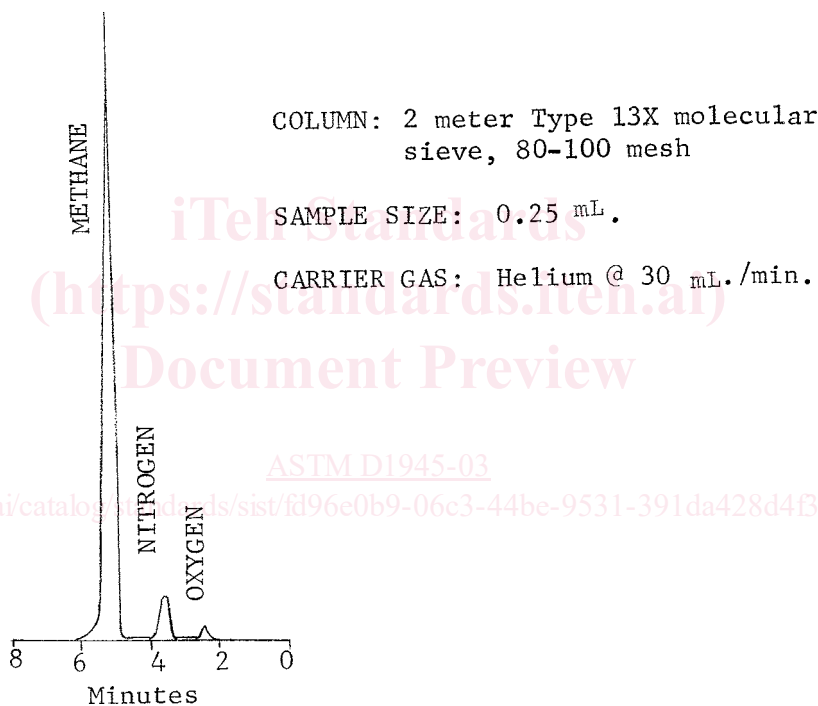SAMPLE SIZE: 0.25 mL.

CARRIER GAS: Helium @ 30 mL./min.

FIG. 3 Separation Column for Oxygen, Nitrogen, and Methane (See Annex A2)

5.8.2.2 *Partition Column*—This column must separate ethane through pentanes, and carbon dioxide. If a recorder is used, the recorder pen must return to the base line between each peak for propane and succeeding peaks, and to base line within 2 % of full-scale deflection for components eluted ahead of propane, with measurements being at the attenuation of the peak. Separation of carbon dioxide must be sufficient so that a 0.25-mL sample containing 0.1-mol % carbon dioxide will produce a clearly measurable response. The resolution (*R*) must be 1.5 or greater as calculated in the above equation. The separation should be completed within 40 min, including reversal of flow after *n*-pentane to yield a group response for hexanes and heavier components. Figs. 4-6 are examples of chromatograms obtained on some of the suitable partition columns.

5.8.3 *General*—Other column packing materials that provide satisfactory separation of components of interest may be used (see Fig. 7). In multicolumn applications, it is preferred to use front-end backflush of the heavy ends.

NOTE 3—The chromatograms in Figs. 3-8 are only illustrations of typical separations. The operating conditions, including columns, are also typical and are subject to optimization by competent personnel.

5.9 *Drier*—Unless water is known not to interfere in the analysis, a drier must be provided in the sample entering system, ahead of the sample valve. The drier must remove moisture without removing selective components to be determined in the analysis.

NOTE 4—See A2.2 for preparation of a suitable drier.

COLUMN–25% BMEE on Chromosorb P,
7 meters @ 25°C
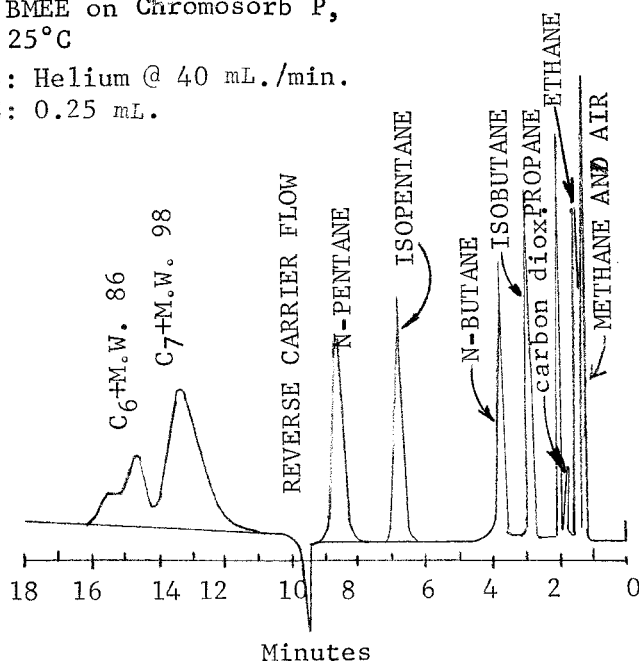CARRIER GAS: Helium @ 40 mL./min.
SAMPLE SIZE: 0.25 mL.

FIG. 4 Chromatogram of Natural Gas (BMEE Column) (See Annex A2)

COLUMN: Chromosorb PAW, 200/500, 10m

CARRIER GAS: Helium @ 40 mL./min.
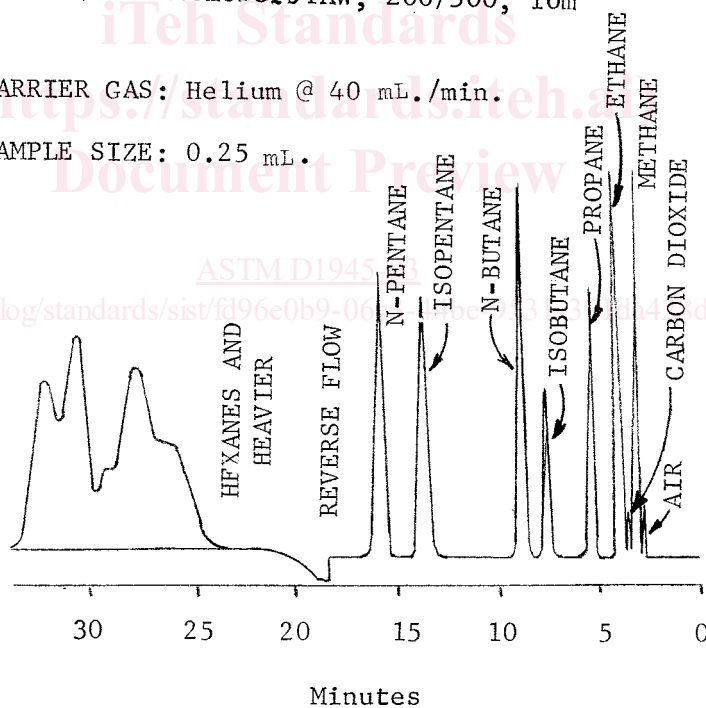
SAMPLE SIZE: 0.25 mL.

FIG. 5 Chromatogram of Natural Gas (Silicone 200/500 Column) (See Annex A2)

5.10 *Valves*—Valves or sample splitters, or both, are required to permit switching, backflushing, or for simultaneous analysis.

5.11 *Manometer*—May be either U-tube type or well type equipped with an accurately graduated and easily read scale covering the range 0 to 900 mm (36 in.) of mercury or larger. The U-tube type is useful, since it permits filling the sample loop with up to two atmospheres of sample pressure, thus extending the range of all components. The well type inherently offers better precision and is preferred when calibrating with pure components. Samples with up to one atmosphere of pressure can be entered. With either type manometer the mm scale can be read more accurately than the inch scale. Caution should be used handling mercury because of its toxic nature. Avoid contact with the skin as much as possible. Wash thoroughly after contact.

COLUMN: DIDP-3meter +DMS-6meter
            @ 35°C.

CARRIER GAS: Helium @ 75 mL./min.
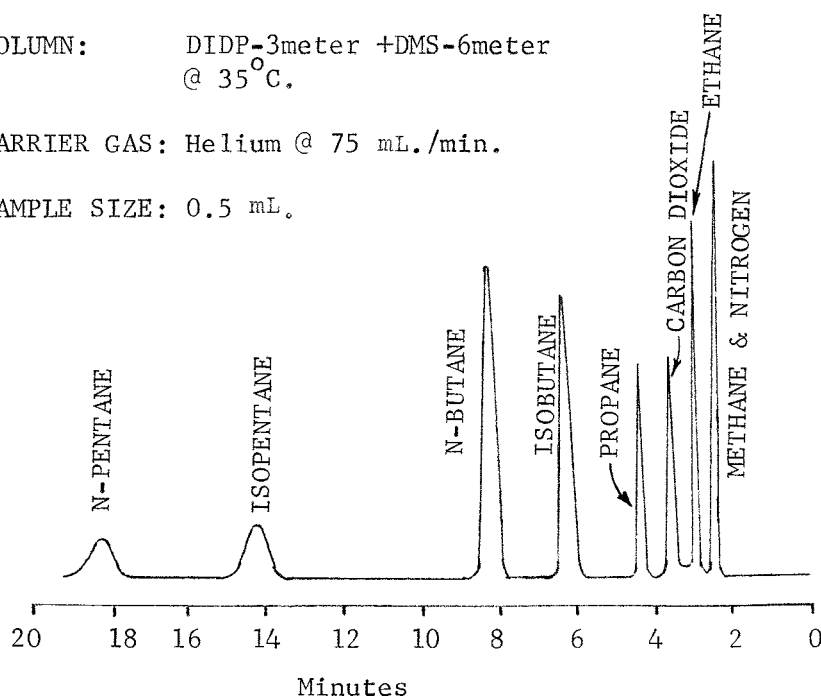
SAMPLE SIZE: 0.5 mL.

FIG. 6 Chromatogram of Natural Gas (See Annex A2)

COLUMN 1: 3 meters x 3mm 152 Squalane
           Chromosorb PAW, 80-100 mesh.

COLUMN 2: 2 meters x 3mm Porapak N
           80-100 mesh.

COLUMN 3: 2 meters x 3mm Molecular Sieve
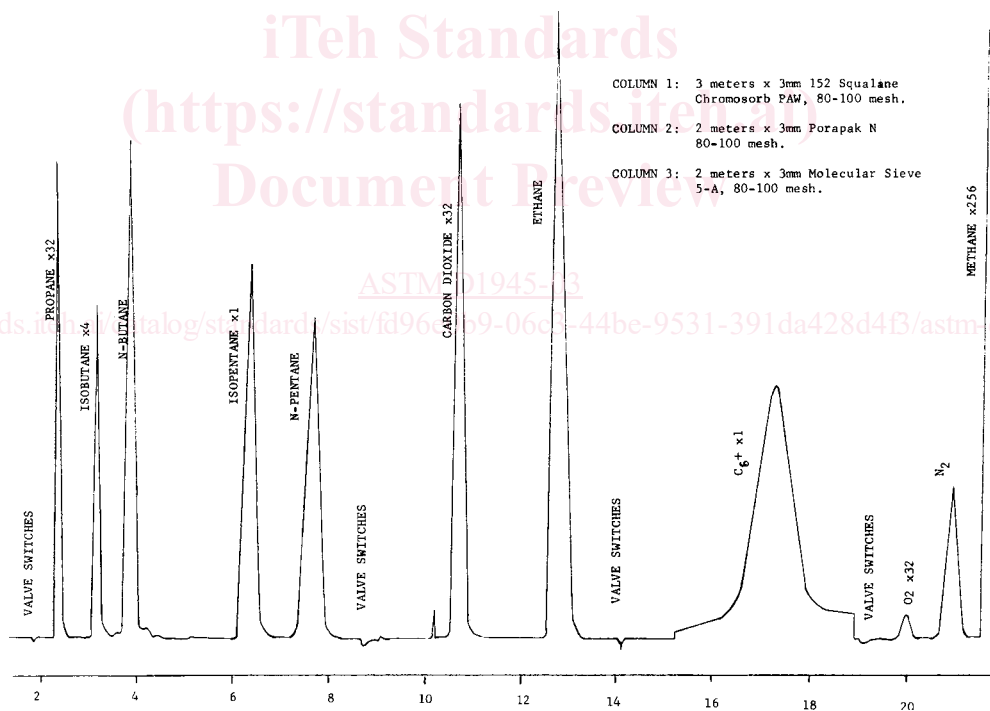   5-A, 80-100 mesh.

FIG. 7 Chromatogram of Natural Gas (Multi-Column Application) (See Annex A2)

5.12 *Vacuum Pump*—Must have the capability of producing a vacuum of 1 mm of mercury absolute or less.

6. Preparation of Apparatus

6.1 *Linearity Check*—To establish linearity of response for the thermal conductivity detector, it is necessary to complete the following procedure:

6.1.1 The major component of interest (methane for natural gas) is charged to the chromatograph by way of the fixed-size sample loop at partial pressure increments of 13 kPa (100 mm Hg) from 13 to 100 kPa (100 to 760 mm Hg) or the prevailing atmospheric pressure.
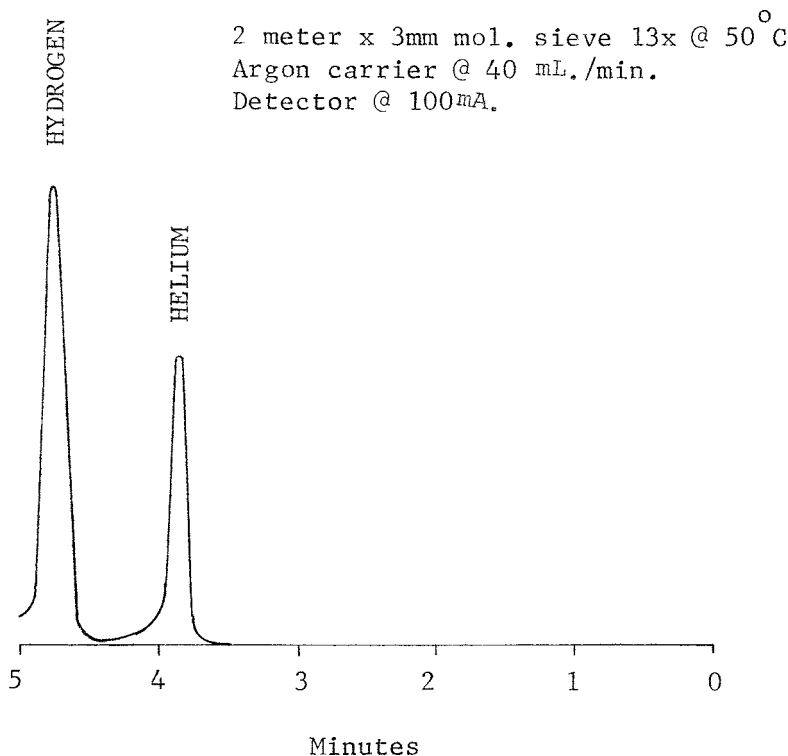
2 meter x 3mm mol. sieve 13x @ 50°C
Argon carrier @ 40 mL./min.
Detector @ 100mA.

FIG. 8 Separation of Helium and Hydrogen

6.1.2 The integrated peak responses for the area generated at each of the pressure increments are plotted versus their partial pressure (see Fig. 9).

6.1.3 The plotted results should yield a straight line. A perfectly linear response would display a straight line at a 45° angle using the logarithmic values.

6.1.4 Any curved line indicates the fixed volume sample loop is too large. A smaller loop size should replace the fixed volume loop and 6.1.1 through 6.1.4 should be repeated (see Fig. 9).

6.1.5 The linearity over the range of interest must be known for each component. It is useful to construct a table noting the response factor deviation in changing concentration. (See Table 2 and Table 3).

6.1.6 It should be noted that nitrogen, methane, and ethane exhibit less than 1 % compressibility at atmospheric pressure. Other natural gas components do exhibit a significant compressibility at pressures less than atmospheric.

6.1.7 Most components that have vapor pressures of less than 100 kPa (15 psia) cannot be used as a pure gas for a linearity study because they will not exhibit sufficient vapor pressure for a manometer reading to 100 kPa (760 mm Hg). For these components, a mixture with nitrogen or methane can be used to establish a partial pressure that can extend the total pressure to 100 kPa (760 mm Hg). Using Table 4 for vapor pressures at 38°C (100°F), calculate the maximum pressure to which a given component can be blended with nitrogen as follows:

$$B = (100 \times V)/i \qquad (2)$$

$$P = (i \times M)/100 \qquad (3)$$

where:
B = blend pressure, max, kPa (mm Hg);
V = vapor pressure, kPa (mm Hg);
i = mol %;
P = partial pressure, kPa (mm Hg); and
M = manometer pressure, kPa (mm Hg).

6.2 . *Procedure for Linearity Check:*

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

6.2.2 Carefully open the needle valve to admit the pure component up to 13 kPa (100 mm Hg) of partial pressure.

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

6.2.4 Repeat 6.2.3 for 26, 39, 52, 65, 78, and 91 kPa (200, 300, 400, 500, 600, and 700 mm Hg) on the manometer, recording the peak area obtained for sample analysis at each of these pressures.

6.2.5 Plot the area data (*x* axis) versus the partial pressures (*y* axis) on a linear graph as shown in Fig. 9.

6.2.6 An alternative method is to obtain a blend of all the components and charge the sample loop at partial pressure over the range of interest. If a gas blender is available, the mixture can be diluted with methane thereby giving response curves for all the components. (**Warning**—If it is not possible to obtain information on the linearity of the available gas chromatograph detector for all of the test gas components, then as a minimum requirement the linearity data must be obtained for any gas