ASTM
INTERNATIONAL

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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 ~~inch-pound~~ SI units are to be regarded as standard. ~~The values given in parentheses are mathematical conversions to SI units that are provided for information only and are not considered~~ No other units of measurement are included in this standard.

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
~~D3588 Practice for Calculating Heat Value, Compressibility Factor, and Relative Density of Gaseous Fuels~~
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.

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.

A Summary of Changes section appears at the end of this 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

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.

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 ±1°C. ±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. 0.5 mL at 100 kPa. 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.

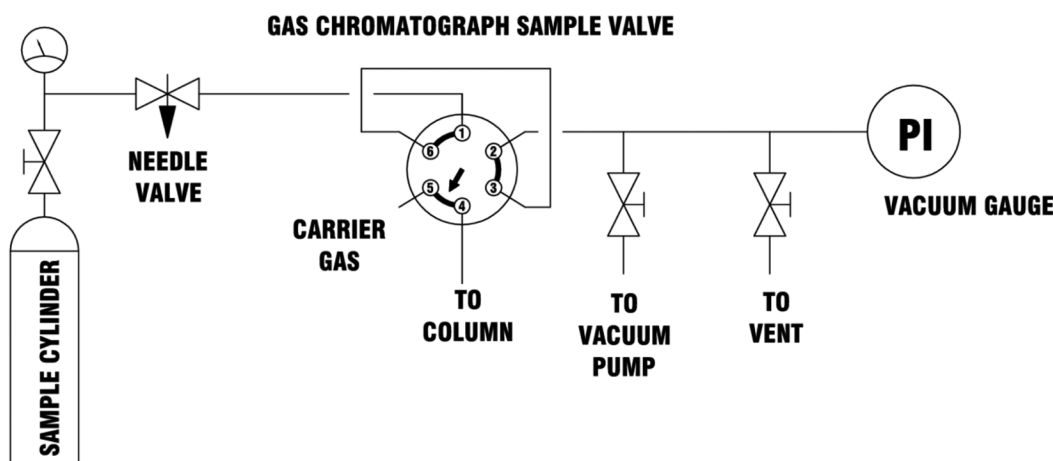5.4.3 An optional manifold arrangement for entering vacuum samples is shown in Fig. 1.

FIG. 1 Suggested Manifold Arrangement for Entering Vacuum Samples

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 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 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:

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

5.8.2.2 *Partition Column*—This column must separate ethane through pentanes, 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 one 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.
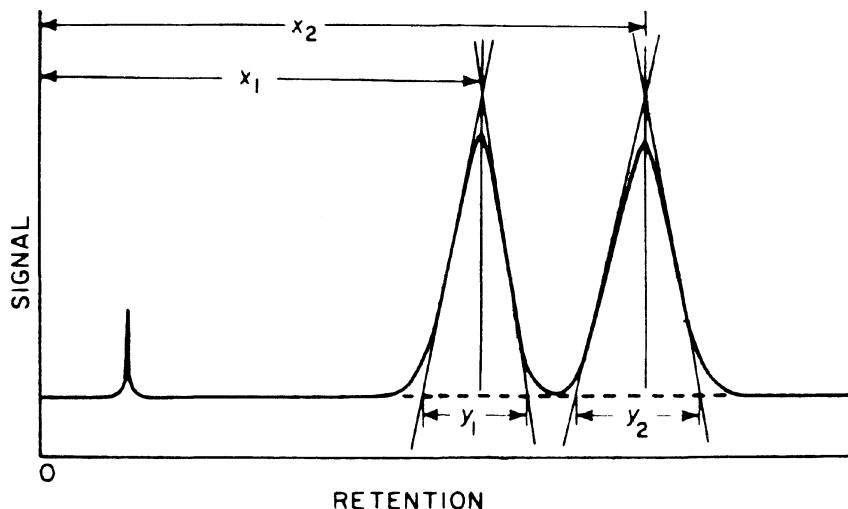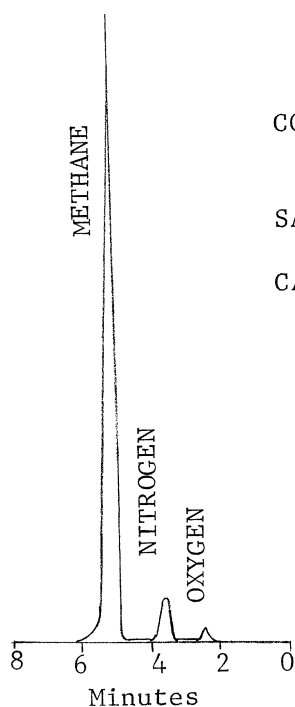

FIG. 2 Calculation for Resolution

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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)

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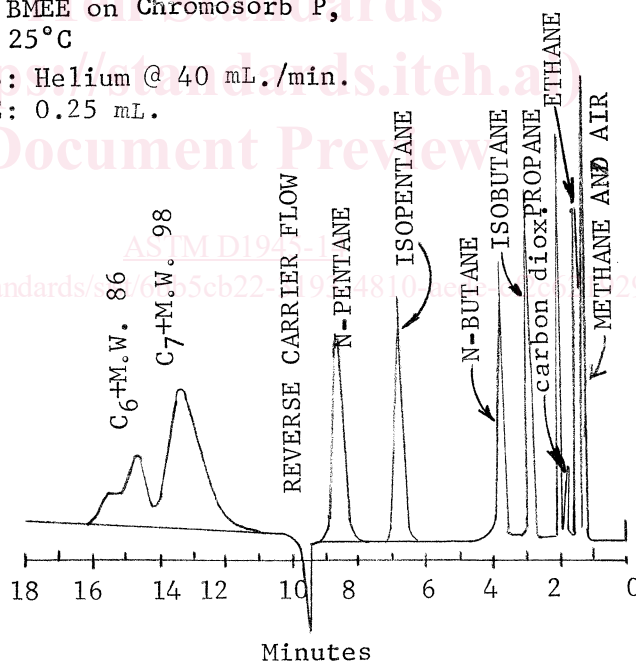CARRIER GAS: Helium @ 40 mL./min.
SAMPLE SIZE: 0.25 mL.

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

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.

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

5.11 ~~*Manometer*~~—*Vacuum Gauge*—~~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~~

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COLUMN: Chromosorb PAW, 200/500, 10m

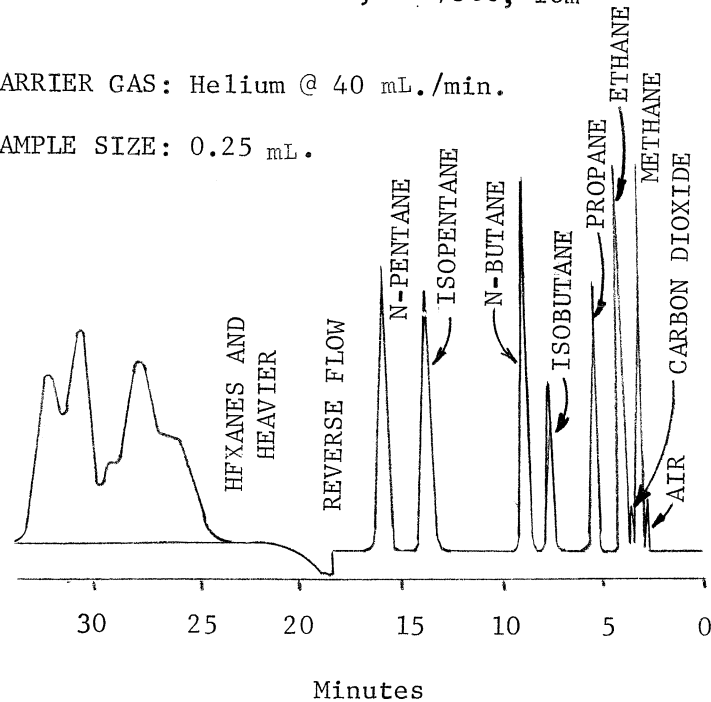CARRIER GAS: Helium @ 40 mL./min.

SAMPLE SIZE: 0.25 mL.

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

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

CARRIER GAS: Helium @ 75 mL./min.

SAMPLE SIZE: 0.5 mL.
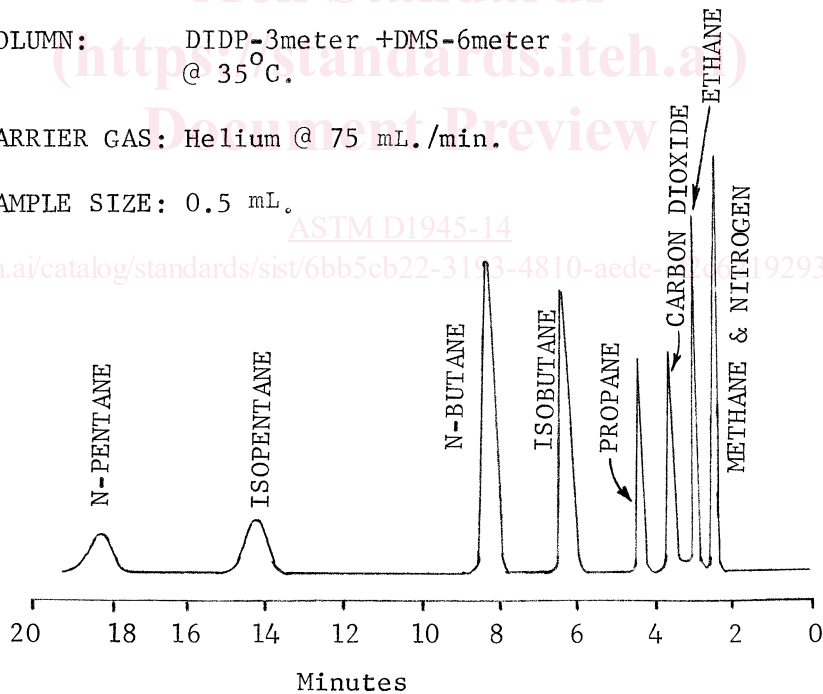
FIG. 6 Chromatogram of Natural Gas (See Annex A2)

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. Any type of vacuum gauge may be used which has a resolution of 0.14 kPa or better and covers the range of 0 to 120 kPa or larger.

5.12 *Vacuum Pump*—Must have the capability of producing a vacuum of 1 mm of mercury 0.14 kPa 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:
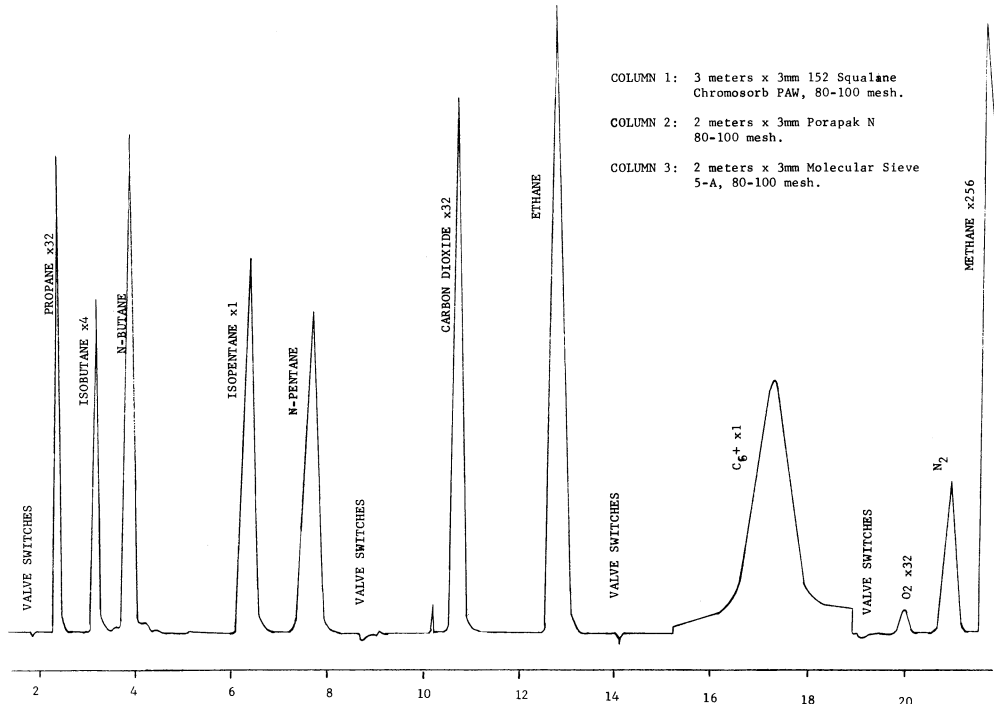
FIG. 7 Chromatogram of Natural Gas (Multi-Column Application) (See Annex A2)
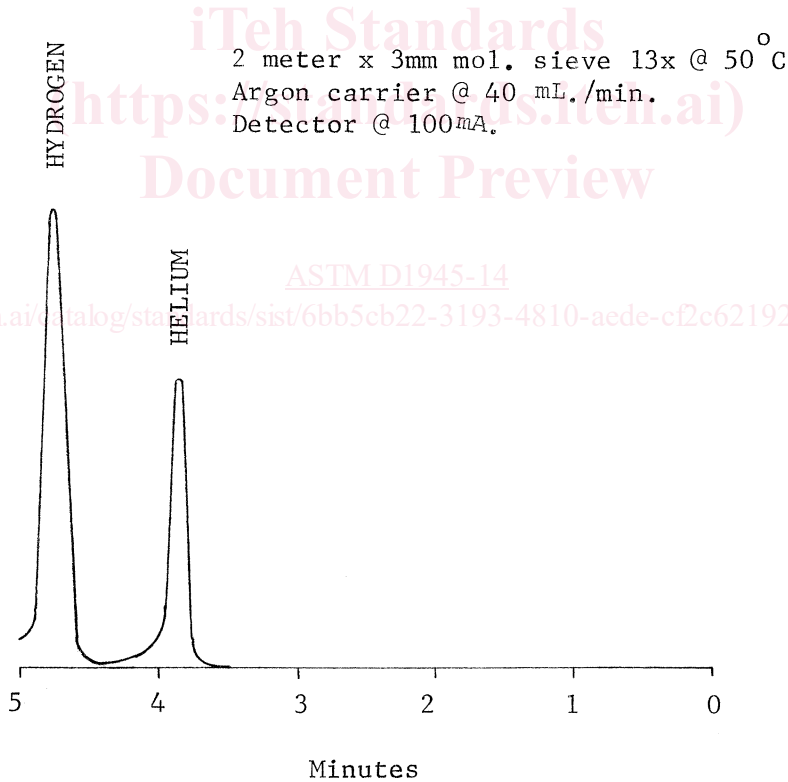
FIG. 8 Separation of Helium and Hydrogen

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.

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).

FIG. 9 Linearity of Detector Response

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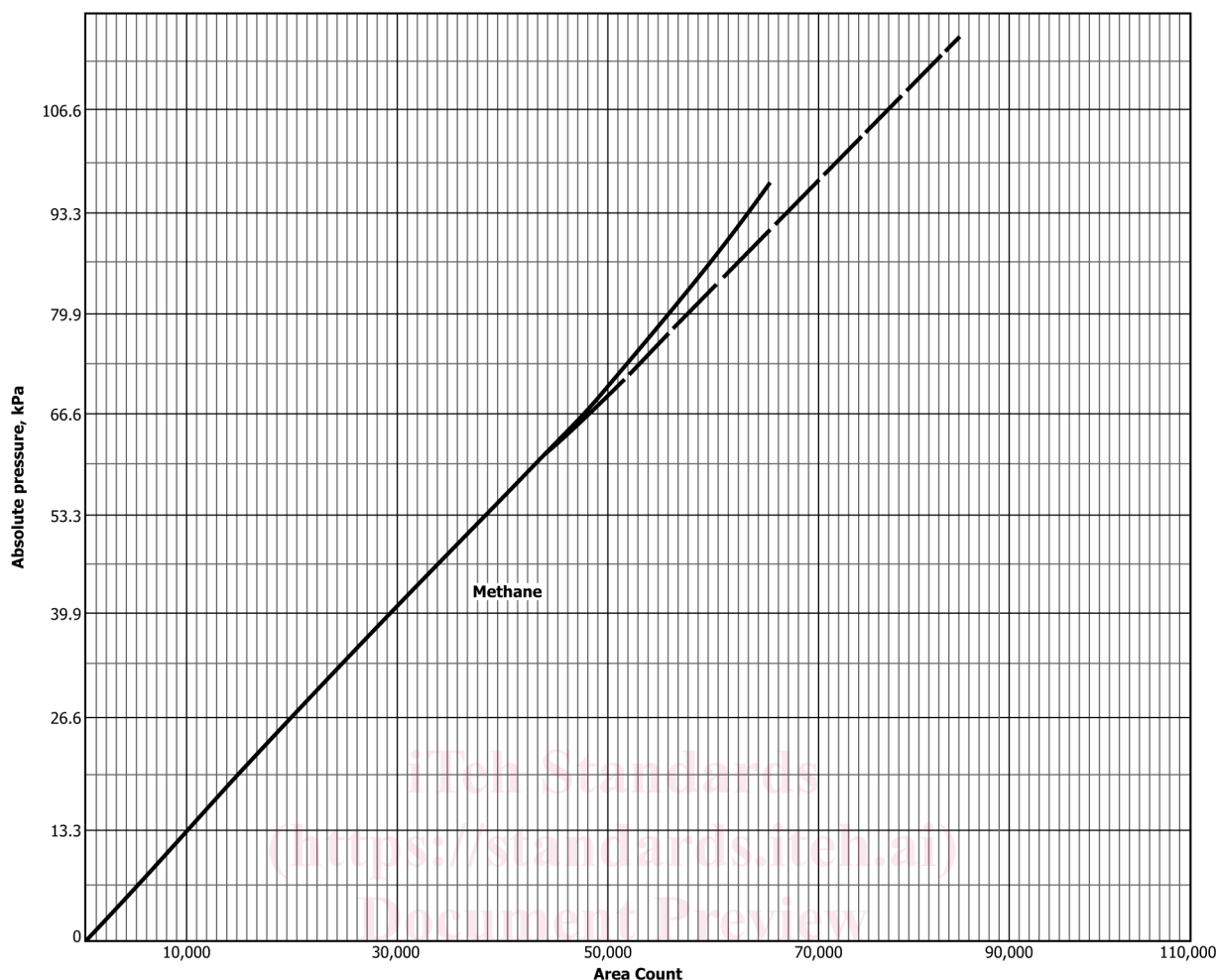
6.1.5 The linearity over the range of interest must be known for each component. It is useful to construct a table noting the response factor deviation in changing concentration. (See Table 2 and Table 3).

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 vacuum gauge reading to 100 kPa (760 mm Hg). kPa. For these components, a mixture with nitrogen or methane can be used to establish a partial pressure that can extend the total pressure

TABLE 2 Linearity Evaluation of Methane

S/B diff = (low mole % – high mole %)∕low mole % × 100			
B area	S mole %	S/B mole %∕area	S/B diff., % on low value
223 119 392	51	2.2858e-07	
242 610 272	56	2.3082e-07	−0.98
261 785 320	61	2.3302e-07	−0.95
280 494 912	66	2.3530e-07	−0.98
299 145 504	71	2.3734e-07	−0.87
317 987 328	76	2.3900e-07	−0.70
336 489 056	81	2.4072e-07	−0.72
351 120 721	85	2.4208e-07	−0.57

TABLE 3 Linearity Evaluation for Nitrogen

S/B diff = (low mole % – high mole %) ∕ low mole % × 100			
B area	S mole %	S/B mole % ∕ area	S/B diff., % on low value
5 879 836	1	1.7007e-07	
29 137 066	5	1.7160e-07	−0.89
57 452 364	10	1.7046e-07	−1.43
84 953 192	15	1.7657e-07	−1.44
111 491 232	20	1.7939e-07	−1.60
137 268 784	25	1.8212e-07	−1.53
162 852 288	30	1.8422e-07	−1.15
187 232 496	35	1.8693e-07	−1.48

to 100 ~~kPa (760 mm Hg).~~ kPa. Using Table 4 for vapor pressures at ~~38°C (100°F),~~ 38 °C, calculate the maximum pressure to which a given component can be blended with nitrogen as follows:

$$B = (100 \times V)/i \tag{2}$$

$$P = (i \times M)/100 \tag{3}$$

where:

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

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~~ vacuum gauge for leaks. (See Fig. 1 for a suggested manifold arrangement.) The sample-entry system must be vacuum tight.

TABLE 4 Vapor Pressure at ~~38°C (100°F)~~[A]

Component	kPa absolute	~~psia~~
~~Nitrogen~~	~~>34 500~~	~~>5000~~
~~Methane~~	~~>34 500~~	~~>5000~~
~~Carbon dioxide~~	~~>5 520~~	~~>800~~
~~Ethane~~	~~>5 520~~	~~>800~~
~~Hydrogen sulfide~~	~~2 720~~	~~395~~
~~Propane~~	~~1 300~~	~~189~~
~~Isobutane~~	~~501~~	~~72.6~~
~~n-Butane~~	~~356~~	~~51.7~~
~~Isopentane~~	~~141~~	~~20.5~~
~~n-Pentane~~	~~108~~	~~15.6~~
~~n-Hexane~~	~~34.2~~	~~4.96~~
~~n-Heptane~~	~~11.2~~	~~1.62~~

TABLE 4 Vapor Pressure at 38 °C[A]

Component	kPa absolute
Nitrogen	>34 500
Methane	>34 500
Carbon dioxide	>5 520
Ethane	>5 520
Hydrogen sulfide	2 720
Propane	1 300
Isobutane	501
n-Butane	356
Isopentane	141
n-Pentane	108
n-Hexane	34.2
n-Heptane	11.2

[A]The most recent data for the vapor pressures listed are available from the Thermodynamics Research Center, Texas A&M University System, College Station, TX 77843.

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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, on the vacuum gauge, 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 component that exceeds a concentration of 5 mol%. Chromatographs are not truly linear over wide concentration ranges and linearity should be established over the range of interest.)

7. Reference Standards

7.1 Moisture-free gas mixtures of known composition are required for comparison with the test sample. They must contain known percents of the components, except oxygen (Note 5), that are to be determined in the unknown sample. All components in the reference standard must be homogenous in the vapor state at the time of use. The concentration of a component in the reference standard gas should not be less than one half nor more than twice the concentration of the corresponding component in the test gas.

Note 5—Unless the reference standard is stored in a container that has been tested and proved for inertness to oxygen, it is preferable to calibrate for oxygen by an alternative method.

7.2 *Preparation*—A reference standard may be prepared by blending pure components. Diluted dry air is a suitable standard for oxygen and nitrogen (see 8.5.1).[3,4]

8. Procedure

8.1 *Instrument Preparation*—Place the proper column(s) in operation as needed for the desired run (as described in either 8.4, 8.5, or 8.6). Adjust the operating conditions and allow the chromatograph to stabilize.

8.1.1 For hexanes and higher, heat the sample loop.

Note 6—Most modern chromatographs have valve ovens that can be temperature controlled. It is strongly recommended in the absence of valve ovens to mount the gas sampling valve in the chromatograph oven and operate at the column temperature.

8.1.2 After the instrument has apparently stabilized, make check runs on the reference standard to establish instrument repeatability. Two consecutive checks must agree within the repeatability limits for the mol % amount present of each component. Either the average of the two consecutive checks, or the latest check agreeing within the repeatability limits of the previous check on each component may be used as the reference standard for all subsequent runs until there is a change in instrument operating conditions. Daily calibrations are recommended.

8.2 *Sample Preparation*—If desired, hydrogen sulfide may be removed by at least two methods (see Annex A2.3 A2.3).

8.2.1 *Preparation and Introduction of Sample*—Samples must be equilibrated in the laboratory at 20 10 to 50°F 30 °C above the source temperature of the field sampling. The higher the temperature the shorter the equilibration time (approximately 2 h 2 h for small sample containers of 300 mL or less). This analysis method assumes field sampling methods have removed entrained liquids. If the hydrocarbon dewpoint of the sample is known to be lower than the lowest temperature to which the sample has been exposed, it is not necessary to heat the sample.

8.2.2 Connections from the sample container to the sample inlet of the instrument should be made with stainless steel or with short pieces of TFE-fluorocarbon. Copper, vinyl, or rubber connections are not acceptable. Heated lines may be necessary for high hydrocarbon content samples.

8.3 *Sample Introduction*—The size of the sample introduced to the chromatographic columns shall not exceed 0.5 mL. (This small sample size is necessary to obtain a linear detector response for methane.) Sufficient accuracy can be obtained for the determination of all but the minor constituents by the use of this sample size. When increased response is required for the determination of components present in concentrations not exceeding 5 mol %, it is permissible to use sample and reference standard volumes not exceeding 5 mL. (Avoid introduction of liquids into the sample system.)

8.3.1 *Purging Method*—Open the outlet valve of the sample cylinder and purge the sample through the inlet system and sample loop or tube. The amount of purging required must be established and verified for each instrument. The sample loop pressure should be near atmospheric. Close the cylinder valve and allow the pressure of the sample in the loop or tube to stabilize. Then immediately inject the contents of the loop or tube into the chromatographic column to avoid infiltration of contaminants.

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[3] A suitable reference standard is available from Scott Specialty Gases Inc., Plumsteadville, PA.

[4] A ten-component reference standard traceable to the National Institute of Standards and Technology (NIST) is available from Institute of Gas Technology (IGT), 3424 S. State St., Chicago, IL 60616.

8.3.2 *Water Displacement*—If the sample was obtained by water displacement, then water displacement may be used to purge and fill the sample loop or tube. (**Warning**—Some components, such as carbon dioxide, hydrogen sulfide, and hexanes and higher hydrocarbons, may be partially or completely removed by the water.)

8.3.3 *Evacuation Method*—Evacuate the charging system, including the sample loop, and the sample line back to the valve on the sample cylinder, to less than 0.1 kPa ~~(1 mm Hg)~~ absolute pressure. Close the valve to the vacuum source and carefully meter the fuel-gas sample from the sample cylinder until the sample loop is filled to the desired pressure, as indicated on the ~~manometer~~ vacuum gauge (see Fig. 1). Inject the sample into the chromatograph.

8.4 *Partition Column Run for Ethane and Heavier Hydrocarbons and Carbon Dioxide*—This run is made using either helium or hydrogen as the carrier gas; if other than a thermal conductivity detector is used, select a suitable carrier gas for that detector. Select a sample size in accordance with 8.1. Enter the sample, and backflush heavy components when appropriate. Obtain a corresponding response on the reference standard.

8.4.1 Methane may also be determined on this column if the column will separate the methane from nitrogen and oxygen (such as with silicone 200/500 as shown in Fig. 5), and the sample size does not exceed 0.5 mL.

8.5 *Adsorption Column Run for Oxygen, Nitrogen, and Methane*—Make this run using helium or hydrogen as the carrier gas. The sample size must not exceed 0.5 mL for the determination of methane. Enter the sample and obtain a response through methane (Note 5). Likewise, obtain a response on the reference standard for nitrogen and methane. Obtain a response on dry air for nitrogen and oxygen, if desired. The air must be either entered at an accurately measured reduced pressure, or from a helium-diluted mixture.

8.5.1 A mixture containing approximately 1 % of oxygen can be prepared by pressurizing a container of dry air at atmospheric pressure to 2 MPa ~~(20 atm)~~ with pure helium. This pressure need not be measured precisely, as the concentration of nitrogen in the mixture thus prepared must be determined by comparison to nitrogen in the reference standard. The percent nitrogen is multiplied by 0.268 to obtain the mole percent of oxygen or by 0.280 to obtain the mole percent total of oxygen and argon. Do not rely on oxygen standards that have been prepared for more than a few days. It is permissible to use a response factor for oxygen that is relative to a stable constituent.

8.6 *Adsorption Column Run for Helium and Hydrogen*—Make this run using either nitrogen or argon as the carrier gas. Enter a ~~1~~ 1 to ~~5-mL~~ 5 mL sample and record the response for helium, followed by hydrogen, which will be just ahead of oxygen (Note 5). Obtain a corresponding response on a reference standard containing suitable concentrations of helium and hydrogen (see Fig. 8).

9. Calculation

9.1 The number of significant digits retained for the quantitative value of each component shall be such that accuracy is neither sacrificed or exaggerated. The expressed numerical value of any component in the sample should not be presumed to be more accurate than the corresponding certified value of that component in the calibration standard.

9.2 *External Standard Method:*

9.2.1 *Pentanes and Lighter Components*—Measure the height of each component peak for pentanes and lighter, convert to the same attenuation for corresponding components in the sample and reference standard, and calculate the concentration of each component in the sample as follows:

$$C = S \times (A/B) \qquad (4)$$

where:
C = component concentration in the sample, mol %;
A = peak height of component in the sample, mm;
B = peak height of component in the standard, mm; and
S = component concentration in the reference standard, mol %.

9.2.1.1 If air has been run at reduced pressure for oxygen or nitrogen calibration, or both, correct the equation for pressure as follows:

$$C = S \times (A/B) \times (P_a/P_b) \qquad (5)$$

where:
P_a = pressure at which air is run and
P_b = true barometric pressure during the run, with both pressures being expressed in the same units.

9.2.1.2 Use composition values of 78.1 % nitrogen and 21.9 % oxygen for dry air, because argon elutes with oxygen on a molecular sieves column under the normal conditions of this test method.

9.2.2 *Hexanes and Heavier Components*—Measure the areas of the hexanes portion and the heptanes and heavier portion of the reverse-flow peak (see Annex A1, Fig. A1.1, and X3.6). Also measure the areas of both pentane peaks on the sample chromatogram, and adjust all measured areas to the same attenuation basis.

9.2.3 Calculate corrected areas of the reverse flow peaks as follows: