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***Draft* Indian Standard**

METHODS OF TEST FOR PETROLEUM AND ITS PRODUCTS [P: 111] ANALYSIS OF LIQUEFIED PETROLEUM GASES (LPG) AND PROPYLENE CONCENTRATES BY GAS CHROMATOGRAPHY

(*First Revision of* IS 1448 Part 111)

(ICS 75.160.20)

Methods of Sampling and Test for Petroleum and related Products of Natural or Synthetic Origin (excluding bitumen) Sectional Committee PCD 01	Last date for receipt of comment 30 October 2023

FOREWORD

(*Formal clause will be added later*)

IS 1448 (Part 111):1983 Method of test for petroleum and its products (P:111) Analysis of liquefied petroleum gases (LPG) and propylene concentrates by Gas Chromatography was adapted from joint publication of ASTM D 2163-77 and IP 264/79 and published in 1983. IP 264/79 has been withdrawn and D 2163 has been revised as ASTM D 2163-23.

The first revision has been brought out to keep pace with the latest technological developments and international practices. In this revision following major changes have been made:

a) Scope of the test method has been extended to determine the concentrations of component in the range of 0.01 to 100 percent by volume.

In the preparation of this standard, considerable assistance has been derived from the following standards:

ASTM D 2163-23	Standard test method for determination of Hydrocarbons in Liquefied Petroleum (LP) Gases and Propane/ Propylene mixtures by Gas Chromatography
ASTM D 6729-20	Standard test method for determination of Determination of Individual components in spark ignition engine fuels by 100 meter capillary high resolution gas chromatography

The composition of the Committee, responsible for the formulation of this standard is given at Annex. *(will be added later*)

In reporting the result of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS 2 : 2022 'Rules for rounding off numerical values (*second revision*)'.

1 SCOPE

1.1 This standard prescribes the method of test for determination of individual hydrocarbons in liquefied petroleum (LP) gases and mixtures of propane and propylene, excluding high-purity propylenein the range of C1 to C5. Component concentrations are determined in the range of 0.01 to 100 percent by volume.

1.2 This test method dose not fully determined hydrocarbons heavier than C5 and non-hydrocarbon materials, and additional tests may be necessary to fully characterize an LPG sample.

2 TERMINOLOGY

2.1 Propylene Concentrate, Concentrate containing more than 50 percent propylene.

3 OUTLINE OF THE METHOD

3.1 Components in a sample of LP gas are physically separated by gas chromatography and compared to corresponding components separated under identical operating conditions from a reference standard mixture of known composition or from use of pure hydrocarbons. The chromatogram of the sample is interpreted by comparing peak areas with those obtained on the reference standard mixture of pure hydrocarbons.

4 SIGNIFICANCE

4.1 The component distribution of liquefied petroleum gases and propylene concentrates is often required as a specification analysis for end-use sale of this material. Its wide use as chemical feedstocks or as fuel, require precise compositional data to ensure uniform quality of the desired reaction products.

4.2 The component distribution data of liquefied petroleum gases and propylene concentrates can be used to calculate physical properties such as specific gravity, vapour pressure, average molecular weight, calorific (heating) value, combustion requirements, and products of combustion. Precision and accuracy of compositional data are extremely important when these data are used to calculate various properties of these petroleum products.

5 APPARATUS

5.1 Gas Chromatograph (GC) — Any gas chromatographic instrument provided with a linear temperature programmable column oven. The temperature control must be capable of obtaining a retention time repeatability of 0.05 min (3 s) throughout the scope of this analysis.

5.2 Detector—A flame ionization detector (FID) having a sensitivity of 0.5 ppm (mole) or less for the compounds listed in Table 1 is strongly recommended.

5.2.1 Other detectors may be used (alone or in series) provided that they have sufficient response, linearity, and sensitivity to measure the components of interest at the concentration levels required.

5.3 Data Acquisition—Any commercial integrator or computerized data acquisition system may be used for display of the chromatographic detector signal and peak area integration. The device should be capable of calibration and reporting of the final response corrected results.

5.4 Sample Introduction—Whether liquid or vapor sampling, the combination of valve injection size and split ratio must be selected such that the required sensitivity is achieved and also that no component concentration in a sample is greater than the detector upper linearity limit.

5.4.1 If capillary columns will be used, then the GC must include a heated splitting type injector that is operated isothermally. Split ratios in the range of 5:1 to 200:1, with a typical value of 100:1, will be used dependent upon the sample injection volume and sensitivity required. If packed columns will be used, then a splitting type injector is not required and a suitable packed inlet port may be used.

5.4.2 Liquid Sampling (recommended)—The GC should be equipped with a liquid sampling valve for introduction of the sample aliquot to the splitting injector. Liquid sampling valves with an internal fixed sample volume between 0.2 to 0.5 µL or a size to provide the minimum detection limits given in the scope have been used satisfactorily. The valve shall be rated for at least 1380 kPa (200 psi) above the vapor pressure of the sample at the valve operating temperature. A shut-off valve shall be provided at the exit of the sampling valve waste port. A 2 to 7 µm packed-screen type filter should be provided at the sample inlet port of the sampling valve to remove possible particulate material from the sample. The valve shall provide for a repeatability of at least 2 percent relative sample volume introduction. The sampling valve shall be located at the GC such that it can be operated at ambient temperature. The use of floating piston sample cylinders is encouraged to minimize or eliminate the volatilization of lighter components into the headspace. Common 80 percent filled LPG storage cylinders should be pressurized with an inert gas such as helium to facilitate liquid transfer and accurate liquid injections. A minimum pressure of 200 psi above sample vapor pressure is recommended. A pressure gauge may be used to make this determination. Before pressurization, verify that the sample cylinder, transfer lines and valves are rated to safely contain the pressurized sample. It is customary to add a check valve between the helium cylinder and the sample cylinder to prevent contamination in the event the sample cylinder is higher in pressure than the pressurizing cylinder.

Table 1 Expected Retention Order and Times

(*Clause* 5.2 ,8.5.2 and 9.1)

Sl No.	**Component**	**Estimated Retention Time (min)**	**Estimated Retention Time (min)**	**FID**	**TCD**
(1)	**(2)**	**(using typical Al_2O_3 PLOT operating conditions) (3)**	**(using typical 100 m Dimethylpolysiloxane column operating conditions) (4)**	**(5)**	**(6)**

(i)	C5 Olefin/$C6^+$ Composite (backflush)	NA[1]	...	x	x
(ii)	Air Composite (O_2, Ar, N_2, Co)	NA[1]	...	x	x
(iii)	Methane	1.9	6.5	x	x
(iv)	Ethane	2.1	6.7	x	x
(v)	Propane	2.7	7.3	x	x
(vi)	Cyclopropane	3.4	...	x	x
(vii)	Propene	3.5	7.2	x	x
(viii)	2-Methyl Propane (Isobutane)	4.0	8.4	x	x
(ix)	Butane	4.2	9.5	x	x
(x)	Propadiene	4.7	...	x	x
(xi)	Ethyne (Acetylene)	5.0	...	x	x
(xii)	Trans-2-Butene	5.5	9.9	x	x
(xiii)	1-Butene	5.6	9.2	x	x
(xiv)	2-Methyl Propene (Isobutene)	5.7	9.1	x	x
(xv)	2,2-Dimethylpropane (Neopentane)	5.9	10.1	x	x
(xvi)	Cis-2-Butene	6.2	10.6	x	x
(xvii)	Cyclopentane	6.7	25.8	x	x
(xviii)	2-Methyl Butane (Isopentane)	6.8	14.0	x	x
(xix)	Pentane	7.2	16.9	x	x
(xx)	1,3-Butadiene	7.5	9.3	x	x
(xxi)	Propyne (Methyl Acetylene)	7.9	...	x	x
(xxii)	>nC5 (Sum C5 Olefins and Heavier)[2]	8.1 until end of run	...	x	x

NOTE

[1] NA denotes Not Applicable.

[2] Sum C5 Olefins and Heavier is greater than nC5 components and it may be speciated and reported individually.

5.4.3 *Vapor Sampling (optional),* A six-port gas sampling valve or a ten-port sampling/column switching valve with 1.6 mm (1⁄16 in.) fittings and a 200 µL fixed sampling loop may be provided. This valve shall be contained in a heated enclosure and operated at a temperature above the boiling point of the highest boiling component in the sample. The use of a 2 to 7 µm frit or packed-screen type filter ahead of the sample introduction port is recommended. The valve shall provide for a repeatability of at least 2 percent relative sample volume introduction.

5.5 Gas Controls—The GC shall be provided with suitable facilities for delivery and control of carrier gas and the detector gases. This will consist of the appropriate tank and down-stream regulators and supply tubing as well as the mass or pressure controls for the precise regulation of the instrument operation.

5.6 Column Series/Reversal Switching Valve—If desired, a multi-port valve mentioned may be used to provide the C5 olefin/C6$^+$ determination for this analysis. The back-flush configuration should be configured according to the manufacturer's recommendations.

6 COLUMNS

Condition all columns used according to the manufacturers' instructions prior to use.

6.1 Analytical Column —The recommended analytical column is a 50 m by 0.53 mm (I.D.) Na_2SO_4 deactivated Al_2O_3 porous layer open tubular (PLOT) column. Relative retention order is dependent upon the deactivation method for the column.

> NOTE — Specifically test the column to ensure that the column does not adsorb propadiene and butadiene. This condition can exist depending upon the degree of column deactivation.

6.2 Routine re-conditioning of the column may be required to maintain column performance. Alternatively, any column(s) that provides the appropriate component separations may be used. Columns (100 m by 0.25 mm (ID) by 0.5 µm film thickness) employed in standard methods.

6.3 Pre-column (optional)—If an initial back flush of the C5 olefins or hexane plus (C6$^+$) components, or both, through the use of the sequence reversal/back flush valve is desired, a second column is required. Any pre-column that provides separation between the components of interest and the composite heavier components may be used. Choices may include lengths of column such as a 10 to 30 m section of 0.53 mm (I.D.) 1 µm film thickness dimethylpolysiloxane or polyethylene glycol capillary column or a 9 to 15 cm section of the same column material as the analytical column or any pre-column that provides the desired retention of C5 olefins, hexanes, and heavier components. This pre-column acts to keep the heavier components away from the analytical column and to back flush the heavier components as a composite peak to the detector for quantization. A pre-column that also has the ability to retain water and oxygenated hydrocarbon compounds is recommended to keep those materials from entering the analytical column.

7 REAGENTS AND MATERIALS

7.1 Carrier Gases—For carrier gases, it is recommended to install commercial active oxygen scrubbers and water dryers, such as molecular sieves, ahead of the instrument to protect the system's chromatographic columns. Follow supplier instructions in the use of such gas purifiers and replace as necessary.

7.2 Hydrogen, 99.995percent minimum purity, < 0.1 ppm H_2O.

> NOTE — Hydrogen is a flammable gas under high pressure.

7.3 Helium, 99.995 percent minimum purity, < 0.1 ppm H_2O.

> NOTE — These materials are flammable and may be harmful or fatal if ingested or inhaled.

7.4 Detector Gases

7.4.1 *Hydrogen,* 99.99 percent minimum purity.

NOTE — Hydrogen is a flammable gas under high pressure.

7.4.2 *Air,* less than 10 ppm each of total hydrocarbons and water.

NOTE — These materials are flammable and may be harmful or fatal if ingested or inhaled.

7.5 Reference Standards

7.5.1 *Purity of Reagents* — Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.5.2 *Reference Gas Mixture* — Individual and mixed component reference materials are commercially available and may be used to establish qualitative and quantitative calibration. The calibration standard mixture should be gravimetrically prepared, supplied with both gravimetric and calculated volumetric concentrations, and certified. Due to the high partial pressure exerted by methane and ethylene, it is recommended that these components be limited to no greater than 0.2 volume percent of the mixture composition. It is strongly recommended that the calibration standards be contained in floating piston cylinders pressurized to at least 1380 kPa (200 psi) above the vapor pressure of the mixture at all times (a constant pressure source is suggested). Common LPG storage cylinders may also be used provided they can be maintained at the required pressure. Liquid mixtures containing levels of each of the analytes listed in Table 1 in a balance of the type of LPG that is being analyzed should be used to calibrate the instrumentation.

NOTE —These materials are flammable and may be harmful or fatal if ingested or inhaled

7.5.2 *Calibration Gas Mixture*—A mixture of known com-position similar in concentration to the samples being analyzed may be used to monitor precision and accuracy. For liquid sampling, it is strongly recommended that the mixture be contained in floating piston or other cylinders pressurized to at least 1380 kPa (200 psi) above the vapor pressure of the mixture at all times (a constant pressure source is suggested).

8 PREPARATION OF APPARATUS

8.1 Set up the instrument in accordance with the manufacturer's instructions or as specified herein.

8.2 Install and condition the column according to manufacturer's instructions. Set the GC instrument to the operating parameters. Allow the instrument to stabilize before proceeding with calibration and sample injections. Typical operating conditions for both PLOT and 100 percent dimethylpolysiloxane columns are provided in Table 2. The conditions provided for the dimethylpolysiloxane column.

8.3 Obtain duplicate chromatograms of the standard or sample, or both. Ensure that none of the peaks obtained have exceeded the upper range limit of the data handling device (at full scale on the data handling device, all peaks are on scale and display symmetrical, Gaussian shapes as opposed to flat peak tops). Peak areas of like components shall agree within 2 percent. Use the same sample size (split ratio) and range for all runs. Example chromatograms are provided in Figs. 1 and 2.

8.4 Liquid Sampling Valve (recommended)—Set valve on and off times to comply with manufacturer's instructions.

8.5 Gas Sampling Valve (optional)—Set valve on and off times to comply with manufacturer's instructions.

8.6 Switching (Back-flush) Valve (optional)—The valve rests in the "off" state, allowing a continuous back flush flow through the pre-column. Before or upon injection of the sample, the valve should be rotated to the "on" position so that the pre-column is placed at the head of the flow path from the sample valve. At a time which must be empirically determined and which is dependent upon the length and type of pre-column used, the valve must be returned to the "off" position, causing the flow to back flush through the pre-column and flush to the detector ahead of components eluting from the analytical column. Determining this switch time may require iterative attempts and interpolation. However, once the time has been determined, it should remain repeatable for all samples of similar composition.

Table 2 Typical Operating Conditions

(*Clause* 8.2)

Sl No. (1)	**Column Type** (2)	**100 percent Dimethylpolysiloxane** (3)	**Al_2O_3 PLOT - Na_2SO_4 deactivated** (4)
(i)	Column Dimensions	100 m by 0.25 mm by 0.5 µm	50 m by 0.53 mm by 15 µm
(ii)	Backflush	No	No
(iii)	Initial Temperature	0 °C	80 °C
(iv)	Initial Hold Time	15 min	1 min
(v)	Program Rate 1	1 °C/min	10 °C/min
(vi)	Final Temperature	50 °C	200 °C
(vii)	Program Rate 2	2 °C/min	...
(viii)	Final Temperature	130 °C	...
(ix)	Program Rate 3	4 °C/min	...
(x)	Final Temperature	270 °C	...
(xi)	Final Hold Time	0 min	12 min
(xii)	Injector Temperature	250 °C	250 °C
(xiii)	Sample Size	0.2 to 0.5 µL	0.2 µL
(xiv)	Split Ratio	175:1 to 275:1	100:1
(xv)	Detector Temperature	300 to 350 °C	250 °C
(xvi)	Fuel Gas Hydrogen Flow	30 to 40 ml/min	40 ml/min
(xvii)	Oxidizing Gas Air Flow	300 to 450 ml/min	400 ml/min
(xviii)	Make-up Gas Type	N_2 or He	He
(xix)	Make-up Gas Flow	30 ml/min	35 ml/min
(xx)	Carrier Gas	He at 2 ml/min (H_2 optional)	He at 6 ml/min
(xxi)	Average Linear Velocity	25 cm/s	45 cm/s
(xxii)	Data Rate	10 to 20 Hz	5 Hz
(xxiii)	Approximate Run Time	140 min	25 min

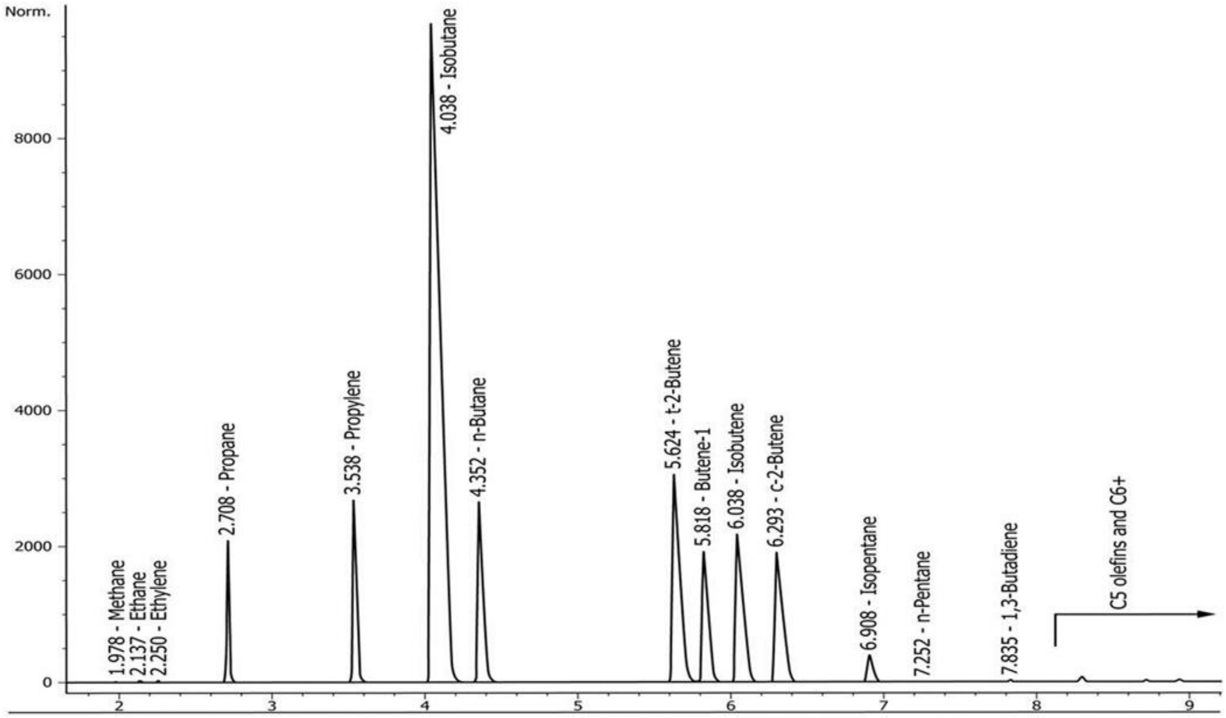

FIG.1 EXAMPLE CHROMATOGRAM USING THE PLOT COLUMN (WITHOUT BACK FLUSH)

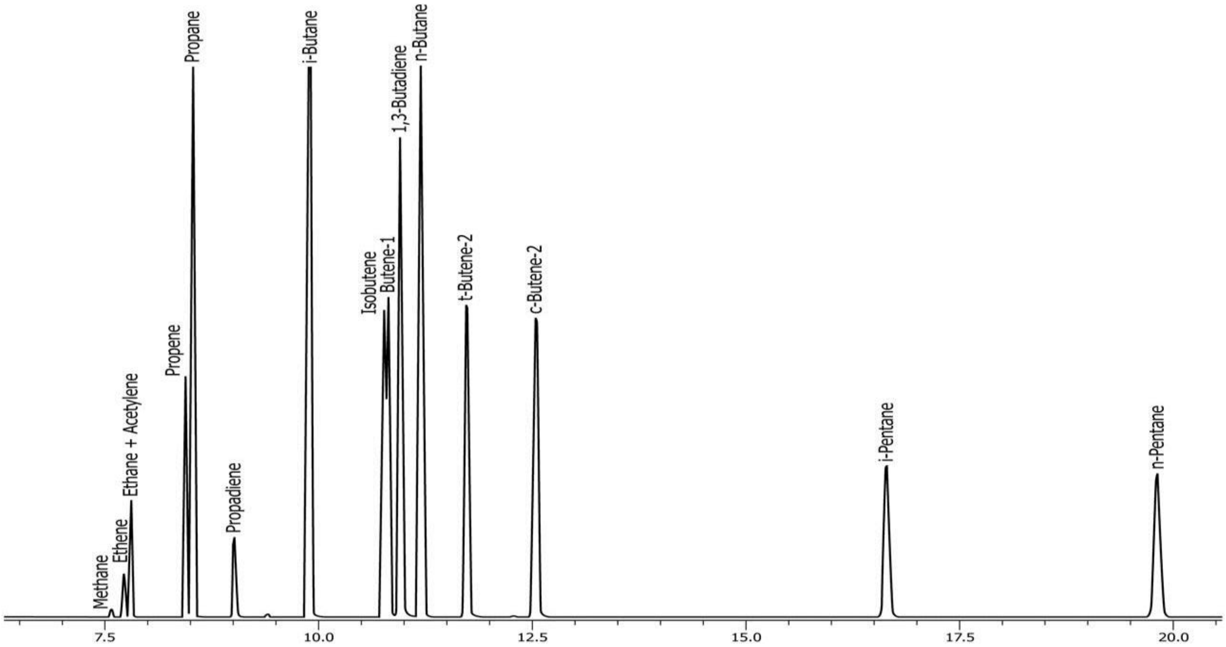

FIG. 2 EXAMPLE CHROMATOGRAM USING THE DIMETHYLPOLYSAILOXANE COLUMN.

9 CALIBRATION AND STANDARDISATION

9.1 Qualitative — Determine the retention times of components by analyzing known reference mixtures in the same manner as the samples (*see* 11). Typical retention times are given in Table 1.

9.2 Quantitative, Hydrocarbons — Use response factors for correction of the detector response of hydrocarbons determined by this test method. Experimental or theoretical response factors may be used.

9.2.1 *Experimental Response Factors* — Determine the experimental response factor of components by analyzing known calibration mixtures under the same conditions of pressure and temperature as the samples (*see* 10). For each component present in the calibration standard, calculate the response factor as given below. (Note that some integrators or computer data systems may use another formula (inverse of the formula given, in some cases) for calculating response factors.) After determining the response factors for each component, analyze a secondary standard as a sample and verify that the concentrations agree with the values for the standard within the precision and bias for this test method as determined by inter laboratory testing.

$$RFi = Ci / Ai$$

where

RFi. = the response factor for component i,

Ci = the known concentration of i, and

Ai = the integrated area of peak i.

9.2.2 *Theoretical Response Factors* – If the samples to be assayed contain only hydrocarbons and a FID is employed for the determination of those components, then theoretical response factors may be applied. The results shall then be normalized to 100 percent.

9.2.2.1 Table 3 provides theoretical mass response factors relative to methane (RRF). Use of these response factors will produce results in mass percent units, which may be converted to other units (liquid volume percent or mole percent) by the user as needed. Alternately, the theoretical response factors may be converted to other units prior to quantification. Individually eluting C5 olefins or hexane-plus components, or both, may be quantified using the same RRF as the $C5^{-}$ / $C6^{+}$ composite peak.

9.2.2.2 It is necessary to compare calculated results to the certified values for a known standard before adopting the calibration. The standard should contain all of the components typically observed in the samples. Results should agree within 5 percent of the certified value. Failure to compare may result from lack of injection split linearity or use of a standard that has not been maintained under pressure

Table 3 Theoretical Mass Relative Response Factors

(*Clauses* 9.2.2.1 *and* 11.2)

Sl No. (1)	Component (2)	RRF_i (3)

(i)	Methane	1.0
(ii)	Ethane	0.937
(iii)	Ethene (Ethylene)	0.874
(iv)	Propane	0.916
(v)	Propylene	0.874
(vi)	Cyclopropane	0.874
(vii)	2-Methylpropane (Isobutane)	0.906
(viii)	Ethyne (Acetylene)	0.813
(ix)	Propadiene	0.834
(x)	Butane	0.906
(xi)	Trans-2-Butene	0.874
(xii)	1-butene	0.874
(xiii)	2-methylpropene (isobutene)	0.874
(xiv)	cis-2-butene	0.874
(xv)	2,2-dimethyl propane (neopentane)	0.895
(xvi)	2-methyl butane (isopentane)	0.899
(xvii)	propyne (methyl acetylene)	0.834
(xviii)	cyclopentane	0.849
(xix)	n-pentane	0.899
(xx)	1,3-butadiene	0.843
(xxi)	C5= /C6$^+$ composite (backflush only)	0.885
(xxii)	> nC5 (C5= and heavier)	0.885

NOTE — All response factors are relative to that of methane according to the following equation:

$$RRF_i = (MW_i / NC_i) \text{ X } (1 / MW_{\text{methane}})$$

where

RRF_i = relative response factor of each component with respect to methane,

MW_i = the molecular weight of the component,

NC_i = the number of carbon atoms in the component molecule, and

MW_{methane} = the molecular weight of methane.

9.3 Quality Monitoring — The primary or secondary standard should be analyzed at least once a week to verify system accuracy, when the test method is in regular use. If the test method is used only occasionally, analyze a primary or secondary standard before each set of analyses.

10 PROCEDURE

10.1 Sampling — Sampling at the sample source and at the chromatograph shall always be done in a manner that ensures that a representative sample is being analyzed. Lack of precision and accuracy in using this test method can most often be attributed to improper sampling procedures.

10.2 Liquid Sample Valve Injection – For propene concentrates, butane samples, or other LPG samples, the sample may be introduced as a liquid by means of a liquid sample valve. It is strongly suggested that the use of a floating piston type sample cylinder be used and that the sample be pressurized to 1380 kPa (200 psi) above the vapor pressure of the sample prior to sampling.

10.2.1 In a hood, prior to connecting the cylinder, invert the cylinder and purge a small aliquot of the sample through the valve on the sample cylinder to remove any moisture or particulate matter which might be present.

10.2.2 Connect the pressurized liquid standard to the sample in port of the liquid sampling valve and close the waste vent shut-off valve. Open the outlet valve on the standard cylinder and open the waste shut-off valve for 10 to 15 s to allow sample to flow through the sampling valve. Flushing the valve several times prior to injection provides some local cooling, and it provides for more repeatable liquid injections. When liquid is flowing through the valve, quickly close the waste shut-off valve, then rotate the liquid sampling valve to inject the sample.

10.2.3 If the back flush option is being used, switch the back flush valve at the pre- determined time elute the $C5^-$ / $C6^+$ composite to the detector.

10.3 Gas Sample Valve Injection (optional) – Vaporize the liquid sample according to the procedures given in 10.3.1 through 10.3.5, or using an on-line heated vaporizing device that is heat traced to the gas sampling valve, as described in 10.3.6. Flash a gas sample loop with 5 to 10 ml or sample, close cylinder valve, and allow the sample pressure to equilibrate to atmospheric pressure (stopped flow) before introducing the sample into the carrier gas stream.

10.3.1 In a hood, prior to connecting the cylinder, invert the cylinder and purge a small aliquot of the sample through the valve on the sample cylinder to remove any moisture or particulate matter which might be present.

10.3.2 Attach a secondary sampling vessel, consisting of two ball valves joined together and having an internal volume of approximately 1 ml to the liquid outlet on the sample vessel.

10.3.3 Evacuate the secondary vessel to approximately 0.13 kPa (1 mm Hg), including the connection to the liquid outlet of the sample vessel. Close all valves.

10.3.4 Slowly open the sample outlet valve of the sample cylinder to fill the connection with liquid. Open the inlet ball valve of the secondary vessel and fill the vessel with liquid. Holding the liquid sample vessel vertically with the secondary vessel on the bottom, open the outlet ball valve and allow a portion of the liquid to purge through the secondary vessel. Shut the outlet ball valve, followed by the inlet ball valve and the sample cylinder outlet valve, in that order. Disconnect the secondary vessel.

10.3.5 Connect the secondary vessel to a container with an approximate volume of 100 ml which is fitted with needle valves or shut-off valves. Open the container valves and evacuate the container and connecting pipe work. Close the container outlet valve and slowly open the secondary vessel outlet valve to allow the liquid sample to vaporize into the evacuated vessel. Close all valves. The 100 ml container will contain a vapor that is representative of the liquid sample and have a gauge pressure of 69 to 138 kPa (10 to 20 psi). This gas may be used to purge the sample loop of the gas sampling valve as described in **11.1**.

10.3.6 Alternatively, an on-line heated vaporizing device, which is heat traced to the gas sampling valve, may be used. The device should consist of a volume of tubing of approximately 10 ml that is encased in a heated block (the block should be a high mass block heated to approximately 60 ^{o}C). The outlet of the tubing should be heat-traced and connected to the gas sampling valve. Connect the liquid sample cylinder to the inlet of the heated tubing. Using the sample cylinder outlet valve, pulse several small aliquots of the liquid sample through the tubing successively. Allow the sample loop of the gas sampling valve to equilibrate to ambient pressure, and then rotate the gas sampling valve to inject the vaporized sample.

11 CALCULATION

11.1 External Standard Calibration Calculation (recommended) – Calculate the concentration of each component as per equation given below. Determine the total amount of hydrocarbons by summing the component concentrations. If the sample is known to contain only hydrocarbons, then the results shall be normalized to 100.00 percent. Occasionally, normalized results will not equal precisely 100.00 percent due to rounding. In this case, small differences are typically added to the largest component. As stated in 1.2, this test method does not fully determine non-hydrocarbon materials and normalization could cause skewed data.

$$SC_i = RF_i \times SA_i$$

where

SC_i = concentration of component i in the sample,

RF_i = response factor for component i, and

SA_i = integrated area for peak i,

11.2 Theoretical Relative Response Calibration Calculation – If a FID is being employed for the determination of those components, then theoretical response factors, as listed in Table 3, may be applied in place of *RFi*. The results shall then be normalized to 100 percent. Use of these response factors will produce results in mass percent units, which may be converted to other units (liquid volume percent or mole percent) by the user as needed. Alternately, the theoretical response factors may be converted to other units prior to quantitation. Quantitation using theoretical response factors does not account for the presence of non-hydrocarbon components. If non hydrocarbon components are present, the results using this calculation method will not be representative or valid.

12 REPORT

12.1 Report the concentration of each component as liquid volume percent (vol. percent) to the nearest 0.01 percent.

12.2 Individually eluted C5 olefins and hexanes-plus components may be speciated and reported separately or summed together into groups.

13 PRECISION AND BIAS

13.1 Repeatability — The difference between two test results obtained by the same operator using 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 values for r in Table 4 only in one case in twenty.

13.2 Reproducibility — The difference between two single and independent results obtained by different operators working in difference laboratories for identical test materials would in the long run, exceed the R values in Table 4 only in one case in twenty.

13.1.3 *Bias* **—** The bias of this test method could not be determined at the time of the inter laboratory study as on reference materials were available.

Table 4 Repeatability and Reproducibility

(*Clause* 13.1 *and* 13.2)

Sl No. (1)	**Component** (2)	**Concentration Range, vol. percent** (3)	**Repeatability (r), vol. percent** (4)	**Reproducibility (R), vol. percent** (5)
(i)	Methane	0.004 - 0.05	0.2 * (X+0.011)	1.44 * (X+0.011)
(ii)	Ethane	0.002 - 2.94	$0.108 * X^{0.65}$	$0.322 * X^{0.65}$
(iii)	Propane	0.96 - 98.22	$0.397E\text{-}01 * X^{0.7}$	$0.17415 * X^{0.7}$
(iv)	Propylene	0.014 - 77.33	$0.661E\text{-}01 * X^{0.66}$	$0.285 * X^{0.66}$
(v)	Isobutane	0.048 - 98.35	$0.427E\text{-}01 * X^{0.4}$	$0.165 * X^{0.4}$
(vi)	n-butane	0.16 - 97.5	$0.546E\text{-}01 * X^{0.45}$	$0.1376 * X^{0.45}$
(vii)	Isopentane	0.005 - 0.543	$0.33E\text{-}01 * X^{0.25}$	$0.53E\text{-}01 * X^{0.25}$
(viii)	n-Pentane	0.012 - 0.829	$0.44E\text{-}01 * X^{0.4}$	$0.93E\text{-}01 * X^{0.4}$
(ix)	C5+	0.009 - 2.58	$0.341 * X^{0.75}$	$1.965 * X^{0.75}$

If LPG standards are reported in liquid volume percent, the following conversion may be helpful to determine the theoretical relative mass response factors. See Table 5.

TABLE 5 Theoretical Mass Response Factor Evaluation for Liquefied Petroleum Gas

Conversion from Volume Percent to Mass Percent

#	Component	Certified Vol. %	×	Relative Density 15.6/15.6 °C (60/60 °F)[A]	=	Certified Vol. % × Relative Density	×	Normalization factor	=	Mass %
1	Ethane	1.800		0.3564		0.64				1.13
2	Propane	13.000		0.5074		6.60		= 100/total		11.62
3	Propylene	10.300		0.5226		5.38		= 1.762		9.49
4	Isobutane	25.800		0.5629		14.52				25.59
5	n-Butane	10.600		0.5841		6.19				10.91
6	trans-2-Butene	7.000		0.6112		4.28				7.54
7	Butene-1	9.930		0.6004		5.96				10.50
8	Isobutylene	14.500		0.6015		8.72				15.37
9	cis-2-Butene	2.880		0.6286		1.81				3.19
10	Isopentane	2.470		0.6246		1.54				2.72
11	n-Pentane	0.024		0.6311		0.02				0.03
12	1,3-butadiene	1.150		0.6272		0.72				1.27
13	Hexane	0.550		0.6641		0.37				0.64
	Total	100.00				56.75				100.0

Calculation of Experimental Mass Response Factors (Relative to n-Butane)

#	Component	Mass %	/	Peak Area	=	Mass RF (MRF)	/	RF n-Butane	=	Experimental Mass RF relative to n-Butane
1	Ethane	1.13		2102		5.38E-04				1.074
2	Propane	11.62		22007		5.28E-04				1.055
3	Propylene	9.49		19931		4.76E-04				0.950
4	Isobutane	25.59		50050		5.11E-04				1.021
5	n-Butane	10.91		21787		5.01E-04		5.01E-04		1.000
6	trans-2-Butene	7.54		15056		5.01E-04				1.000
7	Butene-1	10.50		21042		4.99E-04				0.997
8	Isobutylene	15.37		31409		4.89E-04				0.977
9	cis-2-Butene	3.19		6458		4.94E-04				0.986
10	Isopentane	2.72		5434		5.00E-04				0.999
11	n-Pentane	0.03		55		4.91E-04				0.981
12	1,3-butadiene	1.27		2686		4.73E-04				0.945
13	Hexane	0.64		1306		4.93E-04				0.984

Comparison of Experimental and Theoretical Mass Response Factors

#	Component	Experimental Mass RF relative to n-Butane	–	Theoretical Mass RF relative to n-Butane	=	Delta	;	Verify (+/– 0.05)
1	Ethane	1.074		1.034		0.040		yes
2	Propane	1.055		1.011		0.044		yes
3	Propylene	0.950		0.965		–0.014		yes
4	Isobutane	1.021		1.000		0.021		yes
5	n-Butane	1.000		1.000		0.000		yes
6	trans-2-Butene	1.000		0.965		0.035		yes
7	Butene-1	0.997		0.965		0.032		yes
8	Isobutene	0.977		0.965		0.013		yes
9	cis-2-Butene	0.986		0.965		0.022		yes
10	Isopentane	0.999		0.992		0.007		yes
11	n-Pentane	0.981		0.992		–0.011		yes
12	1,3-butadiene	0.945		0.930		0.015		yes
13	Hexane	0.984		0.977		0.007		yes

[A] See DS4B, *Physical Constants of Hydrocarbon and Non-Hydrocarbon Compounds,* ASTM International, 1991.