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An American National Standard



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Standard Test Method for Analysis of Liquefied Petroleum (LP) Gases and Propene Concentrates by Gas Chromatography¹

This standard is issued under the fixed designation D 2163; 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 determination of the composition of liquefied petroleum (LP) gases. It is applicable to analysis of propane, propene, and butane in all concentration ranges 0.1 % and above.

1.2 *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.*

1.3 The values stated in SI units are to be regarded as standard.

2. Referenced Documents

2.1 ASTM Standards:

D 2421 Practice for Interconversion of Analysis of C₅ and Lighter Hydrocarbons to Gas-Volume, Liquid-Volume, or Weight Basis²

D 2598 Practice for Calculation of Certain Physical Properties of Liquefied Petroleum (LP) Gases from Compositional Analysis²

D 3700 Practice for Containing Hydrocarbon Fluid Samples Using a Floating Piston Cylinder³

3. Terminology

3.1 Definitions:

3.1.1 *propene concentrate*—concentrate containing more than 50 % propene.

4. Summary of Test Method

4.1 Components in a sample of LP gas are physically separated by gas chromatography and compared to correspond-

ing 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 heights or areas with those obtained on the reference standard mixture of pure hydrocarbons.

5. Significance and Use

5.1 The component distribution of liquefied petroleum gases and propene 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.

5.2 The component distribution data of liquefied petroleum gases and propene concentrates can be used to calculate physical properties such as relative density, vapor pressure, and motor octane (see Practice D 2598). Precision and accuracy of compositional data are extremely important when these data are used to calculate various properties of these petroleum products.

6. Gas Chromatograph System

6.1 *Detector*—The detector shall be a thermal conductivity type or its equivalent in sensitivity and stability. The system shall be capable of detecting 0.1 % concentration of any component of interest. For calculation techniques utilizing a recorder, the signal for the concentration shall be at least 5 chart divisions above the noise level on a 0 to 100 scale chart. Noise level must be restricted to a maximum of 1 chart division. When electronic integration is employed the signal for 0.1 % concentration must be at least twice the noise level.

6.2 *Recorder*—A strip-chart recorder and integrator with a full-scale range of 10 mV or less shall be required. A maximum full-scale balance time of 2 s and a minimum chart speed of 1/2 in. (12.7 mm)/min shall be required.

6.3 *Attenuator*—A multistep attenuator for the detector output signal shall be necessary to maintain maximum peaks within the recorder chart range. The attenuator system must be accurate to 0.5 % in any position.

¹ This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.D0.03 on C4 Test Methods Liquefied Petroleum Gas.

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² Annual Book of ASTM Standards, Vol 05.01.

³ Annual Book of ASTM Standards, Vol 05.02.

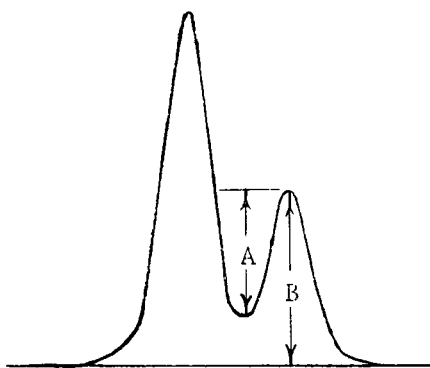


FIG. 1 Illustration of A/B Ratio

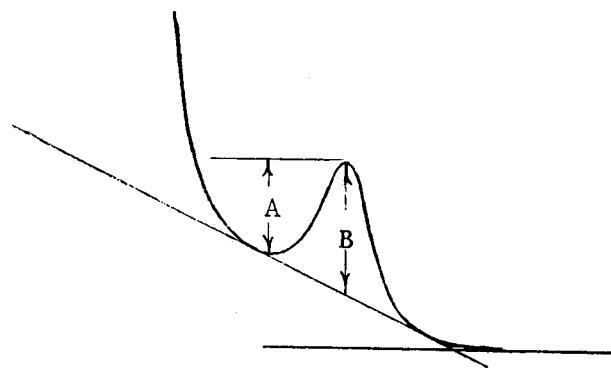


FIG. 2 Illustration of A/B Ratio for Small-Component Peak

6.4 *Sample Inlet System*—Provision shall be made to introduce up to 0.50 mL of the sample. The sample volume must be repeatable such that successive runs agree within 1 mm or 1 % (whichever is larger) on each component peak height.

6.5 *Temperature Control*—The analyzer columns shall be maintained at a temperature constant to 0.3°C during the course of the sample and corresponding reference standard runs.

6.6 *Carrier Gas*—The instrument shall be equipped with suitable facilities to provide a flow of carrier gas through the analyzer column at a flow rate that is constant to 1.0 % throughout the analysis.

6.7 *Columns*—Any column may be used provided all component peaks for compounds present in concentration of more than 5 % are resolved so that the ratio A/B shall not be less than 0.8, Fig. 1

where:

- A = depth of the valley on either side of peak B, and
- B = height above the baseline of the smaller of any two adjacent peaks (see Fig. 1).

For compounds present in concentrations of 5 % or less, the ratio of A/B shall not be less than 0.4. In case the small-component peak is adjacent to a large one, it may be necessary to construct the baseline of the small peak tangent to the curve as shown in Fig. 2.

7. Calibration Standard

7.1 Pure components or calibration standard mixtures⁴ may be used for calibration. If pure components are used, identical volumes of each component are injected into the chromatograph and relative area response factors are determined. These factors are valid for a given instrument and operating conditions and should be redetermined periodically. If pure components are used for calibration, the calculation should be made in mole percent and converted to liquid volume percent (Note 1). Factors repeatable to within 1 % are required. The concentration of each component in the calibration standard mixtures shall be known to within 0.1 %. The concentration of the major component in the calibration standard mixture shall not differ from that of the like component in the sample to be analyzed

by more than 10 % if the peak height method of calculation is used. On propene concentrates, the calibration standard mixtures shall not differ from that of like component in the sample to be analyzed by more than 5 %. Typical composition ranges of suitable calibration standard mixtures are given in Table 1.

NOTE 1—Test Method D 2421 may be used whenever a need exists for such translations.

8. Procedure

8.1 *Apparatus Preparation*—Mount the column suitable for the analysis desired (see Appendix X1) in the chromatograph and adjust the conditions to optimum for the column selected (Table 2). Allow sufficient time for the instrument to reach equilibrium as indicated by a stable base line.

8.1.1 The test method allows the user a wide latitude in choice of instrumentation to make the analysis, and most commercial instrumentation easily meets the requirements defined in the test method. However, only by strict adherence to the calibration procedures outlined in the method can reproducibility between instruments expect to be achieved.

8.1.2 Proper maintenance of instrumentation is critical to continued satisfactory performance of this analysis. Clean sample containers, clean sample inlet systems and clean detectors are mandatory to achieve the precision and accuracy capabilities of this method.

NOTE 2—**Warning:** Samples and reference mixtures are extremely flammable. Keep away from heat, sparks, and flames. Use with adequate ventilation. Cylinders must be supported at all times. Hydrocarbon vapors that may be vented must be controlled to assure compliance with applicable safety and environmental regulations. Vapor reduces oxygen available for breathing. Liquid causes cold burns.

8.2 *Preparation and Introduction of Sample*—Attach the cylinder containing the gas mixture to the sampling valve of the chromatograph so that a liquid phase sample is withdrawn. Adjust the flow rate from the sample cylinder so that complete vaporization of the liquid occurs at the cylinder valve. (An alternative technique is to trap a sample of only liquid phase in a short section of tubing, and then permit the entire sample to vaporize into an evacuated container). Adjust the ratio of the two volumes so that a gage pressure of 69 to 138 kPa (10 to 20 psi) is obtained in the final container. Then use this sample for the analysis. Flush the sample loop for 1 to 2 min at a flow rate of 5 to 10 mL/min before introducing the sample into the carrier gas stream.

⁴ Suitable reference standard mixtures of pure hydrocarbons are available from Scott Specialty Gases, Inc., Plumsteadville, PA.

TABLE 1 Reference Standard Mixtures, Liquid Volume Percent^A

Component	Propane with No Unsaturation	Propane with Low Propene	Propane with High Propene	Butane	Propane-Butane Mixtures	Propene with Low Propene	Propene with High Propene
Ethane	4	4	3	...	2	0.2	0.1
Propane	93	87	57	3	45	4.8	22.6
Propene	...	4	35	...	6	94.9	76.6
n-Butane	1	1	1	64	30	0.1	0.5
Isobutane	1	3	3	25	15
Butene	6	0.2
Isopentane	1	1	1	2	2

^AThe composition values recorded in this table are offered as a guide to laboratories preparing their own mixtures from pure hydrocarbons or to commercial suppliers of standards. In either case, an accurate composition of the standards must be known to analyst.

TABLE 2 Instrument Conditions

	Column Length, m	Column Diameter, mm, OD	Substrate, Mass, %	Temperature, °C	Flow Rate, mL/min	Carrier G
Silicon 200/500	4	6.4	27	90	60 to 70	helium
Benzyl cyanide—silver nitrate	9	6.4	36	40	45 to 55	helium
Hexamethylphosphoramide	9	6.4	17	30	60 to 70	helium
Dimethylsulfolane plus benzyl cyanide and silver nitrate	7	6.4	36	35	60 to 70	helium
Dimethylsulfolane	15	6.4	30	25	30	helium
Hexamethyl phosphoramide	6	3.2	25	28	12	helium
Di-n-butyl maleate	4	6.4	25	28	60	helium
Tricresyl phosphate plus silicone, 550	9	6.4	30	35	70	helium
Methoxy ethoxy ethyl ether	9	6.4	30	30	60	helium

8.2.1 On propene concentrates, the sample may be introduced as a liquid by means of a liquid sample valve or by vaporization of the liquid as above. On propene concentrates having a propene content of less than 80 %, only the alternative technique of trapping a sample of liquid and vaporizing the entire sample into an evacuated container shall be used.

8.2.2 Sampling at the sample source and at the chromatograph must always be done in a manner that ensures that a representative sample is being analyzed. Lack of precision and accuracy in using this method can most often be attributed to improper sampling procedures. (See Test Method D 3700.)

8.3 *Preparation of the Chromatogram*—Obtain duplicate chromatograms of the sample. Adjust the attenuator at each peak for maximum peak height within the recorder chart range. Peak heights of like components shall agree within 1 mm or 1 % (whichever is larger). If a reference standard mixture is used for calibration, obtain duplicate chromatograms of the proper reference standard in a similar manner. Use the same sample size for all runs.

9. Calculation

9.1 *Peak Height Method*—Measure the peak height of each component and adjust this value to the attenuation of the same component in the reference standard mixture. Calculate the percentage by mole or liquid volume of each component as follows:

$$\text{Concentration, liquid volume or mol percent} = (P_s/P_o) \times S \quad (1)$$

where:

P_s = peak height of component in the sample,

P_o = peak height of component in reference standard mixture, and

S = percentage of mole or liquid volume of component in reference standard mixture.

9.2 *Area Method*—Measure the area of each component by multiplying the height of the peak by the width at half height. The width should be measured with the aid of a magnifying glass (Note 3). Adjust the area to the attenuation of the same component in the reference standard mixture.

NOTE 3—The use of planimeters or integrators is permissible provided their repeatability has been established and the resulting repeatability does not adversely affect the repeatability and reproducibility limits of the method given in Section 10.

9.2.1 Calculate the percentage by mole or liquid volume of each component as follows:

$$\text{Concentration, liquid volume or mol percent} = (A_s/A_o) \times S \quad (2)$$

where:

A_s = area of component in sample,

A_o = area of component in reference standard mixture, and

S = percentage by mole or liquid volume of component in reference standard mixture.

9.2.2 If pure components are used for calibration, calculate the composition as follows:

$$\text{Concentration, mol percent} = A_s/A_p \quad (3)$$

where:

A_s = area of component in sample, mm², and

A_p = area sensitivity of component, mm² per percent.