Designation: D7756 – 19

Standard Test Method for
Residues in Liquefied Petroleum (LP) Gases by Gas Chromatography with Liquid, On-Column Injection[1]

1. Scope*

1.1 This test method covers the determination, by gas chromatography, of soluble hydrocarbon materials, sometimes called "oily residue," which can be present in liquefied petroleum (LP) gases and which are substantially less volatile than the LPG product.

1.2 This test method quantifies, in the range of 10 mg/kg to 600 mg/kg (ppm mass), the residue with a boiling point between 174 °C and 522 °C (C_{10} to C_{40}) in LPG. Higher boiling materials, or materials that adhere permanently to the chromatographic column, will not be detected.

1.3 Appendix X3, Appendix X4, and Appendix X6 describe additional applications which could be performed based on the hardware and procedures described in this test method. Appendix X3 describes a test procedure for expanding the analysis range to benzene, Appendix X4 describes a test procedure for the analysis of diisopropanolamine, and Appendix X6 describes a test procedure for the analysis of heavy residues or contaminants from C_{40} to about C_{60} in LPG.

1.4 The values stated in SI units are to be regarded as standard. The values given in parentheses after SI units are provided for information only and are not considered standard.

1.5 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1265 Practice for Sampling Liquefied Petroleum (LP) Gases, Manual Method
D1835 Specification for Liquefied Petroleum (LP) Gases
D2158 Test Method for Residues in Liquefied Petroleum (LP) Gases
D2163 Test Method for Determination of Hydrocarbons in Liquefied Petroleum (LP) Gases and Propane/Propene Mixtures by Gas Chromatography
D2421 Practice for Interconversion of Analysis of C_5 and Lighter Hydrocarbons to Gas-Volume, Liquid-Volume, or Mass Basis
D2598 Practice for Calculation of Certain Physical Properties of Liquefied Petroleum (LP) Gases from Compositional Analysis
D3700 Practice for Obtaining LPG Samples Using a Floating Piston Cylinder
D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance
D6300 Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products and Lubricants
D6667 Test Method for Determination of Total Volatile Sulfur in Gaseous Hydrocarbons and Liquefied Petroleum Gases by Ultraviolet Fluorescence
E355 Practice for Gas Chromatography Terms and Relationships
E594 Practice for Testing Flame Ionization Detectors Used in Gas or Supercritical Fluid Chromatography

3. Terminology

3.1 *Definitions of Terms Concerning Chromatography*—This test method makes reference to many common gas chromatographic procedures, terms, and relationships. Detailed definitions of these can be found in Practices E355 and E594.

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[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.H0 on Liquefied Petroleum Gas.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

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

3.2 *Definitions of Terms Concerning Liquefied Petroleum Gases*—This test method makes reference to the definitions of liquefied petroleum gases as described in Specification D1835.

3.3 *Definitions of Terms Specific to This Standard:*

3.3.1 *high pressure liquefied gas injector, n*—sample introduction device which injects liquefied gas samples under pressure and at room temperature directly onto the chromatographic column thereby maintaining the sample in liquid phase during the injection process.

3.3.2 *pressure station, n*—device that supplies high pressure nitrogen to a suitable sample cylinder and therefore maintains sample in the liquid phase during the injection procedure.

4. Summary of Test Method

4.1 A sample cylinder of LPG is pressurized to 2500 kPa (363 psi) using nitrogen or helium.

4.2 The injection system is flushed with LPG in liquid phase at room temperature.

4.3 After flushing, the injection device is routed to the GC injector port and LPG (25 milliseconds activation time equivalent to 30 µL) is introduced via a high pressure valve and needle which is inserted into a large volume cold on-column injector.

4.4 The gas chromatograph is equipped with a solvent vent which routes most of the LPG light components out of the analytical system and leaves behind the components of interest.

4.5 The oily residue to be determined is retained on a pre-column.

4.6 After venting the LPG, the flow from the pre-column is switched to the analytical column and a temperature program is started.

4.7 Oily residue contaminants are separated and identified based on differences in boiling point temperature.

4.8 Total residue is quantified using area summation of components corresponding to the expected range of C_{10} to C_{40} (174 °C to 522 °C).

5. Significance and Use

5.1 Control over the residue content as specified in Specification D1835 is of considerable importance in end-use applications of LPG. Oily residue in LPG is contamination which can occur during production, transportation, or storage.

5.2 This test method is quicker and much more sensitive than manual methods, such as Test Method D2158, which is based on evaporation of large sample volumes followed by visual or gravimetric estimation of residue content.

5.3 This test method provides enhanced sensitivity in measurements of heavier (oily) residues, with a quantification limit of 10 mg/kg total residue.

5.4 This test method gives both quantitative results and information about contaminant composition such as boiling point range and fingerprint, which can be very useful in tracing the source of a particular contaminant.

6. Apparatus

6.1 *Gas Chromatograph (GC)*—Gas chromatographic instrument equipped with a large volume cold on-column injector (LVOCI), a linear temperature programmable column oven, and a flame ionization detector (FID). The temperature control shall be capable of obtaining a retention time repeatability of 0.05 min (3 s) throughout the scope of this analysis.

6.2 *Data Acquisition*—Any commercial integrator or computerized data acquisition system may be used for display of the chromatographic detector signal and peak area integration.

6.3 *Solvent Vent*—A controlled vent for venting the major part of the matrix.

TABLE 1 Typical Operating Conditions

Oven program	35 °C for 3 min 35 °C to 340 °C at 25 °C/min 340 °C for 10 min
Inlet program	Type: cool on-column Temperature: 65 °C for 3 min 55 °C to 340 °C at 25 °C/min 340 °C for 9 min
Detector settings	Air flow: 400 mL/min Hydrogen flow: 40 mL/min Make up gas flow: 45 mL/min Temperature: 350 °C Data rate: 20 Hz
Column	Retention gap: Sulfinert[A] stainless steel capillary with inner diameter 0.53 mm and length of 5 m Retaining pre-column: 3 m 100 % Dimethylpolysiloxane: 0.53 mm, 2.65 µm Analytical column: 100 % Dimethylpolysiloxane 30 m, 0.32 mm, 0.25 µm
Pressure station	Sample flow: 2 mL/min Nitrogen pressure: 2500 kPa Nitrogen purge pressure: 500 kPa
Liquefied Gas Injector	Injection: 25 ms

[A] Sulfinert is a trademark of SilcoTek, 112 Benner Circle, Bellefonte, PA 16823, www.SilcoTek.com.

6.4 *Retention Gap*—Uncoated stainless steel capillary. Successfully used columns and conditions are given in Table 1.

6.5 *Retaining Pre-Column*—A column with a polydimethylsiloxane stationary phase. Successfully used columns and conditions are given in Table 1.

6.6 *Analytical Column*—A column with a polydimethylsiloxane stationary phase. Successfully used columns and conditions are given in Table 1.

6.7 *Column Coupler—Coupling Device*—Suitable for leak-free coupling of the retention gap to the retaining pre-column. (See Fig. 1 for a schematic overview of the couplings inside the GC oven and the couplings to the solvent vent valve.)

6.8 *Column Splitter*—Splitter suitable for leak-free coupling of the retaining pre-column to one side of the analytical column and the deactivated capillary on the other side. (See Fig. 1 for a schematic overview of the couplings inside the GC oven and the couplings to the solvent vent valve.)

6.9 *High Pressure Liquefied Gas Injector*—A high pressure valve directly connected to a needle which is inserted in the injection port of the GC, after which the valve is triggered in order to introduce a representative aliquot into the GC system without sample discrimination. (See Fig. 2.)

6.10 *Pressure Station*—This shall ensure a sample in liquid phase at a constant pressure. See Fig. 3 for a typical configuration.

6.11 *Typical Column Overview*—See Fig. 1.

6.12 *Typical Operating Conditions*—See Table 1.

7. Reagents and Materials

7.1 *Mineral Oil in LPG Calibration Mixture*—Certified calibration mixture with mineral oil in LPG. The concentration of the mineral oil shall be close to the expected concentration of the contamination in the LPG sample.

7.2 *Mineral Oil in Pentane Calibration Mixture*—Prepare a calibration standard of mineral oil in pentane. Record the weighed value to the nearest milligram of mineral oil and calculate the concentration in mg/kg. The concentration of the mineral oil shall be close to the expected concentration of the contamination in the LPG sample.

7.2.1 Standards that are prepared in pentane, normally liquid at room temperature, should be stored in suitable containers under refrigeration and transferred to sample cylinders prior to use. Alternatively, they may be stored in airtight cylinders.

7.3 *Mineral Oil or Local Hydrocarbon Fraction*—Boiling point range approximately C_{10} to C_{40}. Alternatively, a well-characterized local hydrocarbon fraction, within the range C_{10} to C_{40}, can be used to provide quantitative and qualitative comparison to the contaminant in the sample. Care should be taken to ensure no significant fraction falls outside the C_{10} to C_{40} range.

7.4 *Validation Standard, Mineral Oil in Pentane*—Prepare a validation standard of mineral oil in pentane. Record the exact weighed value to the nearest milligram of mineral oil and calculate the concentration in mg/kg. The concentration of the mineral oil shall be close to the expected concentration of the contamination in the LPG sample.

7.5 *N-alkane Retention Time Standard*—Mixture containing at least C_{10} and C_{40} in a concentration of (nominally) 5 mg/L each, dissolved in pentane or heptane.

7.6 *Solvent*—GC grade pentane.

8. Hazards

8.1 There is a significant fire hazard from LPG, and since the boiling point of LPG can be as low as –41 °C, there is a risk of freezing "burns." Take appropriate safety precautions to prevent ignition or fire, and wear suitable protective equipment to protect against skin contact with LPG.

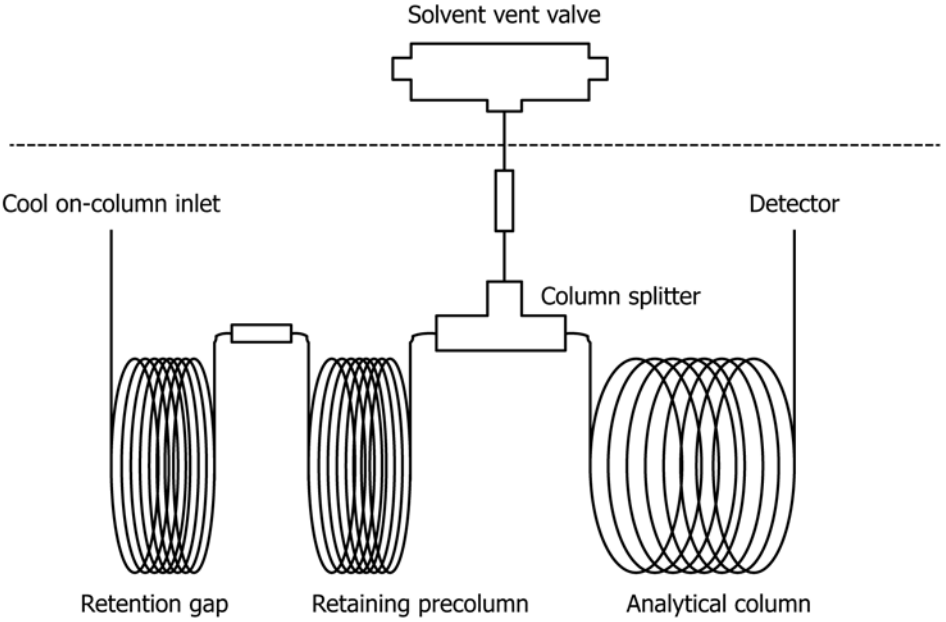

FIG. 1 Overview of the Couplings Inside the GC Oven and the Couplings to the Solvent Vent Valve