Designation: D7756 – 13

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

This standard is issued under the fixed designation D7756; 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, 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 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 and Appendix X4 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, and Appendix X4 describes a test procedure for the analysis of diisopropanolamine in LPG.

1.4 *Units*—The values stated in SI units are to be regarded as standard. The values given in parentheses are for information only.

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

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.

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.

[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**

3.3.2 *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 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.

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.

TABLE 1 Typical Operating Conditions

Oven program	35°C for 3 min 35 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 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.