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.

(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}-C_{40}. Alternatively, a well characterized local hydrocarbon fraction, within the range C_{10}-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}-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.

8.2 An appropriate laboratory ventilation system shall be used.

8.3 An appropriate waste line shall be installed. The pressure station and injector shall be connected to this line. The waste line should vent outside the building.

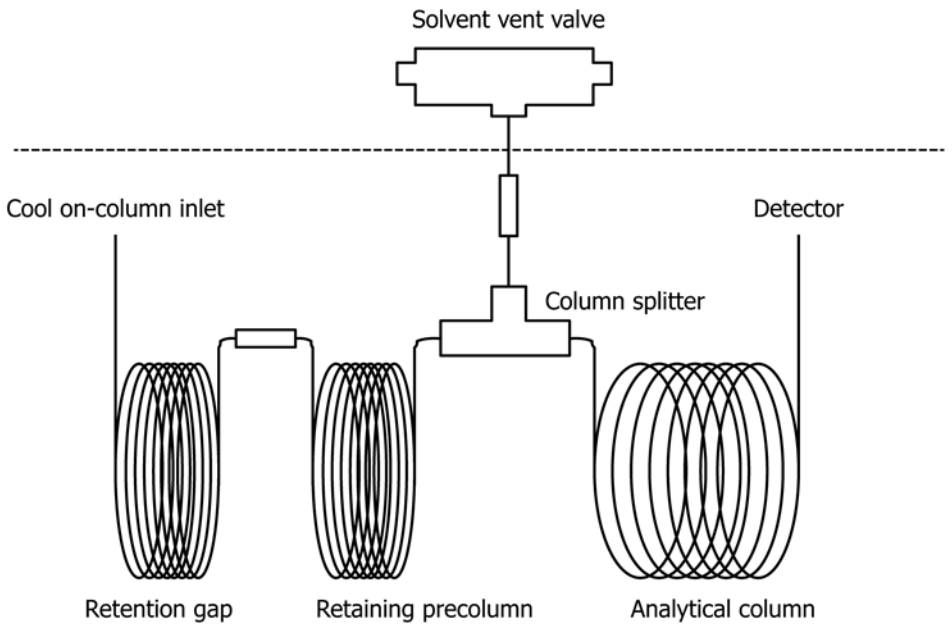


FIG. 1 Overview of the Couplings Inside the GC Oven and the Couplings to the Solvent Vent Valve

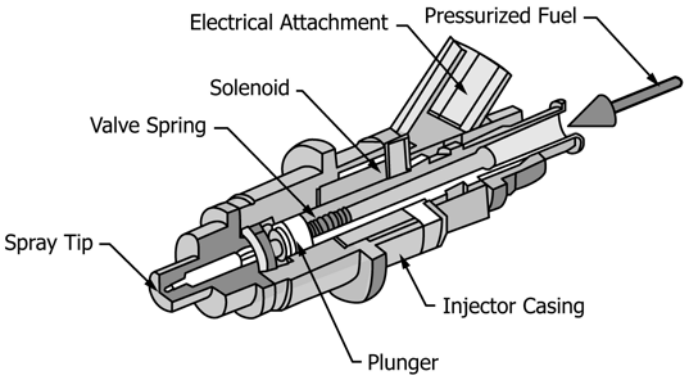
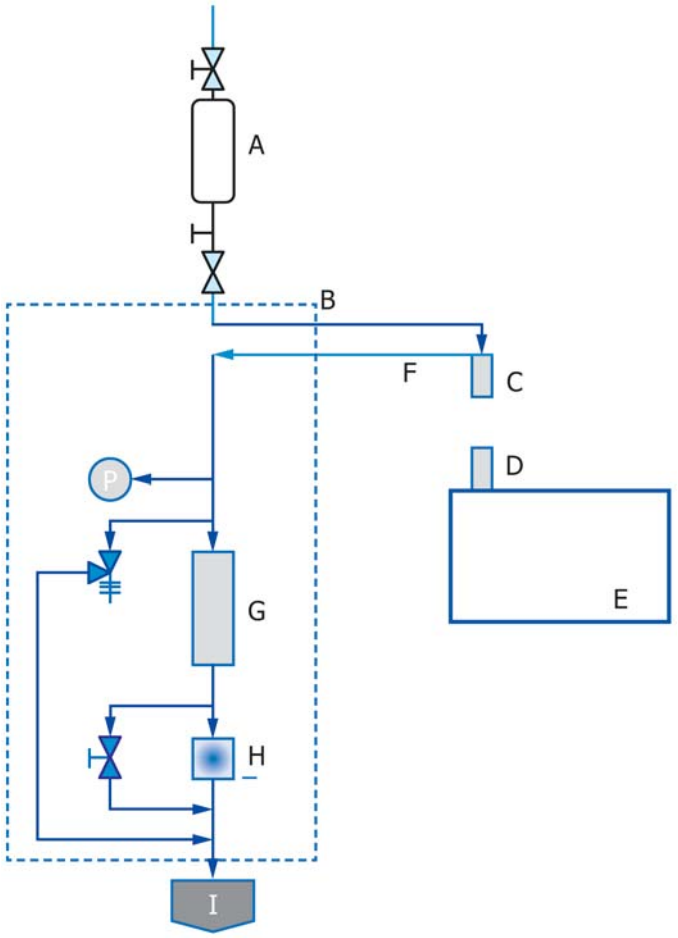


FIG. 2 High Pressure Valve



A	Sample cylinder
B	Sample line in
C	Injection device
D	Cool on column inlet
E	Gas chromatograph
F	Sample line out
G	Rotometer
H	Vaporizer
I	Waste system
P	Pressure gauge

FIG. 3 Typical Configuration of a Pressure Station

8.4 Pressure station, cylinder, injector, and controller shall be grounded appropriately.

9. Preparation of Apparatus

9.1 *Gas Chromatograph*—Install and verify performance in accordance with the manufacturer's instructions. Typical operating conditions are shown in Table 1.

9.2 *Pressure Station*—Install in accordance with the manufacturer's instructions. Purge sample and check carefully for leaks.

9.3 *High Pressure Liquefied Gas Injector*—Install in accordance with the manufacturer's instructions.

9.4 *Column Configuration*—Install the columns as shown in Fig. 1. Use low dead volume connections, and check for leaks.

10. Calibration

10.1 Perform a one point calibration at the startup of the instrument, when the result of the validation sample falls outside the acceptable SQC limits in accordance with Section 14 or after changes in the application hardware or gas supply, or both.

10.2 To verify system linearity over the range of expected sample residues, a linearity check should be performed. More information can be found in Appendix X5.

10.3 Run a blank run, without sample injection. Cycle the GC several times until the baseline is stable. A baseline is stable when the start and end signal (in pA) of two consecutive blank runs are within 5%. An unstable baseline can be caused by a leak, detector gases, or by high boiling point components or materials that have not yet eluted from the column. The signal height (in pA) at the end of an analysis of a calibration, validation, or sample shall be equal or higher than the blank baseline. A signal higher than 5% could indicate a poorly conditioned column or the elution of sample components with a boiling point higher than 522°C. Refer to the datasheet of the column for instructions on conditioning the column.

10.4 Analyze the n-alkane retention time standard (7.6), and establish the retention time for C_{10} and C_{40}. There should be baseline separation between the solvent and the first normal alkane peak (C_{10}). If the separation is not sufficient, adjust the temperature program, re-establish the baseline, and then reanalyze the retention time standard. An example is shown in Fig. 4.

10.5 Analyze the calibration mixture. The calibration mixture is either in LPG or in pentane (7.1 and 7.2).

10.6 Integrate the oily residue by summing the area from C_{10} through C_{40}.

10.7 Determine the response factor by dividing the known concentration by the total area, and use this for the calculation of unknown samples under the assumption that all sample components have the same response factor.

10.8 Analyze the validation sample using the liquefied gas injector. Analyze the validation sample once per day of use before the samples. Repeat the analysis when the result of the validation sample falls outside the acceptable SQC limits in accordance with Section 14.

11. Procedure

11.1 Collect a representative sample according to Practice D1265 or D3700.

11.2 Connect the sample cylinder to the pressure station and pressurize to approximately 2500 ± 200 kPa (363 ± 29 psi). It

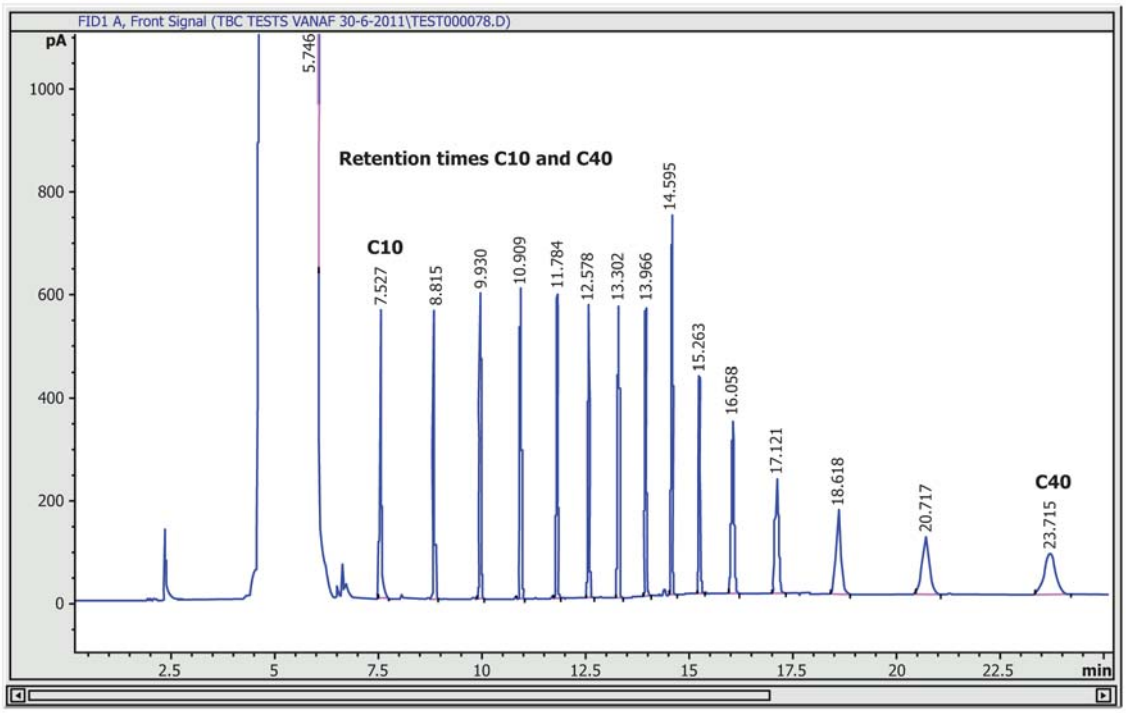


FIG. 4 Chromatogram of C_{10} through C_{40}

is important to maintain and reproduce this pressure as closely as possible to ensure sample size injection repeatability.

11.3 Open the cylinder at both sides and flush the sample for approximately 3 min with a flow rate of about 5 mL/min.

11.4 Inject sample (trigger pulse 25 ms at 2500 kPa, equivalent to approximately 30 µL).

11.5 Analyze each sample in duplicate. If the difference between the results of the two analyses is > 5 %, perform an extra analysis and average the two closest results.

11.6 Close the sample cylinder after injection and repeat 11.3 for the next injection. When all analyses are finished, close the sample cylinder and release the system pressure. Remove the sample cylinder.

11.7 Integrate the oily residue by summing the area from C_{10} through C_{40}.

11.8 To inject the validation sample, fill a sample cylinder with the standard and use the same injection procedure as for LPG samples.

12. Calculation or Interpretation of Results

12.1 Verify whether the separation between the matrix peak and C_{10} is sufficient for correct integration of the residue. An example is shown in Fig. 5.

12.2 Start the integration at the retention time of C_{10} or at the point where the slope of the solvent peak reaches a minimum (the valley). This point should not be higher than two times the value of the baseline in pA.

12.3 Calculation is based on a response factor and correction for the difference in density between the sample and the calibration mixture. Correction for the difference in density between the sample and the calibration standard is performed as in Test Method D6667 (see Appendix X1).

12.4 Calculation of the response factor, using the calibration mixture:

$$Rf = Scg/Ac \quad (1)$$

where:

Rf = Response factor,
Scg = Mineral oil content in the LPG calibration standard or in the standard in pentane in mg/kg weight, and
Ac = Summed area of the peaks in the range of C_{10}-C_{40} in the LPG calibration standard or in the pentane standard.

12.5 Calculation of the sample residue concentration; when the calibration mixture and the sample have the same density:

$$S = Area*Rf \quad (2)$$

where:

S = Mineral oil content in the sample in mg/kg,
Area = Summed area of the peaks in the range of C_{10} -C_{40} in the sample, and
Rf = Response factor = mineral oil content in the calibration standard in mg/kg divided by the area.

12.6 Calculation of the sample residue concentration with correction for the density; to be used when the density of the calibration mixture and the sample differ.

$$S = Area*Rf*Dc/D \quad (3)$$

where:

S = oily residue content in the sample in mg/kg,
Area = Summed area of the peaks in the range of C_{10}-C_{40} in the sample,
Rf = Response factor = mineral oil content in the calibration standard in mg/kg divided by the area,
D = Density of the sample solution at measurement temperature, g/mL, and

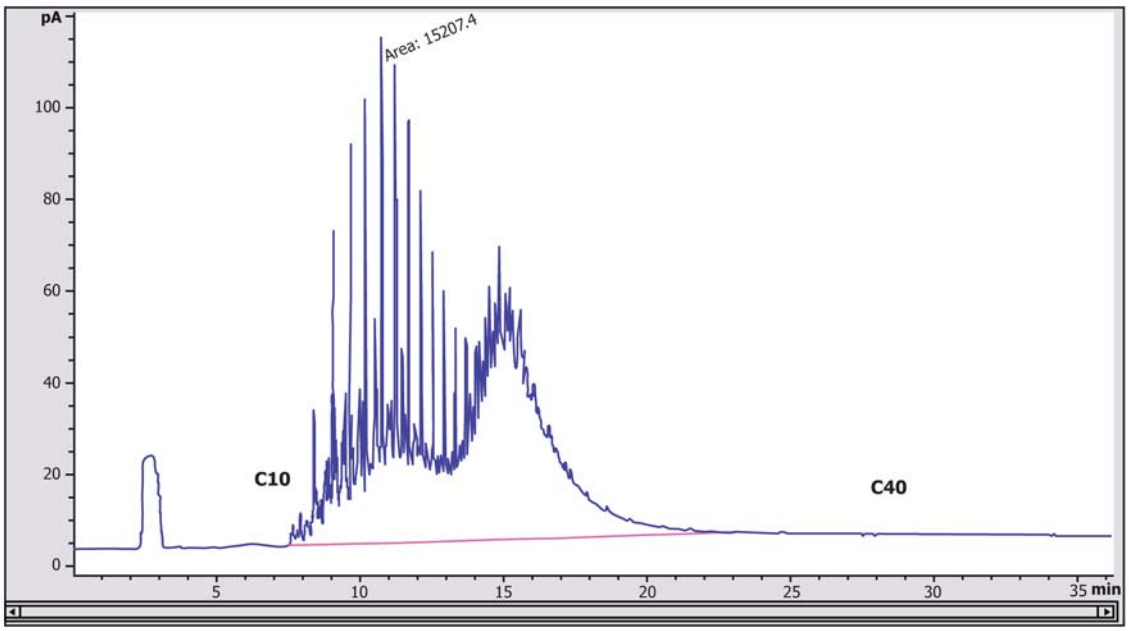


FIG. 5 Chromatogram of 50 mg/kg Mineral Oil

Dc = Density of calibration standard at measurement temperature, g/mL.

13. Report

13.1 Report the results to the nearest mg/kg oily residue in LPG, referencing this test method.

14. Quality Control

14.1 Confirm the performance of the instrument or the test procedure by analyzing validation samples (see 7.4) after each calibration and at least each day of use thereafter.

14.2 When QC/quality assurance (QA) protocols are already established in the testing facility, these may be used when they confirm the reliability of the test result.

14.3 When there is no QC/QA protocol established in the testing facility, Appendix X2 can be used as the QC/QA system.

15. Precision and Bias

15.1 *Precision*—The following precision was determined in accordance with Practice D6300 and Section A21.2.3 of the *Form and Style Manual for ASTM Standards*. This precision is based on an Interlaboratory Study in 2012 which involved the analysis of five samples using 7 independent instrument installations and operators.[3] The range of results applicable to r and R equations listed below is from 6.1 to 640.8 mg/kg. Table 2 provides an example of r and R values at various residue concentrations.

15.1.1 *Repeatability*—The difference between repetitive results obtained by the same operator in a given laboratory applying the same test method with the same apparatus under constant operating conditions on identical test material within short intervals of time would in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in 20.

Repeatability (r) = 0.1453 * $(X)^{0.8292}$ mg/kg

Repeatability standard deviation = Repeatability Limit/2.77

15.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators applying the same test method in different laboratories using different apparatus on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in 20.

Reproducibility (R) = 0.7929 * $(X)^{0.8292}$ mg/kg

Reproducibility standard deviation = Repeatability Limit/2.77

TABLE 2 Example of r and R Values at Various Oil Residue Concentrations

Oil Residue Level (mg/kg)	R	r
10.0	5.35	0.98
50.0	20.32	3.72
100.0	36.11	6.62
250.0	77.20	14.15
600.0	159.54	29.24

15.2 *Bias*—No information can be presented on the bias of this procedure because the results are defined only in terms of this test method.

16. Keywords

16.1 contaminants; gas chromatography; liquefied petroleum gases; LPG; mineral oil; oily residue; residue

[3] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1762. Contact ASTM Customer Service at service@astm.org.

APPENDIXES

(Nonmandatory Information)

X1. DENSITY CALCULATION OF THE LPG AND CORRECTION OF THE RESIDUE RESULT

X1.1 Justification and Methodology Overview

X1.1.1 The mass of the sample injected into the GC using the liquefied injector depends on the pressure of the sample, the time setting for the injection and the density of the sample. An analytical method generally holds the pressure and the time setting constant. A variation in injected mass occurs when there is a difference in composition (and therefore density) between the LPG sample and the calibration material (for example calibration standards prepared in pentane).

X1.1.2 In that case, the final residue result in mg/kg needs to be corrected for the difference in the injected mass. This requires the density of both the calibration matrix and the sample matrix.

X1.1.3 When the sample density has not been determined by direct measurement, it may be calculated according to Practice D2598 using the LPG composition analysis. The density equation given requires the sample composition be in liquid volume %.

X1.1.4 The composition of an LPG is readily determined by GC methods which are generally conforming to Test Method D2163. This test method suggests reporting results in liquid volume % of the major sample components. When available laboratory analytical results are expressed in mass % or mole %, the unit interconversion procedures outlined in Practice D2421 may be used to give the equivalent liquid volume % report.

X1.1.5 The following calculation example uses component properties listed in Practice D2421 and Practice D2598. Values given in GPA 2145 may be substituted if so desired. Refer to the methods for details and updates.

X1.2 Interconversion to Liquid Volume % from Mass % According to Practice D2421

X1.2.1

$$Liquid\ Volume\ \%_x = 100 \times \frac{(Mass\ \ \%_x\ /\ Relative\ density_x)}{\sum_{n=1}^{\#comp}(Mass\ \ \%_n\ /\ Relative\ density_n)} \quad (X1.1)$$

where:

Liquid Volume $\%_x$ = liquid volume percent of all determined components in the sample of which x is one.

#comp = the number of determined components in the sample of which x is one.

Relative Density$_x$ = the value (taken from Practice D2421, Table 2, Column 3) given for each determined component x as a liquid.

Mass$\%_x$ = the weight percent of each determined component taken from GC analysis.

$\sum_{n=1}^{\#comp}(Mass\ \ \%_n\ /\ Relative\ density_n)$ = the sum of the quotients Mass$\%_n$ divided by the Relative Density$_n$ for all determined components.

X1.3 Interconversion to Liquid Volume% from Mole% (Gas Vol%) According to Practice D2421

X1.3.1

$$Liquid\ Volume\ \%_x = 100 \times \frac{(Mole\ \ \%_x \times Volume\ Ratio_x)}{\sum_{n=1}^{\#comp}(Mole\ \ \%_n \times Volume\ Ratio_n)} \quad (X1.2)$$

where:

Liquid Volume $\%_x$ = liquid volume% of all determined components in the sample of which x is one.

#comp = the number of determined components in the sample of which x is one.

Volume Ratio$_x$ = the value (taken from Practice D2421, Table 2, Column 2) given for each determined component x.

$\sum_{n=1}^{\#comp}(Mole\ \ \%_n \times Volume\ Ratio_n)$ = the sum of the quotients Mole $\%_n$ multiplied by the Volume Ratio$_n$ for all determined components.

Mole $\%_x$ = the mole percent of each determined component taken from GC analysis (equivalent to gas volume percent assuming an ideal gas).

X1.3.1.1 Component properties are taken from the tables provided in Practice D2421. Component properties for methane, ethane, propane, iso-butane, normal butane, and pentane are provided in Table X1.1.

X1.4 Relative Density Calculation According to Practice D2598

X1.4.1

$$Relative\ Density_{mix} = \sum_{x=1}^{\#comp}\frac{(Liquid\ \ Volume\ \%_x \times Relative\ Density_x)}{100} \quad (X1.3)$$

where:

#comp = the number of determined components in the sample of which x is one.

relative density$_{mix}$ = relative density of the LPG mixture.

Relative Density$_x$ = liquid relative density of each component of which x is one.

Liquid Volume $\%_x$ = liquid volume% of all determined components in the sample of which x is one.

X1.5 Example Calculation

X1.5.1 A sample calculation using the following hypothetical LPG compositional analysis is given in Table X1.1.The example test result yields an oily residue chromatogram area equivalent to 35 mg/kg in pentane (relative density 0.631).

X1.5.2 *Step 1—Interconversion to Liquid Volume %:*

TABLE X1.1 Component Properties

Component	Mass %
Methane	0.00
Ethane	0.05
Propane	78.45
Isobutane	5.50
N butane	16.00

$$Liquid\ Volume\%_x = 100 \times \frac{(Mass\%_x / Relative\ Density_x)}{\sum_{n=1}^{\#comp} (Mass\%_n / Relative\ Density_n)} \quad (X1.4)$$

Component	Mass%	Divide by Liquid Relative Density[A]	Quotient	Liquid Vol%, Multiply by Normalization Factor (100/191.928)
Methane	0.00	0.3	0.00	0.00
Ethane	0.05	0.35639	0.140	0.07
Propane	78.45	0.50736	154.624	80.57
Isobutane	5.50	0.56293	9.770	5.09
N butane	16.00	0.58407	27.394	14.27
Total	100.00	...	191.928	100.00

[A] Source: Practice D2421, Table 2, Col 3.

X1.5.3 *Step 2—Relative Density Calculation of the Mixture:*

$$Relative\ Density_{mix} = \sum_{x=1}^{\#comp} \frac{(Liquid\ Vol\ \%_x \times Relative\ Density_x)}{100}$$

$$Relative\ Density_{mix} = \left(\frac{0.07 \times 0.35639}{100}\right) + \left(\frac{80.57 \times 0.50736}{100}\right) + \left(\frac{5.09 \times 0.56293}{100}\right) + \left(\frac{14.27 \times 0.58407}{100}\right) = \mathbf{0.521} \quad (X1.5)$$

NOTE X1.1—The resultant relative density is rounded to 3 decimals in accordance with Practice D2598, 5.2.2. However, the result may be reported up to as many significant figures as are used for the component properties.

X1.5.4 *Step 3—Correct for Density Difference between the LPG Sample and Pentane Calibrant:*

$$0.631/0.521 \times 35\ mg/kg = \mathbf{42\ mg/kg}\ \text{oily residue in the sample} \quad (X1.6)$$

X2. QUALITY CONTROL MONITORING

X2.1 Confirm the performance of the instrument or the test procedure by analyzing quality control (QC) sample(s).

X2.2 Prior to monitoring the measurement process, the user of the test method needs to determine the average value and control limits of the QC sample. See Practice D6299 and MNL7.[4]

X2.3 Record the QC results and analyze by control charts or other statistically equivalent techniques to ascertain the statistical control status of the total testing process. See Practice D6299 and MNL7.[4] Investigate any out-of-control data for root cause(s). The results of this investigation may, but not necessarily, result in instrument recalibration.

NOTE X2.1—In the absence of explicit requirements given in the test method, X2.4 provides guidance on QC testing frequency.

X2.4 The frequency of QC testing is dependent on the criticality of the quality being measured, the demonstrated stability of the testing process, and customer requirements. Generally, a QC sample should be analyzed each testing day with routine samples. The QC frequency should be increased if a large number of samples are routinely analyzed. However, when it is demonstrated that the testing is under statistical control, the QC testing frequency may be reduced. The QC sample testing precision should be periodically checked against the ASTM method precision to ensure data quality. See Practice D6299 and MNL7.[4]

X2.5 It is recommended that, if possible, the type of QC sample that is regularly tested be representative of the material routinely analyzed. An ample supply of QC sample material should be available for the intended period of use, and must be homogenous and stable under the anticipated storage conditions.

X2.6 See Practice D6299 and MNL7[4] for further guidance on QC and control charting techniques.

[4] MNL 7, *Manual on Presentation of Data and Control Chart Analysis*, ASTM International.

X3. ANALYSIS OF BENZENE, TOLUENE AND HYDROCARBONS C_7 THROUGH C_{10}

X3.1 This section has been added to the test method to provide guidance for determining heavy residue with a boiling range less than the C_{10} (nominal bp 174°C) given in Section 1. The recovery of benzene (nominal BP 80°C) has been tested successfully.

X3.2 This expansion of the analysis boiling range requires a shorter vent time for the matrix or solvent. A vent time of 6 s gave good recovery of 44 ppm benzene in a pentane matrix. Standard C_{10}+ vent times of 50 to 60 s are the norm with the operational conditions described in Section 6. Care should be taken to examine the degree of separation in the chromatogram between the components of interest and the matrix peak to ensure proper integration for quantitation. See Fig. X3.1.

X3.3 Calibration follows the procedure in Section 10.

X3.4 The total residue may be calculated by summing the individual identified peaks shown with the unresolved C_{10} to C_{40} mineral oil area.

X3.5 The recovery of 44 mg/kg Benzene in comparison with 41 mg/kg Toluene is 98%. The repeatability over four analyses is shown in the following table:

	Nominal Concentration	Average	Standard Deviation	Relative Standard Deviation	Recovery
Benzene	44 mg/kg	40.7	1.38	3.4%	98%
Toluene	41 mg/kg	38.8	1.31	2.9%	100%
n-Heptane	33 mg/kg	31.7	0.62	1.9%	102%
n-Octane	37 mg/kg	35.4	0.79	2.2%	101%

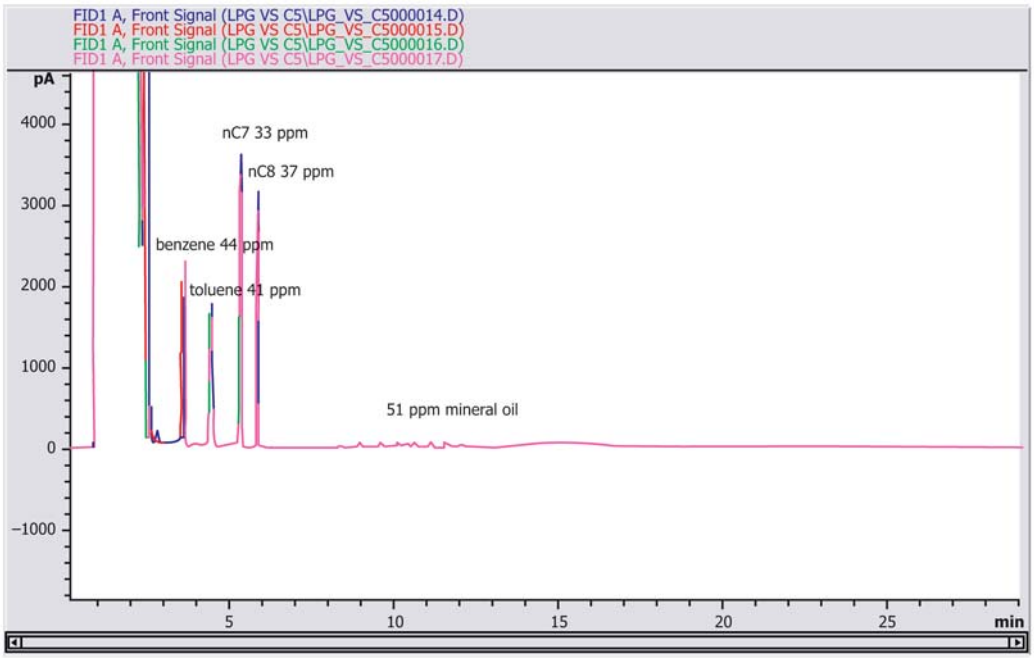


FIG. X3.1 Chromatogram of a Sample Spiked with Benzene, Toluene, Heptane, and Octane Used for Setting the Vent Time

X4. ANALYSIS OF DIISOPROPANOLAMINE (DIPA; CAS No. 110-97-4)

X4.1 This appendix has been added to the test method to provide guidance for the analysis of DIPA (referenced as CAS No. 110-97-4 by the Chemical Abstracts Service) in LPG. See Fig. X4.1.

X4.2 This application requires an amine treated column or a metal column to avoid adsorption of amine on the fused silica. Columns used successfully for this application are the RTX-amine column (30 m by 0.32 mm by 1.0 μm) or the MTX-5

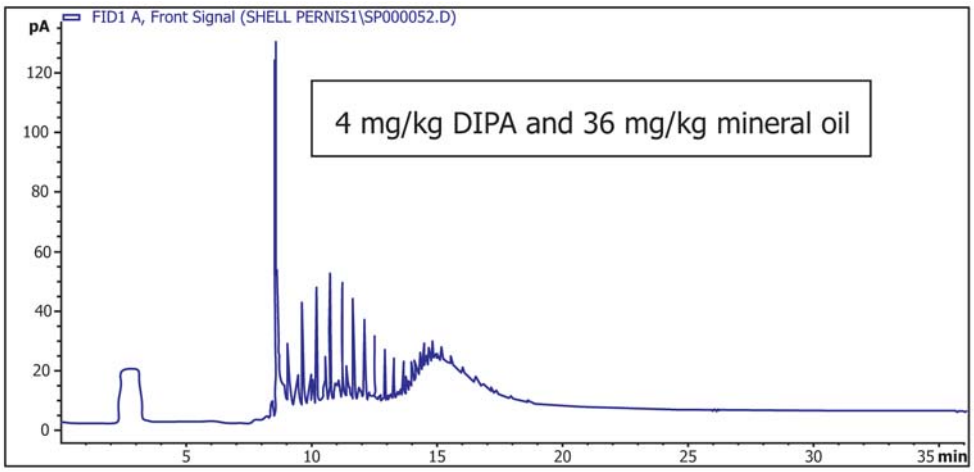


FIG. X4.1 Chromatogram 1 Showing 4 mg/kg DIPA and 36 mg/kg Mineral Oil

column (30 m by 0.32 mm by 1.0 µm). Both columns are available at Restek.[5]

[5] The sole source of supply of the apparatus known to the committee at this time is Restek Corporation, 110 Benner Circle, Bellefonte, PA 16823, www.Restek.com. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

X4.3 Typical conditions, other than the column, are described in Table 1.

X4.4 Calibration follows the procedure in Section 10.

X4.5 The total residue may be calculated by summing the individual identified peaks shown with the unresolved C_{10} to C_{40} mineral oil area. The total DIPA concentration is determined by integrating the DIPA peak.

X5. FID LINEARITY CHECK

X5.1 To verify system linearity over the range of expected sample residue, it is suggested that a range of standards which bracket this expected value be prepared and analyzed after installation or major repair.

X5.1.1 Prepare a mineral oil or site-specific oil standard by weighing to the nearest mg and dissolving in American Chemical Society (ACS) or better pentane or certified LPG. Choose the weighed sample amount and volume of diluent to give a residue concentration at twice the expected concentration in the routine samples.

X5.1.2 Dilute the prepared standard from X5.1.1 1:1(vol/vol) in the diluent (ACS or better pentane or certified LPG) to give a standard roughly equivalent to the expected routine sample residue concentration.

X5.1.3 Prepare a third standard at roughly half the expected routine sample residue concentration by diluting the first X5.1.1 standard 1:3 (vol/vol) with the diluent (ACS or better pentane or certified LPG).

NOTE X5.1—The user may elect to prepare other residue standard concentrations to verify linearity over the range of interest.

X5.1.4 Analyze a minimum of the three described standards according to Section 11.

X5.1.5 Integrate the residue chromatogram, and sum the area of range C_{10}-C_{40}.

X5.1.6 Prepare a plot of area versus nominal concentration in mg/kg (ppm). This plot should give a straight line with a constant slope. The multiple regression correlation coefficient (R^2) should be 0.99 or better.

X5.1.7 Any deviation from linearity indicates nonlinear behavior of the application set-up.

X5.1.8 Nonlinear behavior could be caused by poor control of the injection volume (check the peak shape) or the detector (check the manufacturer manual for correct FID setting). Correct the issue and repeat the linearity check.

SUMMARY OF CHANGES

Subcommittee D02.H0 has identified the location of selected changes to this standard since the last issue (D7756 – 12) that may impact the use of this standard. (Approved June 15, 2013.)

(1) Added 1.3 and 10.2.

(2) Section 15, Precision and Bias, was completely revised.

Subcommittee D02.H0 has identified the location of selected changes to this standard since the last issue (D7756 – 11) that may impact the use of this standard. (Approved Nov. 1, 2012.)

(1) Revised Appendix X1.

(2) Added Appendix X3, Appendix X4, and Appendix X5.