



Standard Test Method for Determination of Residue Composition in Liquefied Petroleum Gas (LPG) Using Automated Thermal Desorption/ Gas Chromatography (ATD/GC)¹

This standard is issued under the fixed designation D7828; 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 residue in LPG by automated thermal desorption/gas chromatography (ATD/GC) using flame ionization detection (FID).

1.2 The quantitation of residue covers a component boiling point range from 69°C to 522°C, equivalent to the boiling points of C₆ through C₄₀ n-paraffins.

1.2.1 The boiling range covers possible LPG contaminants such as gasoline, diesel fuel, phthalates and compressor oil. Qualitative information on the nature of the residue can be obtained from this test method.

1.2.2 Materials insoluble in LPG and components which do not elute from the gas chromatograph or which have no response in a flame ionization detector are not determined.

1.2.3 The reporting limit (or limit of quantitation) for total residue is 6.7 µg/g.

1.2.4 The dynamic range of residue quantitation is 6.7 to 3300 µg/g.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *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

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.

D1835 Specification for Liquefied Petroleum (LP) Gases
D2158 Test Method for Residues in Liquefied Petroleum (LP) Gases
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
E355 Practice for Gas Chromatography Terms and Relationships
2.2 Environmental Protection Agency:³
EPA Method TO-17 Determination of Volatile Organic Compounds in Ambient Air using Active Sampling onto Sorbent Tubes

3. Terminology

3.1 Definitions:

3.1.1 For the definitions of common chromatographic terms, refer to Practice **E355**.

3.1.2 *quality control sample, QC sample, n*—for use in quality assurance program to determine and monitor the precision and stability of a measurement system; a stable and homogenous material having physical or chemical properties, or both, similar to those of typical samples tested by the analytical measurement system. The material is properly stored to ensure sample integrity, and is available in sufficient quantity for repeated long-term testing. **D6299**

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *residue, n*—soluble contaminants in LPG with boiling points from 69°C to 522°C, covering the boiling point range of C₆ to C₄₀ n-paraffins.

3.2.2 *sorbent tube, n*—a tube that contains commercially available adsorbents whose composition is specific to retain the components of interest (residues).

3.2.3 *thermal desorber, n*—a sample introduction technique used in gas chromatography in which residue adsorbed on an adsorbent material is desorbed into a gas chromatograph.

³ Available from United States Environmental Protection Agency (EPA), Ariel Rios Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, <http://www.epa.gov>.

3.2.3.1 *Discussion*—Figs. 1-3 illustrate the flow path and function of the thermal desorber used in this test method.

3.2.4 *thermal desorption, n*—the process of using heat, temperature, gas flow and time to remove adsorbed components captured in a sorbent tube for introduction into a gas chromatograph for analysis.

3.2.5 *time group, n*—in gas chromatography, a set time window used in determining the response (area).

3.2.5.1 *Discussion*—In this test method, the time for response begins after the elution of pentane and stops after the elution of C₄₀ or of the heavier oil being used for this range, with the sum of the integrated peaks within this time providing a total area of the residue.

3.3 Acronyms:

3.3.1 *ATD*—automated thermal desorption

3.3.2 *IS*—internal standard

3.3.3 *LPG*—liquefied petroleum gas

4. Summary of Test Method

4.1 Liquefied Petroleum Gas (LPG) is sampled by Practice D1265 or Practice D3700.

4.2 A single phase sample of LPG is then captured on a fixed volume sample loop (Sampling Cell). The sample is maintained within the sample loop at a pressure above its bubble point as it is released directly onto the hydrocarbon-selective absorbent tube material, thereby trapping the C₆ plus hydrocarbons (residue). The C₅ minus components pass through the sorbent(s). The loop weight containing the sample provides the sample mass.

4.3 The sorbent tube is placed onto the thermal desorber, which desorbs the residue from the tube directly onto the analytical column of the gas chromatograph for separation and quantitation.

4.4 The data handling system acquires the raw data from the flame ionization detector. The processing method, which contains the response factor (RF) and integration parameters from

standards previously analyzed, is applied to the sample, and the mass of residue in the sample is calculated.

5. Significance and Use

5.1 Residue in LPG is a contaminant that can lead to operational problems in some end use applications. Engines, micro-turbines, fuel cells and other equipment may be sensitive to residue levels as low as 10 mg/kg.

5.2 Contamination of LPG can occur during production, transport, delivery, storage and use. A qualitative indication of the contaminants can help track down the source of the contamination from manufacture, through the distribution system, and to the end user.

5.3 This test method is designed to provide a lower detection limit, wider dynamic range, and better accuracy than gravimetric methods like Test Method D2158.

5.4 This test method can be performed with little or no discharge of LPG vapors, compared to Test Method D2158 which requires evaporation of 100 mL of sample per test.

5.5 Sampling for residue in LPG using sorbent tubes can be performed in the field, and the sorbent tubes sent to a laboratory for analysis. This saves significant costs in shipping (weight of tube is approximately 10 grams), and is much safer and easier than transporting LPG cylinders.

5.6 This test method determines total residues from C₆ to C₄₀, compared to a thermal gravimetric residue method such as Test Method D2158 which heat the residue to 38°C, resulting in a lower recovery due to loss of lighter residue components.

5.7 If there is a need to decrease the detection limit of residue or individual compounds of interest below 10 µg/g, the procedures in this test method can be modified to achieve 50 times enhanced detection limit, or 0.2 µg/g.

6. Apparatus

6.1 *Sampling Apparatus*—Refer to Appendix X1 for the typical apparatus and configuration for sampling LPG onto sorbent tubes.

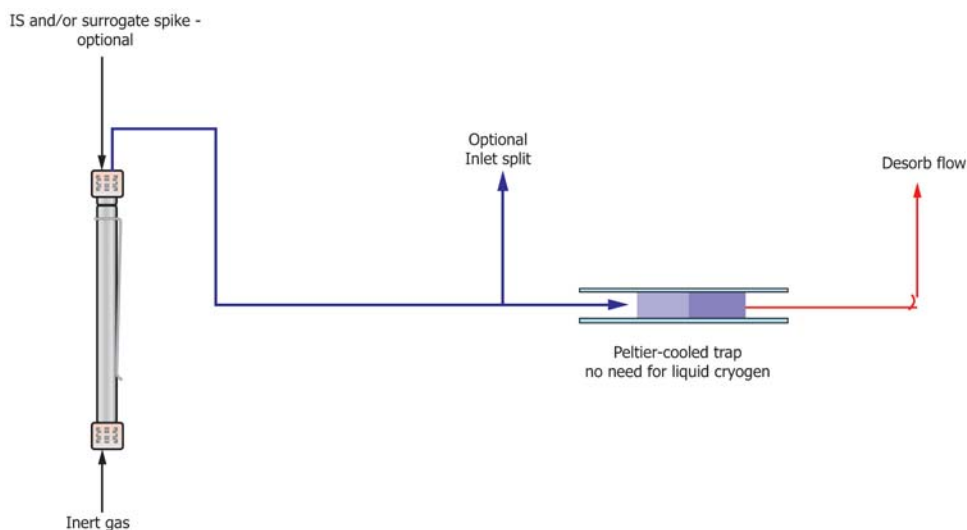


FIG. 1 Sample Tube Desorption (Primary Desorption)

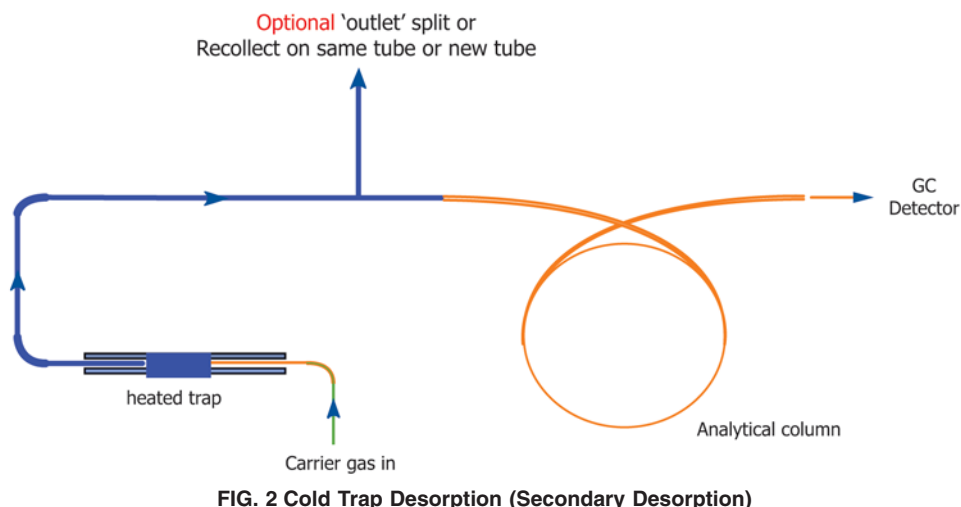


FIG. 2 Cold Trap Desorption (Secondary Desorption)

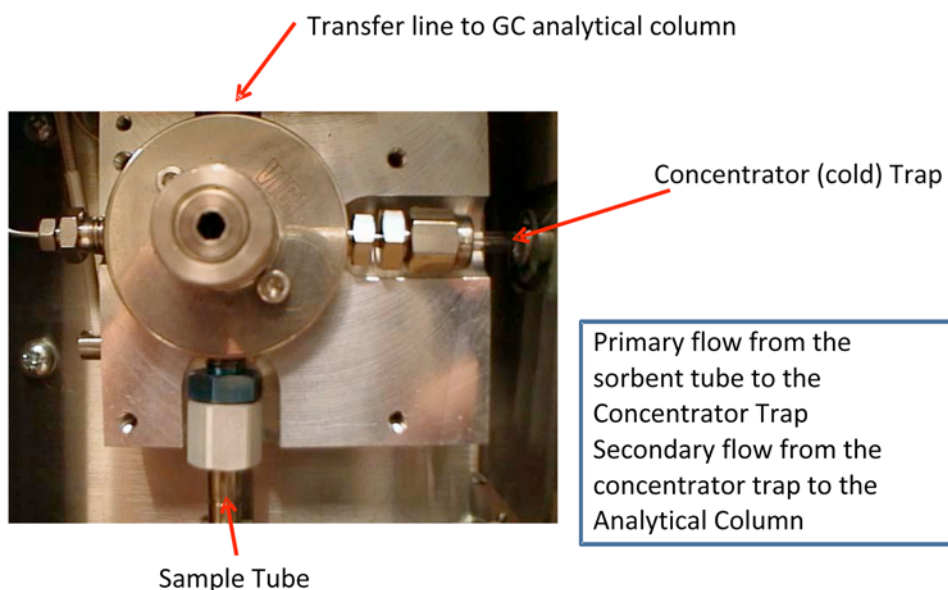


FIG. 3 Valving and Connections in a Thermal Desorber

6.2 Thermal Desorber:

6.2.1 A thermal desorber is necessary to remove the residue from the sorbent tube and introduce it to a gas chromatograph. It shall be designed to hold the sorbent tubes described in 7.4, and be capable of the parameters of temperature and flow as detailed in Table 1.

TABLE 1 Thermal Desorber Parameters

Sorbent Tube	Desorb for 18 min at 375°C at 30 mL/min
Concentrator Trap	Trap Low 5°C; Trap high 380°C; Trap Hold 14 min
Pneumatics	Inlet split 50 mL/min; Outlet split 30 mL/min; analytical column flow 0.8 mL/min
Ambient Purge ^A	Purge for 3 min at ambient temp at 50 mL/min
Transfer Line ^B	290°C
Valve Temp ^B	260°C
GC Cycle Time	34 min

^A A purge is used to rid the tube of residual oxygen and C₅ minus prior to primary desorption.

^B Manufacturer specific parameter. Refer to manufacturer's guidelines for these parameters.

6.2.2 Sorbent Tube Autosampler (Optional)—An autosampler may be used, but is not required. The instrument used to design this test method had a 50-tube automated sampler.

6.2.3 Sample Re-collection (Optional)—Most of the sample being analyzed may be re-collected via the split vent onto the same sorbent tube or onto a new sorbent tube. Sample re-collection allows re-analysis of the same sample if needed, and preservation of the sample if required for further analytical testing or legal retention, etc.

6.2.4 Transfer line configuration to install the thermal desorber to the GC or GC column is vendor specific. Consult with the manufacturer.

6.2.5 Appendix X2 contains the apparatus required for spiking standards onto standard sorbent tubes.

6.3 Gas Chromatograph (GC), configured with a split/splitless injector and a flame ionization detector that is capable of establishing the method parameters as detailed in Table 2 is required.

TABLE 2 Gas Chromatographic Parameters

Oven	35°C for 4 min, ramp 15°C/min to 230°; ramp 10°C/min to 330°C and hold for 3 min
GC Run Time	30 min
Detector temp	340°C
Detector Flows ^A	40 mL/min Hydrogen; 400 mL/min Air

^A Manufacturer specific parameter. Refer to manufacturer's guidelines for these parameters.

6.4 *Capillary Column*—with non-polar stationary phase. A 100% dimethyl polysiloxane phase capillary column with dimensions 20 m × 0.18 mm × 0.2 µm was found to be satisfactory. The column shall separate pentane from hexane with a resolution (R value) of 1.5 or greater.

6.4.1 Residues in the diesel fuel and compressor oil boiling range are summed, so detailed component speciation is unnecessary. If speciation is desired, a high resolution column and optimized GC oven parameters may be used.

6.5 *Balance*, capable of weighing to 0.1mg.

6.6 *Data Handling System (Computer)*, capable of performing timed group integrations, multi-level first order calibrations and using average response factors to calculate the amount of residue in a sample and provide results in a report.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁴ Other grades may be used, provided it is pure enough to be used without lessening the accuracy of the determination.

7.2 *Solvents and Standards*—(**Warning**—many of these chemicals are flammable and the vapors are harmful. Proper ventilation, safety precautions and other personal protective equipment, such as safety glasses, should be used when handling. Benzene is an EPA target carcinogen.)

7.2.1 *Benzene* (only if the retention time is desired).

7.2.2 *Compressor Oil*, residue range from approximately C₁₈ to C₄₀ (range will vary depending upon source).

7.2.3 *Diesel Fuel*, residue range from approximately C₈ to C₂₂ (range will vary depending upon source).

7.2.4 *Dichloromethane*, cleaning and flushing fluid. An alternative appropriate solvent may be used that will dissolve residue to clean the cylinder and be volatile enough to allow its evacuation from the cylinder. It is advisable not to use a solvent that would chromatographically elute in the quantitative time window specified in this test method (C₆ to C₄₀) just in case the evacuation (or evaporation) of cleaning solvent is not complete. To provide method validity, methylene chloride was used as a cleaning solvent.

⁴ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the United States Pharmacopeia and National Formulary, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

7.2.5 *Heptane*.

7.2.6 *Hexane*.

7.2.7 *Iso-octane* (2,2,4-trimethylpentane).

7.2.8 *Liquefied Petroleum Gas (LPG)*—LPG is a fire hazard and can cause freezer burns. Follow local safety protocols regarding released ethane, propane and butane vapors from LPG. Use safety precautions and suitable safety equipment when handling LPG.

7.2.9 *Paraffin Standard*, covering the range from C₆ to C₄₀ at 50 µg/g in pentane (commercially available mixtures may be used).

7.2.10 *Pentane*, high purity HPLC grade having non-detectable residue, as solvent for standards.

7.2.11 *Toluene*.

7.3 *Instrument Gases*:

7.3.1 *Carrier Gas*, 99.999% Ultra High Purity Helium.

7.3.2 *Combustion Gases*, 99.999% Ultra High Purity Hydrogen and Dry Air (some gas chromatographs use a makeup gas for their flames. Follow vendor's instructions).

7.4 *Sorbent Tubes*—Tubes that contain an adsorbent material designed to adsorb residues commonly found in LPG.⁵

7.4.1 Sorbent tubes are shipped and stored with brass end caps isolating adsorbents from ambient air. EPA Method TO-17 mandates a maximum holding time of 30 days after sampling onto tubes. Some studies indicate stability and accuracy of components in sorbent tubes to be six months. A maximum holding time of 30 days after LPG sampling is recommended.

8. Calibration

8.1 External standard calibration technique is used.

8.2 Either multi-level or single-level calibration may be appropriate.

8.2.1 When the concentration range of the samples being analyzed is unknown, it is recommended to use a multi-level calibration that encompasses the varying concentrations of the sample. If a sample amount falls above this calibration range, dilution of the sample or a smaller volume with correction factor is required so that it falls within the calibration range. If a sample amount falls below the reporting limit, the sample amount should be reported as below the reporting limit. It is not accurate to provide a result for a sample that falls outside of the calibration range of the test method.

8.2.2 If the goal is to determine that the residue in the sample is below a maximum limit for residue, and not to report the exact amount of residue, a single-level calibration is sufficient at that concentration.

8.3 To cover the residue range, a component mixture (hexane, heptane, iso-octane, and toluene) is used for the lower boiling point region (gasoline); diesel is used for the mid-range and compressor oil is used for the higher boiling point region. Since speciation is usually not required, a sum of the entire

⁵ The sole source of supply of the sorbent tubes for this test method known to the committee at this time is Perkin Elmer, 710 Bridgeport Avenue, Shelton, CT 06484, www.perkinelmer.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, which you may attend.

residue area is used. The “timed group” start time for this sum is immediately following the elution of pentane and the end point for this sum is when the compressor oil returns to baseline (some compressor oil elutes past C₄₀). Fig. 4 displays this integration noting the time points for the timed group for response (area) from the standard. Fig. 5 is an expansion of this chromatogram on the x-axis demonstrating the separation of pentane (solvent) and hexane.

8.4 Standard Preparation for Multi-Point Linear Least Square Fit—A three or five level calibration is sufficient covering the range of sample concentration.

8.4.1 Solvent Blank—Inject a 1 µL solvent blank onto a sorbent tube prior to preparing standards.

8.4.2 Volatile Stock—Half fill a 5 mL volumetric flask with pentane. Zero (tare) the flask on a balance. Weigh approximately 0.1 g each of hexane, heptane, iso-octane and toluene, recording the mass to the nearest 0.1 mg into the flask by inserting each compound directly into the solvent, then fill to mark with pentane. The final concentration shall be approximately 0.02 g/mL for each of the chemicals dissolved in the pentane stock solution. Calculate the exact concentration based on recorded masses.

8.4.3 Stock #1—Weigh approximately 3.5 g of diesel and 4.0 g of compressor oil (recording the mass to 0.0001 g) into a 10 mL volumetric flask. Add 600 µL of Volatile Stock by inserting stock directly into mixture, and then fill to mark with pentane. This standard contains 1.2 µg/µL volatiles and 750 µg/µL diesel plus compressor oil. Calculate the exact concentrations based on recorded masses.

8.4.4 Stock #2—Fill a 10 mL volumetric flask about half full with pentane. Using a 1 mL gas tight syringe, transfer 1 mL of Stock #1 into pentane and then fill to mark with pentane. This standard contains 0.12 µg/µL volatiles and 75 µg/µL diesel plus

compressor oil. Calculate the exact concentrations based on recorded masses from Stock #1.

8.4.5 Stock #3—Fill a 5 mL volumetric flask about half full with pentane. Using a 0.25 mL gas tight syringe, transfer 0.20 mL of Stock #2 into pentane and then fill to the mark with pentane. This standard contains 0.0048 µg/µL volatiles and 3.0 µg/µL diesel plus compressor oil. Calculate the exact concentrations based on recorded masses from Stock #1.

8.4.6 Transfer the following amounts onto standard sorbent tubes following the procedure outlined in Appendix X2, Spiking Standards onto Sorbent Standard Tubes. In this example, seven concentrations were prepared because of the broad range.

1 µL Stock #3	6 µL Stock #3	0.5 µL Stock #2	2 µL Stock #2	5 µL Stock #2	1 µL Stock #1	2 µL Stock #1
µg on tube	µg on tube	µg on tube	µg on tube	µg on tube	µg on tube	µg on tube
3.00	18.03	37.56	150.24	375.60	751.20	1502.40

8.4.7 The first order curve represents response versus mass on tube, where the y-axis is response of each standard (the time integration starting immediately after the elution of pentane through compressor oil), and the x-axis is µg on tube. Fig. 6 represents a first order plot containing 11 concentrations from 3 to 1517.4 µg with correlation coefficient (r²) of 0.9990.

8.4.8 The correlation coefficient (r²) used for quantitation shall be 0.9900 or greater.

8.4.9 In cases when a single point calibration is acceptable (refer to 8.2.1), use 1 µL of Stock #3 resulting in 3.0 µg of residue standard on tube, or the desired limit of quantitation.

8.5 A paraffin standard covering the range from C₆ to C₄₀ at approximately 50 ppm each should be injected to designate boiling point retention, to locate the time for integration and to

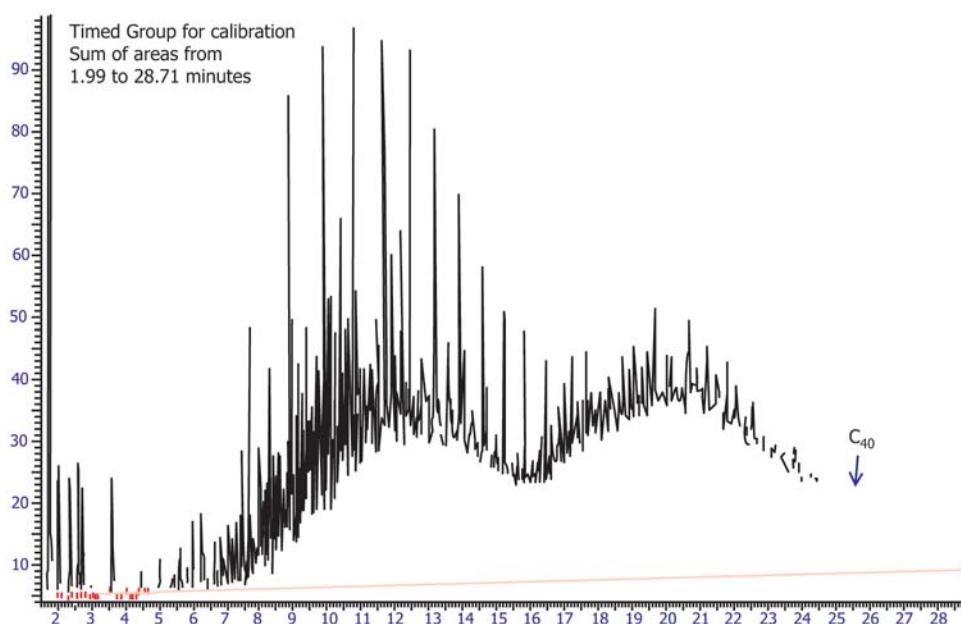


FIG. 4 Standard Chromatogram of Gasoline Surrogate Components, Diesel and Compressor Oil Displaying Integration and Timed Group

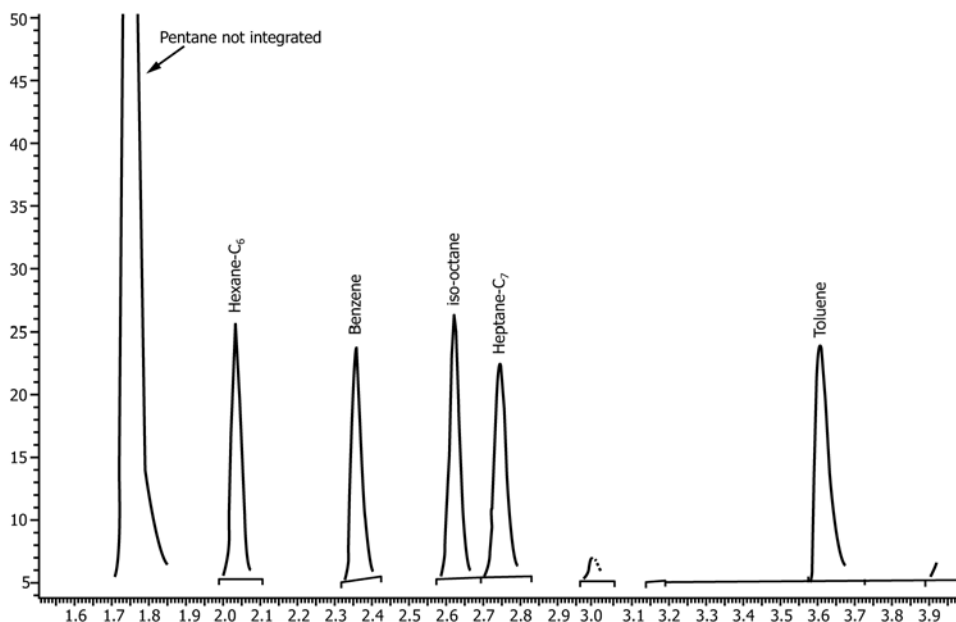


FIG. 5 Expansion of the X-axis (first 5 min) of Fig. 4 of the Standard Chromatogram to Demonstrate Separation of the Lower Boiling Point Hydrocarbons and Separation of Hexane from Pentane

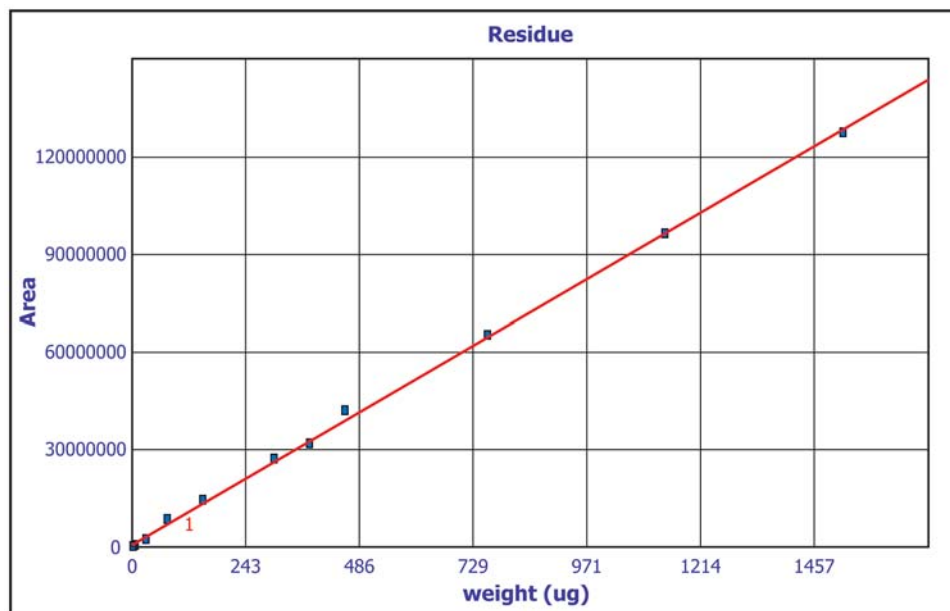


FIG. 6 Calibration Plot of Residue Containing 11 Points from 3 to 1517 μg . Correlation Coefficient (r^2) = 0.9990

ensure recovery of the analytical system. Fig. 7 represents a chromatogram of a paraffin standard used to verify and confirm recovery from C₆ to C₄₀ of the instrument by injecting this standard onto a standard tube. Table 3 documents the results from this standard confirming recovery for residue in this range.

9. Procedure

9.1 Obtain a representative sample of LPG by Practice D1265 or Practice D3700, or collect a sample directly onto a sorbent tube from a sampling point on the LPG system.

9.2 Perform an instrument blank test to ensure the system is not contaminated, by analyzing an empty sorbent tube (a tube without adsorbents). If the system is contaminated after two blank tube injections, consult the manufacturer's manual or consult with vendor customer support to resolve the problem.

9.3 Perform the calibration with standards as described in section 9 to calibrate the test method for quantitation. The instrument parameters found in Tables 1 and 2 should be followed.

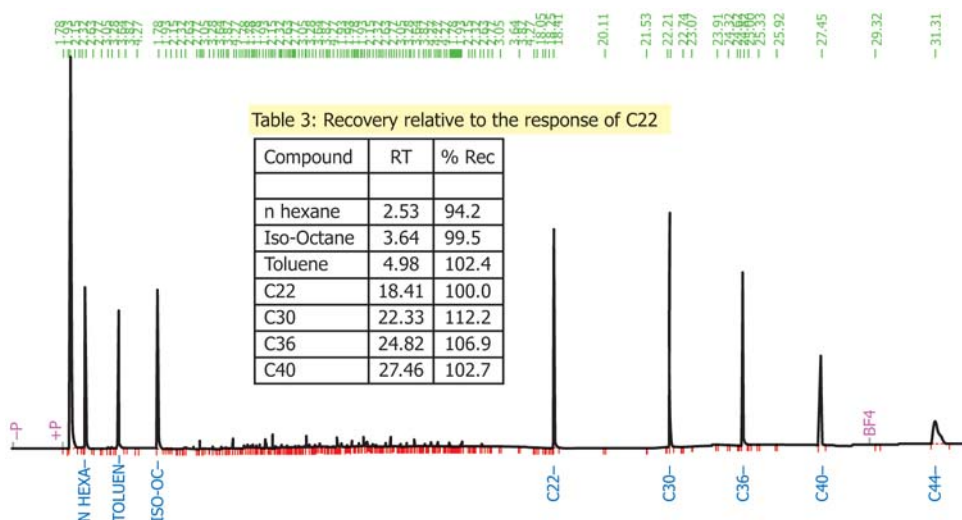


FIG. 7 Paraffin Standard to Confirm Recovery

TABLE 3 Gas Chromatographic Parameters

Compound	RT	% Rec
n hexane	2.53	94.2
Iso-octane	3.64	99.5
Toluene	4.98	102.4
C22	18.41	100.0
C30	22.33	112.2
C36	24.82	106.9
C40	27.46	102.7

9.4 Perform a quality control check prior to running samples to ensure calibration is still valid (refer to Section 11).

9.5 Inject a blank sample after the QC check to ensure carryover has not occurred. The results should be non-detectable or below the limits of quantitation.

9.6 Follow the directions outlined in Appendix X1 to sample onto sorbent tubes. The sampling technique described in Appendix X1 has been found to be satisfactory. Other sample to tube techniques may be employed if the sample is introduced as a liquid and the recovery, as defined in Table 4 of Section 12, is proven to be equivalent or better.

9.7 Analyze the sorbent tube using method parameters described in Tables 1 and 2. Insert the sample mass as the divisor in the sequence so that the proper calculations are performed.

9.8 Calculation of results is performed by the data handling system and results are reported. If the amount of residue in a sample exceeds the calibration range, dilution of the sample or a smaller volume with correction factor is required so that it

TABLE 4 Interim Repeatability and Accuracy

Analyte	Hexane				I-Octane			Heptane		
	LPG Sample Weight (g)	Calculated amount (µg/g)	Actual amount (µg/g)	% Dev	Calculated amount (µg/g)	Actual amount (µg/g)	% Dev	Calculated amount (µg/g)	Actual amount (µg/g)	% Dev
	0.4088	2	1.8	13.3	1.6	1.6	0	1.7	1.7	0
	0.4140	2.1	1.8	14.4	1.6	1.6	0	1.7	1.7	0
	0.4317	1.9	1.8	7.2	1.5	1.6	-6.3	1.6	1.7	-5.9
	0.4269	2	1.8	11.1	1.5	1.6	-6.3	1.7	1.7	0
	0.4274	2	1.8	10.0	1.5	1.6	-6.3	1.7	1.7	0
	0.4143	2	1.8	11.1	1.5	1.6	-6.3	1.7	1.7	0
Std Dev	0.01	0.05			0.05			0.04		
Average	0.42	2.00			1.53			1.68		
%RSD	2.2	2.3			3.4			2.4		
Analyte	Toluene				Diesel and Compressor Oil					
	LPG Sample Weight (g)	Calculated amount (µg/g)	Actual amount (µg/g)	% Dev	Calculated amount (µg/g)	Actual amount (µg/g)	% Dev			
	0.4088	1.8	1.8	0.0	114	132	-14			
	0.4140	1.8	1.8	0.0	113	132	-15			
	0.4317	1.7	1.8	-5.6	102	132	-23			
	0.4269	1.7	1.8	-5.6	107	132	-19			
	0.4274	1.7	1.8	-5.6	104	132	-21			
	0.4143	1.8	1.8	0.0	108	132	-18			
Std Dev		0.05			4.59					
Average		1.75			107.79					
%RSD		3.1			4.3					

falls within the calibration range. If a sample amount falls below the reporting limit, the sample amount should be reported as below the reporting limit. It is not accurate to provide a result for a sample that falls outside of the calibration range of the test method.

10. Quantitation

10.1 Refer to **Appendix X1** and obtain the sample mass. The amount of LPG sampled should be within the range of 0.40 to 0.45 g. Dividing the response factor by sample mass provides the amount of residue in LPG in $\mu\text{g/g}$.

10.2 Calculation of the residue using first order calibration. The equation for a first order fit is:

$$y_s/w_s = mx_s + b \quad (1)$$

where:

y_s = the response of unknown residue (area of timed group),
 m = the slope of first order fit (response/ μg),
 b = the y intercept,
 w_s = the mass of LPG sample (g), and
 x_s = the amount of residue in sample ($\mu\text{g/g}$).

Solving for $x_s = (y_s/w_s - b)/m$

10.3 Calculation of residue using a single point calibration (refer to section 8.2.1):

$$\text{Amount of unknown residue, } x_s = (RF)(y_s/w_s) \quad (2)$$

where:

RF = the response factor which is the concentration of standard (μg) / response of standard (area) using timed group.

10.4 **Fig. 8** represents clean LPG spiked with a residue standard. The concentration of this standard was 7.9 $\mu\text{g/g}$ (C_6 through C_8), 62.9 $\mu\text{g/g}$ diesel and 69.3 $\mu\text{g/g}$ compressor oil

resulting in a total residue concentration in LPG of 139 $\mu\text{g/g}$. Standard mass on tube was 0.4269 g.

10.5 The standard concentration range is from 3 to 1500 μg . Since the sample amount being used is approximately 0.45 g, the method dynamic range is from 6.7 to 3300 $\mu\text{g/g}$.

11. Quality Control

11.1 If a multi-level calibration is being used, follow established laboratory quality control procedures or refer to Practice **D6299** for guidance.

11.2 After the calibration curve is established, a QC check should be injected at the beginning of the sample queue (or batch) to confirm that calibration (the response factor) is still valid. A mid-point concentration level is recommended for a QC. This is performed to ensure accuracy is maintained.

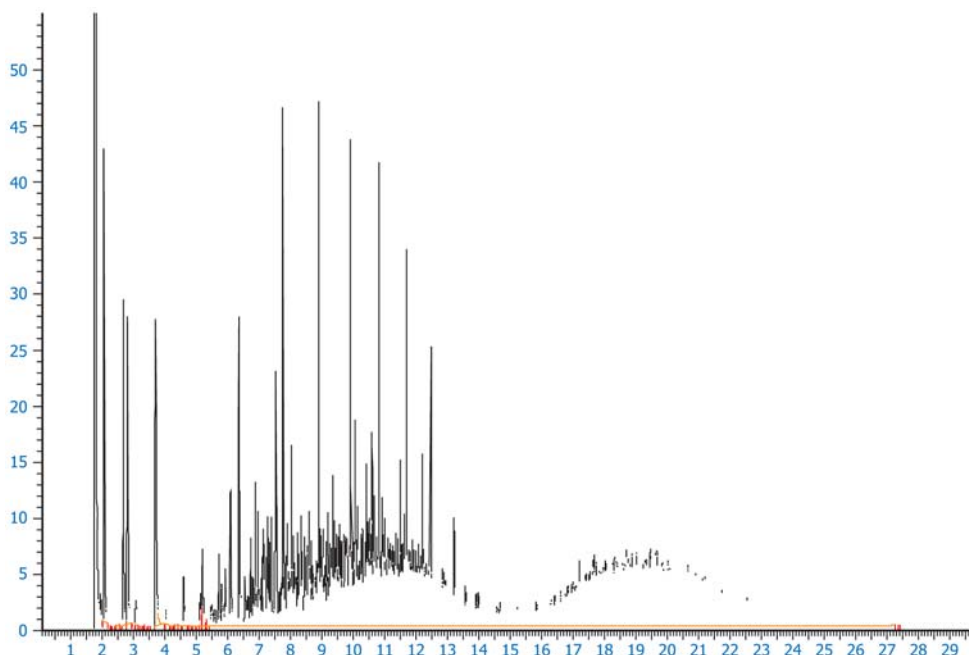
11.3 Follow internal QC procedures, or follow Practice **D6299**, to attain accuracy limits.

11.4 If the calculated amount of a QC is outside of this set accuracy criterion, the system calibration is no longer valid and a new multi-level calibration curve needs to be performed, creating a new response factor to use for quantitation.

11.5 If a single point calibration is employed, two QCs should be used—one at the same concentration as the standard, and the other at the limit of quantitation. The latter confirms the lower limit of detection can still be achieved.

11.6 Confirmation of calibration needs to be performed prior to the start of an analysis when quantitation is required.

11.7 When necessary, retention times should be updated using the quality control standard.



NOTE 1—Propane and butane in LPG are not detected or retained by adsorbents, and therefore do not interfere with residue measurements.

FIG. 8 Chromatogram of 139 $\mu\text{g/g}$ Standard of Gasoline Surrogate Components, Diesel and Compressor Oil in LPG

12. Precision and Bias

12.1 The following temporary precision is in accordance with *ASTM Form and Style*, section A21.2.2. Full precision will be completed within five years as specified in *ASTM Form and Style*, A21.2.3.

12.2 Interim repeatability and accuracy were determined in the same laboratory.

12.3 A standard was prepared in LPG. Total residue amount in LPG was 139 µg/g.

12.4 Table 4 contains the amount of LPG sampled onto the adsorbent tube; the calculated and actual amounts of volatiles (speciated), and of diesel and compressor oil (summed); the precision (%RSD); and the percent deviation from the actual amount. This precision encompasses sampling through analysis.

12.5 % deviation = (calculated amount-actual amount)/actual amount * 100%

12.6 A paraffin standard was prepared in LPG to determine the recovery of the residue range in LPG. The recovery of C₃₆

plus was less in LPG. This may be due to the decrease in solubility of the higher boiling components in LPG compared to the solubility in pentane. Calculating the diesel amount and compressor oil amounts in Table 4 separately, the compressor oil recovery was less.

12.7 Breakthrough experiments were performed to ensure adsorbent was able to retain the target analyte range of residue. Two sorbent tubes were connected together when sampling LPG. If breakthrough does not occur, the second tube in line will be blank because the front tube was able to retain the residue. Eight experiments were conducted to confirm that breakthrough of the residue did not occur even for the most volatile component, hexane. This confirms the suitability of the residue composite sorbent tubes (the sorbent tubes used in this test method) for the analysis of residue in an LPG matrix.

13. Keywords

13.1 gas chromatography; liquefied petroleum gas; LPG; residue; residue in LPG; thermal desorption

APPENDIXES

(Nonmandatory Information)

X1. SUGGESTED METHOD FOR SAMPLING LPG ONTO A SORBENT TUBE AS A LIQUID

X1.1 *Apparatus*—See Figs. X1.1-X1.6.

X1.2 *Sampling Cell*—See Table X1.1.

X1.3 *Sampling System*—See Table X1.2.

X1.4 Procedure

X1.4.1 *Apparatus Preparation*—Refer to Fig. X1.4.

X1.4.2 Ensure all valves are in the closed position to avoid accidental release.

X1.4.3 Fill a 500 mL sample cylinder 50% full (250 mL) with dichloromethane by removing valve VII and filling cylinder directly with a funnel.

X1.4.4 Pressurize the cylinder to 200 psi with nitrogen through VII.

X1.4.5 If multiple samples are to be taken it may be desirable to leave the nitrogen source connected throughout sampling to ensure no loss of pressure.

X1.4.6 Connect V10 to V7.

X1.4.7 Open V10 to fill solvent to V7.

X1.5 Sampling Procedure

X1.5.1 Connect LPG source to V3. If LPG is contained in a sample cylinder go to X1.5.1.1. If source is direct (Pipeline, LPG bullet, tank, etc.) go to X1.5.1.2. Figs. X1.4-X1.6 shows this connection as a dotted line as either scenario is applicable.

X1.5.1.1 *Sample Cylinder*:

(1) Pressurize cylinder to 200 psi with nitrogen or other inert gas.

(2) Connect VI to V3. Go to X1.5.2.

X1.5.1.2 *Direct Source*:

(1) Connect source directly to V3.

X1.5.2 Move V4 to the “load” position.

X1.5.3 Open V1 or the source valve to fill sample V3.

X1.5.4 Open V3.

X1.5.5 Slowly open V3 until liquid LPG is visible exiting T1. As soon as liquid LPG is visible exiting T1 close V3 (Note: ensure proper safe venting procedures are in place).

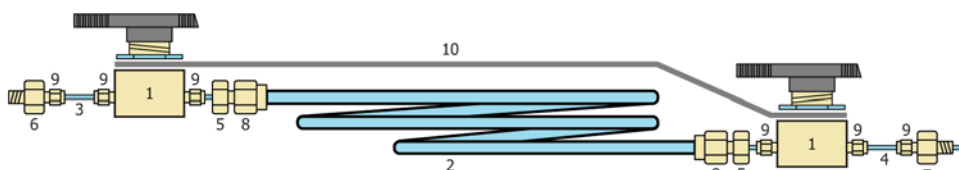


FIG. X1.1 Side View of Sampling Cell

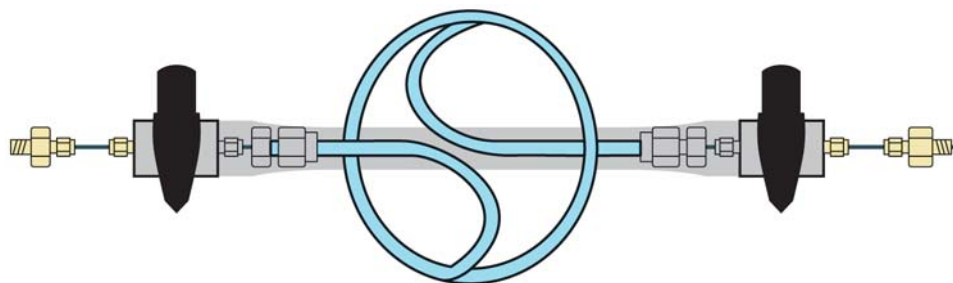


FIG. X1.2 Top View of Sampling Cell



FIG. X1.3 Aluminum Support

X1.5.6 Move V4 to the 'Purge/Clean' position.

X1.5.7 Connect the sample cell V8 to V4 outlet.

X1.5.8 Open V10 (dichloromethane source).

X1.5.9 Move V6 to the 'clean' position.

X1.5.10 Open V7.

X1.5.11 Open V8.

X1.5.12 Open V9 to begin cleaning sampling cell. Purge approximately 3 times the sample loop volume (approximately 2.5 mL). Capture solvent for proper disposal of chlorinated waste.

X1.5.13 Briefly purge solvent through V12 to ensure no residual material is trapped in vent line. Capture solvent for proper disposal of chlorinated waste.

X1.5.14 Close V7.

X1.5.15 Open V5 to nitrogen source.

X1.5.16 Move V6 to the purge position.

X1.5.17 Purge nitrogen for 1 min to ensure all solvent is evaporated from sampling cell.

X1.5.18 Briefly purge nitrogen through V12 to remove any remaining solvent.

X1.5.19 Close V5.

X1.5.20 Remove Sampling Cell and weigh to 0.1 mg. Record the mass as M1.

X1.5.21 Replace Sampling Cell in the system.

X1.5.22 Open V5.

X1.5.23 Open V8 and V9.

X1.5.24 Close V9 to pressurize the system with nitrogen to prevent sample vaporization during sampling.

X1.5.25 Close V8 to isolate the sample cell.

X1.5.26 Close V5.

X1.5.27 Move V4 to 'load' position.

X1.5.28 Open V3 to fill up to sampling cell inlet V8.

X1.5.29 Open V8 to fill the sampling cell.

X1.5.30 Using V9, purge the sampling cell until liquid is visible exiting. Close V9 as soon as liquid LPG is visible. (Use caution as excess LPG purging may result in freeze off of the sample cell outlet.)

X1.5.31 Close V8 to capture the LPG sample in the Sampling Cell.

X1.5.32 Close V3.

X1.5.33 Slowly open V12 to release LPG pressure from the system prior to removing the Sampling Cell.

X1.5.34 Close V12.

X1.5.35 Remove Sampling Cell and weigh to 0.1mg. Record the mass as M2.

X1.5.36 Replace Sampling Cell in the system.

X1.5.37 Open V5.

X1.5.38 Ensure V6 is in the purge position.

X1.5.39 Move V4 to the 'Purge/Clean' position.

X1.5.40 Connect the sorbent tube to the Sampling Cell outlet V9.

X1.5.41 Open V8 to provide nitrogen back pressure on the sample in the Sampling Cell.

X1.5.42 Open V9 and start the timer to begin injecting the captured sample onto the Sample Tube. The tube should begin to get cold and frost may form approximately 1.5 cm from the upper nut. This indicates the LPG is vaporizing within the absorbent material in the Sampling Tube. This vaporization within the tube indicates proper sampling technique.

X1.5.43 Continue purging for 2 min to ensure all the sample has been transferred to the sorbent tube.

X1.5.44 Close V8 and allow any remaining pressure to dissipate through the sorbent tube.

X1.5.45 Remove the sorbent tube for analysis.

X1.5.46 Close V5.

X1.5.47 Open V12 to vent remaining nitrogen pressure then close V12.

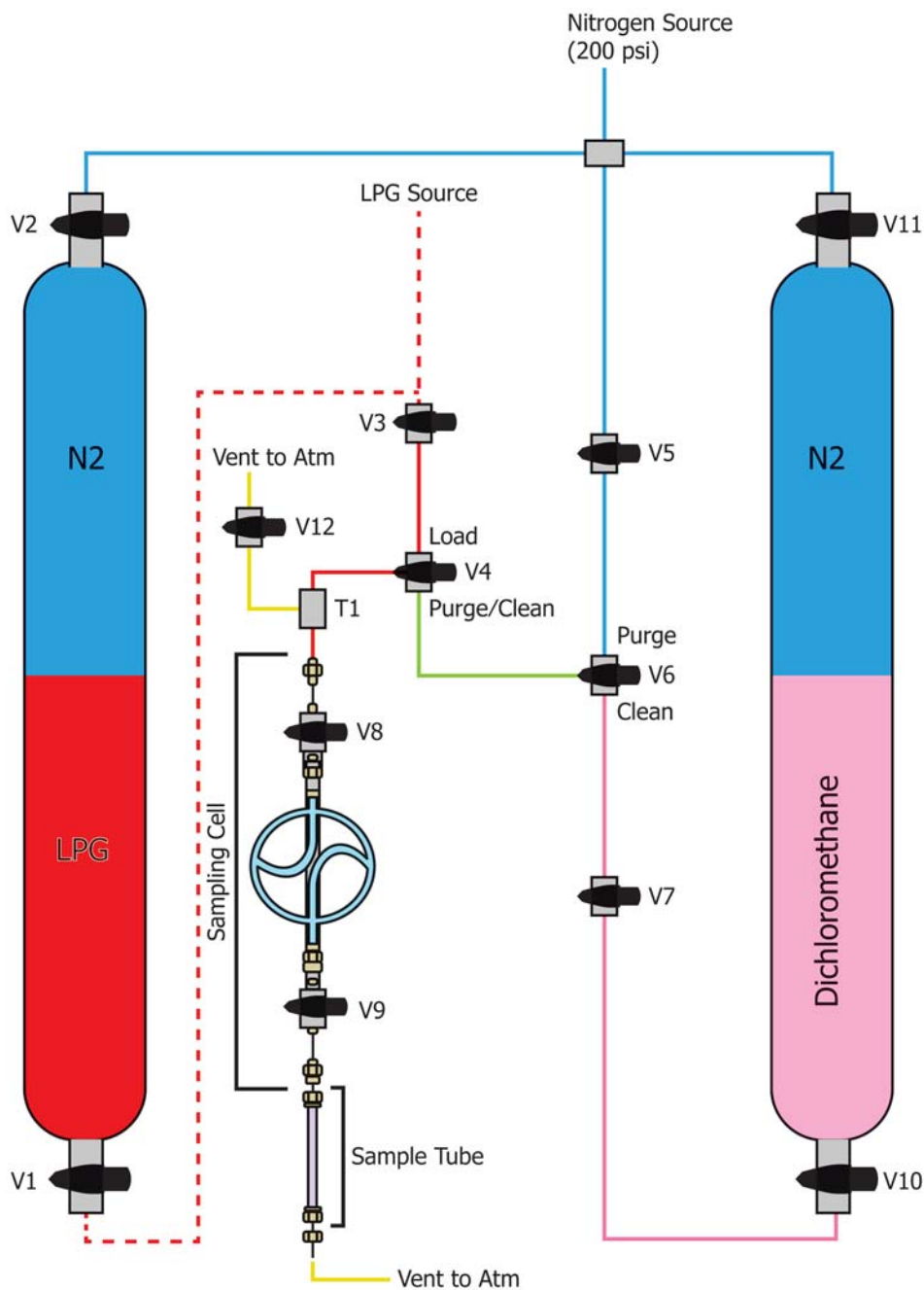


FIG. X1.4 Complete LPG Residue Sampling System

X1.5.48 Repeat procedure for additional samples or replicate sorbent tubes, or both, or to clean—only repeat steps X1.5.7 to X1.5.19.

X1.6 Depressurizing the Sampling System (post sampling)

- X1.6.1 Shut off nitrogen source.
- X1.6.2 Close V2 and V11.
- X1.6.3 Close V1 and direct source valve.
- X1.6.4 Move V4 to the “load” position.
- X1.6.5 Open V3.

- X1.6.6 Open V12 to vent remaining LPG in the system.
- X1.6.7 Remove sampling cell.
- X1.6.8 Disconnect sample cylinder line or direct source line.
- X1.6.9 Close V12.
- X1.6.10 Close V5.
- X1.6.11 Close V10.
- X1.6.12 Move V4 to the “Purge/Clean” position.
- X1.6.13 Move V6 to the “Clean” position.



FIG. X1.5 LPG Residue Sampling System Without Sampling Cell or Sorbent Tube (Initial Sample Purge)

X1.6.14 Open V7.

X1.6.15 Open V12 to release solvent pressure.

X1.6.16 Close V12 and open V5.

X1.6.17 Open V12 to release nitrogen pressure. The system should now be completely depressurized.

X1.7 Calculation

$$S = M2 - M1 \quad (\text{X1.1})$$

where:

$$S = \text{mass of sample,}$$

$M1$ = mass of sampling cell empty, and
 $M2$ = mass of sampling cell with sample.

$M2$ = mass of sampling cell with sample.

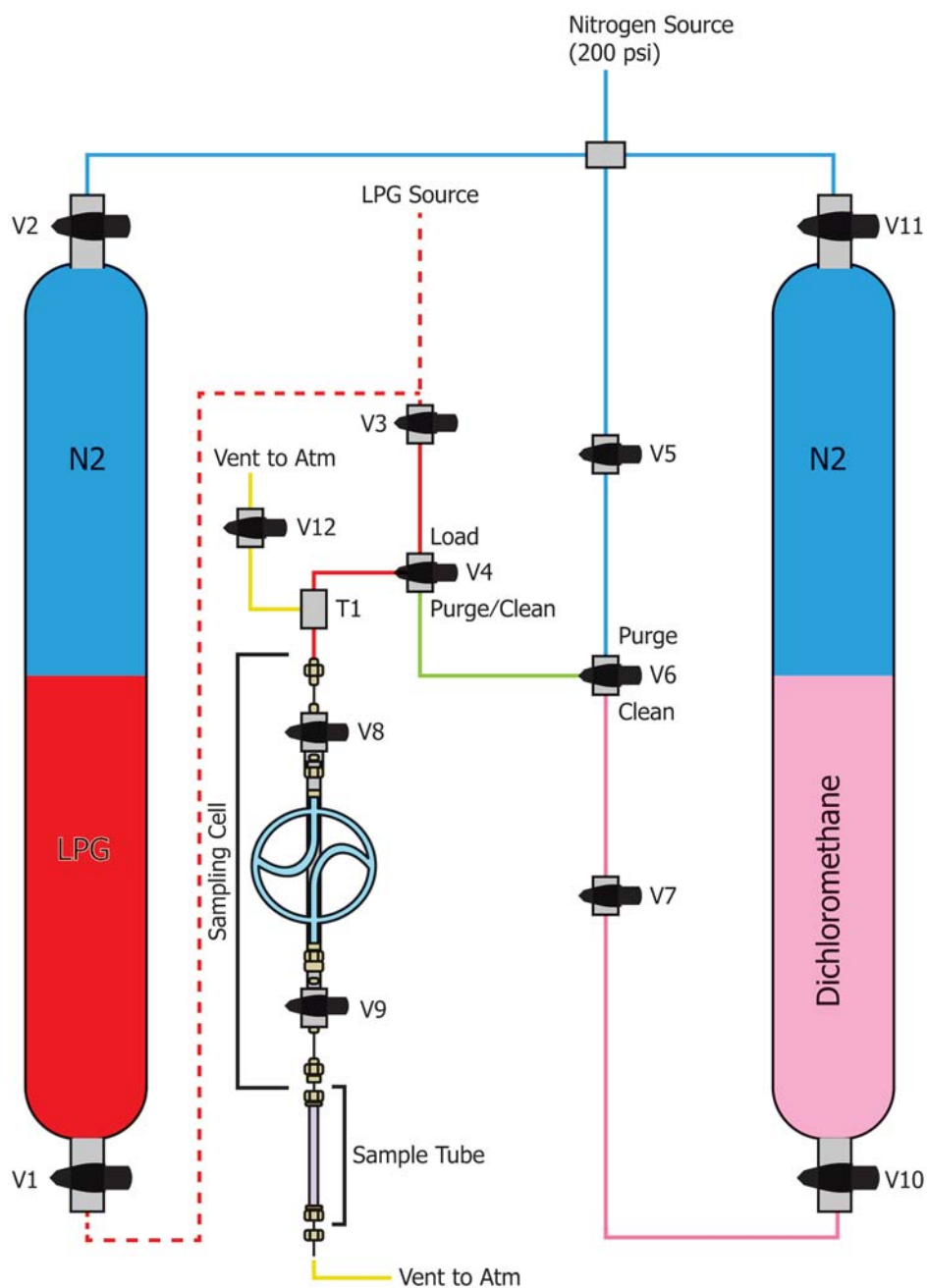


FIG. X1.6 LPG Residue Sampling System Without Sorbent Tube (System Clean and Sampling Cell Fill)

TABLE X1.1 Sampling Cell

Item	QTY	Unit	Description
1	2	Each	Swagelok 1/16 in. ball valve (PN SS-41GS1) - Phenolic Handle
2	13	Inch	1/8 in. Stainless Steel Tubing (0.028 in. wall thickness) - Sample Loop (~0.76 mL)
3	0.8	Inch	1/16 in. Stainless Steel Tubing (0.020 in. wall thickness)
4	2	Inch	1/16 in. Stainless Steel Tubing (0.010 in. ID - 0.026 in. wall thickness)
5	2	Each	Reducer - 1/8 in. male to 1/16 in. female
6	1	Each	Reducer - 1/8 in. male to 1/16 in. male
7	1	Each	Reducer - 1/4 in. male to 1/16 in. male
8	2	Each	1/8 in. Stainless Steel Nut & Ferrule Set
9	6	Each	1/16 in. Stainless Steel Nut & Ferrule Set
10	1	Each	Aluminum Support (12.6 g or less)

TABLE X1.2 Sampling System

Item	QTY	Unit	Description
1	8	Each	Swagelok 1/8 in. ball valve - Phenolic Handle
2	2	Each	Swagelok 1/8 in. 3-way valve - Phenolic Handle
3	1	Each	Swagelok 1/8 in. Tee
3	as req		1/8 in. Stainless Steel Tubing (0.028 in. wall thickness)
4	2	Each	500 mL Stainless steel cylinder (1800 psi MAWP)
5	1	Each	1/8 in. Stainless Steel Cross
6	1	Each	Stopwatch or Timer

Use the minimum amount of tubing between connections to reduce the dead volume of the system.

X2. PROCEDURE FOR SPIKING STANDARDS ONTO STANDARD TUBES

X2.1 A standard tube for this application is a two bed adsorbent tube with 1/4 in. glass wool plugs on each opening.

X2.2 The procedure for spiking a standard onto a sorbent tube is as follows:

X2.2.1 Fill a syringe with the appropriate volume;

X2.2.2 Insert the needle into the glass wool;

X2.2.3 Inject the standard into the glass wool from the side where the weaker adsorbent is located. This direction is marked on the tube with an arrow or is documented with the tube from the supplier;

X2.2.4 Place the tube on a flow stream so that carrier gas grade ultra pure (99.999%) can pass through the tube at a flow rate between 100 and 125 mL/min for 5 min. This flow sweeps the components into the adsorbent. Residue components are retained on the adsorbents, but a quantity of pentane is not retained.

X2.3 It is convenient to use a GC inlet for this gas stream. Connect the tube to the injector and increase the inlet pressure until there is a flow rate of approximately 100 mL exiting tube. Follow the diagram in Fig. X2.1 for the fittings.

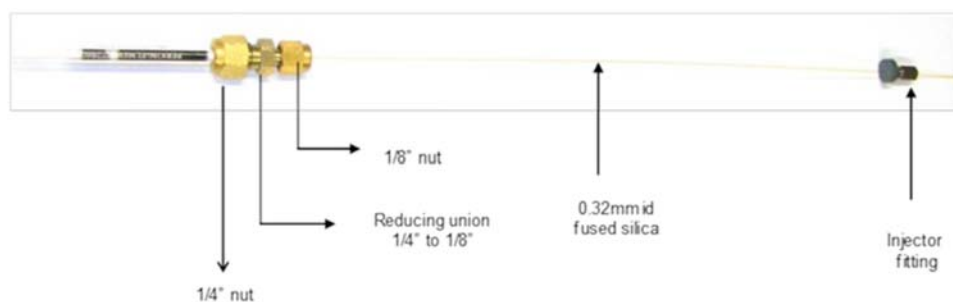


FIG. X2.1 Setup for Spiking Residue Calibration Standard Onto Sorbent Tube

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