# Dual Analysis of Oily Residues in LPG (ASTM D7756/EN 16423) and Hydrocarbon Composition of LPG (ASTM D2163 & ISO 7941)

## Introduction

Control over residue content is essential in end-use applications of automotive LPG. Residues can lead to troublesome deposits that will accumulate and corrode or plug the LPG fuel filter, the low pressure regulators, the fuel mixer or the control solenoids.
LPG can be contaminated with oily residues during its production or transport. Transport contamination can be a result of shared pipelines, valves and trucks used for the distribution of other products. Production sources such as the desulfurization process may contribute sulfur absorbent oil to the LPG stream. Commercial LPG, especially for automotive applications, should comply with current fuel specifications.

**Application Note**

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## Analysis of Oily Residues in LPG

Fuel specifications for oily residue in LPG list ASTM Method D2158 or EN Method 15470-1. ASTM Method D2158 is commonly called the oil stain method. After evaporating 100 milliliters of the LPG stream, the remaining volume of residue is read from the glass evaporation tube.
This volume is one quantification used for fuel specifications. In addition, the residue is dissolved in a solvent and the resulting solution is slowly dripped on the adsorption paper. The size and persistence of the stain which remains on the paper after the solvent evaporates is the other, empirical, quantification of the oily residue in the LPG sample. Both quantifications are not very accurate.

EN 15470 determines the oily residue by performing a gas chromatographic analysis of the residue that remains after evaporation of an LPG sample. EN 15471 uses the weight that remains after evaporation of 100 ml of LPG sample as the quantification.
All of these procedures offer a safety risk due to the required evaporation of flammable LPG samples.

## Compositional Analysis of LPG

The industry needs an alternative which not only quantifies the residue without LPG evaporation but also speeds up the analysis time and determines the hydrocarbon composition of LPG.

*Figure One: Agilent GC & DVLS Liquefied Gas Injector*

Various methods for the determination of hydrocarbon composition of LPG are available, such as ASTM D2163 and ISO 7941.

Da Vinci Laboratory Solutions developed an alternative technique for determination of oily residue in C3 and C4 streams that complies with ASTM D7756 and EN 16423.
This method uses a direct injection technique of the pressurized liquefied gas into the GC by means of the Liquefied Gas Injector (LGI). It provides a safe and accurate method for determining the oily residue.

Adding a liquid sampling valve (LSV) and external GC oven to this instrumentation allows the analysis of the hydrocarbon composition of LPG at the same time from the same sample cylinder.

## Boosting Laboratory Efficiency

## Application Description ASTM D7756/EN 16423

The ASTM D7756/EN 16423 application uses the Liquefied Gas Injector (LGI). This dedicated sampler is able to inject liquefied gases at room temperature directly on the GC column.
The sample is injected under a constant pressure.
The chromatographic analysis after the sample introduction is based on boiling point separation of the oily residues and contaminants.
The total residue is quantified using area summation of the components in the range of C10 to C40.
The result is reported in parts per million (w/w) of residue in LPG.

The GC is configured with the LGI as displayed in Figure One, an on-column injection port, a solvent vapor exit and Flame Ionization (FID) detection.

Figure Two shows the configuration of retention gap and columns. The sample is injected into a Sulfinert® coated stainless steel retention gap. The retention gap is connected to a non-polar retaining pre-column, with an exit for flushing the LPG matrix. After matrix venting, the valve is closed and the flow is directed to an analytical column for the separation of the various contaminants present in LPG.

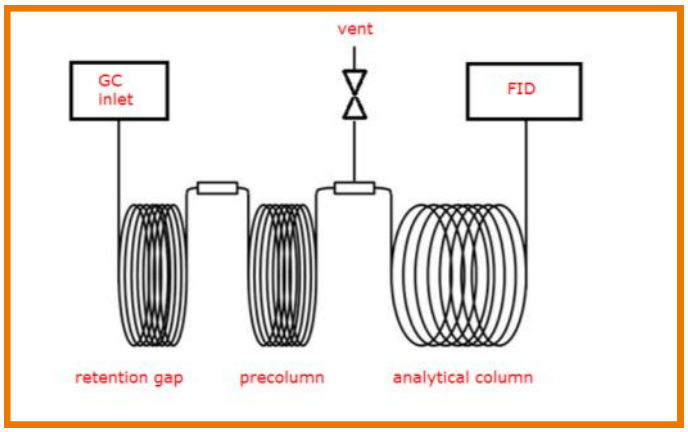



*Figure Two: Column Configuration ASTM D7756*

## Application Description ASTM D2163 & ISO 7941

Most methods for the LPG compositional analysis recommend the use of a liquid sampling valve (LSV) for LPG sample introduction into the GC split inlet.

The analysis of oily residues in LPG and the compositional analysis were combined by mounting the LSV in the 'sample out' line of the LGI.
In addition to the Cool on-Column inlet and detector for the D7756 application, the GC was equipped with an extra Split/Splitless inlet and FID detector for the compositional analysis as shown in Figure Three.

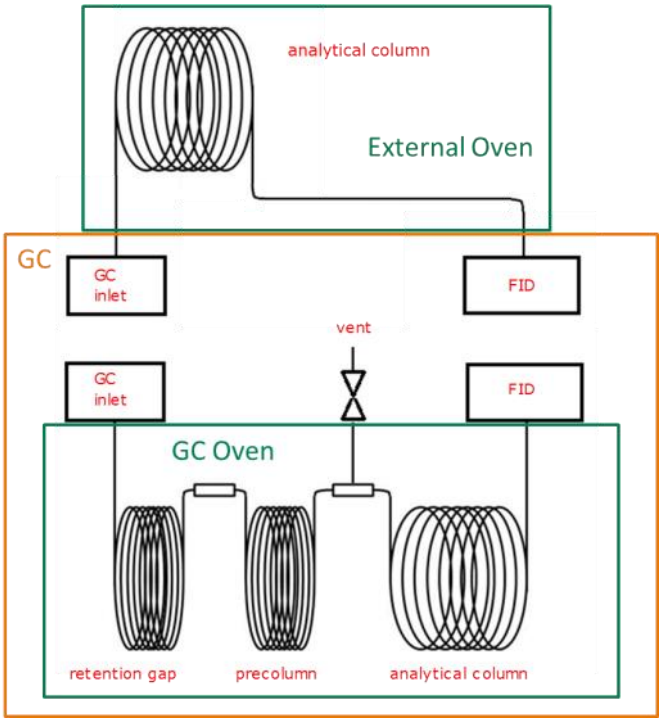



*Figure Three: Column Configuration ASTM D7756 & D2163*

The sample injection in the SSL inlet via the LSV was performed simultaneously with the LGI injection pulse.

The column for the compositional analysis was installed in an external oven, enabling running both the temperature program for the D7756 application and the compositional analysis simultaneously. Table One and Two show the typical instrument parameters .

## Analytical Results

Oily residue was added to automotive LPG. This was performed by preparing a stock solution of a mineral oil standard (RIVM-oil) in n-pentane. The stock solution was added to a sample cylinder and filled with LPG. Total amount of LPG added was determined by weighing the cylinder. A constant pressure of 25 bar was applied.
This sample was analyzed seven times with the above described instrumentation for combined residue in LPG and LPG hydrocarbon composition.

Figure Four shows the chromatogram of the residue analysis (D7756), Figure Five shows the LPG hydrocarbon composition. Table Three shows the precision data.

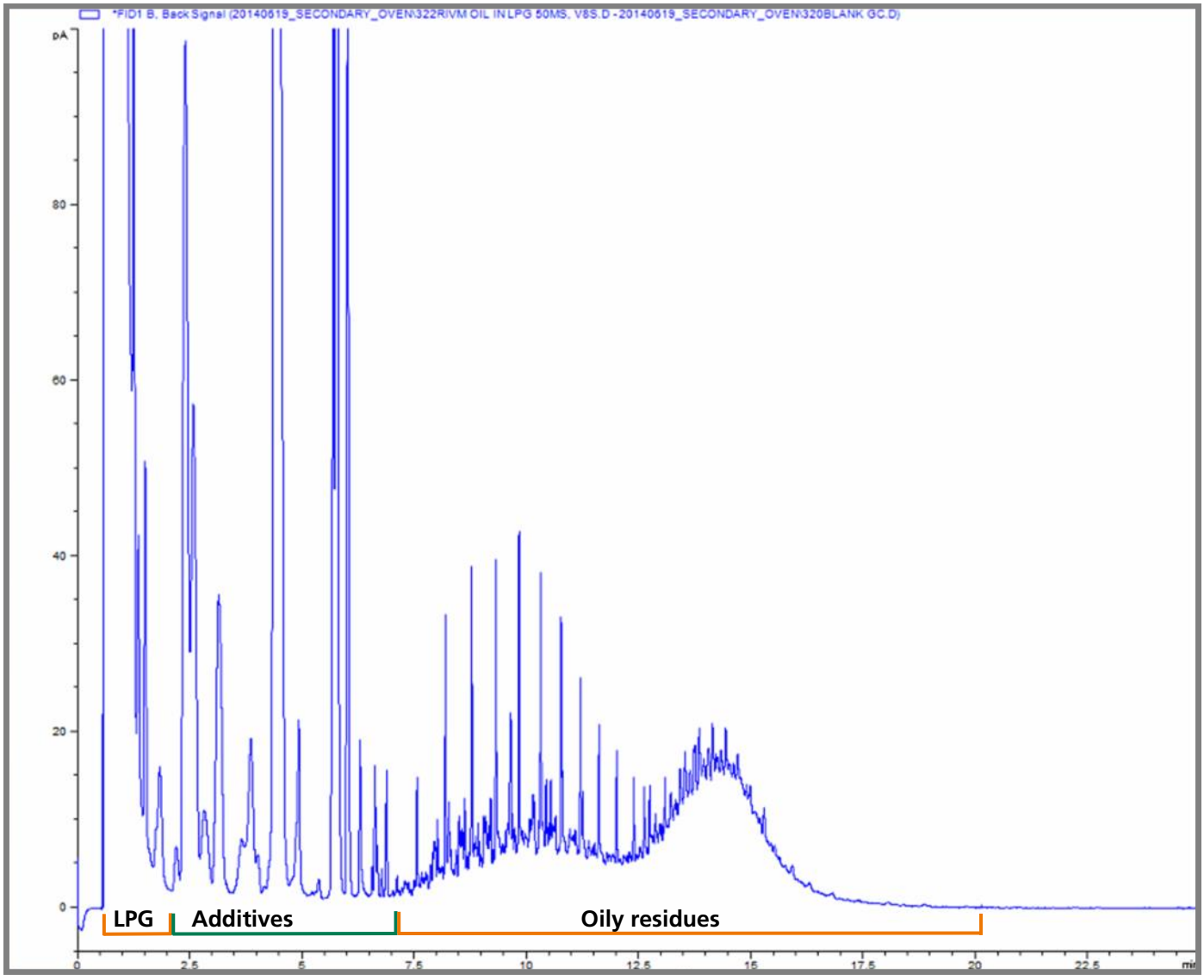
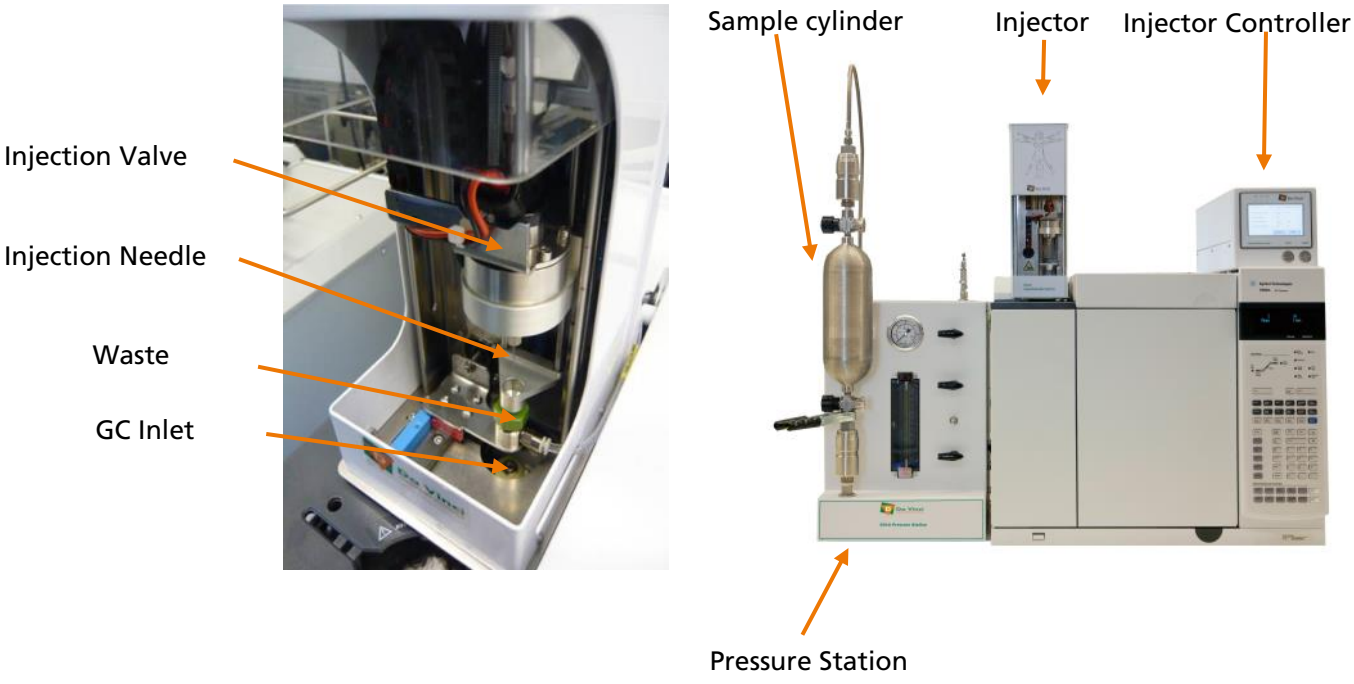



*Figure Four: Chromatogram of the oily residues analysis in commercial LPG (ASTM D7756)*



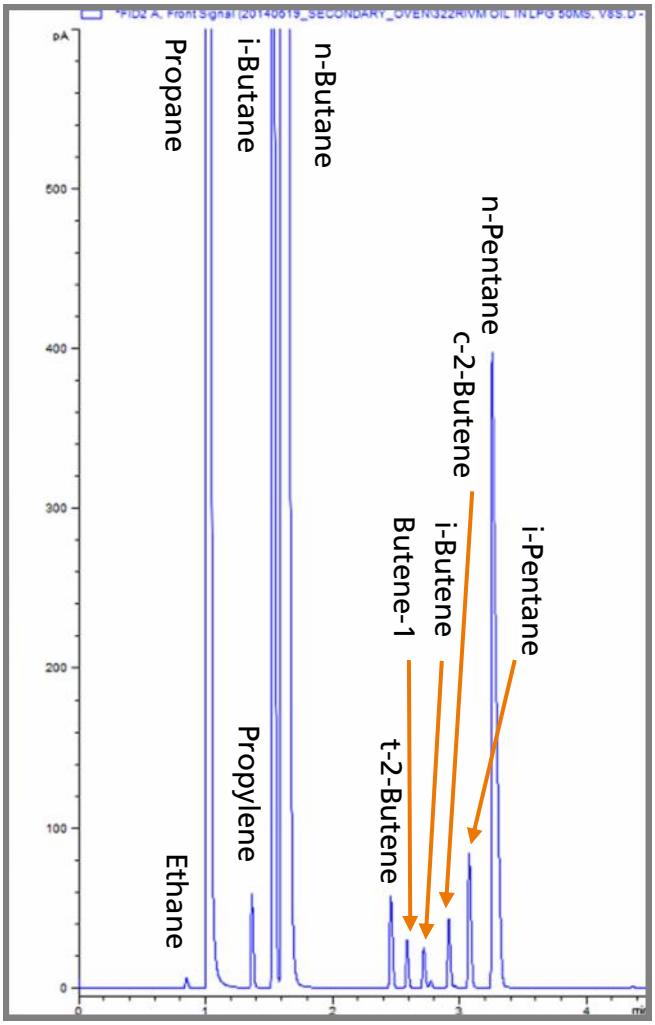



*Figure Five: Chromatogram of the Dual Analysis of the hydrocarbon composition*

| Instrument Parameters<br>Oily Residues in LPG ASTM D7756/EN 16423 | |
|---|---|
| Oven initial | 35°C (3 min) |
| Rate | 25°C/min |
| Oven final | 325°C (10.4 min) |
| Inlet initial | 55°C/min |
| Rate | 25°C/min |
| Inlet final | 325°C |
| Column flow | 6.0 mL/min |
| FID | 325°C |
| Hydrogen flow | 35 mL/min |
| Air | 350 mL/min |
| Solvent vent time | 8 sec |
| LGI injection pulse | 50 ms |

| Instrument Parameters<br>Compositional Analysis ASTM D2163/ISO 7941 | |
|---|---|
| Oven initial | 80°C (0.5 min) |
| Rate | 10°C/min |
| Oven final | 200°C (1 min) |
| Inlet | 250°C/min |
| Split ratio | 1:10 |
| Column flow | 4.0 mL/min |
| FID | 250°C |
| Hydrogen flow | 35 mL/min |
| Air | 350 mL/min |
| LSV sample volume | 0.06 µL |

Table One & Two: Typical instrument parameters

| Method | Oily Residues | Compositional analysis | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | | |
| Component | Oily Residue | ethane | propane | propylene | i-butane | n-butane | t-2-butene | butene-1 | i-butene | c-2-butene | i-pentane | n-pentane |
| Avg. Area Counts | 4935.9 | 8.5 | 29415.9 | 71.7 | 2080.6 | 11117.7 | 83.7 | 42.4 | 38.1 | 59.6 | 123.4 | 1028.0 |
| Stdev | 77.6 | 0.2 | 488.3 | 1.1 | 31.6 | 166.9 | 1.3 | 0.7 | 0.5 | 0.9 | 1.8 | 14.7 |
| %RSD | 1.6 | 1.8 | 1.7 | 1.5 | 1.5 | 1.5 | 1.5 | 1.6 | 1.2 | 1.5 | 1.5 | 1.4 |
| | | | | | | | | | | | | |
| Maximum difference between the calculated concentra-tions of the 7 analyses | 1.343 ppm | 0.009 Vol% | 0.088 Vol% | 0.0004 Vol% | 0.0119 Vol% | 0.074 Vol% | | | | | 0.001 Vol% | 0.01 Vol% |
| Repeatability according to ASTM | 5.159 ppm | 0.0001 Vol% | 0.777 Vol% | 0.020 Vol% | 0.077 Vol% | 0.223 Vol% | | | | | 0.023 Vol% | 0.057 Vol% |

*Table Three: Oily residue according to ASTM D7756 & LPG hydrocarbon composition*

The precision data demonstrate that the repeatability of the results of the analyses with the combined instrumentation for determination of oily residue according to D7756 & LPG hydrocarbon composition according to D2163 complies very well with the precision data of Interlaboratory Studies described by ASTM for both methods.

## Conclusion

The high pressure liquid sampling technique is developed by Da Vinci Laboratory Solutions and introduced in 2010 as the Liquefied Gas Injector (LGI). The LGI is standardized as ASTM D7756 and EN 16423. Adding an external oven with special valve configuration to a high pressure liquid sampling application offers the dual analysis of both oily residues in LPG and LPG hydrocarbon composition.
For the compositional analysis of LPG the LGI application was extended with a valve configuration as described in methods such as ASTM D2163 and ISO 7941. The analytical results demonstrates that the repeatability complies very well with both ASTM D7756 and ASTM D2163.

References:


1. ASTM D7756-13 :Standard Test Method for Residues in Liquefied Petroleum (LP) Gases by Gas Chromatography with Liquid, On-Column Injection
2. ASTM D2163 - 14e1 Standard Test Method for Determination of Hydrocarbons in Liquefied Petroleum (LP) Gases and Propane/ Propene Mixtures by Gas Chromatography
3. ISO 7941:1988 Commercial propane and butane—analysis by gas chromatography
4. Application note: the Analysis of Di-Iso-Propanol-Amine (DIPA) in Liquefied Petroleum Gas (LPG) with the DVLS LGI Injector



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