

## A Safe and Fast Solution for Accurate Quantification of Heavy Residues in LPG by Gas Chromatography: Representative Liquefied Gas Sample Introduction via High Pressure On-Column Injection into a Gas Chromatographic System

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One of the specifications of commercial LPG is the amount of oily residue. Oily residue leads to troublesome deposits that will accumulate and corrode or plug the LPG fuel filter, the pressure regulators, the fuel mixer or the control solenoids. Currently ASTM D2158 or ISO 13757 are used. These methods main disadvantage is that large amounts of LPG need to be evaporated which is a safety risk. The preferred alternative technique is gas chromatography. However, the quantitative analysis of high boiling components in low boiling matrices is an analytical challenge. The limitation is the sample introduction. Residue adsorption on transfer lines, vaporisers and valves lead to cross sample contamination or quantitative bias due to the fractionation of the heavy material.

A new liquefied gas injector is developed by Da Vinci Europe to inject under pressure directly onto the column. The sample remains in liquid phase, at room temperature and without contact with transfer lines, vaporisers or valves and therefore overcomes all limitations of the conventional sample introduction techniques. The chromatography after this representative sample introduction is based on boiling point separation and the total amount is reported in parts per million.

Control over the residue content is essential in end-use applications of automotive LPG. These 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 become contaminated by oily residues during its production or transport. Transport contamination can come from shared pipelines, valves and trucks used for the distribution of other products. Production sources such as the desulfurisation process may contribute sulfur absorbent oil to the LPG stream.

Commercial LPG, especially automotive applications, should comply with current fuel specifications for oily residue as described in ASTM Method D2158[1] or ISO 13757[2].

ASTM Method D2158 is commonly called oil stain method. After evaporating 100 milliliters of the LPG stream, 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 an empirical measure of the oily residue in the LPG sample.

The ISO 13757 method quantifies the oily residue by weighing what remains after evaporation of two kilograms of the LPG. Both of these procedures offer an undue safety risk due to the required evaporation step into the immediate environment.

The industry needs an alternative which not only quantifies the residue without LPG evaporation but also speeds up the analysis time and shortens product certification.

A preferred technique for LPG analysis is gas chromatography. The specification for major components in the LPG stream is already based on gas chromatographic techniques[3]. However, the quantitative analysis of high boiling components in low boiling matrices is an analytical challenge due to the difficulty of representative sample introduction into the chromatographic system. Light end quantification commonly uses injection devices such as high pressure syringes, piston valves, liquid rotary valves or vaporisers. These devices are limited in their ability to deliver a representative injection of higher molecular weight LPG components due to difficulties in controlling the sample pressure and/or temperature at the moment of injection.

Residue adsorption on transfer lines, vaporiser, and valves (heated or unheated) can lead to cross sample contamination or quantitative bias due to the fractionation of the heavy boiling material. Sample injection under pressure directly onto the column is one way to avoid these problems as this ensures the injected sample remains in a liquid phase, at room temperature, and without contact with transfer lines, vaporisers, or valves.

A new approach for LPG GC sample introduction using these design principles has recently been developed by Shell Global Solutions and Da Vinci Europe laboratory solutions. This new approach offers a safe, fast, reproducible and representative on-column sample introduction and analysis of heavy molecular weight components in LPG. The device used for sample introduction is called the Gasoline Direct Injector (GDI), and is based on the standard fuel injection device for gasoline engines. After injection, the GC analysis technique uses a vapor exit function to flush the LPG light end fraction. The oily residue remains on-column and can be separated by boiling point. The result is reported as concentration in ppm and by Carbon number distribution. Analytical column choice aids in specific component separation and identification; for

example an amine column can be used for identification and measurement of DIPA (diisopropanolamine).

This paper gives a brief overview of the configuration of the instrument and its possibilities.

### Experimental

Sample introduction device: the sample introduction principle is based on the "gasoline direct injector" (GDI) commonly used in car engines (Figure 1).

(a) The GDI is filled with the LPG under pressure. (b) After activation of the solenoid, the LPG is sprayed through an on-column needle either to waste for purging or to column for analysis. (c) After injection, the position returns to start position.

The GDI is mounted on a sliding device (Figure 2) which moves the GDI downwards for injection and upwards for waste. An on-column needle is attached to it allowing injection into the gas chromatograph.

The sample cylinder is pressurized to keep the matrix stable during sample charging. The sample flows in a stable liquid phase through the lines. Sample flow can be controlled and routed in discrete bursts through the GDI either to waste or injected directly onto the GC

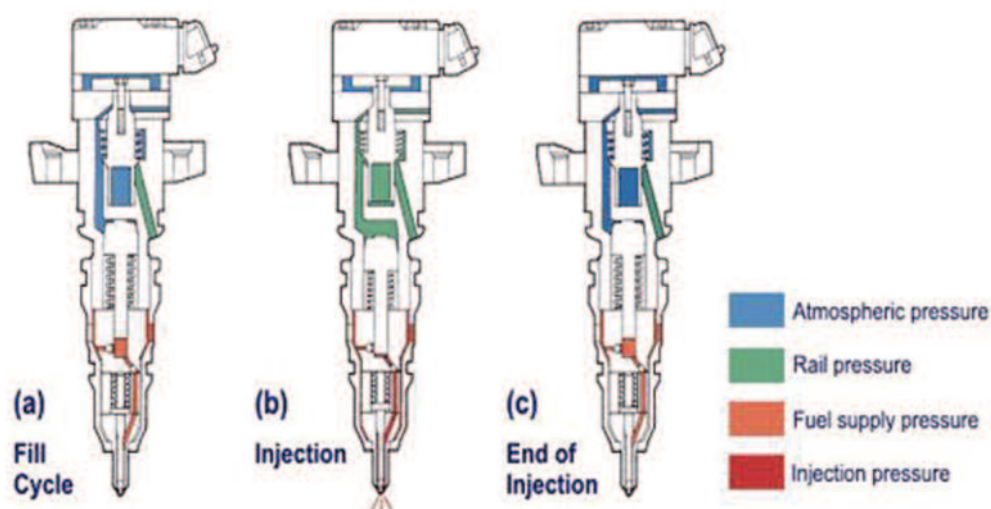


Figure 1: Schematic overview of the different positions of the Gasoline Direct Injector

column. For a representative analysis, the sample must remain in the liquid phase. To ensure this, a device is used that adds high pressure nitrogen to the sample cylinder and controls the outlet pressure (Figure 2). The waste sample is vaporised and safely connected to a central waste system.

This combination of the GDI injector with the pressurization and control station with the electronics will, hereafter, be referred to as the Liquefied Gas Injector (LGI).



Figure 2: GC system dedicated to the Liquefied Gas Injector

On top of GC: Gas Direct Injector (GDI) with an on-column needle attached to it and mounted on a sliding device. GDI is in injection position with an on-column needle inserted into the on-column injector of the GC. Left from GC: Pressure station. This enables sample integrity and representative sample injection. On top of pressure station: Sample container. The sample container is connected to 25 bar nitrogen. When the cylinder is opened, the sample fills the injector. Flow is controlled via a rotor meter in the pressure station designed to allow easy inspection of the sample. Waste LPG leaves the system via a vaporiser installed in the pressure station and connected to an appropriate waste system. Right from the GC: controller with the electronics for the injector.

### GC Analysis

The GC is equipped with an on-column injector and solvent vapor exit. Figure 3 shows the configuration of retention gap and columns. Sample is injected into a 5 meter Sulfinert® coated stainless steel capillary. The retention gap is connected to a 3 meter non polar retaining column, with an exit for flushing the LPG light ends. Subsequently, the exit is closed and the flow is switched to the non-polar analytical column for residue separation by boiling point. Table 1 shows typical settings of the gas chromatograph and column details.

## Results and Discussion:

### Heavy Residue in LPG

Calibration is done by a certified mixture of mineral oil and LPG. Figure 4 shows a chromatogram of mineral oil in LPG. Validation can be done by preparing standards in pentane. This is advantageous with respect to safety and can be conveniently and cheaply prepared by the analysing laboratory. Validation standards can be prepared by weighing the desired concentrations on a calibrated balance. The results are obtained by subtracting a blank run from the sample run. The weight of the residue is the sum of components between C10 and C40. A response factor of 1 is used and area of the sample is compared with the total area of a known standard. The carbon number distribution is determined by injection of a known normal-Alkane distribution sample.

### DIPA in LPG

Automotive LPG is tested for diisopropanolamine (DIPA) after it has been treated for sulfur. The GC analysis using the LGI provides quantitative results for DIPA in LPG (Figure 5). A single GC analysis gives both DIPA content and total mineral oil contamination.

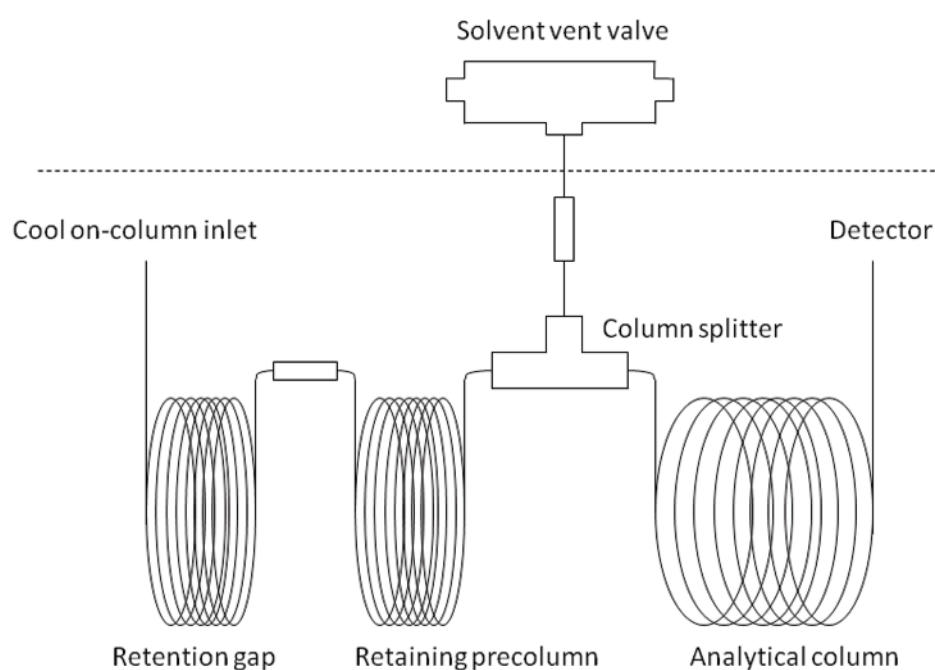


Figure 3: GC column configuration for analysis of LPG injected via Liquefied Gas Injector

Oven program	40 °C for 2 min, 40°C - 340°C at 25 °C/min, 340°C for 10 min
Inlet program	Type: cool on-column Temp: 65 °C for 2 min, 65°C - 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® coated stainless steel capillary with outer diameter of 0.029", inner diameter of 0.021" and length of 33 ft Retaining pre-column: 3 m CP SIL 8CB 3 m, 0.53 mm 0.32 µm Analytical column: HP-1 20 m, 0.25 mm, 0.32 µm
Pressure station	Sample flow: 2 ml/min Nitrogen pressure: 25 Bar Nitrogen purge pressure: 5 Bar
Liquefied Gas Injector	Injection: 25 ms

Table 1: Typical chromatographic conditions and columns for analysis of oily residue in LPG by means of LGI direct injection.

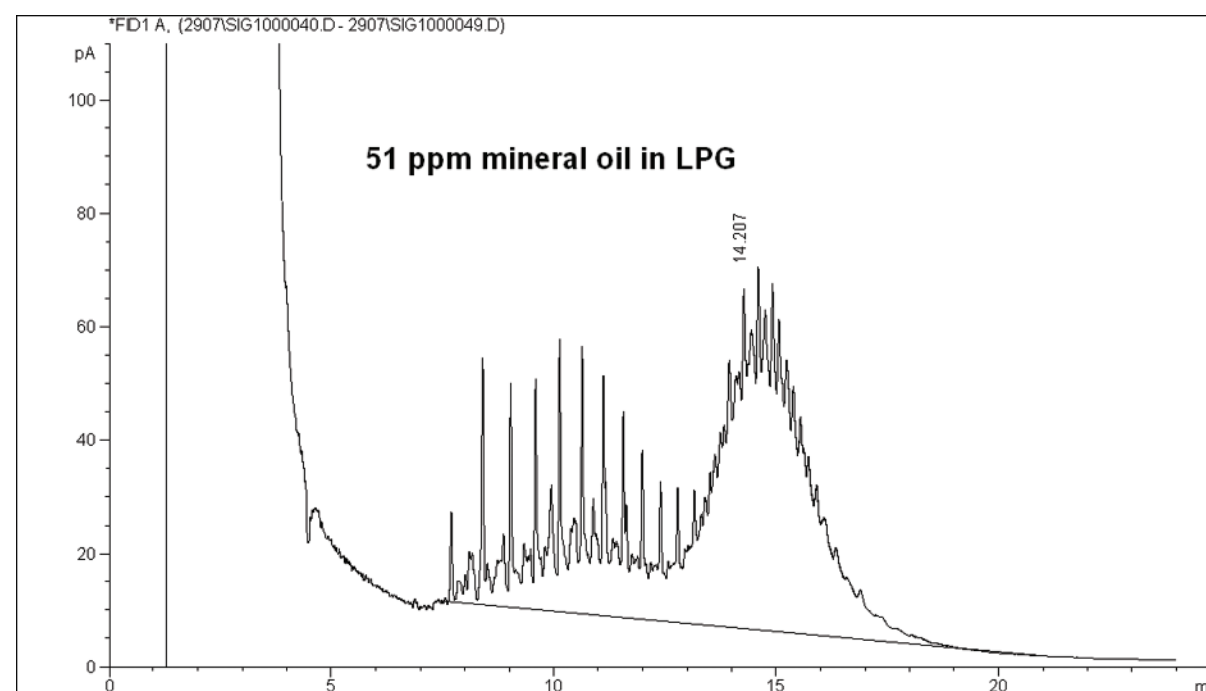


Figure 4: Chromatogram of 51 ppm mineral oil in LPG



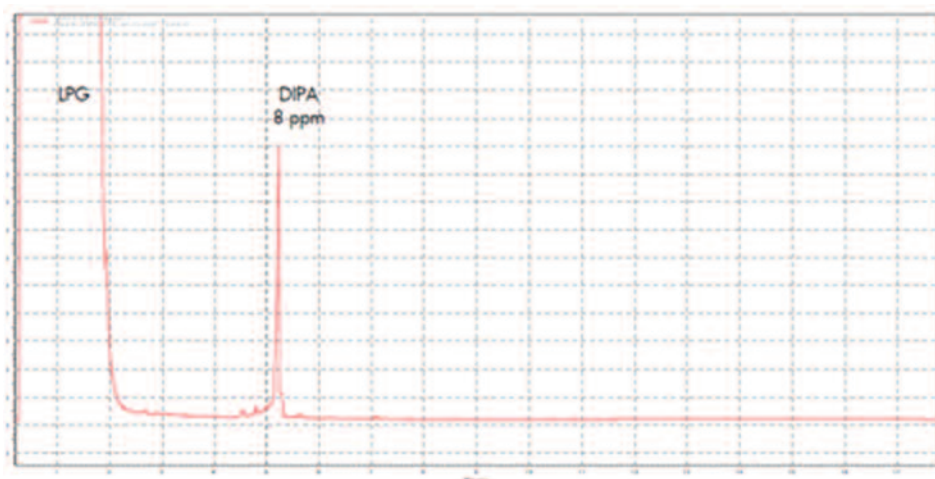


Figure 5: Spiked sample of 8 ppm DIPA in LPG analysed using GC in combination with LGI.

	Mineral Oil	DIPA
Minimum Detection limit	1 ppm	100 ppb
Repeatability	3%	5%

Table 2: Specifications of GC analysis of Mineral Oil and DIPA in LPG using GC in combination with Liquefied Gas Injector.

Sample	Residue Manual Method (mg/kg) ISO 13757	Difference GC - Manual (mg/kg)
1	11	-1.8
2	2	-0.7
3	22	-2.3
4	3	-0.8
5	10	-4.2
6	3	0.5
7	3	1.7
8	10	-0.57
9	1	-2.1
10	14	-0.7

Table 3: Correlation between determinations of heavy residue in LPG determined manually according to ISO 13757 and using GC in combination with Liquefied Gas Injector.

### LGI – GC versus current methods

The minimum detection level for heavy residue in LPG using LGI – GC is 1 ppm, with a repeatability of 5% (Table 2). For DIPA this is 100 ppb and 3% respectively (Table 2). This is far more accurate, convenient, faster and safer compared to the current methods which use evaporation, weighing and oil stain-on-filter-paper examination. Correlations made between the methods are good (Table 3). As there is no partial loss of the C9 to C11 fraction (which bias the results of the ISO 13757 method) the results of the GC/LGI method are generally higher.

Moreover, the injection system uses a closed system and much smaller sample amounts which enhances safety. No evaporation of large LPG volumes to the open air and the attendant monitoring and sample handling is needed. Analysis time is only 24 minutes and, as a result, product release can be approved faster. The chromatographic fingerprint and carbon number distribution is a great help in determining the source and type of the contamination.

### Conclusion:

The industry now has an alternative for the determination of oily residues in LPG. The ASTM D2158 and ISO 13757 methods can be supplemented and eventually replaced by a GC method. This GC method gives the industry a safer, more reliable, and robust method to determine, both qualitatively and quantitatively, LPG residue in less than half an hour. The results are directly comparable to those given by the conventional methods, with far less risk of injury or fire due to sample handling and physically performing the test procedures, with the additional benefits of enhanced accuracy and information, regarding contamination type and source.

### References:

1. ASTM Standard D2158 - 05. Standard Test Method for Residues in Liquefied Petroleum (LP) Gases
2. ISO Standard 13757. Liquefied petroleum gases - Determination of oily residues -- High-temperature method (2006).
3. ASTM D2163 - 07 Standard Test Method for Determination of Hydrocarbons in Liquefied Petroleum (LP) Gases and Propane/Propene Mixtures by Gas Chromatography