The Analysis of Contaminants in Liquefied Gases by Gas Chromatography

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Contaminants in liquefied gases are an analytical challenge. Contaminants are often high boiling or unstable components and their high molecular weight relative to the lighter matrix complicates the introduction of a representative sample into a gas chromatograph. The use of vaporisers, injection valves, and transfer lines is not recommended due to the effects of discrimination, adsorption, and fractionation of these high boiling components during the sample introduction process. Current standardised test methods are not direct injection GC based, and determine dissolved high molecular weight residue by evaporating large volumes of the liquid sample, boiling off the light fraction, and thereby isolating the so called residue. This is then examined for volume or weight, visually inspected, or dissolved in a solvent and injected into a gas chromatograph. These methods are time consuming, have poor precision, and present a health and safety risk.

An alternative gas chromatographic method which features representative liquid phase injection is now available with the development of a new type of GC injector introduced by Da Vinci Europe laboratory solutions, an injector referred to as the Liquefied Gas Injector or LGI. An ASTM standard method for oily residue in LPG (ASTM D7756-11) based on direct on-column injection has recently been balloted and approved and will be available for distribution in December 2011. The LGI complies with this new method.

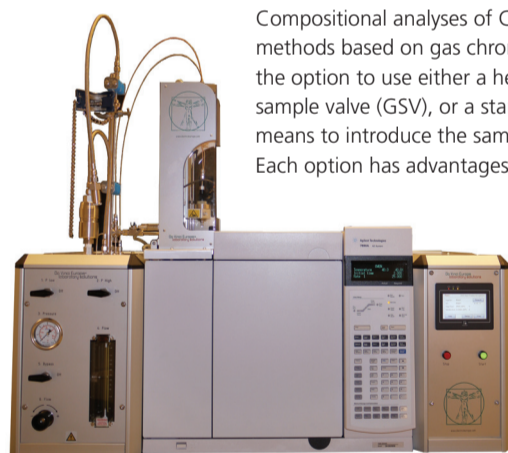## Liquefied Gas Analysis Featuring Injection of Sample in the Liquid or Gas Phase.

Compositional analyses of C3 and C4 streams are generally done by methods based on gas chromatography. Standardised methods offer the option to use either a heated vaporiser in series with a gas sample valve (GSV), or a standalone liquid sample valve (LSV), as the means to introduce the sample into the analytical system. Each option has advantages and disadvantages and both require continuous pressurisation to maintain the pressure of the cylinder contents during the sample purge and injection. Calibration in these methods generally involves the use of external standards and the GC detector calibrant/sample response is directly compared. Therefore both GSV and LSV usage require the same volume of sample and calibrant to be injected.

Figure 1. GC system dedicated to the Liquefied Gas Injector

The use of a LSV makes the injection volume independent of the atmospheric pressure, but attention must be paid to the flow path to ensure the sampling system internal volume is filled and purged with the pressurised sample in liquid phase, free of gas bubbles, solids, or water. The use of a rotometer with a sight glass placed in the flow path is a good option to visually check the condition of the flow contents prior to activating the valve. The sample injection volume of a heated vaporiser with GSV does depend on the atmospheric pressure. Calibration and sample analysis must be performed under the same atmospheric conditions to ensure that the volume injected is the same for both. The purge time and flow of sample through the system must be carefully regulated and duplicated from sample to sample and sample to calibrant. Standard Operating Procedure (SOP) specifications commonly call for several minutes of purge time before the GSV is activated in order to ensure prior sample components have been displaced from the internal volume of the sample system and equilibrium is achieved at the liquid/gas interface of the vaporiser. However, in both approaches there is a tendency for components with a higher boiling point than the gas matrix to deposit in the tubing between the sample cylinder, the vaporiser and sampling valve or the sampling valve and the injection port/column of the GC. The current evaporative test methods define the target "residue" as the material that remains in place after the light ends have flashed, so it is not surprising that at least some of it adsorbs to the tubing between the sample flash and the GC column. Heated sample lines and valves will reduce but not entirely solve this problem. Therefore, when the "residue" itself is the target analyte, the liquid sample cannot be vaporised in an upstream injection system, but must flash in the column, where the residue can be deposited completely and representatively, and where the higher temperature capability of the GC oven can vaporise and move it through the analytical system to the detector.

This ensures accurate quantification of the residue contained in the individual sample charge. What the industry needs is an alternative that takes the precision, speed and convenience provided by gas chromatography in the analysis of the major components of liquefied gas, and applies these advantages to the determination of the dissolved residue. The development of the LGI sample introduction technology provides the means to accomplish this. The conventional evaporative test methodology can now be replaced by a more modern, instrument based approach which is not subject to the limiatations of current GC injection systems.

Liquefied Gas Injector

Da Vinci Europe developed the new type of GC injector in close cooperation with Shell Global Solutions and introduced it in 2010. It has been designated as the Liquefied Gas Injector. This injector is able to inject liquefied gases at room temperatu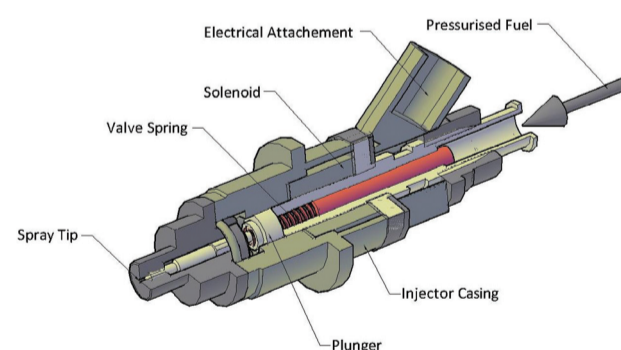re directly on column. The Liquefied Gas Injector is based on the proven "gasoline direct injector" (GDI) used in the automotive industry to inject fuel into the automotive engine combustion chamber.

Figure 2. Schematic overview of the Gasoline Direct Injector

The LGI GDI has been modified and connected to a standard GC injector needle, which can be inserted into existing GC large volume on-column injection systems. Solenoid activation using millisecond timing transfers the pressurised sample through the needle directly on-column. Sample volume can be varied by changing the GDI activation time. For example a 30 ul volume injection occurs when the activation time is 25 ms seconds at a sample pressure of 25 Bar.

The GDI is mounted on a sliding device (Fig. 3) 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.

Figure 3. GDI transformed to a GC injector

Gas Chromatograph

The Gas Chromatograph is equipped with a large volume cool on-column injection port, a solvent vent option and an FID. The typical column configuration is shown in Figure 4.
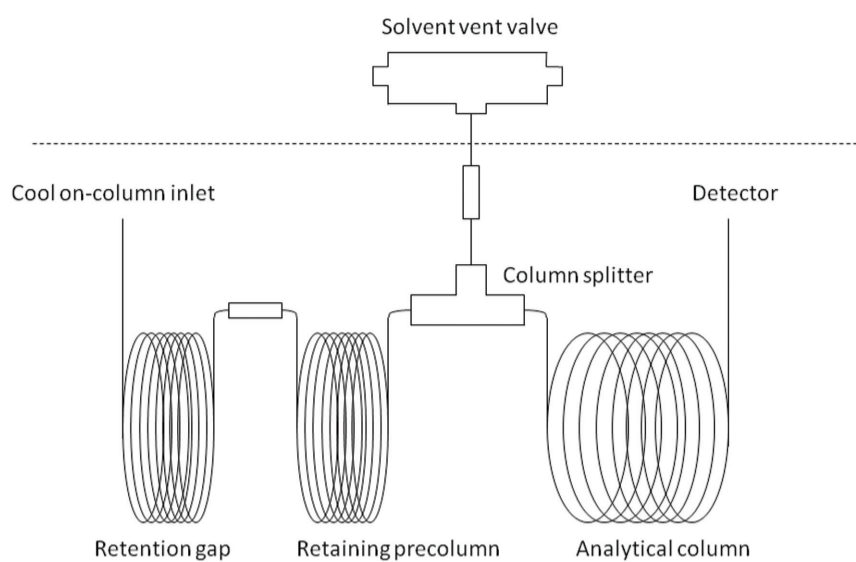

Figure 4. GC column configuration for the analysis of high boiling components, injected via the Liquefied Gas Injector
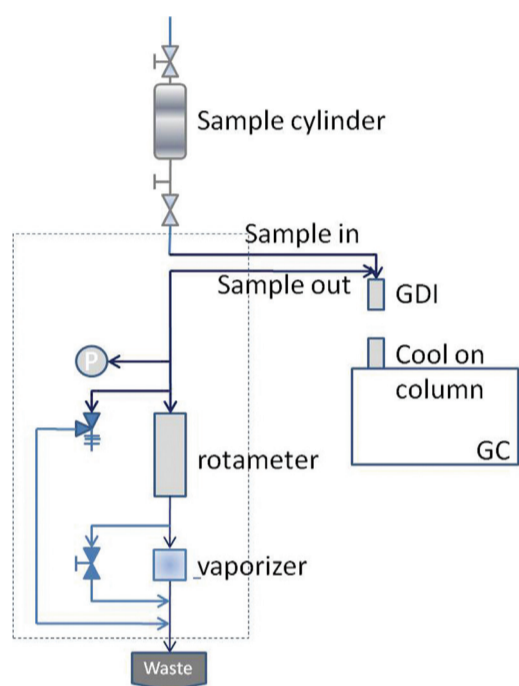

Figure 5. Pressure Station to maintain the sample in liquid phase

Sample is injected into a 5 meter retention gap of Sulfinert® coated stainless steel capillary. This retention gap is connected to a 3 meter non polar retaining column, with an exit for flushing the matrix light ends. Subsequently, the exit is closed and the flow is switched to the analytical column. The selected analytical column is based on the application.

For a representative analysis, the sample must remain in the liquid phase. To ensure this, a device (designated the Pressure Station) is used to add high pressure nitrogen to the sample cylinder and to control the outlet pressure (Fig. 5).

The waste sample is vaporised and safely connected to a central waste system. This combination of the GDI injector with the pressure and control station including the electronics will, hereafter, be referred to as the Liquefied Gas Injector (LGI).

GC System Dedicated to the Liquefied Gas Injector

Figure 1 displays the GC/LGI system. On top of the GC: Gas Direct Injector (GDI) with an on-column needle attached to it and mounted on a sliding device. On the left side of the GC: Pressure station. This enables sample integrity and representative sample injection. On top of the pressure station: Sample container. The sample container is connected to 25 Bar nitrogen. When the cylinder is opened, the sample fills the injector. The rotometer in the pressure station allows easy inspection of the sample. Waste leaves the system via a vaporiser installed in the pressure station and connected to a central waste system or exits the building. On the right side of the GC: electronics to drive the injector and enter the number of purge cycles and GDI activation timing to control injection volume.

Sample Introduction Procedure

The sample cylinder is installed on the pressure station using quick connects. High pressure inert gas (generally nitrogen due to price and availability) is applied to the cylinder. The sample flows in a stable liquid phase through the lines for approximately 3 minutes in discrete bursts. After line flushing is completed, the GDI needle is routed to the GC inlet and the solenoid activated for the set time. A 30 ul volume injection takes 25 ms seconds at a pressure of 25 Bar. The injector then starts the GC and the temperature program.

LGI Application to Mineral Oil in LPG (ASTM D 7756-11)

Control over the residue content in LPG is essential to the end-use applications of LPG. Oily residue in LPG is a contamination which can occur during production, transportation or storage. Current test methods are ASTM D2158, ISO/EN15470 and 15471 and are based on the evaporation of large amounts of the product at atmospheric pressure. The GC with the LGI was setup for the application of oily residue analysis in LPG in the range of C10 through C40

Table 1 is an overview of the typical analysis conditions of the application and figure 6 shows the results of the GC/LGI analysis. Figure 6 is an overlay of chromatograms with oily residue concentration in the range of 10 to 600 mg/kg.

The precision of this method is expressed as follows: Repeatability Limit, mg/kg = 0.09(X + 12) The relative standard deviation was between 2.4 and 4.7%.

Table 1. Analysis conditions for oily residue analysis in LPG

| Oven program	35°C for 3 min, 35-340°C at 25°C/min, 340°C for 10 min
Inlet program	Type: cool on-column Temp: 65°C for 3 min, 55- 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® stainless steel capillary with inner diameter 0.53mm and length of 5m. Retaining pre-column: 3m 100% Dimethylpolysiloxane, 0.53mm 2.65μm Analytical column: 100% Dimethylpolysiloxane 30m, 0.32mm, 0.25μm
Pressure station	Sample flow: 2 mL/min Nitrogen pressure: 2500kPa Nitrogen purge pressure: 500kPa
Liquefied Gas Injector	Injection: 25ms
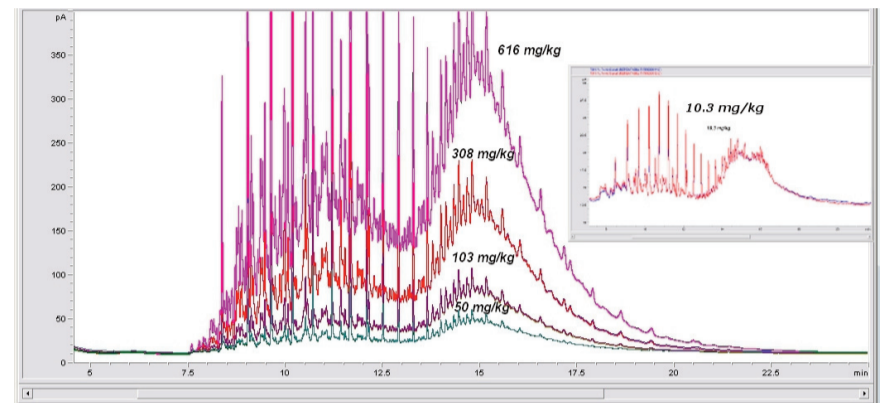
Figure 6. repeatability of oily residue by LGI/GC (ASTM D 7756-11)

Application p-Tertiary-Butylcatechol in Butadiene

p-Tertiary-butylcatechol (pTBC) is commonly added to commercial butadiene in amounts of 50 to 250 mg/kg as an oxidation inhibitor. A current test method to determine the total inhibitor content is ASTM D1157. Similar to other LPG methods, it is based on evaporation of (100ml) butadiene and determines the p-TBC by measuring the absorbance using a photoelectric photometer after adding FeCL3.
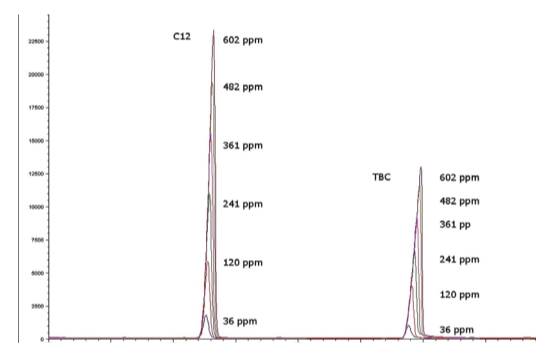

Figure 7. overlay of 6 chromatograms with p-TBC concentration between 36 and 602 mg/kg by GC/LGI

Table 2: relative standard deviation of pTBC by GC/LGI

pTBC concentration in mg/kg	Relative standard deviation
36	2.4%
120	3.3%
241	3.0%
361	1.6%
482	3.3%
602	4.0%

The method is labor intensive and presents a health risk; Butadiene is extremely flammable and a suspected human carcinogen. Therefore the closed sample flush system of the Liquefied Gas Injector is a great improvement in terms of safety. The following chromatogram (Figure 7) is an overlay of 6 chromatograms of different concentrations obtained with LGI/GC and the column configuration described in Table 1 (Application: mineral oil in LPG).

The C12 in the chromatogram of Figure 7 is a marker in the calibration mixture for determining the recovery of the p-TBC.

The repeatability of the ASTM D 1157 method Total Inhibitor Content (TBC) of Light Hydrocarbons in the range of 50 to 500 mg/kg is 10 mg/kg. The LGI/GC method has an analysis time of 15 minutes and the relative standard deviation is less than 4% as shown in Table 2.

Conclusion

The Liquefied Gas Injector opens up the Gas Chromatography technique for complex analysis in C3 and C4 streams such as LPG and Butadiene. The LGI allows repeatable and representative sample introduction of ppm high boiling components without carryover.

The analytical column and detector can be customised to the analyte. Two applications are described in this article. The application for oily residues in LPG has recently been balloted and approved by ASTM as D7756-11. The new ASTM method will be available for distribution in December 2011.

Moreover a proof of principle has been carried out successfully for the analysis of elemental Sulphur and DIPA in LPG.

The LGI/GC is a fast, safe and accurate alternative to current non GC methods and the LGI expands the application range of direct injection GC sample introduction systems.
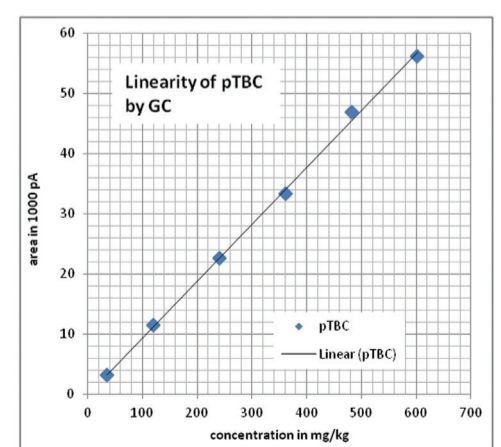

Figure 8. linearity of pTBC by GC/LGI, y = 0.0947x-0.1648, R² = 0.9985