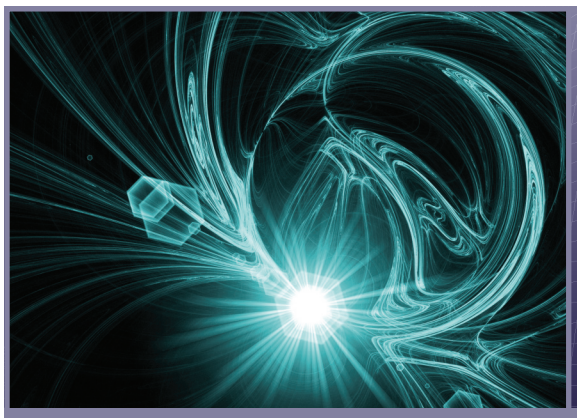

Unique Automated LPG Residue Analysis at ppm/ppb Level by GC

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Analysis of LPG streams is very common on Refinery laboratories. The analysed components have a wide boiling point range, from methane to heavy oil fractions. Global Analyser Solutions offers a comprehensive range of instruments, using 3 different sample injection techniques, covering the complete boiling point range of all components of interest.

LPG samples are normally injected into the GC in gaseous state after vaporisation, using a gas sampling valve (GSV), or directly as a liquid, using a liquid sampling valve (LSV). The latter is the preferred method, avoiding discrimination of heavier components. This technique delivers satisfactory quantitative results for volatile and medium volatile components, provided that the sample pressure is controlled. The required instrument configuration is discussed in this article. The automated analysis of high boiling components like DIPA (diisopropanolamine) and heavy oil fractions in LPG is a real challenge; many laboratories use the labor intensive and risky ISO 13757 method, which dictates evaporation of large amounts of LPG sample, and determination of the residue content by weighing. In this article, the automated and safe analysis of these demanding compounds at low ppm level is described.

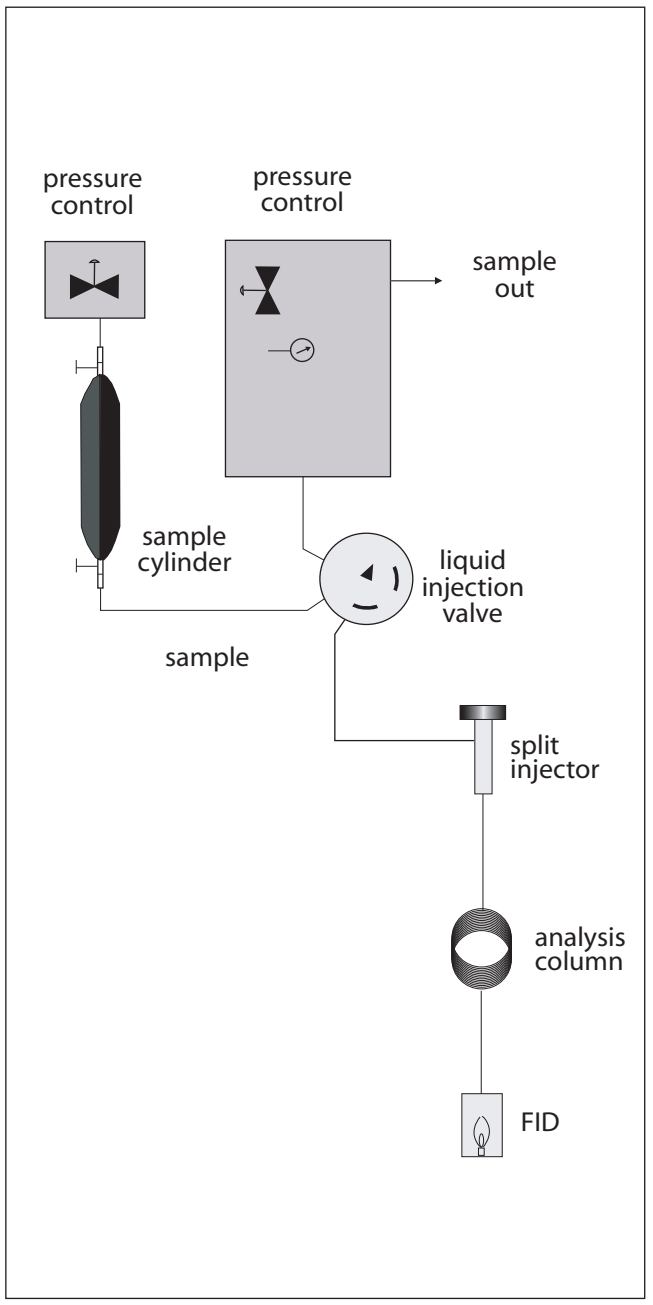

Figure 1: Schematic diagram of the LPG analyser with pressure controlled sample flush of the Liquid Sampling Valve

Analysis of Volatile and Medium Volatile Components

The analysis of volatile and medium-volatile components in LPG streams is widely performed in many laboratories. The sample can be injected in gas or liquid state. In the first method, the sample is gasified using the Vaporiser Facility, which is build around a heated pressure regulator, and subsequently the gas is injected on the column using a gas sampling valve.

When correctly applied, this method is satisfactory for volatile components up to C_4/C_5 hydrocarbons.

In case of medium volatile components, starting at C_5/C_6, liquid injection is preferred to avoid the loss of higher boiling components. The liquid sample is injected by LSV into the heated Split injector for fast evaporation before entering the analysis column. For reliable quantitative results, it is essential that (partial) evaporation of the sample in the sample loop is prevented by all means. This is achieved by raising and controlling the pressure at the sample cylinder and LSV, using pressures up to 20 bar. See figure 1 for the basic configuration. Figure 2 shows the utilised Pressure Facility.

Figure 3 shows chromatogram of the analysis of impurities in propylene with FID detection. In figure 4 PFPD (Pulsed Flame Photometer Detector) detection is applied for selective analysis of sulphur component at ppb level. Both channels can run simultaneously in one GC instrument with two LSVs and two columns, or using only one analysis channel by splitting the column effluent to both detectors. Figure 5 shows the optional autosampler for LPG sample cylinders, with built-in Pressure Facility. A series of 10 cylinders is analysed by pushing only one button. Figure 6 shows the excellent repeatability.

Figure 2: LPG analyser with LSV and Pressure Facility, which is available for different sample cylinder sizes and connectors.

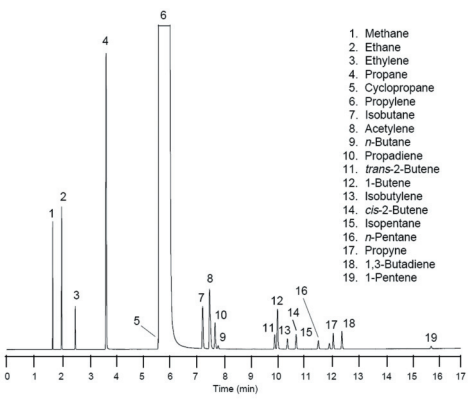

Figure 3: Impurities in propylene at ppm level. FID detection

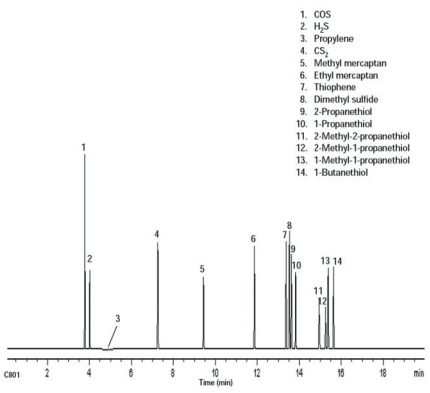

Figure 4: Sulphur components in propylene at ppb level using PFPD detection

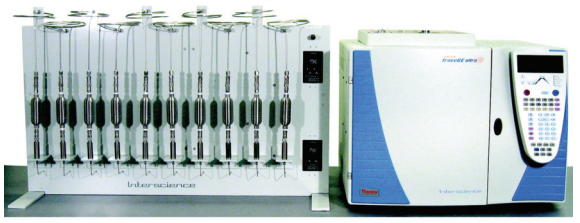

Figure 5: Auto sampler for 10 LPG cylinders. Other position numbers are available on request

Residue Analyis Of LPG Samples

There is also a need for analysing heavier and polar components in LPG, like mineral oil and DIPA. The above mentioned method using LSV is not applicable for these components. In order to keep the sample in liquid state,

Trace GC-FID Instrument Name	I-Butane Area	Butane Area
Trace GC Valve Inj	75405191.00	112744059.00
Trace GC Valve Inj	74606676.00	111717664.00
Trace GC Valve Inj	74925955.00	111509427.00
Trace GC Valve Inj	75377429.00	112744895.00
Trace GC Valve Inj	75092654.00	112570174.00
Trace GC Valve Inj	73793171.00	110533659.00
Trace GC Valve Inj	74145739.00	110950372.00
Trace GC Valve Inj	74078879.00	110862094.00
Trace GC Valve Inj	74135522.00	111265145.00
	Min: 73793171.00	110533659.00
	Max: 75405191.00	112744895.00
	Mean: 74617912.89	111655276.56
	Std Dev: 606575.71	849350.84
	%RSD: 0.81	0.76

Figure 6: Repeatability of the analysis of butane / iso-butane sample using automated liquid injection with the optional autosampler.

the injection valve is normally not heated, and therefore the components of interest are (partially) trapped in the valve and transfer-tubing to the split injector. Subsequently quantitative analysis is not possible. Refinery labs therefore analyse these components as described in ISO 13757 and ASTM D2158. Large amounts of LPG are evaporated in these methods, and the residue content is determined by weighing or measuring the volume. The methods are not very accurate, components of interest may partially evaporate as well, and compounds like anti icing additives give erroneous results. Moreover, the methods are very labor intensive and bring along severe safety risk. For this reason, Da Vinci Europe laboratory solutions BV developed the Liquefied Gas Injector. The method works excellent for mineral oil and DIPA, and the feasibility for other applications is considered, among them are: diesel in ethane, pole oil in ethylene, TBC (tertiary butyl catechol) in butadiene, alcohols in hydrocarbon feed streams and EBHP (ethyl benzene hydro peroxide) in SMPO (styrene monomeer propene oxide).

Working principle and results

The sample is directly transferred from the sample cylinder into the analysis column (on-column injection), using elevated pressure, without using LSV and split injector. Discrimination, fractionation and adsorption of the compounds are avoided in this way. Sample volumes of 10 to 50 ul are injected, resulting in very low detection limits of 100 ppb for DIPA, and 1 ppm for oil (C10-C40) in LPG. The repeatability is respectively 3 and 5 %, which is excellent for this type of analysis. See the chromatograms in figure 7 and 8.

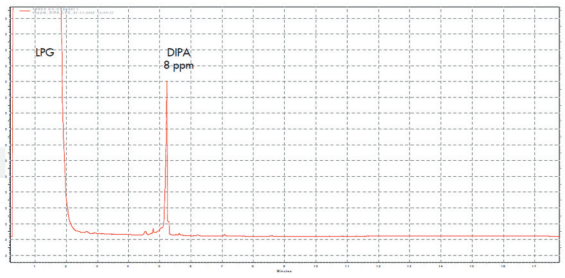

Figure 7: Analysis of DIPA at ppm level in LPG. LDL is 100 ppb, repeatability is 3 %.

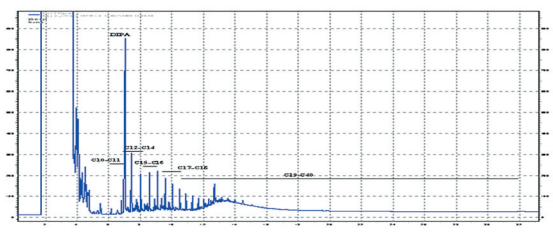

Figure 8: Chromatogram of spiked sample of mineral oil and DIPA. LDL for mineral oil is 1 ppm, repeatability is 5 %. The chromatogram is a fingerprint of the contaminating source, and will therefore help to identify.

Figure 9 shows the DVE Liquefied Gas Injector. The operation is easy and safe: a 250 ml cylinder is connected to the Pressure Facility; after flushing, the sample is injected by the auto sampler. In figure 10, the correlation with ISO 13757 is shown. The evaporation temperature in this method is 105°C, which results in partial loss of C10-C11 components. The presented GC method has no loss at all of these components, and produces high accurate results.

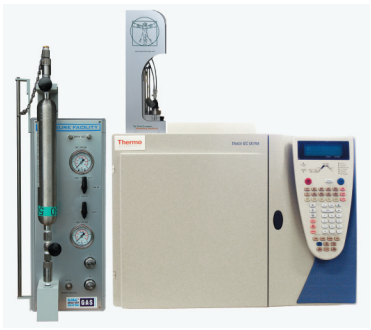

Figure 9: LPG residue analyser with DVE LGI

Sample	Residual 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	-0.0.57
9	1	-2.1
10	14	-0.7

Figure 10: correlation with ISO 13757

Summary

Global Analyser Solutions offers an integral line of products for the analysis of the complete boiling point range of components in LPG and other refinery streams. The unique DVE Liquefied Gas Injector delivers high quantitative results for high boiling components by GC analysis, as an alternative to the labor intensive and dangerous ISO 13757 and ASTM D2158 methods.