GC Analysis of Sulfur Compounds in LPG using the DVLS Liquefied Gas Injector combined with a Sulfur Specific Detector

Introduction

Many sources of liquefied petroleum gases (LPG) contain sulfur compounds that are odorous, corrosive and poisonous to catalysts used in petroleum and chemical refining. The sulfur content of LPG used for fuel purposes is subject to government regulations. For these reasons process feeds and finished products need to be analyzed for sulfur compounds. This application note describes the gas chromatographic analysis of sulfur compounds in LPG using the DVLS Liquefied Gas Injector (LGI) combined with a Sulfur specific detector.

Application Note

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Analysis of LPG

For end-use LPG various standardized specifications are available, including ASTM D1835, EN 589 and ISO 9162, all of which prescribe several tests for sulfur analysis.
Various test methods are available for measuring the total amount of sulfur. Other methods (e.g. D5623, D5303, D5504) are specifically designed for quantification of individual sulfur compounds. These latter methods use gas chromatography for the separation of sulfur compounds and a sulfur specific detector.
The sample is introduced into the GC inlet via a gas or liquid sampling valve (GSV or LSV).

Da Vinci Laboratory Solutions developed the Liquefied Gas Injector, a closed system for the direct injection of liquefied petroleum gases into the GC inlet. The difference to a sampling valve is the direct injection of the liquefied gas via a needle into the GC inlet— similar to an automatic liquid sampler. This avoids contact of the sample with transfer lines, vaporizers or valves and it ensures a good sample transfer into the heated zone of the inlet.

Application Description

The LGI consists of an Injector, a Pressure Station and Controller. The Injector is configured on top of the GC inlet. The Pressure Station is installed next to the GC and ensures that the Injector is filled with the sample in liquid phase.

Figure One: the DVLS Liquefied Gas Injector

The Injector includes the proven fuel direct injection technique used by the automotive industry to inject fuel into the automotive engine combustion chamber.
The LGI was introduced in 2010. It was originally applied for the analysis of oily residue in LPG. This method has been approved as ASTM D7756 and EN 16423.

The current study describes the application of the LGI-GC technique for the analysis of sulfur compounds in liquefied Propane and Butane samples and in a liquid Pentane sample. For the sulfur detection a sulfur specific Flame Photometric Detector (FPD) is used.

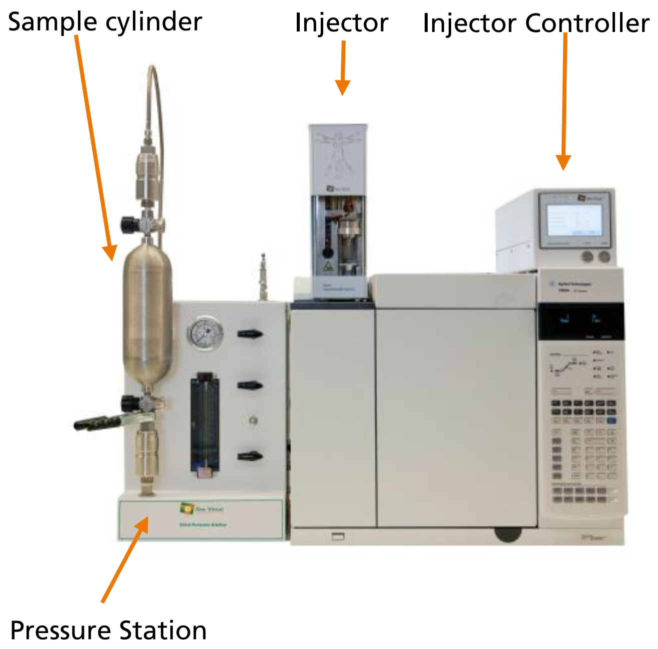

Figure Two: DVLS Liquefied Gas Injector installed on the GC

Analytical Results

The samples were analyzed using the instrument settings as shown in Table One.

The chromatogram of each sample shows one or more sulfur compounds. Based on retention times various peaks could be assigned to specific compounds: Carbonyl Sulfide (COS), Dimethyl Sulfide (DMS) and Dimethyl Disulfide (DMDS).

Instrument Configuration and Settings	
LGI	
Inject pulse	15 ms
Nitrogen sample pressure	25 bar
GC	
Inlet	SSL
Inlet temperature	250°C
Oven	50°C (3 min) → 270°C, 10°C/min
Split ratio	1:1
Columns	PoraBond Phase
Carrier	Helium
Detector	FPD

Table One: Instrument Configuration and Settings

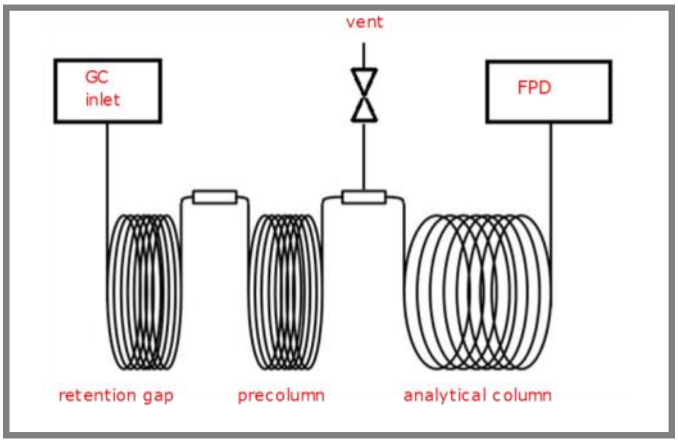

Figure Three: The column configuration of the Liquefied Gas Injector

For quantification a calibration standard of sulfur compounds is prepared in n-Pentane. Results are corrected for the differences in densities between sample and calibration standard according to the procedure prescribed in ASTM D7756 and EN16423.

The Limits of Quantification (LOQs) ranged from 0.18 to 0.27 mg sulfur/kg and the Limit of Detection (LODs) from 0.05 to 0.08 mg sulfur/kg. The LOQ and LOD are defined as, respectively, 10 and 3 times the standard deviation of the noise.

The chromatograms demonstrate that the hydrocarbons, that are present in large amounts, cause quenching of the FPD signal. This is a generally known phenomenon for Flame Photometric Detectors.
Therefore it is important to select the appropriate GC column and set the correct conditions to resolve the coelution of the sulfur compounds with the bulk of hydrocarbons.
Once this has been achieved the instrument will be able to detect a wide range of sulfur compounds. When using a Pulsed Flame Photometric Detector (PFPD) or a Sulfur Chemiluminescence Detector (SCD) the sensitivity of the analysis method can even be increased. An advantage of the SCD detector is that the signal is not influenced by the hydrocarbon matrix.

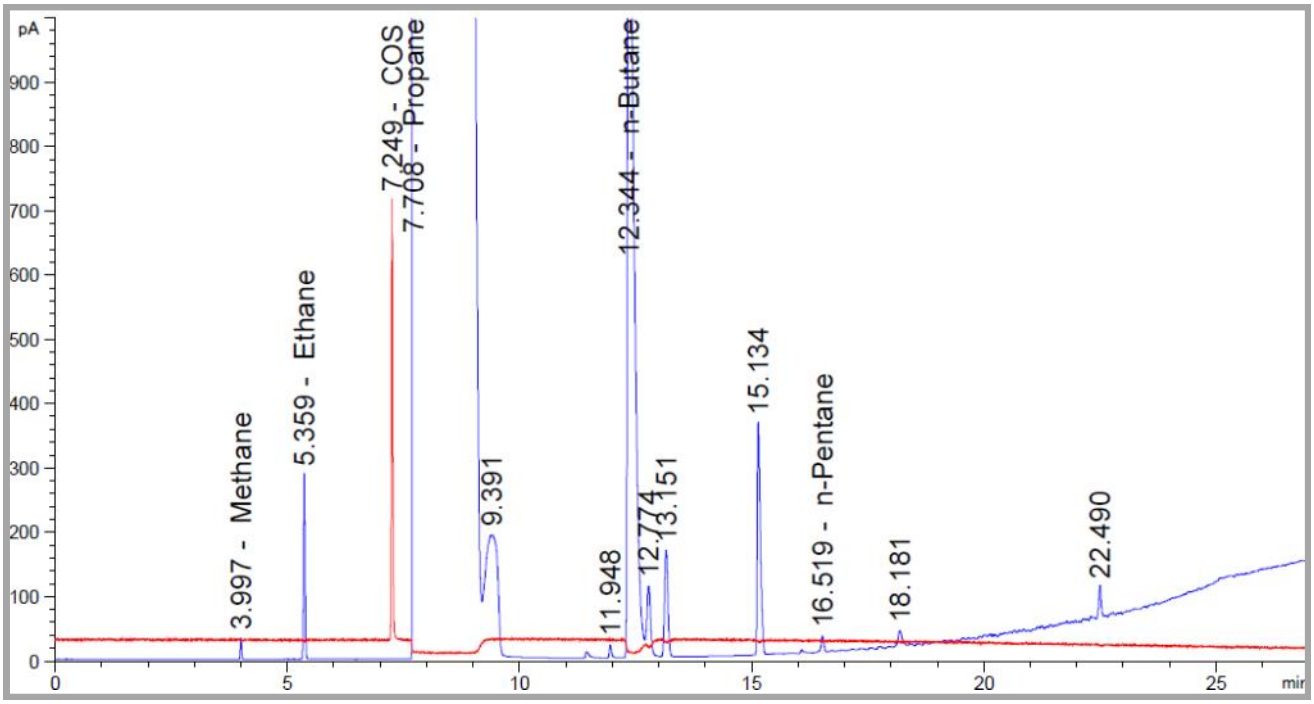

Figure Four: Chromatogram of the LGI analysis of liquefied Propane: FPD signal = red, FID signal = blue

	Sulfur Conc.	%RSD	LOQ	LOD
	(mg Sulfur/kg)		(mg Sulfur/kg)	(mg Sulfur/kg)
COS	0.51	0.6	0.18	0.05

Table Two: Results of the LGI analysis of liquefied Propane

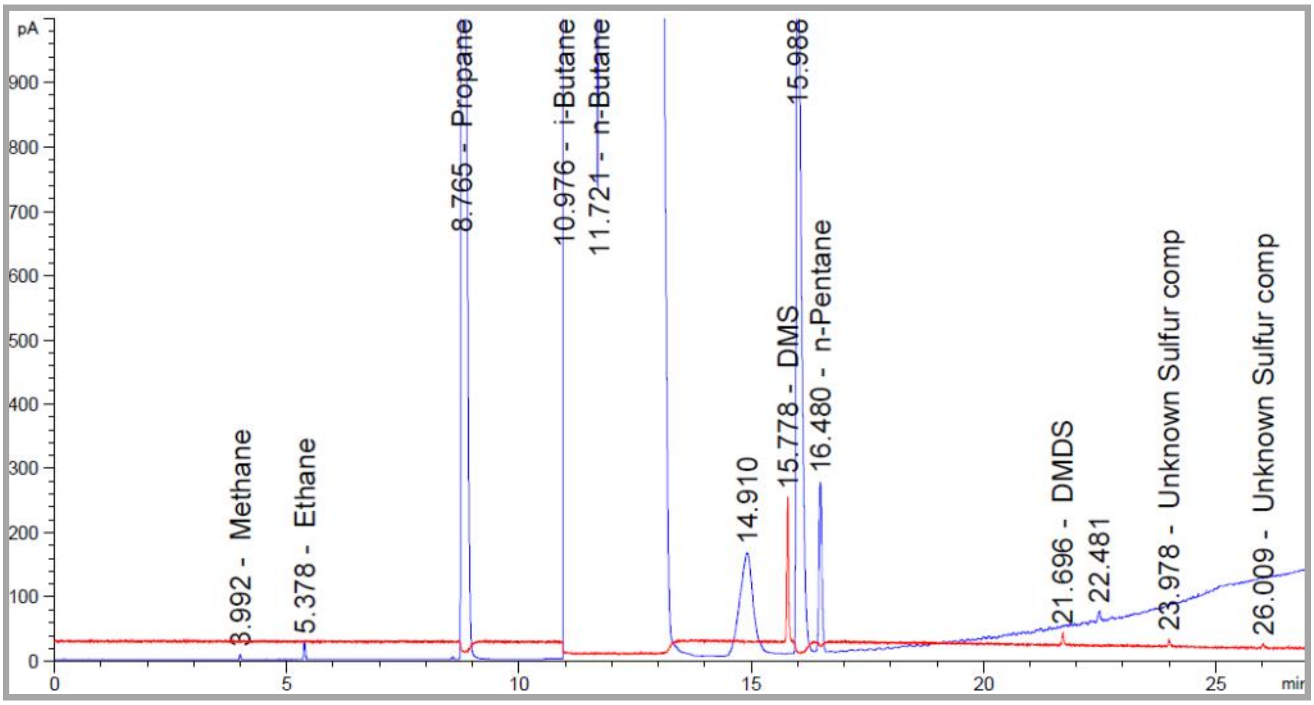

Figure Five: Chromatogram of LGI analyis of liquefied Butane: FPD signal = red, FID signal = blue

	Sulfur Conc.	%RSD	LOQ	LOD
	(mg Sulfur/kg)		(mg Sulfur/kg)	(mg Sulfur/kg)
DMS	0.34	0.3	0.19	0.06
DMDS	0.09	4.3	0.19	0.06
Unknown S comp. Rt 23.979	0.08	3.7	0.19	0.06
Unknown S comp. Rt. 26.008	0.05	2.4	0.19	0.06

Table Three: Results of the LGI analysis of liquefied Butane

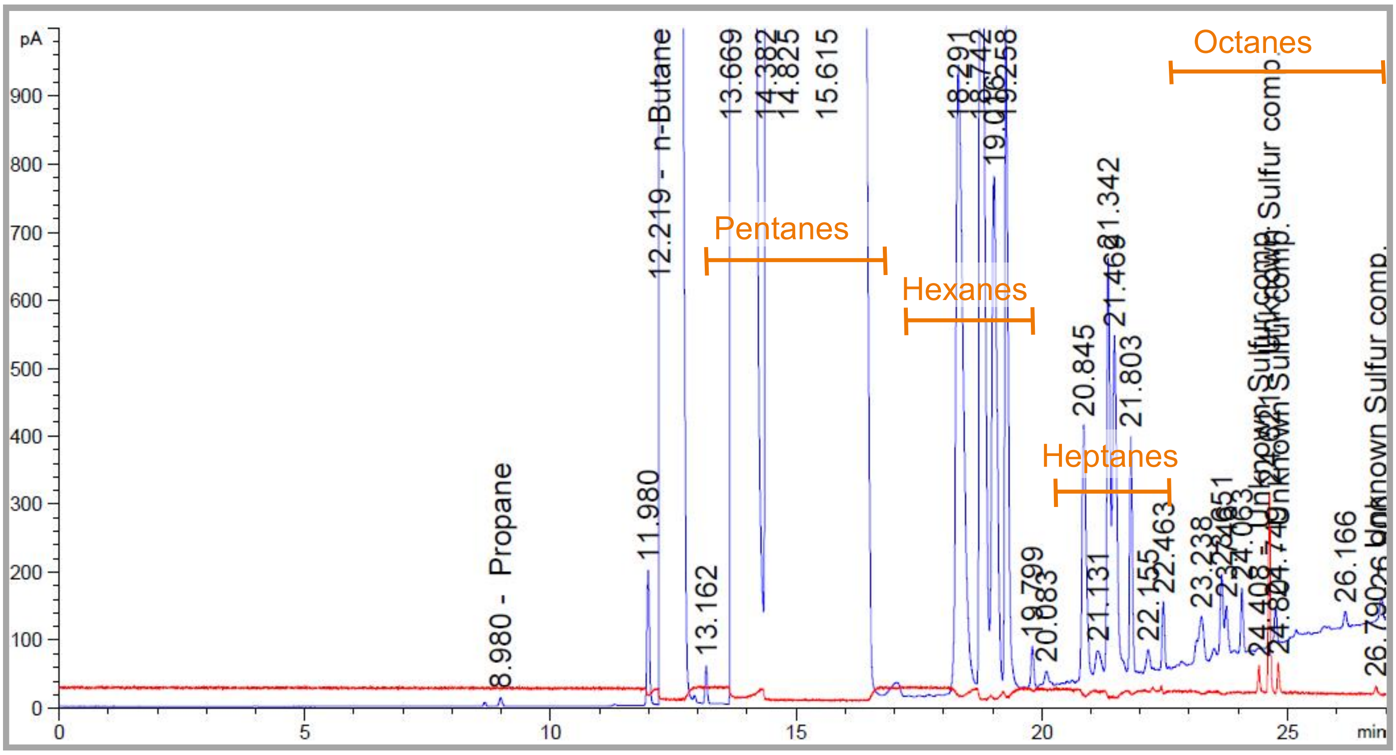

Figure Six: Chromatogram of LGI analysis of liquid Pentane: FPD signal = red, FID signal = blue

	Sulfur Conc.	%RSD	LOQ*	LOD*
	(mg Sulfur/kg)		(mg Sulfur/kg)	(mg Sulfur/kg)
Unknown S comp. Rt 24.408	0.15	1.2	0.26	0.08
Unknown S comp. Rt 24.621	0.40	2.0	0.27	0.08
Unknown S comp. Rt 24.801	0.16	2.0	0.26	0.08
Unknown S comp. Rt 26.790	0.08	3.9	0.20	0.06

Table Four: Results of the LGI analyis of liquid Pentane

Conclusion

The LGI-GC technique has been successfully applied for the analysis of sulfur compounds in liquefied Propane and Butane and also in liquid Pentane. Using a PFD detector LOQs range from 0.18 to 0.27 mg sulfur/kg and LODs from 0.05 to 0.08 mg sulfur/kg respectively. When using an PFPD or SCD detector an even higher sensitivity can be achieved. The LGI-GC technique combined with a sulfur specific detector offers a powerful tool for sulfur control of liquefied petroleum gas samples and liquid pentane samples.

References:

1. ASTM D7756-13 :Standard Test Method for Residues in Liquefied Petroleum (LP) Gases by Gas Chromatography with Liquid, On-Column Injection
2. Application note: The Analysis of Liquid Ethane by On-column Gas Chromatography with the DVLS LGI Injector
3. Application note: Dual Analysis of Oily Residues in LPG (ASTM D7756/EN 16423) and Hydrocarbon Composition of LPG (ASTM D2163 & ISO 7941)

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