The Analysis of Liquid Ethane by On-column Gas Chromatography using the DVLS Liquefied Gas Injector

Introduction

Ethane is an important petrochemical feedstock. The two main sources of ethane are natural gas and petroleum gas; a mixture of gaseous hydrocarbons that arise as a byproduct of petroleum refining. The main use of Ethane is to produce Ethene (also called Ethylene) for the chemical industry. This application note describes the gas chromatographic analysis of liquid Ethane by a direct injection of the sample into the GC injection port using the DVLS Liquefied Gas Injector (LGI).

Application Note

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Liquid Sampling

The Liquefied Gas Injector is an instrument dedicated to a direct injection of liquid gas samples into a GC inlet system. The LGI incorporates an innovative high pressure liquid sampling technique developed by Da Vinci Laboratory Solutions (DVLS).

The direct injection approach of the LGI includes the proven fuel direct injection technique used by the automotive industry to inject fuel into the automotive engine combustion chamber.
The LGI consists of an Injector, a Pressure Station and a Controller.
The Injector is configured on top of the GC inlet.
The Pressure Station is installed next to the GC and keeps the sample pressurized using Nitrogen. This enables a constant pressure of the liquid sample and allows to inject a representative and repeatable amount of the sample. The Controller box on top of the GC drives the injection cycling.

Residue Analysis

The LGI was introduced in 2010. Originally it was developed for the analysis of oily residue with a boiling point range of C10 to C40 in Liquefied Petroleum Gases (LPG), defined as (mixtures of) liquid Propane, Propylene and Butane. The method has been approved as ASTM D7756 and EN 16423.
For the oily residue analysis using the LGI the sample is injected in a Cool on-Column (COC) inlet. The light ends of the matrix are vented through a solvent vent valve. The residue compounds with higher boiling points are retained on a precolumn. After closing the vent valve, the retained compounds are separated on the analytical column.

Boosting Laboratory Efficiency

Figure One: Agilent GC & DVLS Liquefied Gas Injector

Hydrocarbon Composition Analysis

Typical GC set-up for the analysis of the light hydrocarbon composition in liquefied gases is injecting the sample through a Split/Splitless injection port onto an Alumina Plot column (e.g. ASTM D2163 and ISO 7941.

Application Description

The LGI injector is applied for the residue analysis of liquid Ethane using the typical instrument and column setup as shown in Figure Two.
The analysis of the light hydrocarbons with the LGI-GC technique is performed by using a Split/Splitless inlet and an Al_2O_3 Plot column.

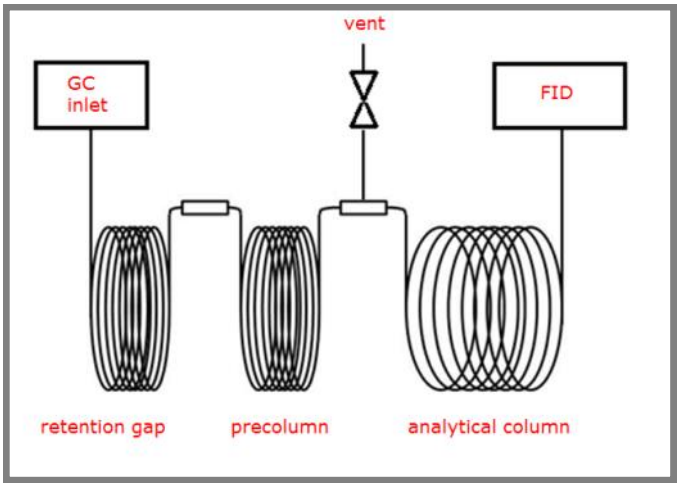

Figure Two: Typical Column Configuration for residue analysis using the LGI

Analytical Results

Residue Analysis

The chromatogram of the residue analysis shows that various impurities are present in this Ethane sample. To determine the boiling point range of these compounds, a retention time calibration standard of n-alkanes was used.
The results demonstrate that the impurities elute in the boiling point range of C5-C8 and C30-C38 n-alkanes.

In line with the ASTM / EN method for residue analysis in LPG a one point calibration using a quantitative standard with Pentane as a solvent was used for quantification. The use of standards in Pentane is convenient and cost-effective as these can be easily prepared at relatively low costs compared to commercial gas standards.

For the current application, a quantitative calibration standard of 21 mg/kg Toluene (retention time 4.719 min) in residue grade Pentane was prepared and analyzed. In case a calibration standard with a different solvent is used the ASTM / EN method prescribes a correction for the difference in the densities of the two solvents.
The relative densities used in the calculation are 0.54 for Ethane and 0.63 for Pentane.

For further characterization of the residue compounds, the system can be extended with a Mass Spectrometer.

LGI Setting Residue Analysis	
Inject pulse	15 ms
Vent open	8 s
N_2 sample pressure	60 bar
GC	
Inlet	COC
Inlet temperature	55°C (3 min) → 325°C, 25°C/min
Oven	35°C (3 min) → 325°C, 25°C/min
Columns	• Sulfinert retention gap • Non polar pre-column • Non polar analytical column
Carrier	Nitrogen
Column flow	6 ml/min
Detector	FID

Table One: Instrument Configuration and Settings for residue analysis

LGI Settings Hydrocarbon Analysis	
Inject pulse	15 ms
N_2 sample pressure	60 bar
GC	
Inlet	SSL
Inlet temperature	240°C
Split Ratio	15:1
Oven	40°C (8 min) → 200°C, 8°C/min
Columns	Alumina Plot column
Carrier	Helium
Column flow	5 ml/min
Detector	FID

Table Two: Instrument configuration and settings for hydrocarbon analysis

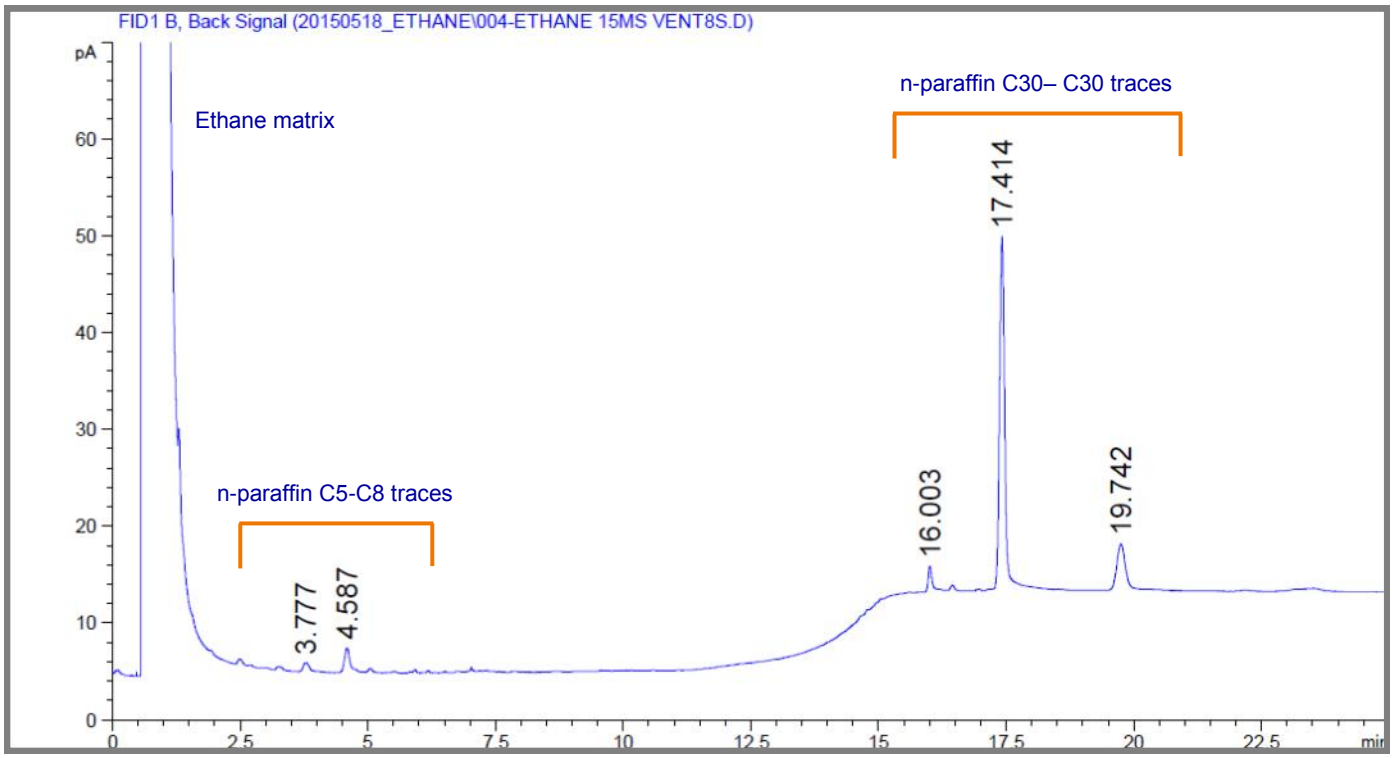

Figure Three: Chromatogram of the LGI analysis of residue in liquid Ethane

	Analysis #1		Analysis #2		Average	
	Area	Conc (mg/kg)	Area	Conc (mg/kg)	Area	Conc (mg/kg)
C5-C8 traces	28.8	0.6	32.9	0.7	30.9	0.7
C30-C38 traces	340.3	7.2	330.2	7.0	335.3	7.1

Table Three: Results of the LGI analysis of residue in liquid Ethane

	Prepared Conc (mg/kg)	Area
Toluene	21	1150.0

Table Four: Results of the LGI analysis of the prepared concentration calibration standard Toluene in n-Pentane

	Area	Conc (%)
Methane	461.1	0.599
Ethylene	0.7	0.001
Propane	193.0	0.251
Propylene	7.9	0.010
i-Butane	3.2	0.004
n-Butane	5.1	0.007
Ethane purity		99.128

Table Five: Results of the LGI analysis of light hydrocarbons in liquid Ethane

Hydrocarbon composition analysis

The chromatogram shows that, beside the major compound Ethane, also some minor amounts of Methane, Ethylene, Propylene, i-Butane and n-Butane are present in the sample.
Calculation of the concentrations is based on normalization. The Ethane purity was found to be 99.1 % as displayed in Table Five.

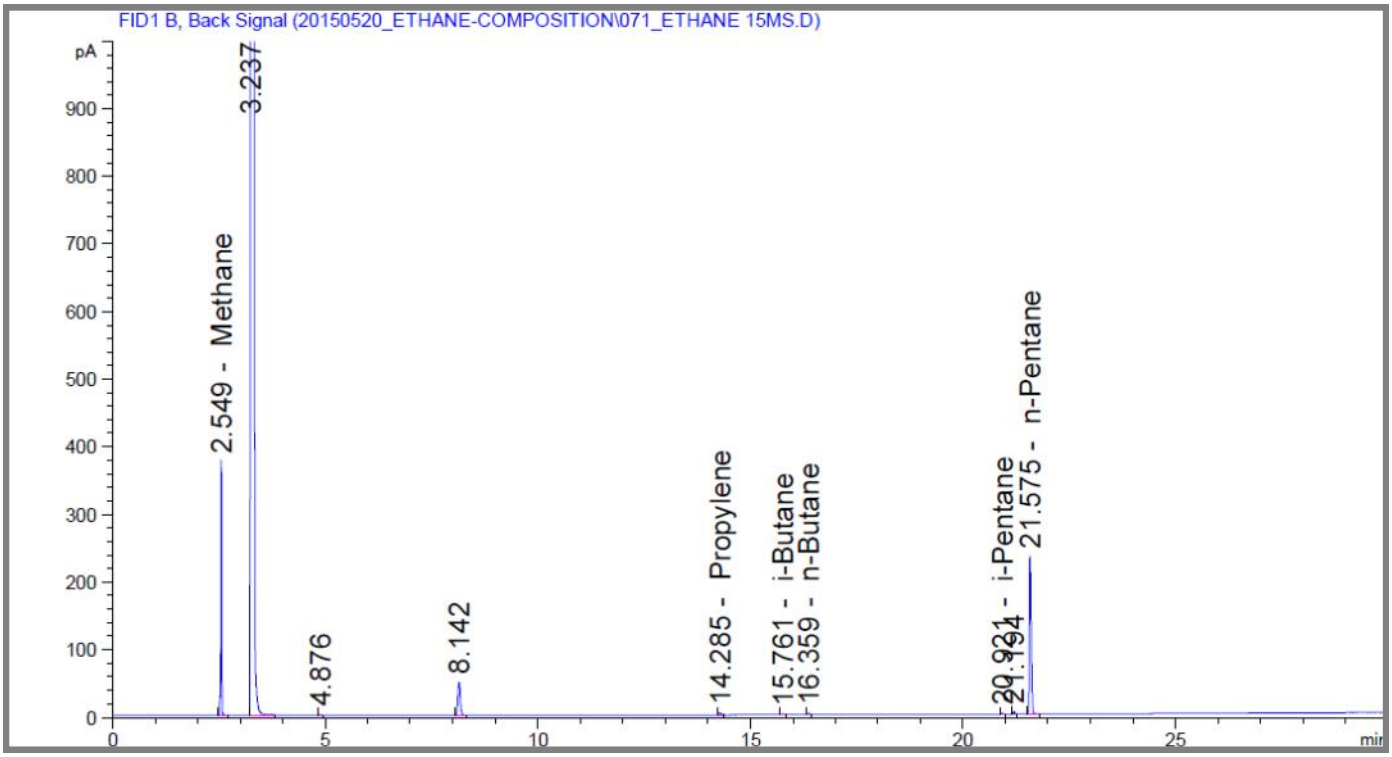

Figure Four: Chromatogram of the LGI analysis of light hydrocarbons of liquid Ethane

Conclusion

The analysis results demonstrate that by applying the LGI-GC technique both the heavy residue content and light hydrocarbon composition of liquid Ethane samples can be determined.

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

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