# The Analysis of Hydrocarbon Composition in LPG by Gas Chromatography using the DVLS Liquefied Gas Injector

## Introduction

Specification of the hydrocarbon composition of LPG is required as traces of hydrocarbon impurities in LPG can negatively effect the fuel quality and processing. The compound distribution data of the hydrocarbons can also be used to calculate properties including relative density, vapor pressure, and motor octane number. This application note describes the gas chromatographic analysis of the hydrocarbon composition of LPG using the DVLS Liquefied Gas Injector (LGI).

**Application Note**

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## Analysis of LPG

Various standard test methods for determining the hydrocarbon composition of liquefied petroleum gases are available, such as ASTM D2163 and ISO 7941. Both of these methods use gas chromatography as the analysis technique. Introduction of the liquefied gas sample into the GC inlet is most commonly performed by means of a liquid sampling valve.

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 LGI instrument was introduced in 2010. It was originally developed for the analysis of oily residue (range C10-C40) in LPG. This method has been approved as ASTM D7756 and EN 16423.

In the current study the LGI injector is applied for determining the hydrocarbon composition of LPG samples with various compositions.

## Application Description

The LGI consists of an Injector, a Pressure Station and a Controller. The Injector is configured on top of the GC inlet as displayed in Figure One.
The Pressure Station is installed next to the GC and ensures that the Injector is filled with the sample in liquid phase. The Controller box drives the injection cycling.
The Injector includes the proven fuel direct injection technique used by the automotive industry to inject fuel into the automotive engine combustion chamber. The liquid sample is injected directly with a needle into the inlet similar as with an automatic liquid sampler. This avoids contact of the sample with transfer lines, vaporizers or valves and allows a good sample transfer into the heated zone of the inlet.

## Analytical Results

For each sample the Normalized Volume percentages (Norm. Vol. %) of the individual compounds are calculated according to ASTM D2163. The Theoretical Volume Response factors (RRFis) as specified in D2163 are used.
For certain compounds these values are not mentioned in this method. In these instances the RRFis are calculated using the sources D2163 refers to.

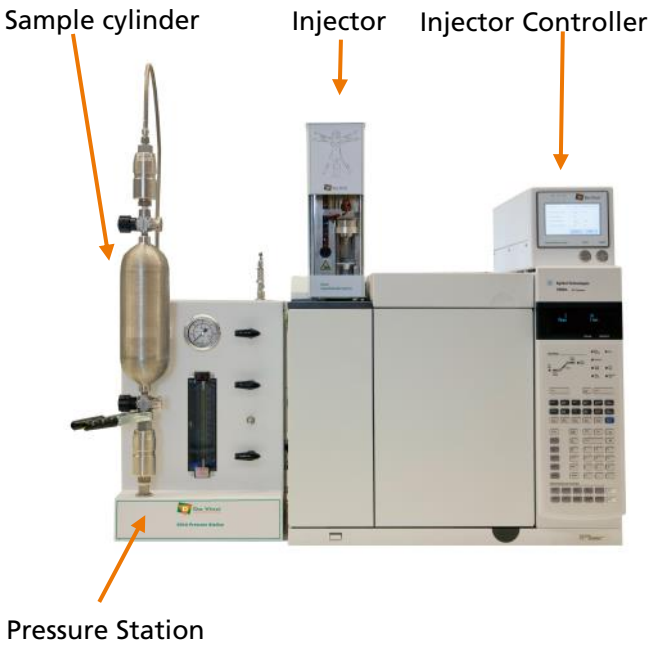


*Figure One: DVLS Liquefied Gas Injector installed on the GC*

ASTM D2163 applies to compound concentrations in the range of 0.01 to 100 volume percent (Vol %). ISO 7941 applies to concentrations > 0.1 mass percent.
Based on the reported chromatograms the Limits of Detection (LOD) are calculated. The LOD is defined as 10 times the standard deviation of the noise. The LODs of all compounds detected in the LPG samples are at least 10 times lower than the lower value D2163 applies to. Most values were even 50 to 300 times lower. This indicates that the current technique offers an excellent sensitivity for determination of hydrocarbons in LPG.

Repeatability is determined by performing seven analyses of the automotive LPG sample. For the major compounds; Propane, i-Butane and n-Butane, the Relative Standard Deviation (RSD) varies between 0.2 and 0.6 %. For the trace compounds with concentrations > 0.01 Vol. % the RSD varies between 0.2 to 2.5 %.

## Conclusion

In the current study the LGI-GC technique has been applied for the analysis of the hydrocarbon composition of LPG samples. The analytical results demonstrate an excellent sensitivity.

| Instrument Configuration and Settings | |
|---|---|
| LGI | |
| Inject pulse | 15 ms |
| GC | |
| Inlet | SSL |
| Inlet temperature | 240°C |
| Oven | Propane, Propylene & Butane: 40°C (8 min) → 200°C, 8°C/min Pentane: 50°C (3 min) → 270°C,10°C/min |
| Split ratio | 1:1 |
| Column | Alumina Plot |
| Carrier | Helium |
| Column flow | 5 ml/min |
| Detector | FID |

*Table One: Instrument Configuration and Settings*

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: The Analysis of Di-Iso-Propanol-Amine (DIPA) in Liquefied Petroleum Gas (LPG) with the DVLS LGI Injector
4. Application note: Dual Analysis of Oily Residues in LPG (ASTM D7756/EN 16423) and Hydrocarbon Composition of LPG (ASTM D2163 & ISO 7941)

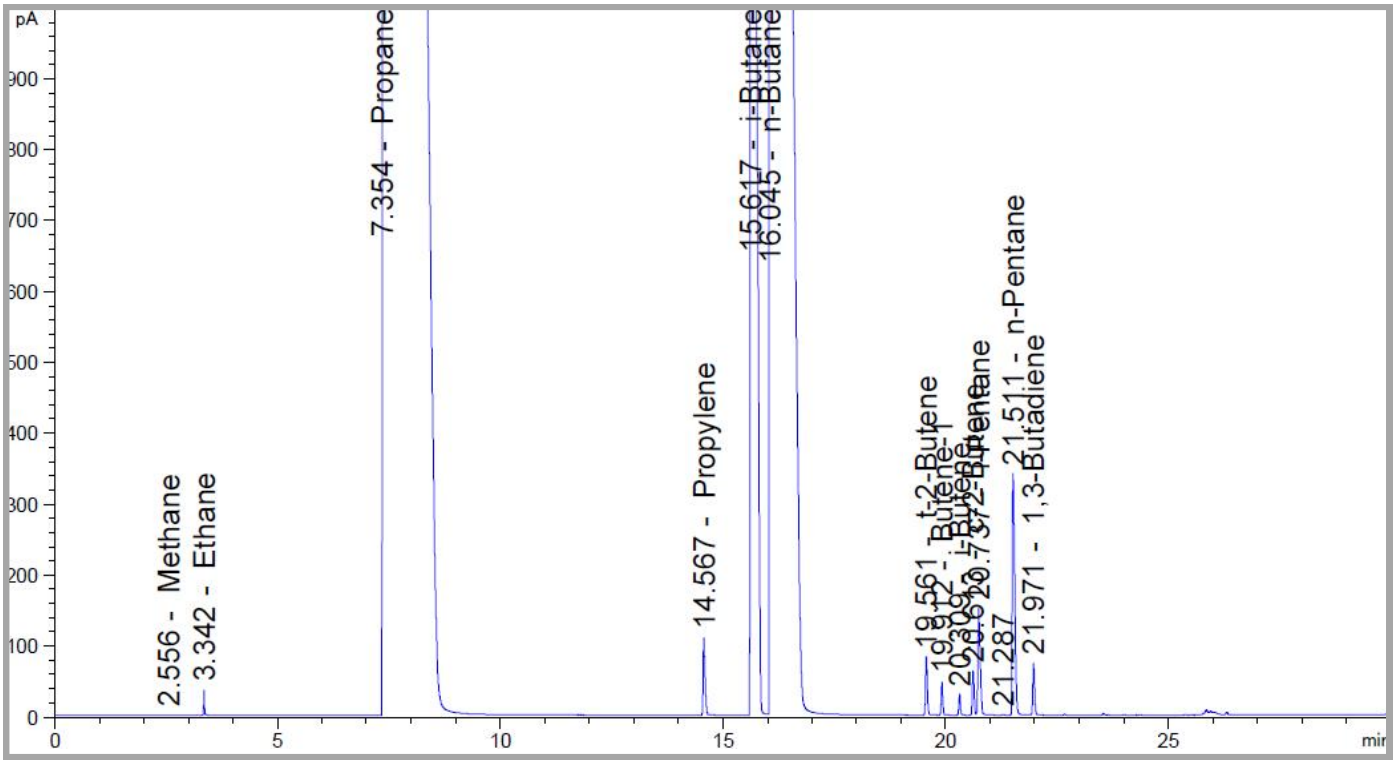


*Figure Two: Chromatogram of the LGI analysis of automative LPG*

| | Average | RSD | LOD |
|---|---|---|---|
| | Norm. Vol.% | Norm. Vol. % | Norm. Vol% |
| Methane | 0.0001 | 13.9 | 0.00006 |
| Ethane | 0.0166 | 0.9 | 0.00004 |
| Propane | 71.8904 | 0.2 | 0.00055 |
| Propylene | 0.0712 | 0.2 | 0.00005 |
| i-Butane | 3.8319 | 0.4 | 0.00012 |
| n-Butane | 23.7136 | 0.6 | 0.00030 |
| tr-Butene | 0.0414 | 1.2 | 0.00004 |
| Butene-1 | 0.0219 | 1.1 | 0.00004 |
| i-Butene | 0.0131 | 1.8 | 0.00004 |
| c-2-Butene | 0.0287 | 1.3 | 0.00004 |
| i-Pentane | 0.1005 | 1.7 | 0.00005 |
| n-Pentane | 0.2359 | 1.4 | 0.00006 |
| 1,3-Butadiene | 0.0347 | 2.5 | 0.00004 |
| Total | 100.000 | | |

*Table Two: Results of 7 LGI analyses of automative LPG*

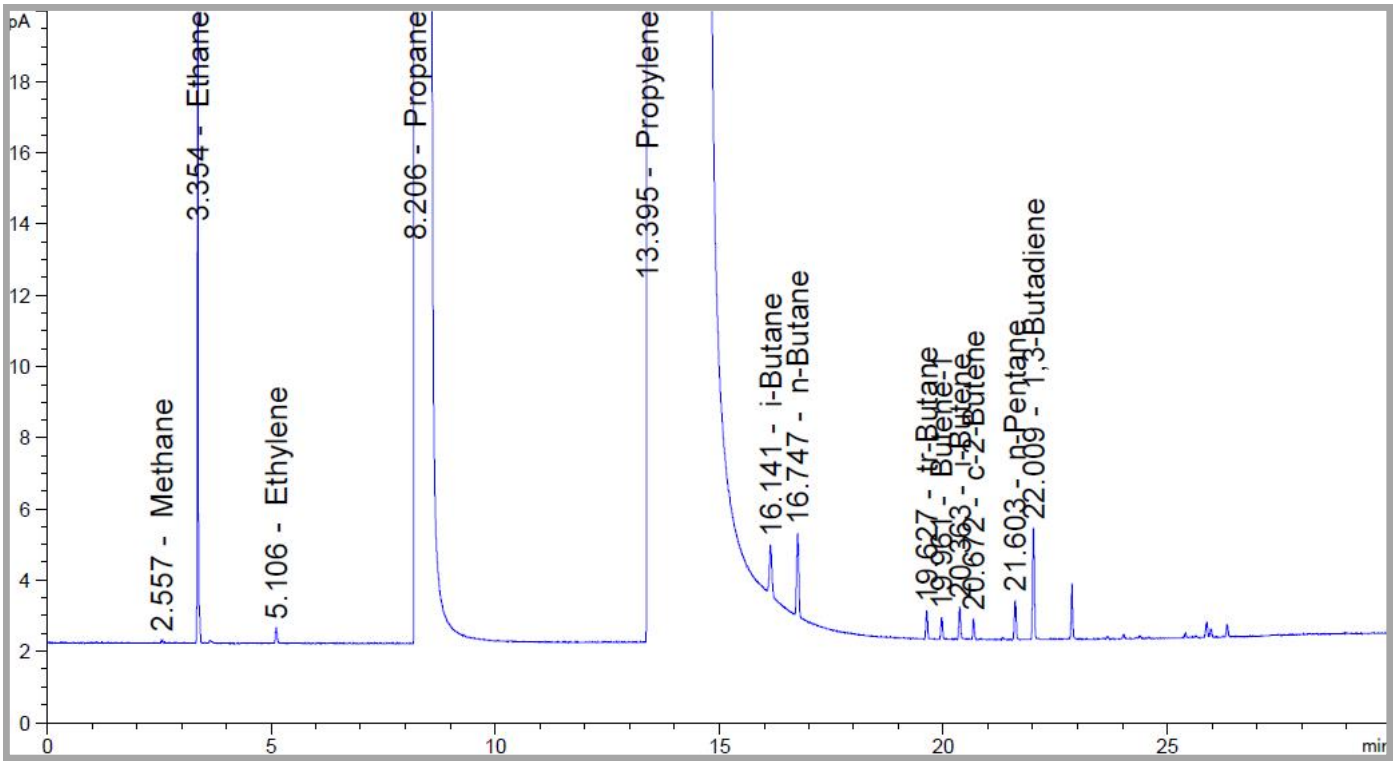


*Figure Three: Chromatogram of the LGI analysis of liquefied Propylene*

| | | LOD |
|---|---|---|
| | Norm. Vol.% | Norm. Vol.% |
| Methane | 0.0001 | 0.00010 |
| Ethane | 0.0126 | 0.00004 |
| Ethylene | 0.0004 | 0.00006 |
| Propane | 5.7348 | 0.00019 |
| Propylene | 94.2447 | 0.00054 |
| i-Butane | 0.0013 | 0.00006 |
| n-Butane | 0.0019 | 0.00005 |
| tr-Butane | 0.0005 | 0.00003 |
| Butene-1 | 0.0004 | 0.00004 |
| i-Butene | 0.0005 | 0.00003 |
| c-2-Butene | 0.0003 | 0.00003 |
| n-Pentane | 0.0007 | 0.00004 |
| 1,3 Butadiene | 0.0018 | 0.00004 |
| Total | 100.000 | |

*Table Three: Results of the LGI analysis of liquefied Propylene*

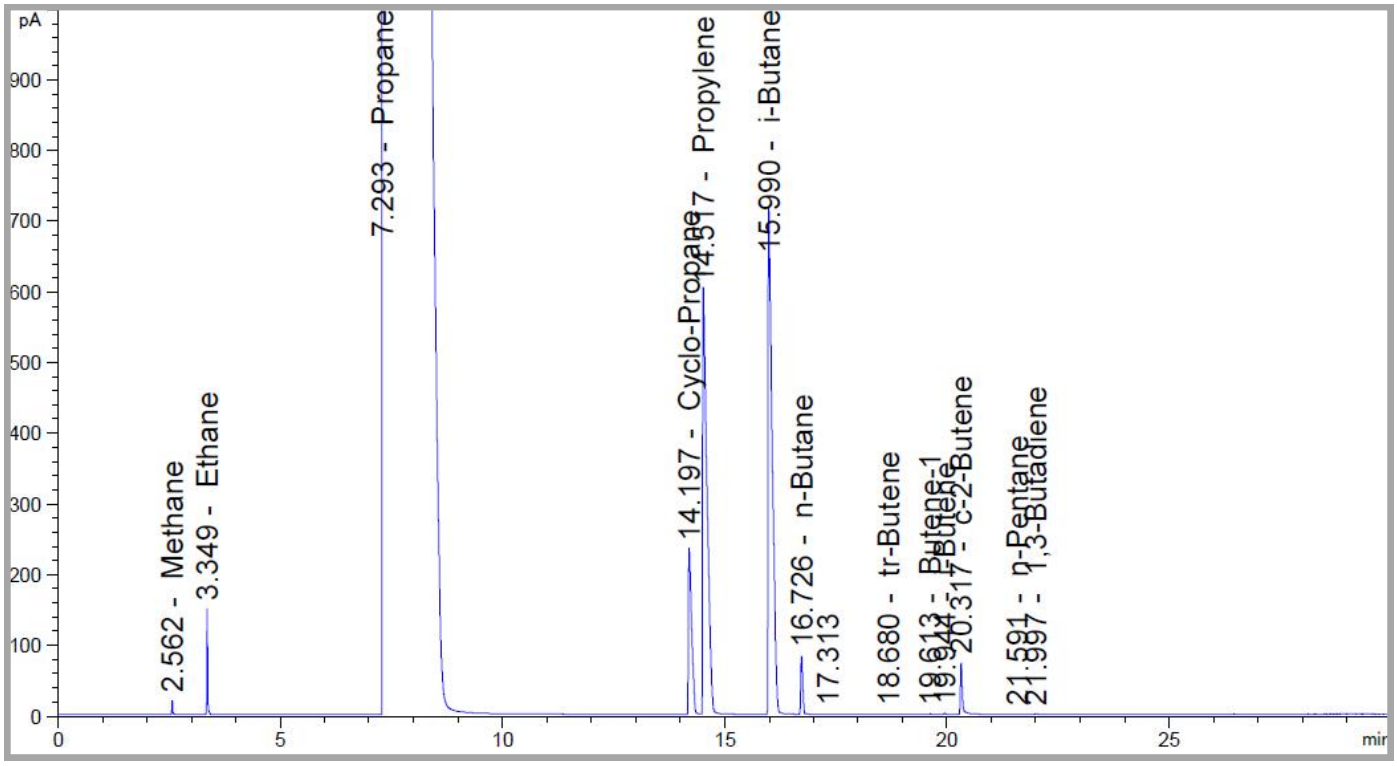


*Figure Four: Chromatogram of the LGI analysis of liquefied Propane*

| | | LOD |
|---|---|---|
| | Norm. Vol.% | Norm. Vol.% |
| Methane | 0.0107 | 0.00006 |
| Ethane | 0.0795 | 0.00005 |
| Propane | 97.6246 | 0.00085 |
| Cyclo-Propane | 0.1907 | 0.00008 |
| Propylene | 0.9730 | 0.00016 |
| i-Butane | 1.0182 | 0.00014 |
| n-Butane | 0.0573 | 0.00007 |
| tr-Butane | 0.0001 | 0.00005 |
| Butene-1 | 0.0001 | 0.00005 |
| i-Butene | 0.0008 | 0.00005 |
| c-2-Butene | 0.0448 | 0.00006 |
| n-Pentane | 0.0000 | 0.00006 |
| 1,3-Butadiene | 0.0003 | 0.00005 |
| Total | 100.000 | |

*Table Four: Results of the LGI analysis of liquefied Propane*

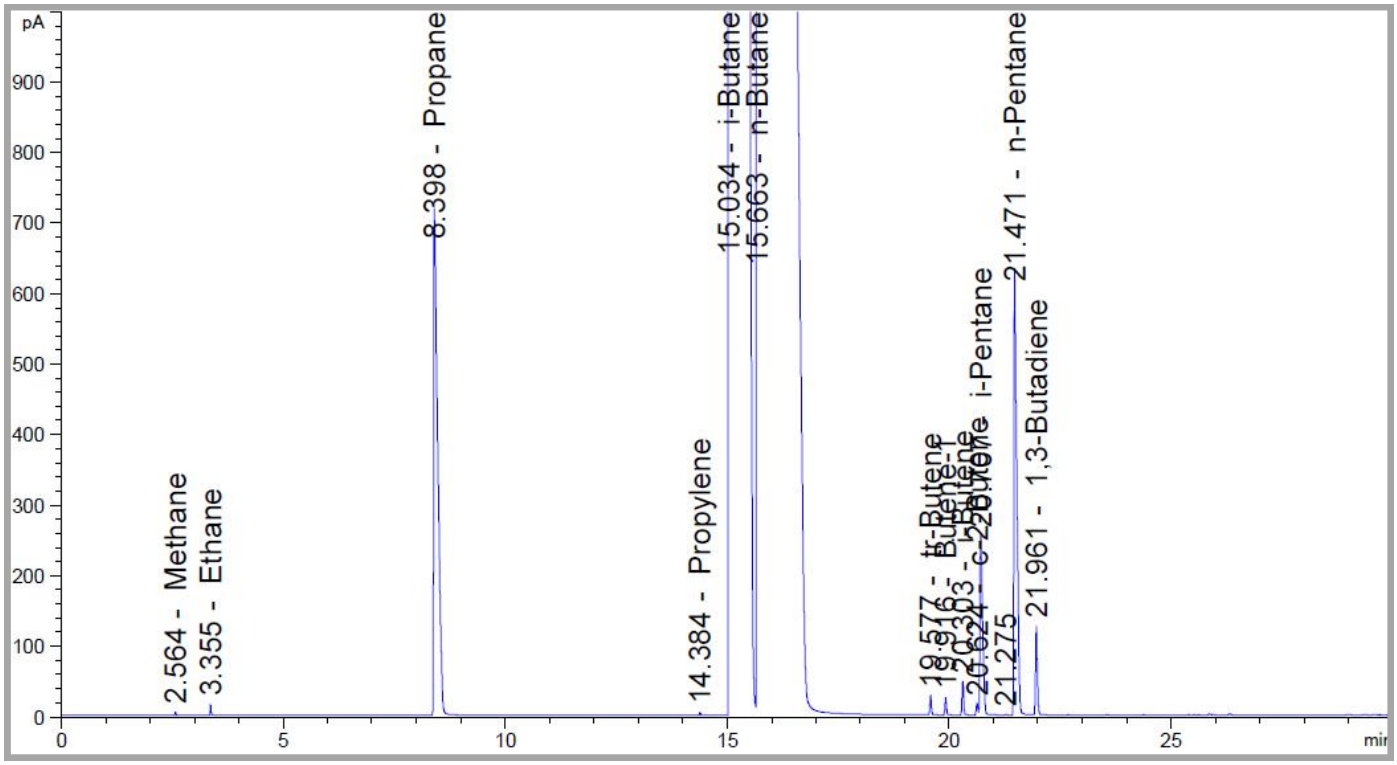


*Figure Five: Chromatogram of the LGI analysis of liquefied Butane*

| | | LOD |
|---|---|---|
| | Norm. Vol.% | Norm. Vol.% |
| Methane | 0.0019 | 0.00004 |
| Ethane | 0.0063 | 0.00004 |
| Propane | 1.0238 | 0.00011 |
| Propylene | 0.0014 | 0.00003 |
| i-Butane | 31.7849 | 0.00028 |
| n-Butane | 66.3553 | 0.00045 |
| tr-Butane | 0.0120 | 0.00004 |
| Butene-1 | 0.0111 | 0.00004 |
| i-Butene | 0.0218 | 0.00004 |
| c-2-Butene | 0.0068 | 0.00003 |
| i-Pentane | 0.1928 | 0.00006 |
| n-Pentane | 0.5196 | 0.00007 |
| 1,3-Butadiene | 0.0623 | 0.00004 |
| Total | 100.000 | |

*Table Five: Results of the LGI analysis of liquefied Butane*

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