Da Vinci
LABORATORY SOLUTIONS



# Liquefied Gas Injector

**Solution for the Sampling and Analysis of Liquefied Gases**

# DVLS Liquefied Gas Injector


## Safe and Representative Sampling of Liquefied Gases

The analysis of impurities and contaminants in liquefied gases is an analytical challenge. The contaminants and impurities are high boiling or unstable components having a high molecular weight, which complicates the sample introduction. Their adsorption on vaporizers, injection valves and transfer lines enlarges the discrimination, adsorption, and fractionation effects. Current test methods are labor intensive and present a safety risk due to the required evaporation of the large volumes of liquefied gas.
Da Vinci Laboratory Solutions (DVLS) developed an alternative and fast gas chromatographic method which features a direct injection of the liquefied gases that eliminates the need for sample evaporation: the Liquefied Gas Injector.

### Liquefied Gas Injector

The direct injection approach of the Liquefied Gas Injector includes the proven fuel direct injection technique used by the automotive industry to inject fuel into the automotive engine combustion chamber.

The LGI is connected to a standard GC injector needle, which is inserted into a GC large volume on-column injection system.
Solenoid activation transfers the pressurized sample through the needle directly on-column.
A sliding device moves the needle downwards for the injection and upwards for purging.

### Pressure Station

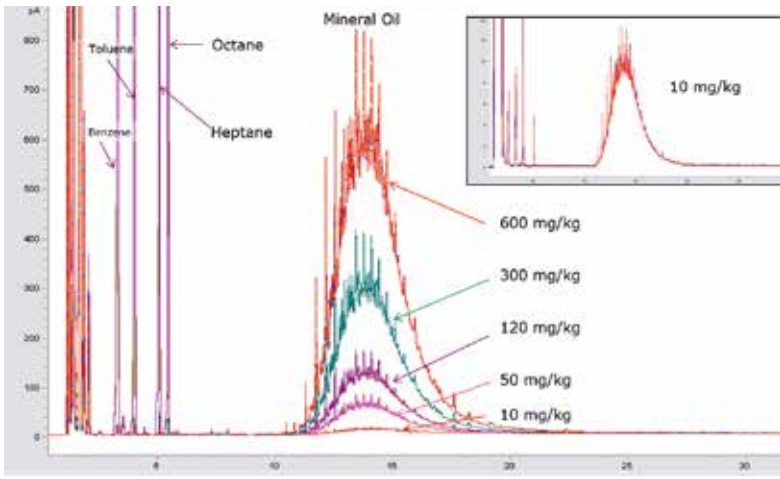
To allow a representative sample injection a Pressure Station is used to keep the sample in a liquid phase during the injection.

The sample cylinder is installed using quick connectors. For liquid samples the Pressure Station adds high pressure Nitrogen to the sample cylinder and controls the outlet pressure and flow.
Optionally the Pressure Station can also be configured for gas samples by including a vaporizer to control the sample evaporation after injection.
The waste sample is vented to a central waste system to ensure laboratory safety.



**Boosting laboratory efficiency**

# DVLS Liquefied Gas Injector




## Analysis of Liquefied Gases

The Liquefied Gas Injector (LGI) is introduced in 2010 and has been standardized as ASTM D7756 and EN 16423 for the analysis of residues in liquefied petroleum gases by gas chromatography. Adapting the hardware setup allows to extend the analysis of oily residues in LPG to a wider application range.

### Key Benefits

- **Safe injection of liquefied gases**
  The direct injection approach of the LGI is based on a proven fuel direct injection technique used by the automotive industry which eliminates the need for sample evaporation.
- **Representative sampling**
  The pressure station ensures that the sample remains in the liquid phase during the injection process.
- **Proven technology**
  Since its introduction in 2010 the LGI has been successfully used by a global installed base of leading oil refineries.
- **Wide application range**
  The LGI determines hydrocarbon composition, impurities, contaminants and sulfur compounds in liquefied gases and nitrogen, carbon dioxide, hydrogen sulfide and hydrocarbons in unstabilized gas condensate.
- **Accurate and fast performance**
  Several case studies demonstrate an excellent and fast performance of the LGI.

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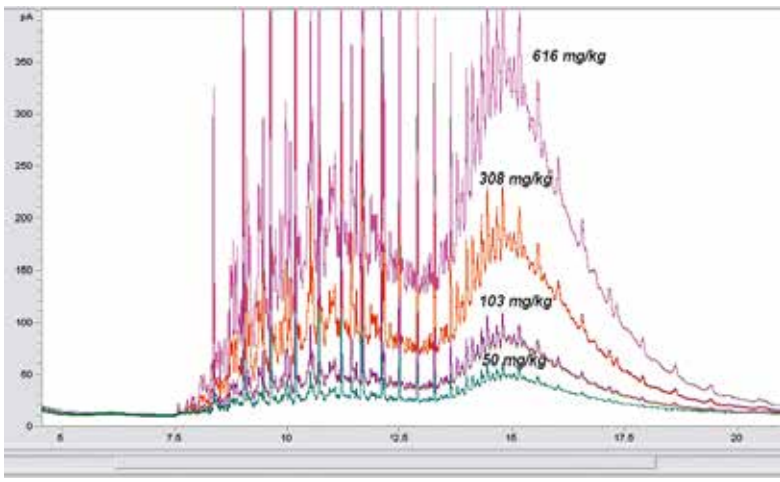
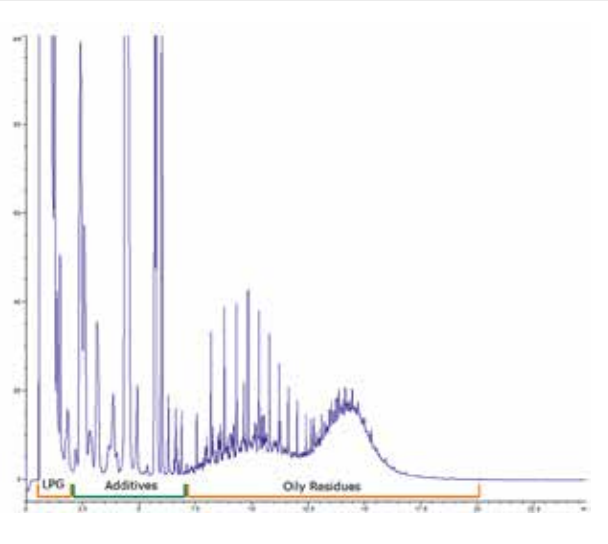



## Application Range

The DVLS Liquefied Gas Injector offers laboratories a proven GC standard for the following applications:

- Oily residues and light contaminants in LPG (ASTM D7756, EN 16423)
- Hydrocarbon composition of LPG (ASTM D 2163, ISO 7941)
- Sulfur compounds in liquefied petroleum gases
- Desulfurization additives in LPG: DIPA, MEA & DEA
- Inhibitors, additives and Dimers in Butadiene: ACN, ρTBC, Butadiene Dimer
- Nitrogen, carbon dioxide, hydrogen sulfide and hydrocarbons in unstabilized gas condensate

## Oily Residues Analysis in LPG (ASTM D7756/EN 16423)




**Specifications:**

- Analysis time < 30 minutes
- Oily residue analysis range of 10 - 600 mg/kg
- LOD individual components < 1 ppm

The ASTM D7756/EN 16423 application uses the Liquefied Gas Injector (LGI). The sample is injected under a constant pressure into a Sulfinert® coated stainless steel retention gap. The retention gap is connected to a non-polar retaining pre-column, with an exit for flushing the LPG matrix. After matrix venting, the valve is closed and the flow is directed to an analytical column for the separation of the various contaminants present in LPG.

The chromatographic analysis after the sample introduction is based on boiling point separation of the oily residues and contaminants. The total residue is quantified using area summation of the components in the range of C10 to C40. The result is reported in parts per million (w/w) of residue in LPG.



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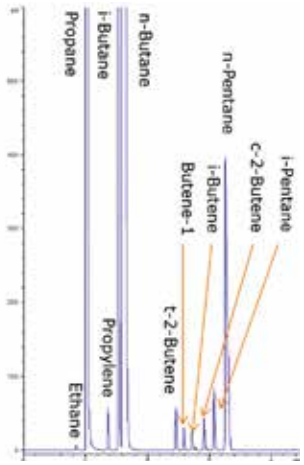
## Dual Analysis of Oily Residues in LPG (ASTM D7756/EN 16423) and Hydrocarbon Composition of LPG (ASTM D2163 & ISO 7941)

The LGI method for determining oily residue in C3 and C4 streams complies with ASTM D7756 and EN 16423. Adding an external oven with a special valve configuration to a high pressure liquid sampling application extends the single analysis to a dual analysis of both the oily residue and the hydrocarbon composition of LPG at the same time from the same sample cylinder.

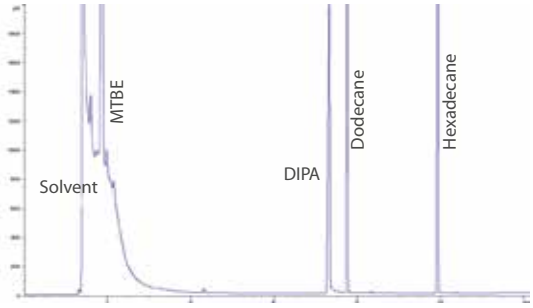
The column for the compositional analysis was installed in an external oven, enabling running both the temperature program for the D7756 application and the compositional analysis simultaneously. Analytical results demonstrate that the repeatability complies very well with both ASTM D7756 and ASTM D2163.




| Component | oily residue | ethane | propane | propylene | i-butane | n-butene | t-2-butene | butene-1 | i-butene | c-2 -butene | i-pentane | n-pentane |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Avg. Area Counts | 4935.9 | 8.5 | 29415.9 | 71.7 | 2080.6 | 11117.7 | 83.7 | 42.4 | 38.1 | 59.6 | 123.4 | 1028.0 |
| Stdev | 77.6 | 0.2 | 488.3 | 1.1 | 31.6 | 166.9 | 1.3 | 0.7 | 0.5 | 0.9 | 1.8 | 14.7 |
| % RSD | 1.6 | 1.8 | 1.7 | 1.5 | 1.5 | 1.5 | 1.5 | 1.6 | 1.2 | 1.5 | 1.5 | 1.4 |
| Maximum difference between the calculated concentrations of the 7 analyses | 1.343 ppm | 0.009 Vol % | 0.088 Vol % | 0.0004 Vol % | 0.0119 Vol % | 0.074 Vol % | | | | | 0.001 Vol % | 0.01 Vol % |
| ASTM Repeatability | 5.159 ppm | 0.0001 Vol % | 0.777 Vol % | 0.020 Vol % | 0.077 Vol % | 0.223 Vol % | | | | | 0.023 Vol % | 0.057 Vol % |

## Analysis of Amines in LPG

To quantify Amines in LPG an LGI system is setup according to ASTM D7756. Analytical tests demonstrate that the LGI repeatability is better than 2% relative and the lower detection limit is far below 1 ppm.

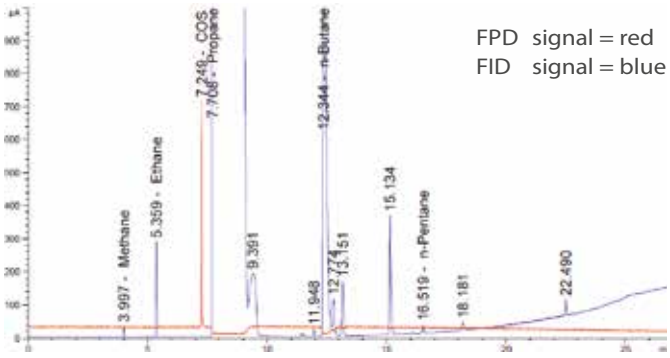


## DVLS Liquefied Gas Injector

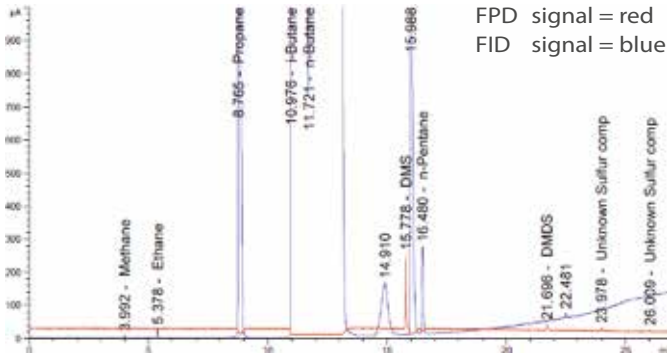

## Analysis of Sulfur Compounds in Liquefied Gases

Several methods are available for the quantification of individual sulfur compounds, that use a GC configured with a sulfur specific detector and a gas or liquid sampling valve for the sample introduction. The LGI method offers several advantages over the sample introduction through a valve as the direct injection avoids contact of the sample with transfer lines, vaporizers or valves.

The LGI application is configured with a sulfur specific Flame Photometric Detector (FPD) for the analysis of sulfur compounds in liquefied Propane, Butane and liquid Pentane.




| | Sulfur Conc. mg Sulfur/kg | % RSD | LOQ mg Sulfur/kg | LOD mg Sulfur/kg |
|---|---|---|---|---|
| COS | 0.51 | 0.6 | 0.18 | 0.05 |

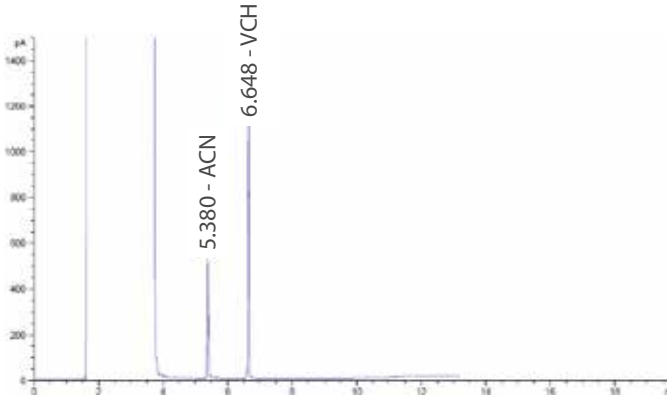



When using an PFPD or SCD detector an even higher sensitivity can be achieved. The LGI-GC technique combined with a sulfur specific detector offers a powerful tool for sulfur control of liquefied petroleum gas samples and liquid pentane samples.

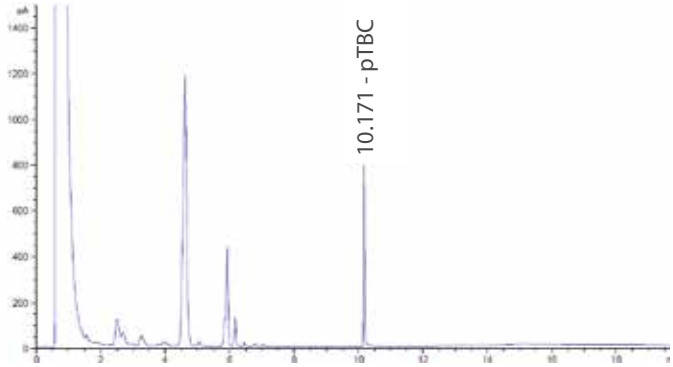
| | Sulfur Conc. mg Sulfur/kg | % RSD | LOQ mg Sulfur/kg | LOD mg Sulfur/kg |
|---|---|---|---|---|
| DMS | 0.34 | 0.3 | 0.19 | 0.06 |
| DMDS | 0.09 | 4.3 | 0.19 | 0.06 |

## Analysis of Inhibitors, Additives and Impurities in Butadiene

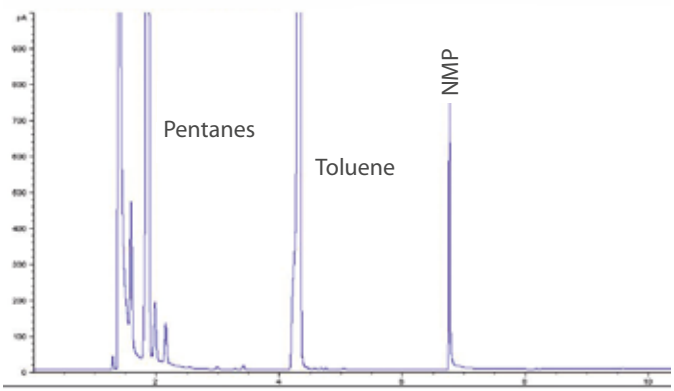
The LGI application dedicated to the analysis of ACN, NMP, VCH and pTBC consists of a GC configured with the LGI, an on-column injection port, a solvent vapor exit and a Flame Ionization (FID) detection.
Analytical tests proof that pTBC can be very well separated from the C3/C4 matrix of LPG. To measure ACN in the C3/C4 matrix a WAX type column is used. Test results demonstrate that this polar column is able to separate ACN and VCH very well, even from a C5 matrix.




| Component | LOQ (mg/kg) | LOD (mg/kg) | RSD % |
|---|---|---|---|
| pTBC | 0.078 | 0.023 | 0.6 |
| ACN | 0.045 | 0.013 | 0.4 |
| VCH | 0.011 | 0.003 | 0.3 |




Controlled handling of Butadiene cylinders, in combination with on-column GC injection, reduces health and safety risks for analysts involved in Butadiene quality control.

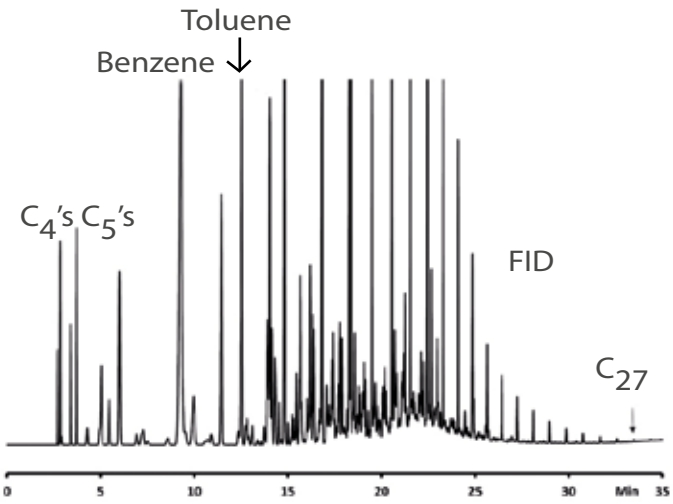


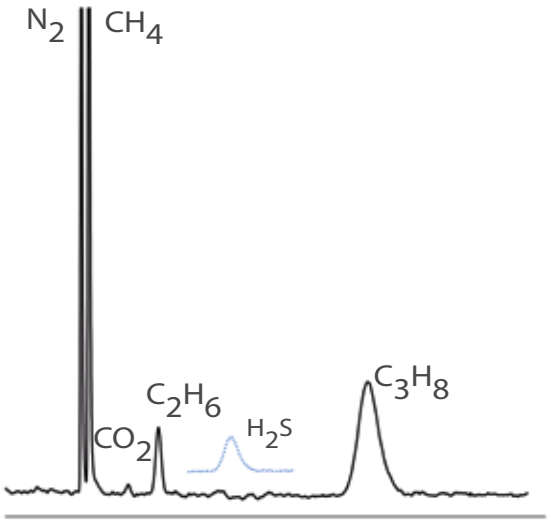

| Component | LOD (mg/kg) | RSD % |
|---|---|---|
| NMP | < 1 | < 2 |

## Analysis of $N_2$, $CO_2$, $H_2S$ and Hydrocarbons in Unstabilized Gas Condensate

The design of the LGI allows liquefied gas analysis with pressures up to 80 bar and requires a single GC run for the analysis of Nitrogen, Carbon dioxide, Hydrogen sulfide and C1-C36+ hydrocarbons in high pressure unstabilized gas condensate.

The sample is kept under pressure by pressurizing the sample cylinder with water or using a piston cylinder.
By applying a two channel system, only one single injection is required. Nitrogen, Carbon dioxide, Hydrogen sulfide, Methane, Ethane and Propane are analyzed using a TCD. C4 up to C36+ are analyzed using an FID. Repeatable results of 1.5% RSD of the normalized area% are found.





**Da Vinci Laboratory Solutions B.V.**

*Visiting address:*
Sydneystraat 5
3047 BP Rotterdam
The Netherlands

*Postal address:*
P.O. Box 12103
3004 GC Rotterdam
The Netherlands

**T** +31 (0)10 258 1870
**F** +31 (0)10 258 1879
**E** solutions@davinci-ls.com
**I** www.davinci-ls.com

**Service Office**

*Visiting address:*
Da Vinci Laboratory Solutions
Chemelot Campus
Building G122.110.02.64
Urmonderbaan 22
6167 RD Geleen (Gate2)
The Netherlands



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