Da Vinci
LABORATORY SOLUTIONS

Liquefied Gas Injector

Solution for the Sampling & Analysis of Liquefied Gases

Analysis 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 includes a direct injection of the liquefied gases that eliminates the need for sample evaporation: the Liquefied Gas Injector.

The Liquefied Gas Injector (LGI) technique is standardized in the ASTM D7756 and EN 16423 methods for the analysis of oily residue in LPG.

The setup of the LGI analysis consists of an Agilent gas chromatograph on which the injector and its controller are installed. The Pressure Station is used for safe and accurate sample introduction of LPG. The analysis parameters are set in the Agilent OpenLab software.

The analysis of the oily residue in LPG is started using the controller. The LGI injects the LPG as a liquid directly into the GC inlet. The analysis of the oily residue is completed within 20 minutes.

Liquefied Gas Injector

The direct injection approach of the Liquefied Gas Injector (LGI) is a safe alternative technique to a liquid sampling valve or manual evaporation.

The LGI uses 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.

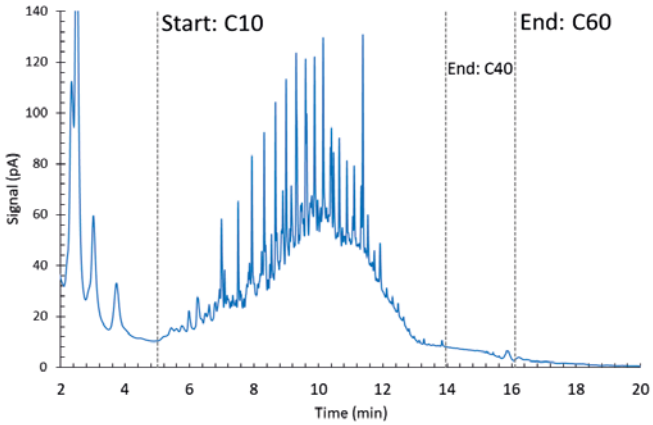
Vaporizer

Pressure Station

For a repeatable introduction into a GC system the liquefied gas sample must remain in a liquid phase under constant pressure during the GC injection. This is especially required for LPG or other liquefied gases.

The sample cylinder is mounted onto the Pressure Station using quick connectors.
For liquefied gas samples the Pressure Station adds high pressure Nitrogen to the sample cylinder to control the outlet pressure and flow. The sight glass enables a visual check of the liquid phase of the sample. The sample is introduced as a liquid using the Liquefied Gas Injector. Optionally the Pressure Station can also be configured with a vaporizer to control the sample waste. The waste sample is vented to a central waste system to ensure laboratory safety.

Application Range of the Liquefied Gas Injector



The Liquefied Gas Injector (LGI) is introduced in 2010 and has been standardized as ASTM D7756 and EN 16423 for the analysis of oily residue 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.

The application range of the DVLS Liquefied Gas Injector includes the following analyses:

- Oily residues and light contaminants in LPG (ASTM D7756, EN 16423);
- Elemental sulfur in LPG;
- Amines in LPG;
- Nitrogen, carbon dioxide, hydrogen sulfide and hydrocarbons in (un)stabilized gas condensate;
- Composition & impurities analysis in butadiene, crude C4 & raffinate (ASTM D2593, D4424, D2426);
- Oxygenate traces in liquid hydrocarbon matrices (ASTM D7423, D7754);
- Benzene and Toluene in LPG (ASTM D7756);
- Hydrocarbon composition of LPG (ASTM D 2163, ISO 7941).

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

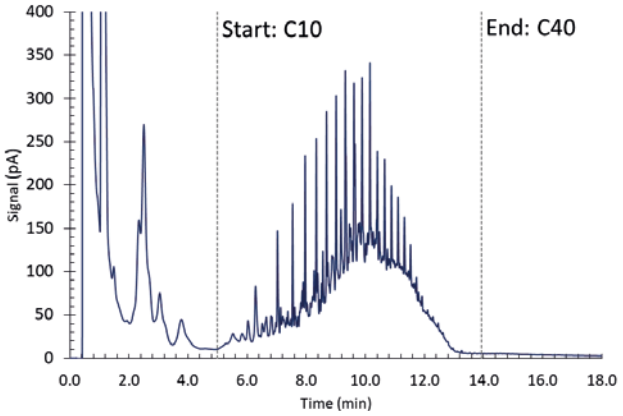
The ASTM D7756/EN 16423 application uses the Liquefied Gas Injector (LGI) to inject the sample injected under a constant pressure into a Sulfinert® coated stainless steel retention gap. The retention gap is connected to a non-polar retaining pre-column, with an exit for flushing the LPG matrix. After 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.

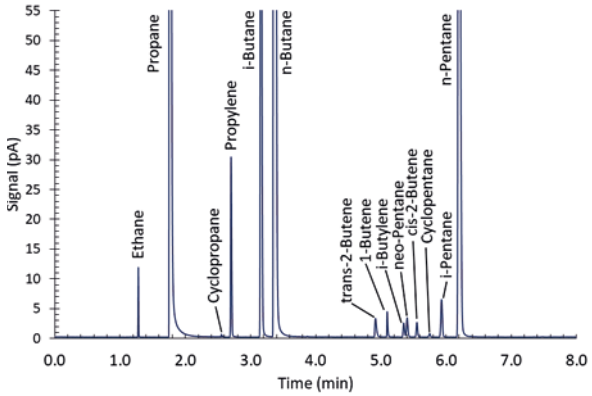
The chromatographic analysis after the sample introduction is based on boiling point separation of the oily residues and contaminants. The total residue is quantified using area summation of the components in the range of C10 to C60. The result is reported in mg/kg of residue in LPG.

Specifications:

- **Analysis time < 20 minutes**
- **Analysis range: 10 - 600 mg/kg**
- **LOD oily residue: 0.5 mg/kg**

Analyses of Composition & Oily Residues in LPG





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 liquid sample valve configuration to a high pressure liquid sampling application allows a simultaneous analysis of the oily residue (ASTM D7756/EN 16423) and the hydrocarbon composition (ASTM D2163 & ISO 7941) of LPG from the same sample cylinder.
Analytical results demonstrate that the repeatability complies very well with both ASTM D7756 and ASTM D2163 methods.

Specifications:

- **Analysis time < 20 minutes**
- **Analysis range C1 - C5: 0.01-100% v/v**
- **Analysis range residue: 10 - 600 mg/kg**
- **LOD residue: 0.5 mg/kg**
- **LOD C1-C5: 0.001 % (10 mg/kg)**

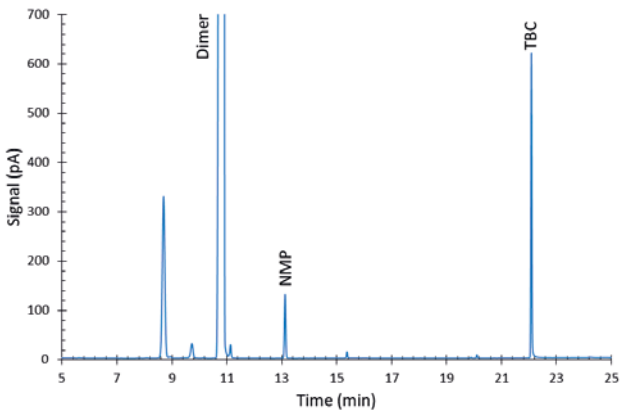
Analysis of Composition & Impurities in Butadiene, Crude C4 & Raffinate

The Butadiene application uses a dual channel configuration to simultaneously determine the hydrocarbon composition and the impurities such as Dimer & inhibitors in 1,3-Butadiene, Crude C4 fractions and Raffinate according to ASTM D2593, D4424, D2426, custom DVLS method and BASF method Part I-2, I-3 & I-7. The front channel is configured for the analysis of:

- Hydrocarbon impurities at ppm level;
- Butylene/Crude C4/1,3-Butadiene/Crude Butadiene/Raffinate composition.

The back channel is configured with a Liquefied Gas Injector for the analysis of:

- Dimer and Styrene content;
- TBC and EC3071 Inhibitors;
- Residual solvents such as NMP, DMF, Toluene and Acetonitril.



The application can also be used as an alternative to ASTM D1157 to determine TBC inhibitor or to ASTM D1025 for the analysis of Residue (C10 - C24 oily residue).

Specifications:

- **Analysis time: 30 minutes**
- **LOD C1-C5 hydrocarbons: < 0.5 mg/kg**
- **LOD BHT, DEHA, dimer, DMF, NMP, residue, styrene, TBC, toluene: < 0.2 mg/kg**

Butadiene Dimer Results (ASTM D2426)

Calibration Matrix: i-Butane
Calibration Standard Density: 0.5629

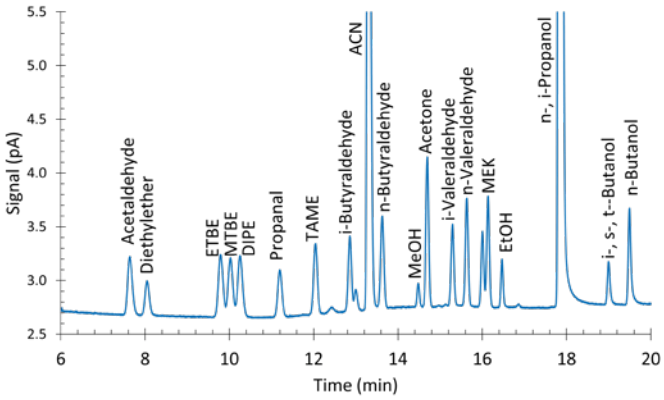
RT [min]	Name	Area	Density	RRF	Amount (mg/kg)
10.871	Dimer	173216	0.8263	0.02000	3171
	Sum	173216			3171

Inhibitor Results (ASTM D1157 Modified)

Calibration Matrix: Ethanol
Calibration Standard Density: 0.7967

RT [min]	Name	Area	Density	RRF	Amount (mg/kg)
22.087	TBC	1540	1.06	0.03970	79
	Sum	1540			79

Analysis of Oxygenate Traces in Liquid Hydrocarbon Matrices



The Low Oxygenates application complies with the ASTM D7423 and D7754 methods to characterize oxygenate traces such as alcohols and ethers, in gasoline & liquid hydrocarbon matrices.

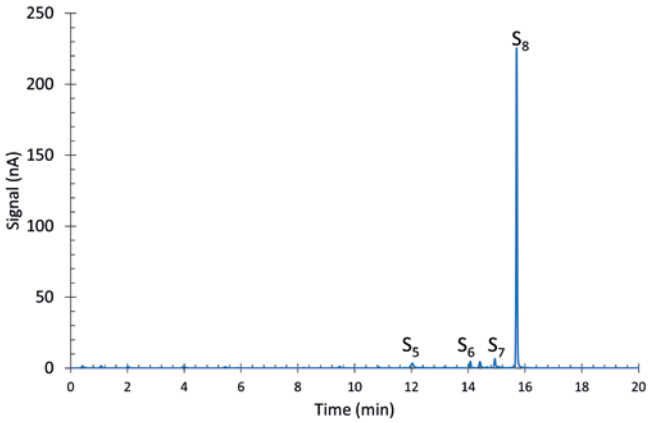
The application is configured with a Deans switching bracket and unique inert Programmable Temperature Inlet (PTI) to determine the oxygenate traces. Adding the Liquefied Gas Injector to the configuration enables to achieve ppb level detection limits for the analysis of trace oxygenates in liquefied gases. The chromatogram shows the trace oxygenates analysis of a 50 -100 ppb standard. The table displays the typical detection limits. The use of the inert PTI will substantially improve the peak shape and response for the oxygenates.

Specifications:

- **Analysis time <25 minutes**
- **Analysis range: oxygenates from 100 mg/kg down to 50 µg/kg**
- **Superior response for heavy oxygenates**
- **LOD individual oxygenates < 10 µg/kg**

Compound	ETBE	MTBE	DIPE	TAME	MeOH	MEK	EtOH	Propanol	i, t, s-Butanol	n-Butanol
Concentration (mg/kg)	1.869	1.656	2.232	1.809	3.57	1.836	2.365	14.50	1.985	1.950
Stdev	0.01	0.01	0.01	0.01	0.11	0.01	0.04	0.12	0.01	0.01
RSD (%)	0.66	0.71	0.57	0.55	3.36	0.68	1.86	0.84	0.53	0.52
r obtained	0.03	0.03	0.04	0.03	0.30	0.03	0.12	0.34	0.03	0.03
LOQ obtained (µg/kg)	<10	<10	<10	<10	11	<10	24	10	<10	<10

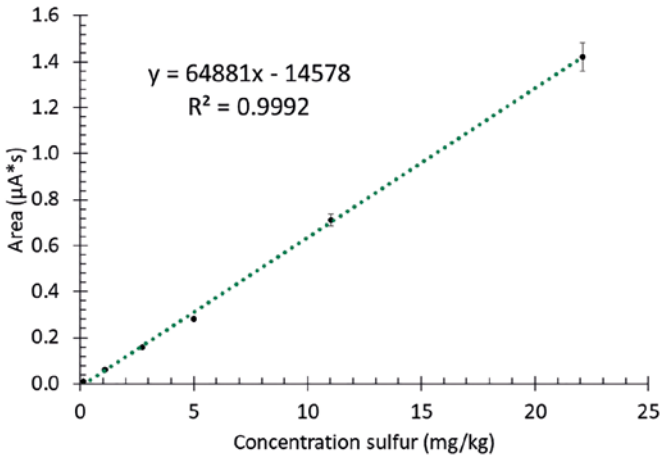
Analysis of Elemental Sulfur in Liquefied Gases



The elemental Sulfur GC application is based on the ASTM D7756 configuration including the DVLS Pressure Station and Liquefied Gas Injector to safely handle and inject LPG samples. The direct injection technique of the LGI ensures full transfer of the elemental sulfur component onto the column.
A Flame Ionization Detector and a Sulfur Chemiluminescence Detector are used to simultaneously detect oily residue and elemental Sulfur.
The calibration curve of the elemental sulfur analysis shows a linear correlation for the analysis range of 0.15 – 22 mg/kg. A study of six LPG samples containing elemental sulfur demonstrates that the Sulfur application analyzes the different amounts of elemental sulfur, ranging from 0.1 to 20 mg/kg S.

Specifications:

- **Analysis time < 20 minutes**
- **Analysis range: 0.1 - 20 mg/kg S**
- **LOD of 0.01 mg/kg S for individual components**



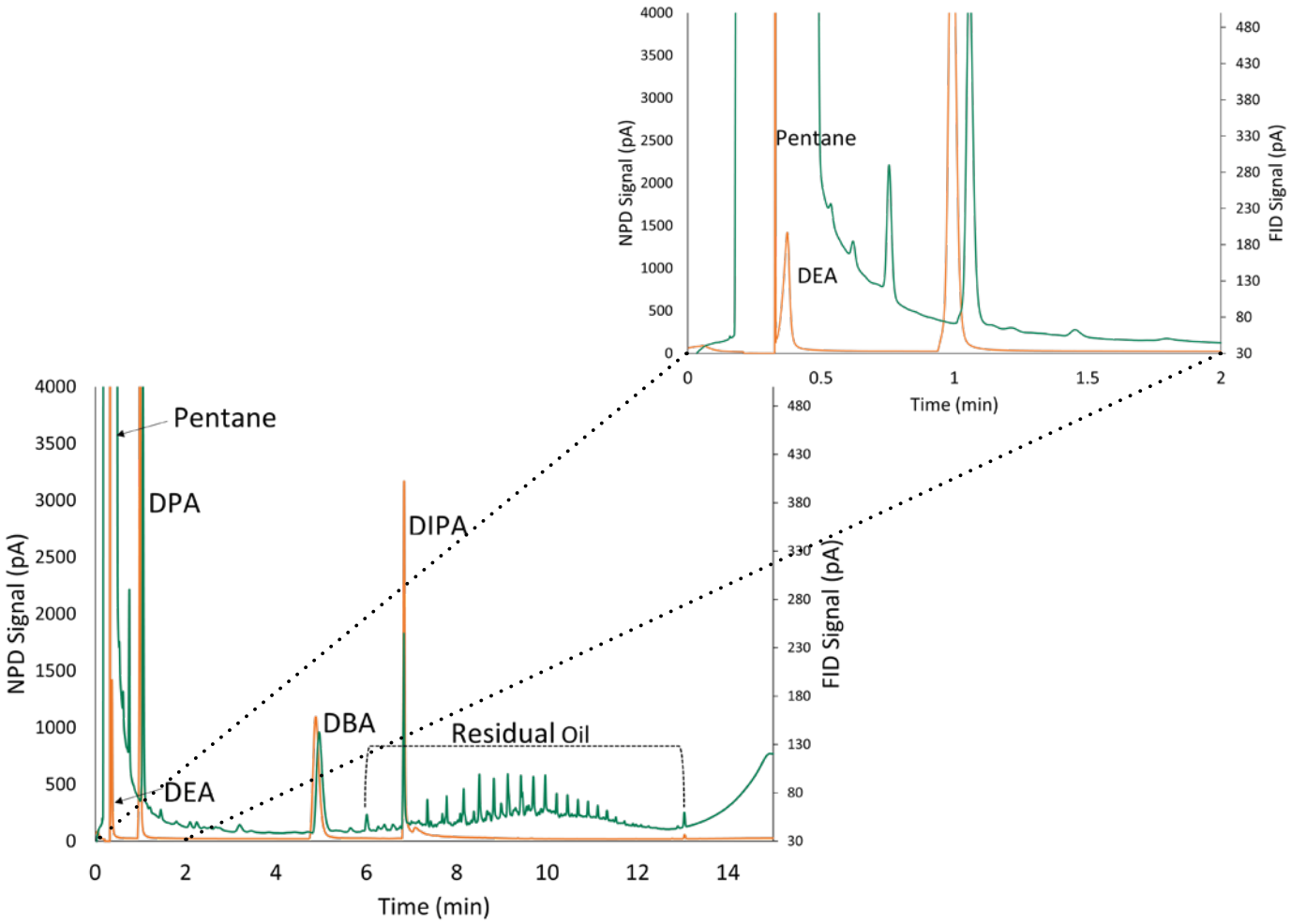
Sample	#1	#2	#3	#4	#5	#6
S_8 (mg/kg S)	14.4	10.8	3.75	3.63	0.70	0.30
RSD of S_8 (%)	7.3	5.4	2.5	2.6	4.4	1.6
Elemental sulfur (mg/kg S)	23.5	18.9	6.65	6.95	0.50	0.46

Analysis of Alkanolamine in LPG

To quantify Amines in LPG an LGI system is configured according to ASTM D7756.
The application uses a Nitrogen Phosphorus Detector (NPD) for a selective nitrogen detection. In a single run both the oily residue and desulfurization agents such as Diisopropanol Amine (DIPA) and Dibutyl Amine (DBA) are determined.

Specifications:

- **Analysis time < 20 minuten**
- **Analysis range: 0.1 mg/kg to 300 mg/kg**
- **LOD amines: 0.001 mg/kg**



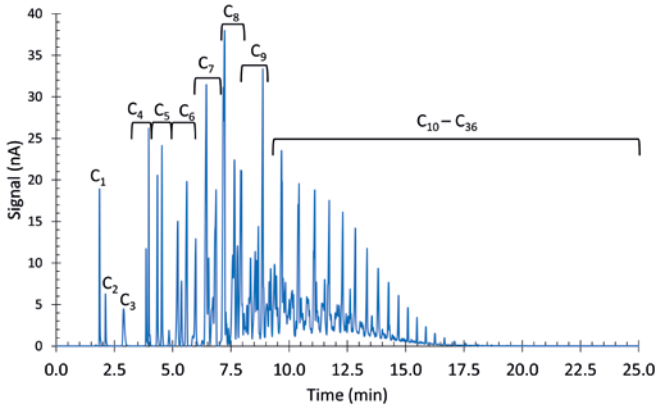
Analysis of N_2, CO_2, H_2S and Hydrocarbons in (Un)stabilized Gas Condensate

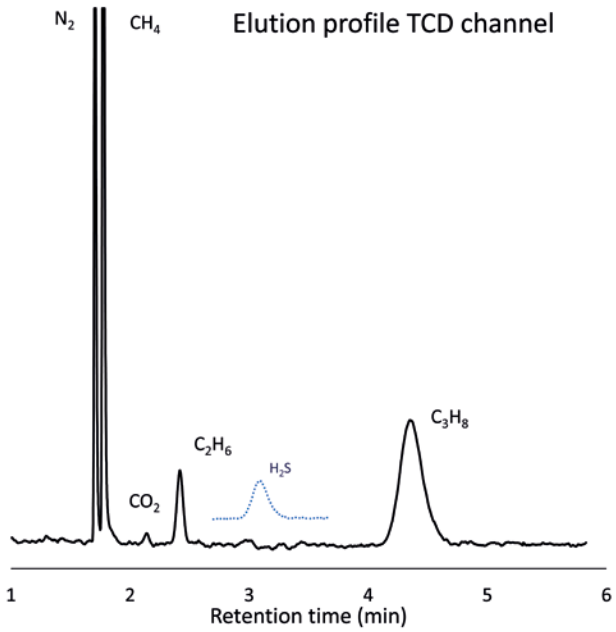
The design of the LGI allows liquefied gas analysis with high pressures and requires a single GC run for the analysis of Nitrogen, Carbon dioxide, Hydrogen sulfide and C1-C36+ hydrocarbons in high pressure unstabilized gas condensate. The sample is kept under pressure by pressurizing the sample cylinder 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.

Specifications:

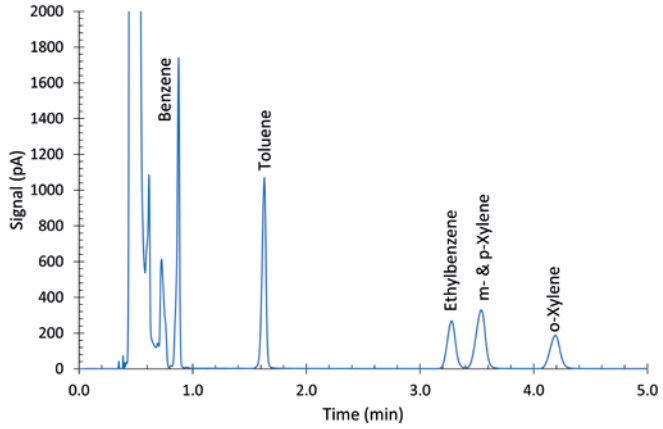
- **Analysis time: 25 minutes**
- **Analysis range permanent gases, H_2S: 0.01% to 100% (m/m)**
- **Analysis range C1-C36+: 0.001 % - 100% (m/m)**
- **LOD permanent gases, H_2S: 0.002 mg/kg**
- **LOD C1 - C36+: 1 mg/kg**





	Nitrogen	CO_2	nC_1	nC_2	nC_3	iC_4	nC_4	iC_5	nC_5	C_6's	C_7's	C_8's	C_9's	C_{10}+
Concentration (m/m%)	0.45	0.025	1.43	0.67	1.26	1.09	2.15	2.30	2.73	0.96	3.70	7.81	9.01	66.4
STDEV	0.02	0.002	0.04	0.02	0.03	0.01	0.02	0.03	0.03	0.002	0.007	0.02	0.02	0.11
RSD (%)	4.65	9.72	2.84	2.94	2.34	0.82	1.12	1.11	1.15	0.21	0.21	0.20	0.24	0.16
R obtained	0.06	0.007	0.11	0.05	0.08	0.02	0.07	0.07	0.09	0.01	0.02	0.04	0.06	0.30

Benzene and Toluene in LPG



The Benzene & Toluene analysis is described in ASTM method D7756 Appendix X3 and includes the Liquefied Gas Injector and Pressure Station. In a single run the application determines both the Benzene, Toluene and oily residue in LPG.

Specifications:

- **Analysis time: 20 minutes**
- **Analysis range: 1 mg/kg to 600 mg/kg**
- **LOD: <0.1 mg/kg**

Key Benefits of the Liquefied Gas Injector

☑ Safe injection of liquefied gases

The direct injection approach of the LGI eliminates the need for evaporating large volumes of liquefied gas.

☑ High repeatability

The direct liquid injection results in an excellent repeatability and it avoids discrimination of high boiling components as there is no transfer to an inlet.

☑ 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 is a dedicated solution to the analysis of heavy components in light matrices such as LPG.

☑ Accurate performance

Several case studies demonstrate an excellent performance. Detection limits of <0.1 mg/kg for individual impurities in liquefied gases are easily achieved.

☑ Standardized method

The LGI is one of the innovations of Da Vinci and has been standardized as ASTM D7756 and EN 16423 for the analysis of oily residue in liquefied petroleum gases by gas chromatography.

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