Application Note

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Determination of Hydrocarbon Composition in Liquefied Petroleum Gas Using the Agilent GC Gasifier and the Agilent 990 Micro GC

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Abstract

It is challenging to analyze liquefied petroleum gas (LPG) with high precision and accuracy. Discrimination and condensation along the transfer line will happen resulting in unsatisfying repeatability. This application note presents a rapid and reliable method for liquefied petroleum gas analysis using the Agilent GC gasifier and the Agilent 990 Micro GC.

Introduction

The precision and accuracy of liquefied petroleum gases (LPG) hydrocarbon component distribution is important for end-use sale of this material. The typical sampling techniques for liquefied petroleum gas involve a high-pressure liquid injection device, a liquid sampling valve, and a gas sampling valve coupled with a vaporizer. Vaporizing is a relatively simple method for such an application. However, most vaporizers in the market suffer from a repeatability problem. In the sampling process, discrimination of the analytes with low and high boiling points may happen due to selective vaporizing and condensing of heavy components along the transfer line.

To preserve the sample's composition from liquid state to gasified state, the Agilent GC gasifier uses a pressure reducing regulator that can create a severe and sudden pressure drop for high-pressurized liquid passing its orifice. This ensures that all compounds vaporize at the same time. Both the regulator and the transfer line are heated to prevent condensation. The tubing in the flow path is deactivated to avoid adsorption of active components. The maximum limit of sample pressure is 1,000 psi. The gasifier output pressure is factory set to 12 psi ±2.5 psi, a safe value to protect the micro GC injection die (maximum tolerance 14.5 psi). It provides a consistent pressure output for samples of different pressures, which is critical to produce reproducible GC performance.

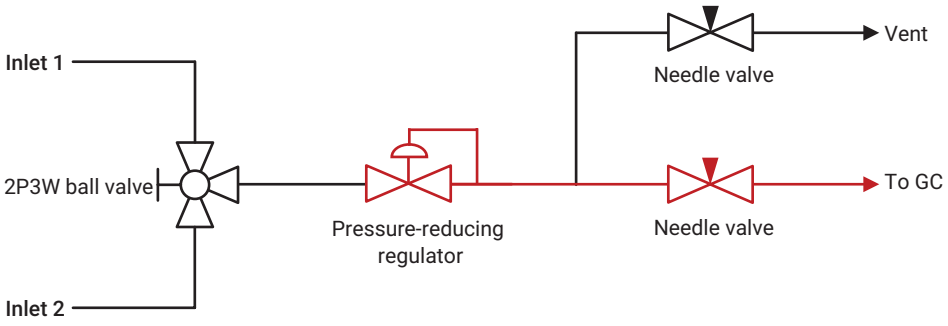
In this application note, the GC gasifier is coupled with the 990 Micro GC to provide fast and reliable analysis of liquefied petroleum gases.

Experimental

The experiments were conducted using a 990 Micro GC configured with a gasifier.

Figure 1 shows how the gasifier couples with the 990 Micro GC. The flow path diagram of the gasifier is shown in Figure 2.

Figure 1. The Agilent G3535A GC gasifier installed on the Agilent 990 Micro GC.



Note: 2P3W = 2-position/3-way, red color denotes heated parts.

Figure 2. The GC gasifier flow path diagram.

An 8 m Agilent J&W CP-Sil 5 CB, backflush channel was used for the hydrocarbon analysis in LPG. The instrument conditions are given in Table 1.

Standard LPG samples were purchased from Air Liquide Corporation. Table 2 shows the sample information.

Table 1. Instrumental conditions.

Gasifier	
Vaporizer Temperature	150 °C
Transfer Line Temperature	100 °C
Agilent 990 Micro GC Agilent J&W, 8 m CP-Sil 5CB, Backflush	
Carrier Gas	Helium
Column Head Pressure	150 kPa
Column Temperature	100 °C
Injection Time	40 ms
Backflush Time	NA
Invert Signal	No
Sample Inlet and Injector Temperature	110 °C

Table 2. LPG standards.

Component (vol%)	Standard 1 (2 Mpa)	Standard 2 (5 Mpa)
Ethane (C2)	0.00460%	0.0900%
Propane (C3)	19.69%	10.81%
iso-Butane (*i*-C4)	20.40%	30.00%
n-Butane (*n*-C4)	58.41%	58.77%
iso-Pentane (*i*-C5)	1.030%	0.101%
1-Pentene (1-C5=)	0.208%	0.104%
n-Pentane (*n*-C5)	0.109%	0.102%
n-Hexane (*n*-C6)	0.0515%	0.0107%
n-Heptane (*n*-C6)	0.0483%	NA
n-Octane (*n*-C6)	0.0491%	NA

Results and discussion

Repeatability

LPG standard 1 is used as hydrocarbon calibration gas. Fifty consecutive runs are conducted. The repeatability for hydrocarbons is excellent with area RSD less than 1% and retention time (RT) RSD of less than 0.2% as listed in Table 3. Figure 3 is the overlapping of 50 chromatograms.

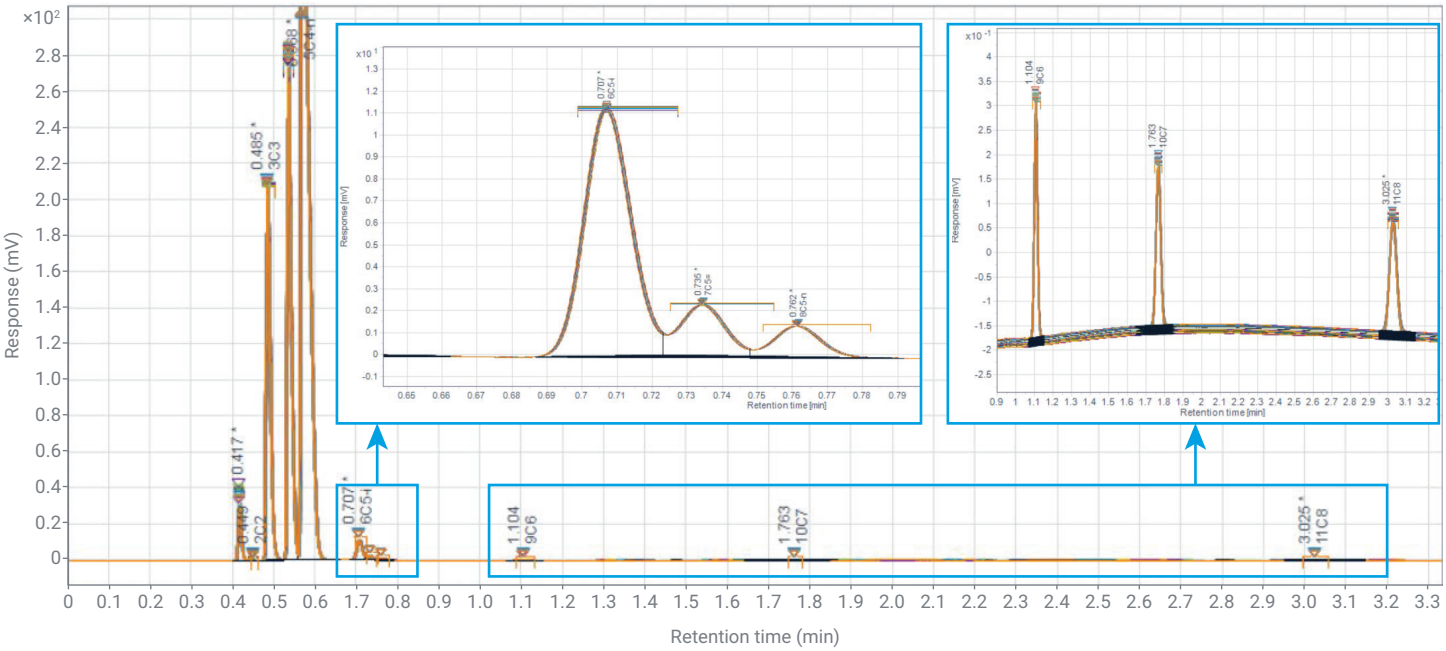


Figure 3. Fifty overlapped runs using LPG calibration standard.

Table 3. Repeatability and experimental $RRF_{n\text{-}C4}$ obtained using LPG calibration standard.

Component	Average (n = 50) RT (s)	RT RSD %	Average (n = 50) Peak Area (mV * s)	Area RSD %	Experimental $RRF_{n\text{-}C4}$
C2	0.449	0.17%	0.029	0.89%	1.49
C3	0.485	0.17%	143.92	0.17%	1.285
i-C4	0.535	0.14%	186.18	0.31%	1.029
n-C4	0.567	0.18%	548.68	0.34%	1
i-C5	0.707	0.13%	10.59	0.40%	0.914
1-C5=	0.735	0.12%	2.18	0.63%	0.896
n-C5	0.761	0.12%	1.35	0.38%	0.759
n-C6	1.104	0.08%	0.62	0.42%	0.781
n-C7	1.762	0.04%	0.63	0.65%	0.722
n-C8	3.023	0.02%	0.68	0.47%	0.683

Carryover

The carryover effect is evaluated by alternating calibration sample run and blank run. Between sample run and blank run, the system is purged using N_2 (Gasifier vent flow 100 mL/min) for 2 minutes. The carryover rate is below 0.4% (<2 ppm carryover for C6+) by comparing the response of each component in blank run and sample run.

Quantitation precision and accuracy

The quantitation accuracy of Micro GC system with the gasifier is evaluated by comparing experimental determined concentration with nominal concentration. LPG standard 2 is analyzed to mimic a real sample under the same experimental condition as the calibration standard. The chromatogram is shown in Figure 4 and the area RSD and RT RSD performance is listed in Table 5.

For each component present in the calibration standard, the average peak area is used to calculate the relative response factor to *n*-butane ($RRF_{n\text{-}C4}$) according to Equation 1.[1] Calibration results are listed in Table 3. The experimental concentration of the LPG standard 2 is then calculated according to Equation 2.[1] The relative error between experimental determined concentration and nominal concentration for each component is less than 10%. While SH/T 0230-2019[1] doesn't have specification on method accuracy, the gasifier-micro GC method accuracy is acceptable for common GC quantitative analysis.

Experimental concentrations obtained by two consecutive LPG standard 2 runs are used to evaluate the method repeatability. The repeatability (r) of the two consecutive runs is calculated according to SH/T 0230-2019[1] and ASTM D2163-14[2] requirements. The calculated r for all components in the LPG standard 2 is less than the average concentration of the two runs as shown in Table 6.

Table 4. Carryover effect.

Peak Area (mV * s)	Sample Run	Carryover Run	Carryover%
C2	0.029	0	0.00%
C3	143.84	0.152	0.11%
i-C4	186.79	0.289	0.15%
n-C4	550.79	0.709	0.13%
i-C5	10.69	0.021	0.20%
1-C5=	2.194	0.003	0.14%
n-C5	1.381	0.002	0.14%
n-C6	0.616	0.001	0.16%
n-C7	0.62	0.002	0.32%
n-C8	0.668	0.002	0.30%

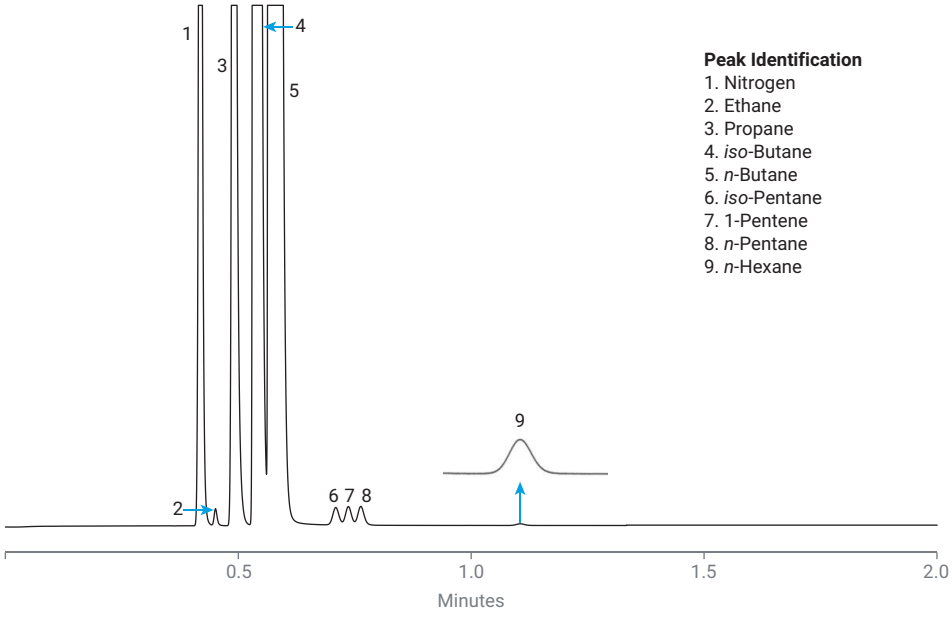


Figure 4. Chromatogram of LPG standard 2.

Table 5. Quantitation accuracy of hydrocarbon in LPG.

Component	Average (n = 10) RT (s)	RT RSD %	Average (n = 10) Peak Area (mV * s)	Area RSD%	Experimental Concentration (Vol%)	Nominal Concentration (Vol%)	Accuracy
C2	0.451	0.07%	0.49	0.33%	0.08%	0.09%	90.90%
C3	0.489	0.08%	75.85	0.31%	10.92%	10.81%	101.00%
i-C4	0.534	0.14%	257.4	0.19%	29.67%	30.00%	98.90%
n-C4	0.566	0.05%	526.89	0.15%	59.01%	58.77%	100.40%
i-C5	0.709	0.05%	1.051	0.36%	0.11%	0.10%	106.60%
1-C5=	0.736	0.05%	1.047	0.13%	0.11%	0.10%	101.10%
n-C5	0.763	0.05%	1.111	0.22%	0.09%	0.10%	92.60%
n-C6	1.105	0.04%	0.127	0.58%	0.01%	0.01%	103.70%

Equation 1

$$f_{vi} = \frac{\frac{V_{Ti}}{A_{Ti}}}{\frac{V_{Ts}}{A_{Ts}}}$$

f_{Vi} : Relative response factor for component i

V_{Ti} : Nominal volume percentage of component i (mol/mol)

V_{Ts} : Nominal volume percentage of Balanced component's (mol/mol)

A_{Ti} : Peak area of component i (mol/mol)

A_{Ts} : Peak area of Balanced component's (mol/mol)

Equation 2

$$V_{Ti} = \frac{f_{Vi} A_{Ti}}{\sum_{i=1}^{n} f_{Vi} A_{Ti}}$$

V_{Ti} : Concentration of component i in the sample

f_{Vi} : Relative response factor for component i calculated by Equation 1.

A_{Ti} : Peak area of component i in the sample

Table 6. Quantitation repeatability of hydrocarbon in LPG.

Hydrocarbon	Experimental Concentration		Repeatability (r)			
Component	Run1 x_1 (Vol%)	Run2 x_2 (Vol%)	Equation $x=(x_1+x_2)/2$	r	$\lvert x_1-x_2\rvert$	Verify→ $\lvert x_1-x_2\rvert<r$
C2	0.0817%	0.0816%	$0.108*X^{0.7824}$	0.0137	0.0001	√
C3	10.944%	10.939%	$0.098*X^{0.550}$	0.3654	0.0056	√
i-C4	29.685%	29.680%	$0.056*X^{0.772}$	0.7673	0.0051	√
n-C4	58.973%	58.983%	$0.086*X^{0.409}$	0.4557	0.0103	√
i-C5	0.107%	0.107%	$0.100*X^{0.864}$	0.0145	0.0001	√
1-C5=	0.105%	0.105%	$0.197*X^{1.068}$	0.0177	0.0003	√
n-C5	0.0940%	0.0942%	$0.044*X^{0.4}$	0.0171	0.0002	√
n-C6	0.0111%	0.0112%	$0.341*X^{0.75}$	0.0117	0.0001	√

Note: C2~1-C5 = repeatability specs are from SH/T 0230-2019, it doesn't include n-C5 and n-C6 specs, listed values are from ASTM D2163-2014.

Conclusion

The Agilent GC gasifier coupled with the Agilent 990 Micro GC is suitable for LPG hydrocarbon composition analysis, providing great area repeatability (RSD <1%) and RT repeatability (RSD <0.2%). The system is fast and can complete a C2~C6 analysis within two minutes. The quantitative precision meets the SH/T 0230-2019[1] standard requirements and it offers acceptable quantitative accuracy (relative error <10%). The device is controlled and monitored via a GC user interface, thus providing a simple, rapid, and convenient method to make reliable LPG analysis.

References

1. SH/T 0230-2019. Determination of composition in liquefied petroleum gases by gas chromatography.
2. ASTM D2163-14. Standard test method for determination of hydrocarbons in liquefied petroleum (LP) gases and propane/propene mixtures by gas chromatography.

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DE.3724074074

Printed in the USA, October 22, 2020
5994-2624EN

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