Application Note
Energy and Chemicals

Agilent GC Gasifier Coupled with Agilent 8890 and 8860 Gas Chromatographs for Pressurized Liquid Sample Analysis

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Abstract

Vaporizing is a simple method for sampling pressurized liquid samples as fractionation can cause unsatisfying precision and accuracy. The Agilent GC gasifier is designed to ensure the flash vaporization of all components in the liquid sample simultaneously. It is also designed to guarantee a gasified sample with constant flow and pressure to the GC system. The deactivated tubing and heated transfer line in the gasifier help eliminate possible adsorption and condensation. Therefore, samples delivered to the GC system are representative. Various pressurized liquid samples were analyzed with this device coupled with both the Agilent 8890 and Agilent 8860 GC systems, including liquified petroleum gases with and without oxygenates and high purity 1-butene. Excellent repeatability is obtained for both hydrocarbons and oxygenates with area RSD below 1% on the 8890 GC.

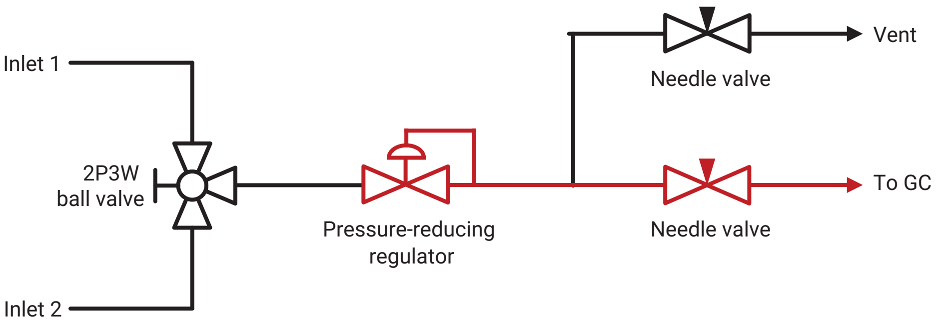
Introduction

The typical sampling techniques for liquefied light hydrocarbons include 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 repeatability problem. During vaporizing, evaporation may occur along with the vaporization process instead of flashing the entire sample into vapor. In evaporation, analytes with low boiling points gasify faster than those with higher boiling points, resulting in fractionation. Also, gasified samples can condensate along the transfer line, especially for high boiling point molecules. This results in the gasified sample not being able to accurately represent the sample from the cylinder.

The Agilent GC gasifier has a pressure reducing regulator to ensure flash vaporizing of all components simultaneously, hence providing the GC system with a representative sample. The vaporizer and transfer line in the gasifier are heated and well insulated to avoid condensation. The tubing in the flow path is deactivated to eliminate a possible adsorption effect. This compact device is installed next to the GC back inlet and controlled by the GC data system. Excellent repeatability is obtained with area RSD below 1% on the 8890 GC. Both hydrocarbons and oxygenates are linear across their typical concentration range with R^2 better than 0.998, providing good quantitative accuracy and precision.

Experimental

The experiments were conducted using an 8890 or 8860 GC. The sampling method is "G3535A Gasifier + 6-port gas sampling valve (GSV)" or liquid sampling valve (LSV). The flow path diagram of the GC gasifier (G3535A) is shown in Figure 1. The "Gasifier + GSV" GC configuration for hydrocarbon-only samples and an oxygenated sample are shown in Figure 2 and Figure 3, respectively. For hydrocarbon-only samples, an Agilent 30 m × 0.53 mm Al_2O_3 column (part number 19095P-M23) or an Agilent 50 m × 0.53 mm Al_2O_3 column (part number 19095P-K25) was used for separation. For samples with



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

Figure 1. The GC gasifier flow path diagram.

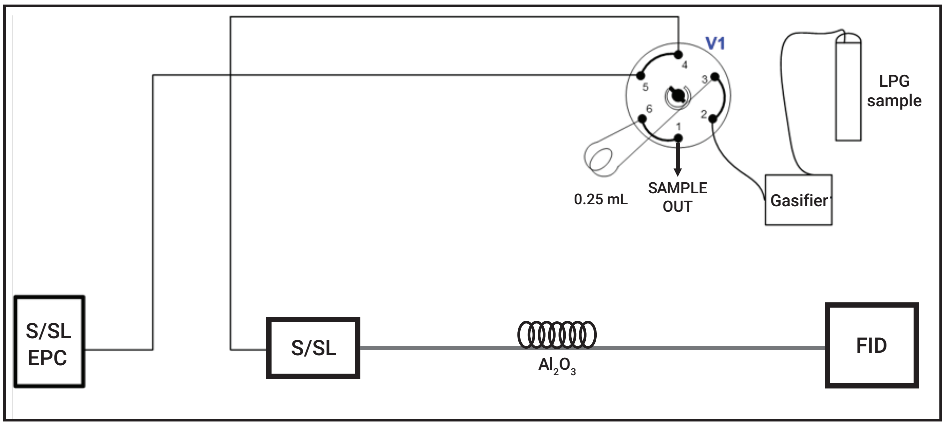


Figure 2. The GC configuration diagram for hydrocarbon-only samples.

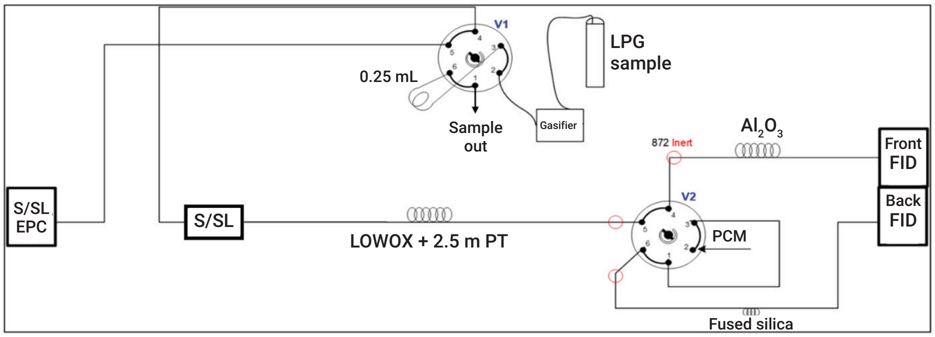


Figure 3. The GC configuration diagram for samples with oxygenate impurities.

oxygenate impurities, the hydrocarbons were quickly eluted through an Agilent 10 m × 0.53 mm Lowox column (part number CP8587) and separated by an Al_2O_3 column. Then, valve 2 switched the sample into the other FID for separation and detection of oxygenates. Tables 1 and 2 show the system experimental conditions.

Standard LPG samples and oxygenates calibration gases were purchased from Air Liquide Corporation. Table 3 shows the sample information.

Table 1. Instrument general conditions.

Parameter	Value
GC	Agilent 8890 or 8860
Injection Source	Agilent liquid sampling valve (LSV) or Agilent gasifier (vaporizer 150 °C, transfer line 100 °C) + gas sampling valve (GSV, 150 °C)
Injection Port	Split/splitless, 200 °C or 250 °C
Sample Size	Liquid sampling valve 0.5 µL Gas sampling valve 0.25 mL
Carrier Gas	Helium
FID	300 °C H_2 30 mL/min; air 400 mL/min; make up N_2 25 mL/min

Table 2. Columns and parameters for various samples.

Standard	Sample No.	Sample Description	Columns	Column Flow (mL/min)	Split Ratio	Temperature Program
NB SH/T 0230-2019	1	1 Mpa-oxygenated LPG	Column1: Agilent HP-AL/M, 30 m × 0.53 mm, 15 µm (p/n 19095P-M23) Column2: Agilent Lowox, 10 m × 0.53 mm, 10 µm (p/n CP8587)	4.5	40	90 °C for 1 min, 6 °C to 168 °C
	2	5 Mpa C1-n-C6	Agilent HP-AL/M, 30 m × 0.53 mm, 15 µm (p/n 19095P-M23)	4.5	40	90 °C for 1 min, 6 °C to 168 °C
	3	2 Mpa C2~n-C5 (Major components are C4)	Agilent HP-AL/M, 30 m × 0.53 mm, 15 µm (p/n 19095P-M23)	4.5	40	90 °C for 1 min, 6 °C to 168 °C
	4	2 Mpa C2~n-C5 (Major components are C3)	Agilent HP-AL/M, 30 m × 0.53 mm, 15 µm (p/n 19095P-M23)	4.5	40	90 °C for 1 min, 6 °C to 168 °C
	5	2 Mpa C2-n-C8	Agilent HP-AL/M, 30 m × 0.53 mm, 15 µm (p/n 19095P-M23)	4.5	40	90 °C for 1 min, 6 °C to 180 °C
	6	Oxygenates calibration gases	Column 2: Agilent Lowox, 10 m × 0.53 mm, 10 µm (p/n CP8587)	4.5	40	90 °C for 1 min, 6 °C to 168 °C
NB SH/T 1492-2004	7	2 Mpa 1-butene (purity >99%)	Agilent AL_2O_3, 50 m × 0.53 mm, 15 µm PLOT/KCL (p/n 19095P-K25)	6.5	40	80 °C for 10 min, 5 °C to 100 °C for 1min, 10 °C to 180 °C

Table 3. Performance comparison between LSV and "Gasifier + GSV" system.

	Volume Relative Response Factor Relative to *n*-Butane ($RRF_{n\text{-}C4}$)								
	Methane (C1)	Ethane (C2)	Propane (C3)	*iso*-Butane (i-C4)	*n*-Butane (n-C4)	*iso*-Pentane (i-C5)	1-Pentene (1-C5=)	*n*-Pentane (n-C5)	*n*-Hexane (n-C6)
"Gasifier + GSV"	4.559	2.489	1.554	1.064	1.000	0.836	0.797	0.826	0.648
LSV	3.836	2.296	1.462	1.035	1.000	0.804	0.803	0.773	0.621
Difference (GSV/LSV)	119%	108%	106%	102.8%	100%	107%	100%	103%	104%

Results and discussion

Discrimination

It is challenging to convert highly volatile liquified hydrocarbons so they vapor instantly without changing the composition. The goal here was to flash vaporize all components at the same time to preserve the sample composition. To achieve this goal, a pressure-reducing regulator was used to create a sudden pressure drop (from several Mpa to less than 0.1 Mpa). The liquid sampling valve injected samples in their original state. The performance between the LSV and the "Gasifier + GSV" were compared to evaluate the possible discrimination effect of the GC gasifier.

A 5 Mpa liquified C1~n-C6 sample (sample 2) was used to evaluate if discrimination exists. For normalization, the average peak area of each component was used to calculate the relative response factor to *n*-butane ($RRF_{n\text{-}C4}$) according to Equation 1.[1] As shown in Table 3, the $RRF_{n\text{-}C4}$ obtained by the LSV method and the "Gasifier + GSV" method for C1 to C6 were close (difference <10%). The difference of methane is 19%, which is understandable since methane has high partial pressure.

Repeatability

The 2 Mpa C2 ~C5 (sample 3) sample was used to demonstrate the repeatability of the gasifier. Twenty consecutive runs were conducted and the repeatability for both hydrocarbons and oxygenates was excellent with area RSD less than 1% and RT RSD less than 0.1% as listed in Table 4. Figure 4 shows the overlapping of 20 chromatograms.

Table 4. Repeatability and experimental RRFn-C4 obtained using LPG calibration standard.

Component	Average (n = 20) RT (s)	RT RSD %	Average (n = 20) Peak Area (pA)	Area RSD %
Ethane (C2)	3.0735	0.031%	11.01	0.59%
Propane (C3)	3.4621	0.030%	245.91	0.57%
Propylene (C3=)	4.1094	0.027%	37.43	0.56%
iso-Butane (i-C4)	4.2119	0.029%	289806.92	0.57%
n-Butane (n-C4)	4.5066	0.026%	28067.25	0.56%
trans-2-Butene (trs-C4=)	5.3298	0.035%	216327.14	0.56%
iso-Pentane (i-C5)	6.8309	0.022%	73.09	0.55%
1-Pentene (1-C5=)	9.4857	0.020%	37.67	0.58%
Dimethyl ether	5.0403	0.027%	1188.03	0.56%
Methyl tertiary-butyl ether	8.5242	0.023%	316.59	0.55%
Methanol	12.4813	0.085%	47.78	0.70%
Acetone	13.6575	0.060%	159.35	0.56%

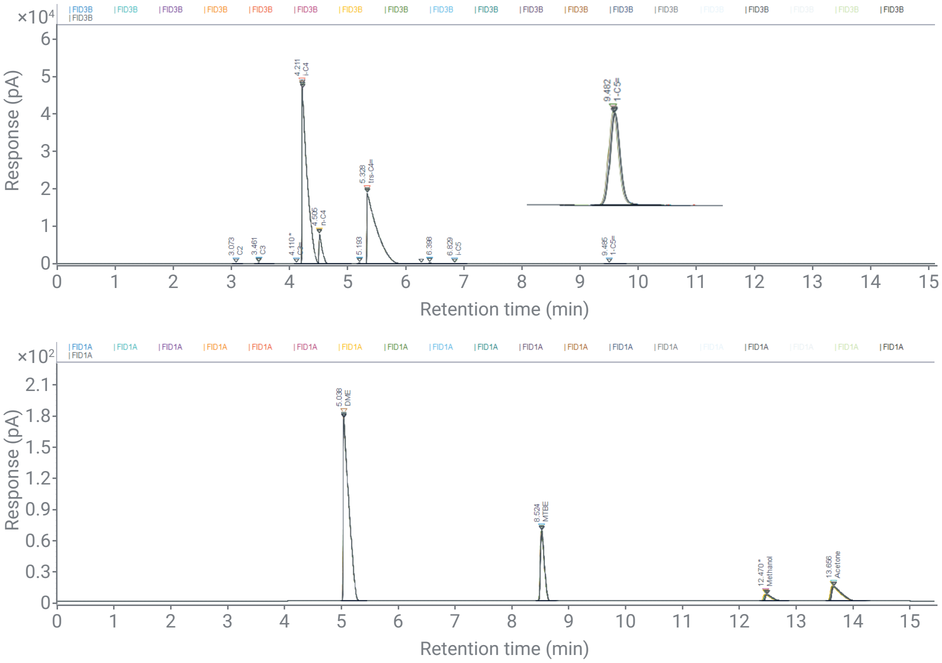


Figure 4. 20 overlapped runs for samples with oxygenate impurities (sample 3).

Carryover

The carryover effect was evaluated by alternating a sample run and a blank run using a 2 Mpa C2 ~C8 sample (sample 5). Between the sample run and blank run, the system was purged using N_2 (gasifier vent flow 100 mL/min, transfer line 30 mL/min) for two minutes. The carryover rate is below 0.1% (<1 ppm carryover for C6+) by comparing the response of each component in the blank run and sample run as listed in Table 5.

Dynamic range

The gasifier is designed to handle liquified petroleum gases with wide concentrations ranges (hydrocarbons in 50 ppm to 100 %, oxygenates in 100 ppm to 40%). Various liquified standard samples (sample 1 ~5) were analyzed to evaluate the linearity of hydrocarbons. Four oxygenates calibration gases were used to establish a calibration curve for dimethyl ether (DME): methyl tertiary-butyl ether (MTBE), methanol, and acetone respectively. The tubing in the new gasifier device was deactivated to eliminate a possible adsorption effect. As shown in Table 6, the linearity for hydrocarbons and four oxygenates across their typical concentration range in LPG samples was good (R^2 >0.998).

Table 5. Carryover effect.

Component	Sample Run (peak area)	Carryover Run (peak area)	Carryover%
Ethane (C2)	4.90	0.00	0.000%
Propane (C3)	18585.49	1.00	0.005%
Propylene (C3=)	17193.55	1.02	0.006%
iso-Butane (i-C4)	49742.88	3.89	0.008%
n-Butane (n-C4)	106382.72	8.89	0.008%
trans-2-Butene (trs-C4=)	52201.84	6.67	0.013%
iso-Pentane (i-C5)	3379.45	0.56	0.017%
n-Pentane (n-C5)	427.69	0.09	0.022%
1-Pentene (1-C5=)	688.00	0.12	0.018%
n-Hexane (n-C6)	202.71	0.07	0.035%
n-Heptane (n-C7)	220.49	0.14	0.064%
n-Octane (n-C8)	251.70	0.24	0.094%

Table 6. Linearity for common hydrocarbons and oxygenates in LPG.

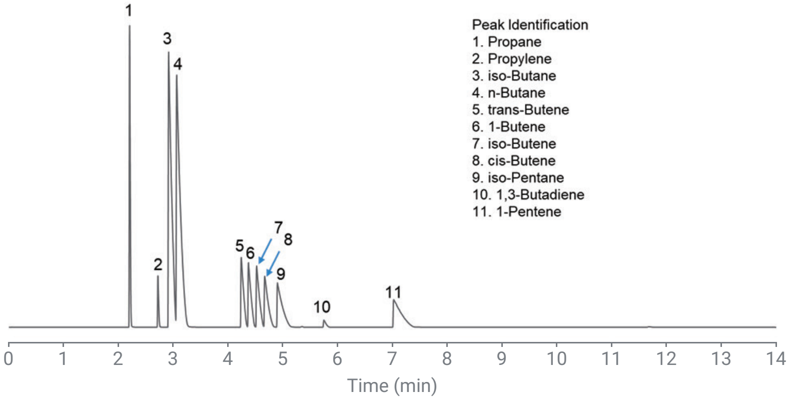
Component	Typical Concentration in LPG (Vol%)	Concentration Level (Vol%)				R^2
Ethane (C2)	0.01%~3%	0.0046%	0.090%	2.90%	NA	1
Propane (C3)	0.05%~95%	0.0568%	9.87%	58.38%	NA	1
Propylene (C3=)	0.01%~95%	0.0109%	1.01%	9.82%	30.00%	0.9999
iso-Butane (i-C4)	0.05%~80%	0.0501%	0.1041%	20.40%	53.48%	0.9997
n-Butane (n-C4)	0.2%~99%	0.205%	5.04%	38.21%	58.87%	0.9994
trans-2-Butene (trs-C4=)	0.01%~40%	0.0120%	5.10%	20.20%	40.20%	0.9980
iso-Pentane (i-C5)	0.01%~3%	0.0105%	0.101%	1.03%	NA	0.9999
1-Pentene (1-C5=)	0.01%~0.5%	0.00542%	0.104%	0.208%	0.498%	0.9981
Dimethyl ether	0.1%~40%	0.0505%	4.99%	9.97%	40.3%	1
Methyl tertiary-butyl ether	0.01%~1%	0.0100%	0.0994%	0.496%	1.01%	1
Methanol	0.01%~1%	0.0101%	0.103%	0.528%	1.03%	0.9999
Acetone	0.01%~1%	0.0100%	0.101%	0.499%	1.03%	0.9998

Sample analysis

Liquified petroleum gas (LPG) with oxygenates: This analysis is conducted according to SH/T 0230-2019.[1] A typical oxygenated LPG chromatogram is shown in Figure 5 and was acquired using sample 1. It was used as a calibration sample for hydrocarbons. Four oxygenate gas samples were used to calibrate oxygenate components. Sample 3 was used as a real sample to evaluate the quantitative accuracy and precision. The quantitative precision met the SH/T 0230-2019 standard requirements[1] and offered acceptable quantitative accuracy (85~115%). Detailed information can be found in Reference 3.[3]

Pressurized high purity 1-butene: This sample was analyzed according to SH/T 1492-2004 for 1-butene purity and impurity analysis.[4] The chromatogram is shown in Figure 6.

Hydrocarbon components chromatogram acquired from back FID



Hydrocarbon components chromatogram acquired from front FID

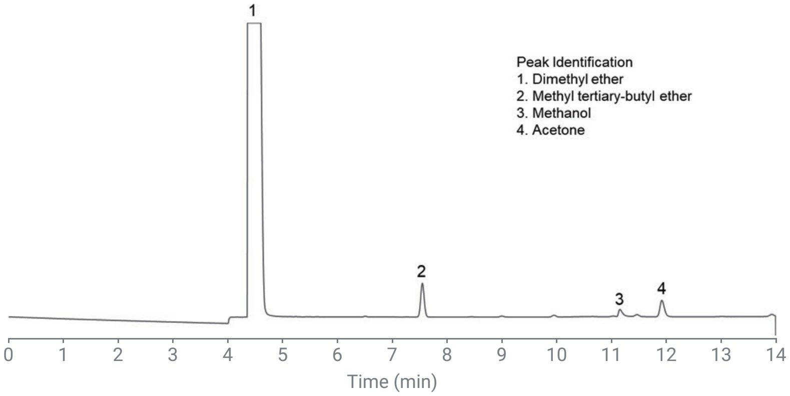


Figure 5. Typical oxygenated LPG GC chromatogram obtained using sample 1 on the Agilent 8890 GC.

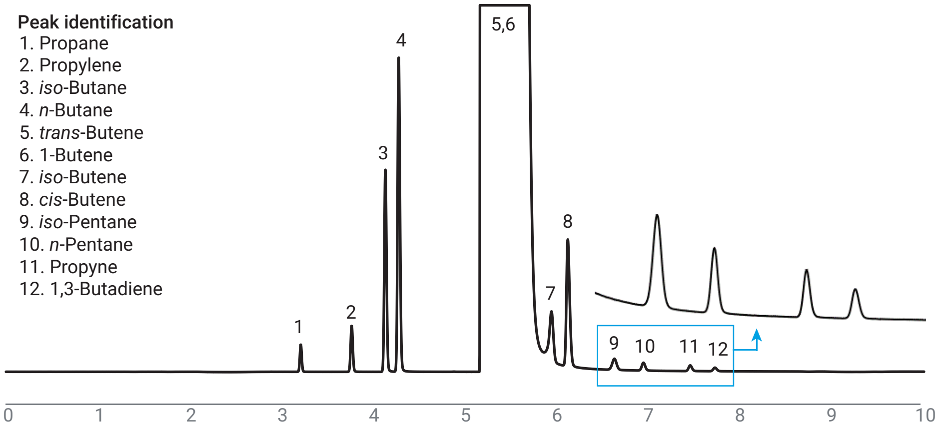


Figure 6. Typical 1-butene GC chromatogram obtained using sample 7 on the Agilent 8890 GC.

Conclusion

The Agilent GC gasifier coupled with the Agilent 8890 or the Agilent 8860 GC is suitable for liquified light hydrocarbon composition (C1 ~C5) and oxygenate impurity analysis. Various pressurized liquid samples were tested on this device with high accuracy, precision, and great area repeatability (RSD <1%). The device was controlled and monitored via the GC user interface, thus providing a simple and convenient method to make reliable LPG analysis.

References

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