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Determination of Hydrocarbon and Oxygenate Composition in Liquefied Petroleum Using the Agilent GC Gasifier and Agilent 8890 GC

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Abstract

It is challenging to analyze liquefied petroleum gas with high precision and accuracy. Discrimination and condensation along the transfer line will happen, resulting in unsatisfying repeatability. Adsorption of active components like methanol can cause loss of sensitivity. In this application note, the Agilent GC gasifier was used to analyze liquefied petroleum gas with oxygenate impurities. The gasifier has a pressure reducing regulator to ensure flash vaporizing of all components simultaneously, hence providing the GC with representative samples. 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 possible adsorption effect. This compact device is installed next to the GC back inlet and controlled by the Agilent 8890 GC data system. Excellent repeatability was obtained with area RSD below 1%. Oxygenates were linear across their typical concentration range with R^2 better than 0.999. The quantitative precision meets the SH/T 0230-2019[1] standard requirements and it offers acceptable quantitative accuracy (85%~115%).

Introduction

The typical sampling techniques for liquefied petroleum gas 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 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 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 1000 psi. The gasifier output pressure is factory set to 12 psi ±2.5 psi. It provides a consistent pressure output for samples of different pressures, which is critical to produce reproducible GC performance.

A couple of liquefied petroleum gas samples were analyzed on this device. Excellent repeatability was obtained (typically within 1%). The linearity of oxygenates is excellent across their typical existed concentration range. Both hydrocarbon and oxygenates are quantified meeting the precision criteria of SH/T 0230-2019 standard.[1] The quantitative accuracy is within 85% to 115%.

Experimental

The flow path diagram of the Agilent GC gasifier is shown in Figure 1. The main components of the gasifier include:

- Two inlets for either gaseous or liquefied samples, switchable by a manual 2-position/3-way valve

- A heated regulator (the vaporizer), with a temperature set and controlled by the GC and displayed in the GC user interface (local UI, web browser, data acquisition software)

- A heated transfer line at a constant 100 °C

- A mechanical needle valve for purging in the vent line

- A mechanical needle valve for gas flow adjustment in the sample line

The experiments were conducted using an 8890 GC configured with a gasifier, two gas sampling valves (GSV), a PCM, a deactivated split/splitless inlet, and two flame ionization detectors (FID). Figure 2 shows the configuration diagram and Figure 3 shows how the gasifier couples with the 8890 GC. LPG samples were first flashed vaporized in the gasifier, then were transferred into the GSV for injection. The hydrocarbons first eluted through an
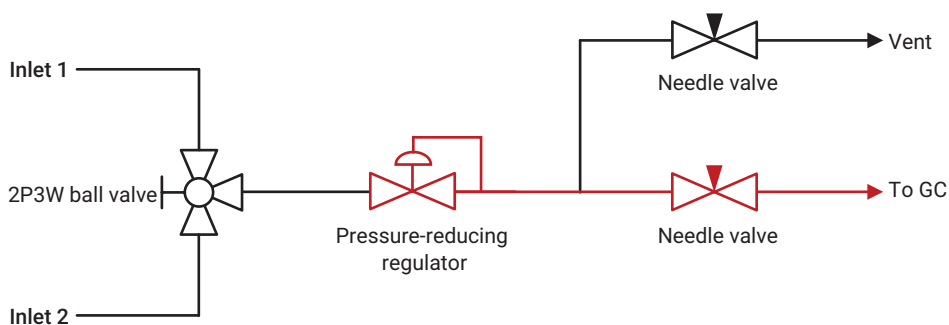
Note: 2P3W = 2-position/3-way, red color denotes heated parts.

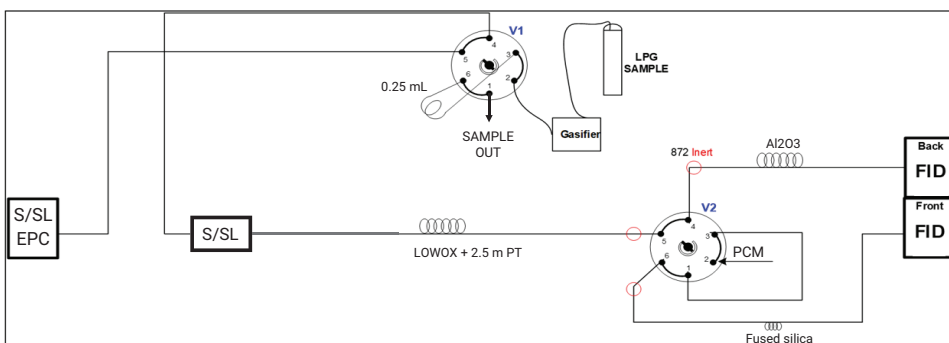**Figure 1.** The GC gasifier flow path diagram.

Figure 2. The 8890 GC configuration diagram.

Figure 3. The Agilent GC gasifier installed on the Agilent 8890 GC.

Agilent Lowox, 10 m × 0.53 mm column (part number CP8587) and separated by an Agilent PLOT Al$_2$O$_3$ "M", 30 m × 0.53 mm column (part number 19095P-M23). Then, valve 2 switched the later-eluted oxygenates sample into the other FID for separation and detection of oxygenates. The sample was run in the split mode using an Agilent split liner (part number 5190-2295). The Agilent OpenLab 2.4 software was used for instrument control, data acquisition, and data analysis. Data were acquired at 5 and 20 Hz. The instrument conditions are given in Table 1.

Standard LPG samples (Table 2) and oxygenates calibration gases (Table 3) were purchased from Air Liquide Corporation.

Table 1. Instrumental conditions.

Parameter	Value
Gas Chromatograph	Agilent 8890A
Gasifier	Vaporizer: 150 °C Transfer line: 100 °C Flow to GSV: 20 mL/min
Gas Sampling Valve	6-Port, 0.25 mL loop, 150 °C
Event	0.01 min Valve 1 On 0.5 min Valve 1 Off 4 min Valve 2 On 14 min Valve 2 Off
SSL	200 °C, split ratio 40:1
Column Flow (He)	4.5 mL/min
Column	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)
Oven	90 °C for 1 min, 6 °C to 168 °C
FID	300 °C H$_2$: 30 mL/min Air: 400 mL/min Makeup N$_2$: 25 mL/min

Table 2. LPG standards.

Component	Standard 1 1 Mpa	Standard 2 2 Mpa
	Concentration (Vol%)	
Propane (C3)	10.80%	0.0596%
Propylene (C3=)	2.03%	0.0104%
iso-Butane (i-C4)	24.30%	53.48%
n-Butane (n-C4)	27.23%	5.04%
trans-2-Butene (trs-C4=)	5.10%	40.20%
1-Butene (1-C4=)	5.06%	NA
iso-Butene (i-C4=)	5.18%	NA
cis-Butene (Cis-C4=)	5.08%	NA
1,3-Butadiene (1,3-C4=)	0.473%	NA
iso-Pentane (i-C5)	4.82%	0.0105%
1-Pentene (1-C5=)	4.82%	0.00569%
Dimethyl ether	5.07%	0.9860%
Methyl tertiary-butyl ether	0.00968%	0.0704%
Methanol	0.0190%	0.0682%
Acetone	0.0100%	0.0688%

Table 3. Oxygenate calibration standards.

Component	Oxygenate Calibration Gas N$_2$ Balance			
	Concentration (Vol%)			
Dimethyl ether	0.0505%	4.99%	9.97%	40.3%
Methyl tertiary-butyl ether	0.0100%	0.0994%	0.496%	1.01%
Methanol	0.0101%	0.103%	0.528%	1.03%
Acetone	0.0100%	0.101%	0.499%	1.03%

Results and discussion

Chromatogram

This application was conducted according to SH/T 0230-2019 (similar to ASTM D2163]).[2] Typical oxygenated LPG chromatograms are shown in Figures 4 and 5, acquired using LPG standard 1. Figure 4 is a hydrocarbon chromatogram acquired by the back FID, and Figure 5 is an oxygenate chromatogram acquired by the front FID.

Quantitation

Hydrocarbon repeatability and calibration

LPG standard 1 was used as hydrocarbon calibration gas. Six consecutive runs were conducted and the repeatability for hydrocarbons was excellent with area RSD less than 1% (Table 4).

The average area for each component was used to calculate the relative response factor to n-butane (RRF_{n-C4}) according to Equation1[1] and listed in Table 5.

Equation 1.

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

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)

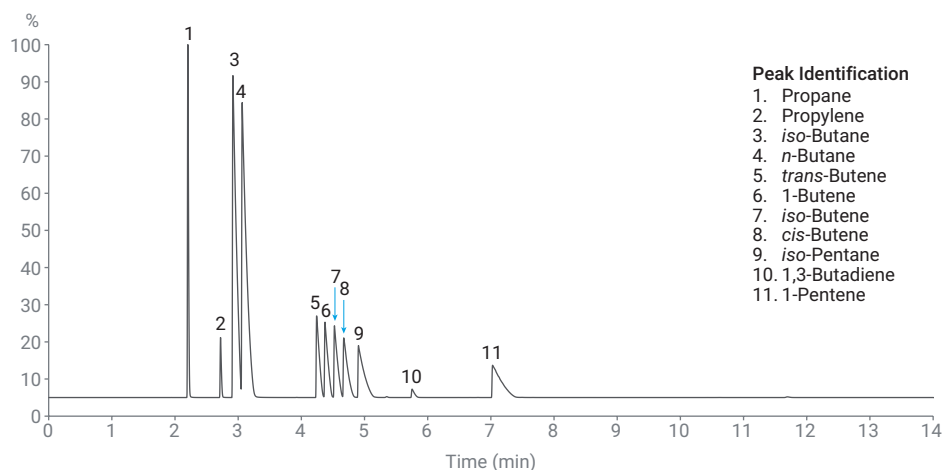A_{Ts} = Peak area of Balanced component's (mol/mol)

Figure 4. Hydrocarbon components chromatogram acquired from Back FID.
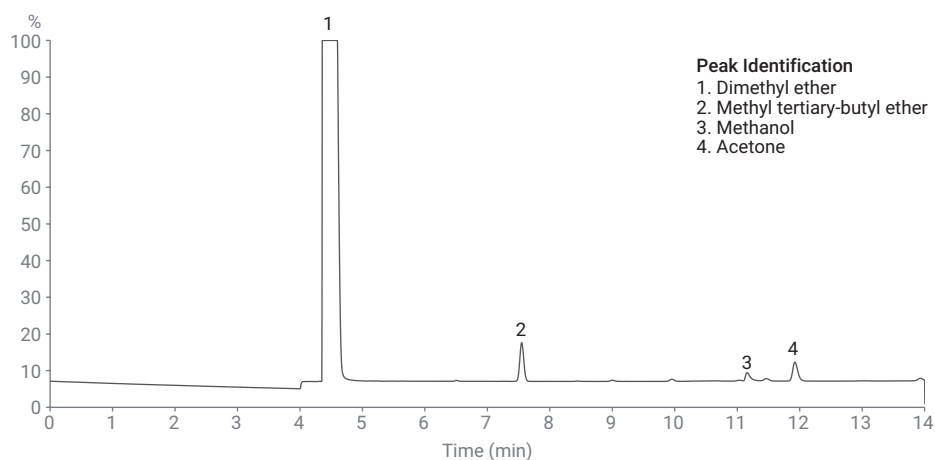
Peak Identification
1. Propane
2. Propylene
3. iso-Butane
4. n-Butane
5. trans-Butene
6. 1-Butene
7. iso-Butene
8. cis-Butene
9. iso-Pentane
10. 1,3-Butadiene
11. 1-Pentene

Figure 5. Oxygenate components chromatogram acquired from Front FID.

Peak Identification
1. Dimethyl ether
2. Methyl tertiary-butyl ether
3. Methanol
4. Acetone

Table 4. Hydrocarbon repeatability.

Run	C3	C3=	i-C4	n-C4	trs-C4=	1-C4=	Cis-C4=	i-C4=	1,3-C4=	i-C5	1-C5=
1	22553.8	4362.9	67025.5	75486.2	13842.0	13834.3	13779.8	14077.9	1368.62	16714.9	16054.0
2	22272.8	4303.9	66497.2	74998.6	13759.2	13764.3	13738.0	14004.3	1358.18	16711.6	15989.9
3	22318.4	4315.1	66528.3	74968.8	13761.1	13769.3	13730.9	14024.6	1358.56	16630.4	15971.4
4	22314.6	4311.4	66694.7	75234.7	13806.2	13808.6	13741.4	14044.4	1362.19	16689.0	16051.7
5	22298.0	4308.0	66656.7	75158.9	13792.3	13796.8	13772.4	14047.5	1361.31	16700.3	15989.4
6	22262.6	4302.4	66463.6	74950.7	13756.6	13758.3	13726.6	14003.9	1357.45	16680.0	15994.9
Average	22336.7	4317.3	66644.3	75133.0	13786.2	13788.6	13748.2	14033.8	1361.1	16687.7	16008.5
SD	108.7	22.8	207.7	206.9	34.0	29.8	22.4	28.6	4.1	31.0	35.2
RSD	0.5%	0.5%	0.3%	0.3%	0.2%	0.2%	0.2%	0.2%	0.3%	0.2%	0.2%

Table 5. Experimental RRF_{n-C4}

Component	C3	C3=	i-C4	n-C4	trs-C4=	1-C4=	Cis-C4=	i-C4=	1,3-C4=	i-C5	1-C5=
RRF_{n-C4}	1.334	1.297	1.006	1.000	1.020	1.012	1.019	1.018	0.959	0.795	0.831

Oxygenate repeatability and calibration

Four oxygenates calibration gases were used to establish the 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 Figure 6, the calibration from four oxygenates across their typical concentration range in LPG samples are quite linear (R^2 >0.999). Table 6 gives a summary of repeatability (n = 10, area RSD <1%) at each concentration level.
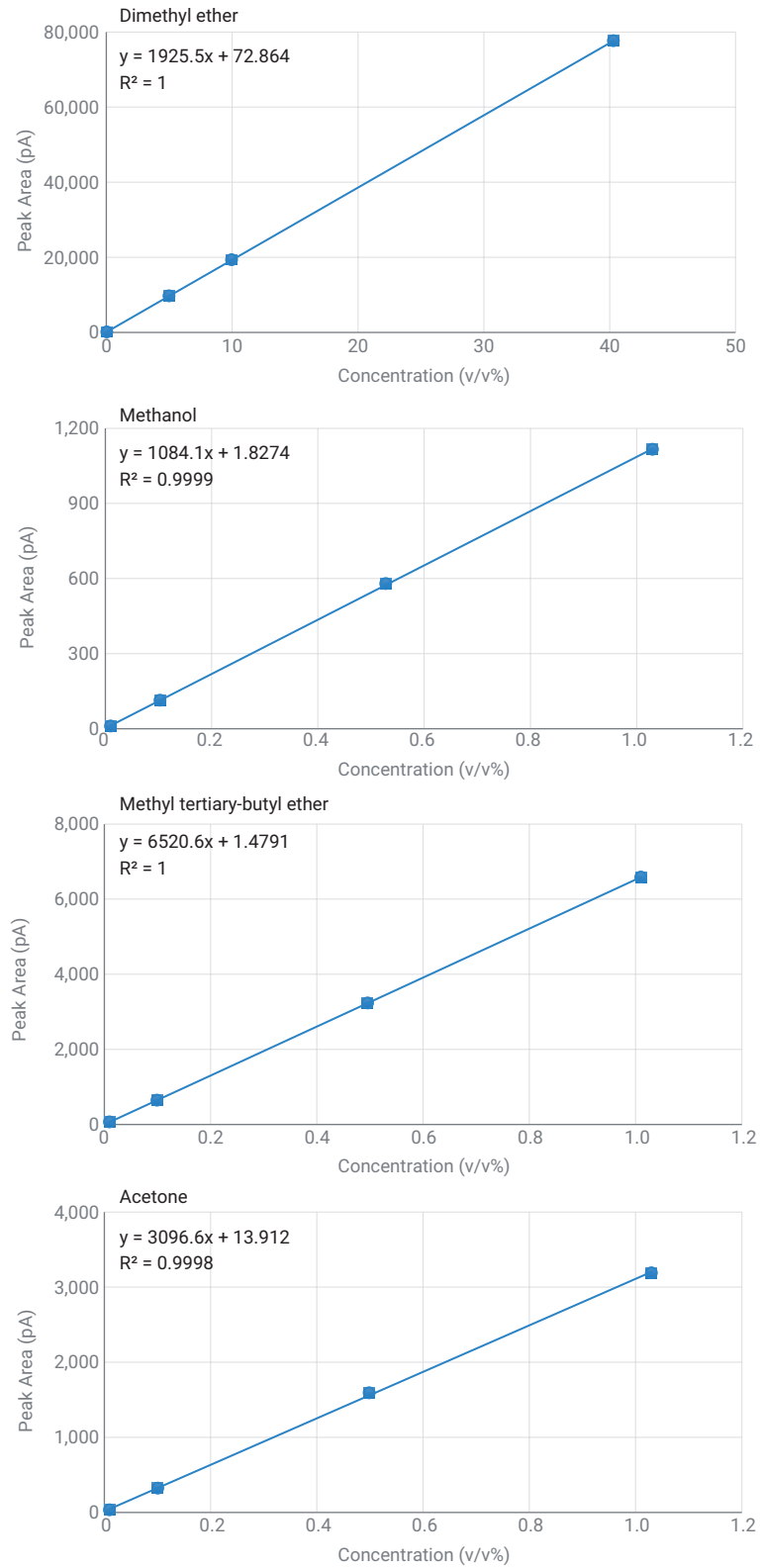

Figure 6. Calibration curves for four common oxygenates existed in LPG.

Quantitation

LPG standard 2 was analyzed as a sample. The average response of two consecutive runs was used to calculate the oxygenates and hydrocarbons concentration according to Equations 2 and 3, respectively. The precision and quantitative accuracy are listed in Table 7. The repeatability for all components meets the SH/T 0230-2019 standard criteria.[1] The quantitative accuracy was then obtained by comparing the experimental concentration with certified concentration, which is within 85% to 115%.

Equation 2.

$$V_{0j} = a_j A_{0j} + b_j$$

V_{0j} = Nominal volume percentage of oxygenate j (mol/mol)

A_{0j} = Peak area of oxygenate j

a_j, b_j = Slope coefficient and intercept of oxygenate j calibration curve

Equation 3.

$$V_{Ti} = \frac{f_{Vi} A_{Ti}}{\sum_{i=1}^{n} f_{Vi} A_{Ti}} \times [100 - \sum_{j=1}^{m} V_{0j}]$$

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

f_{Vi} = Relative response factor for component i calculated by Eq 1.

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

$\sum_{j=1}^{m} V_{0j}$ = Total concentration of m oxygenates calculated by Eq 2.

Table 6. Repeatability and linearity for the four oxygenates analyzed.

Component	Repeatability (area RSD, n = 10)				R^2
	Level 1	Level 2	Level 3	Level 4	
Dimethyl ether	0.18%	0.08%	0.12%	0.11%	1
Methyl tertiary-butyl ether	0.30%	0.09%	0.18%	0.11%	1
Methanol	0.92%	0.49%	0.73%	0.2%	0.9999
Acetone	0.21%	0.11%	0.38%	0.45%	0.9998

Table 7. Quantitation accuracy and repeatability.

Oxygenate Component	Certified Concentration Vol%	Experimental Concentration Run 1 x_1 (Vol%)	Experimental Concentration Run 2 x_2 (Vol%)	Accuracy Run 1	Accuracy Run 2	Repeatability (r) Equation $x = (x_1 + x_2)/2$	r	$|x_1 - x_2|$	Verify → $|x_1 - x_2| < r$
DME	0.986	0.879	0.894	89.2%	90.6%	$0.202*x^{0.749}$	0.185	0.015	√
MTBE	0.0704	0.0730	0.0744	103.8%	105.7%	$0.142*x^{0.876}$	0.014	0.001	√
Methanol	0.0682	0.0619	0.0596	90.8%	87.3%	$0.238*x^{0.870}$	0.021	0.002	√
Acetone	0.0688	0.0699	0.0712	101.6%	103.5%	$0.148*x^{0.676}$	0.025	0.001	√
Propane	0.0596	0.0621	0.0615	104.2%	103.2%	$0.098*x^{0.550}$	0.0212	0.0006	√
Propylene	0.0104	0.0096	0.0094	92.5%	90.2%	$0.039*x^{0.719}$	0.0014	0.0002	√
iso-Butane	53.48	53.19	53.19	99.5%	99.5%	$0.056*x^{0.772}$	1.2037	0.0007	√
n-Butane	5.040	5.156	5.154	102.3%	102.3%	$0.086*x^{0.409}$	0.1682	0.0016	√
trans-2-Butene	40.20	40.48	40.47	100.7%	100.7%	$0.100*x^{0.775}$	1.7601	0.0128	√
iso-Pentane	0.0105	0.0111	0.0111	106.1%	105.4%	$0.100*x^{0.864}$	0.0020	0.0001	√
1-Pentene	0.00569	0.00647	0.00628	113.7%	110.3%	$0.197*x^{1.068}$	0.0009	0.0002	√

Conclusion

The Agilent GC gasifier is suitable for oxygenated LPG analysis, providing great area repeatability (RSD <1%) for both hydrocarbons and oxygenates. The deactivated tubing in the gasifier helps to provide excellent linearity for oxygenates across their typical concentration ranges. The quantitative precision meets the SH/T 0230-2019 standard requirements[1] and it offers acceptable quantitative accuracy. This miniaturized device was installed as close to the GC gas sampling valve as possible to reduce possible cold spots. It is controlled and monitored via the GC user interface, thus providing a simple 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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