Analysis of Biogas with the Agilent 490 Micro GC

Application Note

Energy & Fuels

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Introduction

Biogas is a gas mixture produced by biological processes, from the anaerobic fermentation of organic material such as biomass, manure or sewage, municipal waste, green waste, and energy crops. Swamp gas is a naturally produced biogas.

The main components of biogas are methane and carbon dioxide, with some carbon monoxide and hydrogen. Biogas can be used as biofuel, as a low-cost fuel for any heating purpose. It also has a role in modern waste management to run any type of heat engine, to generate either mechanical or electrical power. To increase caloric values it might be necessary to remove some of the carbon dioxide. Biogas can be compressed, much like liquified natural gas, and used to power motor vehicles. For this purpose it is necessary to remove hydrogen sulfide. Biogas is a renewable fuel, and so it qualifies for renewable energy subsidies in some parts of the world. Due to the increasing interest in biogas, there is a growing demand for fast and efficient analysis technology. That is where the Agilent 490 Micro GC can play a significant role.

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Instrumentation

Depending on the type of biogas to be analyzed, two configurations are available. If the sample contains only permanent gases and the hydrocarbons methane, ethane and propane, a dual channel GC is ideal. If higher hydrocarbons are also present in the sample, a third channel is needed and therefore the quad version of the micro-GC is recommended.

490 Micro GC Gas Chromatograph

Dual channel:

- Channel 1, Agilent J&W CP-Molsieve column
- Channel 2, Agilent J&W PoraPLOT U column

Quad equipped with three channels:

- Channel 1, CP-Molsieve column
- Channel 2, PoraPLOT U column
- Channel 3, Agilent J&W CP-Sil 5 CB column

GC control and data handling software: Agilent chromatography software

Conditions

Table 1. GC conditions

	Inj Time (ms)	Inj Temp (° C)	Column Temp (° C)	Carrier Gas	Pressure (kPa)	Back Flush (s)
Ch1	40	80	80	Ar	150	9
Ch2	100	80	100	He	100	10

Results and Discussion

The sample can be introduced to the 490 Micro GC either pressurized (reduced to max 1 bar) via a Tedlar sampling bag, or by using continuous flow. In this case the sample was pressurized, see Figure 1.

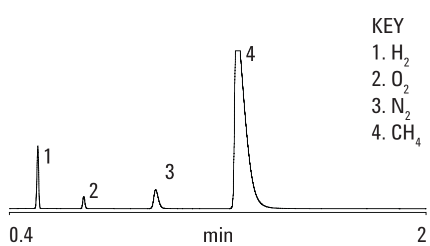

Figure 1. Permanent gases on the CP-Molsieve channel

As biogas and related samples may contain large amounts of CO_2, water and higher hydrocarbons, it was necessary to back flush these components. Water and CO_2, in particular, adsorb to the stationary phase and change chromatographic properties. Higher hydrocarbons eventually elute but cause higher noise and thus reduced sensitivity.

An indication of changed chromatographic properties is a drift in retention time. Table 2 shows repeatability figures on the CP-Molsieve channel. Repeatability figures of retention time and quantity are presented.

Table 2. Repeatability figures for the CP-Molsieve channel

Run #	Tr (min) Hydrogen	Tr (min) Oxygen	Tr (min) Nitrogen	Tr (min) Methane	QTY (%) Hydrogen	QTY (%) Oxygen	QTY (%) Nitrogen	QTY (%) Methane
1	0.5095	0.6858	0.9618	1.2745	1.0253	2.0183	8.0511	84.5107
2	0.5097	0.6858	0.962	1.2748	1.0222	2.012	8.057	82.945
3	0.509	0.6852	0.961	1.2727	1.0375	2.0272	8.0874	88.3207
4	0.5095	0.6857	0.9617	1.2743	1.0239	2.0155	8.0307	83.2869
5	0.5095	0.6858	0.9622	1.2748	1.0292	2.0197	8.0516	85.4475
6	0.5095	0.6858	0.962	1.2743	1.0329	2.0258	8.0664	86.787
7	0.5097	0.686	0.9622	1.2748	1.0306	2.0254	8.0589	85.2073
8	0.5092	0.6853	0.9617	1.2735	1.0365	2.0303	8.0875	88.3182
9	0.5095	0.6858	0.962	1.2745	1.0278	2.0188	8.0446	85.3981
10	0.5098	0.6862	0.9623	1.2753	1.0252	2.0165	8.0182	83.0202
11	0.5093	0.6855	0.9617	1.2736	1.0347	2.0277	8.0754	87.3976
12	0.5092	0.6855	0.9615	1.2735	1.0398	2.0358	8.099	88.1668
13	0.5092	0.6855	0.9617	1.2737	1.0368	2.032	8.0797	87.1916
14	0.5097	0.686	0.9622	1.2752	1.0264	2.0143	8.0082	82.8409
15	0.5092	0.6853	0.9615	1.2735	1.0361	2.0294	8.0688	87.3486
Average	0.5094	0.6857	0.9618	1.2742	1.0310	2.0232	8.0569	85.7458
Std Dev	0.0002	0.0003	0.0003	0.0007	0.0057	0.0073	0.0274	2.0592
RSD %	0.05%	0.04%	0.04%	0.06%	0.55%	0.36%	0.34%	2.40%

The very low relative standard deviation (RSD%) figures in Table 2 clearly show that the CP-Molsieve channel was working with very good repeatability. There was no drift in retention time and the analysis results for quantity were also very repeatable.

Figure 2 shows the chromatogram of the PoraPLOT U channel. Separation of carbon dioxide, ethane, hydrogen sulfide and propane was achieved.

Baseline separation of all components of interest was obtained. Higher hydrocarbons were back flushed to vent, which prevented later eluting components from disturbing the next analysis. The results presented in Table 3 show very good repeatability figures for the PoraPLOT U channel. RSD% below 0.1% for retention times and quantification illustrate the system's suitability for this type of analysis.

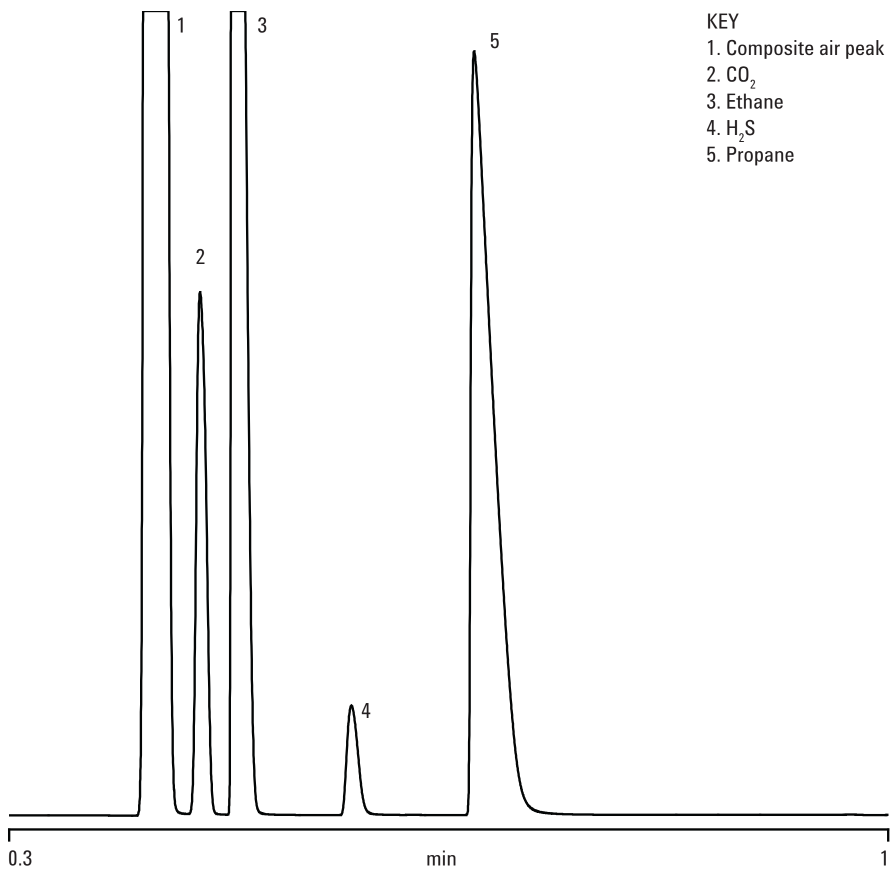

Figure 2. CO_2, H_2S, ethane and propane on the PoraPLOT U channel

Table 3. Repeatability figures of the PoraPLOT U channel

Run #	Tr (min) Air Peak	Tr (min) CO_2	Tr (min) Ethane	Tr (min) Propane	QTY (%) CO_2	QTY (%) Ethane	QTY (%) Propane
1	0.4115	0.4522	0.4833	0.6808	1.9866	4.0032	2.9955
2	0.4113	0.452	0.4832	0.6807	1.988	4.0048	2.9967
3	0.4117	0.4525	0.4837	0.6815	1.9921	4.0121	3.0015
4	0.4117	0.4525	0.4837	0.6813	1.99	4.0073	2.9985
5	0.4115	0.4522	0.4833	0.6808	1.9921	4.011	3.0014
6	0.4115	0.4523	0.4835	0.681	1.991	4.0089	2.9992
7	0.4115	0.4522	0.4835	0.6808	1.9896	4.0059	2.9973
8	0.4113	0.4522	0.4833	0.6808	1.9908	4.0073	2.9986
9	0.4115	0.4522	0.4833	0.6808	1.9927	4.011	3.0027
10	0.4115	0.4522	0.4833	0.6808	1.9912	4.0069	2.9984
11	0.4115	0.4522	0.4833	0.6808	1.9933	4.0113	3.0018
12	0.4115	0.4522	0.4833	0.6807	1.9927	4.0103	3.0008
13	0.4113	0.4522	0.4833	0.6807	1.9908	4.0062	2.9978
14	0.4113	0.452	0.4832	0.6807	1.9928	4.0096	2.9994
15	0.4118	0.4525	0.4837	0.6815	1.9919	4.0076	2.9992

Finally, Figure 3 is a chromatogram of the separation and determination of the (higher) hydrocarbons. The column used was a CP-Sil 5 CB. This extra channel expanded the application range of biogas analysis to blends with C3 and or C4 LPGs.

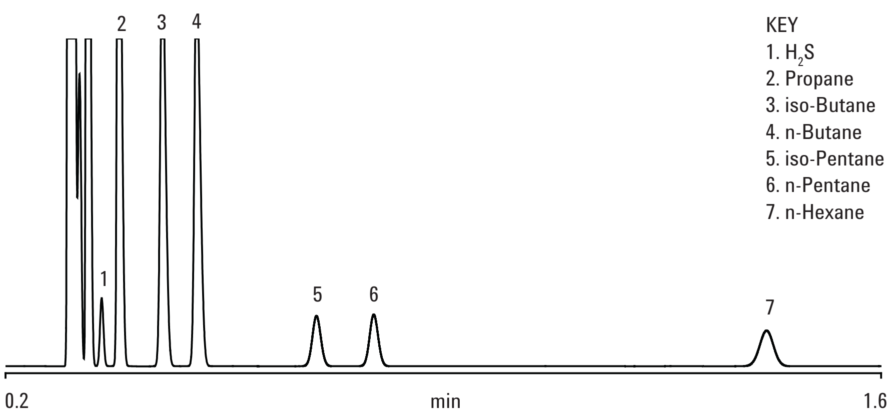

Figure 3. Higher hydrocarbons on the CP-Sil 5 CB channel

Table 4 shows the repeatability figures of the CP-Sil 5 CB channel. Again, very good repeatability figures were obtained. Relative standard deviation was well below 0.05% for retention times and below 0.15% for quantitative measurements.

Table 4. Repeatability figures of the CP-Sil 5 CB channel

Run #	Tr (min) Air Peak	Tr (min) Ethane	Tr (min) Propane	Tr (min) iso-Butane	Tr (min) n-Butane	QTY (%) Ethane	QTY (%) Propane	QTY (%) iso-Butane	QTY (%) n-Butane
1	0.3025	0.3333	0.3833	0.455	0.5107	4.0108	3.0222	0.501	0.5005
2	0.3023	0.3333	0.3833	0.455	0.5105	4.0092	3.0179	0.501	0.5004
3	0.3023	0.3333	0.3832	0.455	0.5105	4.0139	3.0171	0.5007	0.5002
4	0.3023	0.3332	0.3832	0.4548	0.5103	4.0116	3.0136	0.5009	0.5003
5	0.3022	0.3332	0.383	0.4547	0.5102	4.0129	3.0131	0.5007	0.5004
6	0.3023	0.3332	0.3832	0.4547	0.5102	4.0096	3.0111	0.5007	0.5003
7	0.3023	0.3332	0.3832	0.4548	0.5103	4.0102	3.0095	0.5006	0.5002
8	0.3022	0.3332	0.383	0.4547	0.5102	4.0126	3.0104	0.5009	0.5004
9	0.3023	0.3332	0.3832	0.4548	0.5103	4.0119	3.009	0.5007	0.5003
10	0.3023	0.3332	0.3832	0.4548	0.5103	4.0098	3.009	0.5009	0.5003
11	0.3023	0.3332	0.3832	0.4548	0.5103	4.0112	3.0092	0.5011	0.5005
12	0.3023	0.3332	0.3832	0.4548	0.5103	4.0091	3.0078	0.5008	0.5
13	0.3022	0.333	0.383	0.4547	0.5102	4.0128	3.0101	0.5014	0.5007
14	0.3022	0.333	0.383	0.4547	0.5102	4.0099	3.0083	0.501	0.5003
15	0.3022	0.333	0.383	0.4547	0.5102	4.0098	3.0083	0.5009	0.5002
Average	0.3023	0.3332	0.3831	0.4548	0.5103	4.0110	3.0118	0.5009	0.5003
Std Dev	0.0001	0.0001	0.0001	0.0001	0.0001	0.0015	0.0042	0.0002	0.0002
RSD %	0.03%	0.03%	0.03%	0.02%	0.03%	0.04%	0.14%	0.04%	0.03%

490 Micro GC Configuration for Biogas Depends on Sample Type

Regular biogas contains methane, oxygen, nitrogen, carbon dioxide, hydrogen sulfide, and sometimes some hydrogen and carbon monoxide. For this type of sample a two channel 490 Micro GC is perfectly suited. Channel 1, configured with a CP-Molsieve column, will separate and analyze hydrogen, oxygen, nitrogen, methane and carbon monoxide. Channel 2, equipped with a PoraPLOT U column, will analyze carbon dioxide and hydrogen sulfide. This configuration can even be used if ethane and propane are present in the sample. If, however, C4+ hydrocarbons also have to be analyzed, a third CP-Sil 5 CB channel is required, together with the 490 Micro GC QUAD.

Conclusion

All results clearly showed that the system configuration was perfectly capable of analyzing biogas.

The CP-Molsieve channel separated and analyzed permanent gases such as hydrogen, oxygen, nitrogen and methane. With some changes in chromatographic parameters even carbon monoxide can be analyzed on this channel. Higher hydrocarbons, as well as moisture and carbon dioxide, were back flushed to vent ensuring trouble free operation, perfect repeatability and a long column lifetime.

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Published in USA, September 6, 2012

SI-02215

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