Analysis of Biogas Using the Agilent 490 Micro GC Biogas Analyzer

Application Note

Micro Gas Chromatography, Hydrocarbon Processing, Renewable Energy, Biogas Analysis

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Abstract

Biogas is considered a renewable and sustainable energy source and therefore is of great interest worldwide. This application note shows the analysis of biogas, and related samples, using the Agilent 490 Micro GC Biogas Analyzer. Depending on the biogas composition two configurations are available; the Agilent 490 Micro GC Biogas Analyzer for pure biogas analysis and the Agilent 490 Micro GC Biogas Analyzer Extended when biogas is mixed with other hydrocarbon streams, such as natural gas or liquefied petroleum gas (LPG).

Introduction

Biogas is a gas mixture produced through biological processes; from anaerobic fermentation or digestion of organic material such as biomass, manure or sewage, municipal waste and energy crops. The composition of biogas is related to the origin of the organic material; the main components of biogas are methane and carbon dioxide, with some other permanent gases, hydrogen and hydrogen sulfide.

Biogas has a role in modern waste management and can fuel any type of heat engine to generate either mechanical or electrical power. To increase its caloric values it is sometimes necessary to remove some of the carbon dioxide or blend it with other hydrocarbon streams. Biogas can be compressed, much like liquefied natural gas, and used to power motor vehicles. For this purpose, it is essential to remove hydrogen sulfide if present. Biogas is a renewable fuel, and so it qualifies for renewable energy subsidies in some parts of the world.

The increased interest in biogas has resulted in a growing demand for fast and efficient analysis technology to determine its composition. The Agilent Micro GC Biogas Analyzers can play a significant role in achieving this goal.

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The Agilent 490 Micro GC Biogas Analyzers are shipped as a total solution; the analyzers are factory tuned, for optimal separation, and come with final test data, analytical method parameters, a user manual and a check-out sample.

Biogas Analyzer setup and conditions

Based on the Agilent 490 Micro GC, two Biogas Analyzers are available; the configuration required for biogas analysis depends on the sample composition.

For pure biogas analysis, including permanent gases and hydrogen sulfide, the Agilent 490 Micro GC Biogas Analyzer (p/n G3582A#110) is recommended, even ethane and propane can be analyzed with this setup. This Biogas Analyzer consists of a dual channel cabinet including a 10-meter CP-Molsieve 5A with argon as a carrier gas, providing excellent sensitivity and linearity for hydrogen, and a 10-meter CP-PoraPLOT U column channel with helium as carrier gas.

When biogas is mixed with other hydrocarbon streams such as natural gas or liquefied petroleum gas (LPG), the sample contains higher boiling hydrocarbons. To analyze these hydrocarbons the Agilent 490 Micro GC Biogas Analyzer Extended is the analyzer of choice. This Biogas Analyzer Extended (p/n G3582A#111) is a quad channel cabinet Micro GC including three column channels; a 10-meter CP-Molsieve column on argon as carrier gas, a 10-meter CP-PoraPLOT U column and an additional 6-meter CP-Sil 5 CB column on helium as carrier gas for the analysis of higher boiling hydrocarbons. Figure 1 shows the quad and dual cabinet housing for the Agilent 490 Micro GC Biogas Analyzers.

Figure 1. Agilent 490 Micro GC Biogas Analyzers.

Both Biogas Analyzers are equipped with heated sample line and injectors to eliminate any cold spot and prevent possible condensation of moisture, to ensure the integrity of the sample is maintained throughout the sample flow path. Both CP-Molsieve 5A and CP-PoraPLOT U columns have a backflush to vent option, moreover the CP-Molsieve 5A is equipped with the retention time stability (RTS) option. This RTS option consists of additional in-line filters between the electronic gas control and the column module to ensure moisture and carbon dioxide free carrier gas. Moreover the use of the RTS option enables a more efficient backflush of carbon dioxide. This enhances column lifetime and, most importantly, leads to more stable retention times.

Table 1 gives an overview of typical conditions used for the Biogas Analyzers.

Table 1. 490 Micro GC Biogas Analyzer Instrument Conditions

	CP-Molsieve 5A, 10 m	CP-PoraPLOT U, 10 m	CP-Sil 5 CB, 6 m
Column temperature	80 °C	80 °C	60 °C
Carrier gas	argon, 200 kPa	helium, 150 kPa	helium, 150 kPa
Injector temperature	110 °C	110 °C	110 °C
Injection time	40 ms	40 ms	40 ms
Backflush time [1]	11	14	no backflush
Detector sensitivity	auto	auto	auto
Invert signal	yes	no	no
Sample line temperature	110 °C		
Sampling time	30 seconds		

Note [1] Backflush time is column channel dependent and should be fine tuned for each new column.

The sample can be introduced to the Agilent 490 Micro GC Biogas Analyzer either pressurized (maximum limit 1 bar), through a Tedlar sampling bag using the internal sampling pump, or by using a continuous flow sampling mode. When the sample pressure exceeds the 1 bar limit, for example with a liquefied natural gas or liquefied petroleum gas, the pressure should be reduced. The use of the Agilent Micro-Gasifier, a heated pressure reducer, is recommended here.

Results and Discussion

The first column channel, a CP-Molsieve 5A, is used to analyze the permanent gases, including hydrogen, oxygen, nitrogen, methane, and carbon monoxide. Figure 2 shows a chromatogram for this column channel.

As biogas and related samples may contain larger amounts of carbon dioxide, moisture, and higher hydrocarbons it is necessary to backflush these components to maintain the separation effiency of the Molsieve 5A column. Moisture and carbon dioxide tend to adsorb quickly to the Molsieve 5A stationary phase and change its chromatographic properties. This would result, over time, in retention shifts and loss of separation. Higher hydrocarbons will eventually elute, but will cause higher detector noise levels and lead to reduced sensitivity. The backflush to vent functionality on the Molsieve 5A column channel prevents this from happening.

Table 2 shows excellent repeatability figures for both retention time, below RSD 0.05 %, and peak area below RSD 0.1 %, for the compounds analyzed on the Molsieve column channel.

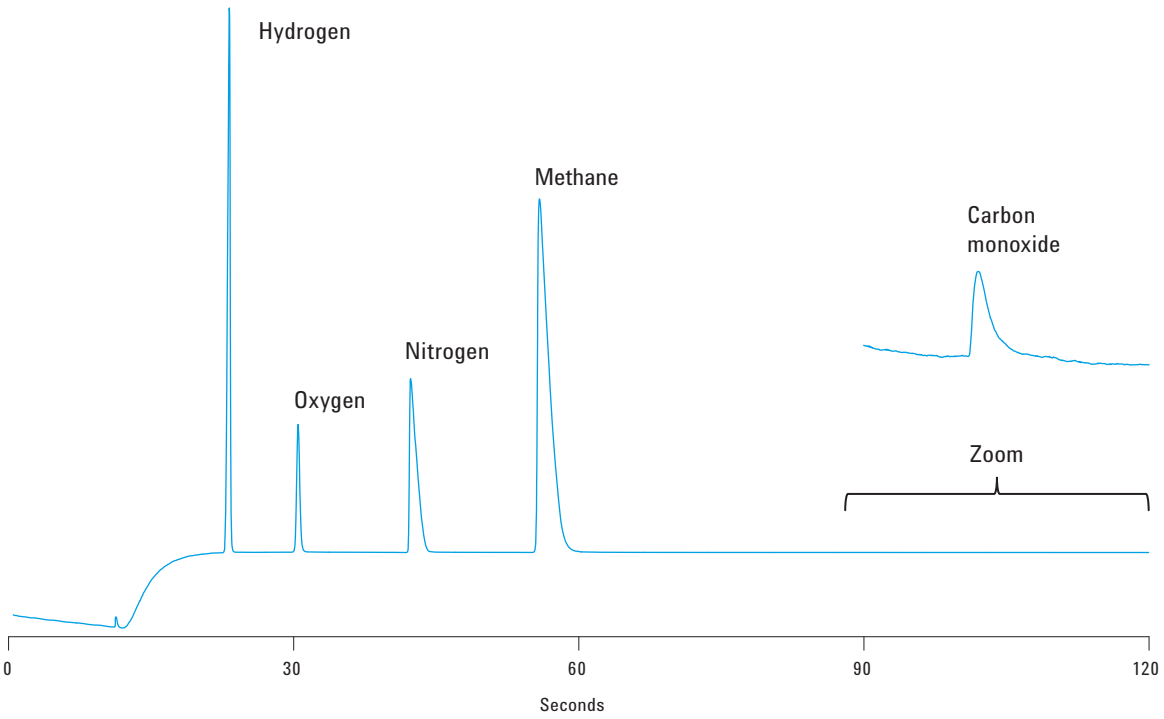

Figure 2. Chromatogram for permanent gases on the CP-Molsieve 5A column channel.

Table 2. Repeatability Figures for Retention Time and Peak Area on the CP-Molsieve Column

Run no.	Hydrogen Rt (sec)	Oxygen Rt (sec)	Nitrogen Rt (sec)	Methane area	Hydrogen area	Oxygen area	Nitrogen area	Methane area
1	23.23	30.46	42.31	55.85	5852426	1594746	4855956	15750694
2	23.22	30.46	42.31	55.85	5852402	1594913	4856189	15752646
3	23.22	30.45	42.30	55.85	5849806	1594074	4853402	15749892
4	23.22	30.45	42.30	55.85	5857044	1596055	4859671	15769519
5	23.22	30.46	42.31	55.86	5853222	1595289	4856426	15762840
6	23.23	30.46	42.30	55.85	5847437	1593546	4853332	15742096
7	23.22	30.45	42.30	55.85	5855831	1596512	4860136	15768153
8	23.23	30.46	42.31	55.86	5846434	1594241	4854710	15745279
9	23.22	30.46	42.30	55.85	5860122	1597659	4864955	15785858
10	23.22	30.45	42.30	55.85	5852819	1595989	4860359	15768762
Average	23.22	30.46	42.30	55.85	5852754	1595302	4857514	15759574
Std. dev.	0.0048	0.005	0.005	0.004	4210	1258	3691	13699
RSD (%)	0.021	0.017	0.012	0.008	0.072	0.079	0.076	0.087

For pure biogas, carbon dioxide and hydrogen sulfide are analyzed on a CP-PoraPLOT U column channel. When biogas is mixed with other hydrocarbon streams, ethane and propane can also be analyzed on this channel. Baseline separation of carbon dioxide, ethane, hydrogen sulfide, and propane is obtained, shown in Figure 2. Higher hydrocarbons present in the sample are backflushed to vent; which prevents late eluting components from interfering in the next analysis.

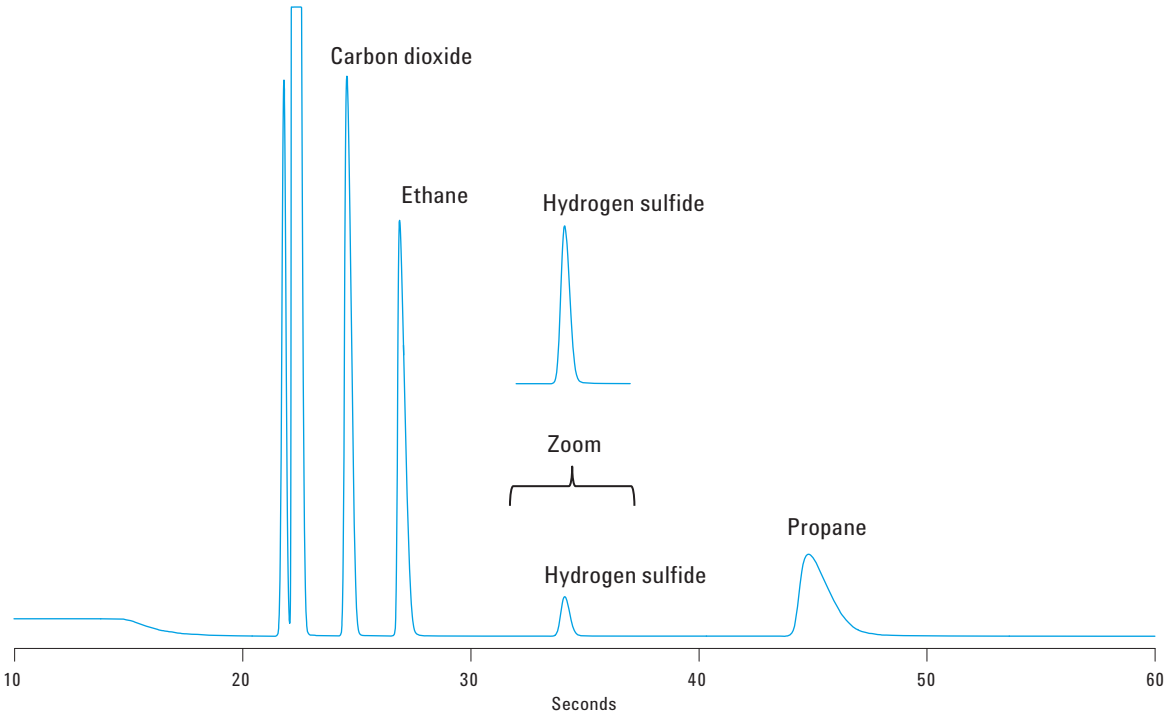

Figure 3. Chromatogram for carbon dioxide, hydrogen sulfide, ethane, and propane on the CP-PoraPLOT U channel.

The stainless steel tubing in the CP-PoraPLOT U channel and the sample inlet of the Micro GC have an UltiMetal deactivation layer, which results in an inert sample flow path and better performance for hydrogen sulfide analysis. Results presented in Table 3 shows very good repeatability figures for hydrogen sulfide and the other compounds (carbon dioxide, ethane, and n-propane) analyzed on the CP-PoraPLOT U channel. Relative standard deviation (RSD %) below 0.02 % for retention time and below 0.15 % based on area illustrates the system's suitability for this type of analysis. Moreover the UltiMetal deactivated sample inlet tubing provides an excellent peak shape for hydrogen sulfide, see Figure 3.

The CP-Molsieve and CP-PoraPLOT U channel, chromatograms as shown in Figure 3, are part of both the Biogas and Extended Biogas Analyzer.

Table 3. Retention Time and Peak Area Repeatability Results for the CP-PoraPLOT U Column

Run no.	Carbon dioxide Rt (sec)	Ethane Rt (sec)	Hydrogen sulfide Rt (sec)	n-Propane Rt (sec)	Carbon dioxide area	Ethane area	Hydrogen sulfide area	n-Propane area
1	24.56	26.87	34.11	44.80	3240882	2662227	320047	2175181
2	24.56	26.88	34.12	44.80	3239148	2660569	319969	2178315
3	24.56	26.87	34.12	44.80	3240617	2662025	320273	2181300
4	24.56	26.87	34.11	44.79	3239973	2661327	320031	2180366
5	24.56	26.87	34.11	44.79	3239006	2661163	319909	2178141
6	24.56	26.87	34.11	44.80	3240134	2661385	319833	2174648
7	24.55	26.87	34.11	44.79	3239972	2661379	320000	2173550
8	24.55	26.87	34.11	44.79	3238407	2660348	319721	2177678
9	24.56	26.87	34.11	44.79	3238332	2660512	320024	2179891
10	24.55	26.87	34.11	44.79	3237012	2659615	319789	2176390
Average	24.56	26.87	34.11	44.79	3239348	2661055	319960	2177546
Std. dev.	0.0048	0.0032	0.0042	0.0052	1197	797	157	2578
RSD (%)	0.020	0.012	0.012	0.012	0.037	0.030	0.049	0.12

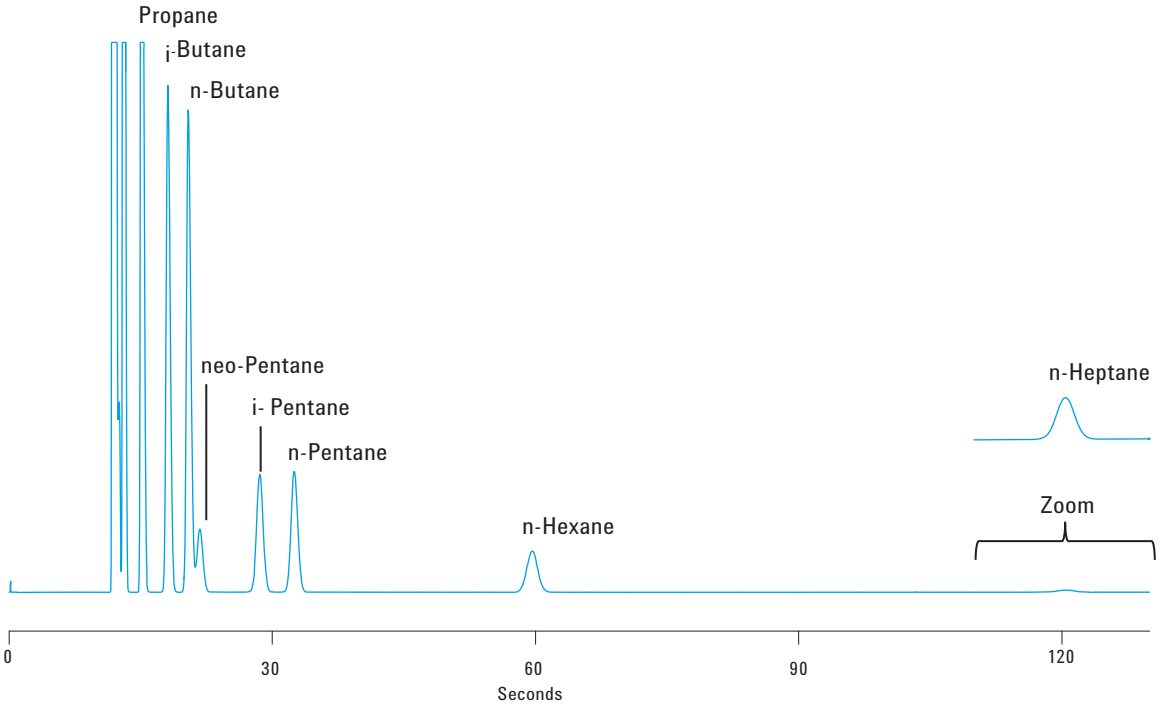

Figure 4. Chromatogram on the CP-Sil 5 CB, separating the hydrocarbons from butanes to n-heptane.

In Figure 4, the chromatogram illustrates the separation and quantification of the higher boiling hydrocarbons as part of the Extended Biogas Analyzer setup; the column used is a CP-Sil 5 CB. This additional channel expands the application range of biogas analysis to blends with natural gas or liquefied petroleum gas (LPG). In this particular case, the biogas was mixed with natural gas.

Tables 4a and 4b show repeatability on the CP-Sil 5 CB channel for the hydrocarbons. The repeatability data of approximately 0.05% for retention times and below the 0.2% mark for peak area can be considered as excellent. Even the partially separated neo-pentane shows a good peak area repeatability performance.

Table 4a. Retention Time Reproducibility Data for the CP-Sil 5 CB Channel

Run no.	i-Butane Rt (sec)	n-Butane Rt (sec)	neo-Pentane Rt (sec)	n-Pentane Rt (sec)	i-Pentane Rt (sec)	n-Hexane t (sec)	n-Heptane Rt (sec)
1	18.10	20.43	21.75	28.58	32.52	59.67	120.66
2	18.10	20.43	21.75	28.58	32.52	59.67	120.69
3	18.10	20.42	21.74	28.58	32.51	59.66	120.70
4	18.10	20.42	21.74	28.57	32.51	59.66	120.71
5	18.09	20.42	21.74	28.57	32.50	59.64	120.72
6	18.09	20.42	21.74	28.57	32.50	59.64	120.72
7	18.09	20.41	21.73	28.56	32.49	59.63	120.72
8	18.08	20.41	21.72	28.55	32.48	59.61	120.73
9	18.08	20.40	21.72	28.55	32.48	59.60	120.72
10	18.08	20.40	21.72	28.54	32.47	59.59	120.74
Average	18.09	20.42	21.74	28.57	32.50	59.64	120.71
Std. dev.	0.0088	0.0107	0.0118	0.014	0.018	0.029	0.023
RSD (%)	0.048	0.053	0.054	0.050	0.054	0.049	0.019

Table 4b. Reproducibility Data, Based on Peak Area, for the CP-Sil 5 CB Column

Run no.	i-Butane area	n-Butane area	neo-Pentane area	n-Pentane area	i-Pentane area	n-Hexane area	n-Heptane area
1	7014680	7186850	1265110	2702141	2781533	1552255	133755
2	7018181	7190966	1264813	2703703	2783345	1553847	133682
3	7018469	7187273	1269047	2704327	2783935	1554441	133642
4	7017302	7188209	1269045	2705176	2784640	1554809	133920
5	7017858	7190794	1264914	2705022	2784520	1554963	133951
6	7024447	7196790	1265962	2707439	2787091	1556518	133959
7	7025658	7196118	1269229	2708459	2787981	1557169	133959
8	7019982	7188645	1270146	2706467	2785715	1555951	133880
9	7018355	7189383	1267352	2706536	2785636	1556096	134091
10	7018173	7190297	1266144	2706696	2785947	1555806	134130
Average	7019311	7190533	1267176	2705597	2785034	1555186	133897
Std. dev.	3315	3418	2043	1888	1865	1439	162
RSD (%)	0.047	0.048	0.16	0.070	0.067	0.093	0.12

Conclusion

The Agilent 490 Micro GC Biogas Analyzer type required depends on biogas sample type. Regular biogas contains methane, carbon dioxide, nitrogen, and sometimes some hydrogen, hydrogen sulfide, and carbon monoxide. For this type of sample, the 490 Micro GC Biogas Analyzer is perfectly suited.

The first column channel, configured with a CP-Molsieve 5A column with argon as carrier gas, will separate and analyze hydrogen, oxygen, nitrogen, methane, and carbon monoxide. Moisture and carbon dioxide, as well as higher hydrocarbons present in the sample, are backflushed to vent, ensuring trouble free operation, perfect repeatability, and a long column lifetime without the need for extensive conditioning procedures. Moreover, this column channel is equipped with a Retention Time Stability option (RTS) to ensure stable retention time on the CP-Molsieve 5A column over time.

The second channel, equipped with a CP-PoraPLOT U column, analyzes carbon dioxide and hydrogen sulfide as part of the biogas sample. This column can even be used when ethane and propane are present in the sample. The sample inlet of the Micro GC and the CP-PoraPLOT U channel are treated with an UltiMetal deactivation process to guaranty good performance for hydrogen sulfide analysis.

When butanes and higher hydrocarbons need to be analyzed, the Agilent 490 Micro GC Biogas Analyzer Extended is recommended. This analyzer, suited for analysis of biogas mixed with other hydrocarbon streams such as natural gas or LPG, is equipped with an additional CP-Sil 5 CB column channel.

All results clearly illustrate that both analyzer configurations are perfectly capable of analyzing biogas and related sample streams. Typical repeatability figures show RSD's around 0.05 % for retention time and RSD's less than 0.2 % for peak area, while the factory specification for peak area repeatability is specified on 0.5% RSD (based on 1 % concentration level propane).

The Agilent 490 Micro GC Biogas Analyzers are factory tuned, including the appropriate settings for the backflush times for the CP-MolSieve 5A and CP-PoraPLOT U columns. The Agilent Biogas Analyzers are shipped with final test data, optimized analytical method, Biogas Analyzer User Manual, and a check out sample kit to have all information available at installation.

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