Application Note

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Biogas Analyzer Based on the Agilent 990 Micro GC

Author

Jie Zhang
Agilent Technologies, Inc.

Abstract

This Application Note presents a method for biogas analysis using two versions of the Agilent 990 Micro GC biogas analyzer. The 990 Micro GC biogas analyzer is intended for pure biogas analysis. The 990 Micro GC biogas analyzer extended is suitable for the analysis of biogas samples mixed with other hydrocarbon streams.

Introduction

Biogas is produced by the anaerobic bacterial breakdown of organic matter. The feedstocks of biogas include different types of organic material. Wastewater, manure, organic industrial waste, and energy crops are the most common feedstocks.

The main components of biogas are methane and carbon dioxide. Methane is a valuable energy source and has a wide range of uses, which is why biogas is used as an alternative energy source. To increase the calorific value of biogas, it is sometimes necessary to remove some carbon dioxide or blend it with other hydrocarbon streams. In addition to methane, carbon dioxide, and some hydrocarbons, other low-percentage gas components in biogas include carbon monoxide, nitrogen, hydrogen, and hydrogen sulfide. Some of the components make no contribution to energy content, and some are corrosive and potentially poisonous. It is important to know the composition and concentration of biogas before adding it to the grid.

The 990 Micro GC provides fast and accurate gas analysis. It accommodates up to two analytical channels in the basic cabinet for gas analysis. Two cabinets can be combined to hold up to four channels for analysis of gases with complex composition, such as refinery gas and natural gas. The Agilent 990 Micro GC biogas analyzers evolved from the 490 counterparts.[1] They address the analysis of biogas with different composition. The 990 biogas analyzers are factory tuned and shipped to customers with optimized method, factory test results, checkout sample, and an operation manual.

Biogas analyzer

There are two types of analyzers based on the 990 Micro GC platform for biogas analysis. The 990 Micro GC biogas analyzer is recommended for pure biogas analysis. It consists of two analytical channels. One is a 10 m Agilent J&W CP-Molesieve 5Å channel for permanent gas, carbon monoxide, and methane analysis, the other is a 10 m Agilent J&W CP-PoraPLOT U channel for carbon dioxide and hydrogen sulfide analysis. Both channels are equipped with a backflush option to protect the analytical column from heavier components and ensure column performance and long-term retention time stability. Retention time stability option (RTS) is a default configuration in the 990 Micro GC 10 m CP-Molesieve 5Å backflush channel.

To increase biogas calorific value, sometimes gas streams containing hydrocarbons are mixed with pure biogas. In such cases, the 990 Micro GC biogas analyzer extended is the choice for biogas composition analysis. The extended analyzer has three channels: channel 1 is 10 m J&W CP-Molesieve 5Å backflush, channel 2 is 10 m J&W CP-PoraPLOT U backflush, and channel 3 is 6 m Agilent J&W CP-Sil 5 CB, straight. Channels 1 and 2 address the analysis of permanent gases, methane, CO, CO_2, H_2S, and light hydrocarbons such as ethane and propane. Channel 3 is for the analysis of higher boiling point hydrocarbons from C_3 to C_9.

Experimental

Tables 1 and 2 show the biogas analyzer configuration as well as the typical analysis conditions of the various channels.

Table 1. Channel configuration of the Agilent 990 Micro GC biogas analyzers.

	Agilent 990 Micro GC Biogas Analyzer	Agilent 990 Micro GC Biogas Analyzer Extended
Channel 1	10 m Agilent J&W CP-Molesieve 5Å, backflush, RTS	10 m Agilent J&W CP-Molesieve 5Å, backflush, RTS
Channel 2	10 m Agilent J&W CP-PoraPLOT U, backflush	10 m Agilent J&W CP-PoraPLOT U, backflush
Channel 3	NA	6 m Agilent J&W CP-Sil 5 CB, straight
Biogas Composition	Hydrogen, oxygen, nitrogen, methane, CO, CO_2, H_2S	Hydrogen, oxygen, nitrogen, methane, CO, CO_2, H_2S, hydrocarbons C_2 to C_9

Table 2. An overview of typical analytical conditions for biogas analyzers.

	10 m Agilent J&W CP-Molesieve 5 Å, Backflush, RTS	10 m Agilent J&W CP-PoraPLOT U, Backflush	6 m Agilent J&W CP-Sil 5 CB, Straight
Carrier Gas	Argon	Helium	Helium
Column Head Pressure	200 kPa	150 kPa	175 kPa
Column Temperature	80 °C	80 °C	70 °C
Injection Time	40 ms	40 ms	40 ms
Backflush Time[1]	10 seconds	11.8 seconds	NA
Invert Signal	Yes	No	No
Sample Inlet and Injector Temperature	110 °C	110 °C	110 °C

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

Results and discussion

Figure 1 shows the chromatogram for permanent gas analysis on the 10 m J&W CP-Molesieve 5Å backflush channel. To analyze hydrogen across the wide concentration range, argon is used as carrier gas. There are large amounts of carbon dioxide in biogas due to its production process. The performance of Molesieve 5Å column is susceptible to moisture and carbon dioxide. To protect the Molesieve 5Å column from CO_2 and moisture, the backflush option was used. By setting the proper backflush time, helium, neon, hydrogen, oxygen, nitrogen, methane, and carbon monoxide elute into the analytical column before the backflush (BF) function is initiated. With BF valve switching, the gas flow in the precolumn is reversed to flush the moisture, carbon dioxide, and other high boiling point hydrocarbons out to vent. In addition, there is a retention time stability (RTS) option installed between the dynamic electronic gas control module and the column module. RTS works as a filter to remove moisture, carbon dioxide, and hydrocarbons from the carrier gas, which is beneficial to long-term RT stability of the Molesieve 5Å channel.

The 10 m J&W CP-PoraPLOT U channel is used for carbon dioxide and hydrogen sulfide analysis. For the biogas mixture with hydrocarbon streams, ethane and propane are also analyzed on the PPU channel. Figure 2 shows the baseline separation of carbon dioxide, ethane, hydrogen sulfide, and propane. Hydrocarbons higher than C_3 are backflushed out of the precolumn to reduce analysis time, which helps generate a clean baseline for the next run. The sample flowpath from sample inlet to the column head of the pre-column is deactivated by the Agilent proprietary UltiMetal technique. It reduces the adsorption of hydrogen sulfide and helps improve the peak shape, making peak integration easier and more accurate, resulting in better repeatability for hydrogen sulfide analysis.

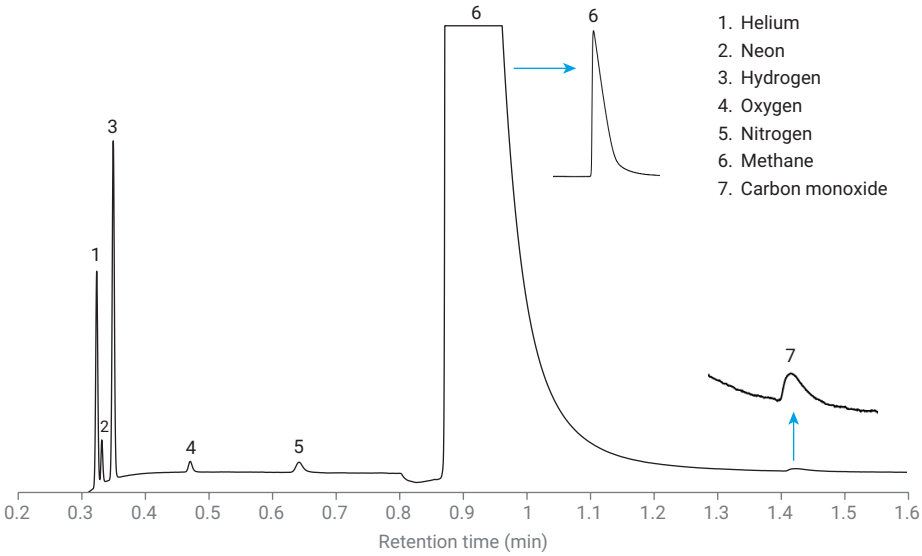

Figure 1. Chromatogram of permanent gases on the Agilent J&W CP-Molesieve 5 Å channel.

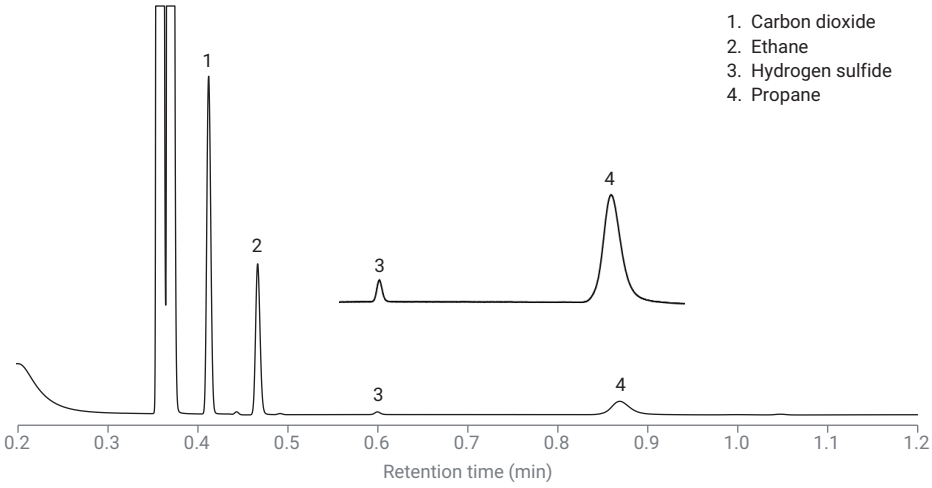

Figure 2. Chromatogram of carbon dioxide, ethane, hydrogen sulfide, and propane on the 10 m Agilent J&W CP-PoraPLOT U backflush channel.

The higher boiling point hydrocarbons from propane to nonane are analyzed on the 6 m J&W CP-Sil 5 CB channel. The chromatograms in Figures 3 and 4 show good separation of the targeted components. This channel helps expand biogas analysis from pure biogas to its mixture with natural gas or liquefied petroleum gas.

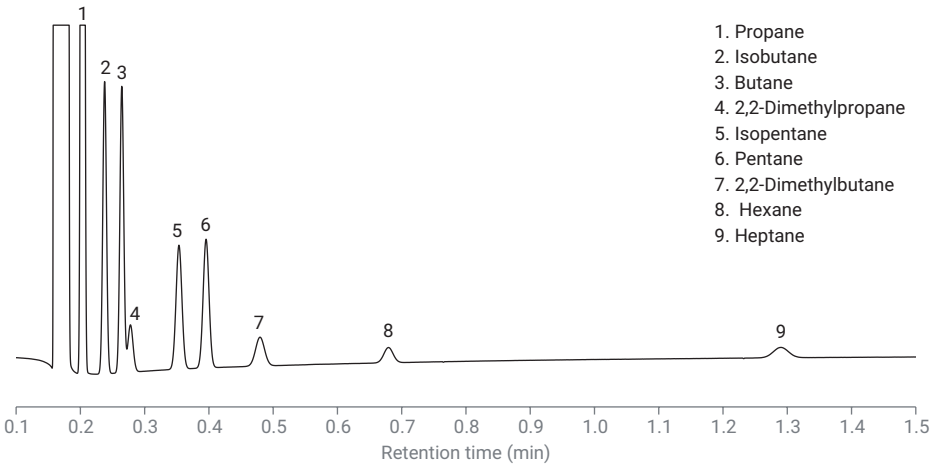

Figure 3. Chromatogram of hydrocarbon mixture from propane to heptane on the 6 m Agilent J&W CP-Sil 5 CB channel.

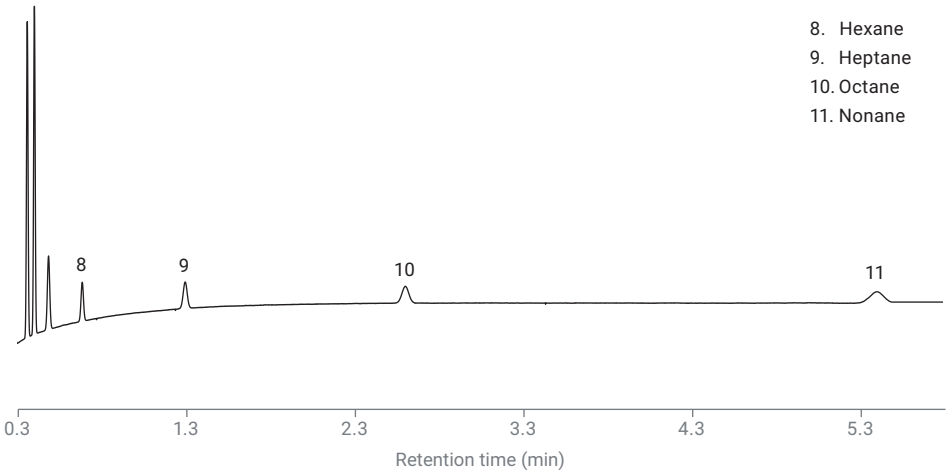

Figure 4. Chromatogram of octane and nonane on the 6 m Agilent J&W CP-Sil 5 CB channel.

Table 3 tabulates the area and retention time repeatability of a simulated biogas sample analyzed by the biogas analyzer extended version. The RT repeatability was from 0.002% to 0.027%. The area repeatability was between 0.032% and 2.0%, mainly depending on compound concentration. Generally, the higher the concentration, the better the quantitation repeatability. Components with concentration higher than 1% are easy to get area repeatability lower than 0.5%, such as methane, CO_2, and ethane. The concentration of He, H_2, O_2, and N_2 in test sample are close to each other, between 500 to 1,000 ppm. To use argon as carrier gas helps dramatically increase the response of H_2 and He, which is why their area repeatability was better than O_2 and N_2. Excellent performance of RT precision and area repeatability in Table 3 is based on the 990 Micro GC's precise pneumatic and thermal control.

Table 3. RT and area repeatability of a simulated biogas sample analyzed on the biogas analyzer extended version.

Compounds	RT (min)	RT RSD%	Area (mv × s)	Area RSD%	Analysis Channel No.
Helium	0.323	0.008	1.004	0.112	1
Neon	0.331	0.008	0.180	0.290	1
Hydrogen	0.349	0.007	1.618	0.060	1
Oxygen	0.470	0.007	0.097	2.0	1
Nitrogen	0.642	0.009	0.172	1.94	1
Methane	0.876	0.019	405.530	0.033	1
Carbon monoxide	1.426	0.027	0.297	1.607	1
Carbon dioxide	0.412	0.007	3.987	0.070	2
Ethane	0.466	0.007	2.011	0.047	2
Hydrogen sulfide	0.599	0.007	0.047	1.102	2
Propane	0.869	0.009	0.786	0.284	2
Isobutane	0.238	0.005	0.787	0.019	3
Butane	0.264	0.005	0.813	0.032	3
Isopentane	0.353	0.004	0.539	0.236	3
2,2-Dimethyl propane	0.278	0.006	0.169	0.121	3
Pentane	0.396	0.004	0.555	0.129	3
2,2-Dimethyl butane	0.480	0.005	0.192	0.337	3
Hexane	0.679	0.006	0.106	1.11	3
Heptane	1.290	0.007	0.118	1.17	3
Octane	2.596	0.017	0.129	1.066	3
Nonane	5.382	0.002	0.137	1.70	3

Conclusion

There are two types of Agilent 990 Micro GC analyzers available for biogas analysis. One is for pure biogas analysis: it is equipped with two channels. The analysis of permanent gases and methane is on the 10 m J&W CP-Molesieve 5Å channel. Argon is used as carrier gas for hydrogen measurement across the wide concentration range. The analysis of carbon dioxide and hydrogen sulfide is on 10 m Agilent J&W CP-PoraPLOT U channel. The coated inert sample flowpath ensures good peak shape of hydrogen sulfide. The J&W CP-Molesieve 5Å and CP-PoraPLOT U channels are configured as backflush options to protect the analytical column from heavy contaminants for better baseline and shorter analysis time.

The biogas analyzer extended version is configured with three channels. Channels 1 and 2 are the same as those used in the basic biogas analyzer. The PPU channel resolves CO_2, H_2S, ethane, and propane. Channel 3 is a 6 m Agilent J&W CP-Sil 5 CB straight channel. It is for higher boiling point hydrocarbon analysis (usually up to C_9). This extended analyzer is suitable for the analysis of biogas mixed with hydrocarbon streams such as natural gas or LPG.

The performance of biogas analyzers is demonstrated by the analysis of a simulated biogas sample. The excellent retention time repeatability (0.002% to 0.027%) and area repeatability (0.032% to 2.0%) guarantees qualitative and quantitative analysis with a high confidence level.

The 990 Micro GC biogas analyzers are trusted biogas analysis solutions. They are factory-tuned with optimal performance, and shipped to users with test results based on a factory checkout sample. The checkout sample will be shipped for on-site analyzer performance re-verification together with a user manual for user operation guidance.

Reference

1. Analysis of Biogas Using the Agilent 490 Micro GC Biogas Analyzer, *Agilent Technologies Application Note*, publication number 5990-9508EN, **2011**.

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