Application Note

Biogas Analysis using Micro GC Fusion®

Introduction

Climate change is accelerating the need for renewable energy sources such as biogas. Biogas is composed of gases produced by the anaerobic digestion of organic compounds. This can happen as a natural byproduct of decomposition, as seen in landfills, or with the use of controlled anaerobic digesters used to break down biomass sources, such as animal or industrial waste. The biogas from those materials can be used for electricity, thermal, transportation, and pipeline gas due to the high energy content of methane, typically 50-75%. The methane content can vary depending on the source of the gas.

Monitoring the composition of biogas is a critical part of keeping the process stable and efficient. In addition, to utilize biogas for pipeline gas, the carbon dioxide (CO_2) content must be reduced to increase the overall percentage of methane and the calorific value. Analytical instruments, such as micro gas chromatographs (GC), monitor and track important changes in gas composition. They provide a fast and reliable gas composition analysis for common biogas components from ppm up to high percent levels.

Gas chromatography is a well-known analytical technique used to separate and quantify gases. A mixed sample, such as biogas, is introduced via a sample inlet and injector onto chemical coated columns in order to separate hydrogen, oxygen, nitrogen, carbon monoxide (CO), carbon dioxide (CO_2), and methane. Once separated, these compounds are quantified using a detector, such as a thermal conductivity detector (TCD). This detector option compares the thermal conductivity of the compound versus a pure carrier gas such as helium or argon, and records the difference. The results are displayed as a chromatogram and a report which contains the concentration of each individual component.

Using chromatography, the composition of each compound can be tracked and monitored over time. Runs are typically only minutes in length and can be run consecutively to ensure the stability and efficiency of biogas plant processes. Chromatography can also be used to analyze inhibitors to the process such as hydrogen sulfide (H_2S).

Benefits of Micro GC Technology

Micro GC Fusion differs from traditional chromatography because it offers a fast analysis in a transportable chassis. Micro GCs can be taken into the field for fast on-site gas analysis, maintaining sample integrity in harsh environments such as landfills. Alternately, the Micro GC can be set up in a fixed location and the small footprint is optimal in limited space conditions.

Micro GC Fusion is a modular instrument containing up to four modules. Each module is a GC in itself, containing an injector, column, and detector. The ability to run up to four modules simultaneously ensures complete results within a few minutes. For the analysis of biogas, a 2-module Micro GC Fusion is recommended.

Micro GC Fusion has the ability to temperature ramp the columns. This ensures that heavy components fully elute from the column, keeping them clean. The temperature ramping also improves peak shape and run time.

Experimental

A 2-module Micro GC Fusion was used to analyze a biogas calibration standard. The composition of the gas and method parameters used in this experiment can be seen in the tables below.

- Module A: RT-Molsieve 5A, 10 m temperature programmable column with a backflush injector and thermal conductivity detector (TCD)
- Module B: RT-Q-Bond, 12 m temperature programmable column with a fixed volume injector and TCD

The molsieve column on module A was configured with a backflush injector due to the high amounts of carbon dioxide (CO_2) present in biogas. The backflush injector utilizes a short pre-column to trap heavier compounds, such as CO_2, and prevent them from entering the analytical column. This minimizes the potential carryover effect of CO_2. In addition, the temperature program also helps ensure any undesired compounds are driven off the columns.

This experiment was conducted using both argon and helium as a carrier gas due to the potential presence of hydrogen in some biogas samples. The thermal conductivities of hydrogen and helium are very similar to each other, meaning the peak sensitivity of hydrogen using helium as a carrier gas would be reduced. Therefore, argon is the recommended carrier gas for samples containing hydrogen. If no hydrogen is present in the sample, helium can be used to provide better sensitivity for the nitrogen, oxygen, methane, and CO peaks.

Compound	Concentration (Mol%)
Hydrogen	1%
Oxygen	1%
Nitrogen	2%
Methane	Balance
CO	0.1%
CO_2	44%

Table 1: MESA Specialty Gas & Equipment calibration gas composition

Carrier Gas	Backflush Time	Temperature Program	Column Pressure	Data Rate	TCD Temperature
Argon	15 s	100°C (125 s) -> 180 C (2°C/s, hold 15 s)	23 psi	100 Hz	70°C
Helium	16 s	100°C (110 s) -> 180 C (2°C/s, hold 30 s)	23 psi	100 Hz	70°C

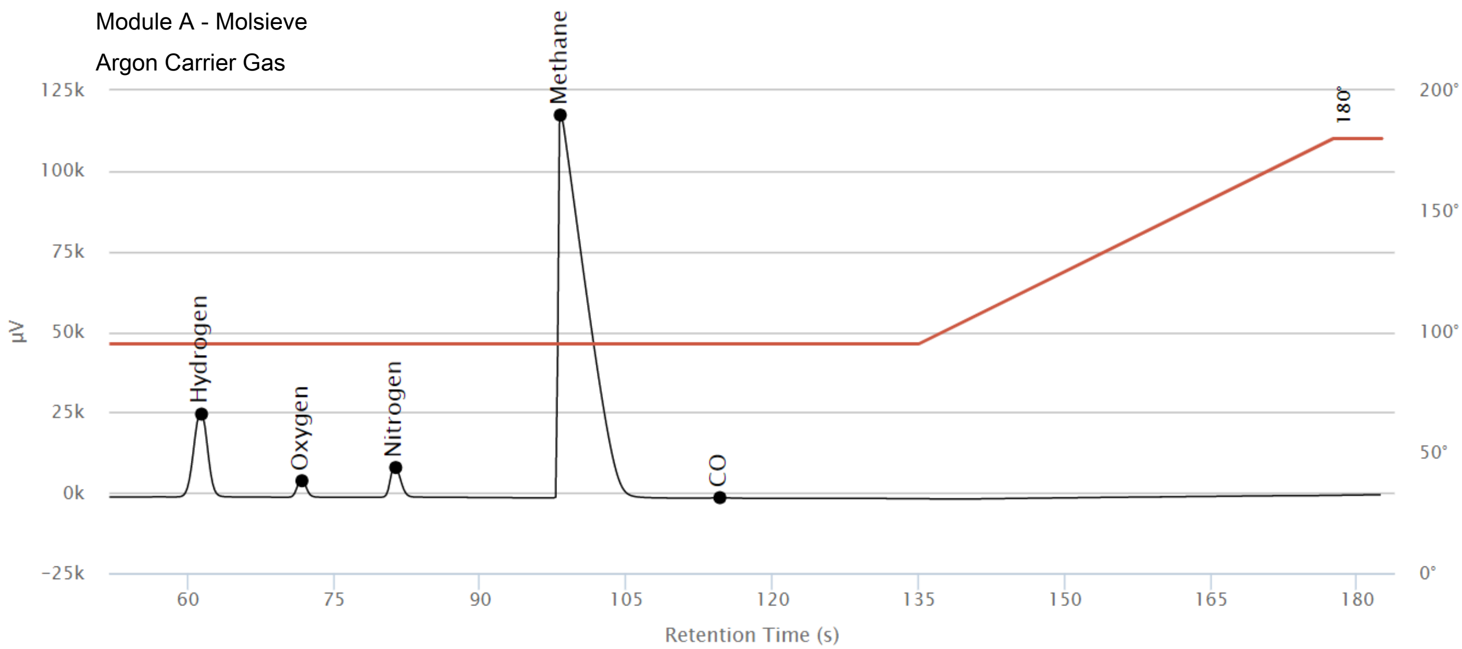
Table 2: Method parameters for Module A - Molsieve

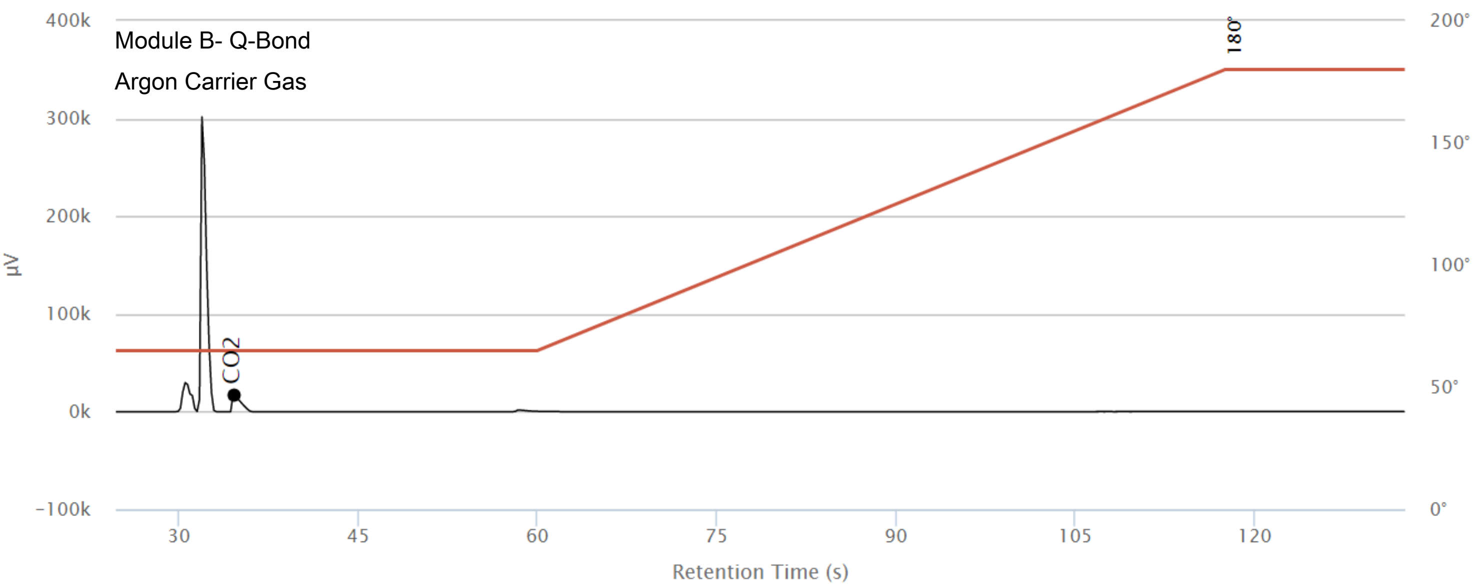
Carrier Gas	Temperature Program	Column Pressure	Data Rate	TCD Temperature
Argon	65°C (60s) -> 180 C (2°C/s, hold 20s)	25 psi	100 Hz	70°C
Helium	65°C (60s) -> 180 C (2°C/s, hold 20s)	25 psi	100 Hz	70°C

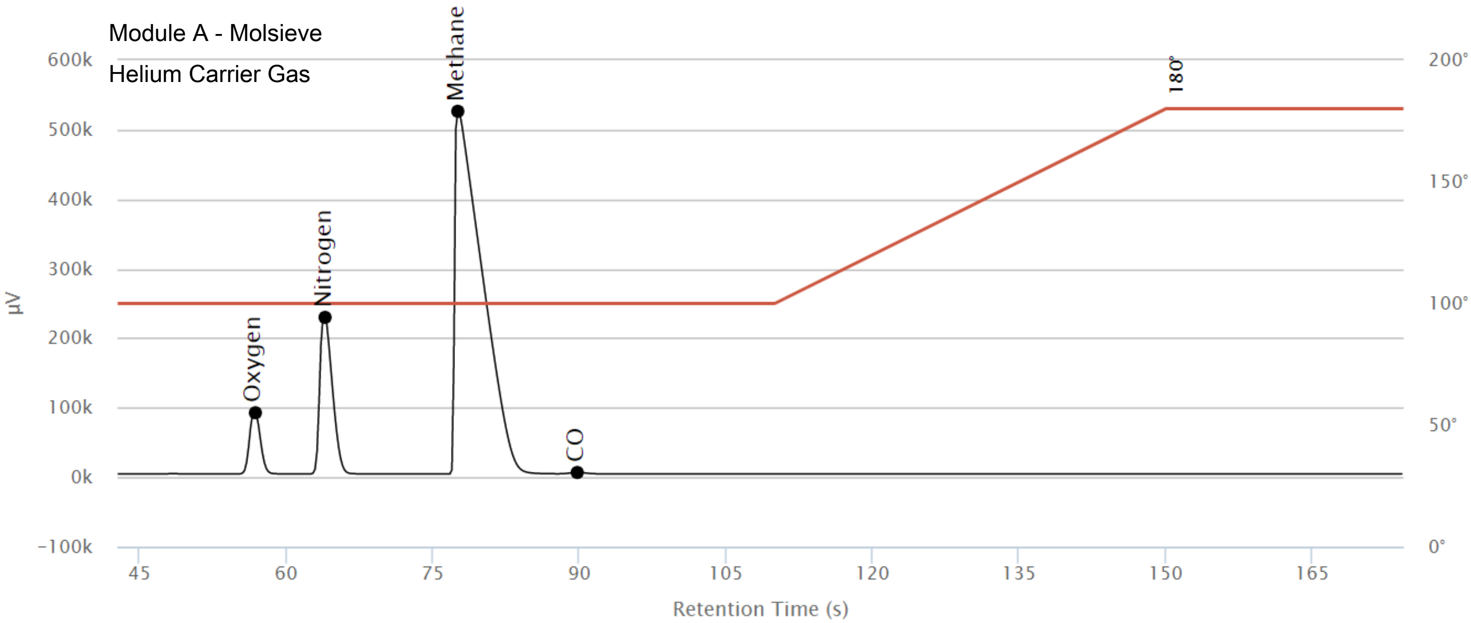
Table 3: Method parameters for Module B - Q-Bond

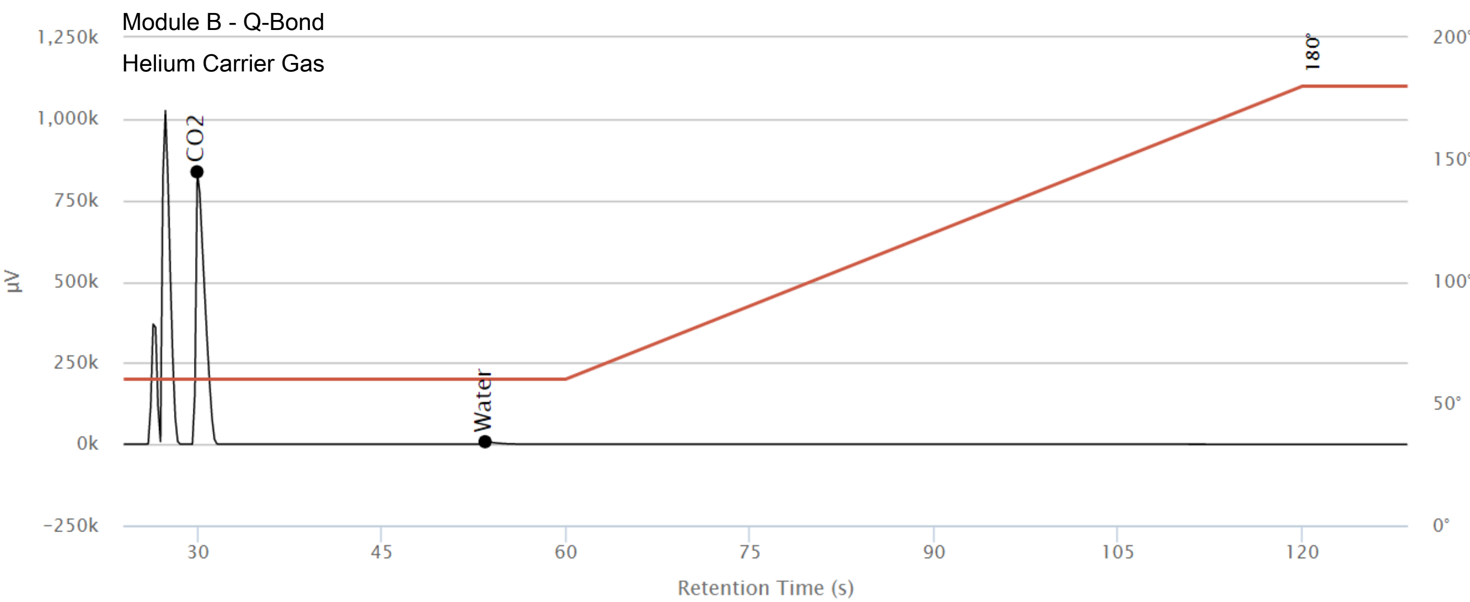
Results

All components in the calibration standard were analyzed within three minutes, on both argon and helium carrier gas, as shown in the chromatograms below.









Ten consecutive runs of each carrier gas were used to calculate the relative standard deviation. All compounds in both argon and helium carrier gas had a peak area %RSD of <1.5% and a retention time %RSD of <0.1%.

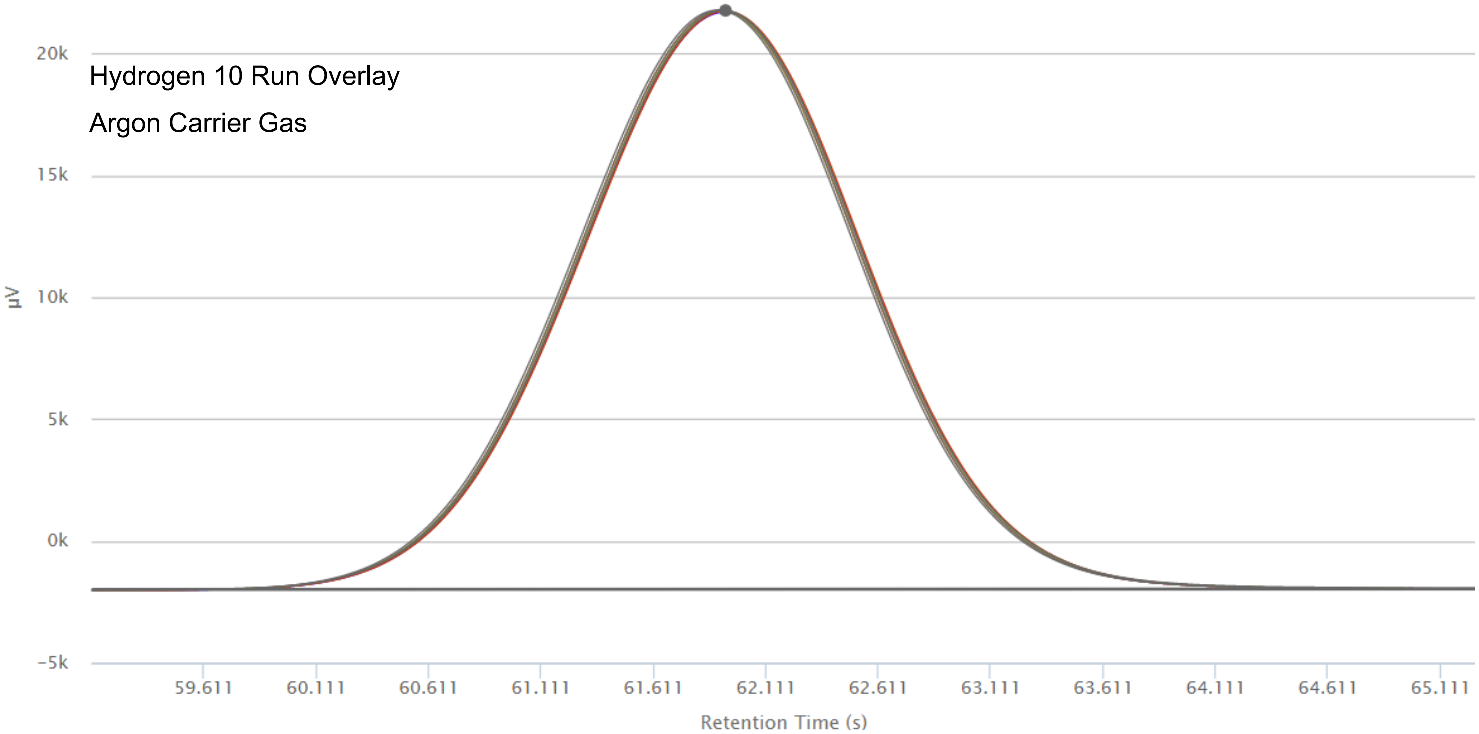
	Hydrogen	Oxygen	Nitrogen	Methane	CO	CO2
Peak area %RSD	0.13%	0.70%	0.81%	0.10%	1.08%	0.11%
Retention time %RSD	0.01%	0.02%	0.02%	0.03%	0.07%	0.01%

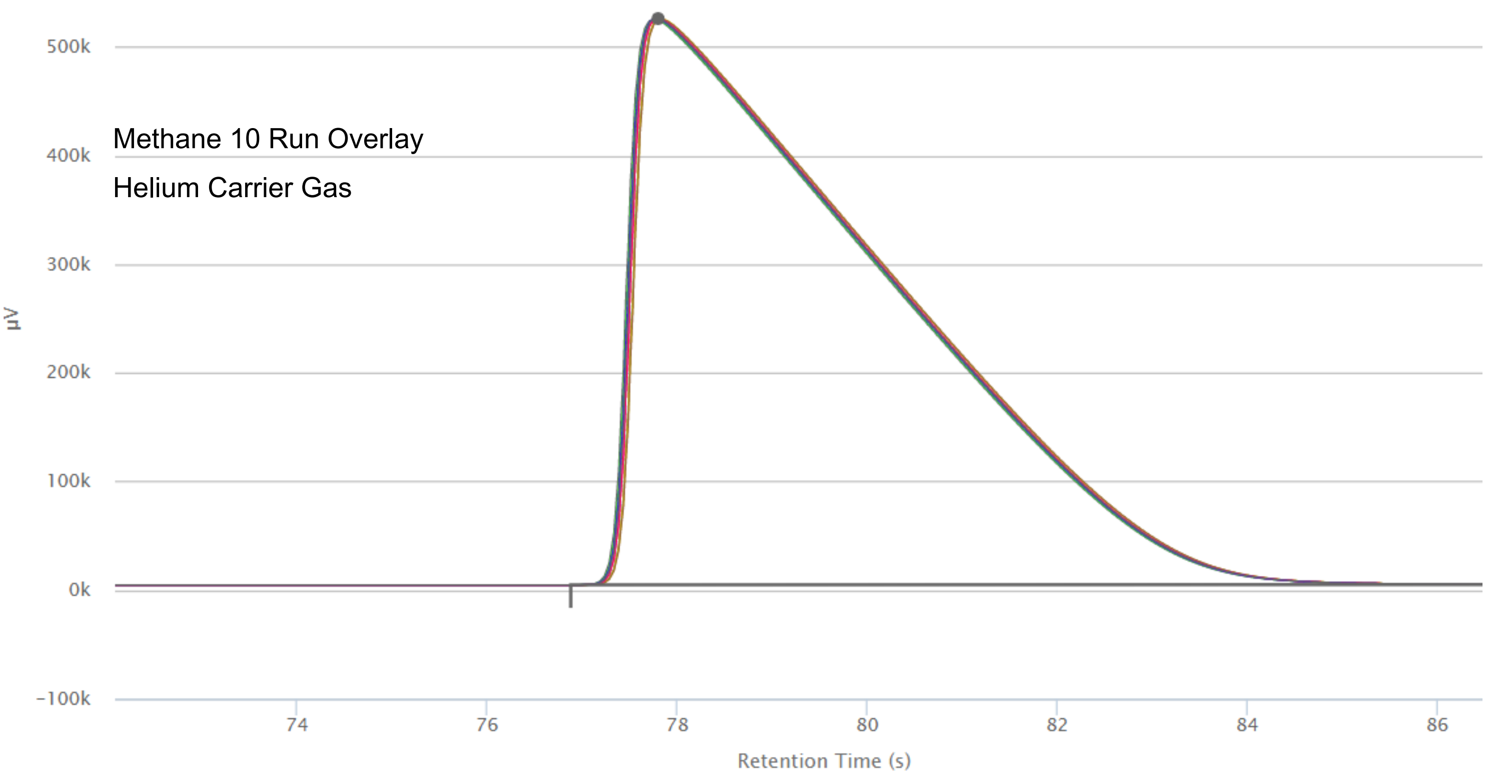
Table 4: Argon carrier gas repeatability

	Oxygen	Nitrogen	Methane	CO	CO2
Peak area %RSD	0.68%	0.69%	0.12%	0.21	0.12%
Retention time %RSD	0.02%	0.03%	0.04%	0.09%	0.02%

Table 5: Helium carrier gas repeatability

The figures below display the last 10 runs for each carrier gas overlaid on each other to demonstrate the repeatability.





Conclusion

Compositional analysis of methane, carbon dioxide, and other fixed gases in biogas is an important factor in ensuring the process in biogas plants is stable and efficient. Gas chromatography is a well-known analytical technique that provides a way to separate and quantify these components. In addition, Micro GC technology provides additional benefits, such as being a fast, transportable option while still providing excellent repeatability.

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