Fast Analysis of Natural Gas Using the Agilent 490 Micro GC Natural Gas Analyzer

Application Note

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Abstract

During production and distribution of natural gas it is of high importance to determine its composition and calorific value because natural gas is bought and sold on its energy content. This application note shows the use of the Agilent 490 Micro GC Natural Gas Analyzer for the analysis of natural gas and the calculation of its heating value. With the 490 Micro GC, Agilent provides ideal solutions for laboratory, on-line and field use.
Introduction

Natural gas mainly consists of methane and variable levels of other hydrocarbons and permanent gases such as oxygen, nitrogen, and carbon dioxide. Different sources of natural gas usually have similar composition but vary in concentration.

Natural gas is traded on its energy content and therefore the analysis of the chemical composition and calorific value is of high importance for all stakeholders. That is where the 490 Micro GC based Natural Gas Analyzer can play a significant role.

The 490 Micro GC Natural Gas Analyzers are shipped as a total solution; the analyzers are factory tuned, for optimal separation, and come with final test data, a complete method, a user manual, and a check-out sample. Easy-to-use software is available for the calculation of all required physical properties, such as heating value and Wobbe index, conform official methods from the American Society of Testing and Materials (ASTM), Gas Processors Association (GPA) and International Standards Organization (ISO).

Natural Gas Analyzer setup

Based on the 490 Micro GC, four Natural Gas Analyzers are available, depending on the composition of the natural gas and the compounds of interest. The configurations and analysis characteristics for all analyzers are shown in Table 1. Additional information for the configurations can be found in Natural Gas Analyzer Data Sheet [1].

The Natural Gas Analyzers are equipped with heated injectors and sample lines, both set to 110 °C in the analyzer method, to eliminate any cold spots and prevent possible condensation of moisture, and to ensure the integrity of the sample is maintained throughout the sample flow path.

Table 1 shows multiple column channels are equipped with a back flush to vent option. To protect the CP-Molsieve 5A stationary phase and maintain the separation efficiency of the molecular sieve column, it is necessary to back flush carbon dioxide, moisture, and higher hydrocarbons. Moisture and carbon dioxide tend to adsorb quickly to the molecular sieve stationary phase change its chromatographic properties. This can result in retention shifts and loss of separation. Higher hydrocarbons will eventually elute, but will cause higher detector noise levels and would lead to reduced sensitivity; the back flush to vent functionality on the Molsieve 5A column channel prevents this from happening. On the PoraPLOT U and HayeSep A channels, the higher hydrocarbons, C4 and higher, are back flushed to vent. This prevents these late eluting components from interfering in the next analysis.

<table>
<thead>
<tr>
<th>Analyzer characteristics</th>
<th>Natural Gas Analyzer A</th>
<th>Natural Gas Analyzer A Extended</th>
<th>Natural Gas Analyzer B</th>
<th>Natural Gas Analyzer B Extended</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micro GC cabinet</td>
<td>Dual with 2 channels</td>
<td>Quad with 3 channels</td>
<td>Dual with 2 channels</td>
<td>Quad with 3 channels</td>
</tr>
<tr>
<td>Column channels installed</td>
<td>HayeSep A 40 cm, without backflush</td>
<td>HayeSep A 40 cm, with backflush</td>
<td>PoraPLOT U 10 m, with backflush</td>
<td>CP-Molsieve 5A 10 m, with backflush and retention time stability option</td>
</tr>
<tr>
<td></td>
<td>CP-Sil 5 CB 6 m, without backflush</td>
<td>CP-Sil 5 CB 4 m, with backflush</td>
<td>CP-Sil 5 CB 6 m, without backflush</td>
<td>PoraPLOT U 10 m, with backflush</td>
</tr>
<tr>
<td></td>
<td>CP-Sil 5 CB 8 m, without backflush</td>
<td></td>
<td></td>
<td>CP-Sil 5 CB 6 m, without backflush</td>
</tr>
<tr>
<td>Analysis</td>
<td>Hydrocarbons C1-C9  Carbon dioxide, Air</td>
<td>Hydrocarbons C1-C12  Carbon dioxide, Air</td>
<td>Hydrocarbons C1-C9  Carbon dioxide, Air, Hydrogen sulfide</td>
<td>Hydrocarbons C1-C9  Carbon dioxide, Air, Hydrogen sulfide, Permanent gases (N₂, O₂, He and H₂)</td>
</tr>
</tbody>
</table>
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. The use of the RTS option enables a more efficient back flush of carbon dioxide. This enhances column lifetime and, most importantly, leads to more stable retention times.

The natural gas sample can be introduced to the 490 Micro GC either pressurized (maximum limit 1 bar), through a Tedlar sampling bag using the internal sampling pump, or by using continuous flow sampling mode. When you need to analyze multiple streams on a single analyzer or you want to connect multiple calibration samples for automated calibration, the use of a stream selector valve is recommended.

To expand the range of samples to Liquid Petroleum Gas (LPG) and Liquefied Natural Gas (LNG), the Micro-Gasifier provides controlled evaporation before the sample is introduced into the gas chromatographic injector for analysis. In addition, high-pressure gas samples can be reduced without creating cold spots, which prevents discrimination in the sample.

Fast Natural gas analysis using the Natural Gas Analyzer A

The first channel in the Natural Gas Analyzer A is equipped with a Haysep A column for separating methane from the composite air peak (nitrogen and oxygen). Carbon dioxide, ethane, and propane are analyzed on this column channel as well. Figure 1 shows an example chromatogram for these compounds.

For the analysis of the hydrocarbons from propane to n-nonane, a second column channel, equipped with a 6-meter CP-Sil 5 CB column, is used. Figure 2a shows a chromatogram on the 6-meter CP-Sil 5 CB for the separation until n-octane; n-hexane elutes in less than 60 seconds and n-octane in just over 3 minutes. Propane is analyzed on both Haysep A and CP-Sil 5 CB column enabling the use of propane as a bridge component. The extended part of the chromatogram obtained with a 6-meter CP-Sil 5 CB column, displayed in Figure 2b, shows the analysis of hydrocarbons until n-nonane.

<table>
<thead>
<tr>
<th>Conditions</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Column temperature</td>
<td>60 °C</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>helium, 260 kPa</td>
</tr>
<tr>
<td>Injection time</td>
<td>40 ms</td>
</tr>
</tbody>
</table>

Peak identification

1. composite air peak
2. methane
3. carbon dioxide
4. ethane
5. propane

Figure 1. Chromatogram for nitrogen, carbon dioxide, and C1 – C3 hydrocarbons on a Haysep A column.
Figure 2a. Chromatogram for C₃ – C₈ hydrocarbon using a 6-meter CP-Sil 5 CB column.

Peak identification
1. propane
2. i-butane
3. n-butane
4. neo-pentane
5. i-pentane
6. n-pentane
7. n-hexane
8. n-heptane
9. n-octane

Figure 2b. Chromatogram for C₈ – C₉ hydrocarbons using a 6-meter CP-Sil 5 CB column.

Peak identification
9. n-octane
10. n-nonane

Analysis up to n-dodecane with the Natural Gas Analyzer A Extended

The extended version of the Natural Gas Analyzer A is used for the analysis of natural gas until n-dodecane. This extended analyzer is equipped with three column channels. First, a HayeSep A column channel is used for separation of composite air peak from methane, carbon dioxide ethane, and propane. This channel is equipped with back flush functionality ensuring that butanes and later eluting hydrocarbons are back flushed to vent. Figure 3 shows an example for the HayeSep A channel, propane is eluting in less than 2 minutes.
The second channel, equipped with a 4-meter CP-Sil 5 CB column with back flush functionality, is used to analyze C3 to C5 hydrocarbons; the chromatogram is shown in Figure 4. N-hexane and higher hydrocarbons are back flushed to vent.

Figure 3. Chromatogram for HayeSep A column with backflush.

Figure 4. Chromatogram for C3 to C5 hydrocarbons on a 4-meter CP-Sil 5 CB.
A third column channel, equipped with a 8-meter CP-Sil 5 CB column, is used to analyze the higher hydrocarbons from n-hexane to dodecane; n-Dodecane elutes in approximately 240 seconds. A natural gas sample sample until n-decane, demonstrated in Figure 5a, is analyzed in less than 2 minutes. Figure 5b displays a hydrocarbon gas mixture from n-hexane until n-dodecane, typical analysis time is 240 seconds.

**Analysis of natural gas including hydrogen sulfide using the Natural Gas Analyzer B**

When your natural gas analysis needs to include hydrogen sulfide, the 490 Micro GC Natural Gas Analyzer B is the analyzer of choice. This analyzer uses a PoraPLOT U column channel for the separation of methane from the composite air peak (nitrogen and oxygen). This column is also used for the analysis of carbon dioxide, ethane, and propane. The chromatogram in Figure 6 shows an example of natural gas on the PoraPLOT U column; total analysis is done in approximately 60 seconds. For the analysis of hydrogen sulfide, the stainless steel tubing in the 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 excellent peak shape ensuring correct analysis of hydrogen sulfide even at ppm level.

Hydrocarbon analysis from propane until n-nonane for the Natural Gas Analyzer B is done with a second channel equipped with a 6-meter CP-Sil 5 CB. This column is identical to the one used for the Natural Gas Analyzer A. The chromatograms for this channel are displayed in Figure 2a and 2b.
Permanent gas analysis using Natural Gas Analyzer B Extended

The Extended version of the 490 Micro GC Natural Gas Analyzer B is equipped with an additional CP-MolSieve 5A column channel for the analysis of permanent gases in your natural gas sample. Helium carrier gas on this channel enables the separation and quantification of oxygen and nitrogen, an example is shown in Figure 7 (top part).

When you need to analyze helium, neon, or hydrogen as well, the use of argon instead of helium as carrier gas is required. The bottom part of Figure 7 shows a chromatogram for the molecular sieve column running with argon as carrier gas. To have the flexibility to change the carrier gas for only the molecular sieve column to argon, this channel is connected to a separate carrier gas inlet at the rear of the micro GC.
Conclusion

Micro GC Natural Gas Analyzer is a genuinely better solution for analyzing your natural gas stream. Whether in the lab, on-line/at-line, or in the field, the “Measure Anywhere” Micro GC provides natural gas analysis in a matter of seconds.

The Natural Gas Analyzer A analyzer combined with a HayeSep A and 6-meter CP-Sil 5 CB column channel is used for the analysis of natural gas. This analyzer will separate methane from air and can analyze up to n-nonane. Carbon dioxide is also analyzed. Total analysis time depends on the hydrocarbons in the sample; up to n-heptane is done in approximately 90 seconds, n-nonane elutes just under 400 seconds.

When you want to analyze until n-dodecane in natural gas, the Natural Gas Analyzer A Extended is required. The 6-meter CP-Sil 5 CB column channel is replaced by two different CP-Sil 5 CB channels. A short CP-Sil 5 CB (4-meter) will analyze from propane to the pentanes; hexane and higher will be back flushed to vent. The second CP-Sil 5 CB channel, with an 8-meter column, is used for analysis of hexane up to n-dodecane.

Figure 8. EZReporter, sample results with calculated physical properties (left), parameter monitoring (middle), and trend analysis (right).
The Natural Gas Analyzer B, equipped with a PoraPLOT U and a 6-meter CP-Sil 5 CB CB column channel, provides fast analysis of natural gas, from the separation of air and methane, carbon dioxide, and hydrocarbons up to n-nonane. This analyzer setup is designed for the analysis of hydrogen sulfide. The stainless steel sample inlet of the system is deactivated using an UltiMetal treatment resulting in excellent peak shape for hydrogen sulfide.

If more detailed analysis of the permanent gases in the natural gas sample is required, the extended version of the Natural Gas Analyzer B is the system of choice. This analyzer is equipped with an additional CP-Molsieve 5A column enabling the separation of oxygen and nitrogen, using helium as carrier gas. When this analyzer uses argon as carrier gas, helium and hydrogen can be detected as well.

The 490 Micro GC Natural Gas Analyzers are factory tuned, including the appropriate settings for the back flush times. The Agilent Natural Gas Analyzers are shipped with final test data, optimized analytical method, Natural Gas Analyzer User Manual, and a check out sample kit to have all information available upon installation.

The analyzer hardware together with your chromatography data system (CDS) of choice provides an easy-to-use and powerful system. The EZReporter software is linked to Agilent CDS, resulting in automatic calorific value/BTU calculations and reports according to American Society of Testing and Materials (ASTM D3588), Gas Processors Association (GPA 2172), and International Standards Organization (ISO 6976).

For more information about the 490 micro GC Natural Gas Analyzer or other Micro GC solutions, visit our website at www.agilent.com/chem/microgc.

References

1. 5991-0301EN; Agilent 490 Micro GC Natural Gas Analyzers; Data Sheet; April 2012.

For More Information

These data represent typical results. For more information on our products and services, visit our Web site at www.agilent.com/chem.