Application Note

Energy and Chemicals

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Fast Analysis of Natural Gas Using the Agilent 990 Micro GC Natural Gas Analyzer

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Introduction

Natural gas is a naturally occurring hydrocarbon gas mixture consisting primarily of methane, but commonly including varying amounts of other hydrocarbons such as ethane, propane, butane and isobutane, pentane and isopentane. Sometimes, a small percentage of carbon dioxide (CO_2), nitrogen, hydrogen sulfide (H_2S), or helium exist together with the hydrocarbons.

Natural gas is a source of energy, used for heating, cooking, and generating electricity. It can also be used as fuel for vehicles and as a chemical feedstock for manufacturing plastic and other important chemicals.

In most parts of the world, natural gas is traded on its energy content. Accurate information on natural gas composition can help generate the correct unit calorific value, which is important for natural gas trading. The traditional approach to natural gas analysis is primarily based on a regular laboratory GC with a complex multicolumn, multivalve configuration. It usually takes 6 to 20 minutes to complete the analysis (depending on the configuration and compounds of interest to be analyzed). Compared to a traditional GC platform, the Agilent 990 Micro GC is much smaller, and consumes much less carrier gas and power. More importantly, it can provide faster natural gas analysis. The 990 Micro GC's analysis approach for complex gas samples is to analyze part of the sample on different channels, then combine and normalize the results from the different channels to give complete information on the whole sample. Since each channel only focuses on a subset of sample, the method is easily optimized for faster speed without compromising resolution.

This study demonstrates four types of natural gas analyzers (NGA) based on the 990 Micro GC platform. Each analytical channel in the analyzer is selected to address part of the natural gas constituents for specific analysis requirement. The analytical method loaded on the analyzer is optimized in the factory and verified by a simulated natural gas standard. To show the validity of the method, all test results will be reproduced at the customer site.

Experimental

Table 1. Channel configurations for the four NGA analyzers.

NGA Analyzers	NGA Analyzer A	NGA Analyzer A Extended	NGA Analyzer B	NGA Analyzer B Extended
G3599A Option	#120	#121	#122	#123
Channel 1	40 cm HayeSep A channel, straight	40 cm HayeSep A channel, backflush	10 m CP-PoraPLOT U, backflush	10 m CP-Molesieve 5Å, backflush, retention time stability option (RTS)
Channel 2	6 m CP-Sil 5CB, straight	4 m CP-Sil 5CB, backflush	6 m CP-Sil 5CB, straight	10 m CP-ParoPLOT U, backflush
Channel 3		8 m CP-Sil 5CB, straight		6 m CP-Sil 5CB, straight
Analysis	Air, CO_2 Hydrocarbons C_1 to C_9	Air, CO_2 Hydrocarbons C_1 to C_{12}	Air, CO_2 Hydrocarbons C_1 to C_9 H_2S	Air, CO_2 Hydrocarbons C_1 to C_9 H_2S Permanent gas (O_2, N_2, He, H_2)

Table 2. Composition of gas standards used for the analyzer test.

Compound	Concentration (mol%)
Simulated Natural Gas	
Nitrogen	1.01%
Oxygen	0.02%
Carbon dioxide	5%
Methane	Balance
Ethane	1.5%
Propane	0.4%
Isobutane	0.05%
Butane	0.05%
2,2-Dimethylpropane	0.01%
Isopentane	0.03%
Pentane	0.03%
2,2-dimethylbutane	0.01%
Hexane	0.005%
Heptane	0.005%
Octane	0.005%
Nonane	0.005%

Compound	Concentration (mol%)
C_6 to C_{10} Hydrocarbons Mixture in Helium	
Hexane	0.005%
Heptane	0.005%
Octane	0.005%
Nonane	0.005%
Decane	0.005%

Compound	Concentration (mol%)
He/Ne/H_2/O_2/N_2 in Methane	
Helium	0.10%
Neon	0.05%
Hydrogen	0.10%
Oxygen	0.05%
Nitrogen	0.10%
Methane	Balance

Table 3. Conditions of each channel for sample analysis.

Channel Type	Column Temperature (°C)	Column Pressure (KPa)	Backflush Time (s)	Carrier Gas
HayeSep A, 40 cm, Straight	60	260	NA	Helium
6 m, CP-Sil 5CB, Straight	70	175	NA	Helium
HayeSep A, 40 cm, Backflush	90	340	150	Helium
4 m, CP-Sil 5CB, Backflush	60	150	11	Helium
8 m, CP-Sil 5CB, Straight	150	200	NA	Helium
10 m, CP-PoraPLOT U, Backflush	80	150	12	Helium
10 m, CP-Molesieve 5Å, Backflush (RTS)	80	200	8	Helium/Argon

NGA analyzers

Two-channel NGA analyzer (Figure 1A)

The sample inlet is at the front of the instrument for easy access. The connections for the carrier gas and column/sample vent are at the back of the GC.

Through the sample inlet, sample is drawn through (in pump mode) or pushed into (in continuous flow mode) the sample loop. The inlet port and its connection tubing to each channel are deactivated for inertness. This is useful in the analysis of low-level active components such as H_2S. The inlet port can be heated to 110 °C to prevent sample condensation.

After the sample purges and fills the sample loop in the injector, the injection valve is switched on, and the sample is injected into the analytical column or precolumn (backflush channel) for analysis. The sample amount injected is controlled by the injection time. Generally, 20 to 100 ms is used for the injection time depending on sample concentration. The longer the injection time, the higher the TCD response. Each channel separates its target compounds and generates a chromatogram. The retention time (RT)of each peak is used for compound identification. Peak response is used for concentration calculation based on the ESTD curve developed on each channel; the final concentration for each component in the whole sample is calculated by concentration normalization of all quantified components.

NGA analyzer extended version (Figure 1B)

The extended version of analyzer accommodates three channels for natural gas analysis. It is the combination of the basic cabinet and channel extension cabinet, which can house up to four channels, controlled by one main board.

The full-color touch screen is provided for better usability. It shows system configuration, and displays the actual value and set points of the pressure and temperature on each channel. Users can easily read firmware version, instrument license, IP address, and other network settings. The information can be displayed in two languages: English and Chinese. It is easy to switch the language through the touch screen. There is a status bar displaying different colors at the bottom of the touch screen to show instrument status. In addition, there is an LED light at the right side of the top assembly to indicate instrument status. It works like a traffic signal:

- Green for system ready at setpoints
- Yellow for not ready
- Red for error
- Flashing green for run

The channel configuration of each analyzer depends on the composition of natural gas or the compounds of interest. The molecular sieve type channel is for permanent gases, methane, and carbon monoxide analysis. The CP-PoraPLOT U type is for H_2S and C_1 to C_3 compounds analysis. The CP-Sil 5CB channel is for the analysis of hydrocarbons heavier than C_2.

The backflush option is used to protect the analytical column. For example, CO_2 and moisture are easily adsorbed on a Molesieve 5Å column, which can result in shifting RT. It takes a long time to condition and recover column performance. If other hydrocarbons enter the molecular sieve channel they will elute after a long time. This not only elongates the analysis time but also increases baseline noise. The backflush option can help trap and flush out the moisture, CO_2, and hydrocarbons ($>C_1$) to protect the Molesieve 5Å analytical column. The PoraPLOT U and HayeSep A columns also have backflush options, which are used to prevent hydrocarbons heavier than C_3 entering the analytical column, to reduce the analysis time on the two channels and to avoid the interference of heavier components on the next run.

Figure 1A. Two-channel NGA analyzer. The red circle indicates the sample inlet.

Figure 1B. Three-channel NGA analyzer. The red circle indicates the sample inlet.

NGA analyzer A

Channel 1: A 40 cm, HayeSep A, straight channel for analysis of air, methane, CO_2, ethane, and propane.

Figures 2A and 2B show chromatograms of the five compounds on this channel. The five targeted components were well resolved. The analysis was completed within two minutes.

Channel 2: A 6 m, CP-Sil 5CB, straight channel for analysis of hydrocarbons from propane to nonane.

Hexane eluted within 50 seconds, and octane eluted in approximately three minutes. Nonane takes approximately five minutes to be detected. Figures 3A and 3B show chromatograms of C_3 to C_9 components. Propane can be analyzed on both channels as a bridge component.

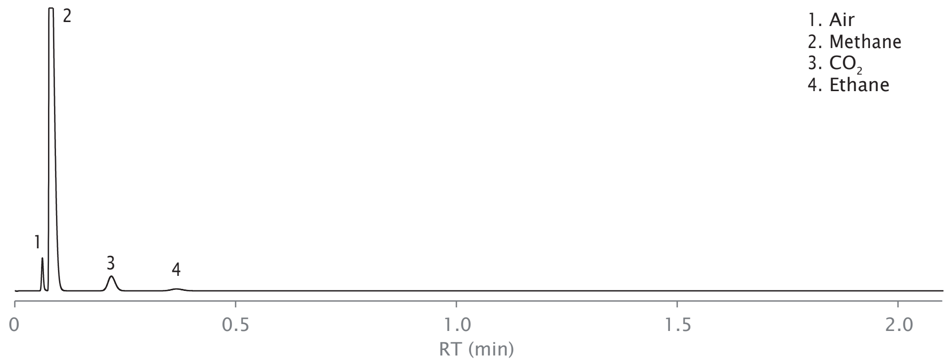

Figure 2A. Air, CO_2, and C_1 to C_3 analysis on the HayeSep A straight channel.

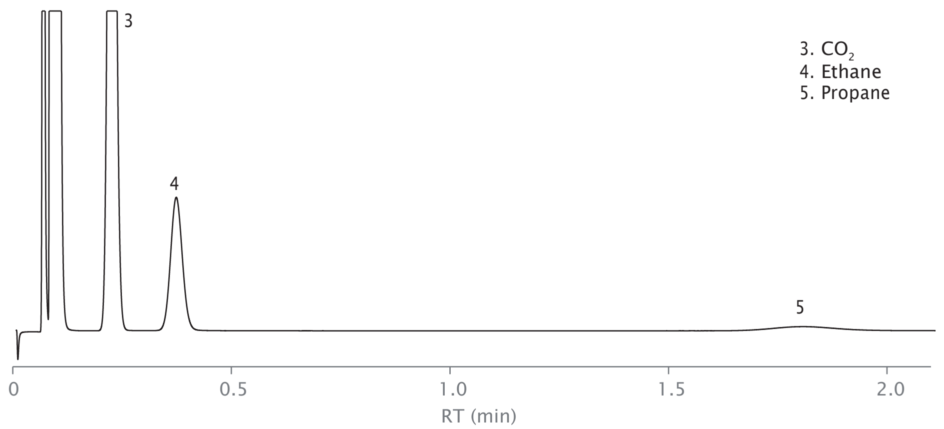

Figure 2B. Enlarged chromatogram for propane on the HayeSep A straight channel.

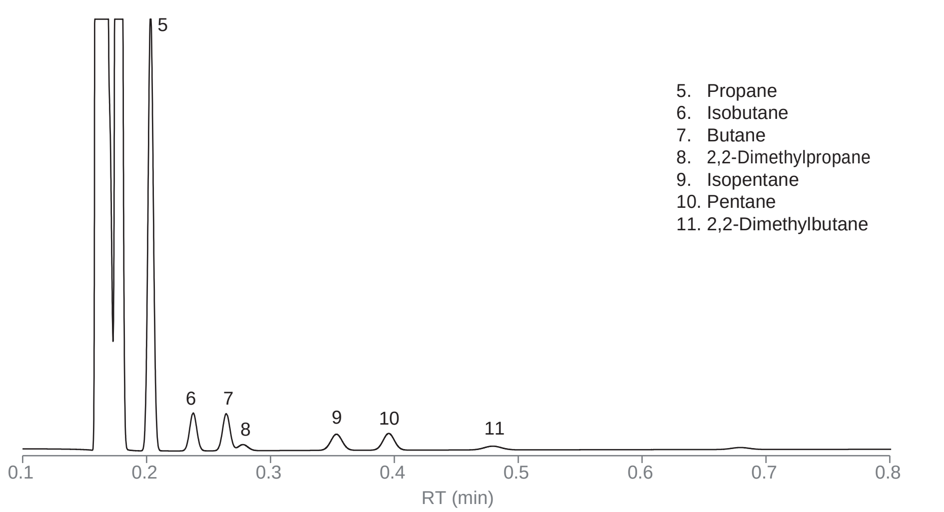

Figure 3A. C_3 to C_5 on the 6 m CP-Sil 5CB channel.

NGA analyzer A extended

Channel 1: A 40 cm, HayeSep A, backflush channel for analysis of air, methane, CO_2, ethane, and propane.

Heavier components (>C_3) **are** backflushed before they entered the analytical channel, ensuring that the analysis can be finished in a shorter time without waiting for their late elution. This also helps prevent their interference in the next run. The HayeSep A column connection in backflush option is different than that in the straight option, so the optimized analytical conditions are different between backflush and straight options. Higher pressure and column temperature are used for fast separation with the HayeSep backflush option. Figures 4A and 4B show the chromatograms of NGA on the 40 cm, HayeSep A, backflush channel.

Channel 2: A 4 m, CP-Sil 5CB, backflush channel for analysis of C_3 to C_5 hydrocarbons.

The components heavier than C_5 were backflushed through the precolumn to the vent port. The analysis was completed within 30 seconds. Figure 5 shows the chromatogram.

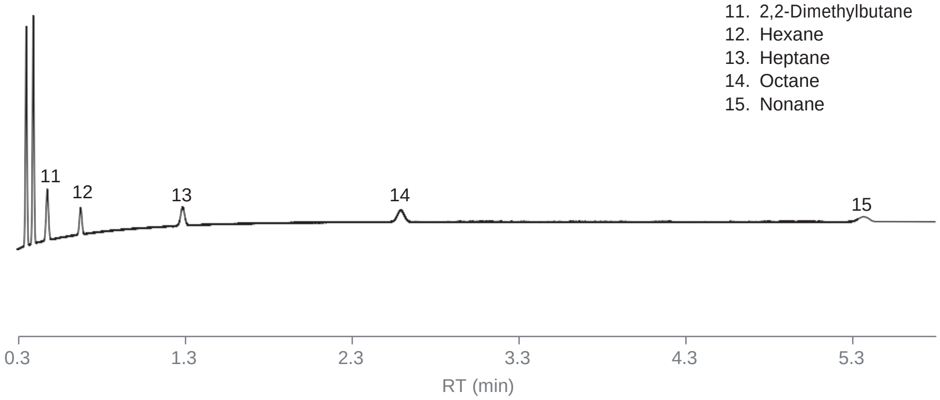

Figure 3B. C_6 to C_9 on the 6 m CP-Sil 5CB channel.

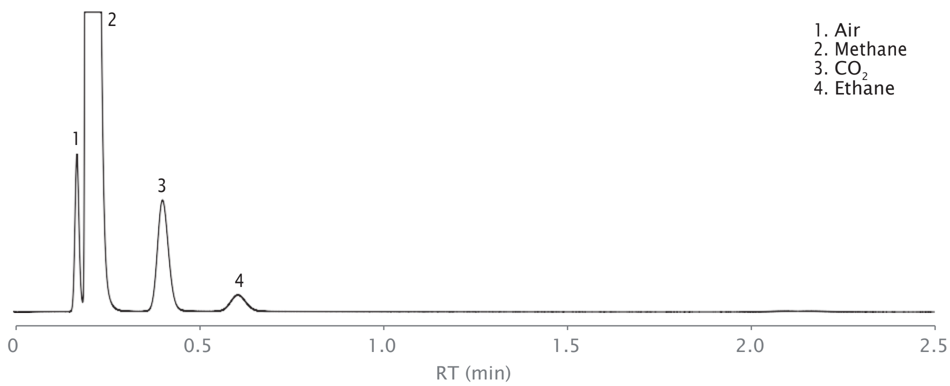

Figure 4A. Air, CO_2, and C_1 to C_3 on the HayeSep A, backflush channel.

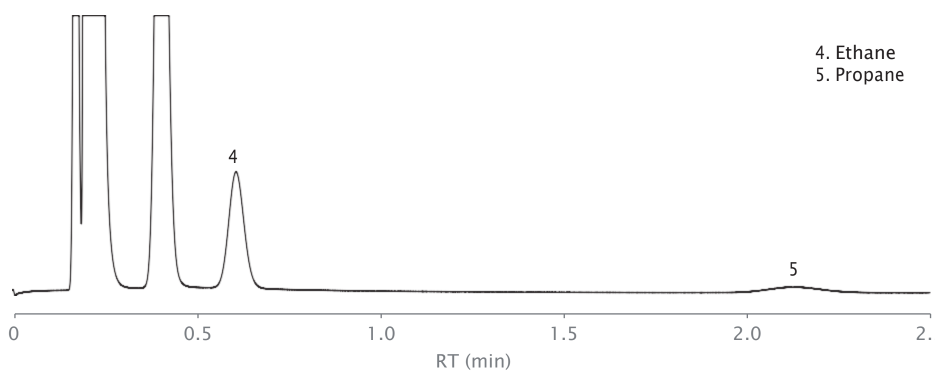

Figure 4B. Propane on the HayeSep A, backflush channel.

Channel 3: An 8 m, CP-Sil 5CB, straight channel for C_6 **and C_6**-plus components analysis.

Figure 6 shows the chromatogram for **C_6** to C_{10} components on the 8 m 5CB straight channel.

Channels 2 and 3 in analyzer A extended not only fulfill the function of channel 2 in analyzer A, but also extend the analysis range of hydrocarbons up to C_{12} without speed compromise. The backflush function of the 4 m CP-Sil 5CB channel **ensures that C_3** to C_5 hydrocarbons are analyzed within 30 seconds without interference from heavy components. The high temperature of 150 °C on channel 3 accelerated the elution of **C_6**/C_6-plus components. To get good separation of hexane and pentane at high column temperature, an 8 m CP-Sil 5CB column is used. The chromatogram (Figure 6) showed that decane eluted at approximately 100 seconds under the optimized conditions. This result is the same as in our previous work on Agilent 490 NGA analyzers.[1]

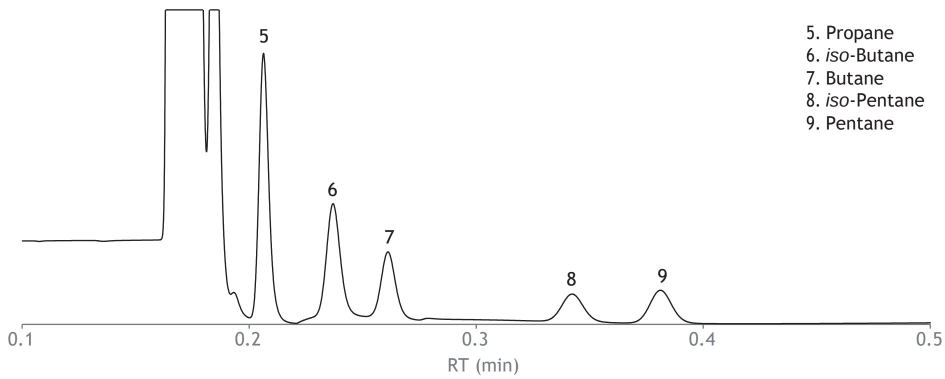

Figure 5. C_3 to C_5 on the 4 m CP-Sil 5CB, backflush channel.

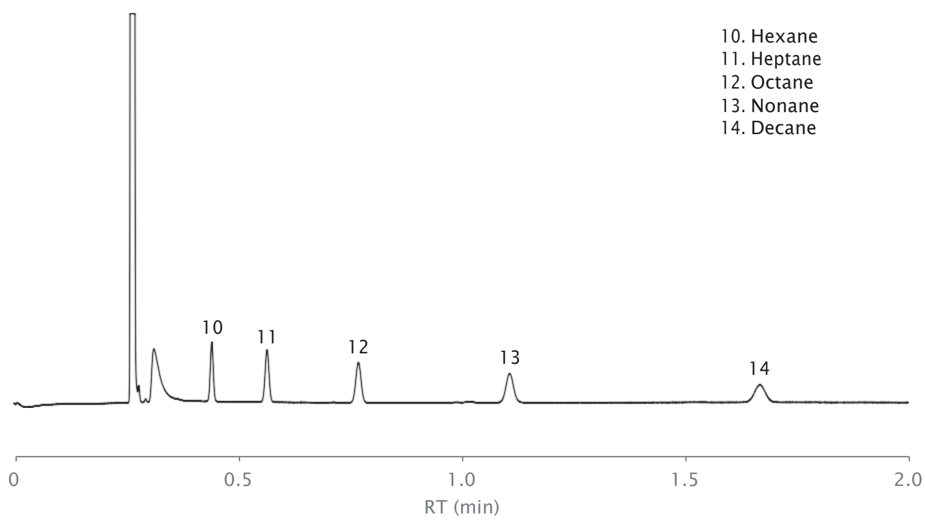

Figure 6. C_6 to C_{10} mixture on the 8 m CP-Sil 5CB channel.

NGA analyzer B

Channel 1: A 10 m, CP-PoraPLOT U, backflush channel for air, methane, H_2S, ethane, and propane analysis.

The measurement of H_2S is important because of the gas quality specification, the corrosive nature of H_2S on pipeline material and the effects of H_2S on utilization equipment. The CP-PoraPLOT U (PPU) column is suitable for H_2S analysis. The 990 Micro GC applies a proprietary deactivation technique to its sample flowpath, which reduces the adsorption of active compounds, improves their peak shape, and helps achieve better detectability for the active components. Figure 7B shows the good peak shape of H_2S on the PPU column. H_2S, methane, and air are well resolved on this channel. The heaviest compound analyzed on this channel is propane. If C_4 and heavier hydrocarbons were analyzed on a PPU channel, they would elute much later with tailing peaks at the applied column temperature. That is why they are analyzed on CP-Sil 5CB channel.

Channel 2: A 6 m, CP-Sil 5CB, straight channel for analysis of propane to nonane.

This channel is the same as that used by NGA analyzer A. For chromatograms, see Figures 3A and 3B.

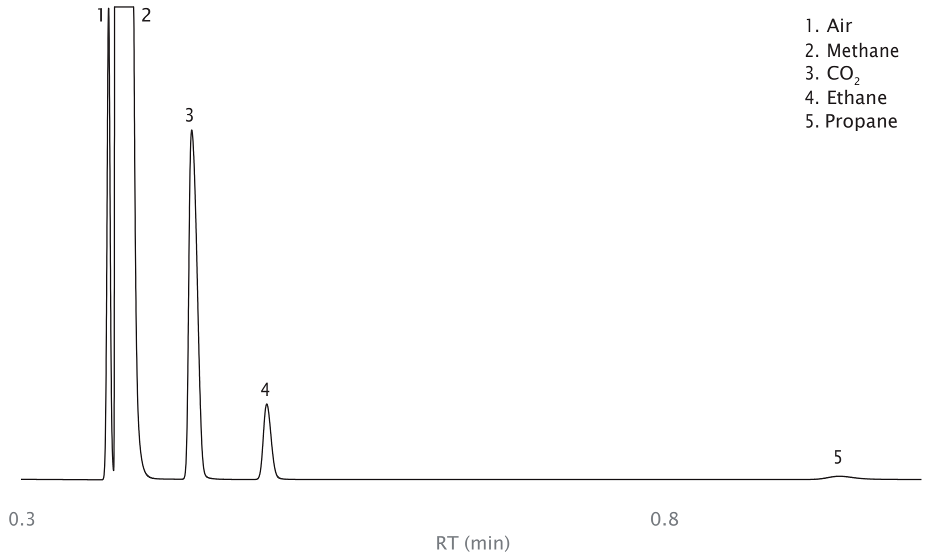

Figure 7A. Air, CO_2, and C_1 to C_3 hydrocarbons on the 10 m CP-PoraPLOT U, backflush channel.

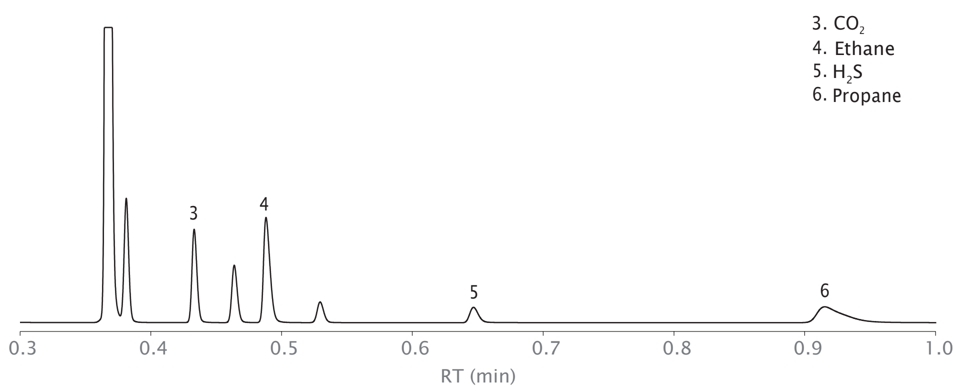

Figure 7B. Hydrogen sulfide on the 10 m CP-PoraPLOT U, backflush channel.

NGA analyzer B extended

Channel 1: A 10 m, CP-MoleSieve 5Å, backflush channel.

The permanent gases in natural gas, including helium, neon, hydrogen, oxygen, nitrogen, and methane are usually analyzed on columns with molecular sieve stationary phase. Compared with other types of stationary phase, Molesieve 5Å achieves baseline separation of permanent gases at or above ambient temperature without expensive coolants.

Both argon and helium can be used as carrier gas. Helium is usually used for nitrogen and oxygen analysis with good detector response. Low concentration helium and full range hydrogen analysis usually uses argon as carrier gas.

Molecular sieve columns are sensitive to moisture and CO_2. That is why a retention time stability option (RTS) is placed between the dynamic electronic gas control (DEGC) module and the analytical column. Working as an inline filter, the RTS traps moisture and CO_2 before carrier gas enters the molecular sieve column, which helps guarantee the long-term retention time stability of this channel.

Figures 8A and 8B show the chromatograms of permanent gases on the MoleSieve 5Å channel with helium and argon as carrier gas. At the tested concentration level (500 to 1,000 ppm), helium and hydrogen are easier to detect with argon as carrier gas.

Channel 2: A 10 m, CP-PoraPLOT U, backflush channel for CO_2, H_2S, ethane, and propane analysis.

Channel 3: A 6 m, CP-Sil 5CB, straight channel for analysis of propane to nonane.

Channels 2 and 3 of analyzer B extended are identical to the two channels used by analyzer B. For chromatograms, see Figures 7B, 3A, and 3B.

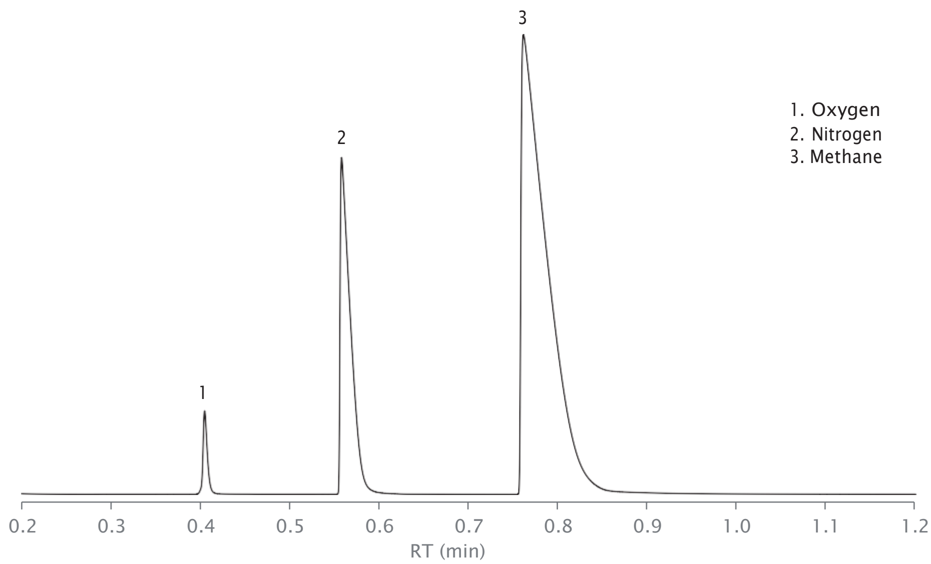

Figure 8A. Oxygen, nitrogen, and methane on CP-Molesieve 5 Å, backflush channel with helium as carrier gas.

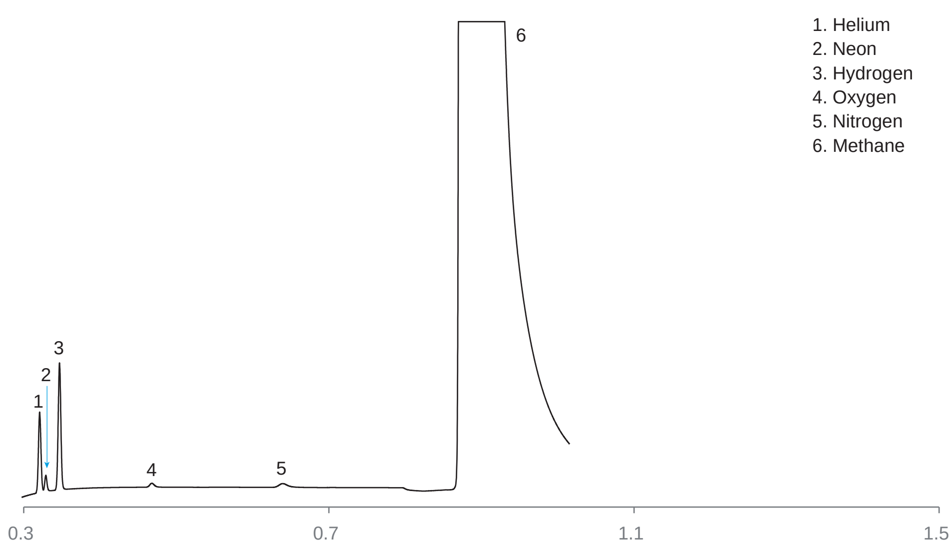

Figure 8B. Helium, neon, hydrogen, oxygen, nitrogen, and methane on the CP-Molesieve 5 Å, backflush channel with argon as carrier gas.

Analyzer RT and response repeatability

For correct qualification and accurate quantitation, instrument repeatability is important. Tables 4A and 4B show the instrument RT and response area repeatability for analyzer A, analyzer B, and B extended in 10 injections. For analyzer B and B extended, RSD% of RT and area are shown on the 10 m CP-PoraPLOT U and molecular sieve channel. The repeatability result of C_4 to C_9 hydrocarbons on the 6 m CP-Sil 5CB channel was the same as that on analyzer A channel 2, as shown in Table 4A. The RT repeatability in the three analyzers is below 0.1%, and area repeatability is in the range of 0.1 to 2%. Excellent repeatability performance were contributed by highly precise pneumatic and thermal control, and stable and sensitive TCD detection.

Table 4A. RT and area repeatability on analyzer A.

Compound	RT/min	RT RSD%	Area (mv × s)	Area RSD%
Nitrogen/oxygen	0.063	0.081	10.73	0.09
Methane	0.079	0.074	426.69	0.04
Carbon Dioxide	0.219	0.022	19.89	0.02
Ethane	0.366	0.014	4.12	0.05
Propane	0.203	0.004	6.685	0.02
Isobutane	0.238	0.002	0.787	0.03
Butane	0.264	0.003	0.813	0.03
2,2-Dimethyl-Propane	0.278	0.005	0.169	0.12
Isopentane	0.353	0.002	0.538	0.22
Pentane	0.396	0.002	0.555	0.11
2,2-Dimethyl-Butane	0.480	0.002	0.191	0.33
Hexane	0.679	0.003	0.106	1.0
Heptane	1.290	0.007	0.118	1.1
Octane	2.596	0.017	0.129	1.00
Nonane	5.382	0.002	0.137	1.90

Table 4B. RT and area repeatability on analyzer B/CP-PoraPLOT U channel and analyzer B extended/CP-Moleseive 5Å channel.

10m, CP-PoraPLOT U, Backflush				
Compound	RT (min)	RT RSD%	Area (mv × s)	Area RSD%
Nitrogen/oxygen	0.368	0.006	12.646	0.34
Methane	0.374	0.001	495.347	0.36
Carbon dioxide	0.414	0.006	23.826	0.37
Ethane	0.487	0.007	4.748	0.37
Propane	0.932	0.014	0.879	0.46
10m, CP-Molesieve 5Å, Backflush				
Compound	RT (min)	RT RSD%	Area (mv × s)	Area RSD%
Helium	0.308	0.006	1.28	0.04
Neon	0.316	0.006	0.231	0.22
Hydrogen	0.333	0.006	2.137	0.06

Physical properties calculation of natural gas

The economic value of natural gas is determined by several key physical properties, including calorific value, compressibility, Wobbe index, and so on. By following international standards, these properties were calculated from the concentration of each identified compound in natural gas and its specific physicochemical parameters. Agilent OpenLab CDS, OpenLab EZchrom, and OpenLab ChemStation are available choices of chromatography data systems for the NGA analyzer to collect data, and identify and quantitate NGA constituents. The quantitation results are fed to the EZReporter software (Figure 9) for calculation of the critical physical properties. EZReport 4.0 follows ASTM D3588, ASTM D2598, GPA 2172, GPA 2177, ISO 6976 and ISO 8973 for natural gas analysis related calculation. The calculation results are available for reporting, monitoring, trend plotting and exporting in EZReport.

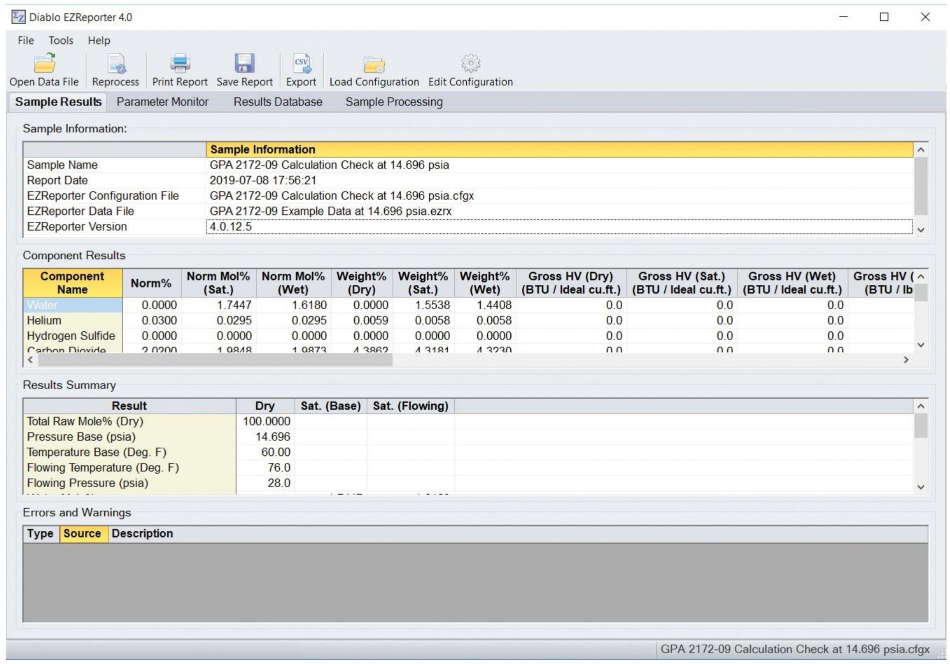

Figure 9. calculation based on GPA 2172-09 by Diablo EZReport 4.0.

Conclusion

This study demonstrates four types of NGA analyzers based on the 990 Micro GC platform. The configuration of each analyzer is determined by the composition of the target natural gas stream. NGA analyzer A resolves air, methane, carbon dioxide, and C_2 to C_6 hydrocarbons within two minutes. The analysis of heavier compounds, up to C_9, can be finished in approximately five minutes. To address the general analysis of natural gas with heavy hydrocarbons up to C_{12} at high speed, NGA analyzer A extended equipped with three channels is used. NGA analyzer B analyzes samples with similar composition as those analyzed by NGA analyzer A but with the additional capability of H_2S analysis. NGA analyzer B extended can address the analysis of permanent gases, H_2S, and other general constituents in natural gas (hydrocarbons up to C_9). The backflush options are used to protect the analytical column from heavier contaminants, and keep each run free from interference of the heavy compounds from the previous run.

Excellent instrument performance is observed in RT and area repeatability, which guarantees qualification and quantitation results with a high level of confidence.

The NGA analyzers can be used in-lab, online, at-line, and in field. They are fast, portable, and energy-efficient solutions for NGA analysis.

Reference

1. Fast Analysis of Natural Gas using the Agilent 490 Micro GC Natural Gas Analyzer, *Agilent Technologies Application Note*, publication number 5991-0275EN, 2011.

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