

# Natural Gas Analysis Using the Agilent 990 Micro GC Equipped with COX and 5CB Channels

## Author

Fang Yue  
Agilent Technologies, Inc.

## Abstract

This application note provides an optional configuration of the Agilent 990 Micro GC system for natural gas analysis, characterized by relatively comprehensive analysis at a low cost. Despite necessary compromises, H<sub>2</sub>, O<sub>2</sub>/N<sub>2</sub>, CO, CO<sub>2</sub>, and C<sub>1</sub> to C<sub>8</sub> alkanes can be analyzed simultaneously with only two channels, with excellent repeatability and a short analysis time (< 5 minutes). The repeatability of gross heating value is below 0.025%, which is a good benchmark in the current market.

## Introduction

Natural gas refers to a mixture of hydrocarbons and nonhydrocarbon gases that are naturally stored in geologic formations, among which hydrocarbons dominate. Natural gas is mainly used as a high-quality fuel, and is priced based on its calorific value in mainstream markets, which requires an accurate analysis of its composition. Usually, natural gas is composed of methane (> 80%), ethane, a small amount of propane, nitrogen, CO<sub>2</sub>, butane, pentane, and trace C<sub>6</sub> to C<sub>8</sub> alkanes. Components of C<sub>9</sub> and above have little effect on its calorific value due to their extremely low content. Recently, there is a new trend to add hydrogen into natural gas to reduce carbon emissions during combustion. Therefore, hydrogen analysis should also be taken into consideration.

The Agilent 990 Micro GC can provide fast and accurate gas analysis with low power and carrier gas consumption, making it an ideal tool for the online analysis of natural gas. In this application, two analytical channels of the 990 Micro GC were used, namely 1 m COX BF and 8 m 5CB. The application of the COX channel enables the simultaneous analysis of H<sub>2</sub>, O<sub>2</sub>/N<sub>2</sub>, CH<sub>4</sub>, CO, and CO<sub>2</sub>, with excellent stability for moisture-containing samples. It takes only five minutes to analyze natural gas (H<sub>2</sub>, O<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub>, C<sub>1</sub> to C<sub>8</sub> alkanes) in one injection, with excellent repeatability for multiple analyses.

## Experimental

The 990 Micro GC system is equipped with a 1 m COX backflush channel, and an 8 m 5CB straight channel. Table 1 shows the experimental conditions. The 1 m COX backflush channel is used to

analyze H<sub>2</sub>, O<sub>2</sub>/N<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub>, and the 8 m 5CB straight channel is used to analyze C<sub>2</sub> to C<sub>8</sub> alkanes. Standard gas was purchased from Air Liquide. Table 2 shows the standard gas components.

**Table 1.** Test conditions for natural gas.

Channel Type	1 m COX, Backflush	8 m 5CB, Straight
Carrier Gas	Argon	Helium
Column Pressure	200 kPa	150 kPa
Injector Temperature	100 °C	100 °C
Column Temperature	65 °C	75 °C
Injection Time	40 ms	40 ms
Backflush Time	4.0 s	NA
Sample Time	30 s	30 s

**Table 2.** Composition of the standard gas.

Standard Gas 1		Standard Gas 2		Standard Gas 3	
Component	Concentration	Component	Concentration	Component	Concentration
H <sub>2</sub>	58.45%	CH <sub>4</sub>	89.04%	H <sub>2</sub>	12.00%
N <sub>2</sub>	2.36%	N <sub>2</sub>	2.04%	N <sub>2</sub>	63.50%
CO	6.17%	CO <sub>2</sub>	2.04%	CO	1.01%
CO <sub>2</sub>	4.97%	C <sub>2</sub> H <sub>6</sub>	2.04%	CO <sub>2</sub>	3.01%
CH <sub>4</sub>	14.10%	C <sub>3</sub> H <sub>8</sub>	2.02%	CH <sub>4</sub>	5.06%
C <sub>2</sub> H <sub>6</sub>	4.04%	n-C <sub>4</sub> H <sub>10</sub>	1.01%	C <sub>2</sub> H <sub>6</sub>	4.06%
C <sub>2</sub> H <sub>4</sub>	3.07%	i-C <sub>4</sub> H <sub>10</sub>	1.01%	C <sub>2</sub> H <sub>4</sub>	2.02%
C <sub>3</sub> H <sub>8</sub>	1.04%	neo-C <sub>5</sub> H <sub>12</sub>	0.20%	C <sub>2</sub> H <sub>2</sub>	1.04%
C <sub>3</sub> H <sub>6</sub>	2.05%	i-C <sub>5</sub> H <sub>12</sub>	0.19%	C <sub>3</sub> H <sub>8</sub>	2.01%
n-C <sub>4</sub> H <sub>10</sub>	1.04%	n-C <sub>5</sub> H <sub>12</sub>	0.20%	C <sub>3</sub> H <sub>6</sub>	1.03%
1-Butene	1.63%	n-Hexane	0.21%	Allene	1.00%
n-Pentane	0.22%			Propyne	1.00%
1-Pentene	0.41%			i-C <sub>4</sub> H <sub>10</sub>	0.31%
n-Hexane	0.12%			n-C <sub>4</sub> H <sub>10</sub>	0.30%
1-Hexene	0.24%			1-Butene	0.30%
n-Heptane	0.03%			i-Butene	0.30%
1-Heptene	0.03%			cis-Butene	0.30%
n-Octane	0.02%			trans-Butene	0.30%
1-Octene	0.02%			1,3-Butadiene	0.30%
				i-Pentane	0.10%
				n-Pentane	0.10%
				1-Pentene	0.10%
				cis-2-Pentene	0.10%
				trans-2-Pentene	0.10%
				2-Methyl-2-butene	0.57%
				n-Hexane	251 ppm
				O <sub>2</sub>	796 ppm

## Results and discussion

The configuration of two channels realized the analysis of  $H_2$ ,  $O_2/N_2$ , CO,  $CO_2$ , and  $C_1$  to  $C_8$  alkanes simultaneously. This system is a lower-cost alternative compared to an NGA analyzer A/B extended (three analytical channels), but some compromises are necessary. Without the PPU channel,  $H_2S$  and COS cannot be analyzed, nor can the unsaturated hydrocarbons of  $C_2$ . Meanwhile, due to the need to analyze  $H_2$  with a content exceeding 1%, helium cannot serve as the carrier gas because of the abnormal thermal conductivity of the  $H_2/He$  mixture. Accurately measuring  $O_2/N_2$  prevents the use of  $N_2$  as the carrier gas, leaving argon as the final choice for the carrier gas. As a result, the sensitivity of  $CO_2$  analysis significantly decreased ( $LDL < 0.1\%$ ). Figure 1A shows the chromatogram of standard gas 1 on the 1 m COX backflush channel.  $H_2$ ,  $N_2$ , CO,  $CH_4$ , and  $CO_2$  were well resolved. To obtain the actual performance on COX for natural gas analysis, a simulated natural gas sample (standard gas 2) was also analyzed and is shown in Figure 1B.

Figure 2A shows the chromatogram of simulated natural gas (standard gas 2) on the 8 m 5CB straight channel.  $C_2$  to  $C_6$  alkanes separate excellently, with n-hexane ( $n-C_6$ ) eluting within 1.5 minutes. For heavier alkanes, as shown in Figure 2B,  $n-C_7$  and  $n-C_8$  still separate well, with a good peak shape on this channel. The maximum analysis time of one injection does not exceed five minutes.

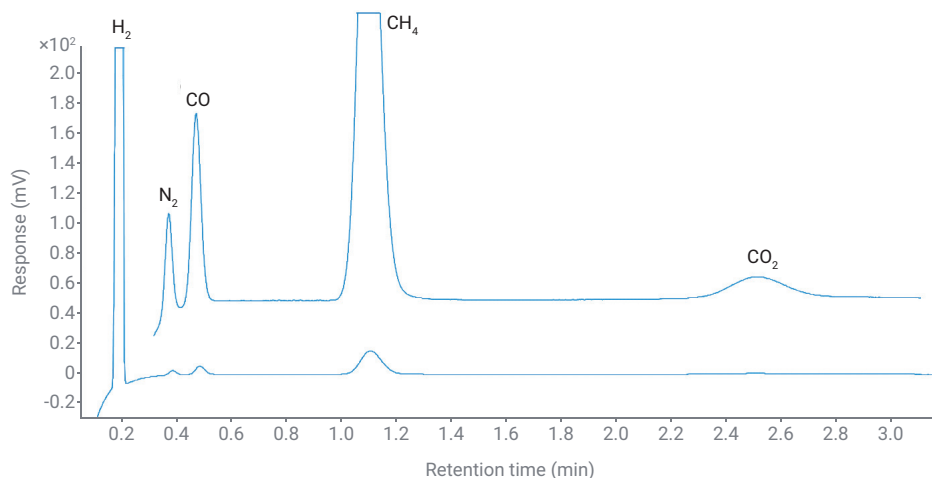


Figure 1A. Chromatogram of standard gas 1 on the 1 m COX backflush channel.

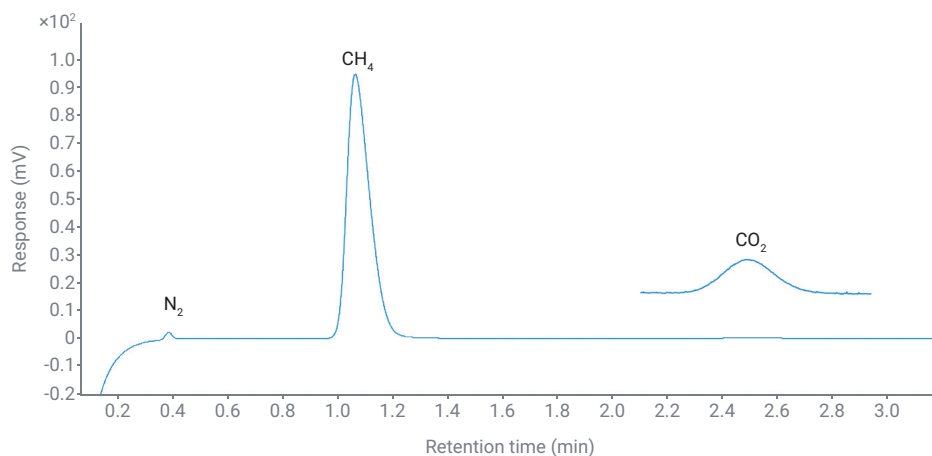


Figure 1B. Chromatogram of standard gas 2 on the 1 m COX backflush channel.

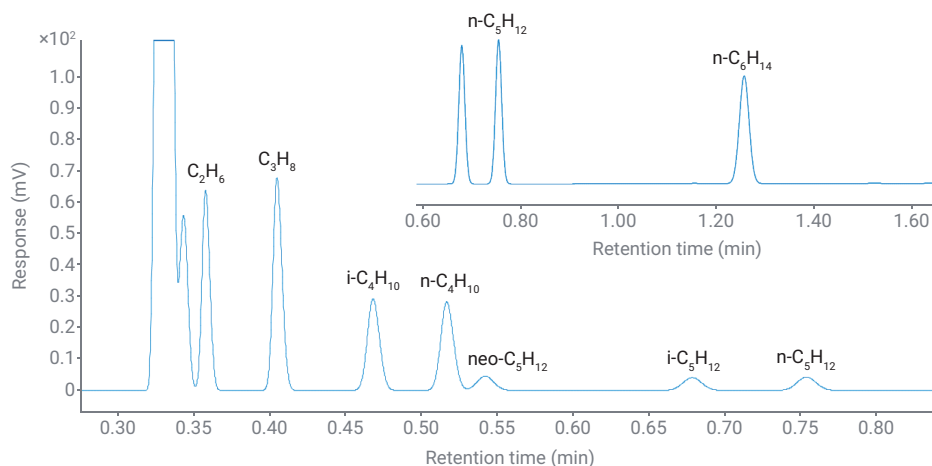
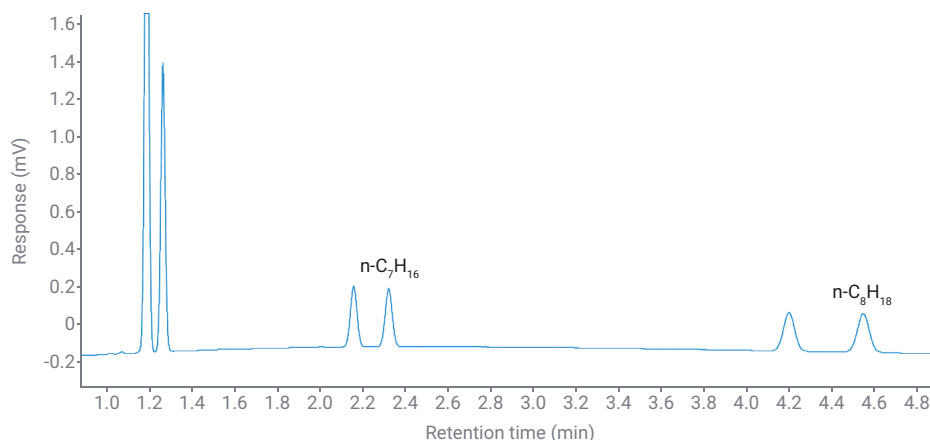


Figure 2A. Chromatogram of standard gas 2 on the 8 m 5CB straight channel.

Table 3 shows the chemical performance of a sequence of 10 sample runs. Note that standard gas 3 was used for the evaluation of the H<sub>2</sub> component on this configuration to ensure that the tested H<sub>2</sub> content is close to that which is added to natural gas. The area %RSD is below 0.5%, except for CO<sub>2</sub> (< 1%), and RT %RSD is below 0.02%, except for CO<sub>2</sub> (< 0.5%), which demonstrates the excellent performance of the 990 Micro GC and provides qualitative results with a high level of confidence.

Table 4 shows the calculated gross heating value (HV) of 10 runs based on standard gas 2. The repeatability is below 0.025%, which is a good benchmark in the current market.



**Figure 2B.** Chromatogram of standard gas 2 on the 8 m 5CB straight channel.

**Table 3.** Retention time, area, and their corresponding repeatability of 10 runs of the standard gas.

Component	Concentration (%)	RT (min)	RT RSD (%)	Area (mV × s)	Area RSD (%)	Analysis Channel
H <sub>2</sub>	12.0	0.191	0.000	270.589	0.0471	1 m COX BF
N <sub>2</sub>	2.04	0.388	0.0143	5.085	0.2843	1 m COX BF
CH <sub>4</sub>	89.04	1.065	0.012	551.620	0.0135	1 m COX BF
CO <sub>2</sub>	2.04	2.500	0.3045	3.446	0.9422	1 m COX BF
C <sub>2</sub> H <sub>6</sub>	2.04	0.359	0.0021	23.686	0.0361	8 m 5CB
C <sub>3</sub> H <sub>8</sub>	2.02	0.406	0.0018	29.116	0.0432	8 m 5CB
i-C <sub>4</sub> H <sub>10</sub>	1.01	0.469	0.002	16.801	0.0366	8 m 5CB
n-C <sub>4</sub> H <sub>10</sub>	1.01	0.518	0.0018	17.129	0.0382	8 m 5CB
neo-C <sub>5</sub> H <sub>12</sub>	0.197	0.543	0.0018	3.640	0.0338	8 m 5CB
i-C <sub>5</sub> H <sub>12</sub>	0.194	0.679	0.0022	3.712	0.0419	8 m 5CB
n-C <sub>5</sub> H <sub>12</sub>	0.199	0.754	0.0025	3.891	0.0352	8 m 5CB
n-Hexane	0.207	1.255	0.0037	4.578	0.0413	8 m 5CB
n-Heptane	0.029	2.316	0.0061	0.735	0.1804	8 m 5CB
n-Octane	0.021	4.545	0.0092	0.829	0.3618	8 m 5CB

**Table 4.** Gross heating value and repeatability based on standard gas 2.

Run No.	Heating Value (kJ/mol)
1	957.89
2	958.17
3	957.86
4	957.96
5	957.74
6	957.41
7	957.82
8	957.82
9	958.02
10	957.80
Average	957.85
RSD (%)	0.021

Table 5 shows the estimated lower detection limits (LDL) of 1 m COX BF and 8 m 5CB, which were obtained under the same experimental conditions described in Table 1. As expected, the sensitivity of CO<sub>2</sub> significantly decreased. The LDL is still lower than 0.1%, which means it can still effectively analyze natural gas components.

**Table 5.** Lower detection limit (LDL) of this configuration.

Component	LDL (ppm)	Analysis Channel
H <sub>2</sub>	20	1 m COX BF
O <sub>2</sub> /N <sub>2</sub>	200	1 m COX BF
CO	200	1 m COX BF
CH <sub>4</sub>	150	1 m COX BF
CO <sub>2</sub>	1,000	1 m COX BF
C <sub>2</sub> H <sub>6</sub>	1	8 m 5CB
C <sub>3</sub> H <sub>8</sub>	1	8 m 5CB
i-C <sub>4</sub> H <sub>10</sub>	1	8 m 5CB
n-C <sub>4</sub> H <sub>10</sub>	1	8 m 5CB
neo-C <sub>5</sub> H <sub>12</sub>	1	8 m 5CB
i-C <sub>5</sub> H <sub>12</sub>	1	8 m 5CB
n-C <sub>5</sub> H <sub>12</sub>	1	8 m 5CB
n-Hexane	1	8 m 5CB
n-Heptane	1	8 m 5CB
n-Octane	1	8 m 5CB

## Conclusion

This application note demonstrates the chemical performance of the Agilent 990 Micro GC system for the analysis of natural gas. This two-channel configuration can analyze H<sub>2</sub>, O<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub>, and C<sub>1</sub> to C<sub>8</sub> alkanes simultaneously, with excellent repeatability and a short analysis time (< 5 minutes) at a low cost. The 990 Micro GC is well-suited for the fast and precise analysis of natural gas, and can provide customers with diversified configurations according to their needs.

## References

1. Permanent Gases on a COX Module Using an Agilent 490 Micro GC. *Agilent Technologies application note*, publication number 5990-7054EN, **2012**.
2. Hydrogen Detection with a TCD using Mixed Carrier Gas on the Agilent Micro GC. *Agilent Technologies application note*, publication number 5991-3199EN, **2013**.
3. Fast Analysis of Natural Gas using the Agilent 990 Micro GC Natural Gas Analyzer. *Agilent Technologies application note*, publication number 5994-1040EN, **2019**.
4. Biogas Analyzer Based on the Agilent 990 Micro GC. *Agilent Technologies application note*, publication number 5994-1376EN, **2019**.