Application Note

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Methanol Analysis in Natural Gas Using an Agilent 990 Micro GC Equipped with the MES (TCEP) Channel

Authors

Fang Yue
Agilent Technologies
(Shanghai) Co. Ltd.

Mou Zongxuan
Xi`an Tiger Electric Technology
Co. Ltd., China

Abstract

This application note presents a method for the analysis of methanol (MeOH) in natural gas on the Agilent 990 Micro GC system. MeOH and its neighboring C_{11} and C_{12} *n*-alkanes on the MES column can be analyzed on a 15 m MES (TCEP) channel with excellent repeatability and a short analytical cycle time (less than three minutes). The lower detection limit (LDL) of MeOH can be as low as 1.4 ppm with a good linear response around it.

Introduction

Natural gas is an important resource that can be used as high-quality, low-pollution fuel and as a carbon source for synthesizing other chemicals. Natural gas usually does not contain MeOH, but MeOH may be introduced during natural gas extraction (or synthesis), purification, and transportation processes. During the natural gas liquefaction process, low temperatures will cause residual MeOH to solidify, blocking valves and pipelines, which endangers production and transportation safety. Therefore, it is necessary to monitor MeOH content in natural gas to ensure the effectiveness of MeOH removal steps prior to liquefaction.

The 990 Micro GC system can provide fast and accurate gas analysis with low power and carrier gas consumption, making it an ideal tool for the online analysis of residual MeOH in natural gas.[1] In this application note, MeOH analysis was performed using the 990 Micro GC system equipped with a MES (TCEP) analytical channel. The MES column enables the rapid analysis of MeOH and its neighboring C_{11} and C_{12} *n*-alkanes. Each run takes less than three minutes to complete, with excellent repeatability for multiple analyses.

Experimental

The 990 Micro GC system was equipped with a 15 m MES (TCEP) straight channel, which is used to analyze MeOH as well as C_{11} and C_{12} *n*-alkanes. Table 1 shows the experimental conditions for this analysis. A standard gas was purchased from Air Liquide, Inc. Using a pressure gauge for partial pressure control, the standard gas was diluted by pure methane in another sample gas cylinder. Table 2 shows the composition of the standard gas and the three corresponding dilutions of this gas (calculated).

Table 1. Experimental conditions for MeOH analysis using the Agilent 990 Micro GC system.

Parameter	Value
Channel Type	15 m MES (TCEP), Straight
Carrier Gas	Helium
Column Pressure	200 kPa
Injector Temperature	110 °C
Column Temperature	65 °C
Injection Time	40 ms
Sample Time	30 s

Table 2. Composition of the standard gas and diluted gases.

Component	Standard Gas Concentration	Diluted Gas 1 Concentration Calculated	Diluted Gas 2 Concentration Calculated	Diluted Gas 3 Concentration Calculated
CH_4	Balance	Balance	Balance	Balance
MeOH	11.1 ppm	9.1 ppm	6.0 ppm	3.2 ppm
n-C_{11}	11.8 ppm	9.7 ppm	6.4 ppm	3.4 ppm
n-C_{12}	11.7 ppm	9.6 ppm	6.3 ppm	3.4 ppm

Results and discussion

Natural gas has an extremely low concentration of hydrocarbons with carbon number greater than 10.[2] Therefore, if the analyte elutes after C_{10}, its analysis will be almost unaffected by the interference of hydrocarbons, helping to lower the detection limit. The MES (TCEP) column, with its high polarity, enables the polar MeOH to elute after *n*-C_{11}, making it an ideal column type for this application.[3] The chromatogram of the standard gas shows that *n*-C_{11}, MeOH, and *n*-C_{12} are well-resolved using this column (Figure 1). The maximum analytical cycle time of one injection did not exceed three minutes.

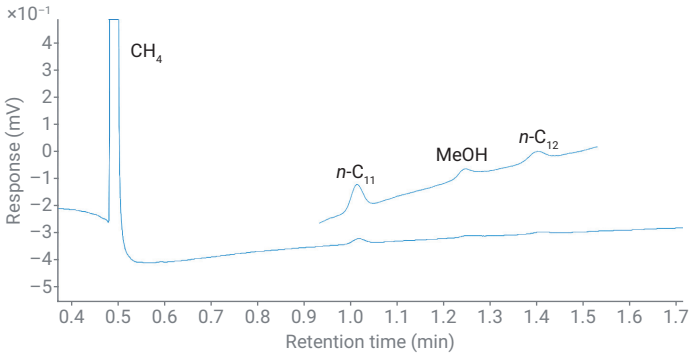

Figure 1. Chromatogram of the standard gas on the 15 m MES (TCEP) straight channel.

Table 3 shows the chemical performance for a sequence of 10 runs of the standard gas. The relative standard deviations (%RSDs) of retention time (RT) and peak area for these components are less than 0.2% and 5%, respectively. These low %RSD values demonstrate the excellent performance of the 990 Micro GC system and its ability to provide quantitative results with a high level of confidence and quality.

Table 3. RT, area, and repeatability (%RSD) for 10 runs of the standard gas.

Component	Concentration (ppm)	RT (min)	RT RSD (%)	Area (mV × s)	Area RSD (%)
n-C_{11}	11.8	1.017	0.0396	0.0357	2.997
MeOH	11.1	1.254	0.1056	0.0163	2.961
n-C_{12}	11.7	1.411	0.1243	0.0170	4.937

The chromatogram of diluted gases 1 to 3 shows that, as the concentrations of *n*-C_{11}, *n*-C_{12}, and MeOH decrease, their peak areas also decrease (Figure 2). However, even at a MeOH concentration of only 3.2 ppm, detection still occurs. For low MeOH concentrations (3.2 to 11.1 ppm), the response factor (RF) of MeOH remains relatively unchanged (RF RSD of 2.41%), demonstrating a good linear response to different MeOH concentrations (Table 4). The LDL of MeOH on the MES (TCEP) channel was calculated to be 1.4 ppm at two times the signal-to-noise ratio (S/N), fully meeting the analysis requirements.

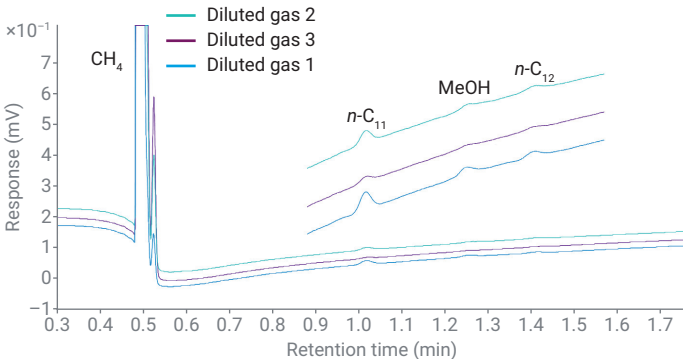

Figure 2. Chromatogram of diluted gases 1 (MeOH 9.1 ppm), 2 (MeOH 6.0 ppm), and 3 (MeOH 3.2 ppm) on the 15 m MES (TCEP) straight channel.

The chromatogram in Figure 3, obtained by the 990 Micro GC PROstation software, shows the analysis of an actual natural gas sample from our customers on the 15 m MES (TCEP) straight channel. No MeOH was observed in the customer sample.

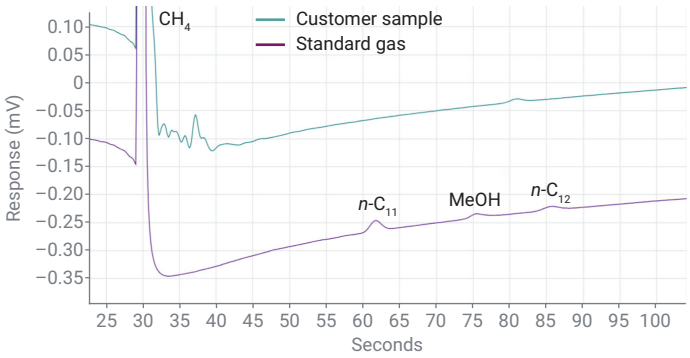

Figure 3. Chromatogram of an actual natural gas sample from customers analyzed on the 15 m MES (TCEP) straight channel.

Table 4. RFs of MeOH at different concentrations and the RF repeatability (%RSD).

MeOH Concentration	Area (mV × s)	RF (mV × s/1)	RF RSD (%)
3.2 ppm	0.0049	1,531.3	2.41
6.0 ppm	0.0088	1,466.7	
9.1 ppm	0.0132	1,450.5	
11.1 ppm	0.0163	1,468.5	

Conclusion

This application note demonstrates the chemical performance of the Agilent 990 Micro GC system for the analysis of methanol (MeOH) in natural gas. The MES (TCEP) channel on the 990 Micro GC system can analyze MeOH and its neighboring *n*-alkanes with excellent repeatability, short analytical cycle time, sufficiently low detection limit, and good linear response. Thus, the 990 Micro GC system is well-suited for the fast and precise monitoring of trace MeOH in natural gas.

References

1. Bajja, M.; van Loon, R. Analysis of Acetone, MeOH, and Ethanol in Air Using the Agilent 490 Micro GC, *Agilent Technologies application note*, publication number 5990-9105EN, **2011**.
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