Application Note

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Analysis of Non-Sulfur Natural Gas Odorants Using the Agilent 990 Micro GC System

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Abstract

In this application note, two non-sulfur odorants, methyl acrylate and ethyl acrylate, were analyzed on the CP-TCEP MES channel of the Agilent 990 Micro GC system. The limit of detection (LOD) and quantitation precision were evaluated using a 11 ppm gas standard. The LOD for methyl acrylate and ethyl acrylate was 1.1 ppm and 1.5 ppm, respectively. For 20 consecutive injections, the response precision was better than 5%, and the retention time (RT) precision was less than 0.1%. Methyl acrylate and ethyl acrylate eluted within 2.2 minutes on the selected analytical channel. These results demonstrate that the 990 Micro GC system can provide a fast and reliable analysis of the sulfur-free odorants in natural gas.

Introduction

To ensure the safe use of natural gas in daily life, odorants are required to be added as an indication of gas leakage. Sulfur-containing compounds such as tetrahydrothiophene (THT) and tert-butyl mercaptan (TBM) are commonly used odorants. These compounds are stable, and at the added concentration, if leakage occurs, they can easily be detected by a person with an average sense of smell. However, over time, THT and TBM will react with the natural gas transport pipeline and the seal elastomer. This reaction will not only increase the risk for leakage but will also consume more odorants and increase costs. Furthermore, THT and TBM will emit sulfur dioxide (SO_2) or sulfide trioxide (SO_3) after combustion. To mitigate the risk for leakage caused by pipe material and elastomer corrosion as well as reduce the environmental effects of SO_2 and SO_3, investigations into alternative non-sulfur odorants have been done.

Methyl acrylate and ethyl acrylate are the world's first commercially available sulfur-free natural gas odorants. Their combined quantity of 8.0 mg/m^3 (approximately 2 ppm) can be detected by individuals with an average sense of smell. These compounds have passed testing related to interactions with pipe materials and elastomers and are compliant with DIN EN ISO 13734 requirements.[1] Both methyl acrylate and ethyl acrylate are suitable for application in natural gas odorization systems. In previous work, the 990 Micro GC system was shown to accurately detect various sulfur odorants in natural gas.[2] Here, its capability of measuring sulfur-free odorants is presented.

Experimental

The 990 Micro GC system was equipped with a 15 m Agilent CP-TCEP MES channel for methyl acrylate and ethyl acrylate analysis. Two gas standards were purchased from Air Liquide Inc., a simulated natural gas sample (gas standard 1) containing approximately 11 ppm methyl acrylate and 11 ppm ethyl acrylate and a second gas standard (gas standard 2) containing approximately 11 ppm *n*-undecane (*n*-C11) and 11 ppm *n*-dodecane (*n*-C12) in methane. The experimental conditions and gas standard information are shown in Table 1 and Table 2.

Table 1. Test conditions for methyl-/ethyl acrylate analysis on the Agilent 990 Micro GC system.

Parameter	Value
Channel Type	15 m CP-TCEP MES Channel, straight
Carrier Gas	Helium
Column Pressure	200 kPa
Injector Temperature	80 °C
Column Temperature	60 °C
Injection Time	40 ms/150 ms

Table 2. Gas standard information.

Gas Standard 1		Gas Standard 2	
Component	Concentration (ppm)	Component	Concentration (ppm)
N_2	2.0×10^4	*n*-C11	11.8
CO_2	2.0×10^4	*n*-C12	11.7
C_2H_6	2.0×10^4	Methanol	11.1
C_3H_8	1.0×10^4	CH_4	Balance
i-C_4H_8	1,000		
n-C_4H_{10}	1,000		
Neo-pentane	200		
Iso-pentane	200		
n-pentane	200		
n-hexane	200		
Methyl acrylate	11.4		
Ethyl acrylate	11.9		
CH_4	Balance		

Results and discussion

Methyl acrylate and ethyl acrylate are the methyl ester and ethyl ester of acrylic acid, respectively. Both are polar compounds. The CP-TCEP MES channel was selected to resolve polar esters from nonpolar hydrocarbons in natural gas, especially from the interference of heavy hydrocarbons such as C10 and C10+ hydrocarbons (not heavier than *n*-C12). This channel is configured with a high polar column with 1,2,3-tri (2-cyanoethoxy) propane (TCEP) stationary phase. As shown in Figure 1, at the applied column temperature and head pressure, methyl acrylate and ethyl acrylate elute in approximately 2 minutes. *n*-Hexane elutes early, close to the balance gas peak on this high polar column. Other light components coelute with methane.

Gas standard 2 was analyzed to show that the hydrocarbons in the natural gas matrix will not interfere with the identification of methyl- and ethyl acrylates. As shown in Figure 2, *n*-C11 and *n*-C12 elute within 1.7 minutes. Their elution is later than the other light hydrocarbons but earlier than the two odorants, which means that the selected column can resolve the two odorants from the natural gas matrix.

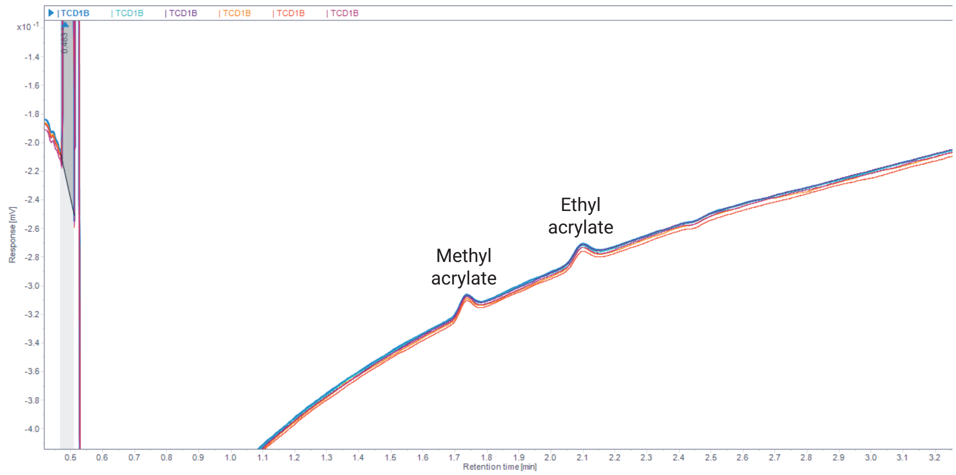

Figure 1. Chromatogram overlay of six injections for gas standard 1.

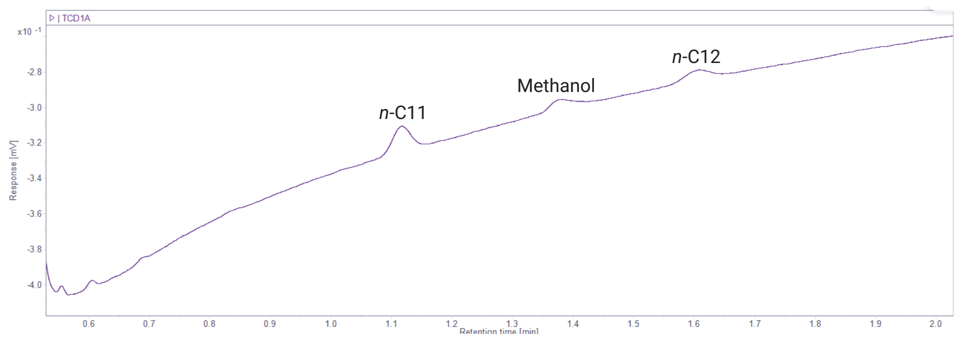

Figure 2. Chromatogram of gas standard 2 showing that *n*-C11 and *n*-C12 elute before the two sulfur-free components. These data indicate that there is no interference from *n*-C11 and *n*-C12 on methyl acrylate and ethyl acrylate identification.

The analytical precision was evaluated based on 20 consecutive injections of gas standard 1. Results were satisfactory considering that the test concentration was at a low ppm level. As shown in Table 3, the RT and area relative standard deviations (%RSDs) are less than 0.1% and 5.1%, respectively.

The LODs for the two components were calculated using the following formula:

$LOD = t \times \%RSD \times C_{compound}$

where t is the single-tailed critical value for 99% confidence for 20 replicate injections; here t = 2.539.

$C_{compound}$ is the analyte nominal concentration.

%RSD is the relative standard deviation of measured concentration.

The calculated LOD was 1.1 ppm for methyl acrylate and 1.5 ppm for ethyl acrylate. As shown in Figure 3, increasing the injection time from 40 ms to 150 ms increases the peak height of the two analytes by approximately 3x, with no notable increase in baseline noise. Thus, a long injection time such as 150 ms can be used for analysis if the added odorant amount is close to the minimum concentration (8 mg/m^3, approximately 2 ppm).

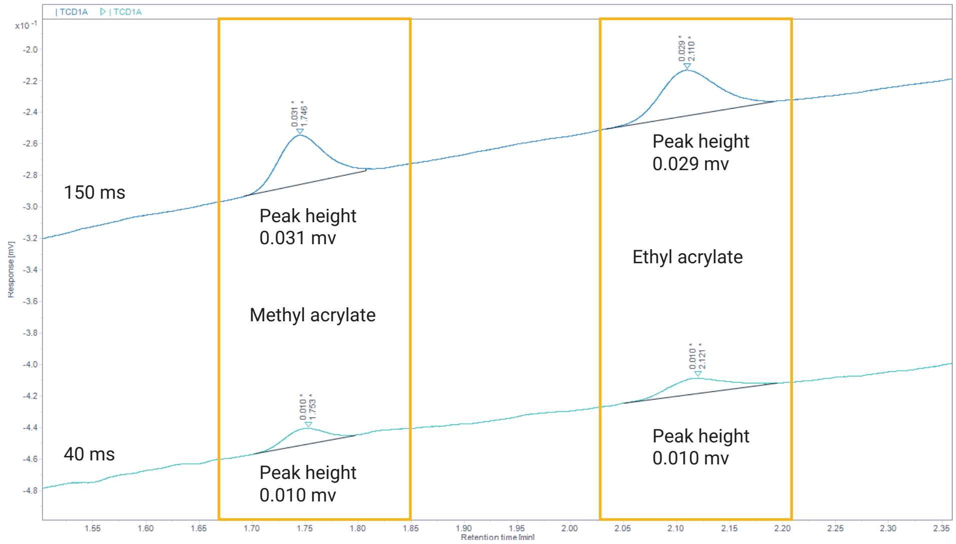

Figure 3. Peak height improvement using 150 ms injection time compared to 40 ms injection time.

A collaborator used the 990 Micro GC system and the CP-TCEP MES channel to test residential-use natural gas with methyl- and ethyl acrylate odorants added. A calibration gas standard containing 5.2 ppm methyl acrylate and 5.4 ppm ethyl acrylate was used, and the same experimental conditions described in the Experimental section were applied (Table 1). Both methyl- and ethyl acrylate eluted within 2 minutes from the standard on this TCEP channel (Figure 4).

At the collaborator site, the area precision of odorants at 5 ppm was 7.1% for methyl acrylate and 3.6% for ethyl acrylate (n = 4). In the real natural gas sample, the two target compounds were detected at 3.5 ppm (methyl acrylate) and 4.3 ppm (ethyl acrylate) based on the single-point external standard (ESTD) method. This corresponds to a total odorant concentration of 30 mg/m^3. The chromatogram for this real natural gas sample is shown in Figure 5.

Table 3. The RT and response results of methyl acrylate and ethyl acrylate in gas standard 1.

Component	Concentration (ppm)	RT (min)	RT RSD (%)	Area (mV × s)	Area RSD (%)	LOD (ppm)	Analytical Channel
Methyl acrylate	11.4	1.738	0.044	0.030	3.826	1.1	CP-TCEP MES
Ethyl acrylate	11.9	2.101	0.078	0.033	5.078	1.5	CP-TCEP MES

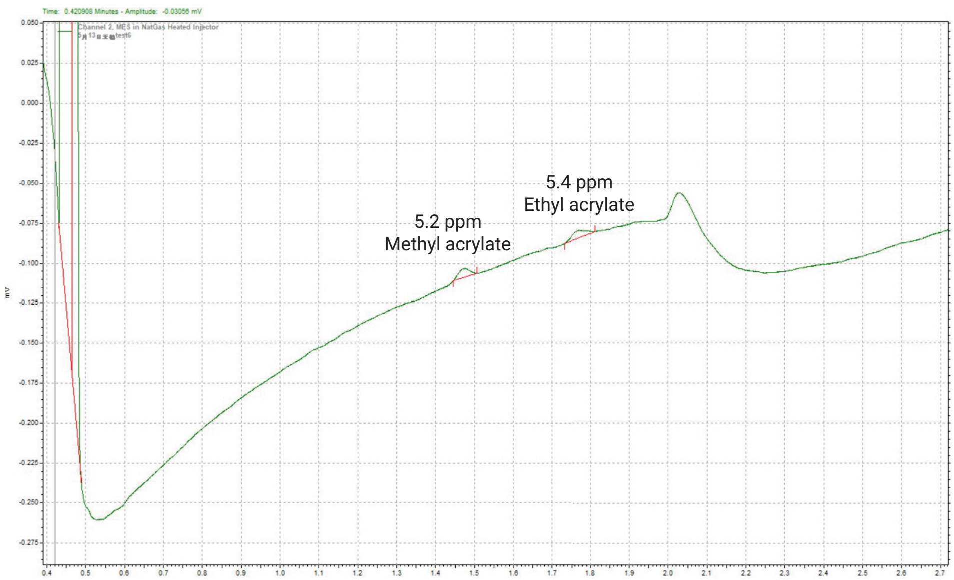

Figure 4. Chromatogram of the collaborator's gas calibration standard on their TCEP channel.

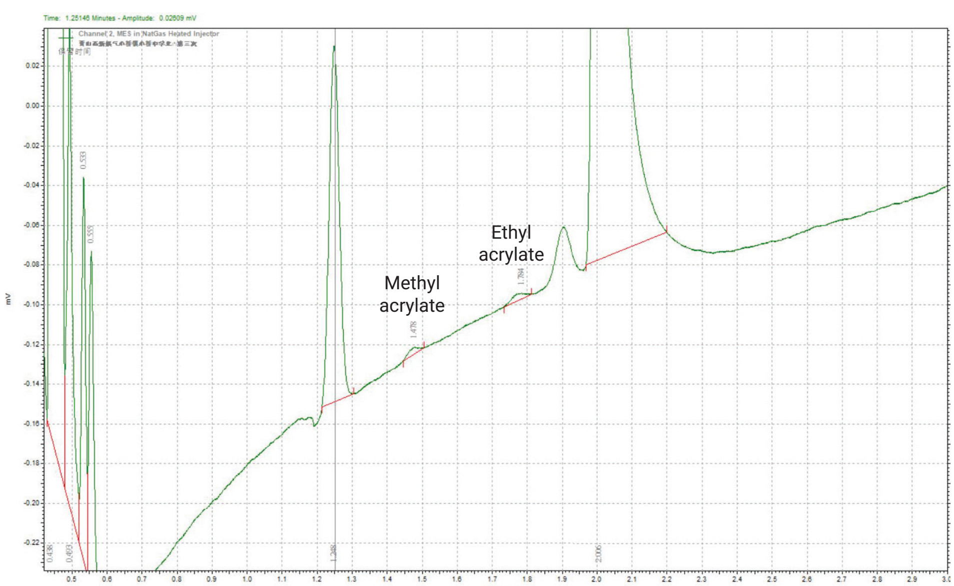

Figure 5. Chromatogram of methyl acrylate and ethyl acrylate detected in a real natural gas sample.

Conclusion

Using the Agilent 990 Micro GC system, methyl acrylate and ethyl acrylate can be separated effectively from hydrocarbon components in natural gas and detected at low ppm concentration levels. The retention time and area precision generated on the CP-TCEP MES channel in 20 consecutive injections demonstrated good system quantitation repeatability and accuracy. The application of this analytical channel to sulfur-free odorant analysis in a real natural gas sample resulted in the detection of methyl- and ethyl acrylate at a combined concentration of approximately 8 ppm. These results show that the 990 Micro GC can provide an effective measurement of non-sulfur odorants in residential-use natural gas.

References

1. Schmeer, F.; Reimert, R.; Kaesler, H.; Henke, F.; Mansfeld, G. Development of a Sulphur-Free Odorant. Presented at the 22nd World Gas Conference, Tokyo, **2003**.
2. Zhang, J. Analysis of Tetrahydrothiophene (THT) in Natural Gas Using the Agilent 990 Micro GC; *Agilent Technologies application note*, publication number 5994-1042EN, **2019**.

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