

Micro GC Fusion® Analysis of Odorants in Natural Gas

Introduction

Sulfur-containing odorants are added to natural gas to allow leaks to be detectable by humans through smell. Numerous factors, including adsorption and oxidation, can cause the odor to fade, which diminishes the smell of the odorant. Ensuring that there is enough odorant present to smell a leak is critical. Common odorants include dimethyl sulfide (DMS), tert-butyl mercaptan (TBM) and thiophene (THT) and are often added so that the concentrations in the gas are at the single-digit ppm level. The type of odorants added and the concentrations levels vary by country, geography, and gas utility company.

Micro GC Fusion is a small, easily transportable gas chromatograph (GC) that allows analysis to be completed directly in the field or in a stationary location. This ensures sample integrity and provides fast, reliable analysis.

Using a single 16 m CP-Sil13CB module, Micro GC Fusion can analyze low ppm levels of DMS, TBM, and THT, within minutes.

If THT is the only odorant being tested, a 4 m CP-Sil19CB module is used to analyze THT in less than a minute.

Either of these modules can be used in combination with a 12 m Q-Bond module and a 10 m Rxi-1ms module to provide a complete analysis of gas quality, with BTU calculations, if desired.

Experimental

An odorant calibration gas was analyzed on Micro GC Fusion using a 16 m CP-Sil13CB column with a large, variable-volume injector and a thermal conductivity detector (TCD). A dilution, using a gas-tight syringe, was conducted to establish a low-level analysis of the odorants. Micro GC Fusion was then connected to a natural gas pipeline to measure odorants directly in a sample.

A separate experiment was conducted using a 4 m CP-Sil19CB column with a large variable-volume injector to analyze THT only. The short length of the column ensures that this analysis is completed quickly.

Calibration gas information is found in the table below.

Component	Odorant calibration gas for 16 m CP-Sil13CB	Odorant calibration gas for 4 m CP-Sil19CB
	Concentration	Concentration
Methyl mercaptan (MM)	3.6 ppm	N/A
Ethyl mercaptan (EM)	3.6 ppm	N/A
DMS	3.5 ppm	N/A
TBM	3.8 ppm	N/A
THT	3.2 ppm	4.1 ppm
Methane	Balance	N/A
Natural gas	N/A	Balance

Method parameters are found in the table below.

Parameter	16 m CP-Sil13CB	4 m CP-Sil19CB
Injection time	300 ms	250 ms
Injector temperature	70°C	70°C
Enhanced injection	On	On
Enhanced injection pressure	40 psi	40 psi
TCD heater	60°C	70°C
TCD delta	5°C	2°C
Column pressure	35 psi	16 psi
Data rate	25 Hz	25 Hz
Column temperature profile and ramp rate	53°C (92s) – 130°C (50s), 1.5°C/s	70°C (120s)
Sample pump time	15 s	40 s
Sample inlet temperature	90°C	90°C

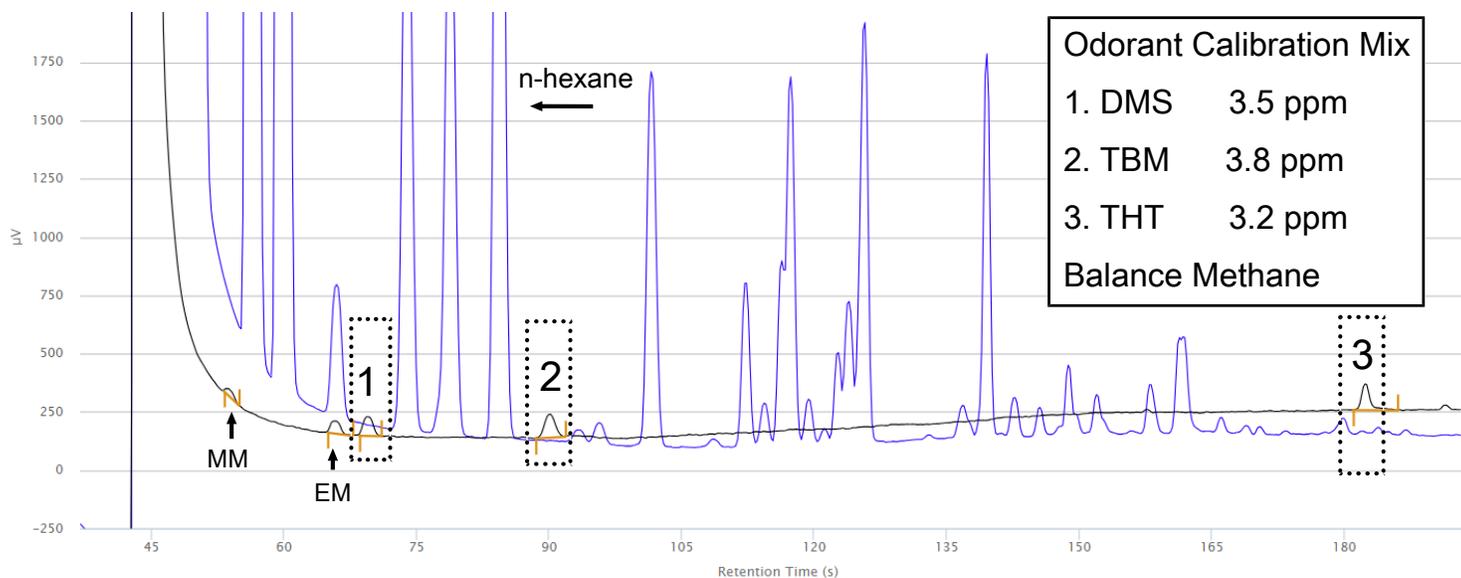
For DMS and TBM analysis without THT on the 16 m column, the method can be run isothermally at 53°C for 100 s.

Results

16 m CP-Sil13CB

Chromatograms were obtained for the analysis of DMS, TBM and THT on the 16 m CP-Sil13CB module. An odorant calibration mix was analyzed, followed by a natural gas calibration mix, containing hexane plus components, to prove that there was odorant separation from the neighboring hydrocarbons.

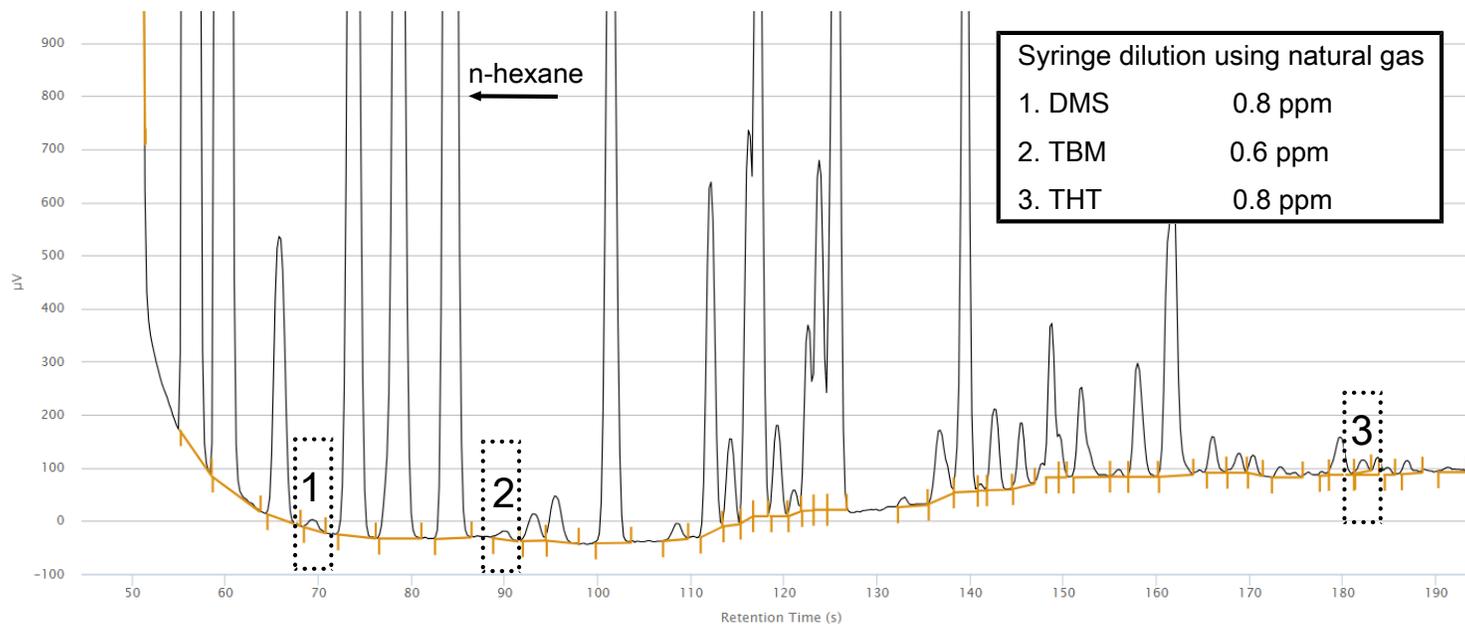
DMS, TBM, and THT were fully separated from neighboring hydrocarbon isomers within four min. Methyl mercaptan and ethyl mercaptan were also present; however, ethyl mercaptan co-elutes with a C6 isomer.



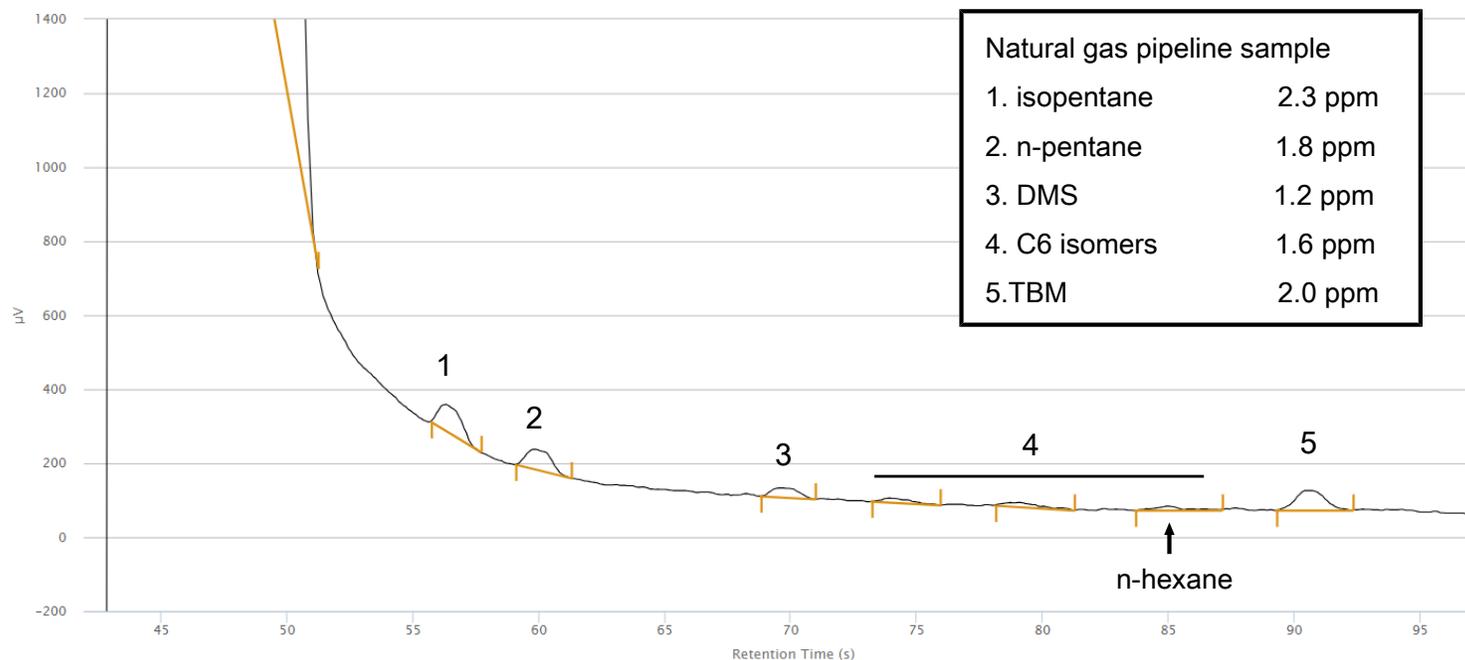
Ten runs were conducted of the odorant calibration gas to determine the percent relative standard deviation (%RSD).

Component	%RSD
DMS	5%
TBM	5%
THT	10%

The Micro GC Fusion thermal conductivity detector (TCD) is extremely sensitive. The dilution below shows the detection of <1 ppm DMS, TBM, and THT. At these low levels, proper peak integration is needed for accurate results.



Micro GC Fusion was connected to a natural gas pipeline source to measure odorants in a natural gas stream. The results show 1.2 ppm of DMS and 2.0 of TBM. THT was not present in the sample.



The following report was generated with Diablo EZReporter software, which works in tandem with Micro GC Fusion software to provide a complete BTU report of natural gas. This report was generated from a Micro GC Fusion configured for both natural gas and odorant analysis.

Gas Quality and Odorant Analysis Report INFICON Micro GC Fusion

Sample Information

Sample Information	
Sample Name	GasLine
Method Name	Odorant
Injection Date	2020-05-12 11:03:01
Report Date	2020-06-18 09:13:50
EZReporter Configuration File	GasQuality.cfgx
Source Data File	ad200171-42d4-4de3-85f7-64a57dbe39d6
Instrument SN	70098752
NGA Phys. Property Data Source	ASTM D3588-98 (2003)

Component Results

Component Name	Module	Ret. Time	Peak Area	Raw Amount	Norm%	User Tag
Nitrogen	moduleA:tcd	29.35	8713.8	0.263	0.264	
Methane	moduleA:tcd	29.87	2405772.4	97.147	97.483	
CO2	moduleA:tcd	35.26	1779.0	0.043	0.043	
Ethane	moduleA:tcd	48.09	93427.1	2.120	2.128	
Propane	moduleA:tcd	91.52	4666.1	0.075	0.076	
iso-Butane	moduleA:tcd	125.77	113.7	0.002	0.002	
n-Butane	moduleA:tcd	133.70	350.5	0.004	0.004	
iso-Pentane	moduleA:tcd	161.14	19.5	0.000	0.000	<0.001
n-Pentane	moduleA:tcd	166.06	19.7	0.000	0.000	<0.001
Hexanes plus	moduleA:tcd	195.00	0.0	0.000	0.000	<0.001
Total:				99.655	100.000	

Pipeline natural gas
individual concentrations

Results Summary

Result	Dry
Total Raw Mole% (Dry)	99.7
Pressure Base (psia)	14.696
Temperature Base (Deg. F)	60.00
Gross Heating Value (Btu / Ideal cu. ft.)	1024.4
Gross Heating Value (Btu / Real cu. ft.)	1026.5
Net Heating Value (BTU / Ideal cu.ft.)	922.9
Net Heating Value (BTU / Real cu.ft.)	924.8
Relative Density (G), Ideal	0.5666
Relative Density (G), Real	0.5675
Compressibility (Z) Factor	0.9979
Gross Wobbe Index, Real	1362.6
DMS, ppm	1.5
TBM, ppm	2.1

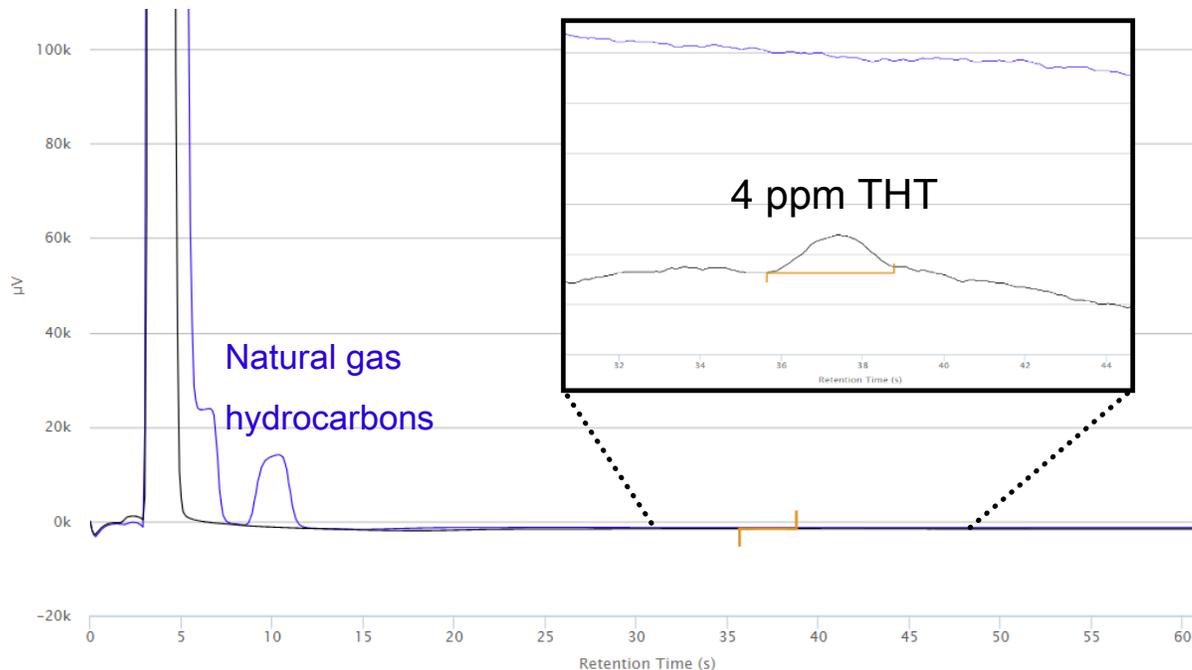
BTU calculations

Odorant concentrations in ppm from
16 m CP-Sil13CB

4 m CP-Sil19CB

If only THT is desired, the 4 m CP-Sil19CB module can be used to analyze THT within 60 s. Natural gas components C1-C5 elute before the THT peak as a group, resulting in full separation from adjacent C6 isomers. The chromatogram below displays the detection of 4 ppm THT.

Due to the THT peak eluting quickly, %RSD values are achievable down to 2-3% for single-digit ppm analysis.



Conclusion

With its speed and detection capabilities, Micro GC Fusion is ideal for analyzing various sulfur-containing odorants on a single 16 m CPSil-13CB module. For rapid analysis of THT only, a 4 m CPSil-19CB module is the best choice. Detection limits and repeatability depend on column module and the specific odorant.