

# Development of a micro-TCD-gas chromatography method to measure mercaptans in biomethane and natural gas

A. Louvat, V. Chadeffaud, C. Senne, JP Leininger

*GDF SUEZ, Centre de Recherche et d'Innovation Gaz et Energies Nouvelles, 361, avenue du Président Wilson – BP33, 93211 Saint Denis La Plaine Cedex.*

## 1. Context

Sulfur in gas comes from two different origins:

- Sulfur present originally in gas
- Sulfur coming from odorant

To prevent impacts on infrastructures, end-users equipment and environment, a maximum content of sulfur is specified. The Technical Committees of the CEN (TC 234 WG 11 and TC 408) are working on natural gas and biomethane quality standards. The sulfur specification (before odorisation) of the current version of the gas quality standard produced by CEN TC 234 is expressed as follow:

- Total Sulfur : below 20 mg(S)/Nm<sup>3</sup>
- Mercaptans : below 6 mg(S)/Nm<sup>3</sup>
- H<sub>2</sub>S and COS : below 5 mg(S)/Nm<sup>3</sup>

This sulfur specification will also be applicable to biomethane.

Usually the quantification of total sulfur content is performed with a gas chromatograph (GC) coupled with a specific detector (*FPD-flame photometric detector* or *PFPD-pulsed flame photometric detector*). The main advantage of this technique is the specificity of the detector. It detects only sulfur compounds. The natural gas matrix is not an issue for the analysis of sulfur traces. These appliances give acceptable results and robust measurements. But they requires high-skilled staff and expensive maintenance (considering the number of interventions required). The time of an analysis is also quite long for process analysis (20-30 minutes). With the increase of biomethane injection points on the network, the analytical follow-up of biomethane quality can become complex. Indeed Mercaptans can be produced by waste anaerobic degradation in the digester and thus occur in biomethane. It seems rather difficult to install a GC with a specific detector on each biomethane injection points. A challenging approach is to find a simple, less expensive and easy-to-use technique to analyze sulfur compounds in general and mercaptans, in particular.

## 2. Description of the material used

In order to develop this mercaptans analysis, we chose to work with a micro-gas chromatograph ( $\mu$ GC). It has the following characteristics:

- $\mu$ GC CP 490 AGILENT
- Stationary phase: CP SIL-13 CB dedicated to TBM analysis
- Detector:  $\mu$ -TCD (thermal conductivity detector)

The analytical method is developed in order to analyze the following mercaptans:

- Methylmercaptan (MM),
- Ethylmercaptan (EM),
- n-Propylmercaptan (NPM),
- Isopropylmercaptan (IPM),
- n-Butylmercaptan (NBM),
- Isobutylmercaptan (IBM),
- Sec-butylmercaptan (SBM),
- Terbutylmercaptan (TBM).

## 3. Strategy of mercaptans analysis by $\mu$ GC

The method development was divided into three steps:

- Step 1: separation of each mercaptan on the analytical module chosen
- Step 2: optimization of the method
- Step 3: characterization of the optimized method

## 4. Results

### 4.1. Separation of each mercaptan on the analytical module chosen

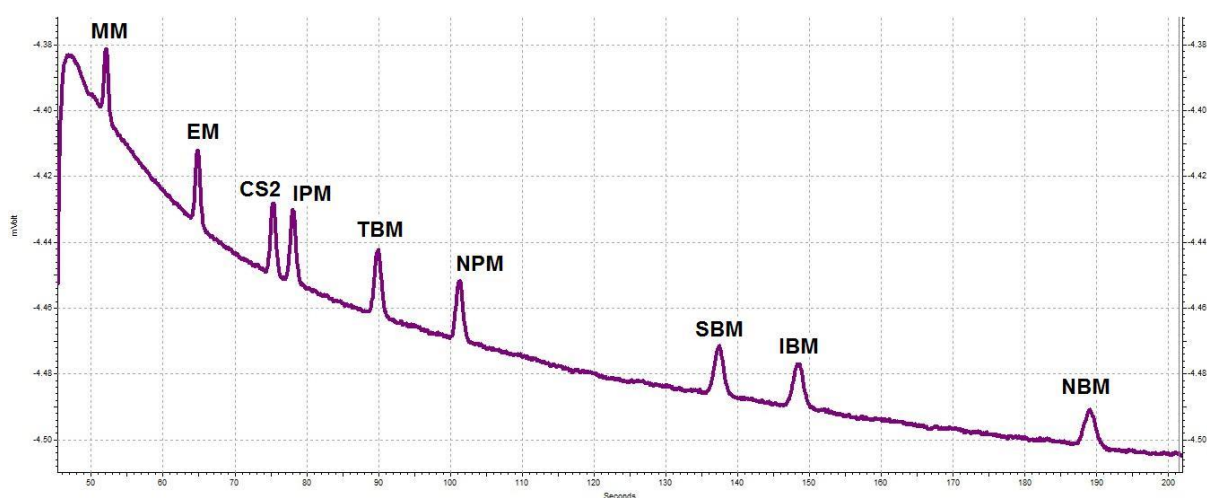


Figure 1 – Mercaptans separation on the analytical module

All the targeted mercaptans are separated. Carbon disulfide (CS<sub>2</sub>) is also present in the gas standard mixture and analyzed by the same method.

With this peaks separation the first step of the method development is achieved.

Four parameters were studied in the method optimization:

- Injection time (ms)
- Column temperature (°C)
- Injector temperature (°C)
- Column pressure (kPa)

All these parameters were modified in the software of the  $\mu$ GC (EZChrom Elite).

Some preliminary tests were performed on the injection time. It was decided to increase the value of the injection time at 250 ms. This value is a good compromise in order to obtain the maximum peak surface area while retaining a Gaussian shaped peak.

For the three others parameters, an design of experiments was performed:

- The column pressure was studied between 135 and 165 kPa
- The column temperature was studied between 50 and 70°C
- The injector temperature was studied between 50 and 70°C

The aim was to maximize the surface area and the peak height of each mercaptan. The software JMP was used to build the design of experiments and analyze the results.

It was also possible to determine the retention time of each mercaptan. The analysis of all the mercaptans is fast. The time of analysis is less than 200 seconds.

## 4.2. Characterization of the optimized method

The optimized method is characterized by:

- The stability of the measurement
- The study of interferences with other biomethane and natural gas compounds
- Linear working range
- Limit Of Detection (LOD) and Limit Of Quantification (LOQ)
- Repeatability/Accuracy

### 4.2.1. Stability of the measurement

The stability of the measurement was checked graphically and calculated with the help of the relative standard deviation (RSD). Three compounds were selected for this study: methylmercaptan, ethylmercaptan and tertibutylmercaptan. 20 runs were realized then the RSDs were calculated:

- at first with all the values,
- then by removing the first 5 measures
- then by removing the first 10 measures.

The results are as follows:

		MM	EM	TBM
RSD (%)	With all value	2.5	4.6	2.0
	By removing the first 5 measures	1.2	0.9	1.3
	By removing the first 10 measures	1.2	0.8	1.4

By removing the first five measures, the RSD is improving and acceptable. Removing 5 or 10 measures does not make a difference in terms of RSD.

**Subsequently, 20 runs will be performed and the first five measures will be removed from statistical data processing.**

#### 4.2.2. Study of the interferences with other biomethane and natural gas compounds

For biomethane, the interferences chosen were : methane, oxygen, nitrogen and carbon dioxide.

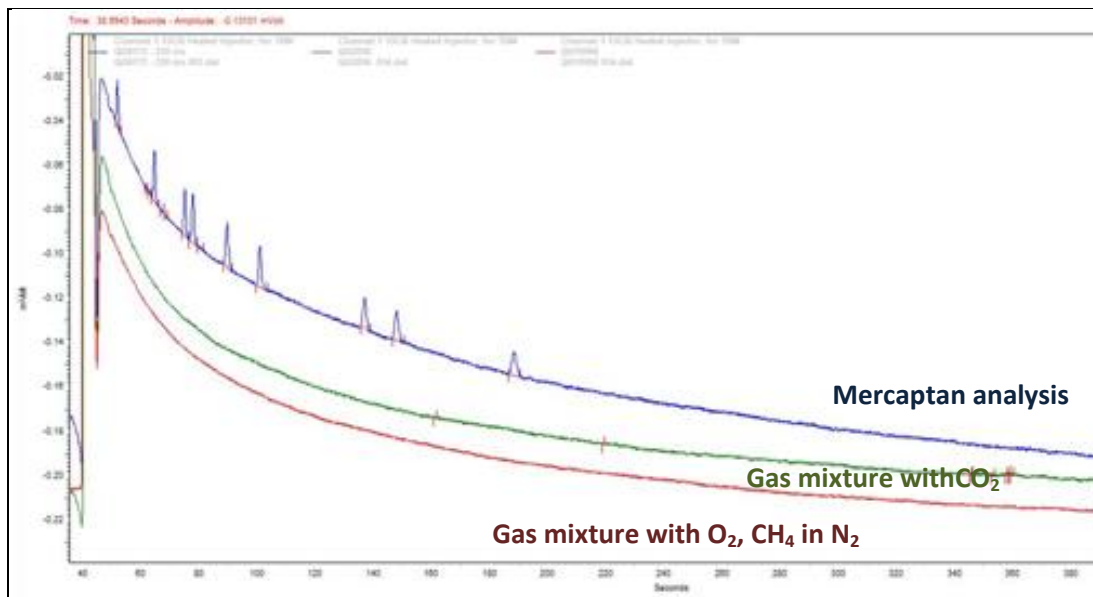


Figure 2 –  
 In blue: mercaptan analysis,  
 in green: gas mixture with 5% of CO<sub>2</sub>,  
 in red: gas mixture with 1% of O<sub>2</sub>, 0.3% of CH<sub>4</sub> in nitrogen

There are no interferences with biomethane compounds.

**This method can analyzed mercaptans in biomethane.**

For natural gas compounds, a typical gas composition was studied as well as a mixture with BTEX compounds.

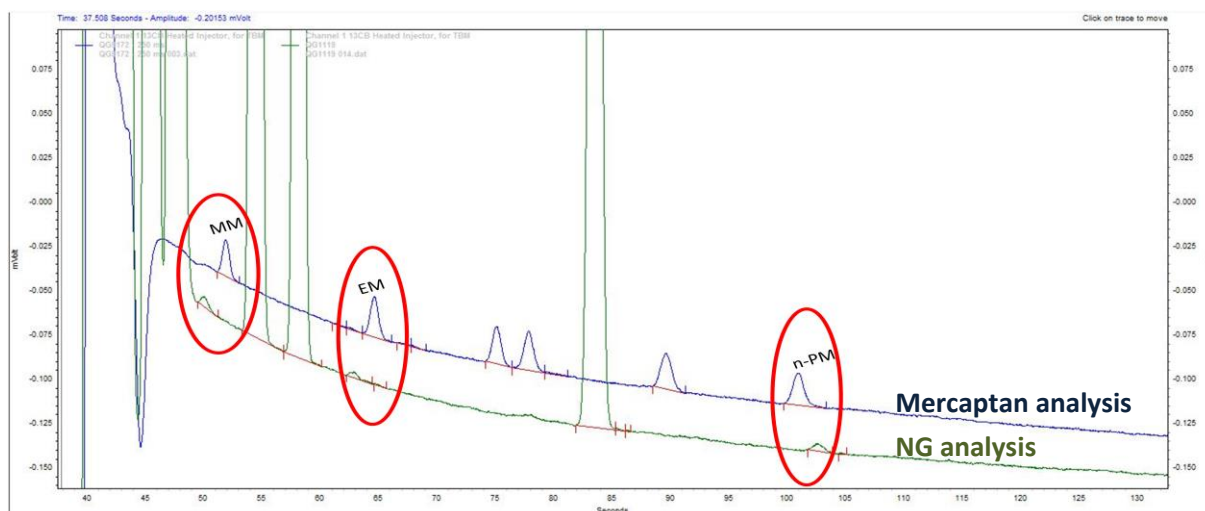


Figure 3 – in green: natural gas analysis, in blue: mercaptan analysis



Figure 4 – in green: BTEX analysis, in blue: mercaptan analysis

We consider that two peaks are separated if the resolution between these two peaks is equal or above 1.5. In this case, the calculated resolution for MM, EM, NPM and SBM and the interferent compound was estimated around 0.8. Statistically, the peak are not separated but the coelution is partial.

**For the analysis of mercaptans in natural gas, a special attention needs to be taken on this analysis of MM, EM, NPM and SBM due to the low resolution between the peaks. To prevent the coelution of the peaks the retention time shifts need to be checked.**

#### 4.2.3. Linear working range and Limit Of Detection (LOD) and Limit Of Quantification (LOQ)

The working range is studied with four level of concentrations: 1, 2, 3 and 4 ppm. For each mercaptan, it is possible to perform a one point calibration passing through the origin because of the linear response of the detector.

The LOD and LOQ were determined graphically by the representation of the mercaptans concentrations and the associated RSDs. We chose to associate a RSD of 15% to the LOQ and a RSD of 50% to the LOD. The results are summarized below.

	LOQ (ppm)	LOD (ppm)	LOQ (mg(S)/Nm <sup>3</sup> )	LOD (mg(S)/Nm <sup>3</sup> )
<b>MM</b>	0.8	0.3	1.1	0.4
<b>EM</b>	0.8	0.3	1.1	0.4
<b>IPM</b>	1.0	0.4	1.4	0.6
<b>TBM</b>	0.6	0.2	0.9	0.3
<b>NPM</b>	0.7	0.2	1.1	0.3
<b>SBM</b>	1.0	0.2	1.4	0.3
<b>IBM</b>	1.1	0.3	1.6	0.4
<b>NBM</b>	1.2	0.2	1.8	0.3
	<b>TOTAL</b>		<b>10.4</b>	<b>3.0</b>

The sum of all the mercaptans' LOD is around 3 mg(S)/m<sup>3</sup> and this value is below the sulfur specification of the European gas quality standard.

#### 4.2.4. Repeatability/Accuracy

For the repeatability of the method, three levels of mercaptans concentrations were studied. The key parameter is the RSD.

	1st level (ppm)	RSD (%)	2d level (ppm)	RSD(%)	3d level (ppm)	RSD (%)
<b>MM</b>	0.73	<b>21.1</b>	1.95	<b>3.1</b>	3.9	<b>2.7</b>
<b>EM</b>	0.75	<b>14.9</b>	2.0	<b>4.2</b>	4.0	<b>2.5</b>
<b>IPM</b>	0.75	<b>20.7</b>	2.0	<b>6.5</b>	4.0	<b>2.0</b>
<b>TBM</b>	0.75	<b>12.8</b>	2.0	<b>4.0</b>	4.0	<b>1.6</b>
<b>NPM</b>	0.75	<b>17.1</b>	2.0	<b>4.2</b>	4.0	<b>4.0</b>
<b>SBM</b>	0.75	<b>22.2</b>	2.0	<b>8.8</b>	4.0	<b>4.1</b>
<b>IBM</b>	0.75	<b>16.9</b>	2.0	<b>8.5</b>	4.0	<b>4.5</b>
<b>NBM</b>	0.75	<b>15.2</b>	2.0	<b>10.7</b>	4.0	<b>4.3</b>

For levels 2 and 3, the RSDs are below 10%. It is quite acceptable for trace analysis of sulfur compounds in natural gas. For the level 1, the RSDs are higher. It could be explained by the fact we are very close to the limit of quantification (LOQ) of the method.

For the accuracy, the results are the following:

	MM	EM	IPM	TBM	NPM	SBM	IBM	NBM
<b>Theoretical values (ppm)</b> (of the gas standard mixture)	<b>3.9</b>	<b>4.0</b>	<b>4.0</b>	<b>4.0</b>	<b>4.0</b>	<b>4.0</b>	<b>4.0</b>	<b>4.0</b>
<b>Uncertainties (%)</b> (of the gas standard mixture)	± 5%	± 5%	± 5%	± 5%	± 5%	± 5%	± 10%	± 5%
<b>Experimental values (ppm)</b>	<b>3.9</b>	<b>3.9</b>	<b>4.2</b>	<b>4.1</b>	<b>4.2</b>	<b>4.0</b>	<b>4.1</b>	<b>4.0</b>
<b>Accuracy (%)</b>	<b>0.1</b>	<b>3.2</b>	<b>4.6</b>	<b>3.4</b>	<b>4.7</b>	<b>0.8</b>	<b>3.7</b>	<b>0.8</b>

The accuracy is below the uncertainties of the gas standard for all the mercaptans.

## 5. Conclusion

**The method can be used for the analysis of mercaptans in biomethane.**

**For the analysis of mercaptans in natural gas, this method can also be used but with some caution. There are possible interferences with MM, EM and NPM.**

**This method needs some improvements to optimize the separation of the co-eluting peaks.**