DEVELOPMENT OF **A MICRO-TCD-GAS CHROMATOGRAPHY** METHOD TO MEASURE MERCAPTANS IN BIOMETHANE AND NATURAL GAS

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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 equipments and environment, 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 current version of the gas quality standard produced by CEN TC 234, whose sulfur specification (before odorisation) will be applicable to biomethane, is expressed as follow:
- Total Sulfur : below 20 mg(S)/Nm^3
- Mercaptans : below 6 mg(S)/Nm^3
- H2S and COS : below 5 mg(S)/Nm^3

With the increase of biomethane injection points on the network, the analytical follow-up of biomethane quality can become complex. Mercaptans can indeed be produced by waste anaerobic degradation in the digester and thus be present in biomethane. GDF SUEZ-CRIGEN has developed a simple and easy-to-use mercaptans analysis by micro-TCD (thermal conductivity detector)- gas chromatography.

Initial settings

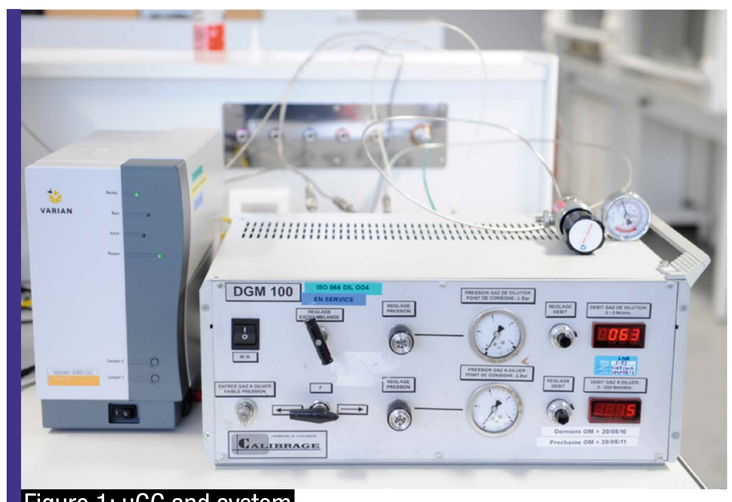

Figure 1: µGC and system of gas dilution

µGC characteristics:

- µGC CP 490 AGILENT
- Stationary phase: CP SIL-13 CB dedicated to TBM analysis
- Detector: µ-TCD (thermal conductivity detector)

List of mercaptans:

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

Methodology used

STEP 1: mercaptan identification with the Agilent method - analysis in 200 sec

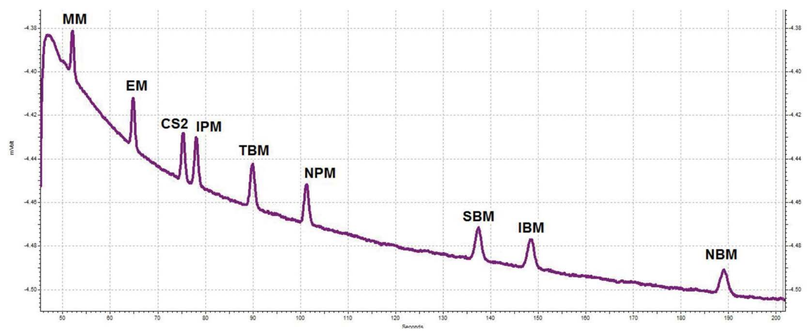

Figure 2: mercaptans analysis by µGC (4 ppm concentration for each mercaptan) [carbon disulfide was also in the gas standard mixture used and analyzed with the method]

STEP 2: method optimization using an experimental design

4 parameters studied and an experimental design:
- Injection time (sec)
- Column temperature (°C)
- Injector temperature (°C)
- Column pressure (kPa)

STEP 3: method characterization using statistic tools

- Stability of the measure → after 5 measures
- Study of interferences with other biomethane and natural gas compounds → no interference with biomethane compounds – Possible interference with some NG compounds
- Repeatability/Accuracy → standard deviation below 5%
- Linear working range → 0-4 ppm
- LOD and LOQ

Table 1: mercaptans LOD (in mg(S)/Nm^3)

MM	EM	IPM	TBM	NPM	SBM	IBM	NBM	TOTAL
0.37	0.41	0.63	0.30	0.29	0.33	0.40	0.34	3.06

Below gas quality standard

Conclusion

- **Mercaptans analysis in biomethane: can be used on field**
- **Mercaptans analysis in natural gas: can also be used but caution must be taken**

→ **possible co-elution peaks with MM, EM and NPM**

→ **Method needs some improvements to optimize the separation of the co-eluting peaks**

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