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GAS QUALITY CONTROL: an interlaboratory study to assess the performance of laboratories methods for sampling and analysis of biomethane samples

DEVELOPMENT OF RENEWABLE ENERGY: industrialization of biomethane pathway in France

The development of renewable energy is a major challenge all over the world, in response to various environmental, geopolitical and economic issues. Biomethane (methane produced after treatment of biogas) to be injected into the grid is one answer. The French Energy Agency (ADEME) scenario developed a pro-active roadmap for biomethane that suggests the production of 30 TWh by 2030 in France.

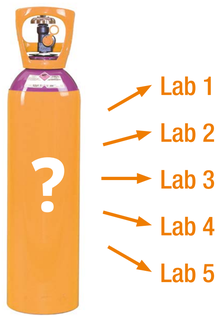
GAS QUALITY CONTROLS: an “exploratory” interlaboratory study carried out on field to evaluate the methods used by laboratories to perform biomethane analysis

Currently, there is no international reference method for biomethane sampling and analysis. ENGIE LAB CRIGEN has validated its methods in laboratories and on field, based on its experience from natural gas.
As it is until now the only laboratory in France which performs such analysis, the aim of the study carried out by ENGIE LAB CRIGEN was to validate the performances of methods used by laboratories to quantify trace compounds in biomethane with reliable results.

Parameter	Range of content	Component in gaz reference mix
Hydrogen (H_2)	0 – 6 %	H_2 at 1 %-mol
Carbon monoxide (CO)	0 – 2 %	CO at 0,05 %-mol
Ammonia (NH_3)	0 – 3 mg/Nm³	No NH_3
Mercury (Hg)	0 – 1 µg/Nm³	No Hg
Total Chloride (Cl)	0 – 1 mg/Nm³	Dichlorobenzene at 3,2 mgCl/Nm³
Total Fluoride (F)	0 – 10 mg/Nm³	Difluoromethane at 1,7 mgF/Nm³
Total Mercaptans	0 – 6 mgS/Nm³	C_2H_5SH at 5,6 mgS/Nm³
Total Sulfurs	0 – 30 mgS/Nm³	C_2H_5SH at 5,6 mgS/Nm³ and CS_2 at 14,6 mgS/Nm³

According to French specifications, 8 parameters need to be controlled when injecting biomethane into the gas grid.

Laboratories were selected on their experience on biogas or air quality monitoring, that require the closest analytical solutions.



A gas “blind” reference mix with indications on the range of contents was sampled by five laboratories. The interlaboratory study was carried out in real conditions on one biomethane site. This enabled to assess the capability of the laboratories to sample gases under pressure on site (sampling devices, adequate materials, security,…).

Then, Z-scores were estimated according to ISO 13528 using the maximum permissible error as the standard deviation of the proficiency assessment.

$$Zi = \frac{\bar{y}_i - \bar{y}_{ref}}{\sigma_R}$$

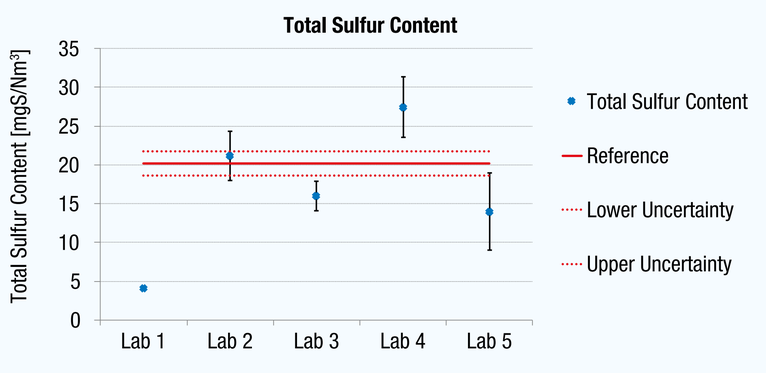
Z-score formula.

RESULTS OF THE STUDY

Parameter / Z-score	H_2	CO	Total chloride	Total fluoride	Total sulfurs	Total mercaptans
Lab 1	-2,1	nc*	nc*	nc*	-5,3	-4,3
Lab 2	4,6	1,5	nc*	nc*	0,3	-1,1
Lab 3	4,6	4,5	-4,6	-0,7	-1,4	-4,6
Lab 4	2,0	1,7	-6,2	nc*	2,4	7,7
Lab 5	nc*	nc*	-4,2	nc*	-2,0	nc*

Z-score results show that laboratoires are not ready yet for biomethane measurements.

Z < 2 Satisfactory result
2 < Z < 3 Questionnable result
Z > 3 Unsatisfactory result
nc* < LOQ : Not calculated, the measurement is below the LOQ



Graphic of results for total sulfurs: a main impact is due to the sampling step.

Tested laboratories do not manage biomethane sampling (materials of the samplers, gas volumes to be sampled, sampling and analysis of gas under pressure, etc.), whereas this step impacts highly the quantification of the targeted compounds (e.g. sulfur compounds according to ISO 19739).

CONCLUSION AND OUTLOOKS

This study was originally a practical way to evaluate and validate sampling and analysis methods for the control of biomethane specifications. But it rather emphasizes the lack of laboratories skills for biomethane sampling.

It means that first of all, the analytical methods of the laboratories need to be validated. This can be carried out by using an interlaboratory campaign. These interlaboratory studies are an interesting way to define the best practices for biomethane sampling and analysis. It can be helpful for any standardization process for the parameters of biomethane.

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