

Siloxane standards generation using LiqMix Cascade

The work described below is a joined project between Axel'One [Axel'One | Plateforme chimie-environnement | Lyon \(axel-one.com\)](http://axel-one.com) and AlyTech SAS

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LiqMix Cascade: A new way to calibrate siloxane analysers

Over the past few years, production of biogas, especially in Europe has seen a steep development. As these products are either used locally to produce electricity through some engines run generators, or injected into the local commercial network, their quality is very important and must be carefully checked.

This developing market has generated a need for a product specification and the corresponding analytical method development. This specification is contained into the EN 16723 documents.

Among the analytical methods, came a standardized test method for siloxanes in biomethane. The Silicone content is due to remain below 0.5mg/m³. This method uses a GC-IMS analysis. One big challenge has been to supply accurate, stable, and traceable gas standards. LiqMix Cascade can create these gas standards using diluted liquid siloxane.



GC-FID calibration on siloxane using LiqMix Cascade

The present study describes a cheaper and easier analytical method to be used in a control laboratory, with on-site generation of calibration gases. The analysis is done on a GC fitted with an FID detector. This analyser is calibrated with multi-level calibration gases. To avoid high cost, long delivery time and short shelf-life calibration gas cylinders, siloxane calibration gases were prepared on site using an AlyTech LiqMix Cascade model. This calibration was done using the Octamethylcyclotetrasiloxane known as D4 siloxane at 98% purity and CAS N° 556-67-2.

System used and parameters description

Axel'One's R&D laboratory is dedicated to industrial analysis and provides online analysis solutions for a consortium of major companies. Equipped with chromatograph, spectrometer, sensor type analyzers as well as a gas or liquid sample generation bench, the Analysis team carries out feasibility studies and aligns industrial needs with innovative solutions from technology providers. All the data shown below were obtained using the GC-FID and recommendation from Axel'One.

The main goal of this study was to calibrate from 5-0.5ppm the GC-FID using LiqMix Cascade. The system used is described below:

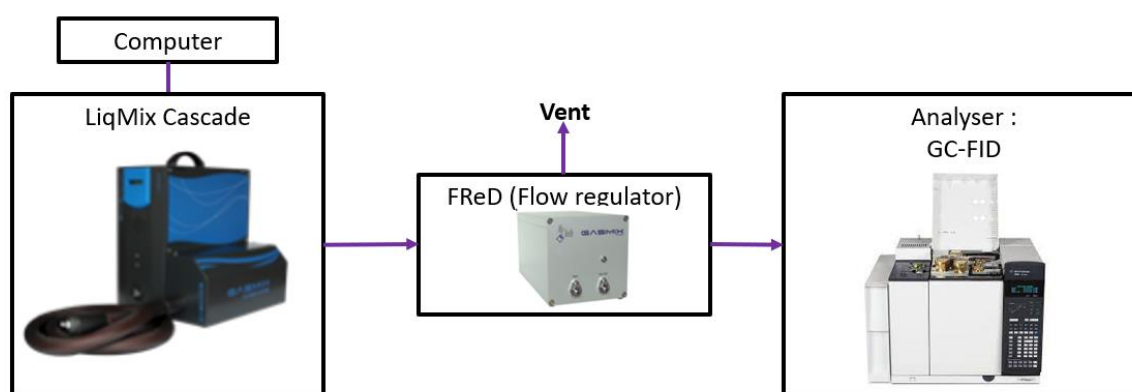


Figure 1: Calibration system scheme.

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The GC-FID parameters were optimized for the D4 calibration following Axel'One recommendations. Here are the instrument parameters and the column used:

Agilent 7890B GC-FID parameters:	
Run Time:	3.5min
Post Run Time:	0.5min
Temperature:	
Setpoint:	80°C
Hold Time:	3.5min
Post Run:	80°C
Inlet:	
Mode	Splitless
Detector:	
	FID
Column Description: DB1	
Model:	125-10HB
Diameter:	530.00 µm
Film thickness:	2.65µm
Length:	10.0m
Void time:	0.179min

Figure 2: GC-FID main method parameters and column description.

Each level of D4 siloxane concentrations were prepared using the LiqMix Cascade and his associated software:



Figure 3: LiqMix Cascade software.

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The LiqMix Cascade parameters as Heating, compounds used, flows and each mixture concentrations can be found on the software report. They are displayed as following:



Project Report

Date: 29/09/2021 08:43
User: NoUser
GasMix S/N: L18-146C
Software revision: 118

Project name: D4 AxelOne 5_05 ppm

Instrument configuration

	Channel 1	Channel 2	Output 1st stage	Dilution 2nd stage
Standard	D4	Air/N2	Air	Air/N2
Min. flow	0,109 g/h	200,0 Nml/min	1,179 Nml/min	100,458 Nml/min
Max. flow	4,99 g/h	5141,795 Nml/min	49,89 Nml/min	5146,49 Nml/min
Analytes	D4 98,0 %			

Heated channels (°C)

LINE	OUTLET	Evaporator
55	60	75

Figure 4: Report of the created project LiqMix Cascade. Compounds and flows used on each channel are displayed.



Project Report

Sequence summary

Mixture 1 of 6:

Description					
Pause before	Mixture	Pause after	Cycle	Replicates	Total duration
00:00:00	00:54:00	00:00:00	00:54:00	1	00:54:00

Relays

	1E	2E	1I	2I
ON	---	---	---	---
OFF	---	---	---	---

Analytes

D4	
Concentration	5,000 ppm
Uncertainty	+/- 0,156 (abs.)

Flows

Channel 1	Channel 2	Output 1st stage	Dilution 2nd stage
1,061 g/h	1534,0 Nml/min	17,6 Nml/min	2985,9 Nml/min

Total flow: 3003,5 Nml/min

Figure 5: Example of report for the 1st mixture created on LiqMix Cascade.

Mixture N°	D4 concentration	Channel 1	Channel 2	Output 1st stage	Dilution 2nd stage
1	5 ppm	1,061g/h	1534,0 Nml/min	17,6 Nml/min	2985,9 Nml/min
2	4 ppm	1,061g/h	1534,0 Nml/min	14,1 Nml/min	2989,4 Nml/min
3	3 ppm	1,061g/h	1534,0 Nml/min	10,6 Nml/min	2993,0 Nml/min
4	2 ppm	1,061g/h	1534,0 Nml/min	7,0 Nml/min	2996,5 Nml/min
5	1 ppm	1,061g/h	1534,0 Nml/min	3,5 Nml/min	3000,0 Nml/min
6	0,5 ppm	1,061g/h	1534,0 Nml/min	1,8 Nml/min	3001,8 Nml/min

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Table 1: Summary of the calibration points parameters used on LiqMix Cascade.

Results

For each concentration prepared by LiqMix Cascade the area of the identified D4 peak is integrated on the chromatogram and his area is measured. As LiqMix Cascade is a dynamic system it allows to obtain multiple GC-FID chromatograms for a single mixture. It can be seen on the next figures:

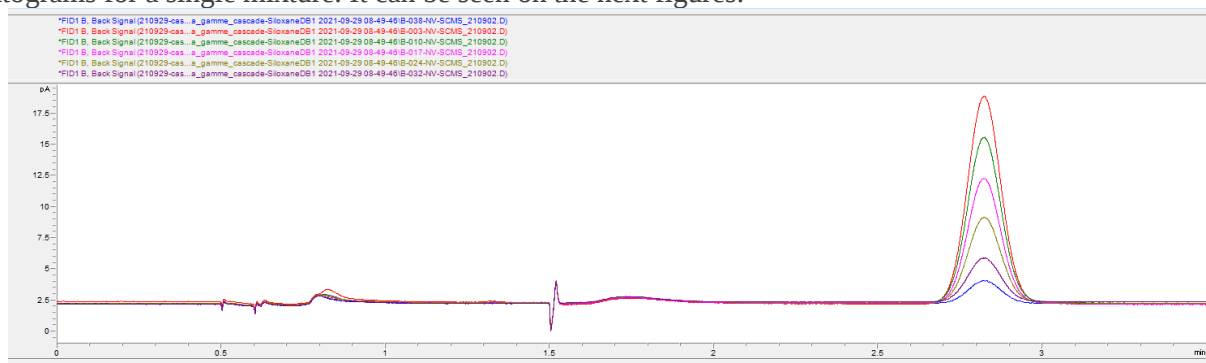


Figure 6: GC-FID D4 Chromatogram.

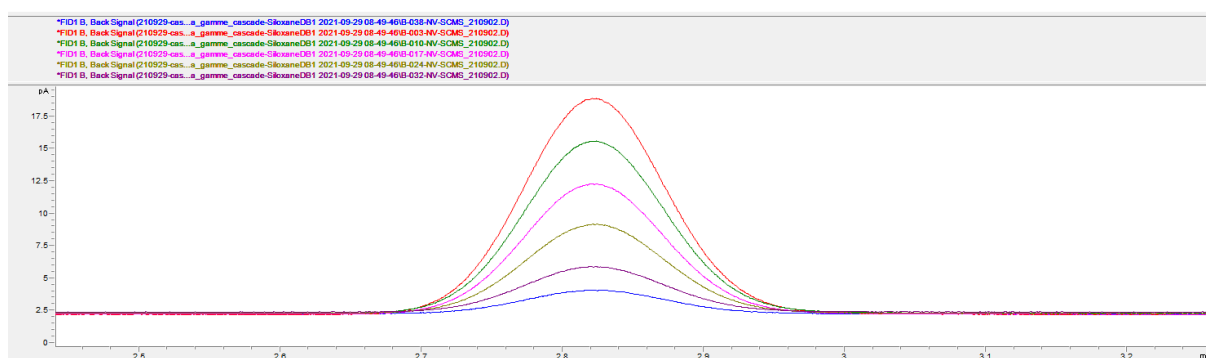


Figure 7: Zoom In of the D4 peak.

D4 concentration over time

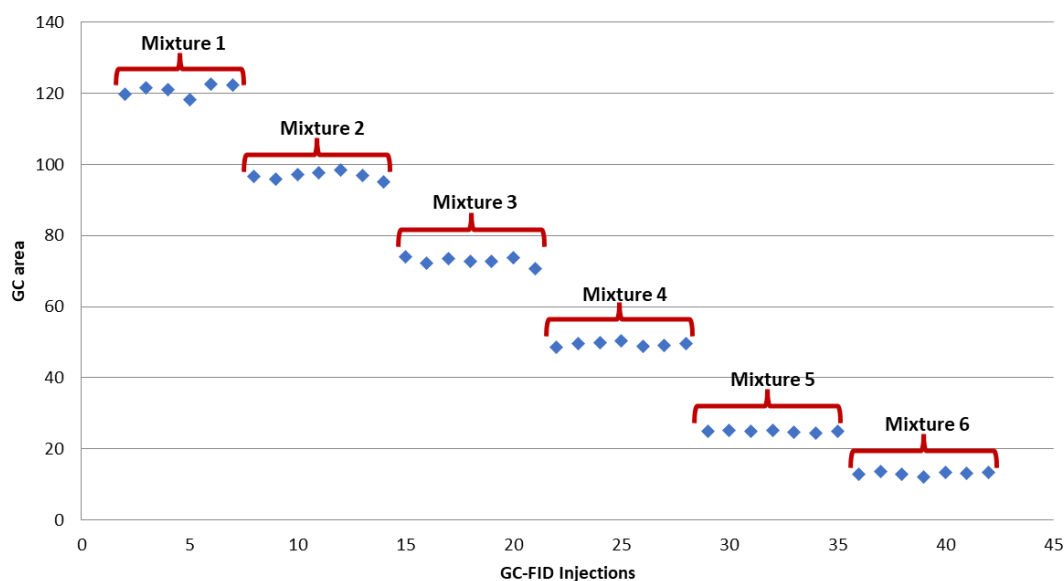


Figure 8: GC-FID Area for the integrated D4 generated on each mixture using LiqMix Cascade

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The average area and the repeatability can be easily calculated and are showed on the next table:

Mixture N°	LiqMix Cascade concentration	GC Area	RSD%
1	5 ppm	121	1,4
2	4 ppm	97	1,1
3	3 ppm	73	1,0
4	2 ppm	49	1,3
5	1 ppm	25	1,2
6	0,5 ppm	13	3,8

Table 2: GC-FID calibration points RSD%

Using these results the calibration curve for the D4 compound on the GC-FID is generated. The experiment was done twice on this occasion and on this next figure are displayed the 2 calibration curves obtained:

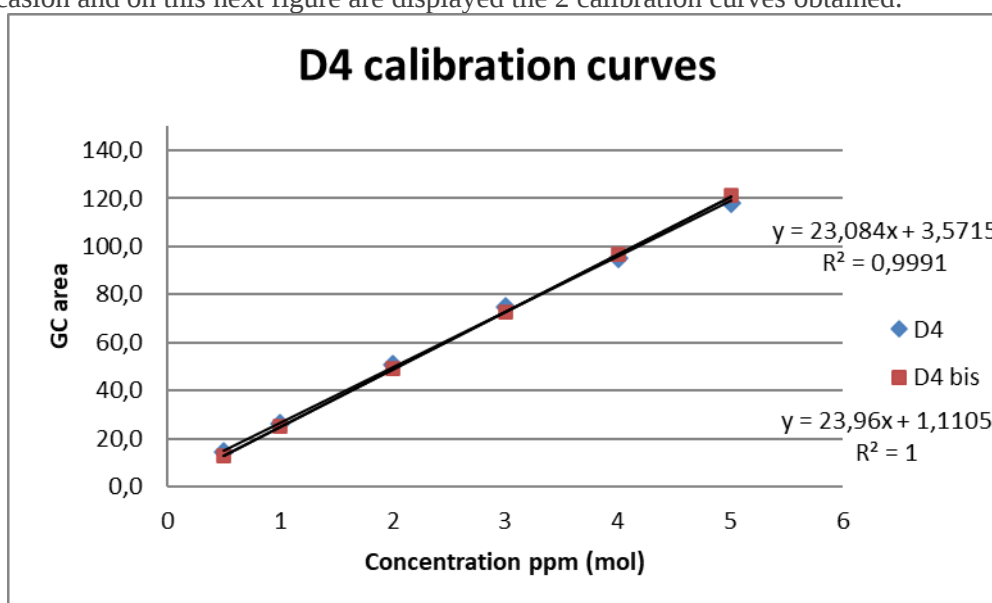


Figure 9: D4 Calibration curves on GC-FID

Both curves are similar and got an $R^2 > 0.999$ with RSD% < 4% for each level. LiqMix Cascade provides accurate, stable, and traceable siloxane standard.

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Calibration using μ GC with TCD detector

The same experiment was done with the μ GC Fusion. The μ GC results were obtained from 50ppm to 3ppm as the LOQ of the μ GC didn't allow to go lower at that time:

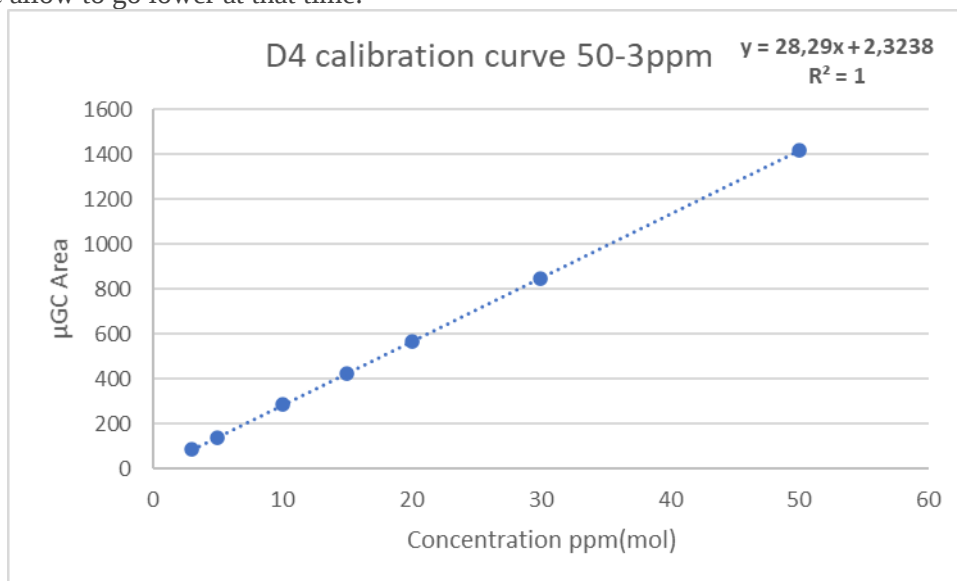
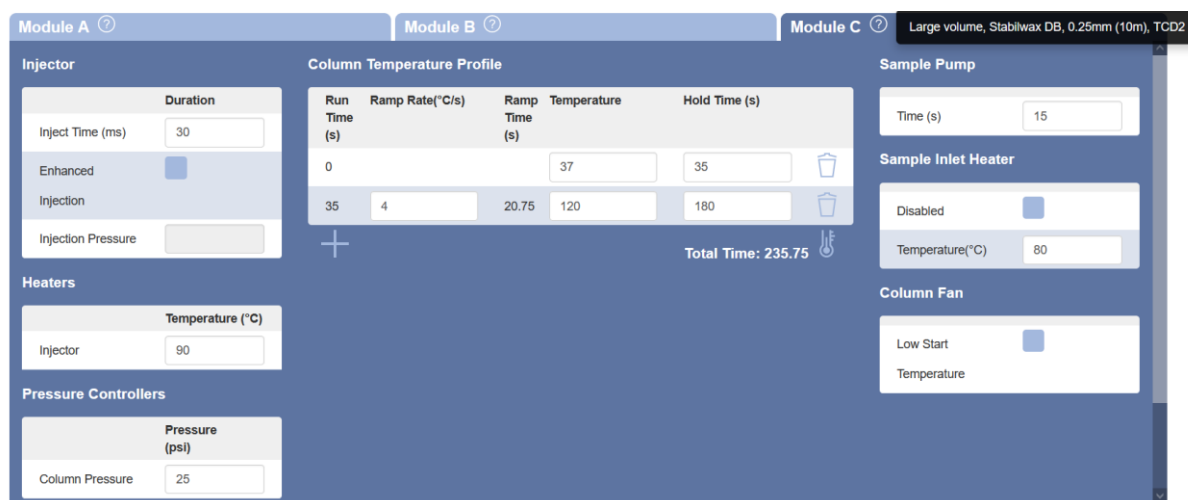


Figure 10: μ GC D4 calibration from 50 to 3ppm using LiqMix Cascade



Run Time (s)	Ramp Rate (°C/s)	Ramp Time (s)	Temperature (°C)	Hold Time (s)
0			37	35
35	4	20.75	120	180

Figure 11: μ GC Method parameters and column used.

Conclusion

The above-described method is a promising alternative to the heavy and involving GC-IMS combined with the use of cylinder calibration gases.

The onsite preparation of the siloxane calibration gases offers multiple advantages: The calibration gases are prepared on demand, at multiple and adjustable concentrations. The final uncertainty on the concentrations is lower than those given on the certificate of the cylinder.

The well-known GC-FID method seems to be a good option for the analysis of siloxane impurities in biogases. The concentration window achievable and demonstrated (0.5 to 50ppm D4) covers most of the current market demand.