Application Note

Siloxanes in Biogas

Precise on-site measurement using GC-IMS Analysis

Introduction

Biogas is produced during the digestion of organic materials in the absence of oxygen and used as alternative source to mainly feed combustion engines (figure 1). It is produced from agricultural waste, municipal waste, plant material, sewage or sludge and green or food waste. Biogas contains mainly methane (CH_4) and carbon dioxide (CO_2).

Due to the presence of silicon containing materials in the waste coming from sources like washing agents, skin care products or waterproofing materials siloxanes are formed. Siloxanes contain silicium (Si), Oxygen (O) and methyl groups (CH_3-) and are generated in their cyclic as well as linear form. Siloxanes, which can be found in biogas are listed in table 1.

Table 1: List of cyclic and linear siloxanes

Siloxane	
Hexamethyldisiloxane	L2
Octamethyltrisiloxane	L3
Decamethyltetrasiloxane	L4
Hexamethylcyclotrisiloxane	D3
Octamethylcyclotetrasiloxane	D4
Decamethylcyclopentasiloxane	D5
Dodecamethylcyclohexasiloxane	D6

Biogas can be upgraded and inserted into natural gas pipelines or burned as fuel in a power generation facility.

Problems occur if the amount of siloxanes in the biogas surpasses a critical value that jeopardizes the valves and pistons of the engine of the power generator through the formation of SiO_2 (figure 2).

Figure 1: Biogas power plant

Therefore, the concentration of siloxanes in the biogas has to be controlled and kept below a maximum level. Nowadays the common way to control the silicium amount is to take a gas sample using a sample bag and analyse it with gas chromatography – mass spectrometry (GC-MS). This causes an important information delay regarding the composition of the gas with respect to its siloxane concentration.

The GC-IMS-SILOX by G.A.S. allows an on-site as well as a 24/7 based on-line monitoring of the individual siloxanes listed in table 1 at very low concentration levels.

Advantages of G.A.S.' GC-IMS-SILOX for siloxane analysis:

- On-site measurements with "one-click" menu
- On-line/continuous monitoring at set intervals
- Very low detection limits (µg/m^3)
- High reproducibility and accuracy
- Very low running and maintenance costs

Figure 2: Defects on engine parts caused by silicon

Experimental Set-up

Using the GC-IMS-SILOX (figure 3) the individual siloxanes are separated by the use of a 30 m SE54 gas chromatographic column operated at 80° C and detected by an ion mobility spectrometer developed by G.A.S.. The experimental parameters of the GC-IMS-SILOX system are listed in table 2. The biogas sample is sucked by an integrated pump with flow of 150mL/min. into the 6-port-valve of the system and by switching the valve injected to the chromatographic column. The total run time for the analysis is 15 minutes. If the detection of D6 is required the run time is approximately 60 min. The system is calibrated using test gases generated by certified permeation tubes. For the automatic re-calibration a certified calibration tube of D4 is used. The tailor made firmware allows the automatic re-calibration of all other siloxanes at the same time.

Table 2: Experimental parameters

Technology	Gaschromatograpy-Ion Mobility Spectrometry
Ionisation Source	Tritium (300MBq - below ex-emption limit in EURATOM)
GC column	30 m (5% Diphenyl, 95 % dimethyl polysiloxane) x 0.44 mm x 0.32. µm FS-SE-54-CB-1
Column Temperature	80°C isothermal
Carrier gas flow rate	15 mL/min
Carrier-/Drift gas	Nitrogen 5.0
Sample Loop volume	1 mL

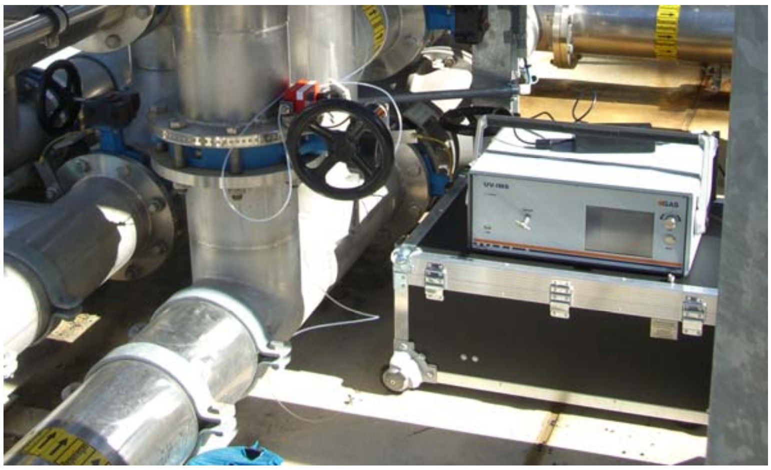

Figure 3: GC-IMS-SILOX on-site at biogas plant

After a measurement run the results are displayed on the screen of the GC-IMS-SILOX (figure 4). Via a current loop the total amount of silicium can be transferred to e.g. a control room for continuous monitoring purposes.

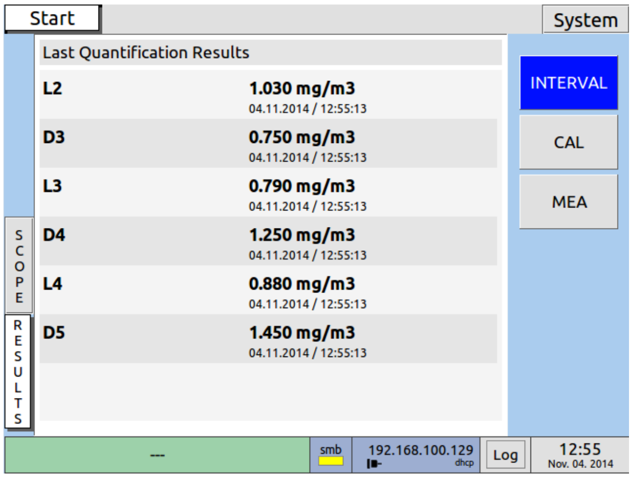

Figure 4: Screen shot of the GC-IMS-SILOX

Results

Figure 5 shows the 3 dimensional IMS-chromatogram of the mixture of L2, L3, L4, D3, D4 and D5. All siloxanes are separated clearly. The individual siloxanes exhibit a characteristic retention and additionally specific drift times in the ion mobility spectra (figure 6). This enables the precise identification of the siloxanes in the presence of the biogas matrix.

The calibration was carried out in the concentration range of 0.1 up to ~ 5 mg/m³. On request lower detection limits down to the µg/m³ range can be realised. The calibration curves for L2, L3, L4, D3, D4 and D5 are shown in figure 6.

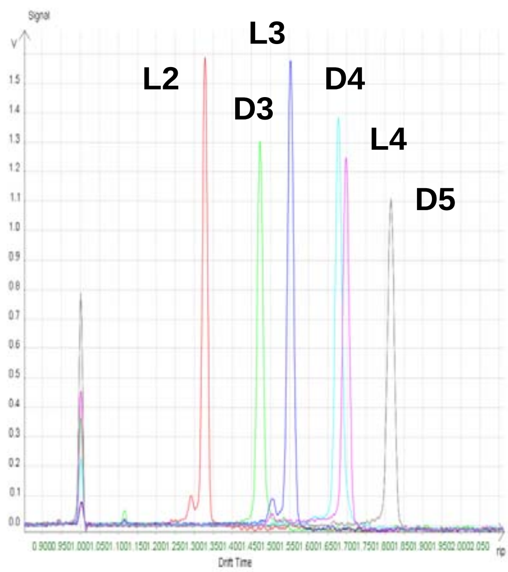

Figure 6: Single ion mobility spectra for L2, L3, L4, D3, D4 and D5 showing characteristic drift times for the generated ions

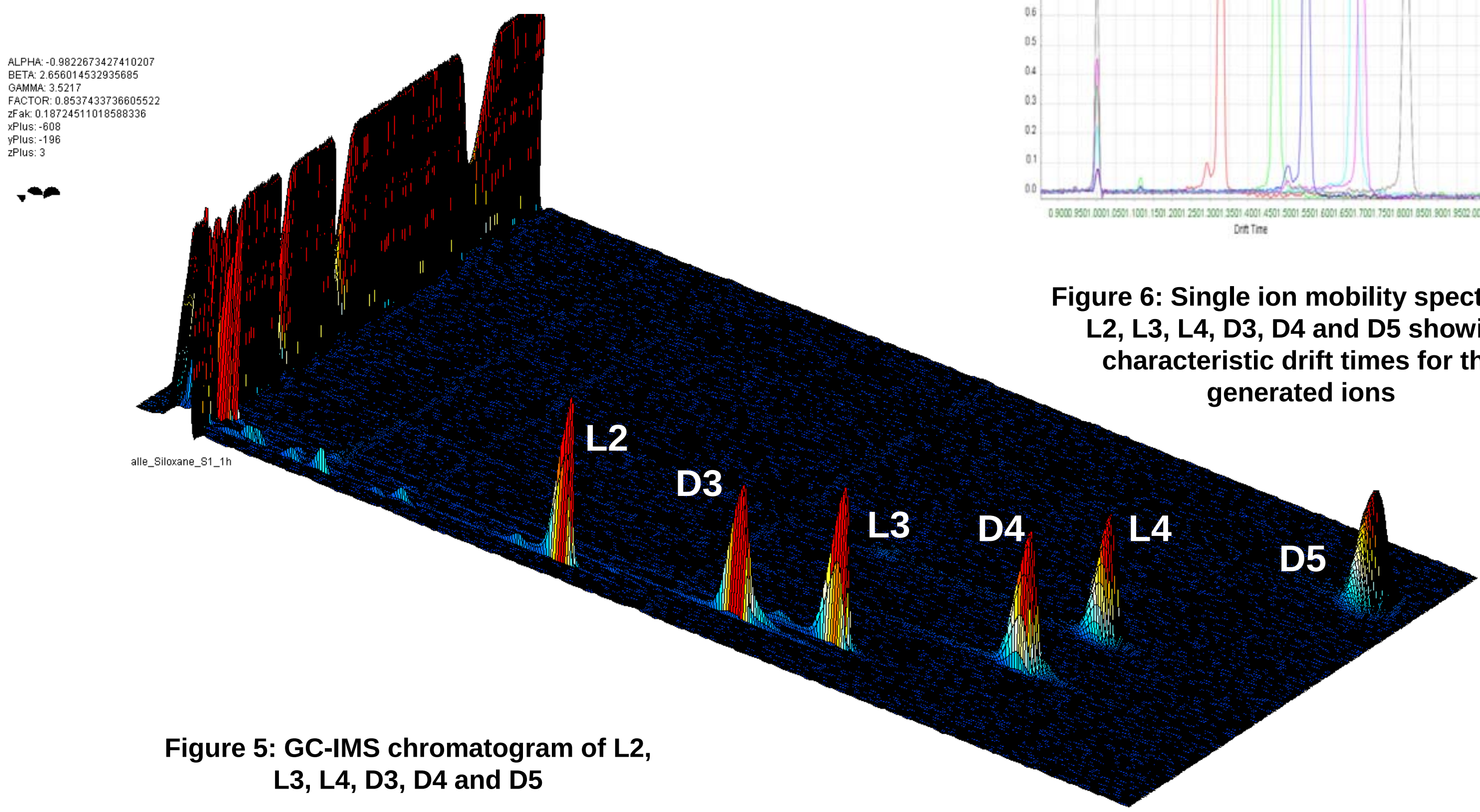

Figure 5: GC-IMS chromatogram of L2, L3, L4, D3, D4 and D5

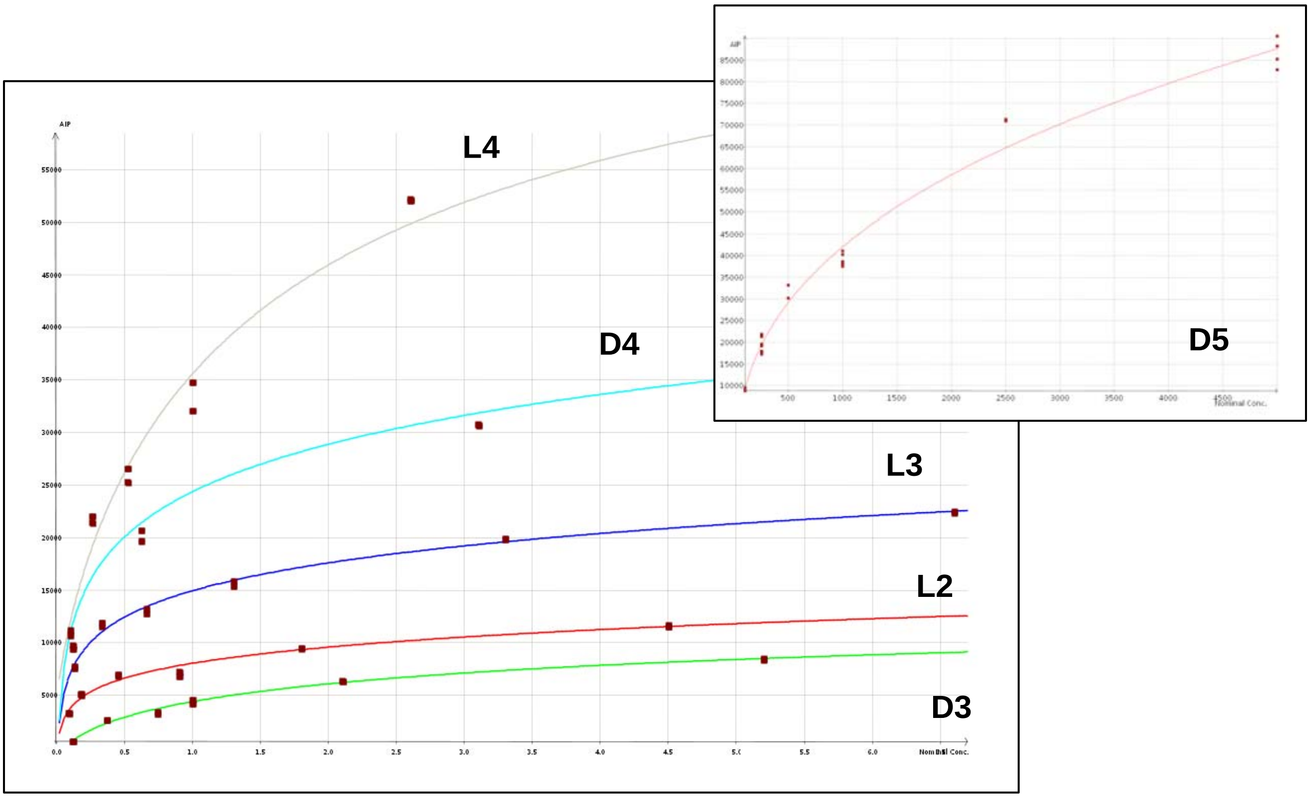

Figure 6: Calibration curves for the individual siloxanes L2, L3, L4, D3, D4 and D5

Summary

The GC-IMS-SILOX is an analytical tool for the precise quantitative determination of the single siloxanes L2, L3, L4, D2, D3, D4 and D5 in biogas and D6 on request. Standard calibrations of the system are carried out in the range of 0.1 mg/m^3 to 5 mg/m^3. On request, detection limits in the low µg/m^3 range can be reached.
The system works fully automatically and can be installed directly at a biogas pipeline. This allows the continuous 24/7 monitoring of siloxanes quantity within the biogas and e.g. to control a filter break through at a very early stage.

The live time of power generator can be extended, expensive re-investment same as costly down times can be avoided. Biogas filters can be used to their optimum life span and unnecessary filter changes can be avoided.

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