On-site Analysis of Siloxanes and Terpenes in Biogas

Application Note

Introduction

Landfill/sewage/bio-gas 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 or municipal waste, plant material, sewage or sludge and green or food waste. Landfill/sewage or bio-gas mainly contains 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/hair care products or waterproofing materials siloxanes are formed.
Siloxanes contain silicon (Si), Oxygen (O) and methyl groups (CH_3-) and are generated in their cyclic as well as linear molecular structure. Typical siloxanes, which can be found in landfill/sewage gas are Hexamethyldisiloxane (L2) or Decamethylcyclopentasiloxane (D5).
When the waste material contains citric fruits (e.g. oranges), conifers (e.g. pine tree), or herbs (e.g. rosemary, bay, thyme, mint and eucalyptus), terpenes are released during fermentation. Well known terpenes are, for example, Cymene, Limonene, and Pinene.

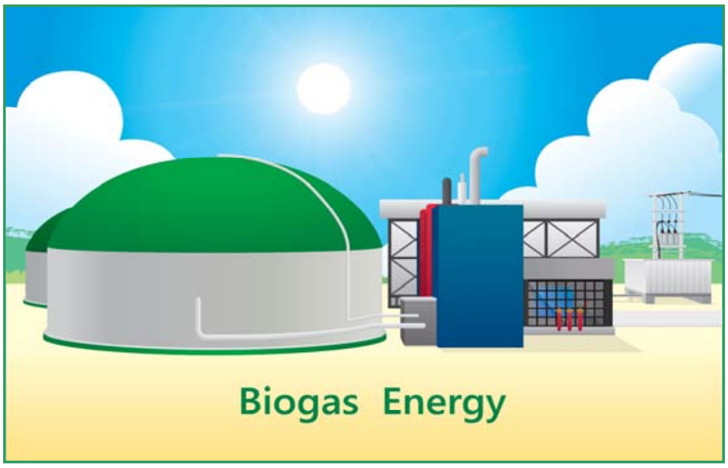

Figure 1: Biogas power plant

In order to recognize the optimal time for a filter change, the **GC-IMS-SILOX** is an adequate measuring device which identifies in online monitoring mode 24/7 the content of siloxanes, 'Total Si' and terpenes. This allows the user to notice an increase in substance concentrations at a very early stage and is therefore a very useful tool to avoid system breakdowns at minimal costs.

Technical Context

Landfill/sewage or biogas can be upgraded and introduced into natural gas pipelines or burned as fuel in power generation facilities.
Problems occur if the amount of siloxanes in the gas stream surpasses a critical level; during the combustion process in the engines Si may fall out as SiO_2-sand which sticks on to the inner surfaces of engines and especially moving parts like valves and/or pistons will be damaged. Therefore, the concentration of siloxanes in the gas has to be controlled and kept below a maximum level.
Gas quality criteria have been specified in EN 16723-1 & 2 with a maximum level for the total of silicon (Si) of 0.3-1.0 mg/m^3.
In addition to the siloxanes, it is just as important to avoid terpenes in the biogas.
The reason for this is that these mask the smell of odorants, such as THT, which is added to the natural gas used in households.

Advantages of GC-IMS-SILOX for sensitive on-site siloxane analysis:

•Standard:
-ASTM D-8455 22

•Sensitivity:
-2-fold separation: GC plus IMS
-Low detection limit of siloxanes: ~0.03 mg/m3

•Easy to use:
-Manual measurement with 'single-click' menu
-Automatic on-line (24/7) monitoring
-Automatic data transfer

•Short runtime:
-Between 20 and 60 minutes

•Low costs:
-Only requires power and nitrogen (5.0)

•EU Patent:
-EP 2 798 343 B1

So far the **common way** to monitor the silicium amount is to **take a gas sample** using a sample bag and analyse it in a remote analytical laboratory using thermo desorption plus gas chromatography-mass spectrometry (TD GC-MS) acc. to EN ISO 16017-1:2000. The lab testing though is highly inefficient as the utility operators are suffering a significant **information delay** regarding filter breakthrough and gas quality. Due to the **high costs** of filter material, filter loads should be used to their maximum capacities. Decisions of changes have to be taken within hours to protect the engines and run the plant within the gas quality related specification range.

The **GC-IMS-SILOX** by G.A.S. (Figure 2) allows an **easy and reliable** on-site test performing a 24/7 on-line monitoring of siloxanes same as 'Total Si' (Si) at **lowest concentration levels.** It further allows the monitoring of **terpene** concentrations.

Figure 2: GC-IMS-SILOX

Experimental Set-up

The GC-IMS-SILOX allows to test for siloxanes on-site (Figure 3) using a by-pass set-up directly connected with the gas pipe. The sample is sucked into the instrument by an integrated pump and circulates through a 6-port-valve into the sample loop. By switching the valve (automatically) the carrier gas feeds the sample into the chromatographic column for the first (matrix) separation before it elutes into the IMS for the second separation step (and co-eluting compounds are separated). This set-up guarantees the exact determination even at low concentration levels.
The total run time for the analysis is compound dependent and lasts up to max. 60 minutes (typical run time of 20 to 40 minutes).


Figure 3: GC-IMS-SILOX on-site at a landfill site

The system is calibrated using test gases generated by certified permeation tubes and double checked by a certified test gas from a cylinder. For highest accuracy requirements the system has an integrated and easy to use **one-point re-calibration** function.
With specific compound concentrations of a certified test gas the customer can recalibrate the system on-site.
Terpenes are not calibrated and reported with in arbitrary units.
Testing parameters of the GC-IMS-SILOX are listed in table 1.

Technology	**Gaschromatography-Ion Mobility Spectrometer (GC-IMS)**
Ionisation Source	**Tritium - Below exemp limit in EURATOM and US NRC licence**
Operating Gas	**Nitrogen 5.0**
Carrier Gas Flow **Drift Gas Flow**	**5 - 15 mL/min (flow ramping)** **150 mL/min**
GC Column	**MXT 5: (5% Diphenyl, 95 % dimethyl polysiloxane)** **30m x 0.32mm x 1.0µm**
Column Temperature **IMS Temperature**	**80°C** **65°C**
Sample Loop Volume	**1000 µL**
Pump Flow	**150 mL/min**

Table 1: Experimental parameters

Operational Aspects and Results

The GC-IMS-SILOX is permanently flushed with nitrogen (5.0 quality) supplied by a cylinder or a nitrogen generator to assure its cleanness and by that its sensitivity. All measurement results are given on the display of the GC-IMS-SILOX (figure 4). The available monitoring mode allows to define and automatically trigger measurements at user defined intervals. Typically 'Total Si' as result is automatically transferred via current loop or MODBUS (TCP) to a control room for process monitoring.

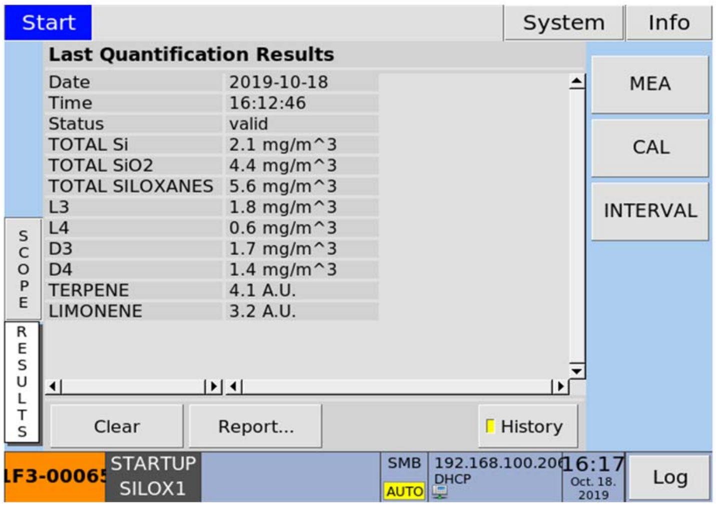

Figure 4: GC-IMS-SILOX result window. L2, L4 and D4, D5 are displayed same as the calculated concentration for total siloxanes, silica and silicon. Terpene and Limonene content are displayed in A.U.

Data Analysis

The individual siloxanes exhibit a characteristic retention and additionally specific drift times in the ion mobility spectra (Figure 5). The GC-IMS-SILOX reports the content of siloxanes same as the 'Total Si' content within the measured gas sample in a fast and userfriendly way. Confirmed by a multi-point calibration (figure 6) an immediate conversion of IMS-signals from defined monitoring areas into siloxane concentrations is assured. On request the GC-IMS-SILOX can test and report the content of Limonene and Terpenes in arbitrary units (A.U.) (Figure 4).

Figure 7 shows three GC-IMS fingerprints of which the first one is a test-gas mixture of L2, L3, D4, L4 and D5 diluted in N2. The 'compound windows', represented as topographic plot, are shown by the red rectangles. Next to this lab sample the GC-IMS fingerprints of real biogas samples are displayed. These samples are taken downstream at the end of the purification process including siloxane condensation and filtering with active carbon. Thanks to its remarkable sensitivity the residual siloxanes can be identified and quantified. The two real samples were taken with 10 days difference and taken from the same organic waste feed. All siloxanes (marked in red) and terpenes (marked in yellow) signal areas are clearly separated from other volatiles present in the biogas. Especially the increase in D4 concentration reveals that the filter is about to be saturated approaching its breakthrough.

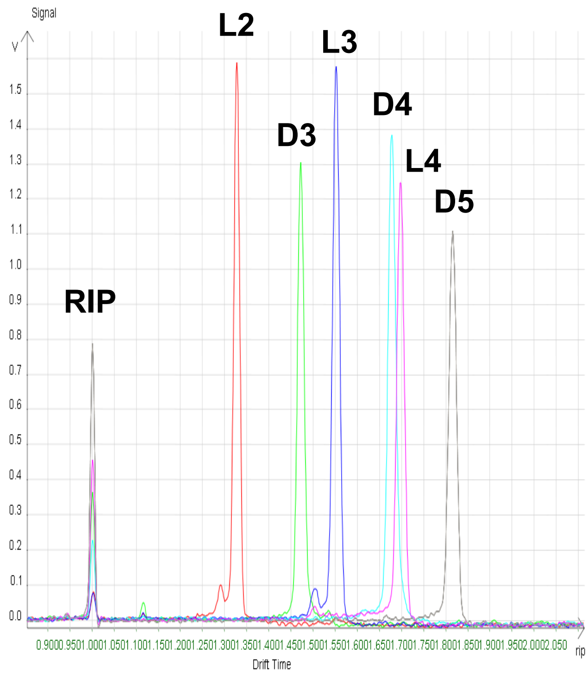

Figure 5: IMS spectra of individual siloxanes

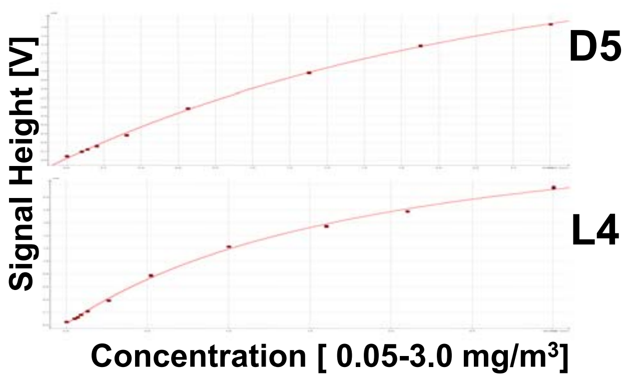

Figure 6: By using certified permeation tubes and sophisticated gas-dilution various headspace concentrations of the siloxanes are achieved to create a multi-point calibration curve; e.g.: D5, L4

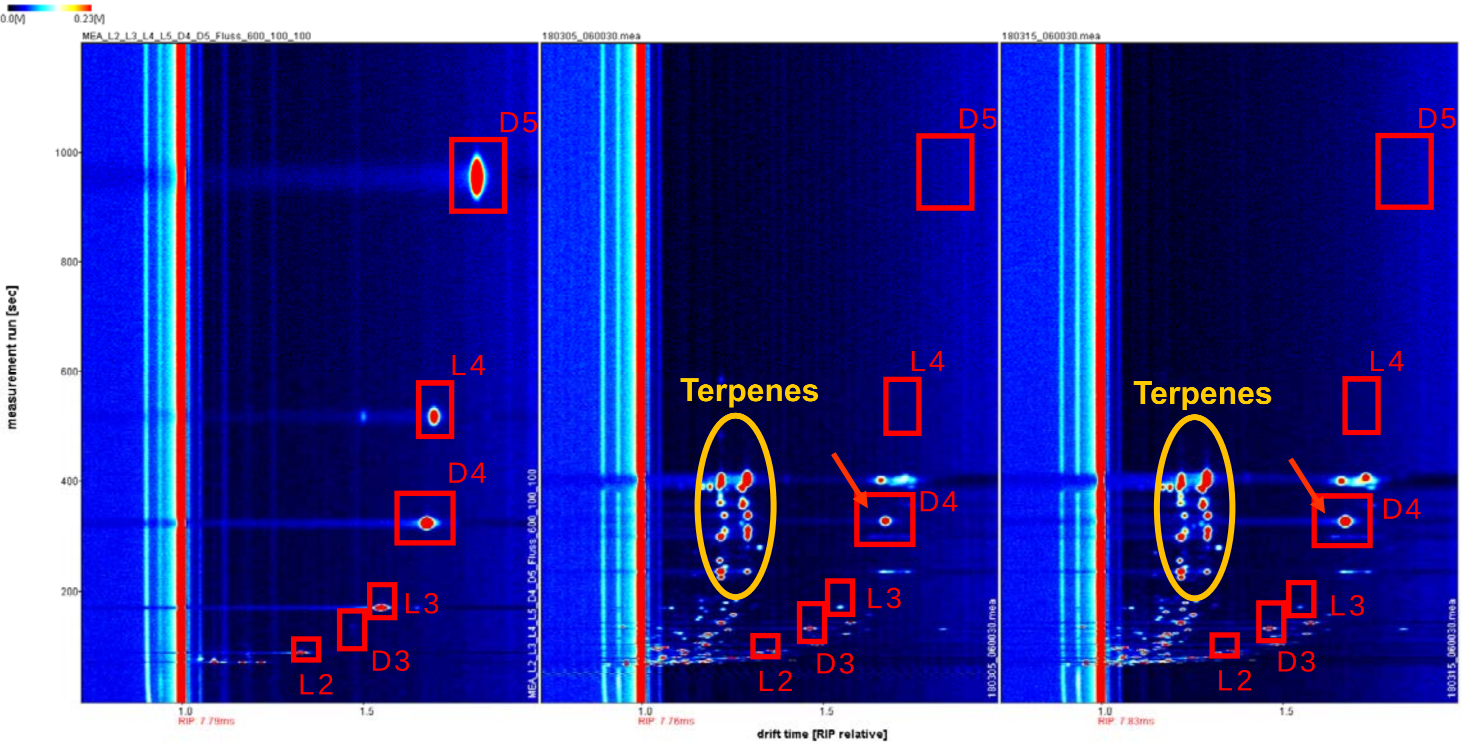

Figure 7: GC-IMS chromatograms of calibration gas in nitrogene (left) and of landfill gas (middle/right)

The sample in the middle is taken 10 days before the one shown in the right chromatogram. D4 concentration is significantly increased from 0.1 mg/m³ to 0.8 mg/m³. Also other markers increase and indicate that a filter-breakthrough is occurring.

Proficiency Test

Since several years, considerable effort has been put into the development of measurement standards for the siloxane content in biomethane and upgraded biogas.

These efforts have paved the path VSL to organise a proficiency test. VSL the National Metrology Institute of the Netherlands, is an internationally authoritative knowledge institute in the field of metrology. The proficiency test aims at assessing the performance of laboratories determining the contents of siloxanes in biomethane and upgraded biogas.

Round Robin 2019: The test was operated in accordance with ISO/IEC 17043.

A gas mixture containing the siloxanes L2, L3, D3, D4 and D5 was prepared and analyzed by GC-FID several times. The concentration for each single siloxane was between 0.4 and 3.0 ppm.

The proficiency of the laboratories was evaluated using Z-scores.

Def.:“A *Z-Score* is a statistical measurement of a score's relationship to the mean in a group of scores.“

A total of seven laboratories signed up for this proficiency test, including G.A.S. using the GC-IMS-SILOX system. Table 2 gives an overview of the Z-scores for each of the 7 laboratories. From the table below it becomes obvious that the results achieved by G.A.S. are satisfactory for all investigated siloxanes.

Lab ID	L2	L3	D3	D4	D5
L001	0.13	-0.13	0.37	0.32	1.04
L002	-0.98	1.24	4.18	3.60	6.33
L003	3.46	1.96	0.86	-0.20	0.95
G.A.S.	-0.62	0.97	1.30	0.01	0.48
L005	-0.15	3.10	2.97	4.12	3.76
L006	0.56	0.84	7.15	0.03	-0.53
L007	0.16	3.47	3.21	6.77	2.44

* |Z|<2 Satisfactory Results
2<|Z|<3 Questionable Results
|Z|>3 Unsatisfactory Results

Table 2: Proficiency test Z-scores* per participant for each component

Summary

- The GC-IMS-SILOX is an analytical tool with an outstanding selectivity and sensitivity starting from 0.03mg/m^3 (5ppb) to precisely quantify the individual siloxanes L2, L3, L4, D2, D3, D4 and D5 in landfill/sewage gas (D6 and other silicon containing compounds on request).

- Calibrations of the system regarding the ’Total Si’ are available from 0.1-5mg/m^3 and by that cover the most relevant range of 0.3 to 1.0 mg/m^3 (acc. to EN 16723-1 & 2). On request, other measurement ranges can be implemented.

- Limonene and Terpenes are reported in arbitrary units (A.U.).

- The system is either operated manually with a single-click menu or works fully automatically and is rugged enough to be installed directly on-site. This allows the continuous (24/7) monitoring of siloxane quantities within the landfill/sewage gas and e.g. to control a filter breakthrough at a very early stage via common protocols.

- By this the lifetime of power generators can be extended, expensive re-investment same as costly down times can be avoided. Filter loads can be used to their optimum life span and unnecessary/early filter changes can be avoided.

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