Sensitive on-site Test of Siloxanes

GAS

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 waste, 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 silicium (Si), Oxygen (O) and methyl groups (CH_3-) and are generated in their cyclic as well as linear molecular structure. Typical siloxanes, which typically can be found in landfill/sewage gas are listed in table 1.

Siloxanes	
Hexamethyldisiloxane	L2
Octamethyltrisiloxane	L3
Decamethyltetrasiloxane	L4
Dodecamethylpentasiloxane	L5
Hexamethylcyclotrisiloxane	D3
Octamethylcyclotetrasiloxane	D4
Decamethylcyclopentasiloxane	D5
Dodecamethylcyclohexasiloxane	D6

Table 1: List of linear and cyclic siloxanes

Technical Context

Landfill/sewage or bio-gas 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 engine and especially moving parts like valves and/or pistons will be damaged (figure 2).

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 mg/m^3.

Figure 1: Landfill site

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 the gas quality. Due to 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. allows an easy and reliable on-site testing and a 24/7 on-line monitoring of siloxanes same as 'Total Si' (Si) at lowest concentration levels.

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

- 2-fold separation of GC plus IMS
- Manual measurement with 'single-click' menu
- Automatic on-line (24/7) monitoring
- Detection limit of siloxanes: ~0.03 mg/m^3)
- High reproducibility and accuracy
- Low costs (needs only power and nitrogen)
- Patent Application (EP12 816 669.1)

Figure 2: Defects on engine parts due to silica

Experimental Set-up

Using the GC-IMS-SILOX (figure 3) allows to test for siloxanes on-site using a by-pass set-up directly connected with the gas pipe. The gas matrix is separated by the use of a gas chromatographic column isothermally operated at 80° C together with a flow ramping for better separation. Subsequently compounds are separated by the IMS, the difference drift time allows to separate co-elutiong compounds. The experimental parameters of the GC-IMS-SILOX system are listed in table 2. If needed the sampling can additionally be improved with a liquid separating (GENIE-) filter to prevent any condensation water can enter the analyzer. The sample is sucked into the instrument by an integrated pump with flow of 150mL/min. and guided through the heated 6-port-valve. By switching the valve a gas sample is taken and introduced to the chromatographic column for the first (matrix) separation step before it elutes into the IMS ionization chamber. The total run time for the analysis is compound dependent and lasts maximum 35 minutes (when incl. L5). If the detection of D6 is required the run time is extended to approximately 60 min. The system is calibrated using test gases generated by certified permeation tubes or certified test gases from cylinders.

For an optimum quantification the system has an easy to use on-site re-calibration function: a one-point calibration is implemented into the customized firmware and as calibration test gas it is possible to use either a certified permeation tube e.g. of D4 or a certified test gas from a cylinder.

Technology	Gas chromatography-Ion Mobility Spectrometry (GC-IMS)
Ionisation Source	Tritium (300MBq - below ex-emption limit in EURATOM)
Carrier-/Drift gas	Nitrogen 5.0
Carrier gas flow rate	Linear flow ramping from 5- 15 mL/min
GC column	30 m (5% Diphenyl, 95 % dimethyl polysiloxane) x 0.44 x 0.32. mm MXT5
Column Temperature IMS Temperature	80°C isothermal 45°C isothermal
Sample Loop volume	1 mL

Table 2: Experimental parameters

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

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. When operated manually by the 'single-click' menu test results are given on the display of the GC-IMS-SILOX (figure 5). The available monitoring mode allows to define and automatically trigger measurements at user defined intervals. Test results output of the total amount of silicon ('Total Si') is provided either via current loop or MODBUS (TCP) and can be transferred to e.g. a control room for continuous process control and engine protection.

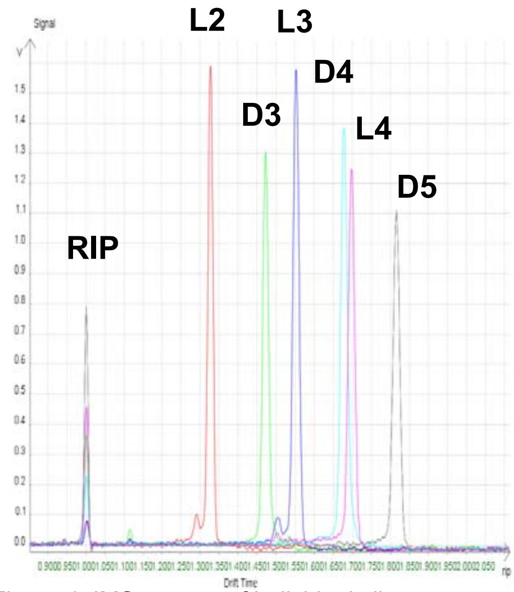

Figure 4: IMS spectra of individual siloxanes

Data Analysis

The individual siloxanes exhibit a characteristic retention and additionally specific drift times in the ion mobility spectra (figure 4). The GC-IMS-SILOX instrument can report the content of siloxanes same as the 'Total Si' content within the measured gas sample in a fast and user-friendly way (figure 5). Underlaying is a thorough calibration effort (figure 6) which makes it possible to immediately convert measured IMS-signals from pre-defined monitoring areas into siloxane contents.

Figure 7 shows three GC-IMS fingerprints of which the first one is a test-gas mixture of L2, L3, D4 and D5 diluted in N_2. The 'compound windows' 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 which also includes 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 originate from the same organic waste feed. All siloxane signal areas are clearly separated from other volatiles (e.g terpenes marked in yellow) present in the bio-gas. Especially the increase in D4 concentration reveals that the filter is about to be saturated approaching its breakthrough.

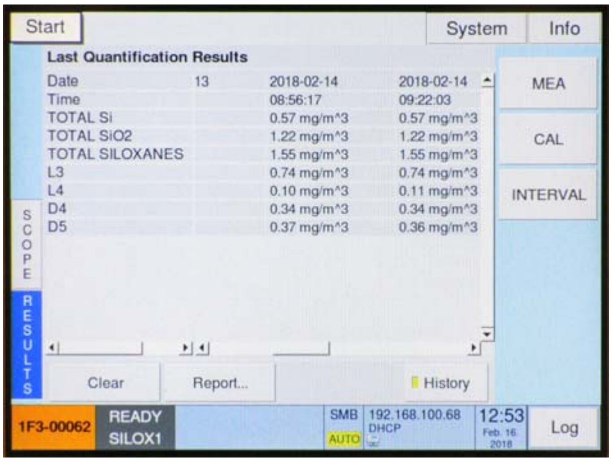

Figure 5: GC-IMS-SILOX result window. L2, L4 and D4, D5 are displayed same as the calculated concentration for total siloxanes, silica and silicon.

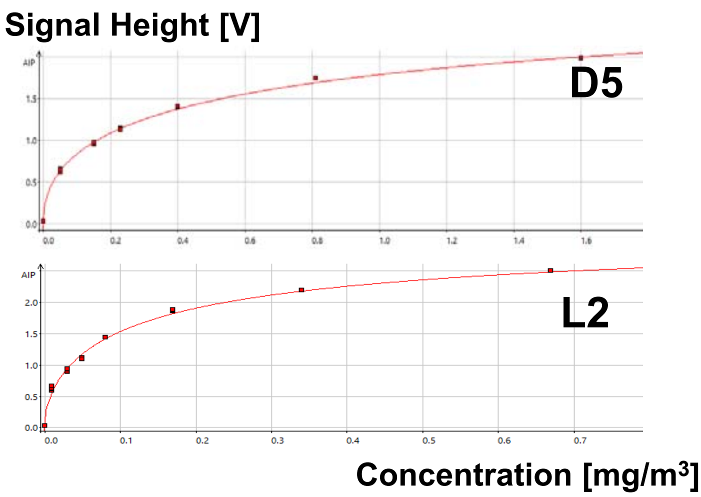

Figure 6: By using certified permeation tubes and sophisticated gas-dilution various headspace concentrations of the siloxanes are achieved to create a calibration curve; e.g.: D5, L2

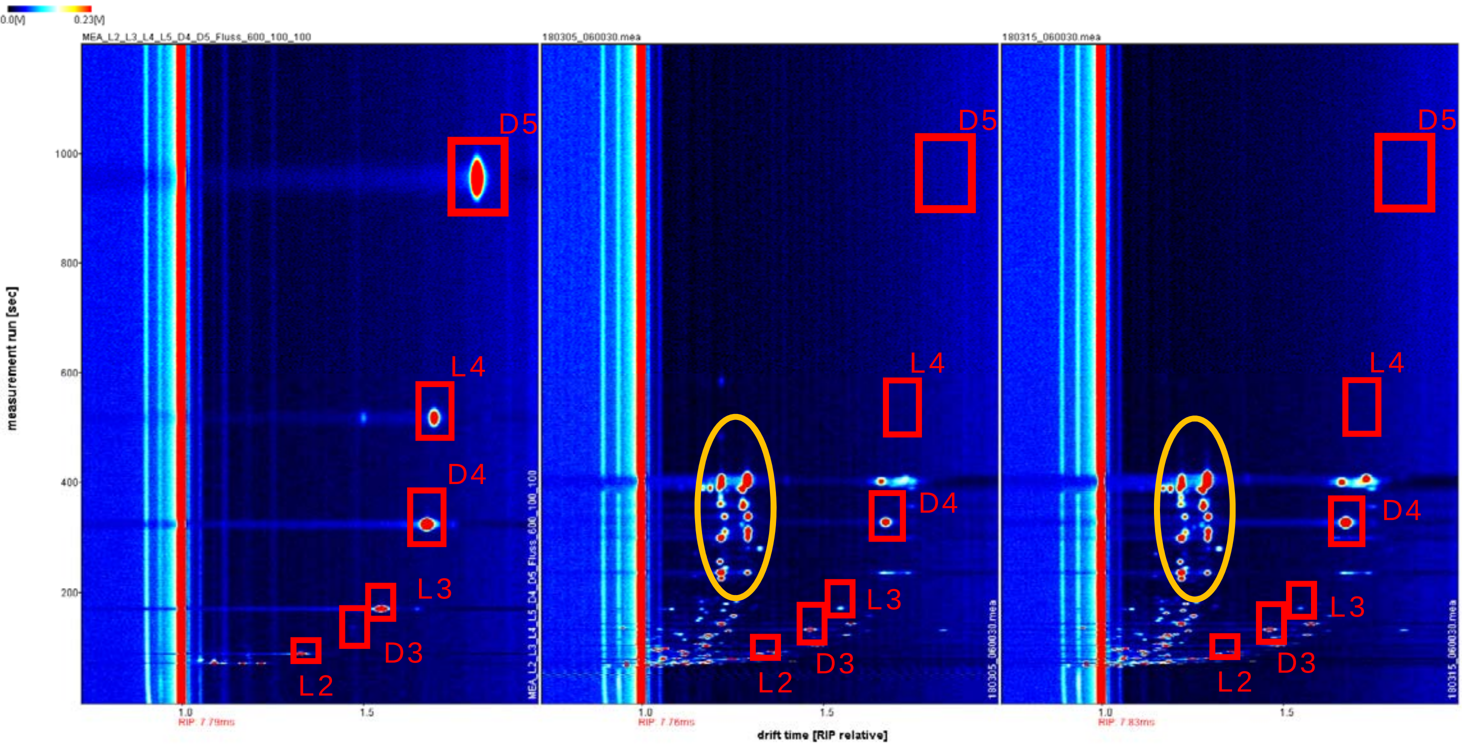

Figure 7**:** 3 GC-IMS chromatograms of landfill gas
Left: A calibration mixture containing L2, L3, D4, L4 and D5 signals marked in red. D3 is not present.
Middle/Right: The complex GC-IMS fingerprints represent real biogas samples. Beside the siloxanes L2, D3, and traces of L3, D4 it is possible to see higher signals from terpenes (yellow oval). 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/m^3 to 0.8 mg/m^3. Also other markers increase and indicate that a filter-breakthrough is occurring.

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.

- 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 life time 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.

Please contact:
G.A.S. Gesellschaft fuer analytische Sensorsysteme mbH, Otto-Hahn-Str. 15, 44227 Dortmund, Germany
Phone : +49 231 9742 6550, Mail: **info@gas-dortmund.de** , Website: **www.gas-dortmund.de**