Siloxane Measurement in Land-Fill Gas via FTIR

What are siloxanes?

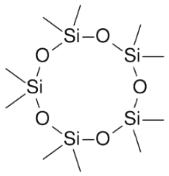

Fig 1 - Siloxane molecules find their way into biogas

The generation of electricity from municipal digesters and land fill is of increasing interest, as the biogas generated is a form of renewable energy. Organosilicon compounds are often present in products such as shampoo and cosmetics, as well as industrial products and lubricants, and they move into land-fill. These volatile compounds find their way into land-fill or digester gases as siloxanes.

Problems caused by siloxanes

Siloxanes are low-level hazards to the atmosphere in terms of their emissions, however when they are combusted in gas engines the hard silica that is produced is very harsh to the moving parts of the gas engine. Ultimately this increase maintenance cost and gives a lower energy output, making the generation of power less efficient. With this ever-growing market, the need for analysis of the siloxane content of the biogas pre-generator is important. A land-fill gas plant operator can determine the amount of siloxane removal of the pre-combustion feed gas. This enables a more cost-effective cleaning system to be employed. They can also determine whether an existing clean-up system is operating effectively.

atmosFIR Solution

There is currently no standard method for gaseous siloxane measurement and to date no on-line gas process monitoring system. The usual method of gas analysis has involved the extraction of a sample gas, via bag or cylinder, and analysis off-plant. Sampling losses of siloxanes inevitably occur, as the sample can be adsorbed on to the sample container wall. The common method of analysis is absorbing into a liquid and analysis via GC-MS or GC-FID, but this is not a direct reading of the gaseous sample.

Protea has developed an analytical model for our atmosFIR FTIR gas analyser that allows speciation of siloxanes on-line. The full spectrum technique of FTIR also allows for the measurement of the main gas components, CH_4, CO_2, NH_3 etc. A range of common siloxane and other species found in land-fill gases has been identified, see Table 1. The siloxanes present can vary from different land-fill sites, different sewage plants and other sources, but Protea has found this list to cover most straight and cyclic siloxane compounds present. Trimethylsilanol, while not a siloxane, can lead to siloxane formation and is so included in the analytical model.

Although absorption features of the siloxane groups are similar, there are small changes in response due to the underlying vibrational frequency difference of the molecules. This enables us to “fingerprint” each species of siloxane and generate an accurate analytical model of the biogas process.

Siloxane Full Name	Component	Boiling Point / °C	Mol. Wt.
Pentamethyldisiloxane	PMDS	86	148.35
Hexamethyldisiloxane	L2	101	162.38
Hexamethylcyclotrisiloxane	D3	134	222.46
Octamethyltrisiloxane	L3	153	236.53
Ocatmethylcylclotetrasiloxane	D4	175-176	296.62
Decamethyltetrasiloxane	L4	194	310.69
Decamethylcyclopentasiloxane	D5	211	370.77
Dodecamethylpentasiloxane	L5	230	384.84
Dodecamethylcyclohexasiloxane	D6	245	444.93
Trimethylsilanol	TMS	98-99	90.12
Methane	CH_4	Background Gas	16.04
Carbon Dioxide	CO_2		44.01
Hydrogen Sulphide	H_2S		34.08
Ammonia	NH_3		17.03

Analysis

The measurement of siloxanes in the Mid-IR spectrum is in the absorption region 850 – 1250cm^{-1}. Here we find the IR absorptions due to the Si-O stretch, with interference from CH_4 at a minimum, See Figure 2.

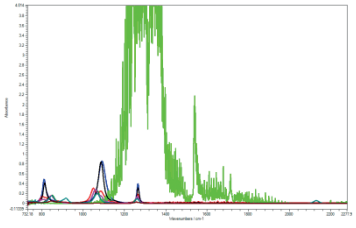

Fig 2 – High levels of methane have little interference with the absorption of siloxanes.

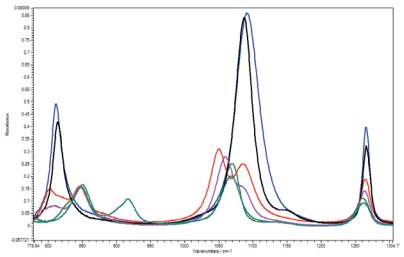

Fig 3– The FT-IR spectra of siloxanes overlap but are subtly different.

Chemometrics

Protea prides itself on the generation of accurate calibration information, and on incorporating this into an application specific chemometric model for the application. For siloxane analysis we use PLS modelling techniques, which are able to find the subtle differences in our calibration spectra, and then use this information to predict concentrations. Thus allowing speciation and quantification of each siloxane.

In addition we also model the interfering responses due to CH_4 and CO_2, to allow us to accurately account for the overlapping absorbances of background gases.

Systems

Protea's atmosFIR FTIR analyser can be supplied with the suitable performance specifications for each application. The detection limits for this standard siloxane analysis model are summarised in Table 2. These values are calculated using our standard product. For customers with specific needs these can be improved upon by making modifications to the hardware and data collection parameters. atmosFIR FTIR analyser use DTGS detectors for siloxane measurements. Other FTIR systems employ the temperature cooled MCT variety of detectors. These MCT detectors have a limited IR detection range and cannot detect all the absorption peaks due to siloxanes. In order to analyse spectral absorptions below 950cm^{-1}, MCT detector require cryogenic cooling – not ideal for fixed, hassle-free continuous monitoring.

Species	PMDS	L2	D3	L3	D4	L4
LDL/ppm	0.0041	0.0215	0.0145	0.0033	0.0144	0.0029
Species	D5	L5	D6	TMS		
LDL/ppm	0.0036	0.0291	0.0036	0.691		

Table 2 – Lower Detectable Limits (LDL) for siloxanes.

Measurements

Resulting data from online runs on land-fill gives the predominant siloxane species in this case to be D4, Octamethylcyclotetrasiloxane, with traces of other siloxanes.

Species	PMDS	L2	D3	L3	D4	L4
Conc. / ppm	0.5	0.66	0.01	0.29	1.25	0.37
Species	D5	L5	D6	TMS	NH3	
Conc. / ppm	0.51	0.01	0.01	1.8	0.59	
Species	CH_4	CO_2				
Conc. / %Vol	43.12	34.47				

Table 3 - Speciated and Total Siloxane Measurements from Land-Fill Gas on Inlet to Chiller

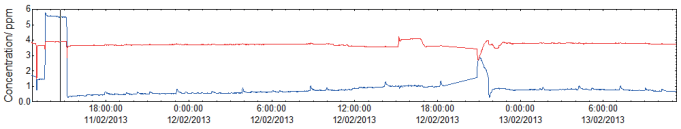

Fig 4 – Trends in D4 and L2 over time measured by Protea analyser software (PAS)

Protea's continuous monitoring systems can be set-up to read speciated siloxanes or Total Siloxanes, whichever is most required. As well as the siloxane measurement, the quantification of background gases of CH_4 and CO_2 helps to control and improve the overall biogas process.

With the power of atmosFIR, we can also identify other species present in biogas, such as NH_3 and sulphurous compounds such as H_2S and Mercaptans. This provides the complete analytical tool for the biogas plant.

Supplier: