

Monitoring Siloxanes in Biogas Using Thermal Desorption Tube Sampling

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Abstract

For the use of biogas as fuel, it is necessary to remove impurities like the siloxanes that can cause significant operational problems in engines. The selection of an efficient sampling technique for biogas analysis is a key step to reliable results. The canister sampling technique have been used, but it's not suitable for heavier siloxanes. In this work, the canister was compared with the sorbent tube sampling technique regarding the quantitative recovery of higher-boiling siloxanes. The subsequent sample analysis was done by a thermal desorption (TD) capillary GC-MS analytical procedure. Canisters showed inherent recovery limitations for lower-volatile siloxane species, resulting in poor recovery. This bias was less apparent when sampling onto tubes.

Introduction

There is an increased need for power generation using biogas from landfill sites, wastewater treatment plants and anaerobic digesters. However, biogas can contain high levels of siloxanes, which are a common addition to consumer products and do not decompose in the activated sludge process. Silicones contained in anti-foaming agents biodegrade to siloxanes. During combustion of biogas, siloxanes are converted to silicon dioxide particles, which build up and can cause significant damage to turbines and other motors. As a result, monitoring the levels of siloxanes in biogas has become an important topic.

Thermal desorption (TD) is an ideal technique for the analysis of trace-level siloxanes in biogas. It provides both analyte concentration and efficient transfer/injection into the GC analytical system. Samples have historically been collected with canisters, but this has proven troublesome, particularly for the heavier compounds¹, which are major impurities of biogas. Considering that sorbent tubes have demonstrated recovery of much higher-boiling VOCs (up to n-C40)², quantitative recovery of these higher-boiling siloxanes should be simple, and demonstrating this was the aim of this study.

Experimental

The study was split into two parts, with analytical standards being prepared on tubes and canisters.

Siloxane analysis using sorbent tubes

A Markes International TD-100™ system (Figure 1), a thermal desorber ideal for high throughput of up to 100 sorbent tubes was used. A mixture of Carbograph™ 2TD and Carbograph 1TD sorbents was used.

A nominal 1000 ng/μL bulk liquid solution was prepared in methanol. The analytes added to the solution are presented in Table 1. A typical chromatogram obtained is displayed in Figure 2. Good chromatography is observed for all the siloxanes in the mix, including the heaviest, D5 and L5. Interestingly, a large amount of D4 is observed, indicating an impurity in the standard solution. TMS is present in much lower quantity than the siloxanes; indeed, it had completely disappeared upon later re-analysis, confirming its instability in methanolic solutions.



Figure 1: Markes' TD-100 automated tube system.

Table 1: Composition of liquid and canister standard

Analyte	Abbreviation	Retention Time (min)	Extracted ion (m/z)
Trimethylsilanol	TMS	12.6	75
Hexamethyldisiloxane	L2	14.9	147
Hexamethylcyclotrisiloxane	D3	21.3	207
Octamethyltrisiloxane	L3	23.8	221
Octamethylcyclotetrasiloxane ‡	D4	28.3	281
Decamethyltetrasiloxane	L4	31.0	207
Decamethylcyclopentasiloxane	D5	34.2	267
Dodecamethylpentasiloxane	L5	37.0	369

‡ - analytical reference standard out of stock - not present in liquid standard

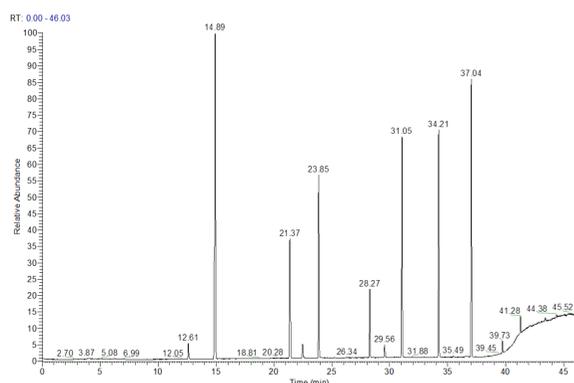


Figure 2: Chromatogram of a 1000 ng/μL siloxane standard in methanol.

Standards were prepared over the range 10–1000 ng/μL. 1 μL of each was spiked onto sorbent tubes using Markes' Calibration Solution Loading Rig™. Good linearity (Figure 3) was observed across the range for compounds L2 to L5, but TMS was not linear due to its degradation in the standard solution.

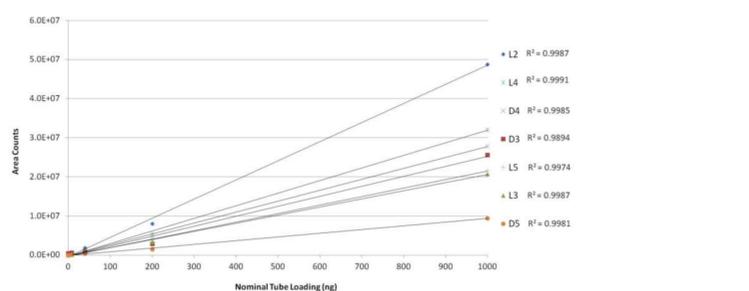


Figure 3: Regression lines for siloxane standards spiked on to sorbent tubes.

Experimental - continuation

Siloxane analysis using Canister

A Markes International CIA Advantage™ system (Figure 4) was used for analysis of the canister samples. The heated flow path (max. 200 °C) maximizes the sample transfer through the system. Internal standard addition conforms to US EPA Method TO-15. The system is able to sample over a wide range of volumes from 0.5 mL to several litres by a combination of sample loop and/or metered flow sampling. Accurately measured volumes are collected on an electrically cooled focusing trap in the UNITY™ thermal desorber/preconcentrator.



Figure 4: Markes' CIA Advantage system.

A canister sample was prepared in a 6 L Summa canister. The canister contained siloxanes and TMS at a nominal concentration of 55 ppbv in nitrogen. Volumetric samples were taken from the canister over the range 10–500 mL. A typical chromatogram obtained is displayed in Figure 5. The difference between the tube and canister samples is quite marked. The absence or low recovery of the least volatile siloxanes (L4, D5 and L5) is quite apparent from the canister sample, and is demonstrated further by the drop-off in response for the linearity studies (Fig. 7).

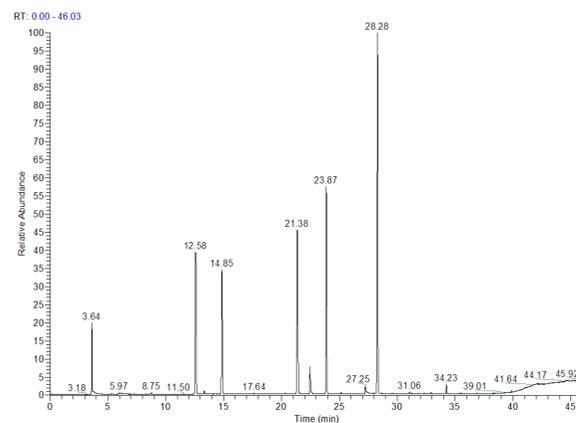


Figure 5: Chromatogram of a 500 mL sample of 55 ppbv siloxane canister standard in nitrogen.

Linearity is best observed for the most volatile species, TMS and L2, where the regression is excellent, indicating good performance of the CIA Advantage system. As the volatility reduces, so does the linearity, as recovery at higher volumes drops off. This gives an indication that recovery of semi-volatile siloxanes is more difficult from canisters than tubes.

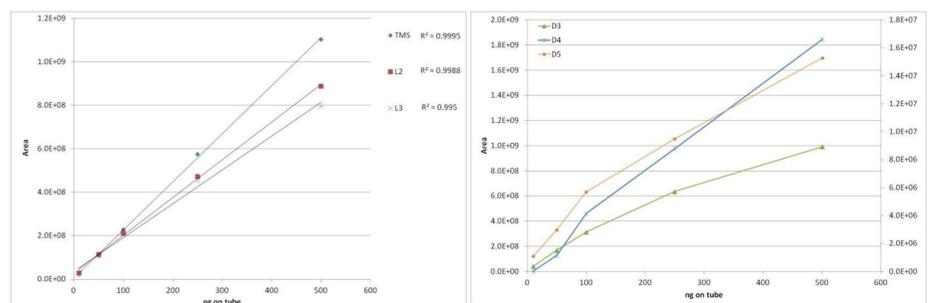


Figure 6: Regression lines for a canister siloxane standards. The curve for D5 is plotted against the secondary vertical axis to allow it to be displayed to scale.

Further work

Real-world samples will be collected, and sorbent tubes compared directly with canister samples.



With sorbent tubes, samples can be collected with either the Easy-VOC™ grab-sampler (Figure 7) or the ACTI-VOC™ constant-flow pump (Figure 8). The ACTI-VOC is a robust low-flow pump for sampling vapour-phase organic compounds (VOCs) onto sorbent tubes. Being lightweight, easy-to-use and intrinsically safe, ACTI-VOC is ideal for use in a wide range of air and gas sampling applications.



Figure 7: Markes' Easy-VOC grab-sampler.



Figure 8: Markes' ACTI-VOC constant-flow sampling pump.

Further work will also consider the effect of matrix on the samples, as landfill biogas is highly humid. A hydrophobic tube with graphitized carbon black will be used (in the standards tests carried out, a mixture of Carbograph 2TD and 1TD was used). Sample sizes will also be kept low to avoid collection of excess water on the tubes, aided by dry-purging of the tubes to help remove any residual water prior to chromatography.

Conclusion

This short study has demonstrated that the TD-100 tube-sampling system and the CIA Advantage canister sampler can analyze siloxane species.

There is clear evidence that canisters show inherent recovery limitations during the analysis of lower-volatility siloxane species, resulting in poor recovery. This bias is less apparent when sampling onto sorbent tubes and using the TD-100 system for analysis.

References

- S. Saeed *et al.*, Comparison of impinger and canister methods for the determination of siloxanes in air, AMWA Symposium of Air Quality Measurement Methods and Technology, San Francisco, CA, 13–15 November 2002.
- Markes International, Application Note 053, Quantitative recovery of high boiling point (>450 °C) semi-volatiles organic compounds using thermal desorption coupled to GC-MS.