Monitoring of Siloxanes in Landfill and Digester Gas using Advanced Silonite™ Coated Canisters

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Abstract

A complete monitoring solution for the measurement of Siloxanes from 10-2500 PPBv in Landfill and Digester Gas is presented.   Stainless steel vacuum sampling canisters with a newly improved Silonite ceramic surface improves the storage and recovery of siloxanes out through L5/D6 with demonstrated holding times of at least 2 weeks.   Improvements in GCMS sample preconcentration systems allows all siloxanes from Trimethyl Silanol (TMS) through D6 to be analyzed in a single GCMS analysis, with linear calibrations from 10 - 2500 PPBv, with or without the use of liquid nitrogen. A new robotic autosampler is also presented that creates only momentary contact with the sample, vastly reducing carryover and memory effects relative to previously used rotary valve autosamplers that maintain contact with the sample for up to several days.   Calibration curves, method detection limits, and holding time studies are presented.

Background

The accurate measurement of siloxanes in landfill and waste water digester gas continues to grow in importance.   The use of Siloxanes in cosmetics, shampoos, and an ever growing number of consumer products is continuing to increase the concentration of these compounds in waste water and landfills.   Due to the high volatility of Siloxanes with a molecular weight below 450 g/mole, relatively high concentrations of siloxanes are able volatilize into the methane biogas that is produced during wastewater treatment. More and more facilities are being constructed to produce energy by burning the biogas to produce electricity, but the presence of siloxanes results in the production of Silicon Dioxide (SiO2) deposits during combustion.   These deposits reduce the life span of the turbines, resulting in larger investments in plant maintenance.   Filtering systems are being used to reduce siloxane concentrations prior to the combustion process, but the efficiency of the filters must be evaluated regularly to ensure that breakthrough has not significantly occurred.   Accurate monitoring of volatile siloxanes is necessary to maintain the longest possible operation of the power generation systems without costly interruptions.

Several methods for collection and analysis of siloxanes have been shown in the literature, including collection by SUMMA canisters, Tedlar bags, impingers, and adsorbent media. Typically, the whole air technique using canisters has been preferred due to the ease of sampling, lower detection limits, and improved quantitative accuracy. Unlike hydrocarbons where carbon forms the back bone of the molecule, siloxanes have a repeating silicon oxygen structure that tends to be less stable than hydrocarbons, creating a challenge for their collection and accurate analysis days or weeks after collection. The lower level of chemical stability make siloxane collection on adsorbent tubes followed by thermal desorption unreliable.

However, whole air collection into vacuum sampling canisters leaves the sample unconcentrated and in the gas phase while awaiting analysis where reactions of siloxanes can be virtually eliminated.

The key to stability of siloxanes is to keep them in the gas phase rather than adsorbed where surfaced induced catalysis can alter their concentrations. Therefore, it is important to use canisters with properly passivated internal surfaces that will not adsorb siloxanes. Earlier attempts to use metal oxide lined SUMMA canisters showed poor recovery of L5, D5, and D6 Siloxanes. Recently, however, a new ceramic coating called Silonite-S is allowing the heavier Siloxanes to also remain in the gas phase for 2 or more weeks after sampling, allowing the accurate quantitation of all volatile Siloxanes. Although neither L5 or D6 tend to be the higher concentration constituents of Landfill and Digester Gas, their concentrations are not insignificant, and they are good indicators of the overall performance of the analytical system. When L5 and D6 numbers are consistent, the accurate measurement of more abundant D4/D5 compounds is ensured.

Getting the sample to the analyzer while still at or near original concentrations of the collected siloxanes is only the first challenge. Managing a large number of samples without carryover is yet another. Concentration systems originally developed for ambient levels of VOCs at low to sub PPB concentrations relied heavily on 16 position rotary valve autosamplers to automate the introduction of samples into the GCMS preconcentrator. Long exposures to these inlet lines with sample canisters connected for 1-3 days or more does not cause an issue for ambient air analysis where all compounds are expected to be within 20x of the method detection limits. However, siloxane measurements may see concentrations vary from 5 to 5000 PPB, so a 1% carryover of the previous sample can result concentrations that are well above the reporting level. To reduce carryover issues, the Entech 7650-M Autosampler was used that only makes contact through a single heated transfer line which is moved

Figure 1 *Silonite-S 1.4L Canister with advanced internal surface coatings providing longer holding times and improved recoveries of the full range of linear and cyclic siloxanes.*

from canister to canister. After sample extraction through a momentary connection through the canister's Micro QT valve, the transfer line is immediately flushed to prevent the absorption and ultimate carryover of the previous sample into the next analysis. This momentary contact and then flushing with UHP nitrogen to clear the inlet line was found to be critical in achieving a linear calibration and minimizing carryover for the heavier siloxanes.

Entech has also introduced the Model 7200 Preconcentrator in the last 3 years that improves flow path inertness and overall system performance. For this application, the 7200 was operated in a mode where cryo cooling was unnecessary to preconcentrate and desorb the TMS through D6 compounds. The 7200 performs a faster injection out of the M2 Tenax trap than does its predecessor, the 7100A, allowing all compounds from TMS through D6 to be quantified in a single analysis. Calibrations, MDLs, and holding time studies have been conducted to show the improvements

Figure 2   The 7650-M/7200 was used for this study on an Agilent 7890/5975. The 7650-M is the only multi-canister autosampler available that uses a single inlet to analyze all canisters, with only momentary contact being made in order to maximize recovery and minimize carryover.

the viscosity to allow accurate syringe transfer into a Silonite canister in the next step. See Table 1 for the amounts used to create the initial cocktail. To create the high level 250PPBv gas phase standard in a 15L Silonite canister, 1.73ul of the cocktail and 250ul of water were injected directly through the stem of the nitrogen filled clean canister with the valve removed to ensure 100% delivery into the canister. Water was added to simulate the relative humidity in ambient air. The canister valve was reattached, and the canister was pressurized to 54 psia (psi absolute) with UHP Nitrogen. After 1 day of equilibration, the 250 ppbv standard was further diluted down to 10 PPBv into a 6L Silonite canister using an Entech model 4700 Precision Dilution System . Both the 250 PPBv and 10 PPBv standard were used to perform the method validation and GCMS calibration.

An advanced version of the Entech Silonite canister was used for this study. The Silonite-S surface was specifically engineered to maximize the recovery of gas phase Siloxanes through L5/D6. The analytical

Experimental

Neat material for all siloxane components were obtained from Sigma Aldrich. A simple Excel spreadsheet was created to determine the volume or weight of each siloxane needed to make an equimolar standard. This amount was added to a vial along with a 2 equimolar volume of hexane to reduce

|	Trap	Sweep	M1-M2	M2-M3
M1 Empty Trap	140C	140C	140C	
M2 Tenax Trap	35C	35C	35C	230C
M3 Focuser	NA	NA	NA	40
Volume (cc)	25cc	75cc	NA	
Flowrate	100ccm	100ccm	NA	

Table 2 - 7200 Trapping Conditions for Siloxane enrichment prior to GCMS Analysis

Table 1 - Neat amounts of Siloxane added to a vial to create the working, liquid cocktail. From this 1.73ul was injected into a 15L canister and pressurized to 54 psi absolute to create the 250PPBv high level standard

Analyte	MW	Density	uL of Analyte
Hexane	86	0.655	26.3
Trimethyl Silanol	90	0.950	9.5
Hexamethyldisiloxane (L2)	162	0.764	21.2
Hexamethylcyclotrisiloxane (D3)	222	1.12	19.8 (mg)
Octamethyltrisiloxane (L3)	236	0.820	20.7
Octamethylcyclotetrasiloxane (D4)	296	0.956	31.0
Decamethyltetrasiloxane (L4)	310	0.854	36.0
Decamethylcyclopentasiloxane (D5)	370	0.958	38.6
Dodecamethylpentasiloxane (L5)	384	0.875	44.0
Dodecamethylcyclohexasiloxane (D6)	445	0.959	46.4

Figure 3 Siloxane sampler. Fully coated to eliminate adsorption during sampling. Includes an internal restrictor to slow down the sampling rate so that the collection can stop after the vacuum has risen from 30" to 10" Hg to keep water from condensing in the canister even when sampling at slightly elevated temperatures up to 35 deg C at 100% relative humidity. In the laboratory, the canister can be pressurized by a factor of 2x using dry, UHP nitrogen without any condensation of water. Keeping the canister completely homogeneous (gas phase with no water condensation) is important to ensure recovery of all siloxanes
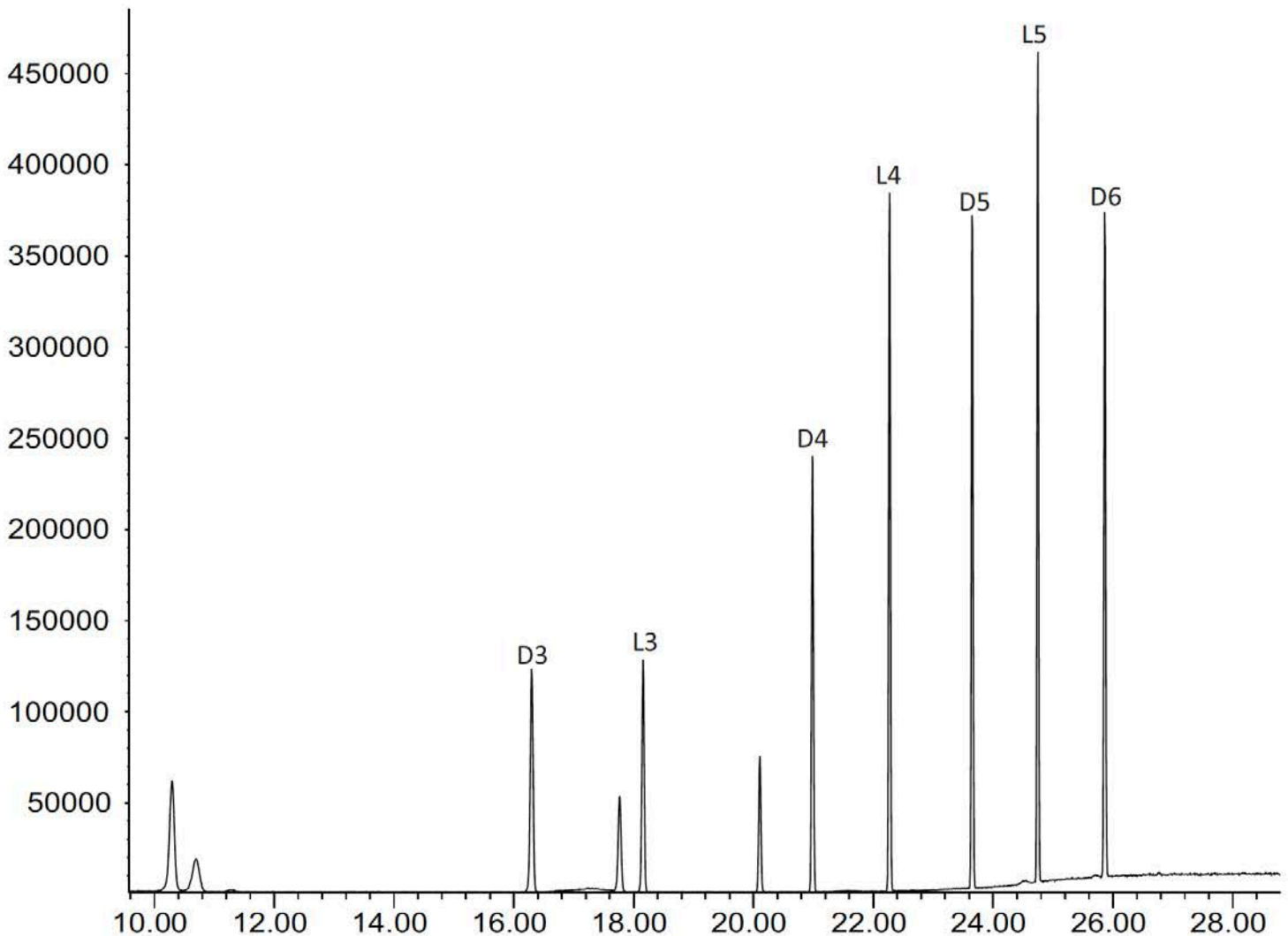
Figure 4 Typical Siloxane analysis showing a 25cc of a 100PPB calibration standard. Calibration standards can be made up using minimal amounts of hexane to create an overall mixture which can be expanded into a canister via syringe transfer.

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Analyte	RF1 10 ppbv	RF2 20 ppbv	RF3 40 ppbv	RF4 100 ppbv	RF5 250 ppbv	RF6 500 ppbv	RF7 1000 ppbv	RF8 2500 ppbv	Avg RF	% RSD
Trimethyl Silanol	0.491	0.539	0.524	0.437	0.47	0.562	0.574	0.531	0.516	9.05
Hexamethyldisiloxane (L2)	1.413	1.707	1.793	1.857	1.357	1.56	1.629	1.656	1.622	10.7
Hexamethylcyclotrisiloxane (D3)	1.591	1.801	1.946	2.084	1.576	1.816	1.919	1.611	1.793	10.4
Octamethyltrisiloxane (L3)	1.081	1.266	1.337	1.419	1.105	1.276	1.373	1.061	1.24	11.3
Octamethylcyclotetrasiloxane (D4)	0.565	0.558	0.52	0.536	0.399	0.469	0.429	0.286	0.47	20.3
Decamethyltetrasiloxane (L4)	0.234	0.28	0.309	0.35	0.262	0.323	0.306	0.221	0.286	15.6
Decamethylcyclopentasiloxane (D5)	0.613	0.677	0.699	0.751	0.541	0.69	0.606	0.465	0.63	14.9
Dodecamethylpentasiloxane (L5)	0.169	0.203	0.22	0.248	0.172	0.232	0.217	0.177	0.205	14.4
Dodecamethylcyclohexasiloxane (D6)	0.234	0.3	0.323	0.361	0.245	0.327	0.33	0.255	0.297	15.6

Table 3 *Siloxane calibration from 10PPBv to 2500PPBv.*

system consisted of an Entech Instruments model 7200 sample preconcentrator with a 7650-M robotic autosampler, coupled to an Agilent Technologies 7890/5975 Gas Chromatograph/Mass spectrometer. Preconcentration parameters are summarized in Table 2. A 0.32mm ID x 60m, 1um PDMS column was used (35C for 4 min, then ramping to 230C, 5 min hold). The MS was operated in full scan EI mode scanning from 33-450 amu.

A sample volume of 25cc was chosen which provided detection down to 2-3 PPBv and quantitation out through 2500PPBv without dilution, as this is the range typically encountered in Digester and Landfill gas.

Results

Figure 1 shows a photo of the system presented, including the 7200 Preconcentrator and the 7650-M robotic autosampler. Figure 2 shows a cut open Silonite-S can, revealing the inert coating used to keep Siloxanes in the gas phase. This same coating is used on the tubing throughout the 7200 and 7650-M, resulting in GC column - like inertness that prevents loss of Siloxanes during sample storage and preconcentration. Figure 3 shows a typical chromatogram with good recovery out through L5/D6 as indicated by the peak heights observed when running an equa-molar concentration standard. Methods were evaluated using both a cryogen free approach as shown here, verses a cryofocusing approach. Both showed good recovery

out through L5/D6, although Trimethylsilanol did show improved performance with cryofocusing due to its higher volatility. However, the unique ions exhibited by TMS should allow good quantitation even with the broader peaks obtained without Liquid Nitrogen refocusing.

The calibration curve shown in Table 3 was made by analyzing 25, 50, 100, and 250 cc of the 10 PPBv standard and 25, 50, 100, and 250cc of the 250 PPBv standard. The electron multiplier of the mass spectrometer was lowered by 200 eV from the autotune value to prevent saturation at concentrations above the 1000 PPBv level, although this will undoubtedly be mass spectrometer dependent. In addition, a split tee in the GC oven was added to further perform a 3:1 split during injection. All compounds showed a linear response well within requirements of other EPA canister based methods. However, attempts to create linear calibrations without going through the single heated line of the 7650-M failed to create a linear response for D5, L5, and D6, all of which showed %RSDs greater than 40%. Only by using the 7650-M to draw the sample directly from the canister into the heated transfer line, followed by flushing the heated line with UHP Nitrogen to complete the delivery of the entire Siloxane mixture to the 7200 was it possible to create consistent recoveries and linear calibrations.

Table 4 shows the results of a Method Detection Limit (MDL) study obtained by analyzing seven replicates of a 10 PPBv standard at a 25cc each. The reproducibility of the system is shown to be quite

Analyte	MDL-1	MDL-2	MDL-3	MDL-4	MDL-5	MDL-6	MDL-7	Mean	SD	MDL
	ppbv	ppbv	ppbv	ppbv	ppbv	ppbv	ppbv			
Trimethyl Silanol	10.4	10.5	10.1	9.77	9.85	10.1	9.81	10.1	0.289	0.9
Hexamethyldisiloxane (L2)	10.0	10.0	9.89	9.71	9.62	10.2	9.95	9.91	0.194	0.6
Hexamethylcyclotrisiloxane (D3)	10.4	10.6	10.5	10.1	9.95	10.2	10.2	10.3	0.231	0.7
Octamethyltrisiloxane (L3)	10.2	10.4	10.0	9.53	9.77	10.0	9.98	9.98	0.281	0.9
Octamethylcyclotetrasiloxane (D4)	11.9	11.6	11.4	11.1	11.1	11.4	10.9	11.3	0.341	1.1
Decamethyltetrasiloxane (L4)	10.3	10.4	10.5	9.51	9.48	9.97	9.46	9.95	0.462	1.5
Decamethylcyclopentasiloxane (D5)	11.3	11.1	10.9	10.5	10.3	11.0	10.4	10.8	0.385	1.2
Dodecamethylpentasiloxane (L5)	9.36	9.33	9.38	8.7	8.14	8.90	8.72	8.93	0.460	1.4
Dodecamethylcyclohexasiloxane (D6)	9.71	9.73	9.47	9.26	8.95	9.38	8.95	9.35	0.321	1.0

Table 3   *Calculated detection limits based on 7 repeat injections from a single 10PPB level canister.   These may be better called LODs, as all injections were from a single canister. Recovery variation using 6 different Silonite-S canisters over a two week period is shown in Table 4.*

	2 Week Holding Time % Recovery Results					
Analyte	Can 1	Can 2	Can 3	Can 4	Can 5	Can 6
Trimethyl Silanol	103	103	102	101	102	98
Hexamethyldisiloxane (L2)	103	97	97	101	104	103
Hexamethylcyclotrisiloxane (D3)	102	93	95	98	99	99
Octamethyltrisiloxane (L3)	101	92	94	99	100	100
Octamethylcyclotetrasiloxane (D4)	99	98	98	91	93	93
Decamethyltetrasiloxane (L4)	97	89	94	92	91	92
Decamethylcyclopentasiloxane (D5)	93	94	98	90	89	89
Dodecamethylpentasiloxane (L5)	87	95	100	90	90	88
Dodecamethylcyclohexasiloxane (D6)	80	95	98	82	84	81

Table 4   *Six Silonite-S canisters filled to 100PPB with siloxane standard and then analyzed after 2 weeks. D6 showed the greatest fluctuations, but all canisters were at or above 80% recovery. Recovery includes the combined effect of losses in the canisters, losses during sample preparation, and variations in detection. In general, the data meets the requirements of other canister methods such as EPA Method TO15.*

good, and independent of the particular siloxane being measured. MDLs of 1 PPBv are not particularly important, as concentrations of Siloxanes at these levels are not thought to produce significant SiO2 deposits upon combustion, but it does show that there is more than enough sensitivity with this approach. Typically, it's system cleanliness rather than ultimate sensitivity that affects method detection limits when measuring siloxanes. System cleanliness has been greatly improved by using the 7650-M robotic autosampler that reduces transfer line exposure to the sample to literally seconds rather than hours or days.

Table 4 shows the long term stability of the siloxane mixture in 1.4L Silonite-S canisters. Six Silonite-S canisters were filled with the siloxane mixture at 100 PPBv and were stored for two weeks, then analyzed to determine the percent recovery. All compound showed an 80% or greater recovery after 2 weeks. In previous papers utilizing canisters for Siloxanes, L5/D6 have shown very low recoveries, but the superior inertness of Silonite-S canisters and the extremely inert flow path and short exposure times in the 7650-M/7200 have eliminated surface adsorption and other losses that were contributing to incomplete recoveries.

Conclusion

A superior approach for siloxane measurement from Trimethylsilanol to Dodecamethylcyclohexasiloxane (D6) has been presented. A linear calibration from 10 to 2500 PPB has been shown, allowing most samples to be analyzed without prior dilution. The enhanced inertness of a next generation sampling canister with a special Silonite-S internal coating helps to keep heavier siloxanes in the gas phase to allow their proper measurement a full 2 weeks after sampling. Using a robotic canister autosampler ensures complete flushing of the sample to the preconcentration traps, providing reliable recovery of heavier L5 and D6 siloxanes which can be substantially attenuated using classical rotary valve autosamplers.

Limiting canister sample collection to less than atmospheric pressure and then pressurizing with dry nitrogen in the laboratory can help to reduce the potential for water condensation in the canister which might in turn lead to reduction in gas phase siloxane concentrations. An additional 2x dilution is not expected to affect the ability to achieve quantitative measurements down to 10PPBv based on the MDLs presented here of 1-2 PPBv.

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