

# **Comparison of Impinger and Canister Methods for the Determination of Siloxanes in Air**

**Presented at the AWMA Symposium on Air Quality Measurement Methods and Technology  
San Francisco, CA, November 13-15, 2002**

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## **ABSTRACT**

This paper compares canister and impinger methods for the analysis of siloxanes in air by gas chromatography/mass spectrometry (GC/MS). Siloxanes are frequently found in commercial and consumer products such as detergents and cosmetics. Most low molecular weight siloxane compounds volatilize quickly into the atmosphere; however, some end up in wastewater or landfills when consumer rinse or discard products. Siloxanes have recently emerged as one of the most difficult contaminants to control in sewage and landfill biogases. The biogas can be used to fuel internal combustion engines or turbines that drive electrical generators. Trace impurities in the biogas can form a residue upon combustion and can contribute to reduced engine lifetime. The presence of silicon in the residue combined with the volatility of some siloxanes prompted increased emphasis on improved sample collection and analytical detection of siloxanes.

The first method in the comparison is based on drawing gas phase samples through a series of midjet impingers and analyzing for dissolved siloxanes using GC/MS instrumentation. The second method is based on collecting a whole air sample in an evacuated canister and analyzing for siloxanes using GC/MS instrumentation. This paper compares the performance of each method in terms of sample collection, standard/sample preparation, initial/continuing calibration, and recovery of selected siloxanes over time.

## INTRODUCTION

Siloxanes are frequently found in commercial and consumer products such as detergents, shampoos, deodorants, and cosmetics<sup>1</sup>. Most low molecular weight siloxane compounds volatilize quickly into the atmosphere and eventually degrade into carbon dioxide, silica, and water<sup>1</sup>. Some siloxanes, however, end up in wastewater or landfills when consumers rinse or discard products. Most operators of wastewater treatment facilities and landfills have not heard of siloxanes because they are not odiferous or hazardous to the environment<sup>1</sup>. However, when operators begin to collect the sewage digester gas or landfill gas for energy applications, siloxanes emerge as one of the most difficult contaminants to control in the biogas. The problem generally appears when the biogas is used to fuel internal combustion engines or turbines that drive electrical generators. Although the biogas is primarily methane and carbon dioxide, it frequently contains trace impurities that form a residue upon combustion<sup>2</sup>. The combustion residues can contain calcium, sulfur, zinc, and silicon compounds and are a primary contributor to reduced engine lifetime<sup>3</sup>. The presence of silicon in the residue combined with the volatility of some siloxanes has prompted increased emphasis on improved techniques for sample collection and analytical detection of siloxanes<sup>3</sup>.

The first method in the comparison is based on drawing gas phase samples through a series of midget impingers and analyzing for dissolved siloxanes using GC/MS instrumentation. The second method is based on collecting a whole air sample in an evacuated canister and analyzing for siloxanes using GC/MS instrumentation. This paper compares canister and impinger methods for the analysis of siloxanes in air by gas chromatography/mass spectrometry (GC/MS). The following sections describe the performance of each method in terms of: 1) sample collection procedures; 2) analytical specifications including quality control, standard and sample preparation; 3) initial and continuing calibration; and 4) hold time studies for siloxanes recovery.

## Sample Collection

Table 1 summarizes the two techniques for collecting a gas phase sample from a biogas collection and energy conversion system. The biogas can be collected as a whole air sample with a Summa canister that is evacuated prior to sampling. Alternatively, the biogas can be drawn through an impinger such that the siloxanes are concentrated in the impinger solution. Note that the impinger sampling technique differs from whole air sampling in that the biogas matrix (i.e., mostly methane and carbon dioxide) is not collected.

**Table 1.** Sample Collection Specifications.

Specifications	Impinger Method	Canister Method
Media	One pair of 24 mL borosilicate glass vials and midget impingers in ice bath	Evacuated Summa canister, 6 or 1 L volume

Impinger Solution	Up to 15 mL methanol	N/A
Media Hold Time	30 days from date of certification	30 days suggested
Sampling Volume	Up to 20 L	N/A
Sampling Rate	112 mL/min for 180 minutes suggested	N/A
Sample Handling	Cap vials and keep chilled at $4 \pm 2^{\circ}\text{C}$	Keep at room temperature
Hold Time to Analysis	21 days	7 days

### ***Impinger Method Sample Collection***

Collecting a biogas sample for the impinger method involves a series of two impingers containing methanol as the solvent. Siloxanes present in the gas phase dissolve in the chilled methanol solution and the vials are subsequently capped and kept chilled until analysis. A needle valve and rotameter are used to adjust and measure the flow rate of sample through the impingers. The suggested media hold time is 30 days and the suggested sample hold time until analysis is 21 days.

The user must determine optimum sampling rate and volume to achieve the data quality objectives of the sampling program. Sampling rates from 100 to 1,000 mL/min are appropriate as long as there is not significant loss of impinger solution. The amount of sample air drawn through the impingers and the amount of solvent in the impinger determine the final reporting limit concentration. The more sample air drawn through the impingers equates to more target constituent concentrated in the solution and thus lower reporting limits. The sampler must be careful not to over sample and saturate the solution. Less impinger solvent equates to lower reporting limits, but has less capacity to dissolve the target constituents. A suggested scenario involves filling each impinger with 6 mL of methanol and sampling at a flow rate of 112 mL/min for 180 minutes. This arrangement results in a sampling volume of approximately 20 L.

### ***Canister Method Sample Collection***

Collecting a biogas sample for the canister method involves a Summa canister that has previously been cleaned and evacuated. Siloxanes present in the gas phase are collected with the biogas matrix as a grab sample of 6 L (or 1 L) volume. The sampler is encouraged to allow the canister to achieve ambient pressure conditions (i.e., no residual vacuum in the canister) to minimize the dilution factor associated with subsequent pressurization at the laboratory for analysis. If the process feed line is pressurized, the sampler can pressurize the 6 L canister to a maximum of 5 psig (or 15 psig for a 1 L canister). Sample fill times for 6 and 1 L canisters are normally 16 and 3 seconds, respectively. A particulate filter should be used to prevent particulate matter from fouling the valve and entering the canister.

## Analytical Method

Table 2 summarizes the analytical specifications of the two methods. Both methods use GC/MS instrumentation and follow instrument operating procedures and quality control criteria specified in SW-846 Method 8000B<sup>4</sup>. The methods incorporate a method detection limit (MDL) study conducted annually per 40 CFR and an initial calibration (ICAL). Every 12-hour period of operation involves a tuning check of the GC/MS system, a continuing calibration verification (CCV), and a laboratory control spike (LCS). Laboratory blanks are run before samples are analyzed and a duplicate sample analysis is performed on 10% of the samples. The addition of three internal standards (IS) and one surrogate complete the rigorous quality control for the methods. The methods mainly differ in how the sample and standard are prepared.

**Table 2.** Instrument and Standard Specifications.

Specifications	Impinger Method	Canister Method
Instrumentation	GC/MS	GC/MS
Loading Interface	Direct injection	Direct injection or sample loop
Load Volume	1.0 $\mu$ L	1.0 mL
Internal Standards (IS)	3	3
Surrogates	1	1
IS Recoveries	-50 to 200% of CCV for blank & samples	-50 to 200% of CCV for blank & samples
IS Retention Time (RT) Window	$\pm$ 0.06 min of RTs in daily CCV	$\pm$ 0.06 min of RTs in daily CCV

### *Impinger Method Standard and Sample Preparation*

The standard for the impinger method is prepared in methanol. A 1.0  $\mu$ L aliquot of sample from the impinger vial is injected directly into the GC column and analyzed by a MS detector in the full scan mode<sup>5,6</sup>.

### *Canister Method Standard and Sample Preparation*

Preparing the standard for the canister method is more involved than the impinger method<sup>7,8,9,10</sup>. The first step is similar to the impinger method except that the standard is prepared in hexane. The second step is to heat the injection port of the canister to 140-150°C with heat tape. Next, the standard solution is injected into the evacuated canister with a micro syringe. The standard canister is then pressurized to 5 psig with dry, ultra-high purity (UHP) nitrogen and agitated for 8 hours. The standard

canister can then be used after a total of 24 hours has elapsed. Prior to sample analysis, the internal standards and surrogate are prepared in a Tedlar bag filled with dry, UHP nitrogen.

The sample canister is pressurized to 5 psig with dry, UHP nitrogen. A syringe is used to prepare a 1.0 mL aliquot comprised of 0.8 mL sample from the sample canister and 0.2 mL internal standard/surrogates mix from the Tedlar bag. The aliquot is injected directly into the GC column and analyzing by a MS detector in the full scan mode. Alternatively, the aliquot for the internal standards/surrogate or sample can be introduced through a sample loop.

## Calibration

Development of the two methods targeted eight specific siloxane compounds shown in Table 3. The calibration specifications for both methods are summarized in Table 4. Initial calibration for both methods involved a minimum of five points and a second source check. Continuing calibration for both methods involved a CCV, and LCS. Note that only one source was identified for D<sub>6</sub> and a second source check and LCS could not be performed.

**Table 3.** Target Siloxane Compound List.

<b>Compound</b>	<b>Abbr.</b>	<b>Mol. Wt.</b>	<b>Boiling Pt.</b>
1,1,3,3-Tetramethyldisiloxane	-	134	70°C
Pentamethyldisiloxane	-	148	86°C
Hexamethyldisiloxane	MM	162	101°C
Octamethyltrisiloxane	MDM	237	153°C
Hexamethylcyclotrisiloxane	D <sub>3</sub>	222	188°C
Octamethylcyclotetrasiloxane	D <sub>4</sub>	297	175°C
Decamethylcyclopentasiloxane	D <sub>5</sub>	371	210°C
Dodecamethylcyclohexasiloxane	D <sub>6</sub>	444	245°C

**Table 4.** Calibration Specifications.

<b>Specifications</b>	<b>Impinger Method</b>	<b>Canister Method</b>
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Calibration Range (5-point calibration)	1.0 to 160 $\mu\text{G}/\text{mL}$ <sup>(1)</sup>	0.5 to 5.0 ppmv
ICAL Acceptance Criteria	RSD $\leq$ 30% for standard compounds	RSD $\leq$ 30% for standard compounds
CCV and LCS (12-hour period)	70-130% for standard compounds	70-130% for standard compounds

(1) The reporting limit for D<sub>6</sub> is 2.0  $\mu\text{G}/\text{mL}$

### ***Impinger Method Calibration***

Six compounds (pentamethyldisiloxane, MM, MDM, D<sub>4</sub>, D<sub>5</sub>, and D<sub>6</sub>) passed the quality control criteria for the calibration as summarized in Table 5. Two compounds (1,1,3,3-tetramethyldisiloxane and D<sub>3</sub>) failed the calibration criteria for different reasons. 1,1,3,3-Tetramethyldisiloxane appeared to degrade quickly (in a matter of hours) at room temperature. Poor responses were measured regardless of concentration at room temperature. Compound D<sub>3</sub> appeared to be unstable (i.e., chemical reactions took place) producing other compounds. When D<sub>3</sub> was analyzed by itself, two other compounds appeared (unknown-1 with ions 207, 223, 193 and unknown-2 with ions 207, 297, 223). When D<sub>3</sub> was analyzed in a mixture of the eight targeted siloxanes, three additional compounds appeared (unknown-3 with ions 267, 281, 133, unknown-4 with ions 281, 147, 267, and dodecamethylpentasiloxane). Both 1,1,3,3-tetramethyldisiloxane and D<sub>3</sub> were removed from consideration for the impinger method due to their lack of ruggedness and predictability. For the impinger method, five siloxanes (pentamethyldisiloxane, MM, MDM, D<sub>4</sub>, D<sub>5</sub>) were speciated in a calibration range from the reporting limit of 1.0  $\mu\text{G}/\text{mL}$  (i.e., the low point on the curve) to an upper limit of 160  $\mu\text{G}/\text{mL}$ . The fifth compound, D<sub>6</sub>, was speciated at a higher reporting limit of 2.0  $\mu\text{G}/\text{mL}$ .

### ***Canister Method Calibration***

Four compounds (pentamethyldisiloxane, MM, MDM, and D<sub>3</sub>) passed the quality control criteria for the calibrations as summarized in Table 5. In developing the canister method, liquid standard dissolved in hexane was used to prepare the gas standard in the canister. Liquid standard dissolved in hexane appeared more stable than standard dissolved in methanol. The use of hexane in the standard resulted in the elimination of 1,1,3,3-tetramethyldisiloxane from consideration since it elutes prior to hexane. To protect the GC/MS from damage, a solvent delay is programmed that vents hexane and all prior eluting compounds. For the canister method, four siloxanes were speciated in a calibration range from 0.5 to 5.0 ppmv.

Although compounds D<sub>4</sub>, D<sub>5</sub>, and D<sub>6</sub> typically demonstrated acceptable linearity (<30%RSD), they exhibited erratic recovery in the daily calibration standard. Over a 7-day period, the daily calibration recovery of D<sub>4</sub>, D<sub>5</sub>, and D<sub>6</sub> varied significantly. The recovery of D<sub>4</sub>, D<sub>5</sub>, and D<sub>6</sub> ranged from 125% to 161%, 117% to 174%, and 99% to 234%, respectively. The erratic behavior of these compounds is

possibly due to their high boiling points. It is possible that these compounds were not completely in vapor phase within 24 hours of pressurization. The time interval required for complete vaporization varied for each compound. The high (245°C) boiling point of D<sub>6</sub> made it nearly impossible to achieve complete vaporization.

**Table 5.** Initial Calibration Results.

<b>Compound</b>	<b>Impinger Method</b>	<b>Canister Method</b>
1,1,3,3-Tetramethyldisiloxane	Failed, degrades quickly	Removed from target list
Pentamethyldisiloxane	Passed	Passed
MM	Passed	Passed
MDM	Passed	Passed
D <sub>3</sub>	Failed, unstable	Passed
D <sub>4</sub>	Passed	Failed, erratic
D <sub>5</sub>	Passed	Failed, erratic
D <sub>6</sub>	Passed	Failed, erratic

### Hold Time Study

Two hold time studies were conducted on the compounds that successfully passed the ICAL to determine stability over time in each sample media. The criterion for the study was measuring recovery between 70-130% past 7 days. The hold time study results are summarized in Table 6.

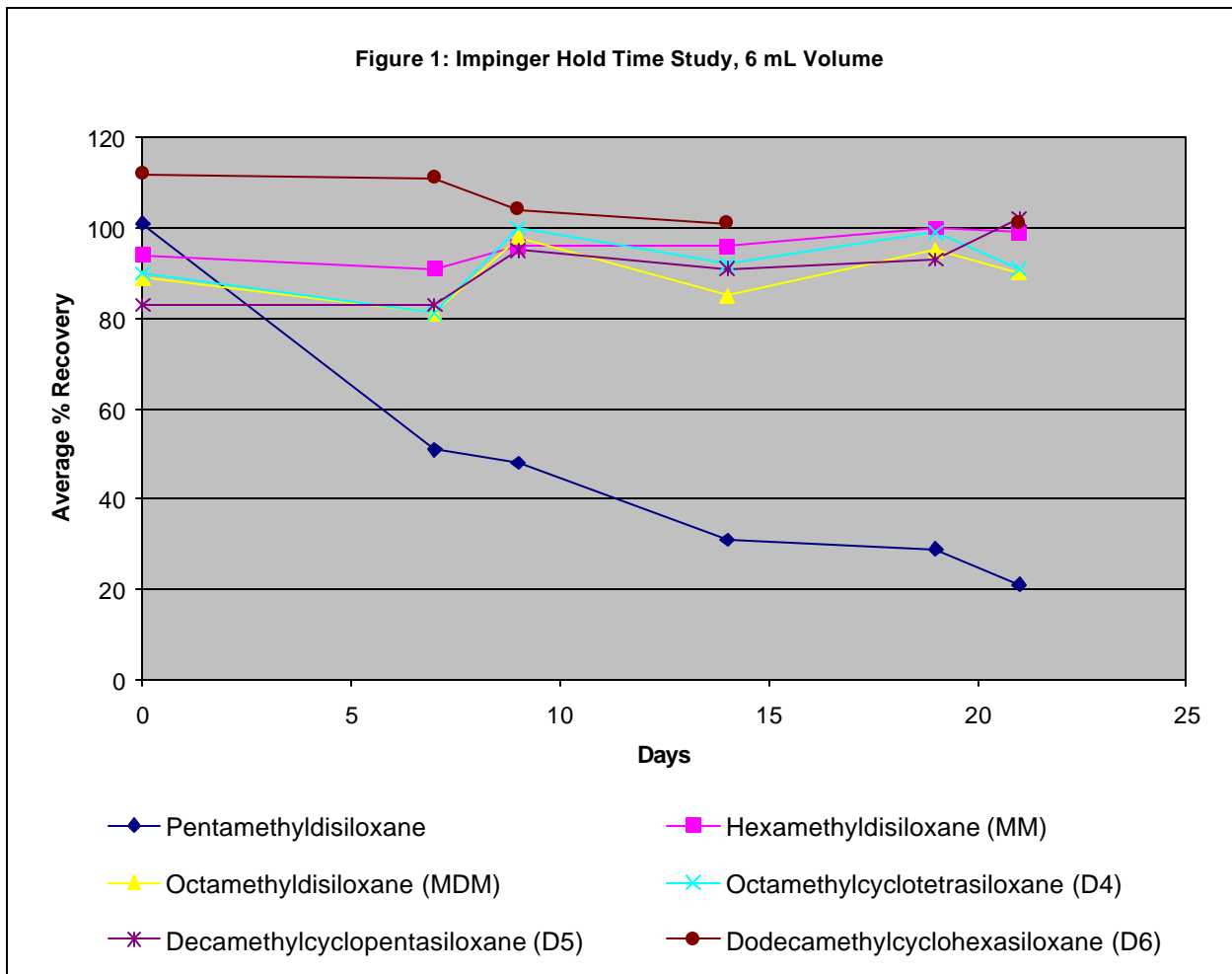
**Table 6.** Hold Time Study Results.

<b>Compound</b>	<b>Impinger Method</b>	<b>Canister Method</b>
1,1,3,3-Tetramethyldisiloxane	N/A	N/A
Pentamethyldisiloxane	Failed (< 7 days)	Passed (> 7 days)
MM	Passed (> 21days)	Passed (> 7 days)
MDM	Passed (> 21days)	Passed (> 7 days)
D <sub>3</sub>	N/A	Passed (> 7 days)
D <sub>4</sub>	Passed (> 21days)	NA
D <sub>5</sub>	Passed (> 21days)	NA
D <sub>6</sub>	Passed (> 21days)	NA



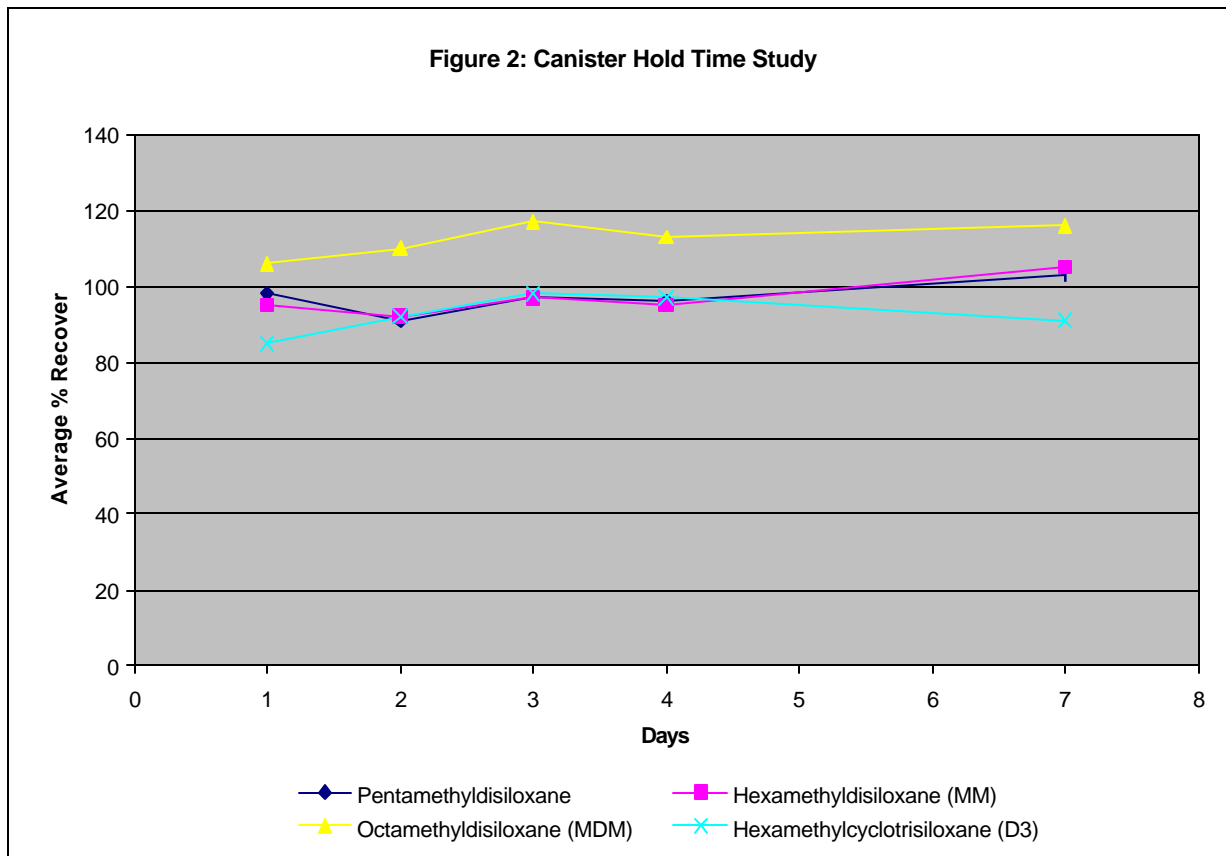
### Impinger Method Hold Time Study

The study began by preparing a solution of methanol spiked with 10  $\mu\text{G}/\text{mL}$  of the six siloxanes passing the ICAL (pentamethylsiloxane, MM, MDM, D<sub>4</sub>, D<sub>5</sub>, and D<sub>6</sub>) in methanol. Aliquot volumes of 6, 15, and 25 mL were prepared in borosilicate vials and stored at  $4 \pm 2^\circ\text{C}$ . The hold time study involved analyzing a total of 54 samples: triplicate samples of each aliquot volume at day 0, 7, 9, 14, 19, and 21. The percent recoveries were calculated for each siloxane compound based on the daily standard. Figure 1 plots the average recovery of the triplicate samples for the six siloxane compounds in the 6 mL vials. Recovery of compounds MM, MDM, D<sub>4</sub>, D<sub>5</sub>, and D<sub>6</sub> was acceptable up to day 21. The recovery was independent upon aliquot volume. Recovery of pentamethylsiloxane was poor and declined to approximately 60% by day 7 and to 20% by day 21. Pentamethylsiloxane was removed from consideration for the impinger method due to lack of acceptable recovery within a reasonable hold time (e.g., 7 days).



### Canister Method Hold Time Study

The study began by preparing 5 canisters spiked with concentrations of the 4 siloxanes passing the ICAL (pentamethyldisiloxane, MM, MDM, and D<sub>3</sub>) between 0.6 and 0.8 ppmv. The sample canisters were agitated for 8 hours and then set aside until a total of 24 hours had elapsed. The hold time study involved analyzing aliquots from each of the 5 canisters at day 1, 2, 3, 4, and 7 plus nearly 50% duplicates. The percent recoveries were calculated for each siloxane compound based on the initial calibration standard. Figure 2 plots the average recovery of the 5 aliquots for the four compounds. Recoveries of compounds pentamethyldisiloxane, MM, MDM, and D<sub>3</sub> were acceptable through day 7.



## CONCLUSION

Table 7 summarizes the comparison of the two methods. In terms of sample collection, the canister method is simple and fast requiring only 16 seconds to passively fill a 6 L canister. The impinger method requires experience with solution sampling and patience since sampling intervals can last up to three hours. In terms of preparing the standard and sample, the impinger method is simple and fast by incorporating an autosampler. The canister method involves complicated steps to introduce the liquid standard into the canister and wait over 24 hours for the standard to vaporize. Siloxanes with high boiling points may never completely vaporize and recovery is erratic. In terms of calibration, each method favored a subset of the eight siloxanes targeted. For the impinger method, six compounds

passed the calibration criteria and 1,1,3,3-tetramethyldisiloxane and D<sub>3</sub> failed due to instability. For the canister method, four compounds passed the calibration criteria while D<sub>3</sub>, D<sub>4</sub>, and D<sub>5</sub> failed due to erratic behavior and 1,1,3,3-tetramethyldisiloxane was removed due to instrument requirements. The hold time study further reduced the compound list for the impinger method. Pentamethyldisiloxane recovery was poor and dropped to 60% by day 7.

**Table 7.** Method Comparison Summary.

<b>Specifications</b>	<b>Impinger Method</b>	<b>Canister Method</b>
Sample Collection	Complicated, active sampling (pump may be required), slow	Simple, passive sampling, fast
Standard/Sample Preparation	Simple, fast	Complicated, slow
Compound List	MM, MDM, D <sub>4</sub> , D <sub>5</sub> , and D <sub>6</sub>	Pentamethyldisiloxane, MM, MDM, D <sub>3</sub>
Reporting Limit	1.0 µG/mL <sup>(1)</sup> or ~ 50 ppbv (assuming 6 mL methanol and 20 L air volume)	0.5 ppmv

(1) The reporting limit for D<sub>6</sub> is 2.0 µG/mL

At this point in the method development, there are two main reasons why the impinger method compares more favorably than the canister method. The first reason concerns the fact that according to available literature, D<sub>4</sub> and D<sub>5</sub> are the major siloxane species found in landfill and sewage biogas<sup>10</sup>. Although the canister method speciates four siloxanes, the inability to quantify D<sub>4</sub> and D<sub>5</sub> render the method impractical for most data users. The second reason concerns the analytical sensitivity required by the data user. Once siloxanes have been identified in the biogas at elevated concentrations, engine manufacturers and facility operators often focus on processes to remove the siloxanes. Low reporting limits in the parts per billion by volume (ppbv) range are required to demonstrate the effectiveness of the siloxane removal equipment. With a reporting limit of 0.5 parts per million by volume (ppmv) or 500 ppbv, the canister method is approximately 10 times less sensitive than the impinger method.

To complete the canister method development, further studies are suggested in the following areas.

- 1) Standard Preparation: vary the injection port temperature, eliminate the use of solvent, blend the standard in a sample cylinder capable of pressurization greater than 5 psig
- 2) Matrix Interference: determine if moisture or other hydrocarbons interfere with the determination of siloxanes

- 3) Field Sampling: compare recovery of siloxanes in landfill and sewage biogas collected simultaneously with impingers and canisters

## ACKNOWLEDGEMENTS

Air Toxics Ltd. would like to acknowledge the following individuals for assistance in developing the canister method: Sherman S. Chao of Analytical Solution, Willobrook, IL and Ed Wheless and Wade Huang of Los Angeles County Sanitation District, Whittier, CA.

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