

A SUMMARY OF AVAILABLE ANALYTICAL METHODS FOR THE DETERMINATION OF SILOXANES IN BIOGAS

Heidi C. Hayes
Air Toxics Ltd.
Folsom, CA

Sepideh Saeed
Air Toxics Ltd.
Folsom, CA

Guy J. Graening
Air Toxics Ltd.
Folsom, CA

Sandia Kao
Air Toxics Ltd.
Folsom, CA

ABSTRACT

The importance of measuring siloxanes has increased with the recent growth of the landfill-gas-to-energy (LFGTE) market. Siloxanes and other biogas impurities can form a residue upon combustion in engines that may increase maintenance and reduce engine lifetime. A siloxanes analysis can assist with either determining if a biogas purification system is needed, or if a system is already in place, determining if it is operating properly. To date, various methods have emerged to measure siloxanes involving different sampling techniques and detectors. This paper summarizes the available methods for the determination of siloxanes in air to enable members of the LFTGE industry to select the most appropriate method for their application.

This paper presents information not only from method development by Air Toxics Ltd., but also from available technical literature by analytical laboratories, environmental consulting firms, and trade conferences. The specific sample collection techniques to be compared are:

- Collecting a whole air sample in a Summa™ canister; and
- Drawing sample air through methanol-filled impingers;
- Drawing sample air through a charcoal sorbent tube.

The specific analytical detectors to be compared are gas chromatography (GC) coupled with a:

- Flame ionization detector (FID);
- Atomic emission detector (AED); and
- Mass spectrometer (MS).

This paper specifically compares the performance of collection and analytical methods in terms of:

- Ease of sampling;
- Collection of a representative sample;
- Siloxane recovery;
- Detector selectivity and availability;
- Reporting limit; and
- Calibration techniques.

INTRODUCTION

Biogas is naturally produced from microbes degrading organic substances in landfills and wastewater treatment plants. One byproduct of this reaction is methane which typically comprises 50 to 60% of the biogas. As an alternative to releasing this greenhouse gas to the environment or simply flaring the gas, plant operators can utilize biogas to generate energy. The high methane content of the biogas provides a medium grade fuel with a heating value ranging from 550 to 680 British Thermal Units per cubic feet of gas (Liang et al., 2002). However, when operators begin to collect landfill and digester gas for energy conversion, trace impurities in the biogas often present an operational challenge.

Siloxanes are one of the most difficult trace compounds to control in the biogas. Siloxane compounds are commonly found in commercial and consumer products, such as cosmetics, lotions and detergents. While some siloxanes quickly volatilize into the atmosphere, other less volatile compounds end up in the biogas. Table 1 lists some typical siloxane compounds and their properties. When the biogas is combusted, siloxanes oxidize to form silica. The formation of silica in the combustion engine is problematic since silica is abrasive and also acts as a thermal and electric insulator. As a result, combustion engine performance may be greatly reduced and post combustion catalysts may be less effective (Slezak et al., 2002, Liang et al., 2002).

Siloxane analysis of the biogas can assist the plant operator in determining whether a siloxane removal system is

TABLE 1. VARIOUS SILOXANES AND THEIR PROPERTIES

Compound	Abbreviation(s)	Molecular Weight	Boiling Point (°C)
Pentamethyldisiloxane	-	148	86
Hexamethyldisiloxane	L2, MM	162	101
Octamethyltrisiloxane	L3, MDM	237	153
Decamethyltetrasiloxane	L4	311	194
Dodecamethylpentasiloxane	L5	385	230
Hexamethylcyclotrisiloxane	D3	222	134
Octamethylcyclotetrasiloxane	D4	297	175-176
Decamethylcyclopentasiloxane	D5	371	210
Dodecamethylcyclohexasiloxane	D6	445	245

needed or whether the removal system is operating correctly. Various analytical methods for the determination of siloxanes have been applied to the analysis of biogas. Sampling techniques typically include collecting a whole air sample using a Summa canister, drawing gas sample through solvent filled impingers, or drawing gas through a sorbent tube. The collected samples can then be analyzed using various instrumentation including gas chromatography coupled with a flame ionization detector (GC/FID), an atomic emission detector (GC/AED), and a mass spectrometer (GC/MS). The performance and applicability of each method is summarized. The differences between two specific methods, impinger GC/MS and canister GC/AED and GC/MS, are discussed by comparing the method results of a real digester gas.

SAMPLE COLLECTION TECHNIQUES

Canisters: Whole Air Sampling

Using the canister collection method, siloxanes present in the gas phase of the biogas are collected as a whole air grab sample. Collection of a biogas in a canister utilizes a clean and evacuated Summa™ canister. The evacuated canister and a particulate filter are attached to the process feed line and the canister valve is opened to fill the canister with sample (Saeed et al., 2002b). After collection, the canister valve is closed and the sample is sent to the laboratory for analysis.

Other whole air collection media are available and have been determined to be less suitable than canisters for the collection of siloxanes. Hagmann et al. (1998) concluded that the performance of bags and glass containers was not acceptable. Sample bags utilizing silicone septa and adhesives resulted in high blank levels of siloxanes, while glass containers demonstrated high adsorption of siloxanes on the glass walls.

Impingers: Liquid Adsorption

Collecting siloxanes using an impinger sampling train involves drawing the biogas sample through a series of

solvent filled impingers. The siloxanes in the biogas dissolve in the chilled solvent. A needle valve and rotameter after the second impinger adjusts and measures the flow rate through the train. If the feed line is not pressurized, a sample pump is required. After the desired sampling duration, the vials are capped and returned to the laboratory for analysis.

Using the impinger collection method requires optimization of the flow rate and sampling duration to meet data quality objectives. The siloxane reporting limit is a function of the volume of biogas drawn through the impingers and the volume of the impinger solvent. The sampler must be careful not to over sample and exceed the capacity of the impingers. Sampling large biogas volumes to achieve lower reporting limits may result in saturation of siloxanes in the first impinger vial and subsequent breakthrough to the second vial. Using a reduced solvent volume will lower reporting limits, and reduce the capacity to dissolve siloxane target. A suggested sampling rate is 112 mL/min for 180 minutes resulting in a total sample volume of 20 L.

Several solvents have been utilized in the impinger collection method for siloxanes (Hagmann et al., 1998), but the most widely used is methanol. The use of methanol impingers for the collection of siloxanes was the result of a 1997 siloxanes investigation conducted by a landfill consortium. The general protocols are outlined by Niemann (1997), and a more detailed approach is described by Saeed et al. (2002a).

Sorbent: Solid Adsorption

Siloxanes can also be collected by drawing the biogas through a solid sorbent designed to trap the siloxanes. The sample train is similar to the impinger train with the tube replacing the methanol impingers. A sample pump is required if the feed line is not pressurized. Like the impingers, the flow rate and the sample duration must be measured to determine the total volume sampled. After sampling is completed, the sorbent is shipped to the laboratory for extraction and analysis.

As with the impingers, care must be taken not to over sample and exceed the capacity of the sorbent tube. Most sorbent tubes have a front half and a back half that can be extracted and analyzed separately to monitor breakthrough.

Various sorbent materials and corresponding desorption solvents have been evaluated in the literature. Adsorption on activated charcoal followed by desorption with carbon disulfide, benzyl alcohol, and dichloromethane resulted in poor recoveries as did XAD-2 and XAD-4 with hexane desorption (Hagmann et al., 1998). Niemann (1997) describes collection using a coconut charcoal tube and desorption using MIBK for adequate recovery of D4. Wheless and Gary (2002) also describe the use of coconut charcoal tubes with good performance for D4.

Discussion

Each collection method for siloxanes has its advantages and disadvantages that should be considered when designing a sampling plan. Several factors to consider are the ease of sampling, the homogeneity of the biogas, and the recovery of the target compounds from the media. Table 2 summarizes the advantages of each sampling method.

Ease of sampling: Of the collection methods discussed, canister sampling provides the sampler with the easiest set up and shortest sampling time. No sample rates need to be determined and optimized, no sample pump or additional hardware is needed, and the evacuated canister fills in seconds. In contrast, the suggested sampling time for impingers and sorbents ranges from 30 minutes to 3 hours (Niemann, 1997, Saeed, 2002a). Impinger collection also requires an ice bath in the field. Unlike canisters, both impingers and sorbents should remain chilled for delivery which generally necessitates prompt return to the laboratory.

Collection of a representative sample: Another difference between the collection methods is the canister collects a grab sample while the impinger and sorbent methods collect an integrated sample. The canister grab sample represents a point in time characterization of the process stream. Because the canister fills in seconds, the concentration of siloxanes in the biogas gives the data user a snap shot of the biogas composition. Depending on the fluctuations of the process feed, this snap shot may or may not be representative of the typical siloxane concentrations introduced into the combustion engine. Alternatively, the impinger and sorbent methods require collection of the biogas sample over a specified time period, effectively averaging fluctuations in siloxane concentrations.

Siloxane recovery: D4 and D5 are the predominant siloxanes found in biogas (Hagmann et al.,

2001). However, according to Wheless and Gary (2002), the siloxane profile of digester gas appears to be different than that of landfill gas. Whereas digester gas siloxane content is typically greater than 90% D4 and D5, landfill gas may contain significant levels of other siloxanes such that D4 and D5 may represent slightly more than the majority for some samples (Wheless and Gary, 2002). Consequently, a suitable collection method must first and foremost effectively recover D4 and D5, but should also provide data on the remaining siloxanes.

Siloxane recovery data indicate that methanol impingers may perform better than canisters for the less volatile cyclical siloxanes such as D4, D5, and D6, while canisters appear to be superior to impingers in recovering pentamethyldisiloxane and D3. Little published information was found on the specific recoveries from a charcoal tube. Wheless and Gary (2002) reported acceptable recovery of D4 and erroneously high D3 levels using this media.

Low canister recovery of several of the less volatile siloxanes has been described in the literature. Schweigkofler and Niessner (1999) found that recovery of D5 was less than 90%, and D6 could not be quantified using a canister method due to its low volatility and low recovery from a canister. Saeed et al. (2002b) discovered erratic behavior of three of the less volatile cyclic siloxanes (D4, D5, and D6) in a prepared standard over the course of a seven day period, making quantification of these compounds in the samples uncertain. The source of the erratic behavior was unclear. Loss of recovery in the canister may be observed due to physical adsorption to the canister surface or due to chemical reactions. Surface effects typically become more significant with increasing boiling point and polarity (Brymer et al., 1996). In contrast, the methanol impinger demonstrated recoveries above 80% for D4, D5, and D6 as well as L2 and L3 over a 21 day period.

Two siloxanes proved to be unsuccessful utilizing the methanol impinger approach, pentamethyldisiloxane and D3. Recovery of pentamethyldisiloxane dropped to 60% in the course of 7 days. D3 proved to be unstable in the methanol standard and could not meet calibration criteria (Saeed et al., 2002b). The canister method proved superior over the impinger method for the recovery of D3 and pentamethyldisiloxane with recoveries over 80% over a 7 day period (Saeed et al., 2002b).

ANALYTICAL TECHNIQUES

The analytical techniques applied to the analysis of siloxanes are numerous and provide the data user with varying levels of specificity and accuracy. Most analytical techniques for siloxane analysis utilize a gas chromatograph (GC) to separate the sample into its

TABLE 2. COMPARISON OF COLLECTION TECHNIQUES

Performance Criteria	Canister	Impinger	Sorbent tube
Ease of sampling	Excellent	Poor	Fair
Representative sample	Fair/Poor	Excellent	Fair
D4/D5 Siloxane recovery	Fair	Excellent	Fair/Poor

components followed by detection using various detectors. The most commonly used detectors and calibration techniques are briefly described and the advantages and limitations of each are discussed.

Analytical Detectors

Detectors commonly used for the analysis of siloxanes include the flame ionization detector (FID), the atomic emission detector (AED), and mass spectrometry (MS). The flame ionization detector is a general purpose detector. Compounds are ionized in a hydrogen/air flame and the amount of ions produced is approximately proportional to the number of carbon atoms present in the compound. In general, any compound containing a carbon-hydrogen bond such as a siloxane will generate a peak.

The AED is more sophisticated than the FID and can simultaneously monitor various emission wavelengths that are characteristic of various atoms. The computer can then sort the data and produce chromatograms made up of peaks from the sample that contain only one element. In the case of siloxanes, the characteristic emissions from silicon and carbon are monitored for compound confirmation and measurement (Chao, 2002).

The MS is also a sophisticated detector which bombards the compound with electrons fragmenting the compound into characteristic charged ions. This fragmentation pattern can be compared to a standard or to a reference library to identify the compound structure.

Discussion

Several factors to consider when selecting an analytical method for siloxane analysis are the selectivity of the detector, availability, analysis cost, and sensitivity. Additionally, various calibration techniques can be employed to provide the data user with differing levels of detail and accuracy. A comparison of the analytical techniques is summarized in Table 3.

Detector selectivity: Of the analytical detectors, the FID is the least selective for siloxanes. Any carbon containing compound may be detected by the FID. Given the complex composition of a typical biogas, identification and quantification of siloxanes are difficult if not impossible. Non-target peaks coeluting with siloxane compounds may lead to false positive identification of siloxanes and high bias for the siloxane quantification. The AED provides an additional filter and can selectively

display compounds containing silicon. This capability minimizes interference from other organic compounds present in the biogas and leads to a more accurate identification and quantification of the siloxanes. The MS takes the selectivity another step and provides specific compound structural information based on the peak's fragmentation pattern and mass ions. Specific mass ions are acquired allowing for the quantification of a compound in the presence of coeluting compounds. The MS also provides the data user with the flexibility of identifying other non-calibrated compounds. Identification is performed by matching the unknown spectra to compounds in the spectral library.

Availability and analysis cost: Of the three detectors, the FID and MS are more commonly used in environmental laboratories. Few environmental laboratories have AED capabilities. The analysis cost is typically related to the sophistication of the instrumentation and the level of expertise and time needed for data reduction. As a result, FID analysis is typically a low cost analytical option relative to the AED and the MS. Additionally, MS is generally a more economical solution than AED analysis.

Reporting Limit: The actual reporting limit is a function of instrument sensitivity and sample load volume. In the case of impingers and sorbent tubes, the reporting limit is also a function sample volume and impinger volume or desorption solvent volume. Given all these factors, each analytical approach can be optimized to reach reporting limits typically less than 0.50 ppmv. Schweigkofler and Niesser (1999) were able to achieve limits of detection of less than 1 ppbv Silicon by concentrating up to 200 mL of the biogas using a cryogenic trap prior to analysis by GC-MS/AED.

Calibration: Several calibration techniques are available for each detector and provide the data user with differing levels of quantification and information. One calibration method is a direct analysis of the specific target siloxanes at varying concentrations. From this data, a calibration curve is constructed for each compound and the appropriate response factor is used to calculate the siloxane concentration. This direct calibration technique can, of course, be used for each analytical technique and for any media. Direct calibration provides the data user with the most accurate data and provides detailed speciation of the siloxanes. However, since preparation of

TABLE 3. COMPARISON OF ANALYTICAL TECHNIQUES

Performance Criteria	FID	AED	MS
Detector selectivity	Poor	Fair	Excellent
Availability	Excellent	Poor	Fair/Excellent
Cost	Excellent	Poor	Fair
Reporting Limit	<0.50 ppmv possible	<0.50 ppmv possible	<0.50 ppmv possible

the gas phase siloxanes is time consuming and difficult (Saeed, 2002b, Chao, 2002), direct calibration techniques are not always used for siloxanes in whole air canister samples.

Another calibration technique used is an indirect calibration of the siloxanes. In this case, a single component standard is used to calibrate the instrument for all the siloxanes. This technique works well for the AED method since it is an equal molar response detector. This means that a silicon atom has relatively the same response in any molecular structure. Chao (2002) describes this simple and quick calibration technique as a way to determine total silicon concentration using only a few siloxane compounds. However, this technique does not validate individual siloxane compound recovery through the analytical system and may provide less accurate quantification of the siloxane compounds.

CASE STUDY

To evaluate several of the available collection methods and analytical techniques, biogas samples were collected from a pressurized feed line at the Sacramento Regional Waste water Treatment Plant in Elk Grove, CA. Two samples were collected through chilled methanol impingers and sent to Air Toxics, Ltd. for subsequent analysis by GC/MS. Additionally, four canister samples were collected for analysis. Three canisters were sent to the LA County Sanitation District laboratory for GC/MS analysis and one canister was sent to Analytical Services, Inc. for GC/AED analysis. The less commonly used sorbent tube collection method was not evaluated in the case study. Additionally, the FID methodology was not included in the study given its poor selectivity for siloxanes.

Collection of the samples through the methanol impingers required about 30 minutes of set up time. The sampling time required for two samples required a total of 6 hours (3 hours for each sample). Collection of the canister samples took seconds and four canisters were collected in less than 15 minutes.

The siloxane results from the three laboratories are compiled in Table 4. Each laboratory provided a different target siloxane list with the AED results reported as total Silicon. Both sets of GC/MS data were mathematically converted to total Silicon to allow for direct comparison of results.

The data set, although limited, highlights several similarities and differences between the analytical methods. The impinger and canister methods all reported D4 and D5 as the major components of the biogas. Although the GC/AED report reflected only the Total Silicon, the report indicated qualitatively that the sample composition was mainly D4 and D5. However, the concentrations of D4 and D5 in the impingers were 2.5 to 6 times higher in the impingers than in the canisters analyzed by GC/MS. The canister GC/AED data did not speciate D4 and D5, but comparison of the Total Silicon results between the methods support the higher siloxane recoveries observed in the impingers relative to the canisters.

Possible reasons for higher siloxane results include actual variations in the biogas siloxane composition or lower recovery of D4 and D5 from a canister. The impingers were collected over two 3-hour intervals, one in the morning and one in the afternoon. After the second impinger was collected, the canisters were collected. If the biogas siloxane composition varied significantly over the course of the day, the canister grab sample may not necessarily compare to the impinger samples.

Alternatively, the D4 and D5 discrepancy may be due to potential recovery difficulties of these compounds out of a canister due to canister surface interactions or reactions with the biogas matrix. It is interesting to note, however, that D6, a compound known to recover poorly from a canister, was detected in Canister 3 by GC/MS. This compound was below the reporting limit for the impinger samples.

SUMMARY

Given the various collection and analytical techniques for siloxanes in biogas, several factors should be considered when setting up the tests. These factors include: ease of sampling, collection of a representative sample, recovery of the targeted siloxanes, selectivity of the analytical detector, the availability of the instrumentation, needed reporting limits, and calibration techniques.

Weighing all these factors, impinger collection followed by GC/MS analysis is a preferable method for the collection of siloxanes in biogas. The impinger method results in an integrated sample with good recovery of D4 and D5. Use of the GC/MS for analysis results in

TABLE 4. COMPARISON OF SILOXANES IN DIGESTER GAS

Siloxane	Impinger 1 _a GC/MS (ppmv)	Impinger 2 _a GC/MS (ppmv)	Canister 1 _b GC/MS (ppmv)	Canister 2 _b GC/MS (ppmv)	Canister 3 _b GC/MS (ppmv)	Canister 4 _c GC/AED (ppmv)
D3	NA	NA	0.11	<0.26	<0.24	NA
D4	0.53	0.65	0.15	0.21	0.17	NA
D5	2.0	2.8	0.47	0.66	0.72	NA
D6	<0.081	<0.079	<0.040	<0.040	0.060	NA
L2	<0.11	<0.10	<0.29	<0.24	<0.22	NA
L3	<0.076	<0.071	<0.21	<0.18	<0.16	NA
L4	NA	NA	<0.17	<0.14	<0.13	NA
L5	NA	NA	<0.13	<0.11	<0.10	NA
Total Si	12	16	3.3	4.1	4.6	6.2_d

Notes: NA = Not Analyzed; a = Air Toxics Ltd data; b = LA County Sanitation District data; c = Analytical Solutions, Inc. data; d = Report indicated that sample was composed mainly of D4 and D5.

definitive quantification of the siloxanes and a direct calibration is used.

The canister collection method provides a quick and easy sampling method, but in our case study, the D4 and D5 results were significantly lower than the impinger collection method for both the GC/MS and GC/AED. The specific cause of the lower results is not known, and more studies need to be conducted to determine whether the difference is due to sample composition variability, poor recovery from a canister, or another factor.

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