Method Development for the Synthesis of Anaerobic Digester Biogas within the Laboratory Environment

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Thesis submitted to the faculty of the Virginia Polytechnic Institute and State University in partial fulfillment of the requirements for the degree of

Master of Science
In
Environmental Engineering

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December 16, 2014
Blacksburg, Virginia

Keywords: biogas synthesis, siloxane, anaerobic digester, wastewater treatment plants, gas chromatography-mass spectrometry

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ABSTRACT

Biogas, a gaseous mixture produced during decomposition of organic matter, is a renewable, easily generated and common byproduct of anaerobic digestion at wastewater treatment plants (WWTP), landfills and agricultural operations. There is growing interest in researching and utilizing the energy potential associated with its combustion. Siloxanes, a family of volatile organic silicon compounds, pose large impediments to biogas usage due to the formation and precipitation of silicon dioxide within combustion devices. Removal of siloxanes prior to combustion is therefore a growing endeavor. Research was performed to synthesize a representative gas stream produced from anaerobic digesters within WWTP. Methane, carbon dioxide and hydrogen sulfide were combined with humidity and gaseous siloxane in levels characteristically seen exiting anaerobic digesters. A methanol impinger train was utilized to sample the biogas composite. Gas chromatography-mass spectrometry (GC-MS) was used to determine gas-phase siloxane concentrations in the gas stream effluent for the purposes of confirming the generation of a consistent and reproducible biogas stream.

ACKNOWLEDGMENTS

This research was fully funded by Hamption Roads Sanitation District (HRSD) in Virginia Beach, Virginia. I would like to express my sincere gratitude and thanks to HRSD for their financial support and help throughout the research. This project would not have occurred without the support and backing provided by them.

I would like to express my deepest appreciation and thanks to Dr. Gregory Boardman, my advisor throughout my tenure as a graduate student. Dr. Boardman provided immeasurable guidance, insight, wisdom and support throughout my graduate tenure, both as a professor in the classroom and as my advisor for my research. Dr. Boardman is extremely active in the professional community and has a passion for both teaching and learning and was critical to my growth as a graduate student. I have nothing but the utmost respect for him and am very fortunate for the experience I received working with him. Dr. Steven Cox, an academic committee member of mine, also graciously provided his help and expertise throughout the research process, I would also like to thank him. Dr. Cox was paramount to the work conducted, from the initial design process all the way through completion, and I was very fortunate to have him as an asset for direction and assistance during my project. I would also like to thank the last academic committee member, Dr. Charles Bott, who was the direct connection between the research being conducted at Virginia Tech to HRSD. Dr. Bott was highly patient and worked hard to maintain in contact with Virginia Tech through his busy schedule, while providing additional guidance and ideas from Virginia Beach. Immense thanks go out to all three of my academic committee members.

I would also like to thank the other individuals who, although not necessarily directly connected to the research, were extremely helpful with completing the research. Jody Smiley, who helped me with all things in the laboratory, was nothing but gracious and determined to ensure that I learned how to successfully analyze data for the researching purposes. Without her I would not have any of the data presented in this report. Thank you Julie Petruska, who strove to teach me and all other students the importance of following directions and focusing on the details. Julie keeps our department running efficiently and without incident and is a great instructor. Dr. Yaoxing Wu, who was a great friend and peer that helped with all of the day-to-day successes and failures and encouraged me to forge on when issues arose. Thanks are due for Pei Yao, who came on towards the end of the research and assisted before continuing on with additional work of her own. Special thanks are owed to Berth Lucas, who keeps track of all students in our department and helps with anything and everything.

I would like to express my gratitude to Kaitlin Blackwell, an undergraduate researcher who worked on the research with me during her hectic undergraduate workload. I would also like to thank my labmates and peers Kat Phetxumphou, Stephanie Countess, Drew Vance, Sheldon Masters, Amanda Sain and Matthew Chan. Having their friendship and point of view greatly assisted the research. Special thanks goes out to Jennifer Lawall, who listened and supported me endlessly during my graduate tenure and was an amazing cheerleader and friend.

Finally, I would like to thank my family. My parents and siblings have pushed me to become the man I am today, and I owe everything I have to them. My sincere gratitude goes out to them.

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CHAPTER 1 – Introduction

Anaerobic digestion is a viable and effective method for treating primary and waste activated sludge (biosolids) in a conventional wastewater treatment plant (WWTP). When compared to aerobic treatment, it possesses inherent benefits and is therefore widely used. These benefits include, but are not limited to, high waste stabilization, a partial removal of pathogens and reduction in solids (Riffat, 2013; Metcalf and Eddy, 2003). Additionally, anaerobic digestion has a better energy balance when compared to aerobic digestion due to the production of methane within the biogas byproduct formed. The biogas, and subsequent methane, can be collected and used as a renewable energy source either on site or in other locations (Metcalf and Eddy, 2003). Using the methane as an energy source on-site has become a growing endeavor in an effort to offset the extensive energy costs associated with continuously operating a wastewater treatment plant. When comparing multiple plants, biogas makeup varies depending upon the municipalities and industries served. Even individual WWTP can see variations in the biogas it produces on a day-to-day basis due to the myriad of different inputs received. Typical biogas constituents remain the same but their levels can vary depending up the influent. Biogas is typically composed of methane (50-70%), carbon dioxide (30-45%), nitrogen (<1%) and trace compounds such as hydrogen sulfide and siloxanes (Accetola et al., 2008; Osorio and Torres, 2009; Rasi et al., 2011; Schweigkofler and Neissner, 2001). The value of the biogas is due to the methane, allowing the gas to be used in combustion engines and turbines. Conversely, contaminants within biogas can lead to problems, with siloxanes posing the greatest issue.

Siloxanes are a volatile group of synthetic organosilicon compounds. They are found in WWTP biogas and have become popular in recent years in a variety of consumer goods, including health and beauty products such as deodorants, creams and lotions, as well as in mechanical products as an alternative to traditional greases, oils and lubricants (Dewil et al., 2007; Gislon et al., 2013; Wheless and Pierce, 2004). Siloxanes find their way into WWTPs by transport within residential and industrial wastewater and gray water. Due to their low water solubility siloxanes are difficult to remove within WWTP processes and consequently congregate within the biogas produced. Siloxanes pose an issue when biogas is used in an engine or turbine. When raised to combustion temperatures, siloxanes transform to silicon dioxide, which in turn precipitates out of the gas and solidifies on the interior of combustion device. This leads to a buildup of silicon dioxide and can render the engine inoperable (Ajhar et al., 2010a; Arnold, 2009; Dewil et al., 2006; Glus et al., 1999; Sudeep and Deshesses, 2008). This impairment potential accompanying siloxanes has caused engine manufacturers to place strict limitations on siloxane levels allowed in fuel sources, including biogas (Soreanu et al., 2011). These levels are extremely low, sometimes in the ppb range. It is economically favorable for biogas pretreatment instead of engine maintenance, leading to the growth in research in the field.

Despite research efforts in recent years, selecting the best system for siloxane removal remains a substantial issue. Some of the more promising techniques include solid adsorption, refrigeration and liquid absorption (Ajhar et al., 2010a). Solid adsorption has the greatest support; however, there is still disagreement about which solid media is the most effective. Many varieties of activated carbon and silica gels exist that have been shown to successfully remove siloxane from gaseous streams, and are generally considered among the best solid media options (Ajhar et al.,

2010a; Pierce, 2005). Additionally, various siloxane capture techniques have been tested, including methanol impingers, Tedlar bags and evacuated Summa canisters. Each collection method has benefits and drawbacks associated with them; however, methanol impingers produce liquid samples whereas Tedlar bags and Summa canisters produce gaseous samples. Methanol impingers therefore have a significant advantage in the ease of use and benefit of complementing GC-MS analysis. GC-MS analysis can be completed with Tedlar bags and Summa canisters, but gaseous injection has drawbacks when compared to liquid injection. The usefulness of GC-MS analysis resides in the many different compounds that can be observed, allowing researchers to test for multiple siloxanes simultaneously. There are certain drawbacks associated with GC-MS, but they can be easily overcome. One issue is the potential for reporting error within the device, which can be remedied by including an internal standard within the samples. Another problem, the tendency for the device to become less accurate over time, can be successfully remedied with regular cleaning and tuning of the device.

Testing solid media is a time consuming and arduous process, made even more difficult by the fact that siloxane levels and species can vary in biogas. In an attempt to successfully test siloxane removal techniques and technologies, researchers must first be able to determine exactly how much of each individual siloxane is present in the testing biogas, without the levels changing drastically over an extended time period. For this reason, being able to synthesize a biogas of known CH_4, CO_2, H_2S, siloxane and humidity levels would be paramount in allowing researchers to apply biogas treatment methods to compare siloxane removal processes. A synthesized gas stream representative of biogas from WWTPs coupled with effective siloxane collection and

analytical techniques would allow researchers to produce information and data regarding siloxane treatments that would greatly benefit the scientific community.

CHAPTER 2 – Literature Review

Introduction

With the growing push for sustainability, people across the globe have been looking to find renewable energy sources. Wind, solar, geothermal and hydroelectric powers have been relatively popular alternatives to conventional energy sources for many decades now. The push to find more and more ways to create energy from unconventional methods has not been limited to those listed above. Biogas utilization has become a hot topic since the late 20th century, as well. A relatively newer energy alternative when compared to some of the other options available, biogas is currently a smaller energy field, but has the potential to grow and become a highly popular and viable endeavor. Finding newer renewable sources and technologies will only continue as many nations accept the need to become more "green."

Biogas refers to the production of a gaseous compound that occurs from the decomposition of living matter. Biogas production is commonly associated with landfills, wastewater treatment plants (WWTP), animal production activities, commercial composting and agricultural food industry operations (Abatzoglou and Boivin, 2008, Holm-Nielsen et al., 2009). Biogas production is dependent upon physical, chemical and microbial processes, and therefore is very sensitive to the environmental conditions affecting it (Aguilar-Virgen et al., 2014). Biogas typically shows similar major components regardless of where it is generated, however certain differences are observed when comparing the diverse environments in which the biogas is produced. For example, WWTP biogas could have trace compounds not found in landfill or agricultural biogas due to the difference in influent.

Using the biogas produced in any operation offers two very large positives: (1) due to a high energetic content, biogas can offset energy costs, and (2) releasing biogas into the environment largely contributes to the greenhouse gas emissions due to the presence of methane and carbon dioxide (Abatzoglou and Boivin, 2008). The energy potential in biogas is directly related to the presence of methane, considering that it can be combusted in engines, turbines, boilers and burners. In an attempt to improve and/or reach complete combustion of biogas, much work and research has been conducted into removing contaminants. Of the many contaminants that biogas can contain, siloxane has been labeled as one of the most serious (Ajhar and Melin, 2006).

Siloxanes are a subgroup of silicon compounds commonly found in biogases, generally in higher concentrations from WWTP than landfills (Wheless and Pierce, 2004). They are volatile, man-made organics containing silicon, oxygen and methyl groups in various linear and cyclic configurations (Wheless and Pierce, 2004). The term, siloxane, is a direct reference to the compounds makeup: silicon, oxygen and an alkane (Ortega and Subrenat, 2009). When referring to siloxanes, linear forms are denoted with an L, cyclical with a D, and both are followed by a number referring to the number of silicon atoms in the compound. Siloxanes are found in many different consumer and industrial goods, including such health and beauty products as detergents, makeup, deodorants and creams and are subsequently released into the environment through a wide variety of sources (Dewil et al., 2007; Gislon et al., 2013; Wheless and Pierce, 2004). Siloxane sources and uses are increasing due to their inherent positive benefits: aroma-free, widely available and exempt from volatile organic compounds (VOC) regulations (McBean, 2008). Due to their varying uses, siloxanes tend to accumulate in landfills and WWTP at different levels and in different amounts for individual species. For instance,

Octamethylcyclotetrasiloxane (D_4) tends to be the predominant species in landfill gas, whereas D_5 is the siloxane of most abundance in digester gas (Ajhar et al., 2010b). The variation of siloxane makeup can be attributed to the different silicon-containing compounds entering each environment.

Siloxanes are non-toxic, somewhat hydrophobic and have high thermal stability and low flammability (Ryckebosch et al., 2011). Because of their lower water solubility and adsorptive nature siloxanes do not accumulate in the water phase, but rather partition to the sludge flocs of biosolids in WWTP (Appels et al., 2008b). Their propensity to accumulate in the biosolids within a WWTP leads to the siloxane partitioning to biogas generated from treatment of the solids. The concentration of siloxanes within biogas is dependent upon the wastewater characteristics and therefore varies both temporally and spatially – levels and species found will be different over time and at separate WWTPs. Bletsou et al. (2013) did not find a consistent pattern regarding siloxane levels within a WWTP after completing a survey comparing wastewater influent and effluent over an extended time period. However, the greater the use of materials containing silicon leads to more silicon entering WWTP and higher levels of siloxanes in the resulting biogas (Rasi et al., 2011).

Table 1 outlines specific characteristics of the siloxanes of interest in this study. In addition to siloxanes, other silicon based compounds have been found in biogas, including trimethylsilanol (Raich-Montiu et al., 2014), considered the most volatile of the volatile methyl siloxanes (VMS) (Piechota et al., 2012).

Table 1 - Physical characteristics of selected siloxane species. Information was collected from McBean, 2008[(1)]; Schweigkofler and Neissner, 2001[(2)]; Wheless and Pierce, 2004[(3)].

Siloxane Species	Abbreviation	MW (g/mol) [3]	Boiling point (°C) [1,2]	Vapor pressure (kPa) [3]
Octamethyltrisiloxane	L_3	236	153	0.520 at 25 °C
Decamethyltetrasiloxane	L_4	310	194	0.073 at 25 °C
Dodecamethylpentasiloxane	L_5	384	230	0.009 at 25 °C
Octamethylcyclotetrasiloxane	D_4	297	176	0.173 at 25 °C
Decamethylcyclopentasiloxane	D_5	371	211	0.053 at 25 °C

Wastewater Treatment Practices

There are many different methods in use today, each with their own pros and cons. Of the various treatment options available, the activated sludge (AS) process has become the conventional method. This process involves collecting all wastewater, transporting it to a centralized plant for treatment and then discharging it after completion. There are myriad methods for treatments associated with AS, however a common theme with those involves the separation of liquids and biosolids. Of the available biosolid management practices, aerobic and anaerobic digestion (AD) are the primary methods employed in most WWTP.

Anaerobic digestion was first discovered more than a century ago and has since evolved and been modified to the conventional treatment systems seen today (Angenet et al., 2004; McCarty and Smith, 1986). Anaerobic digestion refers to the process of treating biosolids in an oxygen deficient environment. The advantages associated with anaerobic treatment include: (1) a high degree of waste stabilization, (2) low production of waste biological sludge, (3) low nutrient requirements, (4) no oxygen requirements, (5) the production of methane and (6) works with many different post-treatment methods to recover useful byproducts like ammonia or sulfur (Angenent et al., 2004; Lettinga, 1995; McCarty, 1964). Within a WWTP that employs AD,

typically all sludge or biosolids removed throughout the various phases of treatment end up combined within a large tank or reactor. This tank is continuously monitored to ensure certain parameters are being met. Important variables for consideration in AD include retention time, mixing, pH, temperature, nutrient levels, the absence of toxic chemicals and appropriate feed characteristics (Parkin and Owen, 1986). Ensuring complete control over these variables within ranges appropriate for sufficient digestion is necessary for bacterial health and therefore optimum operation.

The production of methane, or methanogenesis, occurs in four phases in anaerobic digesters. The stages are referred to as (1) hydrolysis, (2) acidogenesis, (3) acetogenesis and (4)methanogenesis (Appels et al., 2008a). The methanogenesis process is illustrated below in Figure 1. In total, five distinct microbial communities are involved in the anaerobic digestion process.

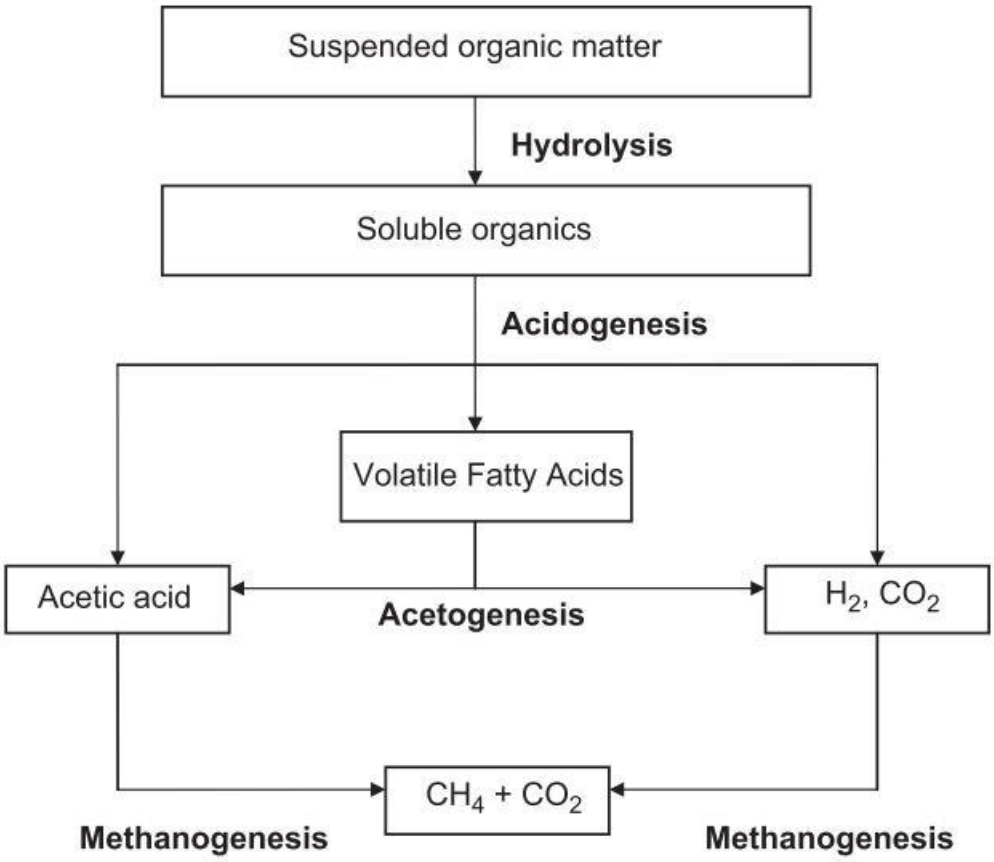

Figure 1 - Four stage process involved in methanogenesis (Appels et al., 2008a).

Biogas produced from an anaerobic digester at a WWTP is typically comprised of 50-70% methane, 30-45% carbon dioxide and small amounts of nitrogen and any number of other contaminants; e.g. hydrogen sulfide, siloxanes and halides (Accetola et al., 2008; Osorio and Torres, 2009; Rasi et al. 2011; Schweigkofler and Neissner, 2001). Research has been conducted into various methods of removing the contaminants, though the greatest focus has been directed towards both hydrogen sulfide and siloxanes. Hydrogen sulfide has potential to cause corrosion (Osorio and Torres, 2009; Tippayawong and Thanomponchart, 2010) and can be found in digester gas in levels from 37.5 mg/m^3 up to over 1,500 mg/m^3 (Wheless and Pierce, 2004). Siloxanes tend to foul up engines via solid precipitation (Dewil et al., 2006; Glus et al., 1999;

McBean, 2008; Soreanu et al., 2011) and have been observed in digester gas from 16 mg/m^3 up to 400 mg/m^3 (Rasi et al., 2006).

The issues associated with siloxane arise when biogas reaches combustion temperatures. When this occurs, siloxane compounds are converted to a silicon dioxide precipitate which then builds within the combustion chamber (Ajhar et al., 2010a; Sudeep and Deshusses, 2008). Silicon dioxide forms crystalline structures, having properties similar to glass (Arnold, 2009). The substance accumulates throughout engines, including pistons, cylinders, valves and oils and can reach thicknesses of several millimeters on solid surfaces (Ohannessian et al., 2008). The substrate formations on solid surfaces can be extremely abrasive and lead to physical damage within the combustion chamber, necessitating an increase in the frequency with which operators must perform maintenance; e.g. stripping the engine down and manually removing the solids from pistons, cylinder heads and valves (Environment Agency, 2010). Silicon dioxide accumulation in oil requires an increase in the frequency of oil changes as well (Ajhar et al., 2010b).

In addition to the physical damage that can occur from silicon dioxide formation, other detrimental effects have been observed. Silicon residues act as thermal insulators, contributing to the overheating of engine parts (McBean, 2008). The residues also exhibit electrical insulation characteristics and can depress the function of spark plugs (Dewil et al., 2006).

Siloxane Collection Techniques

Many different siloxane collection techniques have been proposed and tested. Some of the more popular methods include methanol impinger trains/series, whole-air containers (canisters or

bags) and sorbent tubes. Although each method allows for the capture of gaseous samples, methanol impinger trains lead to the capture of siloxanes in a liquid matrix. Tedlar bags and canisters leave the siloxane in a gaseous matrix; and, sorbent tubes, as the name would imply, adsorb of siloxanes on a solid. For each of these methods, stainless steel or polytetrafluoroethylene (PTFE) tubing and connections are recommended to prevent siloxane interactions within the apparatus (Air Toxics Ltd., 2002; American Public Health Association et al., 1999).

The impinger method of collection involves the use of two midget impingers containing an absorbent liquid of the researcher's choice. The impingers are filled with a known volume of the selected solvent and organized in a series. When sampling is conducted, impingers are submerged in a cool water bath and the gas stream of interest is directed through them. Siloxanes are dissolved within the solvent matrix and the samples are then stored in a chilled environment until further analysis. Adjusting the volume of solvent, as well as the time of sampling, allows the researchers to control the amount of siloxane that is captured in the solvent. The amount of siloxanes collected in the solvent is directly related to the amount of gas drawn through the train, and also coincides with a lower sampling error (Saeed et al., 2002). The researchers must adjust the volume of solvent and length of sampling to ensure siloxane capture is within a range of concentrations suitable for their analytical purposes. Additionally, the researchers must ensure that sampling trials are short enough so as not to completely saturate the first impinger with siloxane. Impingers are typically arranged in series in order to determine whether breakthrough within the first impinger occurs and adjustments to collection process are utilized to prevent breakthrough when witnessed.

Whole-air containers can come in different shapes, sizes and materials. However the two most common containers used for siloxane capture are evacuated canisters and sampling bags. Canisters are available in varying volumes, dependent upon how much sample is required for analysis, but are almost always made of stainless steel. The evacuated canister method requires a simple grab sample of the gas stream. The researcher connects the canister to the gas line and allows the canister to reach ambient pressure conditions, thereby ensuring there is no dilution of the gas. Particulate filters are available and recommended during collection to ensure that no particulate matter enters the canister or fouls the apparatus (Saeed et al., 2002). Sampling bags are used in a similar manner. Bags are usually made of PTFE, polyethylene-terephthalate-nylon-aluminum (PET-NY-AL-CPE) or polyvinyl fluoride (PVF) and come in various sizes (Mariné et al., 2012). Bags are simply filled with gas and placed in storage for analysis. Methods to ensure bags are leak-proof and uncontaminated before sampling are capable of being performed as well, depending upon the researchers concerns. PVF bags are marketed by Tedlar as a universal gas sampling method and are among the more widely used collection techniques. In both whole-air collection methods siloxanes are captured at their concentration within the biogas at the time of sampling (Raich, 2011).

Sorbent tube methods involve filling a stainless steel tube with a known volume of adsorbent and connecting the tube to the biogas stream. The adsorbent matrix can be chosen specifically for the experiment; however, activated carbon and silica gel are two popular options. The adsorbent tubes can be connected in a series, similar to methanol impingers, with two equal or different volumes of sorbent within each tube. Typically an air pump is connected to the biogas stream so

that the flow rate is consistent and allows for optimum adsorption conditions. This flowrate is chosen dependent upon the volume and type of matrix within the tubes. After siloxane capture has occurred, desorption of the siloxanes is required for analysis (Mariné et al., 2012).

Each of these methods has inherent pros and cons. Because of this, there is disagreement on the best collection technique and no standard method is recommended (Mariné et al., 2012; Narros et al., 2009). In terms of ease of use, canisters tend to be the simplest process. Both bags and solid canisters simply require connecting the device to a gas stream and allowing the container to collect until full. After collection, the containers can be transferred and stored until ready for analysis. The impinger collection has the benefit of being capable of allowing the researchers to directly control the concentration of siloxanes captured. This is helpful if the analytical device to be used requires siloxanes be within a certain concentration range. Sorbent tubes are needed if trimethylsilanol is to be captured, because methanol impingers are ineffective (Narros et al., 2009).

For each of the aforementioned methods, there is concern about the sorption of siloxane to the materials. Narros et al. (2009) noticed a lower level of D_4 and D_5 using the impinger method combined with Tedlar bag collection (*ex situ*) when compared with direct impinger sampling (*in situ*). They hypothesized the loss of siloxane to be attributed to adsorption of the two compounds onto the bag's lining. Additionally, high losses of L_4, D_4 and D_5 were observed when Tedlar bags were equipped with o-ring-sealed stainless steel fittings (Ajhar et al., 2010b). Other researchers observed no differences when sampling directly from a source (with impingers using n-hexane as solvent or sorbent tubes) versus sampling from Tedlar bags combined with the impinger and

sorbent tube (Raich-Montui et al., 2014). Extended storage is a concern with Tedlar bags in regards to total concentrations. Mariné et al. (2012) noted a decrease in siloxane response with storage as low as 24 hours. Additionally, there is concern with reusing Tedlar bags due to adsorption of siloxanes onto the liner. The biggest drawback associated with sorbent tubes is the extra step required (desorption) for analysis. Desorption can be done thermally (Mariné et al., 2012; Narros et al., 2009) or via a solvent (Raich-Montui et al., 2014). Sorbent tubes also can pose issues when collecting ultra-volatile chemicals at ambient temperature (Mariné et al., 2012).

Siloxane Analysis Technologies

Analysis of siloxanes can be completed with multiple technologies. Gas Chromatography (GC) can be used in combination with Mass Spectrometry (MS), Flame Ionization Detector (FID) or Atomic Emission Detector (AED). Likewise, Inductively Coupled Plasma (ICP) can be combined with MS or Optical Emission Spectrometry (OES) for analysis; however, these methods are used for determination of total silicon content, as opposed to siloxane levels. For this reason, GC-MS is the most used method of analysis for siloxanes (Companioni-Damas et al., 2012).

Siloxane Removal Technologies

Numerous siloxane removal techniques, including: adsorption (via liquid and solid media as well as membranes), absorption, refrigeration, peroxidation, permeation membranes and biofiltration have been studied and show varying levels of success (Ajhar and Melin, 2006; Ajhar et al., 2010a; Ajhar et al., 2010b; Ajhar et al., 2012; Appels et al., 2008b). A preference towards adsorption media in general has grown in recent years (Pierce, 2005). Of all of the removal techniques, the most widely used to reduce VMS concentrations is adsorption with activated

carbon (Ajhar et al., 2010a), however this is still disagreement as to whether activated carbon is the best media available.

Due to the inconclusive opinion on solid media adsorption, research has been conducted on various solid media options and some information is available describing its variety and effectiveness. Common adsorbents for siloxane removal are carbon or silica based, however molecular sieves and membranes are also used. Many companies have developed and marketed products for solid adsorption, offering anything from universal approaches to customized products for individual streams based on siloxane species makeup. Using a media tailored specifically for the biogas stream is useful due to the competitive adsorption of contaminants (Ajhar et al., 2010a; Dewil et al., 2006). In addition to the individual siloxane species competing for sorption sites, it is reasonable to believe that hydrogen sulfide may compete as well (Schweigkofler and Niessner, 2001). Matsui and Imamura (2010) completed a study comparing twenty two activated carbons, two molecular sieves and a silica gel. In their study, they concluded that the molecular sieves adsorbed the least amount of siloxane D_4, the activated carbons the highest and the silica gel in between the two. They also noted a significant variation in the removal within the various activated carbons tested. Their observation - activated carbon producing the highest siloxane adsorption - agreed with that of Schweigkofler and Neissner's (2001), who tested polymer beads, a molecular sieve, a silica gel and two carbon based adsorbents. Gislon et al. (2013) saw "inadequate" adsorption from two zeolite samples and one silica gel, but much better results with five different activated carbons.

Certain variables can affect siloxane removal regardless of media. These include humidity and temperature of the biogas stream and adsorption environment (Arnold, 2009; Cabrera-Codony et al., 2014; Ortega and Subrenat, 2009). According to Cabrera-Codony et al. (2014), there is a decrease in siloxane removal performance of activated carbon when humidity is present. Ortega and Subrenat (2009) observed the same trend as well. In this instance it is believed that water adsorbs to the material, preventing siloxane adsorption. Ortega and Subrenat (2009) also noted a lower siloxane adsorption capacity coinciding with an increase in temperature, a result typical of VOC's.

Physical and chemical characteristics of the adsorbent media have also been studied and shown to affect siloxane removal. Those characteristics include pore volume, pH and BET surface (Matsui and Imamura, 2010). In fact, adsorption capacity is believed to be directly related to BET surface (Ortega and Subrenat, 2009), and activated carbon media typically has higher BET surface levels than both silica gel and molecular sieves. Matsui and Imamura (2010) noted significantly higher siloxane removal performance using certain activated carbons than silica gel and correlated this to higher BET surface area and pore volume. As to be expected, though, not all activated carbons are alike, and certain types perform better or worse than others. Of the twenty two activated carbons tested alongside the sole silica gel under Matsui and Imamura (2013), the adsorption ratio of D_4 (wt%) ranged between 5-20%, with the silica gel performing just above 10%.

It is important to note there are limitations associated with the alternative siloxane removal methods and they are therefore utilized much less. Cryogenic condensation, or refrigeration, is

effective, but expensive (Dewil et al., 2006). Wheless and Pierce (2004) observed a 50% removal of siloxanes using refrigeration, 95% removal with advanced refrigeration. Peroxidation was shown to reduce siloxane levels by approximately 50% or greater (Appels et al., 2008), however for a more complete removal a second treatment step would be required (Ortega and Subrenat, 2009). Absorption studies suggest that complete elimination of siloxanes can be difficult to attain at elevated gas flow rates due to the volatility of siloxanes (Ryckebosch et al., 2011). Furthermore, Ryckebosch et al. (2011) mention multiple solvent absorption options are available, however two of the more effective solvents include strong acids and bases, which are detrimental to the environment as well as hazardous to handle. Schweigkofler and Neissner (2001) saw efficient siloxane removal with both half-concentrated sulfuric acid and concentrated nitric acid, but also noted the hazards associated with them. There is potential to combine multiple siloxane removal methods to get complete elimination, but because solid adsorption is so effective and, when compared to combing multiple other methods, less costly, the spread and use of these technologies has been limited.

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CHAPTER 3 – Method Development for the Synthesis of Anaerobic Digester Biogas within the Laboratory Environment

Abstract

Biogas, a gaseous mixture produced during decomposition of organic matter, is a renewable, easily generated and common byproduct of anaerobic digestion at wastewater treatment plants (WWTP), landfills and agricultural operations. There is growing interest in researching and utilizing the energy potential associated with its combustion. Siloxanes, a family of volatile organic silicon compounds, pose large impediments to biogas usage due to the formation and precipitation of silicon dioxide within combustion devices. Removal of siloxanes prior to combustion is therefore becoming a common practice. Research was performed to synthesize a representative gas stream produced from anaerobic digesters within WWTP. Methane, carbon dioxide and hydrogen sulfide were combined with humidity and gaseous siloxane in levels characteristically seen exiting anaerobic digesters. A methanol impinger train was utilized to sample the biogas composite. Gas chromatography-mass spectrometry (GC-MS) was used to determine gas-phase siloxane concentrations in the gas stream effluent for the purposes of confirming the generation of a consistent and reproducible biogas stream.

Keywords

Biogas synthesis

Siloxane

Anaerobic digester

Wastewater treatment plants

Gas chromatography-mass spectrometry

Introduction

Anaerobic digestion is a viable and effective method for treating primary and waste activated sludge (biosolids) in a conventional wastewater treatment plant (WWTP). When compared to aerobic treatment, it possesses inherent benefits and is therefore widely used. These benefits include, but are not limited to, high waste stabilization, a partial removal of pathogens and reduction in solids (Riffat, 2013; Metcalf and Eddy, 2003). Additionally, anaerobic digestion has a better energy balance when compared to aerobic digestion due to the production of methane within the biogas byproduct formed. The biogas, and subsequent methane, can be collected and used as a renewable energy source either on site or in other locations (Metcalf and Eddy, 2003). Using the methane as an energy source on-site has become a growing endeavor in an effort to offset the extensive energy costs associated with continuously operating a wastewater treatment plant. When comparing multiple plants, biogas makeup varies depending upon the municipalities and industries served. Even individual WWTP can see variations in the biogas it produces on a day-to-day basis due to the myriad of different inputs received. Typical biogas constituents remain the same but their levels can vary depending up the influent. Biogas is typically composed of methane (50-70%), carbon dioxide (30-45%), nitrogen (<1%) and trace compounds such as hydrogen sulfide and siloxanes (Accetola et al., 2008; Osorio and Torres, 2009; Rasi et al., 2011; Schweigkofler and Neissner, 2001). The value of the biogas is due to the methane, allowing the gas to be used in combustion engines and turbines. Conversely, contaminants within biogas can lead to problems, with siloxanes posing the greatest issue.

Siloxanes are a volatile group of synthetic organosilicon compounds. They are found in WWTP biogas They have become popular in recent years in a variety of consumer goods, including

health and beauty products such as deodorants, creams and lotions, as well as in mechanical products as an alternative to traditional greases, oils and lubricants (Dewil et al., 2007; Gislon et al., 2013; Wheless and Pierce, 2004). Siloxanes pose an issue when biogas is used in an engine or turbine. When raised to combustion temperatures, siloxanes transform to silicon dioxide, which in turn precipitates out of the gas and solidifies on the interior of combustion device. This leads to a buildup of silicon dioxide and can render the engine inoperable (Ajhar et al., 2010a; Arnold, 2009; Dewil et al., 2006; Glus et al., 1999; Sudeep and Deshesses, 2008). This impairment potential accompanying siloxanes has caused engine manufacturers to place strict limitations on siloxane levels allowed in fuel sources, including biogas (Soreanu et al., 2011). These levels are extremely low, sometimes in the ppb range. It is economically favorable for biogas pretreatment instead of engine maintenance, leading to the growth in research in the field.

Despite research efforts in recent years, selecting the best system for siloxane removal remains a substantial issue. Some of the more promising techniques include solid adsorption, refrigeration and liquid absorption (Ajhar et al., 2010a). Solid adsorption has the greatest support; however, there is still disagreement about which solid media is the most effective. Many varieties of activated carbon and silica gels exist that have been shown to successfully remove siloxane from gaseous streams, and are generally considered among the best solid media options (Ajhar et al., 2010a; Pierce, 2005). Additionally, various siloxane capture techniques have been tested, including methanol impingers, Tedlar bags and evacuated Summa canisters. Each collection method has benefits and drawbacks associated with them; however, methanol impingers produce liquid samples whereas Tedlar bags and Summa canisters produce gaseous samples. Methanol impingers therefore have a significant advantage in the ease of use and benefit of complementing

GC-MS analysis. GC-MS analysis can be completed with Tedlar bags and Summa canisters, but gaseous injection has drawbacks when compared to liquid injection. The usefulness of GC-MS analysis resides in the many different compounds that can be observed, allowing researchers to test for multiple siloxanes simultaneously. There are certain drawbacks associated with GC-MS, but they can be easily overcome. One issue is the potential for reporting error within the device, which can be remedied by including an internal standard within the samples. Another problem, the tendency for the device to become less accurate over time, can be successfully remedied with regular cleaning and tuning of the device.

Testing solid media is a time consuming and arduous process, made even more difficult by the fact that siloxane levels in biogas can vary. In an attempt to successfully test siloxane removal techniques and technologies, researchers must first be able to determine exactly how much of each individual siloxane is present in the testing biogas, without the levels changing drastically over an extended time period. For this reason, being able to synthesize a biogas of known CH_4, CO_2, H_2S, siloxane and humidity levels would be paramount in allowing researchers to apply any number of biogas treatment methods to compare siloxane removal processes. A synthesized gas stream representative of biogas from WWTPs coupled with effective siloxane collection and analytical techniques would allow researchers to produce information and data regarding siloxane treatments that would greatly benefit the scientific community.

Objectives

1. To develop a method for synthesizing a gas stream in lab representative of one produced from a typical anaerobic digester at a wastewater treatment plant.
2. To develop a reliable system for production and characterization of a consistent gas stream.

Materials and Methods

Chemicals and Gases

All chemicals, gases and solvents used in this study were analytical grade or higher. Each of the five siloxanes used: Octamethylcyclotetrasiloxane (D_4, CAS no.: 556-67-2, 98%), Decamethylcyclopentasiloxane (D_5, CAS no.: 541-02-6, 97%), Octamethyltrisiloxane (L_3, CAS no.: 107-51-7, 98%), Decamethyltetrasiloxane (L_4, CAS no.: 141-62-8, 97%) and Dodecamethylpentasiloxane (L_5, CAS no.: 141-63-9, 97%) were purchased from Sigma-Aldrich, St. Louis MO. The internal standard (IS), Phenanthrene-d10 mix (CAS no.: 1517-22-2), was manufactured by Restek and purchased from Fisher Scientific Co., Hampton, NH. The surrogate (Surr), p-Terphenyl-d14 (CAS no.: 1718-51-0), was manufactured by Supelco and purchased from Sigma-Aldrich Inc., St. Louis, MO. The gases: carbon dioxide (CO_2), methane (CH_4), and methane blended with hydrogen sulfide (CH_4/H_2S) were purchased from Airgas Inc., Radnor Township, PA.

The methanol used as a solvent and for cleaning purposes (Optima grade, CAS no.: 67-56-1, 99.9%) was purchased from Fisher Scientific Co., Hampton, NH. The acetone used for cleaning purposes (Optima grade, CAS no.: 67-64-1, 99.8%) and methylene chloride used for surrogate

dilution (Stabilized/Certified ACS, CAS no.: 75-09-2) were also purchased from Fisher Scientific Co., St. Louis, MO.

Apparatus Setup - Overview

A laboratory system was utilized to develop a gas stream that simulated the biogas typically found exiting anaerobic digesters at WWTP. The influent gas stream was created by combining carbon dioxide with a hydrogen sulfide and methane blend before diffusing siloxanes into the stream. Regulators were connected to each gas tank and the pressure exiting the tanks was kept below 30 psi. Gas flows from the tanks were independently controlled by two mass flow controllers (MFCs; model SEM-3330M) by Stec Inc. The MFCs were connected to a computer running LabVIEW 2012. LabVIEW was used to directly control each individual MFC via a cDAQ-9174 chassis holding two modules: NI 9264 analog output module and NI 9219 universal analog input. The interface allowed for control of the gas flowrate in a range of 0-500 mL/min per MFC. All gas stream lines from gas tanks to the sorption column were made of 1/8" stainless steel in order to prevent any chemical buildup or interactions within the lines. For this reason, stainless steel Swagelok connections were also used to connect all lines. A schematic of the apparatus is illustrated in Figure 2.

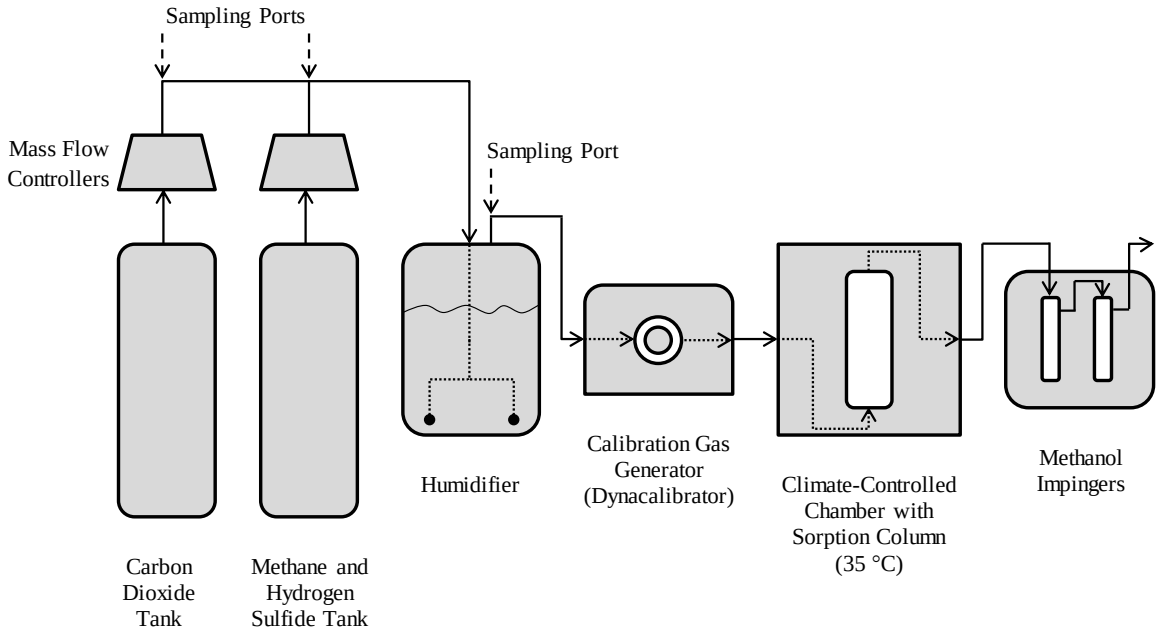

Figure 2 - Schematic drawing of biogas synthesis apparatus.

Apparatus Setup – Gas Stream

For the purposes of synthesizing a typical biogas stream, the test gas mixture was approximately 65% CH_4 and 35% CO_2 with H_2S levels around 45 ppm. After combining the CO_2 and CH_4 gas streams into one mixture, the flow was directed into a humidifier, allowing for the relative humidity to be raised to approximately 50%. The humidifier consisted of a modified glass jar containing diffusion stones that were submerged in distilled water. Upon exiting the humidifier the exiting stream was then sent through a Dynacalibrator (VICI Dynacalibrator Constant Temperature System model 190) to allow for the siloxanes of interest to be added to the stream. The Dynacalibrator, or calibration gas generator as it is sometimes referred to, is a device that can be set to hold an internal chamber to a set temperature. The internal chamber can be accessed from the exterior, allowing for diffusion vials containing liquid compounds of the users choice to be placed inside. The purpose of the device is to allow the liquid compounds within the diffusion vial to be introduced to a gas stream consistently and with little variation. For the researchers

purposes, the Dynacalibrator was set to a constant temperature of 90°C. A diffusion vial containing the liquid siloxanes sat within the diffusion chamber of the Dynacalibrator. Using liquid siloxanes allows customization of each trial to a specific mixture of siloxanes. Experimental trials were conducted with solely D_5, a mixture of D_4 and D_5 and a mixture of all five siloxanes. For trials involving all five siloxanes, siloxanes were mixed using a strict molar ratio. The mixture was calculated using vapor pressures as a base estimate of diffusion levels. A ratio of vapor pressures was used to determine the molar ratio needed for the siloxane mixture to ensure siloxane diffusion rates in the preferred range seen in a typical biogas. Initial trials were completed using the setup described with mixed results. After examining the data thoroughly the dynaclibrator was replaced with a newer version (same model). After replacing the dynacalibrator the results showed a decrease in variability.

Once siloxanes were added to the gas mixture, the gas stream was directed into an empty sorption column contained within an oven (Precision Scientific Thelco Laboratory Oven, model 4) at 35° C. The sorption column was 22 cm tall with a 2 cm inner diameter. The total volume of the column was 69 mL. This column allowed the gas stream to travel through it with a superficial velocity (flowrate/cross-sectional area) greater than 5 ft/min using the desired gas flowrate of 500 mL/min. The column was also selected to provide for an acceptable empty bed contact time (EBCT). The EBCT and superficial velocity were chosen due to a recommendation from David Herrera of Cabot Norit Activated Carbon, a supplier of activated carbons (AC) that are commonly used for siloxane adsorption (Personal communication, 2014). The recommended EBCT was greater than two seconds, but less than 60 seconds. An EBCT too high would make removal difficult due to time constraints. An EBCT too low would expose siloxanes to the media

for too short of a time period. The superficial velocity used in practice with activated carbon is in the range of 5-20 fpm, therefore 5 ft/min was chosen as the minimum superficial velocity. Although no media was placed in the column, the column was incorporated into the experiments to aid in a future phase of the work.

Apparatus Setup – Gas Collection and Analysis

After travelling through the sorption column, the gas stream was then passed through a methanol impinger train in order to collect the siloxanes for analysis. Teflon tubing was used after the sorption column due to its pliability, allowing for easy manipulation of the gas stream. This permitted ease of both sampling and subsequent venting of the exiting gas out of the laboratory. Teflon Swagelok connections were used after the sorption column to connect the methanol impinger sampling train to the gas stream. Two sets of methanol impingers were used for gas collection: SKC Inc. (model 225-36-1) and Bendix (model 7202). Both impinger sets were standard nozzle midget impingers, 25 mL maximum volume. Given a known siloxane concentration, known volume of methanol per impinger, and a set sampling time, estimation of the total siloxane mass that would be captured in the impinger train is easily calculated. Upon completing a trial, the methanol mixture was transferred to a 2 mL GC-MS vial and diluted with methanol in order to keep the siloxanes of interest within a range of 1-5 mg siloxane/L methanol for analytical purposes. In addition, a known amount of phenanthrene-d10 was added to each GC-MS vial to be analyzed as an internal standard. Samples were stored in 2 mL GC vials at 0° C until being analyzed on the GC-MS, typically for no longer than a week.

Samples were analyzed by means of a Thermo Scientific GC-MS (models Focus and DSQ II). The use of GC-MS allowed for direct evaluation of the methanol samples to determine how

much of each individual siloxane species was present. Before any data could be collected, the GC-MS required a calibration curve to be generated using known standards. After synthesizing the standards and generating a calibration curve, samples from preliminary trials were collected and analyzed in order to ensure that: 1) the methanol impingers collected all of the siloxanes diffused, and 2) the GC-MS data were consistent with the siloxane diffusion rates determined gravimetrically.

Quality Control – Sample Analysis

In order to ensure the quality and accuracy of the data collected, multiple quality assurance steps were taken. All standards for calibration curves were created using siloxane solutions diluted with optima grade methanol. Dilutions were made using gastight syringes and volumetric flasks (Pyrex Co., USA, sized 2mL, 5 mL and 10 mL). Standards for the calibration curve were generated with both a surrogate (p-Terphenyl-d14) and an internal standard (phenanthrene-d10 mix), in addition to all five siloxane species of interest. Liquid surrogate solution was produced by dissolving 20 mg, measured with a mechanical balance accurate to five decimal places, of p-Terphenyl-d14 into 2 mL of methylene chloride (measured with a 2 mL volumetric flask), producing a 10,000 mg/L solution. The standards used for the calibration curve included: 0.10, 0.25, 0.50, 1.00, 2.00, 5.00 mg siloxane/L methanol. All standards and samples were stored at 0° C; the internal standard and surrogate solutions were stored at 5° C.

As part of sampling, the surrogate was placed into the methanol impingers, and the internal standard was placed into GC-MS vials with the impinger samples. Both the internal standard and surrogate were analyzed in the GC-MS and results were given along with the siloxane results. The results for the surrogate were compared with the initial concentration within the impingers

before sampling to determine if any losses occurred in the impinger sampling method. The GC-MS was programmed to use the internal standard results for automatic calibration. Minimum detection limit (MDL) and minimum reporting limit (MRL) were calculated for each siloxane species with the GC-MS. This was necessary due to the low level and small range (0-5 mg siloxane/L MeOH) at which the GC-MS could detect siloxanes. The MDL and MRL levels were calculated using the method outlined in EPA document 815-R-00-006.

Quality Control - Glassware

All glassware was cleaned in a four-step process to ensure cleanliness and limit contamination. The cleaning process entailed three rinses with distilled water, three rinses with nanopure water filtered by a Vaponics Inc. device (Aries model), one rinse with optima grade acetone, and a final rinse with optima grade methanol. The glassware was then allowed to air dry completely. Gastight syringes (Hamilton Co., USA, sized 10 µL, 50 µL, 500 µL and 10 mL) were all rinsed three times with optima grade methanol before and after each use.

Quality Control – Gas Stream

Gas flow readings were necessary to ensure proper biogas makeup within the gas stream. For this purpose, a Mini-Buck flow calibrator model M-5 (A.P. Buck Inc, Orlando, FL) was used to take flow readings in three separate locations within the gas stream. The results allowed for the confirmation of CO_2 and CH_4 levels using gravimetric analysis, in addition to the verification of total effluent gas flow. H_2S levels are also vital to the successful synthesis of the biogas stream. Therefore proper analysis is necessary to determine the levels within the stream. Airgas Inc. provided CH_4/H_2S tanks pre-mixed with variability down to H_2S ppm levels. In-house analysis was conducted on their end and the results of such are provided with each tank. Using this information, along with an Industrial Scientific MX6 iBrid multigas monitor (Oakdale, PA)

permitted the collection of H_2S readings within the apparatus. Using the multigas monitor, readings were taken upon exiting the CH_4/H_2S source, after combination with CO_2 (before entering humidifier), and upon exit of humidifier. The location of the third H_2S reading was selected to ensure that H_2S was not exiting the gas stream by dissolving into the liquid H_2O within the humidifier.

Quality Control – Humidity and Temperature

Humidity and temperature are important aspects that must also be accounted for in order to effectively synthesize a representative WWTP biogas. For this purpose, a humidification system was included within the biogas stream and a climate-controlled chamber was used to house a portion of the system. Both humidity and temperature were monitored during initial trials to determine the level of consistency that was possible using the installed system. A Lascar data logger (model EL-USB-2-LCD, Whiteparish, England) allowed for the collection of temperature and humidity data during trials. The data logger was placed directly within the gas stream in a glass column in the climate controlled chamber and recorded readings of temperature and humidity every 30 minutes. After completion of a trial the data logger was connected to a computer and data were downloaded for analysis.

Experimental Trials – Sample Collection

Typical trials were performed between three and five days. Experiments were begun by first filling a diffusion vial with 7 mL of the siloxanes. Most trials were completed with all five siloxanes; however, trials with solely D_5 and a combination of D_4 and D_5 were also completed for comparison. With all five siloxanes, the volumes of each placed into the diffusion vial were as follows: 30 µL of L_3, 120 µL of L_4, 150 µL of D_4, 1.2 mL of L_5 and 5.5 mL of D_5. These volumes were selected in order to satisfy a specific diffusion range for each siloxane. The aim

was to keep diffusion of D_5 around 75-85% of total siloxane diffusion, D_4 around 5-10% of the total and then have L_4, L_5 and D_3 contribute the remaining amount. Using gastight syringes, the siloxanes were measured and then transferred into the diffusion vials in order of least to most volume. Therefore, 30 µL of L_3 was transferred to the diffusion vial, then 120 µL of L_4, and so forth until all five siloxanes had been transferred. After the diffusion vial was filled with the siloxanes, it was weighed on a mechanical balance (accurate to 0.01 mg). The vial was then placed into the dynacalibrator, which was set to 90°C. The time was recorded, along with initial mass.

Two impingers were connected in series to ensure siloxane loss did not occur. The impingers were filled with 25 mL of optima grade methanol measured from a 25 mL graduated cylinder. The methanol was added to the impinger vials, along with 50 µL of the liquid surrogate compound, 10,000 mg/L p-Terphenyl-d14. This volume of surrogate provided for a total concentration of 20 mg/L in the impingers. The impingers were then taken to a digital scale (accurate to 0.01 g) for weighing, and the mass was recorded. Impingers were handled while wearing powder-free nitrile gloves and careful consideration was made to ensure cleanliness. After weighing, they were placed in a cold water bath in a cooler and connected to the gas stream. The connections were made with Teflon Swagelok connectors and 3.125 mm Teflon tubing. Samples were collected over 20 minutes, before the impingers were disconnected from the gas stream. The impingers were then dried using Kimtech Kimwipes before being weighed on the digital scale. The mass was recorded to determine if any methanol was lost during the sampling process.

Using a gastight syringe, 50 µL aliquots of samples were removed from each impinger and placed into GC-MS vials. Duplicates of each sample were made, so two vials were used for impinger A, two vials for impinger B. In addition to the 50 µL of sample, 450 µL of optima grade methanol was also placed into the GC-MS vials (in order to make a 1:10 dilution) along with 2 µL of the internal standard, 1,000 mg/L phenanthrene-d10. After dilution the final concentration of internal standard became 4.0 mg/L., and final concentration of surrogate solution became 2 mg/L. The GC-MS vials were then placed in a freezer set to 0° C for storage until analysis. The impinger glassware was cleaned using the glassware cleaning process outlined above and set aside to dry. Impinger samples were taken in this way for multiple days, allowing the determination of siloxane diffusion over a period of time.

Experimental Trials – Sample Analysis

Upon completion of a given trial, the diffusion vial was removed from the dynacalibrator and allowed to cool to room temperature (approximately one hour). The diffusion vial was then weighed on a mechanical balance. The mass of the vial with contents and time of removal from the dynacalibrator were recorded. Using the time, along with the corresponding change in mass, the mass transfer of siloxanes from liquid to gaseous form was calculated. This information, in conjunction with the total flow-rate of the carrier gas, was used to estimate the concentration of total siloxanes in the gas stream. These steps allowed for the development of the methods that were used for gravimetric analysis.

At the same time, all impinger sample vials were taken to the GC-MS for analysis. Standard curves were generated from fresh standards of all five siloxanes as well as the surrogate. Each standard received the same spike of internal standard as the impinger samples for comparison (2

mg/L MeOH). Impinger samples were analyzed on the GC-MS and compared to the new standard curve to determine the levels of the individual siloxanes, as well as the surrogate concentration. These data were also compared with the estimation of total siloxanes in the gas stream. The data produced by the analysis of the GC-MS were utilized to determine how accurate the GC-MS was compared to the gravimetric analysis, as well as how consistent the siloxane diffusion was over a day-to-day basis.

The siloxane compounds within the samples were analyzed using Thermo Scientific GC-MS models Focus and DSQ II, respectively. Using an AI/AS 3000 model autosampler, 1.00 µl of sample was injected into the injection inlet at base temperature 250 °C. Using helium as the carrier gas, in split mode with a 10:1 split ratio, the sample entered the Restek GC column (model Rxi®-5Sil MS, 30m x 0.25m ID x 0.50 µm df) at a column flow rate of 1 mL/min. The initial oven temperature was set to 60 °C and immediately increased to 165 °C at a rate of 15 °C/min. Upon reaching 165 °C the rate was increased to 45 °C/min until reaching the final temperature of 300 °C, where it was held constant for 2 minutes. The transfer line between the GC and MS was heated to 310 °C. The MS operated in SIM mode for the entirety of analysis and followed the program described in Table 2.

Table 2 - Mass spectrometry analytical program.

Time (min)	ATMU Observed	Compound
Start-4.0	221	L_3
4.0-5.0	281	D_4
5.0-5.8	207	L_4
5.8-6.6	355	D_5
6.6-8.0	147	L_5
8.0-End	188, 244	IS, Surr

These atmu values were used to identify the five individual siloxanes, internal standard and surrogate. Using Thermo Scientific Xcaliber software the peak areas of the seven compounds were integrated to identify and quantify the values by comparing the sample peak areas to that of the standard curve. A chromatogram showing relative abundance of each compound as well as the retention times for each is displayed in Figure 3 below. The seven peaks, one for each compound, are well represented and do not overlap, allowing successful analysis without contamination between individual compounds.

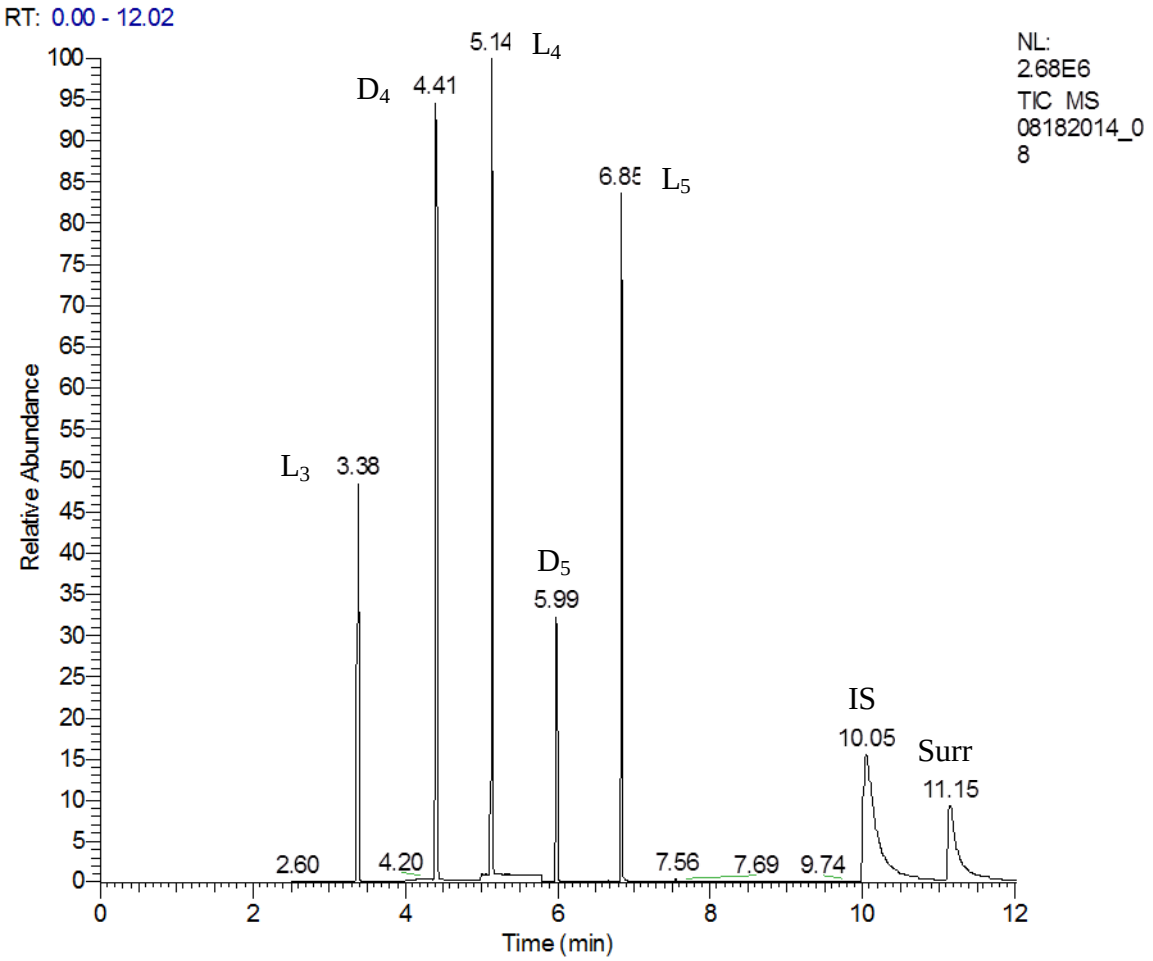

Figure 3 - Chromatogram displaying relative abundance and retention time of all siloxanes, internal standard and surrogate compounds.

Results and Discussion

Biogas Composition

Biogas composition within WWTP is typically comprised of 50-70% methane, 30-45% carbon dioxide and small amounts of nitrogen and any number of other contaminants; e.g. hydrogen sulfide, siloxanes and halides (Accetola et al., 2008; Osorio and Torres, 2009; Rasi et al. 2011; Schweigkofler and Neissner, 2001). It is therefore necessary to demonstrate the capability of designing a successful method of synthesizing a gas stream with those characteristics. Using MFC devices to control both the CO_2 and CH_4/H_2S tanks allows for fine-tuning of the method to ensure that the two largest constituents of the gas stream were within proper range. The flow calibrator took gas flow readings from both sources (after exiting MFCs), along with total effluent flow (after CO_2 and CH_4/H_2S combination) at system exit. Data from the flow calibrator readings are displayed in Table 3.

Table 3 - Flow and composition of CO_2 and CH_4/H_2S within gas stream.

Gas Source	Flow (ml/min)	Makeup (%)
CO_2	160 ± 2	~32
CH_4/H_2S	340 ± 2	~68
Total	500 ± 4	100

Outside of CH_4 and CO_2, H_2S and siloxane provide a small, but important, presence within biogas. Siloxane is considered the most serious contaminant (Ajhar and Melin, 2006).

Additionally, siloxane and H_2S are a primary focal point; in the form of potential removal techniques. Ensuring that those two contaminants can be effectively introduced and maintained within the gas stream is therefore vital to synthesizing a representative biogas stream. AirGas, Inc. provided a pre-mixed gas tank of CH_4 with 73.16 ppmv H_2S (according to their in-house analysis). The multigas monitor was used to determine H_2S levels within the gas stream at three locations: (1) upon exiting the CH_4/H_2S gas source, (2) after combination with CO_2 prior to entering the humidifier, and (3) upon exiting the humidifier. Data from multigas monitor readings are displayed in Table 4.

Table 4 - H_2S levels at three locations within system (n = 10).

Sampling Location	H_2S Level (ppm)
Source	73.16
Pre-humidifier	43.2 ± 0.7
Post-humidifier	41.8 ± 0.8

Humidity and temperature levels of a typical biogas found at a WWTP are typically consistent and important variables. The goal for the research was to reach a biogas temperature of 35° C and a relative humidity as high as possible. Using the data logger, data were collected for both of these parameters during initial trials. The results of the data, collected continuously over nine days, are displayed in Table 5.

Table 5 - Average temperature and relative humidity levels within system (n = 2775).

Temperature (°C)	Humidity (%)
34.3 ± 0.6	49.7 ± 3.3

Humidity levels were remained at approximately 50% relative humidity with temperature close to 35 °C during the course of the trials. These data were collected using the data logger placed within the gas stream channel within the climate controlled chamber. Humidity levels were thus recorded in an environment warmer than that of the humidification device, which was held at room temperature, defined as 23 °C. Change in temperature was approximately 12 °C. Relative humidity is defined as partial pressure divided by saturation vapor pressure. Saturation vapor pressure at 35 °C is 5.6 kPa and 2.8 kPa at 23 °C. Therefore we can estimate relative humidity immediately exiting the humidification device as 100% relative humidity.

Siloxane Analysis – Gravimetric Estimations

Ensuring siloxane concentrations were within ranges possible in WWTP biogas was the primary goal of the research. The use of trial and error allowed for the proper adjustment of the calibration gas generator settings to increase siloxane concentration to a high level while still remaining within the typical ranges observed in the field. This was achieved by adjusting the temperature setting of the dynacalibrator and the composition of the siloxane mixture before taking samples and analyzing results. Depending upon the siloxane levels, adjusting the sampling time with methanol impingers and the dilution factor allowed for the optimization of the setup. By altering each of those components, a representative siloxane concentration was achieved. Confirming siloxane levels were on the higher end of the observable range became an informal goal in order to prepare the setup for future work investigating siloxane treatment. It was the belief of the researchers that higher siloxane levels would improve future research in the field by potentially leading to a decrease in time necessary for siloxane removal studies.

Using gravimetric calculations, it was possible to estimate the siloxane levels within the gas stream. These calculations were made via mass readings collected before and after trials, along with time of input and output. Change in mass and change in time were then used to determine the diffusion rate and concentration using simple computations. The mean, standard deviation (SD) and coefficient of variation (standard deviation/mean, CV) were calculated using the data gathered. Table 6 displays data concerning siloxane measurements using gravimetric information at three different temperature settings within the dynacalibrator. These data were used during initial trial and error in order to determine the optimal temperature setting for the dynacalibrator. Initially, 98 °C was tested, then 95 °C and finally 90 °C. It was hypothesized that the diffusion rates and concentrations were directly correlated with the temperature setting of the dynacalibrator, although the data collected were with the first dynacalibrator and showed high levels of variability. Data at each temperature were gathered using all five siloxanes (L_3, L_4, L_5, D_4 and D_5) in the diffusion vial and represent trials from one to four days.

Table 6 - Comparison of mean siloxane diffusion and concentrations within gas stream at three different dynaclibrator temperatures. Gravimetric estimations.

Temperature (° C)	Siloxane Diffusion (g/min)	Siloxane Concentration (mg/m^3)
98 (n = 9)	9.25×10^{-5}	185
95 (n = 10)	5.03×10^{-5}	101
90 (n = 8)	5.31×10^{-5}	106

Table 7 - Comparison of mean, standard deviation and coefficient of variation of siloxane concentration at three different dynacalibrator temperatures. Gravimetric estimations.

Temperature (° C)	Mean (mg/m^3)	SD	CV
98 (n = 9)	185	30.6	0.17
95 (n = 10)	101	17.8	0.18
90 (n = 8)	106	16.1	0.15

After comparing the three temperature settings for the dynacalibrator, 90 °C was chosen as the ideal temperature for the purposes of continuing the research due to the concentration being close to the desired range and the smaller coefficient of variation compared to the two other temperature settings. The first dynacalibrator was removed in favor of a newer version (same model) in the hope that variability would be decreased. The data with the new dynacalibrator are displayed in Table 8 below. This newer arrangement became the optimized system and represents the final organization of apparatus. Different mixtures of siloxanes were used for the optimized trials in an effort to determine whether this affected total siloxane diffusion and overall concentration within the gas stream. The differences in trials are as follows: three trials contained a mixture of all five siloxanes, one trial contained solely D_5, and one trial contained D_4 and D_5.

Table 8 - Siloxane diffusion rates and concentration within gas stream at 90 °C. Gravimetric estimations.

Siloxanes	Diffusion Rate (g/min)	Siloxane Concentration (mg/m^3)
D_5	4.24×10^{-5}	84.69
D_4 & D_5	5.15×10^{-5}	103.1
L_3, L_4, L_5, D_4 & D_5	4.31×10^{-5}	86.10
L_3, L_4, L_5, D_4 & D_5	4.25×10^{-5}	84.93
L_3, L_4, L_5, D_4 & D_5	5.21×10^{-5}	104.3

Table 9 - Mean, standard deviation and coefficient of variation of gravimetric measurements at 90 °C from trials containing all siloxanes (n = 3). Gravimetric estimations.

Mean (mg/m^3)	SD	CV
91.8	8.86	0.097

Data from Table 9 compare the mean, standard deviation and coefficient of variation of trials containing all siloxanes using gravimetric estimations. Siloxane levels within the finalized biogas settings remained within a range of 85-104 mg total siloxanes/m^3 gas flow. These levels, although on the higher end of those found within a WWTP, appear to be consistent and reproducible, according to the analytical data observed. The data suggest that there was little difference between individual siloxane diffusion compared to a mixture of all five siloxanes. This observation allows for effective analysis for many different endeavors in siloxane research, including individual siloxane analysis or different combinations of siloxane species. Siloxane levels found in biogas produced at a WWTP fluctuate temporally and spatially based on silicon entering WWTPs and are therefore difficult to approximate due to the varying influent they receive (Bletsou et al., 2013). Therefore in order to successfully synthesize a representative biogas, it is necessary to ensure that each aspect of the gas stream in consistent and adjustable to allow for the ease of use.

Siloxane Analysis – GC-MS Analysis

In addition to gravimetric estimations, GC-MS analysis allows for effective siloxane assessments within gas streams. Using the methanol impinger technique, samples were capable of being taken any time from start to finish during each experiment. Benefits of this method included the allowance of routine sampling, and therefore increased data for comparison and analysis. Daily methanol impinger samples were collected during the optimized 90° C trials, permitting increased siloxane diffusion and concentration information. Siloxane fluctuations are common within WWTP biogas, however a goal of this research was to limit this phenomenon as much as possible in an effort to improve consistency and replicable applications. Daily sampling permits

the determination of siloxane concentration fluctuations within the apparatus over the course of each experiment.

Because the GC-MS analyzes for all five siloxanes individually, it is possible to see the individual siloxane levels during each trial. Figures 4 and 5 below display siloxane concentrations over a four day trial. The data were collected using GC-MS analysis during the final trial containing all siloxanes and are presented as individual and total siloxane concentrations.

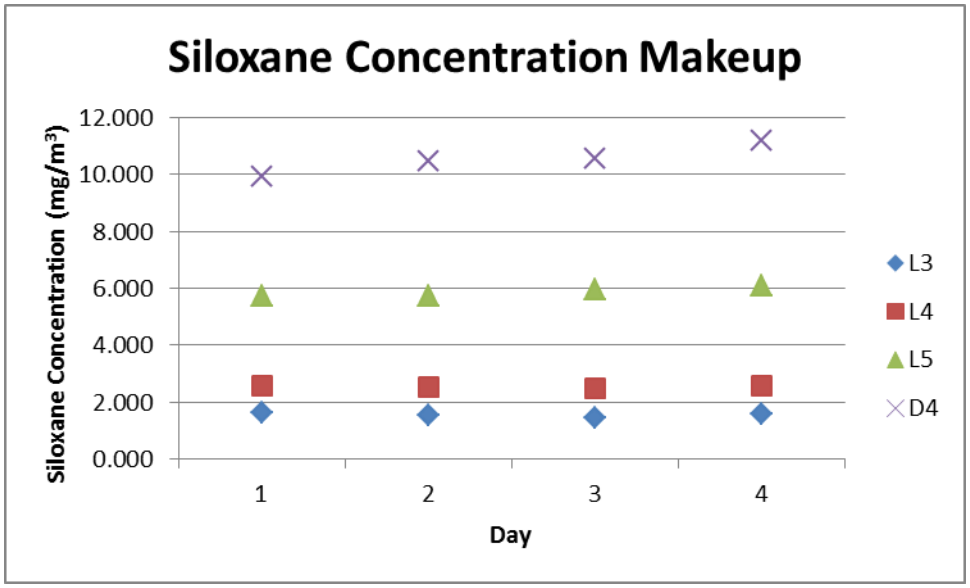

Figure 4 - Siloxane analysis over four days, third trial containing all siloxanes. Results produced by GC-MS analysis.

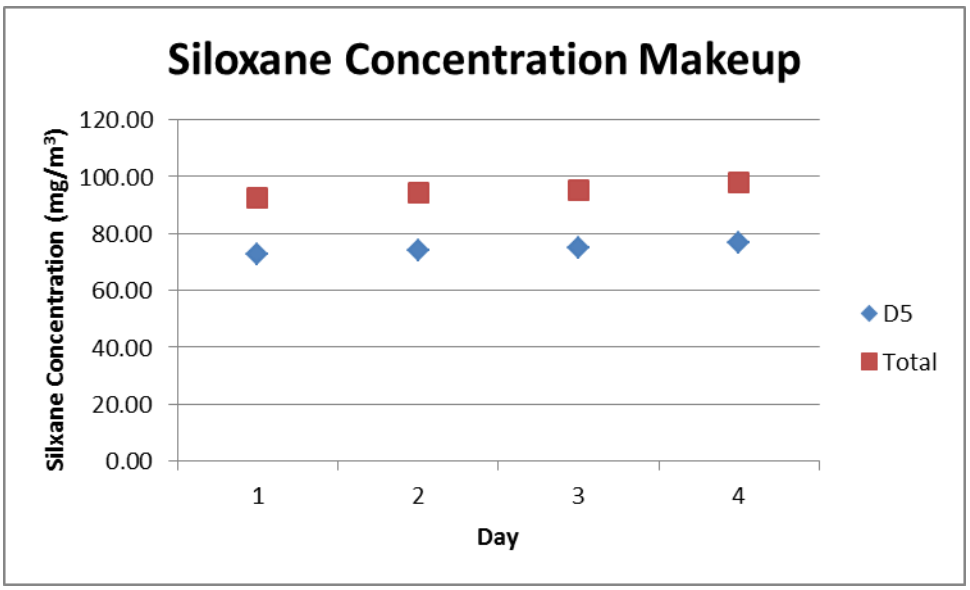

Figure 5 - Siloxane analysis over four days, third trial containing all siloxanes. Results produced by GC-MS analysis.

From Figures 4 and 5 above it is possible to see that using the apparatus settings for the optimized trials, D_5 was observed at concentrations above 60 mg/m^3 within the gas stream. The siloxane D_5 makes up the greatest portion of the total siloxane concentration, followed by D_4, L_5, L_4, and L_3. The above two figures provide a visualization of the daily makeup and fluctuation of individual and total siloxane levels during the course of a four day experimental trial.

Using the GC-MS data from the three trials with all five siloxanes, it is possible to combine the information to determine overall trends with the method developed. Table 10 below shows the overall percent makeup of each individual siloxane over the course of four days. Information displayed is mean values from the three trials containing all five siloxanes. Data were collected using GC-MS analysis.

Table 10 - Percent makeup of siloxane species over the course of four day trials (n = 3). GC-MS analysis.

Day	L_3	L_4	L_5	D_4	D_5	Total
1	5%	3%	6%	12%	73%	100%
2	5%	3%	6%	12%	74%	100%
3	4%	3%	6%	12%	75%	100%
4	4%	3%	6%	11%	76%	100%

The GC-MS data from the three trials containing all five siloxanes allow the determination of mean values for both total and daily siloxane concentration in mg/m^3 and is displayed in Figure 6 below. For the three trials, overall mean of siloxane concentrations was calculated as 119 mg/m^3 and is displayed in Figure 6 as a red line. Additionally, mean daily siloxane concentrations and minimum and maximum daily levels are displayed.

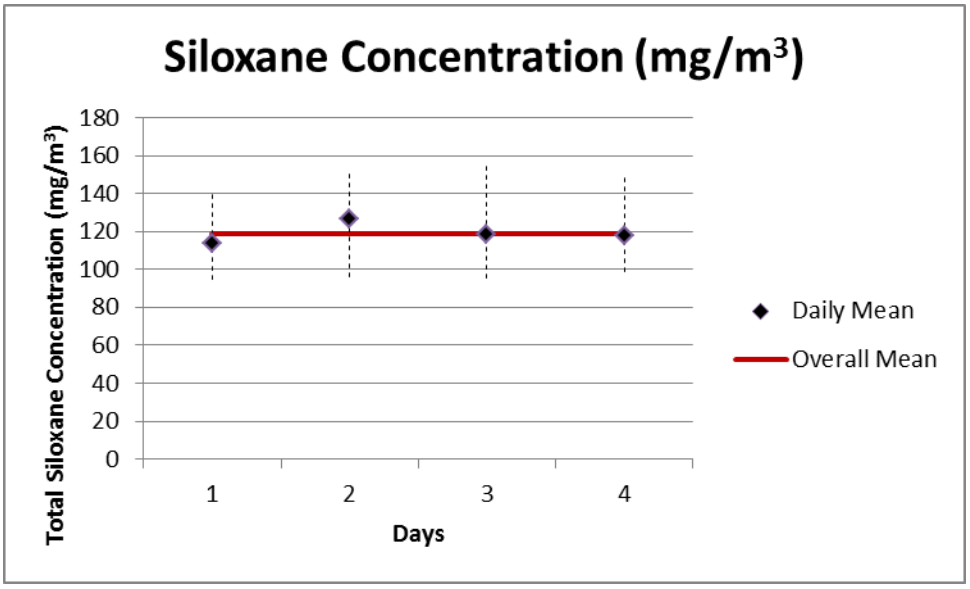

Figure 6 - Siloxane concentration daily mean, overall mean and range over four days for trials containing all five siloxanes. Results produced by GC-MS analysis.

The data for siloxane concentration, standard deviation, coefficient of variation, and surrogate recovery from each individual trial, including that of solely D_5 and of D_4 and D_5, are displayed in

Table 11 below. Data for the trial containing D_4 and D_5 produced D_4 results greater than those of the calibration curve. Therefore the GC-MS could not provide accurate readings of the samples and no conclusions can be drawn from these data. For this reason the data for concentration, standard deviation and coefficient of variation are not applicable (N/A). Mean siloxane concentration, standard deviation, coefficient of variation, and surrogate recovery of the three trials containing all five siloxanes are displayed in Table 12 below. Surrogate recovery for the second trial containing all five siloxanes is only from one day. Three of the four days showed either vastly high levels or no surrogate, it is assumed the GC-MS was in error.

Table 11 - Total siloxane concentration, standard deviation, coefficient of variation and surrogate recovery data from each optimized trial. GC-MS analysis.

Siloxanes	Concentration (mg/m^3)	SD	CV	Surrogate Recovery
D_5	117.5	6.39	0.054	112%
D_4 & D_5	Above GC-MS Range	N/A	N/A	N/A
L_3, L_4, L_5, D_4 & D_5	113.9	12.7	0.11	92.0%
L_3, L_4, L_5, D_4 & D_5	148.3	5.43	0.037	*116%
L_3, L_4, L_5, D_4 & D_5	95.11	2.09	0.022	82.4%

* Surrogate data from one day only*

Table 12 - Mean concentration, standard deviation, coefficient of variation, and surrogate recovery of all trials containing all siloxanes (n = 3). GC-MS analysis.

Concentration (mg/m^3)	SD	CV	Surrogate Recovery
119.1	6.7	0.057	89.1%

Siloxane Analysis – Gravimetric vs. GC-MS Analysis

Gravimetric estimations and GC-MS analysis can be compared to determine the similarity between the two analytical methods. Table 13 below shows the results of both analytical methods for each of the five optimized trials. The trial containing both D_4 and D_5 produced

results greater than those the GC-MS device could reasonably report; therefore no conclusions can be drawn from these data.

Table 13 - Comparison of gravimetric and GC-MS analysis for all trials.

Siloxanes	Gravimetric Estimation (mg/m^3)	GC-MS Estimation (mg/m^3)
D_5	84.69	117.5
D_4 & D_5	103.1	Above GC-MS Range
L_3, L_4, L_5, D_4 & D_5	86.10	113.9
L_3, L_4, L_5, D_4 & D_5	84.93	148.3
L_3, L_4, L_5, D_4 & D_5	104.3	95.11

When comparing the gravimetric estimations to the data produced by the GC-MS, we see a small disparity. The mean data derived from both gravimetric estimations and GC-MS analysis for the trials containing all five siloxanes are displayed in Table 14. Although the data between the two analytical methods do not match perfectly, the information collected does show low variability with both gravimetric estimations and GC-MS analysis. The discrepancy between the two analytical methods can be attributed to both human and instrumental error. Gravimetric estimations involve the use of very sensitive mechanical balances that require immense care and regular calibration. Likewise, GC-MS is also highly sensitive and necessitates the same high level of fine-tuning and calibration. For these reasons, it is not incorrect to believe that small error could occur with both gravimetric and GC-MS analysis. The important information that can be gathered from both analytical calculations is that consistency of the optimized system was high and error was low; for both analytical methods, precision is high.

Table 14- Comparison of gravimetric and GC-MS data for siloxane concentration, standard deviation and coefficient of variation within optimized trials containing all five siloxanes.

Data	Mean (mg/m^3)	Std Dev	CV
Gravimetric	91.8	8.9	0.097
GC-MS	119	6.7	0.057

Conclusions

Using laboratory methods and materials, it was possible to synthesize a representative WWTP biogas containing CH_4, CO_2, H_2S, humidity and siloxanes with the ability to control the levels of each individual component. This method, as presented above, has been shown to be consistent for a time period of up to four days. The method outlines two different analytical techniques that can be used in conjunction with the apparatus to determine siloxane concentration within the gas stream by way of diffusion from liquid to gaseous form. Siloxane characterization of the gas stream is possible using GC-MS analysis, permitting future research to be conducted in the field of biogas treatment methods for removal of humidity, siloxane and H_2S individually or simultaneously.

Acknowledgments

This work was sponsored by the Hampton Roads Sanitation District (HRSD) of Virginia.

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CHAPTER 4 – Summary and Conclusions

As stated in Chapter 3 the objectives of this report were as follows:

1. To develop a method for synthesizing a gas stream in lab representative of one produced as a biogas from a typical anaerobic digester at a wastewater treatment plant.
2. To develop a reliable system for production and characterization of a consistent gas stream.

With regards to objective 1, a laboratory method was developed for synthesizing a representative WWTP biogas using materials and devices. This method allows for the complete control of each individual constituent: CH_4, CO_2, H_2S, siloxanes and humidity. Using the method developed for this report, it was possible to adjust the gas stream to ensure each component was within ranges typically observed in biogas exiting anaerobic digesters at WWTPs. A secondary goal of maintaining siloxane levels at a higher range was also met. This goal was proposed in order to allow further work to be conducted exploring biogas treatment in the form of siloxane removal. In addition, this method allows for future work in humidity and H_2S treatment.

In regards to objective 2, both sampling and analytical techniques were used to ensure that the system was reliable and characterization of the stream was attainable. Sampling of the biogas can occur at multiple locations within the stream and at exit, ensuring consistency is maintained. Additionally, two analytical techniques were tested for characterization of siloxane levels. One method, gravimetric estimations, allowed for total siloxane diffusion calculations. The second method, GC-MS, allowed for individual siloxane species characterizations. With the use of

sampling and analytical techniques, it is possible to perform sufficient characterization and ensure reliability of the biogas stream.

In summary, the gas stream developed is representative of a biogas found exiting an anaerobic digester at a WWTP. It contains CH_4, CO_2, H_2S, siloxanes and humidity at consistent levels. These levels can be adjusted for multiple purposes, while maintaining consistency over the course of four days. Individual component levels can vary within a WWTP biogas; however a reliable stream can be produced using the method developed for this report, allowing for further research to be completed in lab without worry of constituent levels fluctuating.

APPENDIX A – Additional Tables and Figures

Table A1 - Gravimetric data from initial 98 °C dynacalibrator trials.

Siloxanes	Δ Time (mins)	Δ Mass (g)	Diffusion Rate (g/min)	Concentration (mg/m^3)
L_3, L_4, L_5, D_4 & D_5	7834	0.65775	8.40E-05	167.9
L_3, L_4, L_5, D_4 & D_5	2634	0.30343	1.15E-04	230.4
L_3, L_4, L_5, D_4 & D_5	1637	0.16861	1.03E-04	206.0
L_3, L_4, L_5, D_4 & D_5	1592	0.15226	9.56E-05	191.3
L_3, L_4, L_5, D_4 & D_5	1463	0.11142	7.62E-05	152.3
L_3, L_4, L_5, D_4 & D_5	3995	0.31094	7.78E-05	155.7
L_3, L_4, L_5, D_4 & D_5	10029	0.75423	7.52E-05	150.4
L_3, L_4, L_5, D_4 & D_5	1567	0.13884	8.86E-05	177.2
L_3, L_4, L_5, D_4 & D_5	2999	0.3514	1.17E-04	234.3
Average			9.25E-05	185.1
Std Dev			1.53E-05	30.65
Error			0.17	0.17

Table A2 - Gravimetric data from initial 95 °C dynacalibrator trials.

Siloxanes	Δ Time (mins)	Δ Mass (g)	Diffusion Rate (g/min)	Concentration (mg/m^3)
L_3, L_4, L_5, D_4, D_5	1351	0.0603	4.46E-05	89.27
L_3, L_4, L_5, D_4, D_5	1221	0.07623	6.24E-05	124.9
L_3, L_4, L_5, D_4, D_5	3211	0.17752	5.53E-05	110.6
L_3, L_4, L_5, D_4, D_5	1173	0.05666	4.83E-05	96.61
L_3, L_4, L_5, D_4, D_5	1378	0.06908	5.01E-05	100.3
L_3, L_4, L_5, D_4, D_5	1352	0.06479	4.79E-05	95.84
L_3, L_4, L_5, D_4, D_5	1359	0.07016	5.16E-05	103.3
L_3, L_4, L_5, D_4, D_5	1401	0.04262	3.04E-05	60.84
L_3, L_4, L_5, D_4, D_5	5834	0.28301	4.85E-05	97.02
L_3, L_4, L_5, D_4, D_5	5563	0.35341	6.35E-05	127.1
Average			5.03E-05	100.6
Std Dev			8.88E-06	17.76
Error			0.18	0.18

Table A3 - Gravimetric data from initial 90 °C dynacalibrator trials.

Siloxanes	Δ Time (mins)	Δ Mass (g)	Diffusion Rate (g/min)	Concentration (mg/m^3)
L_3, L_4, L_5, D_4, D_5	3017	0.11223	3.72E-05	74.40
L_3, L_4, L_5, D_4, D_5	2783	0.1632	5.86E-05	117.3
L_3, L_4, L_5, D_4, D_5	2779	0.17198	6.19E-05	123.8
L_3, L_4, L_5, D_4, D_5	2868	0.12891	4.49E-05	89.90
L_3, L_4, L_5, D_4, D_5	5763	0.2987	5.18E-05	103.7
L_3, L_4, L_5, D_4, D_5	4320	0.22398	5.18E-05	103.7
L_3, L_4, L_5, D_4, D_5	1440	0.08123	5.64E-05	112.8
L_3, L_4, L_5, D_4, D_5	7178	0.44464	6.19E-05	123.9

Average	5.31E-05	106.2
Std Dev	8.06E-06	16.12
Error	0.15	0.15

Table A4 - Gravimetric data from optimized 90 °C dynacalibrator trials.

Siloxanes	Δ Time (mins)	Δ Mass (g)	Diffusion Rate (g/min)	Siloxane Concentration (mg/m3)
D_5	4406	0.18658	4.235E-05	84.69
D_4 & D_5	5776	0.29767	5.154E-05	103.1
L_3, L_4, L_5, D_4 & D_5	5807	0.24998	4.305E-05	86.10
L_3, L_4, L_5, D_4 & D_5	6306	0.26778	4.246E-05	84.93
L_3, L_4, L_5, D_4 & D_5	7061	0.36813	5.214E-05	104.3

Average	4.63E-05	92.6
Std Dev	4.53E-06	9.05
Error	0.10	0.10

Table A5 – GC-MS data from trial containing solely D_5 (optimized, 90 °C).

Days	D_5 (mg/L)	Concentration (mg/m^3)	Recovery
1	4.4365	111	113.28%
2	4.7885	120	113.30%
3	4.4945	112	108.71%
4	5.0765	127	109.35%

Average	117.5	111.16%
Std Dev	6.39	0.02
Error	0.054	0.019

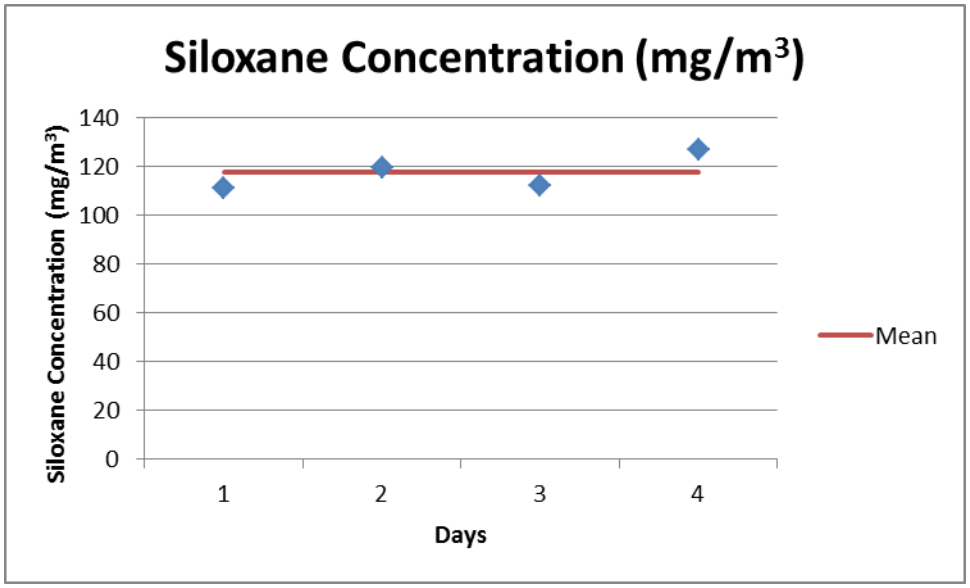

Figure A1 - Siloxane concentration over four days, trial containing solely D_5 (optimized, 90 °C). GC-MS analysis.

Table A6 - GC-MS data from trial containing both D4 and D5 (optimized, 90 °C).

Days	D_4 (mg/L)	D_5 (mg/L)	Total Siloxanes (mg/L)	Concentration (mg/m^3)	Recovery
1	6.666	4.457	11.123	278.1	107.13%
2	6.192	4.514	10.707	267.7	106.37%
3	4.583	3.858	8.441	211.0	76.84%

Average	25225.42%	96.78%
Std Dev	29.46	0.14
Error	0.12	0.15

Data was above limit of GC-MS and therefore no conclusions can be drawn from data.

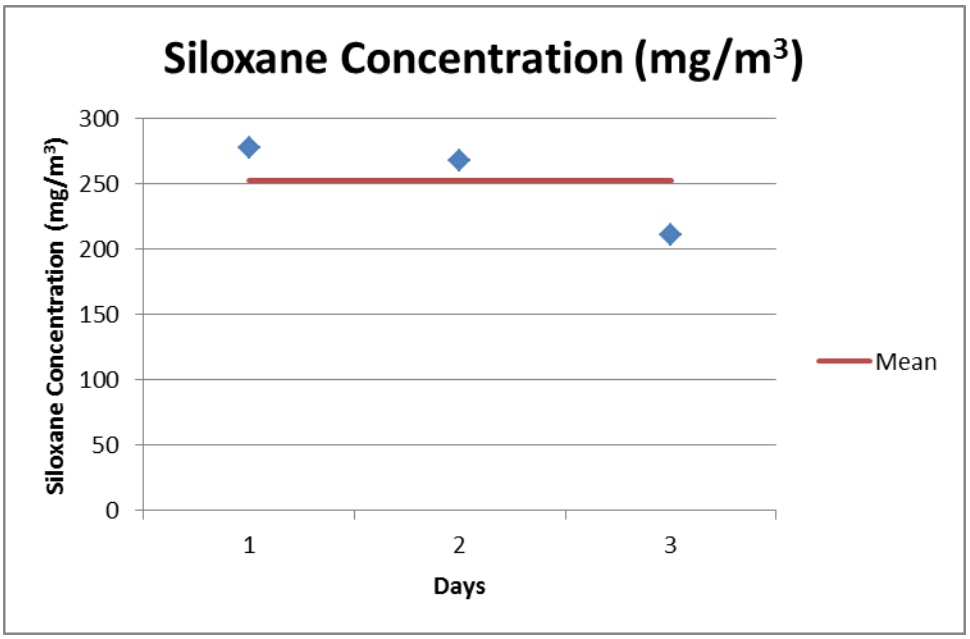

Figure A2 - Siloxane concentration over three days, trial containing D4 and D5 (optimized, 90 °C). GC-MS analysis.

Data was above limit of GC-MS and therefore no conclusions can be drawn from data.

Table A7 - GC-MS data from first trial containing all siloxanes (optimized, 90 °C).

Days	L_3 (mg/L)	L_4 (mg/L)	L_5 (mg/L)	D_4 (mg/L)	D_5 (mg/L)	Total Siloxanes (mg/L)	Concentration (mg/m3)	Recovery
1	0.364	0.161	0.274	0.628	2.939	4.366	109.1	88.97%
2	0.435	0.183	0.287	0.766	3.761	5.431	135.8	78.97%
3	0.312	0.133	0.227	0.525	2.996	4.193	104.8	98.09%
4	0.293	0.128	0.235	0.485	3.099	4.240	106.0	102.29%

Average	113.9	92.08%
Std Dev	12.71	0.09
Error	0.11	0.10

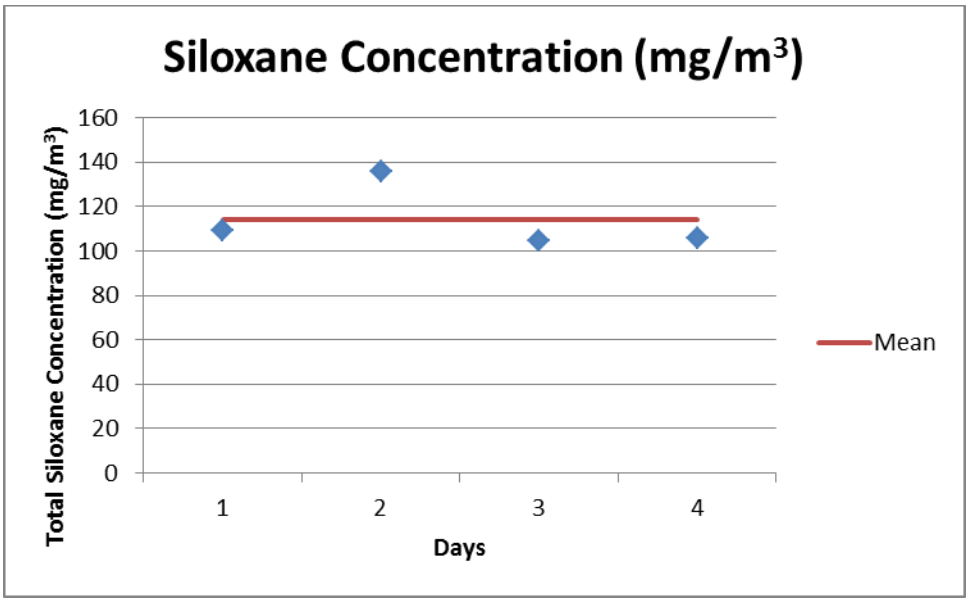

Figure A3 - Siloxane concentration over four days, first trial containing all siloxanes (optimized, 90 °C). GC-MS analysis.

Table A8 - Siloxane makeup over four days, first trial containing all silocanes (optimized, 90 °C). GC-MS analysis.

Days	L_3	L_4	L_5	D_4	D_5	Total
1	8%	4%	6%	14%	68%	100%
2	8%	3%	5%	14%	69%	100%
3	7%	3%	5%	13%	71%	100%
4	7%	3%	6%	11%	73%	100%

Table A9 – GC-MS data from second trial containing all siloxanes (optimized, 90 °C).

Days	L_3 (mg/L)	L_4 (mg/L)	L_5 (mg/L)	D_4 (mg/L)	D_5 (mg/L)	Total Siloxanes (mg/L)	Concentration (mg/m^3)	Recovery
1	0.276	0.217	0.372	0.663	4.063	5.590	139.7	N/A
2	0.264	0.233	0.382	0.699	4.448	6.026	150.7	N/A
3	0.271	0.218	0.364	0.736	4.594	6.183	154.6	N/A
4	0.218	0.215	0.345	0.692	4.467	5.937	148.4	115.75%

Average	148.3
Std Dev	5.43
Error	0.037

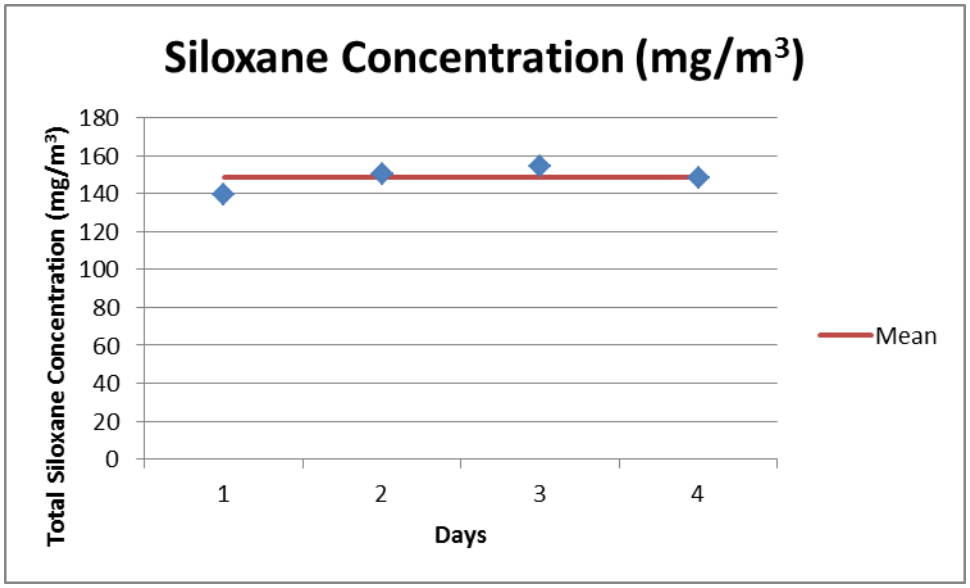

Figure A4 - Siloxane concentration over four days, second trial containing all siloxanes (optimized, 90 °C). GC-MS analysis.

Table A10 - Siloxane makeup over four days, second trial containing all siloxanes (optimized, 90 °C). GC-MS analysis.

Days	L_3	L_4	L_5	D_4	D_5	Total
1	5%	4%	7%	12%	73%	100%
2	4%	4%	6%	12%	74%	100%
3	4%	4%	6%	12%	74%	100%
4	4%	4%	6%	12%	75%	100%

Table A11 - GC-MS data from third trial containing all siloxanes (optimized, 90 °C).

Days	L_3 (mg/L)	L_4 (mg/L)	L_5 (mg/L)	D_4 (mg/L)	D_5 (mg/L)	Total Siloxanes (mg/L)	Concentration (mg/m^3)	Recovery
1	0.065	0.103	0.230	0.398	2.900	3.696	92.39	78.51%
2	0.062	0.102	0.230	0.419	2.966	3.778	94.44	80.29%
3	0.058	0.100	0.238	0.423	2.999	3.817	95.43	79.53%
4	0.064	0.103	0.245	0.447	3.070	3.928	98.19	87.26%

Average	95.11	81.40%
Std Dev	2.09	0.03
Error	0.02	0.04

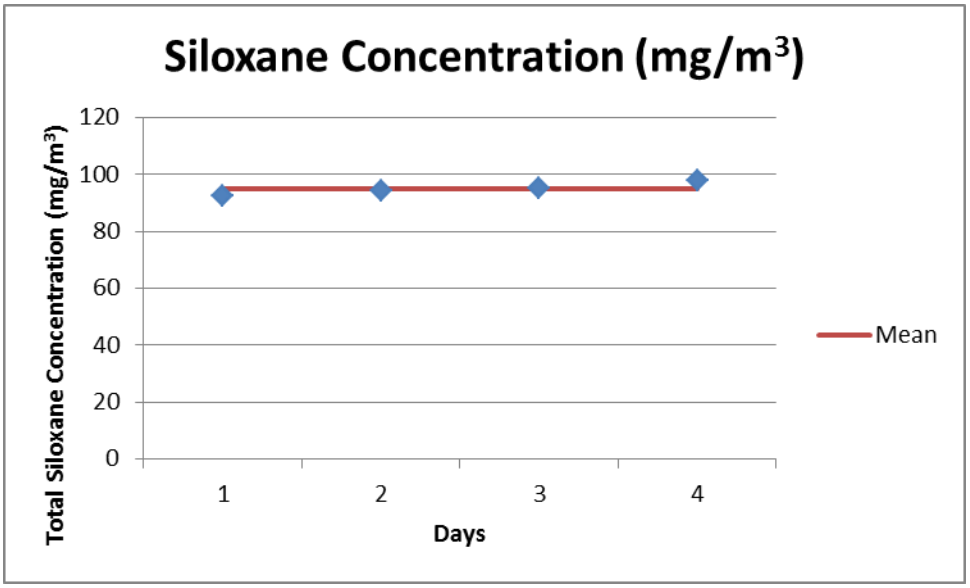

Figure A5 - Siloxane concentration over four days, third trial containing all siloxaes (optimized, 90 °C). GC-MS analysis.

Table A12 - Siloxane makeup over four days, third trial containing all siloxaes (optimized, 90 °C). GC-MS analysis.

Days	L_3	L_4	L_5	D_4	D_5	Total
1	2%	3%	6%	11%	78%	100%
2	2%	3%	6%	11%	79%	100%
3	2%	3%	6%	11%	79%	100%
4	2%	3%	6%	11%	78%	100%

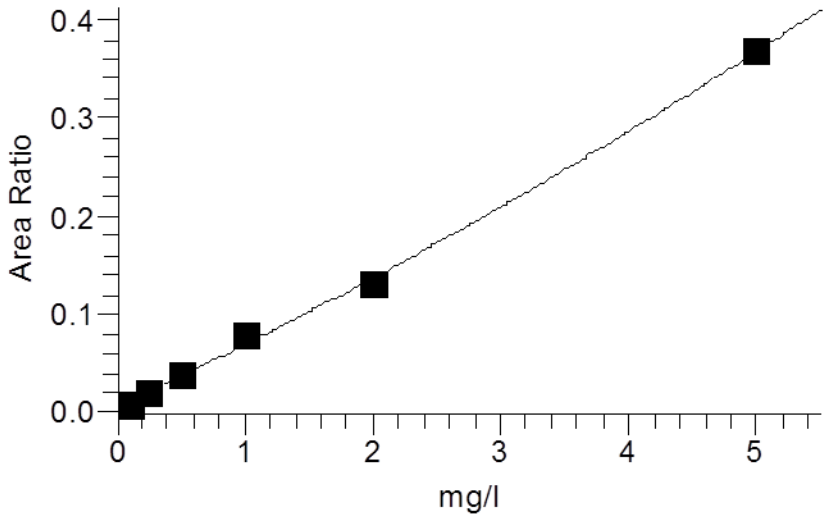

Figure A6 - Octamethyltrisiloxane (L_3) Calibration Curve

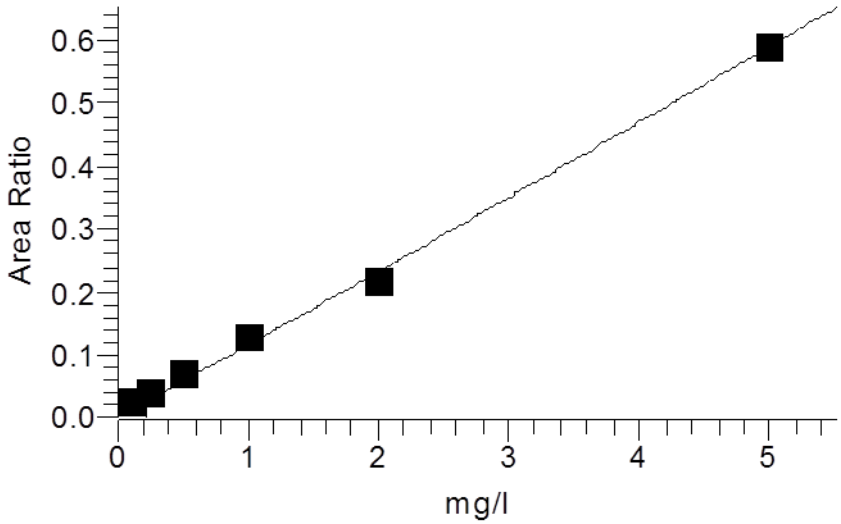

Figure A7 - Octamethylcyclotetrasiloxane (D_4) Calibration Curve

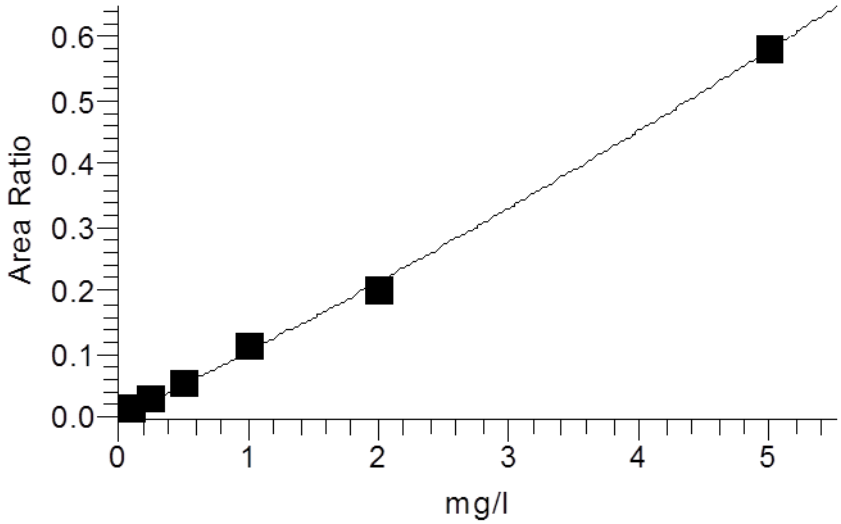

Figure A8 - Decamethyltetrasiloxane (L_4) Calibration Curve

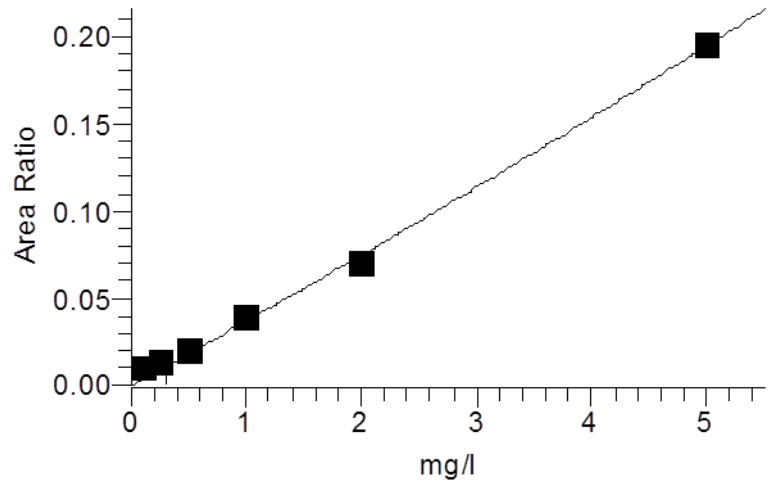

Figure A9 - Decamethylcyclopentasiloxane (D_5) Calibration Curve

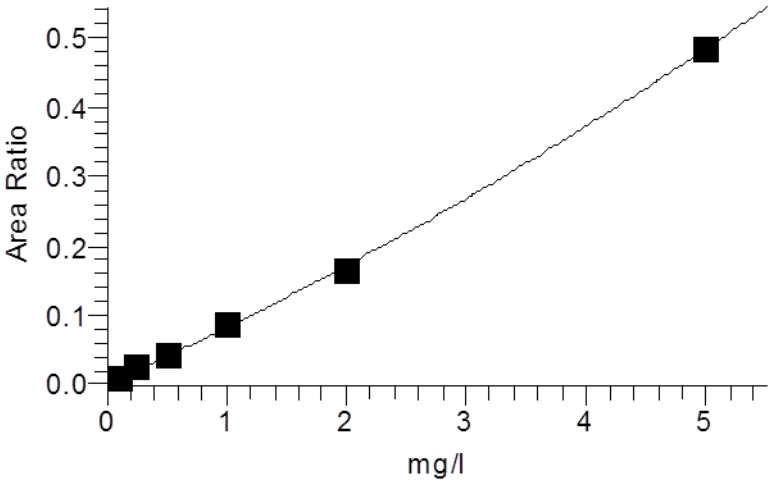

Figure A10 - Dodecamethylpentasiloxane (L_5) Calibration Curve

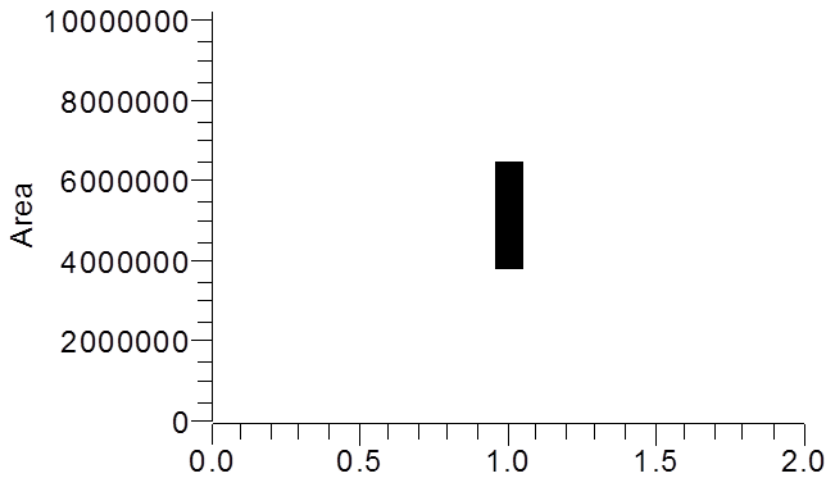

Figure A11 - Internal Standard Response from Calibration Curve