

Gas Chromatography Calibration Curve for Siloxanes analysis.

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Abstract

The ability to determine the concentration of an unknown sample is highly important in every scientific research. This work focuses on the construction of a calibration curve for the analysis of siloxanes concentration in an anaerobic digester. The siloxanes of interest were the octamethylcyclotetrasiloxane (D4) which has a negative effect on the conversion of biogas into energy and is harmful to mechanical equipment. For this purpose, fourteen samples having methanol as solvent and octamethylcyclotetrasiloxane (D4) as solute, with concentrations ranging between 0.01 % V/V and 1 % V/V, were prepared and analyzed through gas chromatography. The resulting percentage areas helped to the construction of a calibration curve. Only samples in the range 0.031 % V/V – 0.115 % V/V followed a linear trend as expected.

Keywords

Gas Chromatography, Siloxanes, Calibration Curve, Octamethylcyclotetrasiloxane, Percentage area.

1. Introduction

Due to the depletion and price increase of fossil fuels as well as their harmful effects on the environment, current waste management policies favor the development of renewable energies (Mckendry, 2002). The world is going to undergo a revolution due to the forecasted ability of the gas industry to produce bioenergy from biomass. The production of biomethane – a green substitute of natural gas – is growing in Europe and the United-States of America (Hilaire et al., 2017).

Biogas originated from landfills and sewage treatment plants is an attractive renewable fuel that can be used as a feedstock for cogeneration plants, internal combustion engines and fuel cells. However, due to various biomass inputs (e.g. agricultural wastes, sludges from sewage treatment plants, etc.), production processes (e.g. anaerobic digestion, municipal solid waste (MSW) landfills), seasonal effects and purification processes (e.g. gas scrubbers, pressure swing adsorption, membranes for biogas upgrading), the composition and quality of biogas and biomethane produced is difficult to assess. The exploitation of biogas is therefore usually limited by the harmful trace constituents, such as H₂S, mercaptans and siloxanes. Among these pollutants, volatile methyl siloxanes (VMSs) have the most detrimental effect on biogas utilization for energy production (Li et al., 2014).

As the material in a landfill or digester decomposes and generates biogas, the siloxane molecules enter the biogas stream as a vapor. During combustion these siloxanes undergo a phase change from a vapor to a solid silicon dioxide powder. This abrasive powder adheres to all surfaces downstream of the point of combustion, reducing heat transfer, blocking flow and increasing wear. Frequent overhaul is often required to prevent total equipment failure. The increased equipment maintenance and parts failures can significantly increase project costs while the downtime and reduced efficiency significantly decreases revenue (Energy, 2015).

The reduction of siloxane vapors prior to combustion to eliminate siloxane powder build up may be critical to the profitability of your biogas to energy project. In projects requiring the use of post combustion catalysts, siloxane vapor reduction is an absolute necessity.

To address this issue, a lab-scale anaerobic digester was developed and its performance for octamethylcyclotetrasiloxane (D4, selected as a model VMS) removal from the produced biogas was monitored. This report focuses on the building of a calibration curve enabling D4 conversion from percentage area to concentration in the digester (%V/V), through gas chromatography.

2. Literature Review

2.1 Siloxanes

Biogas utilized for energy production needs to be free from organic silicon compounds, since their burning has disastrous effects on turbines and engines; organic silicon compounds in the form of siloxanes can be found in biogas produced from urban wastes, due to their enormous industrial use in synthetic product, such as cosmetics, cleansing agents and paints (Gislon et al., 2013).

A siloxane is any chemical compound composed of units in the form of R_2SiO ($R = H$ or HC group). Silicones are macromolecules containing a polymer backbone of alternating silicon and oxygen atoms with organic side groups, such as methyl, phenyl or vinyl, attached to silicon. The word siloxane is derived from the words silicon, oxygen, and alkane. Siloxanes are volatile, liquid compounds and tend to be quite persistent in their environments (Carbon). In some cases, siloxane materials are composed of several different types of siloxide groups; these are labeled according to the number of Si-O bonds. However for the purpose of this study, the octamethylcyclotetrasiloxane (D4) will be used as VMS model.

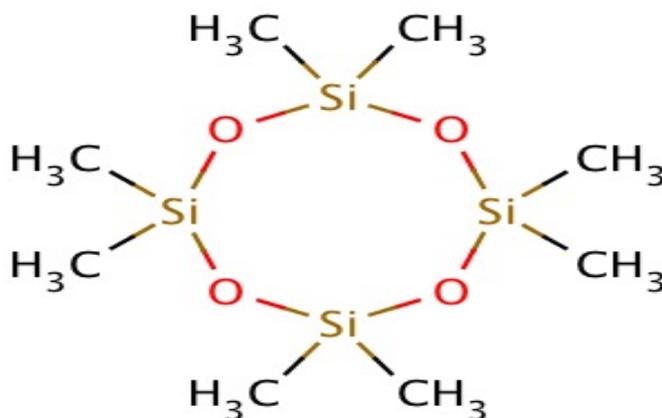


Figure 1: Octamethylcyclotetrasiloxane (Biotechnology)

These silicone-based compounds are used in cosmetics to soften, smooth, and moisten. They make hair products dry more quickly and deodorant creams slide on more easily. They are also used extensively in moisturizers and facial treatments. Siloxanes can also be found in medical implants, water-repelling windshield coatings, building sealants and lubricants (Foundation). Siloxanes are widely used in consumer products such as paints and cosmetics, as well as in medical products because they are characterized by their high stability, physiologic inertness and lubricating properties. The stability of siloxanes makes them to be, in general, very persistent once released in the environment. In recent years, several studies highlighted that some siloxanes may have endocrine disrupting properties and effects on the reproduction, which may cause concern about their effect on humans and the environment (Sanchez et al., 2010).

While composed primarily of methane and carbon dioxide, biogas also contains a host of contaminants including moisture, hydrogen sulfide, and Non Methane Organic Compounds (NMOCs). The most problematic NMOCs are called “siloxanes” which are a family of man-made organic compounds used in the manufacture of cosmetics, hygiene products, foods, and industrial coatings. The use of these compounds is increasing rapidly - and so is their presence in landfills and waste water (Energy, 2015). Siloxanes have been promoted as environmentally friendly substitutes of very harmful as chlorofluorosolventes (P.E. perchlorethylene), used in dry cleaning of clothing. There are more than 10,000 applications listed for siloxanes, and the number is expected to grow 10 more times in the next 5 years old (Foundation). The residue of these products is inevitably deposited in landfills and dragged along with the discharge of municipal and industrial water. Once you start the process of anaerobic digestion of organic matter,

siloxanes are mixed with biogas which is used in power generation facilities. The main varieties of siloxanes in biogas which pollute landfills and sewage treatment plants are of cyclical D3, D4 and D5, and linear L2 and L3 (Foundation). The presence of VMS in biogas can greatly reduce the efficiency of energy recovery from biogas. Typical total organic silicon compound are in the range of 3-24 mg/cm³. During combustion, siloxanes are converted into silicon dioxide deposits, leading to abrasion of engine parts or the build-up of layers that inhibit essential heat conduction or lubrication. The deposits may cause changes in geometry to the combustion chamber, inducing higher emissions of carbon monoxide and formaldehyde, possibly violating air emissions regulations (Ajhar et al., 2009).

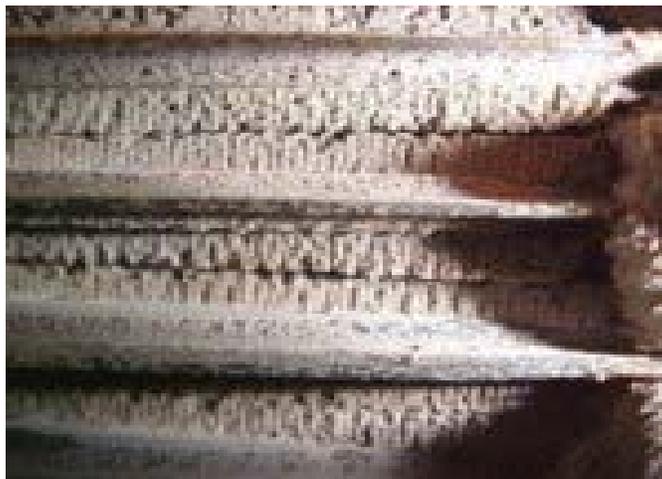


Figure 2: Siloxane build up on a turbine recuperator (Cambio-Evolution)

In order to determine mechanisms allowing the removal of siloxanes from digesters and biogas, a lab-scale anaerobic digestion plant was built and set to run in two successive phases: without and with a bed of zeolite. However, for this study to be successful, the first step would be to define a method of determining the concentration of siloxanes, in particular D4. The chosen method was gas chromatography (GC) that uses atomic detection (AED). The chromatography with mass spectrometry (GC-MS) would have been preferable. The coupling of gas chromatography (GC) with mass spectrometry (MS) has developed into one of the most sensitive and selective analytical methods for the separation, identification, and identification of components of complex organic mixtures. It gives a two-dimensional identification consisting of both a GC retention time and a mass spectrum for each component of the mixture. However, this dual approach is particularly expensive and not readily available in most of African Educational Institutions (Horii et al., 2008).

2.2 Gas Chromatography

The creation of gas chromatography is generally associated with the names of Nobel Prize Laureate Archer Martin and his colleagues Richard Synge and Anthony James. Martin and Synge experimented with separation of amino acid mixtures and, while conducting experiments in 1941, they developed liquid partition chromatography. After more intensive research, they invented gas-liquid chromatography, leading to them being awarded the Nobel Prize (Kolomnikov et al., 2018).

Gas chromatography is a term used to describe the group of analytical separation techniques used to analyze volatile substances in the gas phase. In gas chromatography, the components of a sample are dissolved in a solvent and vaporized in order to separate the analytes by distributing the sample between two phases: a stationary phase and a mobile phase. The mobile phase is a chemically inert gas that serves to carry the molecules of the analyte through the heated column. Gas chromatography is one of the sole forms of chromatography that does not utilize the mobile phase for interacting with the analyte. The stationary phase is either a solid adsorbant, termed gas-solid chromatography (GSC), or a liquid on an inert support, termed gas-liquid chromatography (GLC) (Texts, 2015).

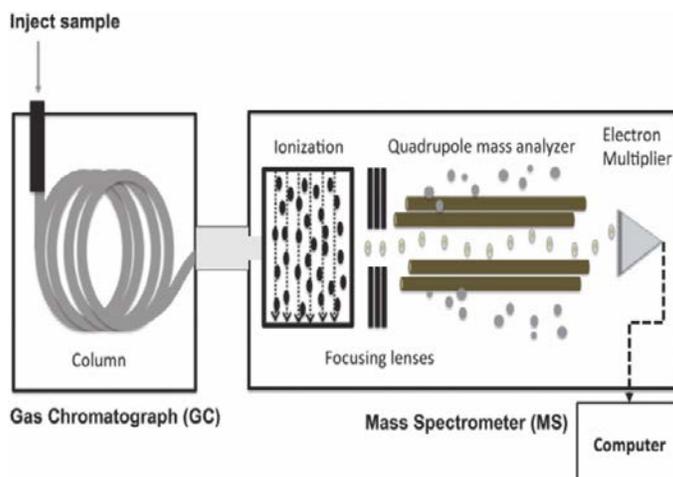


Figure 3: Schematic diagram of a gas chromatography quadrupole mass spectrometer (GC/MS) (Gate)

Carrier gas: The carrier gas must be chemically inert. Commonly used gases include nitrogen, helium, argon, and carbon dioxide. The choice of carrier gas is often dependent upon the type of detector which is used. The carrier gas system also contains a molecular sieve to remove water and other impurities (University).

Sample injection port: For optimum column efficiency, the sample should not be too large, and should be introduced onto the column as a "plug" of vapor - slow injection of large samples causes band broadening and loss of resolution. The most common injection method is where a micro syringe is used to inject sample through a rubber septum into a flash vaporizer port at the head of the column. The temperature of the sample port is usually about 50°C higher than the boiling point of the least volatile component of the sample. For packed columns, sample size ranges from tenths of a microliter up to 20 microliters. Capillary columns, on the other hand, need much less sample, typically around 10-3 mL (University).

Columns: There are two general types of column, packed and capillary (also known as open tubular). Packed columns contain a finely divided, inert, solid support material (commonly based on diatomaceous earth) coated with liquid stationary phase. Capillary columns have an internal diameter of a few tenths of a millimeter. They can be one of two types; wall-coated open tubular (WCOT) or support-coated open tubular (SCOT). Both types of capillary column are more efficient than packed columns (University)

An excessively high column temperature results in very short retention time but also in a very poor separation because all components mainly stay in the gas phase. However, in order for the separation to occur the components need to be able to interact with the stationary phase. If the compound does not interact with the stationary phase, the retention time will decrease. At the same time, the quality of the separation deteriorates, because the differences in retention times are not as pronounced anymore. The best separations are usually observed for temperature gradients, because the differences in polarity and in boiling points are used here (Chem.Ucla.Edu, 2016).

Data handling: data handling was originally by purely manual measurement of peak heights. It was recognized that Peak area measurement was fundamentally better and could be obtained approximately by measuring the peak height and the width of half height. Such an approach was satisfactory for simple mixtures but was totally impractical for mixtures containing perhaps 100 components in widely differing concentrations. Early integrators consisted of mechanical or electromechanical devices such as the ball and disk integrator and integrating amplifiers but were limited in range and speed of response. The mid 1960s saw the introduction of the first generation of electronic integrators and a little later the use of mainframe computers to handle data from a number of instruments simultaneously. The large amounts of data produced by open-tubular columns (especially when coupled to a mass spectrometer) can now be handled by a personal computer. The data can be acquired, manipulated, and displayed in real time and can be stored electronically almost indefinitely for record purposes (Dyson, 1994).

2.3 Calibration Curve

Calibration curve is a method in analytical chemistry. It is used to determine or measure the concentration of a particular substance in a sample. This is done by comparing this sample of unknown concentration to a set of standard samples whose concentration is known (Panel, 2017).

Calibration curves are used to understand the instrumental response to an analyte and predict the concentration in an unknown sample. Generally, a set of standard samples are made at various concentrations with a range that includes the unknown of interest and the instrumental response at each concentration is recorded. For more accuracy and to understand the error, the response at each concentration can be repeated so an error bar is obtained. The data are then fit with a function so that unknown concentrations can be predicted. Typically the response is linear, however, a curve can be made with other functions as long as the function is known. The calibration curve can be used to calculate the limit of detection and limit of quantitation.

When making solutions for a calibration curve, each solution can be made separately. However, that can take a lot of starting material and be time consuming. Another method for making many different concentrations of a solution is to use serial dilutions. With serial dilutions, a concentrated sample is diluted down in a stepwise manner to make lower concentrations. The next sample is made from the previous dilution, and the dilution factor is often kept constant. The advantage is that only one initial solution is needed. The disadvantage is that any errors in solution making—pipetting, massing, etc.—get propagated as more solutions are made. Thus, care must be taken when making the initial solution (University of Virginia).

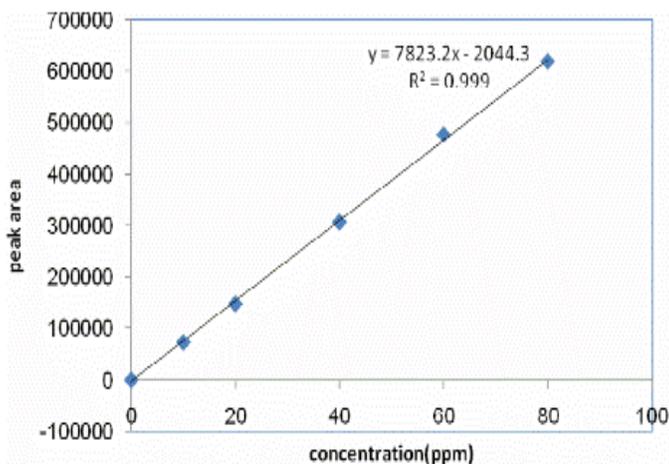


Figure 4: Bio analytical calibration curve (Simulation, 2012)

3. Experimental

3.1. Materials

The only chemicals used in the study was Octamethylcyclotetrasiloxane D4, Methanol, Nitrogen as a carrier gas and hydrogen for the oven heat source.

3.2. Experimental setup

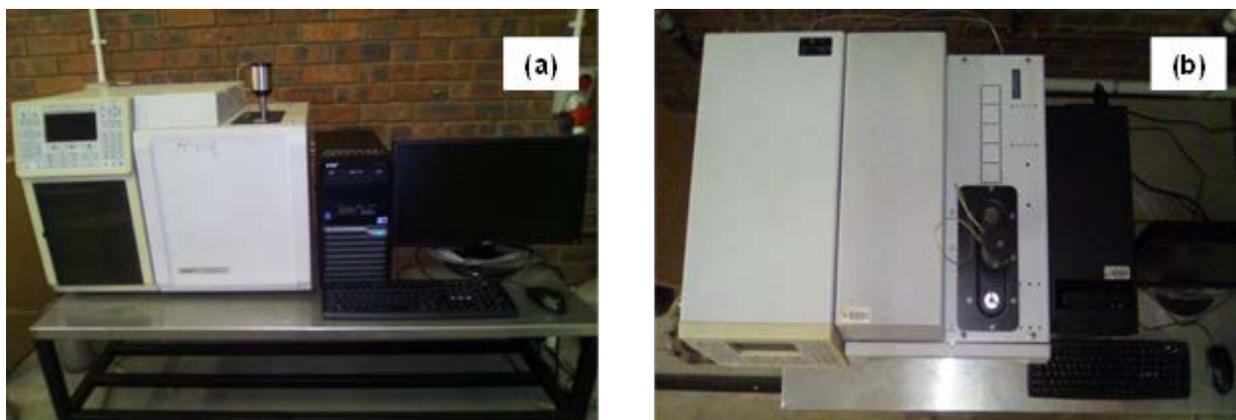


Figure 5: Varian CP-3800 Gas Chromatograph (GC)

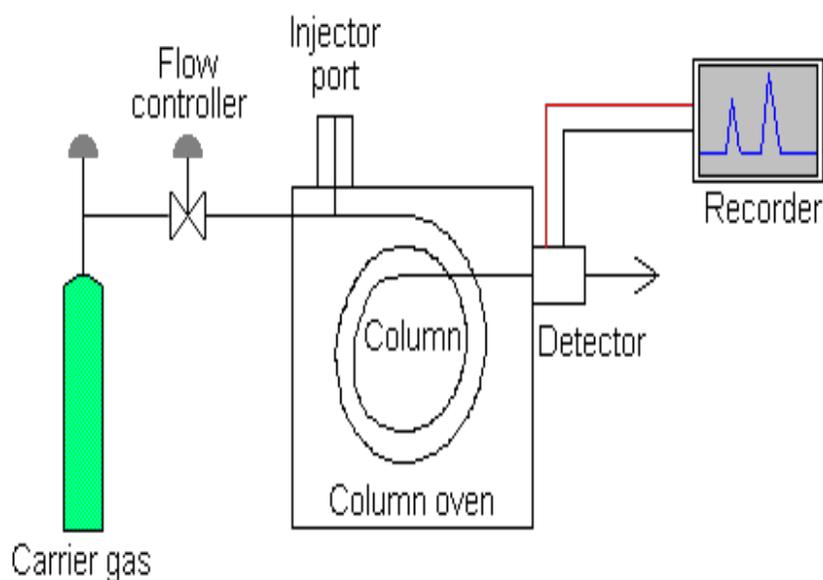


Figure 6: Gas Chromatograph Piping and Instrument Diagram

3.3. Experimental Procedure

Fourteen samples within this range were prepared in different vials, considering methanol as the solvent and D4 as the solute. Before analyzing the fourteen samples through gas chromatography, a sample of pure D4 was injected into the gas chromatograph column to determine D4 peak appearance time in the 33 minutes retention time set as part of the analysis method, after the software, galaxy, was open for parameters control and the carrier gas was open. The peak appearance time was determined to be 16 minutes. Thus, the fourteen samples were run following the same operating conditions (method) and the surface areas values corresponding to the 16 min peaks heights were recorded and plotted against their corresponding concentrations on an excel spread sheet.

4. Results and Discussion

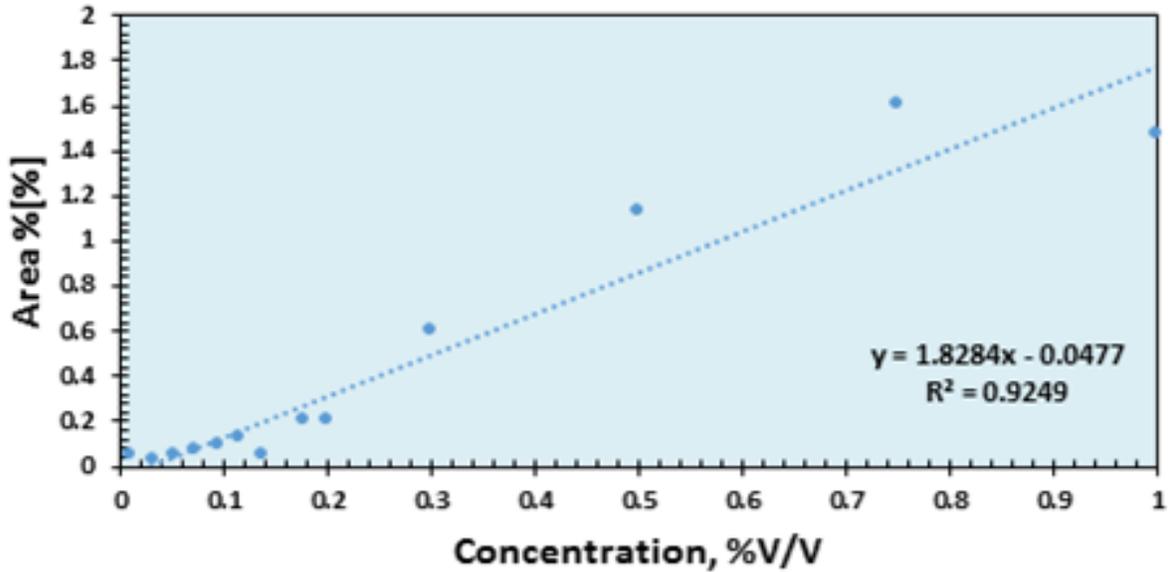


Figure 7: D4 percentage area as a function of concentration

As indicated by Fig 7, the percentage area of the first sample of concentration 0.01 %V/V was 0.048 %. It decreased to 0.029 % for the second sample of concentration 0.031 % V/V. Between 0.031 %V/V and 0.115 %V/V, the percentage area linearly increased from 0.029 % to 0.124 % following an equation of the form $y = mx+b$, implying that the first analyzed sample was probably faulty due to contamination or human error while sampling precise volumes of methanol and D4 from their containers for mixing in the corresponding vial. However, at 0.136 %V/V the percentage area drastically deviated from the linear trend formed by the previous measurements. At 0.178 % V/V, the percentage area approached the linear trend, but the gap between the linear trend and percentage area values concentration increased as concentration increased as well. This is due to the fact that precise volumes of methanol ranging between 9.90 mL and 9.98 mL were required in this interval and human error could have easily been introduced.

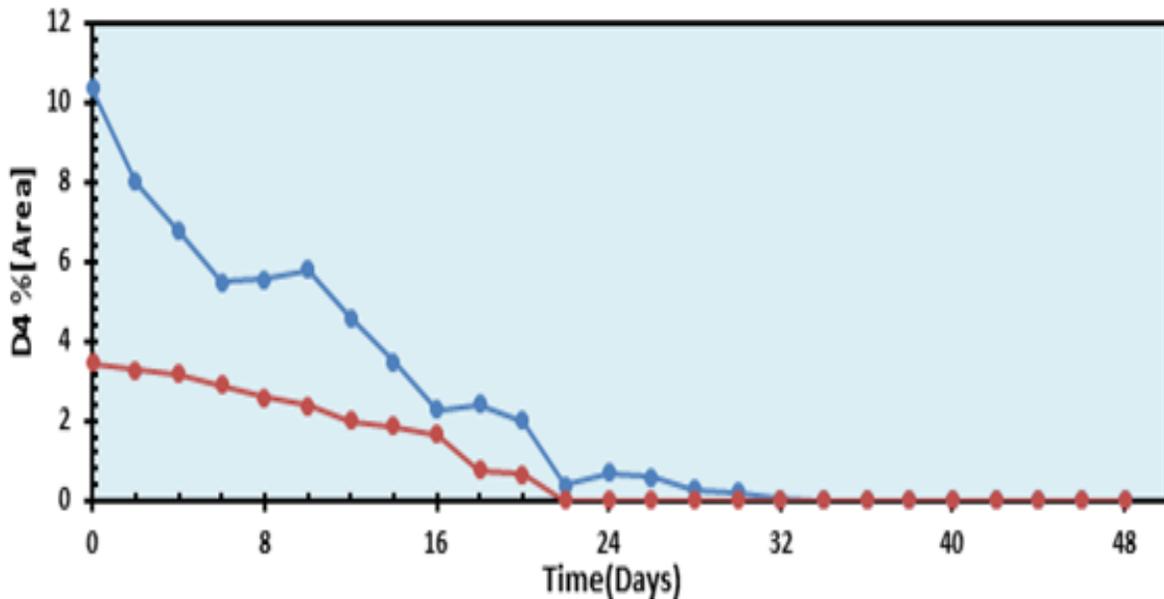


Figure 8: Measured D4 data from Gas Chromatograph

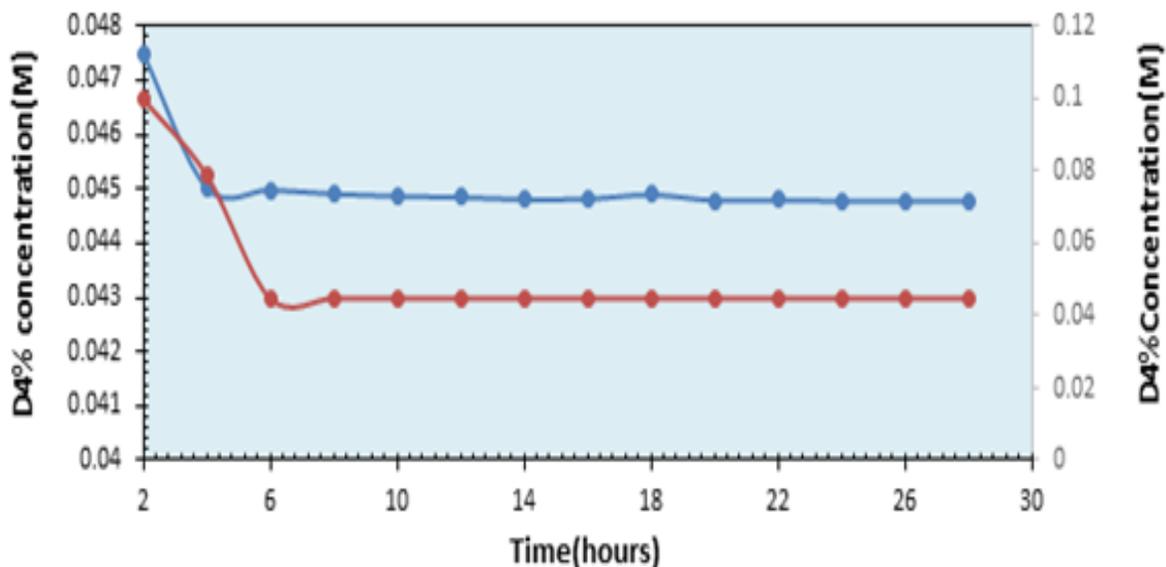


Figure 9: Interpreted D4 data using calibration curve to find volumetric concentration

Fig. 8 shows the measured D4 data from a study conducted in percentage area from the gas chromatograph and Fig. 9 shows the interpreted results using the calibration curve to find volumetric. Several days of data from Fig. 8 was averaged and interpreted using Fig. 7 to generate Fig. 9. Referring to Fig. 9 the left hand axis denotes a scale for the lower curve and the right hand axis for the upper curve. As shown in Fig. 8 and 9 one can use a calibration curve as depicted in Fig. 7 to determine volumetric fractions when using a Gas Chromatograph. This is applicable when there is not access to a Gas Chromatograph Mass Spectrometer which does this automatically; though the latter is more accurate it is also much more expensive.

5. Conclusion

The objective of this study was to build a calibration curve to analyze siloxanes through Gas Chromatography. The selected concentration range was 0.01 % V/V – 1 % V/V. However, after analyzing the fourteen samples specially prepared for calibration, the resulting data points didn't all follow a linear trend as expected. The reasons behind this deviation were the contamination of samples and human error while preparing the samples. Nevertheless, the data followed a linear trend in the percentage area range 0.029 % - 0.124 % corresponding to concentration values ranging between 0.031 % V/V – 0.115 % V/V.

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Biographies

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Molelekoa James Mosesane holds a Master's Degree in Chemical Engineering and a B-Tech Project Management Degree. He is currently employed by Tshwane University of Technology and studying towards a Master's of Business Administration (MBA). He lectures laboratory classes and design experiments for undergraduates; supervise WIL (P1 and P2), B-Tech and Masters chemical engineering students. His expertise includes, project management, laboratory management and maintenance, commissioning of pilot plants, liaising with industry, research collaborations and working on different projects for his students.