Polymer Sorbent Materials For The Extraction Of Organic Compounds

A thesis presented for the award of Doctor of

Philosophy (Pharmacy)

January 2023

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Abstract

This thesis describes how modifying PDMS can influence the polymer's sorbent properties towards organic compounds in aqueous matrices. Where each new sorbent's extraction performance was measured through TD-GC-MS and characterized through various analytical techniques.

Chapter 1: Gives a brief introduction to the analytical techniques used within the thesis whilst outlining the current state-of-the-art PDMS modification techniques reported in recent literature.

Chapter 2: Provides the detailed design of experiment and the corresponding materials used for each results chapter.

Chapter 3: This chapter shows the results and discussions section for the encapsulation of amines with PDMS. In which each PDMS-based material demonstrated variable sorptive extraction properties towards organic compounds in aqueous solutions compared to PDMS. However, each material presented thermal instability and extraction performance dropped over time.

Chapter 4: Highlights how bonding amines to PDMS improved the thermal stability of the sorbent material. However, the TD-GC-MS results showed little variance in extraction performance compared to that of the currently used PDMS, unlike that of the encapsulated method.

Chapter 5: This section looked at how a novel preparation technique aimed to incorporate established commercially available sorbents within the PDMS. These bi-phasic sorbents were tested for organic compound extraction via TD-GC-MS. The results showed that the PDMS-Tenax GR outperformed all other sorbents for most of the tested organic compounds. Whilst demonstrating both chemical and thermal robustness. The main issue around this section was how to scale-up the material preparation step.

Chapter 6: This chapter provides an overview of the results obtained during the thesis while highlighting the areas of improvement. Future works state the direction this research should move based on the result obtained.

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Acknowledgments

Abbreviations

BPA   Bisphenol A

CA   Contact Angle

CAR   Carboxen

CWR   Carbon Wide Range

DMA   Dimethylamine

DVB   Divinylbenzene

EDCs   Endocrine-Disrupting Chemicals

FTIR   Fourier-Transform Infrared Spectroscopy

GC   Gas Chromatography

HPLC   High-Performance Liquid Chromatography

IUPAC   International Union of Pure Analytical Chemistry

LogP   Partition Co-efficient

MS   Mass Spectrometry

MW   Molecular Weight

PA   Polyacrylate

PAH   Polycyclic Aromatic Hydrocarbons

PDMS   Polydimethylsiloxane

PCBs   Polychlorinated Biphenyls

PEG   Polyethylene Glycol

PPCPs   Pharmaceutical and Personal Care Products

SBSE   Stir Bar Sorptive Extraction

SEM   Scanning Electron Microscope

SPME   Solid-Phase Microextraction

SVOC   Semi-Volatile Organic Compound

TD   Thermal Desorption

TMA   Trimethylamine

UV   Ultraviolet

VOC   Volatile Organic Compound

Chapter 1: Introduction

1.1   Scientific Question

Analytical chemistry has an important role in monitoring the quality and safety of our environment, allowing us to study the chemical and physical properties of substances we come in contact within our everyday life[1]. Today, we have several different formats of analytical equipment and methods which allow us to profile chemicals from various industries such as forensic science, clinical analysis or environmental to name a few[2]–[4]. However, in some instances what we wish to be analysed would require sample preparation due to not being compatible with the equipment or not easily removed from its natural environment to a laboratory facility. Such example of this would be the removal of organic contaminants from river systems [5].

HiSorb, a high capacity sorptive extraction probe is used across a vast range of analytical sectors as a sample preparation technique. HiSorb is a solvent-free technique that utilises a polydimethylsiloxane (PDMS) sorptive phase to efficiently extract organic analytes prior to analysis through Thermal Desorption-Gas Chromatography-Mass Spectrometry (TD-GC-MS). PDMS was the chosen sorbent due to favourable properties such as chemical inertness and robustness [6]. However, the hydrophobic surface chemistry (LogP > 3) of the PDMS makes the polymer sorbent efficient at extracting the complimentary, hydrophobic organic compounds [7]. Therefore, this project will address the need for new sorbent materials to extract organic compounds which have a greater range of affinity for organic compounds than the currently used PDMS.

The aim of the project would be to modify the PDMS material through various modification techniques. Each new PDMS-based material's performance at extracting organic compounds from aqueous matrices will be measured through the TD-GC-MS analysis whilst profiling both physical and chemical properties through further analytical techniques described within. With this project being industry-funded, commercial considerations such as cost of material would be taken into consideration. Overall objective for this project would be to widen the product portfolio for Markes International HiSorb and therefore broaden its current application basis.

1.2   Gas Chromatography

The International Union of Pure Analytical Chemistry (IUPAC) definition of chromatography states that it is a physical method of separation in which the components to be separated are distributed between two phases, one of which is stationary (stationary phase) while the other moves (mobile phase) in a definite direction [8]. Gas chromatography consists of a vaporized sample being injected into the machine via the injection port to where the carrier gas is located [9]. The carrier gas is typically inert to prevent any interactions taking place with itself and the sample [10]. From here the sample is passed through to the column.

The column contains a stationary bed which has a large surface area, and the composition of this stationary bed is chosen dependent of the experiment being run [11]. Such options include compounds that are polar or non-polar. The various types of stationary beds will each have a different affinity for the analytes within the sample matrix leading to separation as the analytes elute at different rates [12]. The affinity of the analyte for the stationary phase can be measured in chemical terms as the partition coefficient, K_d. Where K_d is the ratio of the amount of analyte adsorbed to the stationary phase to the amount of analyte remaining in the carrier gas [13]. Thus, providing the following equation:

$$K_d = q/C$$

Equation 1.1: Calculation of partition coefficient K_d, where the distribution coefficient, C is the amount of analyte remaining in the carrier gas and q is the amount of analyte adsorbed onto the stationary phase.

The larger the value of K_d the greater the affinity the analyte has for the stationary phase [14]. Furthermore, the column tends to be a long coil as the longer the column, the greater the separation of the compounds. Once the sample has eluted from the column, the detector monitor's and records which compounds eluted at which rates. The detector displays the signals received in a graphical form for analysis, also known as a chromatogram (Figure 1.1).
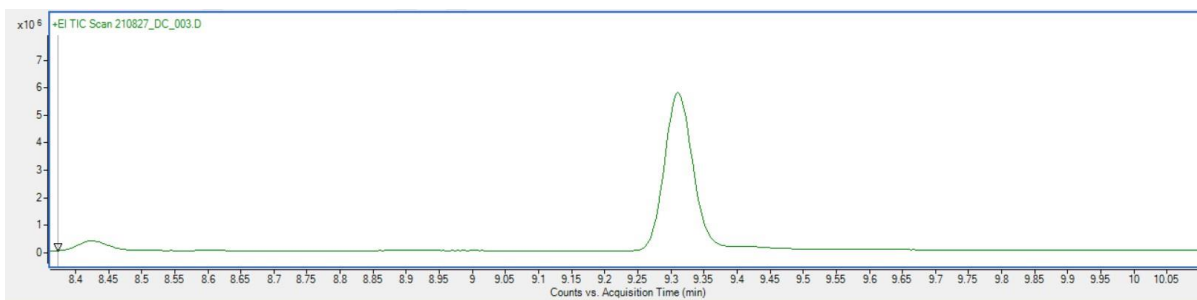
Figure 1.1: Representative peak from chromatogram.

The chromatogram is a two-dimensional plot of response *vs* time. Each compound elutes from the machine at a specific time which is dependent on their chemical structure and how their structure interacts with the column when passed through. The concentration of each compound can be calculated by measuring the area under each peak and how this value of area corresponds to a calibration curve of known concentrations for that compound.

1.3 Mass Spectrometry

Mass spectrometry (MS) is an analytical technique that precisely measures the molecular masses of individual compounds and atoms by converting them into charged ions [15]. The mass spectrometer uses the principle of electric and magnetic fields to deduce the mass of unknown molecules (Figure 1.2). The mass spectrometer ionizes the analytes leaving a charge on each species within the sample. The reason for the charge is that the ions when charged are easier to manipulate into moving in the direction of the detector.
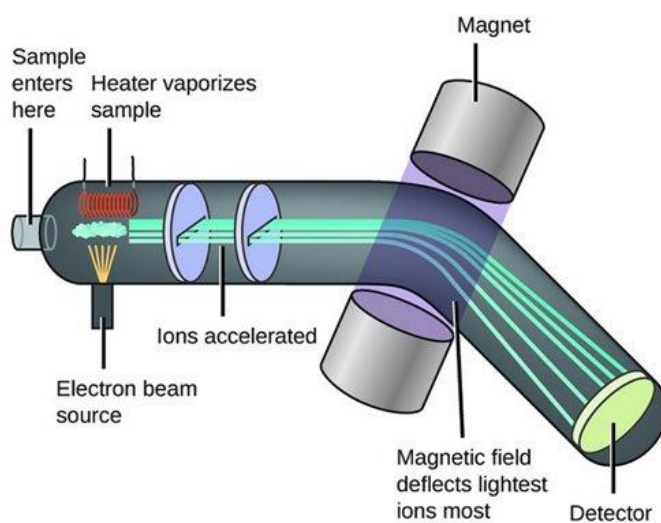
Figure 1.2: Schematic representation of mass spectrometry [16].

Mass spectrometry can be broken down into 3 simple steps.

1. Ionization – this step requires the ionization of the analytes through the addition/removal of electrons or protons forming gas-phase ionic molecules or atoms [17]. The sample may be solid, liquid or gaseous and placed into the mass spectrometer. A high voltage difference is created within the machine and the high voltage difference creates an electric current. This electric current collides with the sample leading to the ionization of the sample mixture, leaving a positive charge on the molecules [18]. The ionization process is undertaken in negative pressures and leads to the fragmentation of compounds within the sample.

2. Separation – the ionized molecules or atoms are now separated according to their individual mass-to-charge ratios [19]. This is done by accelerating the positively charged particles and subjecting them to an electric and magnetic field. The particles differentiate through the various deflections before reaching the ion detector. The ion detector calculates the radius curvature that the positively charged species took on its way to reaching the detector. The mass of the molecule is deduced through the equation:

$$m = (qrB_1B_2) / E$$

Equation 1.2: Mass spectrometry equation where: m = molecular mass, q = charge on particle, r = radius each particle is deflected in magnetic field, B = energy or intensity of the magnetic field, E = ion accelerating voltage.

3. Analysis – the data obtained is displayed in the form of a mass spectrum (Figure 1.3). The mass spectrum displays the relative abundance of ions as a function of the mass to charge ratio. Identification of the structures is determined either through known masses or the fragment patterns displayed on the spectra.
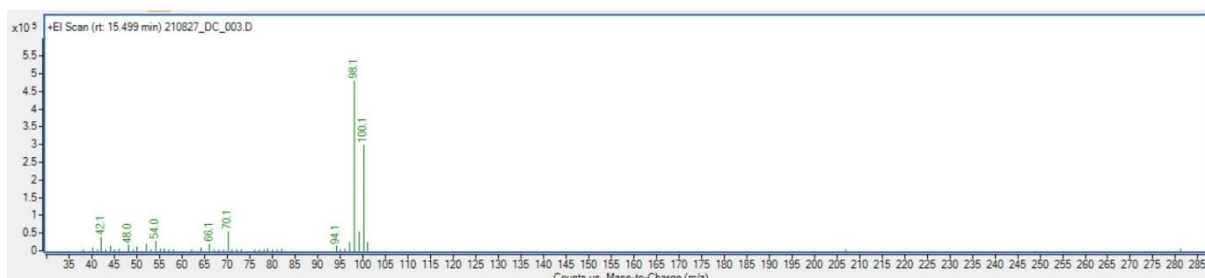
Figure 1.3: The mass spectra for toluene d8.

Mass spectrometry equipment has the capabilities to deduce the structure of a molecule as well as quantitatively measure the analyte levels [20]. Such characteristics has made mass spectrometry one of the most used comprehensive analytical techniques currently being used by scientists across many disciplines such as physics, chemistry and pharmaceutical sciences.

1.4   Gas Chromatography-Mass Spectrometry

Gas chromatography-mass spectrometry (GC-MS) is an analytical technique that detects trace levels of analytes through the combination of gas chromatography and mass spectrometry [21]. This two-part system uses the same protocols that are described in the previous sections where the sample is firstly separated by the different chemical properties associated with each of the molecules in the sample mixture. Upon elution from the gas chromatography machine, the molecules are directly passed into the mass spectrometer. Here the separated molecules are captured and ionized into distinguishable charged fragments prior to acceleration through the machine. Each of the fragments are then analysed based upon their mass-to-charge ratio. GC-MS systems can distinguish between a vast range of compounds enables making them widely used across several industrial sectors in-particular food & drink [22], environmental monitoring [23] and clinical studies [24].

1.5   Thermal Desorption

Thermal desorption was introduced in the 1970's to overcome issues that surrounded sample preparation for conventional GC analysis [25]. It was found that packing injector liners with sorbent material allowed for the adsorption of a fixed volume of gas prior to separation. However, many issues surrounded this initial technique including loss of volatile substances and large errors within the results, all be it the first example of single-stage thermal desorption.

Sample preparation is the treatment of a sample into a state that is efficient for analysis, where thermal desorption is one of the most prominent within the analytics of chemical industry [26]. Furthermore, it is said to be the most powerful and versatile of all gas chromatography sample introduction technologies allowing for trace-level analysis of volatile

molecules that would not be possible with alternative preconcentration techniques such as solvent extraction [27]. Thermal desorption can be interpreted as an extension of GC [26]. The apparatus serves as a multi-purpose tool in the sampling and preparation of analytes. Furthermore, the selected samples can have a tailored concentration prior to injection into the GC equipment. Thermal desorption concentrates volatile and semi-volatile organic compounds within an inert gas stream prior to injection into the GC equipment (Figure 1.4). The alteration to the concentration of the volatile organic compounds leads to the improvement on detection limits, allowing the GC equipment to detect trace amounts within samples as low as a part per trillion (ppt) level. Thermal desorption has an impact on the quality of results when applied in tandem with GC or GC-MS analysis. The sample preparation results in reduced peak widths and an overall improvement on the chromatography performance.

The first step of single-stage thermal desorption requires the direct sampling of volatile materials onto a sorbent tube (Figure 1.4). The adsorbed material undergoes extensive heating before being purged into the injection port of the GC machine via an inert flow of gas. This allows for any substance that was originally adsorbed onto the sorbent tube, to be thermally desorbed into the GC machine and separated into its individual components.

Single-stage is the simplistic approach to thermal desorption. Alternatively, a two-stage thermal desorption method allows for the improvement on the already powerful technique with the introduction of a multi-stage process (Figure 1.5). This entails the continuous process of extraction and desorption into smaller volumes of gas. This concentrates the samples of interest, enhancing sensitivity and detection limits. In principle, this equipment can be used to monitor a range of compounds in the air or sample, firstly by pumping the gaseous samples through a sorbent sampling tube over a set period. The volatile or semi-volatile gases that are retained onto the sorbent tube are desorbed into an inert carrier gas of a set volume. The inert gas that contains the sample re-adsorbs the sample onto a smaller piece of sorbent material, also known as the cold trap. From this, the gaseous analytes can be quantitatively thermally desorbed into the GC inlet in as little as 100μL of inert carrier gas. Thus, providing a sample with a substantially improved concentration which leads to the increased sensitivity and detection limits for the chromatography separation process. Furthermore, through the multiple step process of trapping the gaseous analytes, it is possible to remove unwanted

impurities through a purge to vent system, quantitatively retaining the compounds of interest prior to injection into the GC machine.
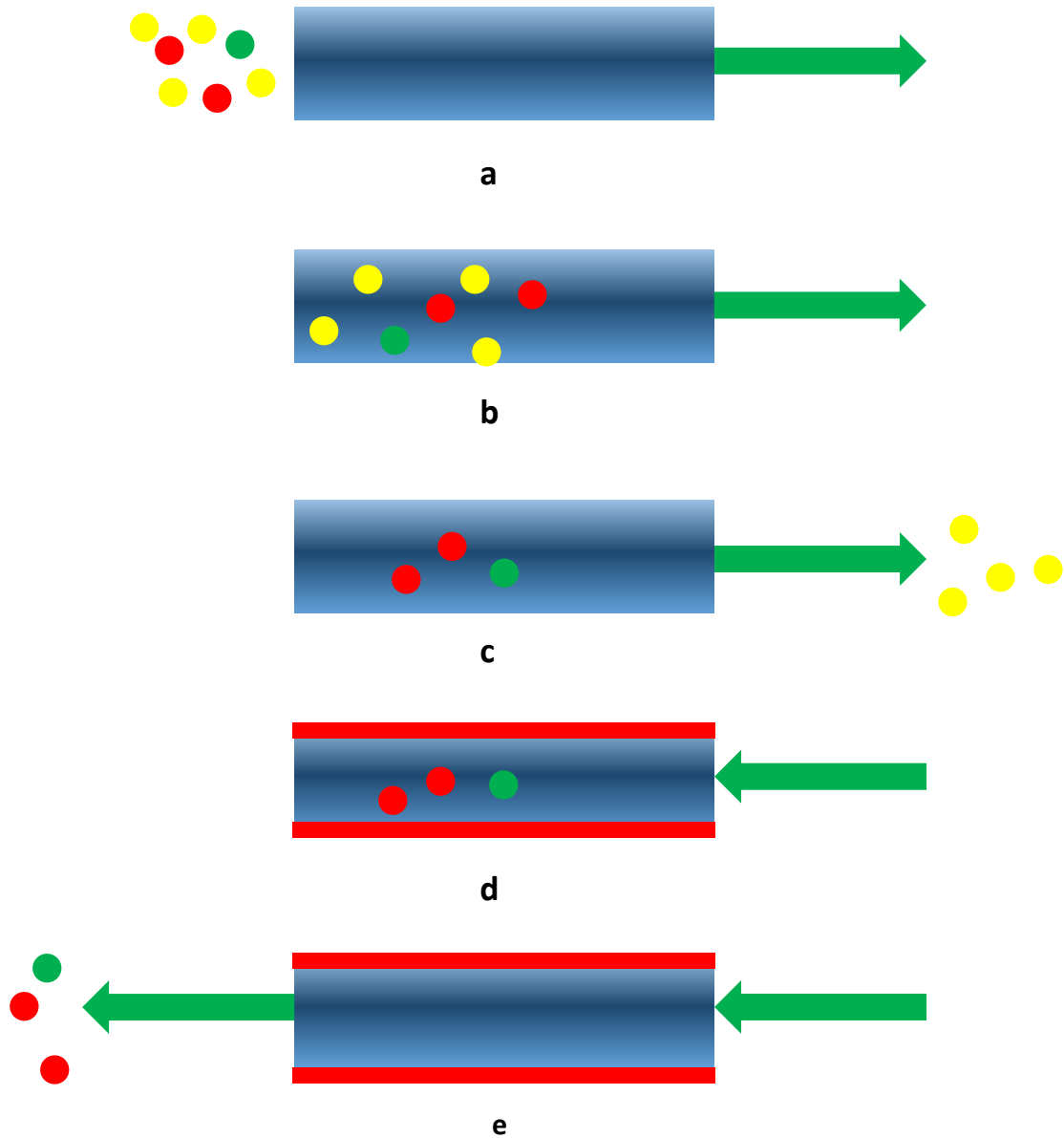
Figure 1.4: Schematic describing the single-stage thermal desorption process. Sample matrix is injected and carried through the column via an inert flow of gas (a). Sample passes onto the sorbent material within the column, where compounds of interest adsorb onto the sorbent surface (b). Lighter molecules such as N_2 pass through the sorbent tube (c). The sorbent tube is heated in a reverse flow of carrier gas in a process called back flushing (d). Compounds of interest desorb from the surface of the sorbent and are released into the inert flow of gas (e).
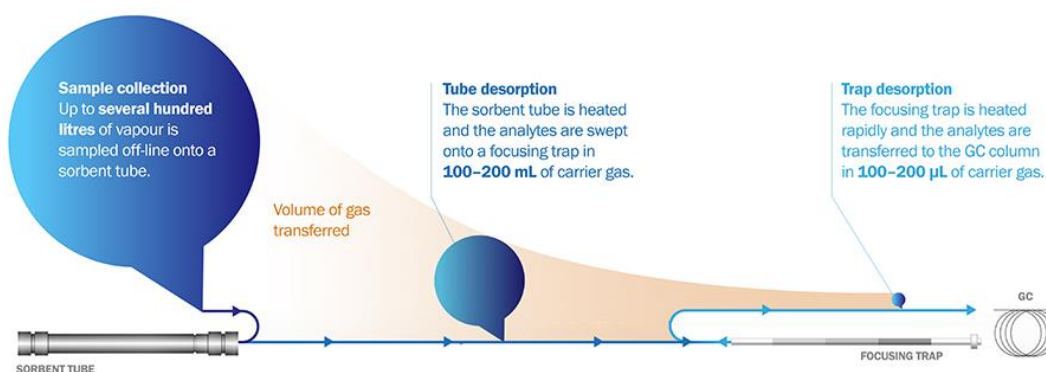
Figure 1.5: Schematic representation of the two-step thermal desorption process [26].

1.6   Thermal desorption *vs* Solvent Extraction

Like thermal desorption, solvent extraction is a common sample preparation technique used within industry and laboratories for chromatography [28]. The method simply consists of the transfer of a solute from one solvent to another with both solvents being immiscible or partially immiscible with each other [29]. The two solvents of choice tend to be an aqueous mixture with the other being a non-polar organic liquid. The method is simplistic, consisting of a mixing step followed by a separation step. However, such disadvantage of solvent extraction is that too vigorous of mixing can lead to a difficult separation step as emulsification of the two layers takes place, expressing the importance of choosing the two correct immiscible solvents at the beginning of the experiment. Another disadvantage to this extraction technique is that it is not possible to transfer to 100% of the retained analytes to the analytical instrumentation, with recovery values being as low as 20% [30]. This is the main advantage of thermal desorption when compared to solvent extraction. Thermal desorption can easily allow for over 95% desorption efficiency given that the experiment meets up to the analytical conditions such as sorbent, temperature and flow rate [31]. This high desorption percentage is due to the constant purging of the compounds into the inert gas as the rising temperature releases the compounds within the matrix as vapours.

Another advantage of thermal desorption over solvent extraction is reduced interference and lower detection limits [32]. During solvent extraction there may be solvent interference. This effect can have an impact on the results of the analysis such as peak masking, signal quenching and baseline disturbance. Without the use of solvents in thermal desorption,

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solvent interference is not an issue. Furthermore, thermal desorption is a preferred technique to due attributes such as being less labour intensive and requiring little or no sample preparation [33].

1.7   Evolution of Thermal Desorption Technology

Contaminated drinking water led to many birth defects within the United States during the 1970's [34]. As a result, a simplistic mode of sampling the water systems were introduced. In response to this, The US Environmental Protection Agency (EPA) developed a purge-and-trap GC-based test that allowed the monitoring of VOCs within the drinking water that was contaminated in the 1940's and 50's by chemical industries [35]. Around the same time was the development of the 'Coker Cooker' which consisted of ¼" O.D tubes designed by Environmental Monitoring Systems Ltd. for the containment of samples and sorbents. This late 1970's thermal desorption model is considered as the first commercial use of thermal desorption technology offering the consumer simple single-step desorption properties with a primary use of monitoring air pollutants within the workplace of the petrochemical industry [36]. Overall, this primitive piece of apparatus operated sufficiently. However, the need to meet certain criteria which included the need for a packed column, only analysis of stable compounds and performance within a narrow concentration and volatility window limited its applications and left room for improvement.

The Working Group 5 (WG5) of the UK Health and Safety Committee on Analytical Requirements (HSE CAR) also convened in the late 1970's to discuss the applications of both diffusive sampling and thermal desorption [37]. At the time, the choice of quantitatively monitoring air was undertaken by personal sampling pumps, however the WG5 believed diffusive sampling could be an inexpensive, alternative option. Eventually, the group decided to base their samplers on the ¼" O.D sorbent tubes that were earlier designed for the Coker Cooker machinery. Characteristics such as practical in size, non-susceptible to air speeds and suitable for both pumped and passive sampling made the ¼" O.D sorbent tubes provided the foundations for the future developments.

As previously mentioned, thermal desorption has a greater ability of separating compounds within a mixture compared to solvent extraction [32], [33], [38], [39]. Furthermore, the WG5

noticed that thermal desorption overcame toxicity issues that were associated with the charcoal/CS$_2$ extraction methods that were employed at the time. These advantageous characteristics of thermal desorption led to the WG5 exploring an automated service for sampling with today's protocols such as leak testing and pre-purging.

WG5 believed that this mode of thermal desorption had greater potential than what was expressed through single-stage thermal desorption [40]. With the sampling tubes containing large quantities of sorbent material and a requirement of several millilitres of gas for extraction, they looked to improve on the sensitivity of the device which resulted in greater resolution spectra. The resulting product was a two-stage thermal desorption apparatus that contained a capillary cryogen focusing trap between the sample tube and the separating column. The process involves the adsorption of analytes to the sorbent within the sample tube. Once adsorbed, the analyte is desorbed from the primary sample tube onto the cryogen cooled focusing trap, prior to once again being desorbed into the separating column via a smaller volume of carrier gas. Reducing the volume of carrier gas increased sample concentration prior to analysis by the gas chromatography equipment leading to improved peak shape and sensitivity.

One of the first recorded models to incorporate the cryogen focusing trap was the Chrompack CTC unit. Results showed improved peak shape and sensitivity in comparison to single-stage thermal desorption methods. Albeit improved results, the cryogen focusing trap blocked with ice and the general running costs of the machinery were expensive as it required 6L of liquid nitrogen per hour to run [41]. In response to the limiting factors associated with the Chrompack CTC, PerkinElmer responded with the release of the ATD (Automated Thermal Desorption) 50 in 1981 [42]. The ATD 50 machine provided the first real breakthrough in thermal desorption analysis. Combining sorbent tubes with an electrically cooled focusing trap, the ATD 50 essentially provided a means of quantitatively measuring the retention time of a vast range of volatile compounds at a low cost with no ice formation within the cryogen trap. The ATD 50 had further features such as a rapid heating rate of 60°C/s on the stainless-steel focusing trap which meant fast desorption of the analyte into the column and an overall improved peak shape. The introduction of a heated rotatory valve located in the flow path of the desorb unit allowed for the isolation of the sorbent tube from the column. This enabled

the user to undergo stop-flow leak tests and pre-purging of the air to vent before the desorption step within each sample run.

The ATD 50 thermal desorption equipment made the initial step towards an easy and simplistic pre-sampling method to gas chromatography. This led to increasing interest from scientists of various backgrounds and increasing the demand for this level of pre-sampling technology [40]. Several limitations with the ATD 50 were highlighted, such as the flow path and desorption temperatures. The specifications of the ATD 50 machines were a maximum flow path temperature of 150°C, desorption temperatures of 250°C in the sorbent tube and 300°C in the cryogen cold trap [40]. These temperature limits were not efficient enough for the detection of carbon chains over C_{26} which became an issue for scientists who at the time were eager to use thermal desorption for the monitoring of various carbon-based substances within the environment. Such examples of these carbon-based analytes include polychlorinated bisphenols (PCBs) and phthalates who have boiling points greater than 300°C [39], [43]. Furthermore, there was growing interest in the monitoring of small molecular, volatile compounds within the atmosphere and to quantitatively examine these range of compounds under ambient conditions [38], [41]. Unfortunately, this was not possible with the conventional sorbent tubes at room temperature due to the pressing issues of harmful environmental gases causing adverse health effects to those living within urban environments [44]. Thermal desorption seemed to be well suited as a solution to the demand for a near real time evaluation of the air pollutants causing health conditions within the population. The thermal desorption equipment was adjusted to easily sample the air within the atmosphere and focus the contaminants directly to the cryogen focusing trap [45]. Such examples of how thermal desorption equipment can have a positive impact on society led to increased awareness and improved investments during the 1990's.

Such improvements during the 1990's included the optimisation of the cryogen focusing trap. To this day the cryogen focusing trap is operated through an electrically cooled/sorbent-packed focusing traps during two-stage thermal desorption. However, parameters such as type of material used, internal diameter, sorbent bed length, cooling/heating efficiencies and desorption rate were and currently are still be improved. Modern instrumentation consists of inert materials such as quartz, to be heated up to rates of 100°C/s and allow for efficient desorption of flows as low as 1.5ml/min to optimize method sensitivity [46]. Backflush

desorption is a term used to describe the carrier gas flowing in the reverse direction to that of the air flow during desorption [47]. Using backflush desorption in tandem with a sorbent bed that consists of various sorbents, the thermal desorption equipment can measure a wide range of analytes with various volatilities [48].

Prior to adsorption onto the cryogenic focusing trap, samples have a variety of methods of being introduced into the gas chromatography equipment. One such methods is direct introduction via solid-phase microextraction (SPME).

1.8   Sampling – Solid-Phase Microextraction

Sampling options associated with thermal desorption include vapour monitoring, use of sorbent tubes/traps, canisters with bags or direct desorption of homogeneous liquids or solids [47]. However, in-terms of obtaining target analytes for analysis via gas chromatography, solid-phase microextraction (SPME) tends to be the preferred use. SPME was developed by Pawliszyn as a new sampling technique using a fused-silica fibre that had an appropriate outer coating called the stationary phase [49]. This extraction method consisted of direct adsorption of analytes from the sample onto the fibre coating. This allowed the user to save time through a greener process that did not include the use of solvents, all while improving the detection limits of their samples [49]. SPME is currently sold commercially in various forms from different suppliers. One such example of these supplier is Merck (Table 1.1). SPME fibre assemblies sold by Merck contain fibres which vary in terms of polarity and thickness of coating on each fibre. In tandem with consistent sampling time, the analyst can expect highly consistent and quantifiable results from low concentrated volatile analytes [50]. Merck offer a range of SPME fibres including polydimethylsiloxane (PDMS) and various multi-phase derivatives, each of which are sold with recommended 24- or 23-gauge needles for auto sampling.

***SPME-Overcoated*:**

Samples that contain a high-background such as various fats and sugars within food products can stick to SPME fibres [51]. This leads to the reduce life expectancy of the fibre and may also result in the contaminants being transferred to the GC machine and interfering with the chromatographic analysis. Providing an overcoat of PDMS to the existing PDMS/DVB coating

reduces these issues as the PDMS serves as a barrier between the contaminants within the matrix and the fibre.

Table 1.1: Range of SPME Fibre Assemblies available from Merck.

Type of SPME Fibre	Composition of SPME fibre	Film thickness – d_f (µm)	Needle size (ga)	Price per needle (£)
SPME-Overcoated	Polydimethylsiloxane/Divinylbenzene (PDMS/DVB) fibre overcoated with a layer of PDMS	75 µm (65 µm of coating + 10 µm of overcoating)	23 ga	150.00
SPME Metal Alloy	Carboxen/Polydimethylsiloxane (CAR/PDMS)	85 µm	23 ga	364.00
	Divinylbenzene/Carboxen/Polydimethylsiloxane (DVB/CAR/PDMS)	50/30 µm Divinylbenzene/Carboxen	23 ga	364.00
	Polydimethylsiloxane/Divinylbenzene (PDMS/DVB)	65 µm	23 ga	364.00
	Polydimethylsiloxane (PDMS)	100 µm	23 ga	367.00
Carboxen/Polydimethylsiloxane (CAR/PDMS)	Carboxen/Polydimethylsiloxane (CAR/PDMS)	75 µm	24 ga	94.00
		75 µm	23 ga	98.67
		85 µm	24 ga	94.00
		85 µm	23 ga	108.33
Polydimethylsiloxane/Divinylbenzene (PDMS/DVB)	Polydimethylsiloxane/Divinylbenzene (PDMS/DVB)	65 µm	24 ga	94.00
		65 µm	23 ga	98.67
Divinylbenzene/Carboxen/ Polydimethylsiloxane (DVB/CAR/PDMS)	Divinylbenzene/Carboxen/Polydimethylsiloxane	50/30 µm (Divinylbenzene/Carboxen)	24 ga	94.00
		50/30 µm Divinylbenzene/Carboxen	23 ga	108.33
Polydimethylsiloxane (PDMS)	Polydimethylsiloxane (PDMS)	7 µm	23 ga	108.33
		7 µm	24 ga	99.00
		30 µm	23 ga	108.33
		30 µm	24 ga	99.00
		100 µm	23 ga	98.66
		100 µm	24 ga	94.00
Polyacrylate (PA)	Polyacrylate	85 µm	24 ga	99.00
		85 µm	23 ga	108.33
Carbowax-Polyethylene Glycol (PEG)	Carbowax-Polyethylene Glycol (PEG)	60 µm	23 ga	108.33

Carboxen/Polydimethylsiloxane (CAR/PDMS):

SPME metal alloy:

The SPME metal alloy fibres consist of the addition of a metal alloy to the needle, plunger and fibre core. The selected metal alloy provides great flexibility to the SPME system with a plunger of greater thickness to reduce the chance of breakage as well as a needle with thinner walls in comparison to the traditional stainless-steel alternative. Furthermore, the metal alloy used is more inert than the stainless-steel needles. There is a range of metal alloys available where the composition of the fibre, the length of the needle and the thickness of the bonded phase all vary.

This form of SPME analysis targets molecules of a low molecular weight of approximately 30-225. The process is particularly used in the sample preparation of GC-MS rather than using the solvent extraction technique. Such examples of this type of SPME fibre being used is within the extraction of volatile cheese extracts via the static headspace method [52], and the determination of the concentrations of molecules such as 2-heptanone [53] and dimethyl sulphide [54].

Polydimethylsiloxane/Divinylbenzene (PDMS/DVB):

The PDMS/DVB SPME fibres mainly vary in film thickness (d_f) of 60 μm and 65 μm, respectively. This has an influence on its applications, where the 60 μm fibres are recommended for HPLC analysis of amines and polar compounds. However, for analysis of more volatile polar compounds such as alcohols, it is recommended to use the 65 μm PDMS/DVB fibres as they possess greater adsorption efficiency and a faster rate of release [55].

Divinylbenzene/Carboxen/Polydimethylsiloxane (DVB/CAR/PDMS):

A 50/30 μm divinylbenzene/carboxen film thickness on a PDMS fibre is used within SPME for extraction of analytes that range from C3-C20 (MW 40-275) and can measure up to trace amounts of compounds within this range.

Polydimethylsiloxane (PDMS):

The PDMS fibres are used for the adsorptive capabilities across the non-polar range. For analysis of analytes across the non-polar semi-volatile or large molecular weight range it is recommended to use PDMS fibres with a film coating of either 7 or 30 μm. These thickness' possess greater extraction efficiency than the extraction probes of 100 μm PDMS thickness across this range, while the fibres of 100 μm thickness are used for non-polar compounds with a low molecular weight and high volatility.

Polyacrylate (PA):

Polyacrylate probes sold by Sigma-Aldrich consist of a film thickness of 85 μm for extraction of polar semi-volatiles of MW 80-300. Such applications of the manual sampling SPME Polyacrylate probes have been recorded in the detection of insecticides within water samples [56], determination of chlorophenols in landfill leachates [57], and the extraction of free fatty acids within milk [58].

Carbowax-Polyethylene Glycol (PEG):

PEG SPME probes are designed for the extraction of alcohols and other polar molecules with a MW 40-275.

Gerstel offer an advancement of the fibre coated probes provided by Sigma-Aldrich (Table 1.2). The Gerstel Twister enables efficient extraction of organic compounds from aqueous matrices based of Stir Bar Sorptive Extraction (SBSE) technology. Gerstel Twister prides itself on being a solvent-free technique with efficient extraction of up to 1000-fold greater sensitivity than conventional SPME techniques [59]. This is due to a large sorbent volume in tandem with stirring allows for extraction and concentration of analytes to the surface of the stirrer bar from a large sample matrix. Once the analytes are adsorbed to the surface of the sorbent, they are typically desorbed using thermal desorption.

The Gerstel Twister detects and extracts low concentrations of organic compounds from aqueous matrices for characterisation and quantification via gas chromatography. This has led to many applications of the Gerstel Twister such as the detection of PAH in marine tissues [60], pesticides in water [61] and 2,4,6-TCA in wine [62]. Each of these compounds has been successfully extracted from aqueous environments using the non-polar phase, PDMS. The

PDMS sorbent on the Gerstel Twister compliments the non-polar hydrocarbons within the aqueous samples, providing a surface for the hydrocarbons to adsorb onto in preparation for analysis.

Table 1.2: Comparison of the Gerstel PDMS Twister and EG/Silicone Twister [59].

	PDMS Twister	EG/Silicone Twister
Phase	Polydimethylsiloxane (PDMS)	Polydimethylsiloxane (PDMS / Ethylene glycol (EG) – copolymer on an inert metal grid for mechanical stabilization
Enrichment	Unspecific adsorption of non-polar compound with a log p > 4. The polarity range can be extended by adding salt to the sample (salting out).	Unspecific adsorption of non-polar compounds, additionally specific binding of polar hydrogen bond donors, such as phenols.
Application examples	Pesticides in water. Polycyclic Aromatic Hydrocarbons (PAHs) in marine tissues. 2,4,6-Trichloroanisole (2,4,6-TCA) in wines. Flavour compounds in foods.	Flavour compounds in beverages.

The Gerstel PDMS Twister specialises in the extraction compounds with a partition coefficient (log P) value of greater than 3 [63]. This leaves a large spectrum of compounds that cannot be extracted using the standard PDMS Twister. To improve on this, Gerstel published a paper in 2011 that compared the PDMS Gerstel Twister with a novel ethylene glycol (EG) and silicone based combined sorbent phase for efficient stir bar sorptive extraction (SBSE) [64]. Each Twister was compared across three drink beverages whiskey, wine and fruit juice for their qualitative flavour profiles of each beverage. It was found that the EG-silicone could extract a broader range of compounds from whiskey, wine and multivitamin juices compared to the PDMS Twister. With the addition of EG in the sorbent phase, polar compounds that included volatile esters, fusel alcohols and phenol-based compounds were successfully extracted. All compounds adsorbed to the surface of each Twister were analysed and quantified using GC-MS. Where it was found that the EG-silicone Twister quantifiably extracted more compounds compared to the PDMS Twister. However, due to the hydrophobic nature of the PDMS surface

long carbon-chain ethyl esters, lactones and terpenes were successfully extracted using the PDMS twister.

Some benefits of SMPE comprise of efficient extraction capabilities and less solvent and sample manipulation. Such qualities are the reason SPME is one of the leading extraction technologies across various areas of chemical analysis including environmental and food monitoring [65]. The technique was revolutionised by PAL Systems with the introduction of the PAL SPME arrows. The main objective of the PAL SPME arrow was to improve on the limited capabilities of existing SPME models such as mechanical stability and the small phase volumes of the sorbent on each fibre [66].

To improve on the mechanical stability of the SPME apparatus, the PAL SPME arrow introduced two sized probes, with outer diameters of 1.1 and 1.5 mm respectively (Table 1.3). The larger outer diameter probes provided an increased surface area as well as improved robustness compared to conventional SPME devices. Furthermore, the PAL SPME arrow gets its name from the arrow-shaped tip that allows for ease of penetration of vials and injector septa. The intuitive design leads to full protection of the sorbent material, preventing loss of analytes adsorbed to the surface. Another highlighted aspect of the PAL SPME Arrow is the ability to analyse matrices via immersive or headspace extraction, expanding on the apparatus' versatility in analysing both volatile and semi-volatile analytes.

The PAL SPME Arrow benefits from improved rate of extraction, sensitivity and robustness which results in greater productivity and lower running costs for the consumer [67]. Similarly to the Gerstel Twister, PAL SPME Arrows comes with a choice of sorbent material which allows the user to select a phase most complimentary to their target analytes.

**Table 1.3:** Various fibre types of the PAL SPME Arrow with relative diameter and phase thickness [66].

Fibre Type	Diameter (mm)	Phase Thickness (d_f)
Polydimethylsiloxane (PDMS)	1.1mm	100 μm
	1.5mm	250 μm
Acrylate (Polyacrylate)	1.1mm	100 μm
Carbon Wide Range/Polydimethylsiloxane (Carbon WR/PDMS)	1.1mm	120 μm
Divinylbenzene/Polydimethylsiloxane (DVB/PDMS)	1.1mm	120 μm

PAL SPME Arrow has a larger phase volume compared to conventional SPME apparatus. This large volume of sorbent gives PAL SPME Arrow apparatus improved sensitivity towards the extraction of target analytes. This was well demonstrated by Kremser et al where they evaluated the extraction efficiency of the PAL SPME Arrow on freely dissolved polycyclic aromatic hydrocarbons (PAHs) in water [66]. For comparable results, the sorbent of choice for both the PAL SPME Arrow and classical SPME fibres was PDMS. The three main areas of comparison analysed were limits of detection, the reliability of the fibres and extraction yields. Results showed that PAL SPME Arrow was superior to conventional SPME fibres at the extraction of the PAHs. Data showed a greater quantity of PAHs were extracted in PAL SPME Arrows and was concluded that this was due to the increased volume of sorbent. Further research that compared PAL SPME Arrow to conventional SPME fibres was undertaken by Helin et al. This research investigated the extraction efficiency of each technique on short chain aliphatic amines in aqueous samples [68]. The two target analytes for the SPME Arrow and SPME Fibre within the aqueous matrices were trimethylamine (TMA) and dimethylamine (DMA). The results revealed that there was a greater percentage volume of DMA and TMA recovery when using the PAL SPME Arrow in comparison to the SPME Fibre (Figures 1.6 & 1.7). Furthermore, evidence showed that when the sample was spiked with 100μL of 5mg/L DMA solution that the PAL SPME Arrow maintained efficient extraction capabilities, however the SPME fibre's extraction affinity for DMA dropped (Table 1.4). As previously explained, the SPME fibre have a small surface area. The paper describes that the small surface area of the

SPME fibre led to competitive adsorption at the surface. In other words, there was saturation at the surface of the Polydimethylsiloxane/Divinylbenzene/Carboxen (PDMS/DVB/CAR) SPME fibre when attempting to extract the DMA. This concluded why the data showed reduced adsorption of DMA compared to that of the PAL SPME Arrow which had a larger surface area and overall sorbent volume. The paper continued to explore a solution to the competitive adsorption on the SPME fibre. With findings suggesting that reducing extraction time would prevent this limitation however, this would be at the expense of sensitivity on the instrument.
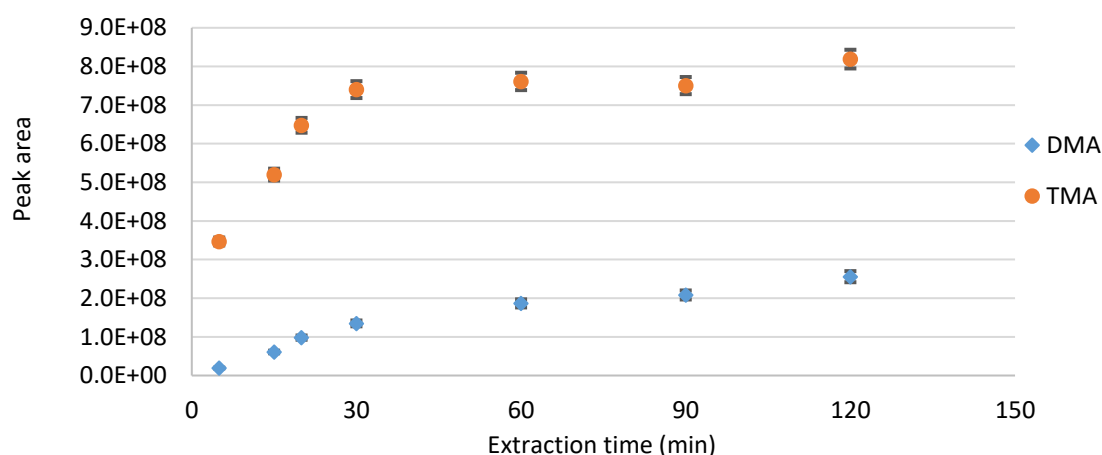
Figure 1.6: Extraction time profiles of dimethylamine and trimethylamine obtained from extractions performed with SPME Arrow (PDMS/CAR 1000) [68].
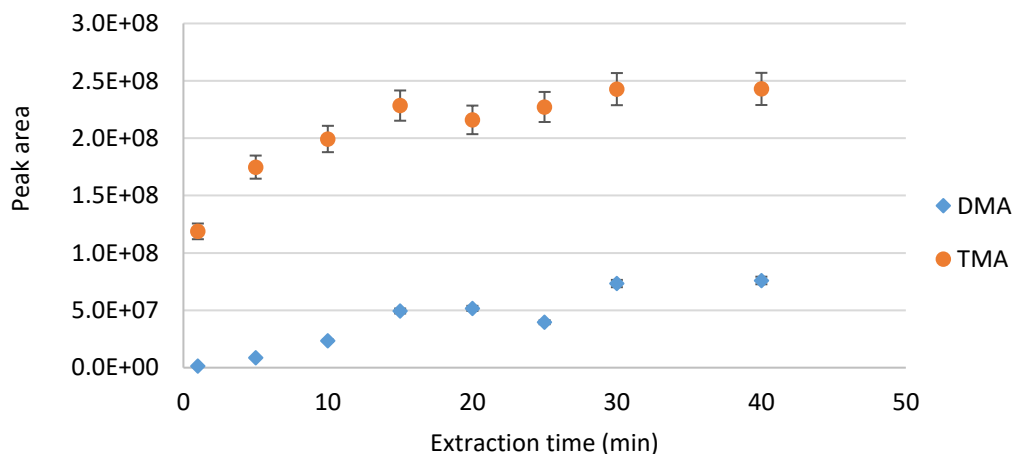
Figure 1.7: Extraction time profiles of dimethylamine and trimethylamine obtained from extractions performed with PDMS/DVB/CAR SPME fiber [68].

Table 1.4: A comparison of PAL SPME Arrow and SPME Fibre in the adsorption of trimethylamine (TMA) and dimethylamine (DMA) [68].

Sample Type (Analyte)	PAL SPME Arrow (PDMS/CAR 1000)	SPME Fibre (PDMS/DVB/CAR)
Effluent (DMA)	79 ± 1 µg/L	80 ± 7 µg/L
Effluent spiked (DMA)	167 ± 2 µg/L	137 ± 10 µg/L
Effluent (TMA)	120 ± 2 µg/L	134 ± 1 µg/L
Influent (DMA)	81 ± 5 µg/L	N/A
Influent (TMA)	120 ± 8 µg/L	N/A

Overall, it can be concluded that SPME is a highly successful tool for sample preparation, with great versatility in extracting a wide range of analytes. However, the characteristics of the fibres such as phase thickness makes these probes easily breakable, non-reusable and subject to competitive adsorption [69] [70].

1.9   Markes International

Markes International is a specialist manufacturer of instrumentation for detection of trace-level volatile and semi-volatile organic compounds (VOCs and SVOCs) [71]. In-particularly, Markes International have expertise in thermal desorption (TD) technology as a pre-concentration technique in the analysis of VOC and SVOCs. Markes International manufacture a vast range thermal desorption equipment that cover 3 modes, sorbent tube analysis, on-line sampling analysis and cannister/bag sampling [72]–[74]. However, the most recent of these was the release of Centri.

1.9.1 Centri

Markes have described Centri as a breakthrough in sample automation and concentration of VOCs and SVOC analysis via GC-MS [75]. Centri offers the user improved sensitivity, unattended sampling and pre-concentration of VOCs and SVOCs across liquid, solid and gaseous matrices [76].

Centri was designed to overcome several analytical issues such as:

- Time-consuming sample preparation that is associated with liquid-liquid extraction or solid phase extraction[77].
- The need for improved sensitivity for the analysis of VOC and SVOC compounds within solid or liquid matrices.
- The ability to run several samples with differing injection techniques and workflows, off a single platform.

Offering the analyst [78]:

- Improved sensitivity – where analytes can be detected at levels as low as part per trillion via cryogen-free analyte trapping technology.
- Improved versatility – successful analysis of a greater range of VOCs and SVOCs in solid, liquid or gaseous forms.
- Improved sample throughput – can run integrated sequences of multiple sampling techniques and run in 'overlap' mode, for unattended operation.
- Cryogen-free analyte trapping – improved sensitivity with the option to purge any water or solvents in the system.
- Recollection of split flows – presented within each injection mode, once the sample has been run it is re-collected and stored. This allows for re-analysis of direct samples while avoiding the lengthy process which is sample preparation.
- Cryogen-free and solvent-free operation – this reduces the cost per sample while making the analytical process more environmentally friendly.
- Barcode readers and TubeTAG technology – allowing the samples to be easily tracked.

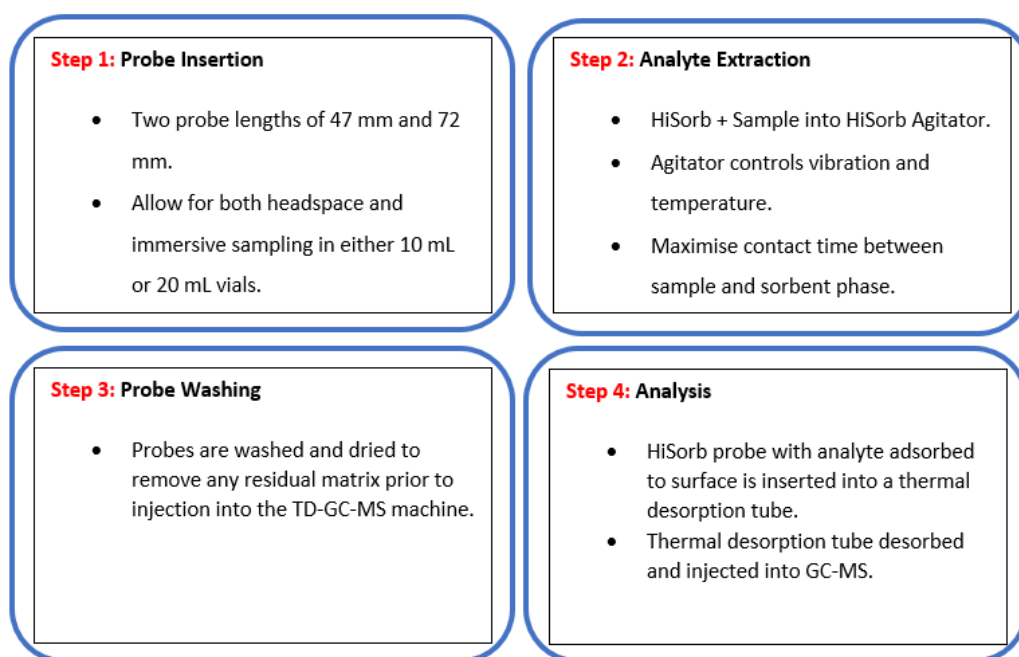Centri can be operated in 4 different sampling modes [78]:

- HiSorb
- Headspace and Headspace-trap
- SPME and SPME-trap
- Thermal desorption

1.9.2 HiSorb

HiSorb technology was developed by Markes International as an innovative, labour-saving sampling technique for the analysis of VOCs and SVOCs in liquids and solids via TD-GC-MS [79]. As an extension of thermal desorption, HiSorb consists of a polydimethylsiloxane (PDMS) sorbent phase which removes analytes from complex matrices via sorptive extraction (Figure 1.8). This has led to improved capabilities of thermal desorption, with trace level analysis of analytes across various disciplines such as aroma profiling and quality control [80]. With improved detection limits within the part per trillion level, HiSorb aimed to improve on conventional techniques such as SPME. The process of HiSorb is relatively simple and comprised of 4 steps, insertion, extraction, washing and analysis (Figure 1.9). All of which can be automated on the Centri platform.

Figure 1.8: HiSorb probes and immersive sampling of organic compounds [79].

Step 1: Probe Insertion

- Two probe lengths of 47 mm and 72 mm.
- Allow for both headspace and immersive sampling in either 10 mL or 20 mL vials.

Step 2: Analyte Extraction

- HiSorb + Sample into HiSorb Agitator.
- Agitator controls vibration and temperature.
- Maximise contact time between sample and sorbent phase.

Step 3: Probe Washing

- Probes are washed and dried to remove any residual matrix prior to injection into the TD-GC-MS machine.

Step 4: Analysis

- HiSorb probe with analyte adsorbed to surface is inserted into a thermal desorption tube.
- Thermal desorption tube desorbed and injected into GC-MS.

Figure 1.9: Shows the 4-stage procedure for HiSorb to remove analytes from the sample mixture and inject into the GC-MS.

The 3 key benefits associated with using HiSorb compared to conventional techniques such as SPME are:

- Time and cost savings due to complete automation on the Centri platform
- Increased sensitivity due to superior phase size
- Robustness

The robust HiSorb equipment allows for automated, unattended sample preparation with improved extraction efficiency. HiSorb is a quicker, more environmentally friendly alternative to solvent extraction. This leads to faster sample preparation for lower costs as solvent consumption and disposal is eliminated. Furthermore, each probe is re-usable reducing the costs associated with buying a probe for each sample run. Similarly to the PAL SPME Arrow previously discussed, the HiSorb probe contains a large volume of PDMS increasing the surface area of the probe compared to conventional SPME Fibres. The large sorbent volume provides the HiSorb probe with lower detection limits and improved sensitivity. HiSorb prides itself on being a versatile, easy to use piece of equipment. This is achieved through the probe's ability to analyse complex sample matrices via immersive or headspace analysis. Furthermore, HiSorb is compatible with all leading TD-GC-MS machines available on the market, allowing the consumer to benefit from HiSorb without the costs of updating all their equipment.

Centri was launched in the Spring of 2018 and uses robotic technology to fully automate the multi-mode sampling and concentration system for GC-MS. In combination with Centri, HiSorb can provide the consumer the ability to automate high capacity sorptive extraction from liquids and solids.
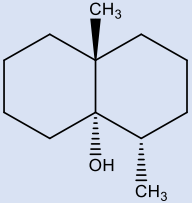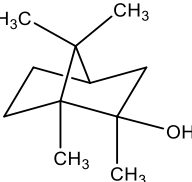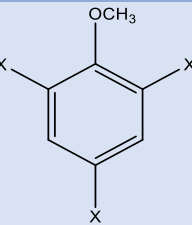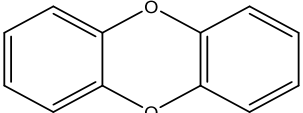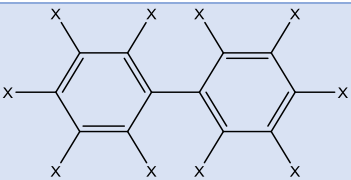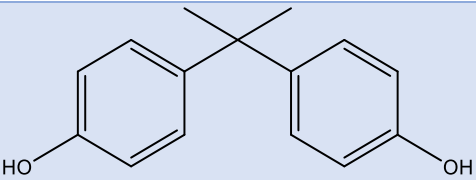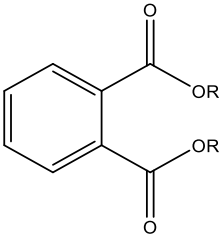
HiSorb provides high capacity sorptive extraction properties for a wide range of target analytes, across many analytical sectors. Such applications for HiSorb include environmental monitoring, food and drink profiling or medical diagnostic to name a few [81][82][58].

Water analysis is another particularly useful application of HiSorb. Drinking water can be prone to contamination by naturally occurring compounds such as geosim, methyl isoborneol (MIB) or trihaloanisoles.

As such, the removal of these trace-level organic compounds is a pro-longed issue for drinking water providers [84][85]. These organic compounds can be detected by the human nose at a concentration as low as 10 ng/L (10 ppt). All-be-it non-toxic, these compounds can provide an unfavourable earthy odour. Early detection, for example at the water plant, can raise alarms that these compounds are present and therefore improve the water company's chance to correct the contamination with appropriate action. Due to the relatively high volatility of the compounds, GC was the recommended mode of analysis. However, due to the considerably low concentrations of the contaminants within the sample, thermal desorption pre-concentration is required. HiSorb has been demonstrated as an appropriate tool within the pre-concentration technique. As the target compounds within the water supply exhibit hydrophobic characteristics, extraction with a PDMS stationary phase was efficient and successful to trace-level concentrations due to the large volume of sorbent used.

The application of HiSorb stretches beyond just drinking water when overcoming issues that surround water treatment. Another major issue for water treatment plants is the presence of SVOCs such as pharmaceuticals and personal care products (PPCPs). PPCPs are an emerging area of environmental contamination within water systems. Their presence at low concentrations within water systems can lead to physiological effects such as unwanted growths throughout various organisms including humans [86]. The extent of PPCP contamination appears across several different water systems such as groundwater, marine water, drinking water, surface water, soils and sediments at very low concentrations.

Table 1.5: Various molecules that are currently extracted using HiSorb [84][87].

Application	Name	Molecular Weight (M)	Chemical Structure	Boiling point (°C)	Detection level
Water Odours	Geosmin	182.31		270	ppt
Water Odours	2-Methylisoborneol	168.28		207	ppt
Water Odours	Trihaloanisole X=Cl 2,4,6-Trichloroanisole	-		-	-
Water SVOCs (EDCs)	Dibenzo-1,4-dioxin	184.19		283.5	ppt
Water SVOCs (EDCs)	Polychlorinated biphenyl	-		-	ppt
Water SVOCs (EDCs)	Brominated flame retardant	-		-	ppt
Water SVOCs (EDCs)	Bisphenol A	228.29		220	ppt
Water SVOCs (EDCs)	Phthalate (esters) Bis(2-ethylhexyl) benzene-1,2-dicarboxylate	-		385°C	ppt

A wide range of substances are thought to disrupt the action of hormone receptors in humans called endocrine-disrupting chemicals (EDCs) [88]. Some examples of these include dioxin and dioxin-like compounds, polychlorinated biphenyls (PCBs), brominated flame retardants, pesticides and components of plastics such as bisphenol A (BPA) and phthalates. The reported effects of these compounds at low concentrations are believed to be linked with adverse effects within humans such as cancer, obesity, type 2 diabetes, low semen quality and genital malformations [89][90]. Due to these reasons, EDCs are a growing issue and area of interest to analytical scientists. With a lack of information surrounding the amounts of the SVOCs within the water systems and their ecological effects, there is a current demand to monitor these. Monitoring can start to answer questions such as where is the source of the SVOCs? What are the most important routes of exposure? How are the levels effected by environmental factors? At what level is it hazardous? What are the underlying mechanisms of action [87]?

Through monitoring with HiSorb technology, more is being learnt about the effects of contaminants within the water systems. The process involves the rapid sampling at the site of an ongoing pollution event, where the HiSorb probe efficiently extracts the contaminants from the aqueous environment to the surface of the PDMS sorbent. Subsequently allowing analysis by TD-GC-MS which will then qualitatively and quantitatively measure the contaminants.

Another important application of the HiSorb apparatus is across the food and beverage industry [91]. With many different types of VOCs contributing to the flavour of drinks. To understand the profiles each beverage can help the manufacturer understand the products in greater depth and lead to improvement by identifying the factors that affect the customers perception. The VOCs of a beverage may also give indictors to whether the product has expired, with uncharacteristic odours and contaminants. The main issue that surrounds sampling from beverages is the ability to separate the volatile substances from the bulk components such as water, ethanol or acetic acid in order to avoid the overload of the analytical system. As previously mentioned, sampling vapours onto sorbent tubes with analysis through thermal desorption is useful to measure volatiles within liquids. As it provides the high level of concentration enhancement that is needed for detailed chemical analysis and profiling. In terms of sampling the VOCs from beverages, sorptive extraction

using HiSorb probes is an efficient method of extracting the less volatile compounds from an aqueous sample when compared to the more traditional approaches such as extraction and distillation.

HiSorb technology can be utilised to extract VOCs within liquids (immersive) or gases (headspace). One of the most recent applications of HiSorb is within the field of medical devices and demonstrates headspace analyte extraction [92]. This simplistic method utilises HiSorb technology to detect and quantify key biomarkers for respiratory disease and liver impairment. Targeting VOCs such as aldehydes, ketones and alkanes associated with these diseases were collected onto the HiSorb phase prior to analysis through TD-GC-MS. With HiSorb technology's ability to extract trace level biomarkers, a large step towards breath-based diagnostics for lung disease and liver impairment has been made, with work continuing to identify more key biomarkers across several other diseases and illnesses.

Overall, HiSorb technology has demonstrated versatility across several application areas. However, with only a single PDMS phase available HiSorb is subject to a limit on which analytes are extracted from a sample. To improve the performance of HiSorb and expand the area of application there is a requirement to expand the number of available phases. This will allow HiSorb to compete with the more established extraction techniques such as SPME.

1.10   Polydimethylsiloxane Modification

Polydimethylsiloxane (PDMS) is a polymer belonging to the siloxane family (Figure 1.10). The PDMS empirical formula is $CH_3[Si(CH_3)_2O]_nSi(CH_3)_3$ where n represents the number of monomer units within each polymer chain. PDMS is one of the most well-used silicon-based polymers due to several desirable characteristics such as biocompatible [93], viscoelastic [94] and chemically inertness [95]. Crosslinking within the PDMS induces a hydrophobic surface with a low surface tension and energy. This allows the polymer to become resistant to swelling against most polar solvents including water and methanol. However, PDMS and its corresponding hydrophobic properties have been proven a useful, cost-effective tool in the removal of hydrophobic contaminants within aqueous/polar environments [84][87].
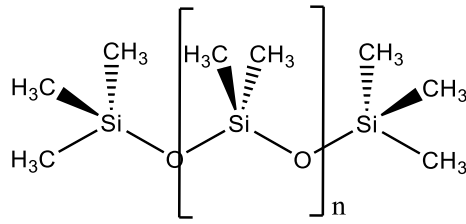
Figure 1.10: Chemical structure of PDMS.

1.10.1 Plasma Treatment

Much research has been carried out in recent years investigating how PDMS can be modified to possess more hydrophilic properties [96]. The majority of research that introduces hydrophilic characteristics to PDMS have focused on surface properties of the polymer [97]. A well-practiced method of surface modification to PDMS is the application of plasma treatment [98][99]. The plasma treatment devices used in PDMS modification commonly have an electrical coil that generates a partially ionized gas comprising of electrons, ions, neutral atoms and molecules [100]. Some of the commonly used gases for PDMS modification include argon, oxygen or nitrogen with each establishing a hydrophilic layer at the surface [101][102][103]. Exposing the PDMS surface to these reactive species introduces more polar silanol (Si-OH) terminal groups in reward of non-polar methyl groups (Si-CH$_3$). This technique has been predominantly investigated to improve the adhesion between PDMS and glass surfaces in microfluidic devices [104].

Gomathi's research group studied the effects of oxygen and nitrogen plasma on the physiochemical properties, in particularly the hydrophilicity, of PDMS to improve the material's biocompatibility [105]. Results from this experiment showed that using nitrogen or oxygen plasma induced a hydrophilic surface characteristic within PDMS (Figure 1.11). The group decided to use oxygen and nitrogen plasma for comparison with untreated PDMS. Untreated PDMS tends to have a low surface energy with leads to the hydrophobic nature and low adhesion properties. However, once treated with plasma the surface energy values and polarity of the samples increase.
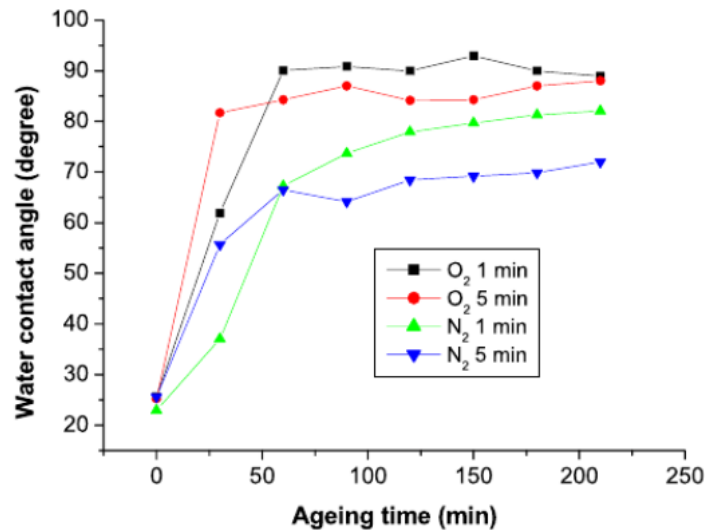
Figure 1.11: Ageing analysis of plasma treated PDMS [105].

Contact angle measurements are a well-established technique for the measuring the hydrophilicity at the surface of the material [106][107]. The contact angle of a deionised water droplet at the surface of the untreated PDMS was shown to be approximately 106° (Table 1.6). Within the experiment, contact angles reached a low of approximately 25° at time = 0 due to the plasma surface modification. However, a key issue that surrounds the oxidisation of PDMS surfaces through plasma treatment, is the eradication of the newly formed hydrophilic surface and regeneration of the hydrophobic surface over the first 30 minutes (Figure 1.11). The restoration of the hydrophobic surface can be explained through a couple of mechanisms [101]. First of which features the migration of low molecular weighted PDMS monomer chains from the bulk to the surface of the polymer material. When the surface undergoes modification via plasma treatment, this destabilizes the thermodynamics of the material surface. As such, the low molecular weight PDMS monomers migrate from the bulk to the surface, to compensate and remove the modified polymer chains that induce the thermodynamically unstable surface. Another possible explanation included the natural physical recovery of the PDMS due to the elastic property of the polymer. These mechanisms of recovery explained the dramatic increase in contact angle values over the first 30 minutes of exposure to air for each piece of treated PDMS. The recovery continued for approximately 90 minutes of air exposure, where the samples hydrophilic property stabilized. PDMS samples that were treated with O_2 for 1 minute showed the most hydrophobic recovery with an

average contact angle of 89° and the samples that were exposed to N_2 plasma for 5 minutes showing the least recovery with an average contact angle of 72°.

Table 1.6: Contact angle, surface energy and polarity of untreated PDMS and plasma treated PDMS. DI = Deionised water, FA = Formamide, DIM = Diiodomethane. γ = surface free energy, γ_p = surface free energy of polar, γ_d = surface free energy of polar [105].

Sample	Contact Angle (°)			Surface Energy (N/mm^2)			Polarity
	DI	FA	DIM	γ_p	γ_d	γ	
Untreated	106 ±2	87 ±1	81 ±2	0.92	15.81	16.7	0.05
O_2 – 1min	89 ±2	60 ±1	76 ±1	6.58	15.47	22.1	0.30
O_2 – 5min	88 ±1	48 ±2	79 ±1	8.71	14.44	23.2	0.38
N_2 – 1min	82 ±2	34 ±2	57 ±2	6.62	26.06	32.7	0.20
N_2 – 5min	72 ±2	28 ±1	63 ±1	13.4	19.87	33.3	0.40

The research group of Tan investigated the effectiveness of a secondary extended oxygen plasma treatment on the hydrophobicity of PDMS surfaces within a closed microchannel [102]. One of the variables used in this study was different oxygen plasma exposure times on the secondary round of treatment. Similarly to Gomathi's research, the group measured contact angles of liquids at the surface of the PDMS to determine any change to the hydrophilicity. The findings revealed that increasing the oxygen plasma exposure time at the PDMS surface reduced contact angle and increased hydrophilicity [102]. The hydrophilicity of the treated PDMS within the microfluidic channels was measured over 6 hours in ambient air. It was found that the devices with the PDMS samples that were treated with just 100 or 200 seconds of plasma, recovered to a hydrophobic state after just 3 hours. However, results showed that exposing PDMS samples to 300, 400 or 500 seconds of oxygen plasma recorded no hydrophobic recovery with contact angles of 60°. Furthermore, atomic force microscopy (AFM) showed that as the length of oxygen plasma treatment increased, the surface of the PDMS became smoother which reduced the rate of hydrophobic recovery. One issue surrounding this paper was the values for the contact angles. For a planar PDMS sample,

exposure to lengthy times of oxygen plasma would produce contact angles of less than 10° at time = 0. Within this study, at time = 0 a contact angle was recorded to be 17°. This increase in contact angle could be explained by a lower concentration of oxygen reactive species reaching the surface of the PDMS due to the shape of the microfluid device. It would have been interesting to see the effects of secondary oxygen plasma on a planar PDMS surface as it would be a more direct exposure to the oxygen radical for the PDMS. Another investigation within the paper stated that induced hydrophilic surface characteristic of PDMS can be attained for more than 7 days via storage in deionised water or a vacuum. This study showed that stabilizing the thermodynamically unstable surface prevents the low molecular weighted PDMS fragments regenerating a hydrophobic surface.

## 1.10.2   Ultraviolet Treatment

An alternative approach to physical modification of PDMS is the application of Ultraviolet (UV) treatment. Although UV is known to not be as oxidising as plasma treatment over the same period of time, a major benefit is that the UV treatment penetrates the material better than plasma, allowing for oxidation further within the bulk of the material [108]. This is advantageous as a greater depth of oxidized PDMS within the sample will produce a slower regeneration time of the original hydrophobic surface. Research presented by Efimenko investigated the effects of oxygen on PDMS during UV treatment [109]. Contact angle measurements were recorded for PDMS samples that were UV treated in either oxygen-rich or oxygen-deprived. It was deduced that the modified PDMS samples which were exposed to a UV treatment with oxygen for up to 60 minutes had reduced contact angle values of 10° and high surface energies of $72mJ/m^2$ compared to contact angles of 110° and surface energy values of $20mJ/m^2$ in PDMS samples not exposed to oxygen. This experimental evidence showed that the presence of oxygen significantly changed the surface energy PDMS making an oxygenated atmosphere a vital aspect of the modification process. The high surface energy within UV and oxygen exposed modified PDMS was characterised through fourier-transform infrared (FTIR) spectroscopy. This data showed the presence of hydroxy (-OH) functionality at the surface of the PDMS samples. Overall, this paper demonstrated an efficient, physical method of surface modification to PDMS, with improved hydrophilic behaviour of PDMS after exposure to UV in oxygen compared to untreated PDMS. This paper demonstrates how

exposure time affects contact angle measurements. However, a critic of this paper is the lack of investigation surrounding the sustainability of modification. With knowledge that PDMS surfaces regenerate after plasma treatment [110], it would be interesting to see how UV treatment differentiates and whether oxygenated species situated within the bulk influence contact angle measurements and hydrophobic regeneration.

1.10.3   Chemical treatment

Chemical treatment of PDMS surfaces is an alternative method to PDMS modification. Brook et al. investigated the effects of thiol-ene click chemistry on the hydrophobic PDMS surface [111]. The reported intention was to improve the hydrophilicity of PDMS while avoiding the unwanted characteristics such as surface cracking and hydrophobic recovery that are associated with other modification methods. The group successfully produced a thiol functionalized PDMS surface via base-catalysed equilibration (Figure 1.12). The first step of the mechanism consisted of the nucleophilic attack of hydroxy ions at the surface of the PDMS material. This allows for the addition of the coupling agent $(MeO)_3Si(CH_2)_3SH$ (MTS). These nucleophilic reactions lead to the formation of silanolate ions (R_3SiO^-). The silanolate ions undergo a further series of nucleophilic reactions that leads to the formation of MTS oligomers, depolymerisation of the PDMS chains and the tethering of MTS in various forms to the PDMS surface.

Techniques such as XPS or fluorescent labelling would be efficient at deducing whether thiols are present at the surface of the PDMS. However, these broadly used techniques are used as a qualitative tool rather than quantitative. To quantitatively measure the amount of thiol present techniques such as titration and Ellman's reagents were considered. The concentration of thiols at the surface of the PDMS was monitored using two complementary titration methods: 4,4-dithiodipyridine (DTDP) titration and iodine titration, respectively. It was understood that applying each of these techniques would allow independent analysis of thiols at the surface of the PDMS and the bulk.
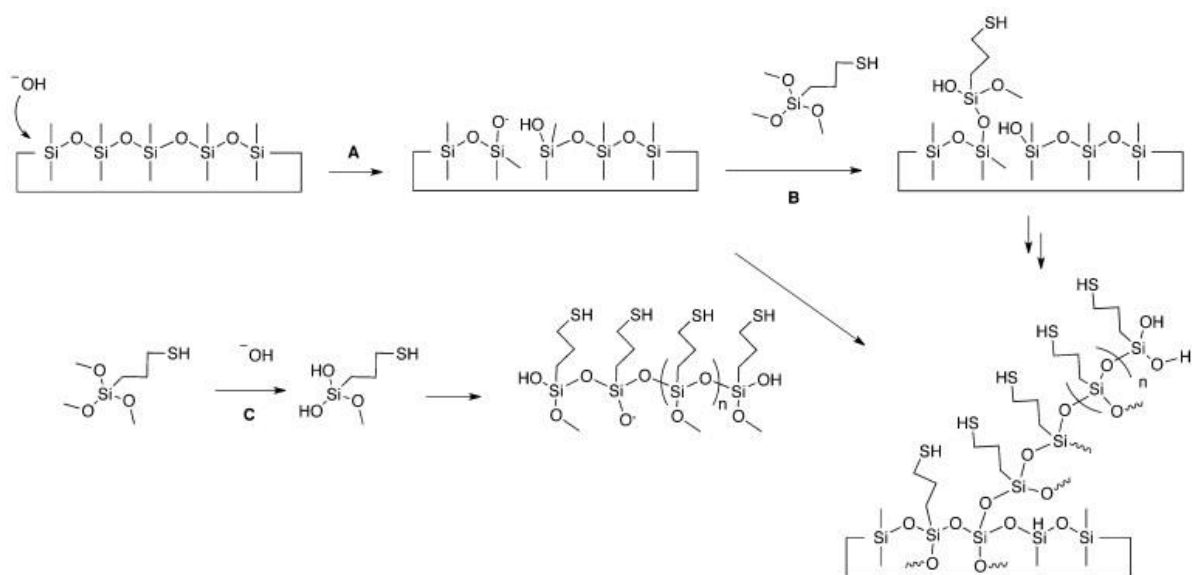
Figure 1.12: Schematic illustration of the process to introduce thiols to the surface of PDMS. (A) reaction with the silicone; (B) reaction at $(MeO)_3Si(CH_2)_3SH$ (MTS); and (C) metathesis at the elastomer interface [111].

DTDP titration was undertaken in DMSO which is an unfavourable solvent for PDMS. Due to the unfavourable interaction between PDMS and DMSO, the DTDP reagent only reacts with thiols at the surface of the PDMS. The nucleophilic substitution reaction sees the formation of 4-thiopyridone and can be measured spectrophotometrically at 347nm (Figure 1.13). Within the iodine titration, an oxidation of iodine to iodide causes the formation of a covalent bond between the sulphur atoms. Unlike DTDP titration, the iodine titration oxidation takes place at the surface and within the bulk of the PDMS. The reason for this being that the titration takes place in a toluene solution which swells the PDMS allowing access to the bulk elastomers. The absorbance of an iodine solution can be seen at 497nm, therefore the concentration of thiols on the surface and within the PDMS can be determined by a loss of intensity as iodine oxidizes to iodide.

A major focus around PDMS modification is the prevention of the hydrophobic recovery as the hydrophiles are replaced at the surface by the hydrophobic silicone chains. Utilising DTDP and iodine titrations to quantify thiols at the surface compared to the surface and bulk provided an opportunity for Brook et al [111]. In-order to measure the hydrophobic recovery of the thiol modified PDMS materials, the results of the two titrations over time were compared to calculate the effect of bulk modification on PDMS hydrophobic recovery.
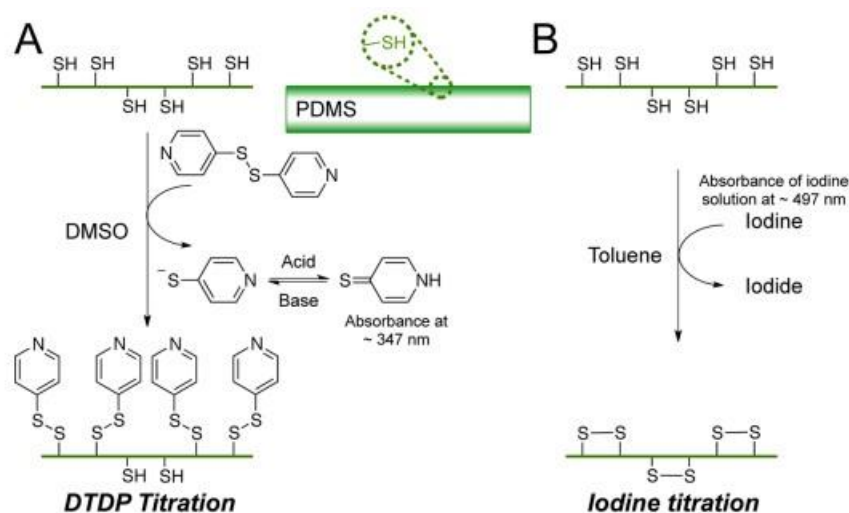
Figure 1.13: Quantitative analysis of thiols at the surface of the PDMS via DTDP titration and within the surface layer via iodine titration [111].

The results showed that after just 2 hours the concentration of thiols based on the DTDP titration dropped over 50% indicating a significant loss of thiols from the surface. However, over the same time the iodine titration showed a smaller, less significant drop from 78nmol/cm^2 to 62nmol/cm^2. This represents little loss of thiol concentration throughout the whole PDMS elastomer. After 4 hours, the concentration of the thiols became close to zero for the samples measured with DTDP titration while iodine titration showed little change. After 6 hours, the samples underwent swelling/deswelling in DCM. This allowed for the rearrangement of the elastomers within the PDMS and what was found was that approximately 25% of the original thiols were present at the surface as they became accessible for titration by DTDP.

A major advantage of obtaining a thiol surface is the ability to undertake thiol-ene click chemistry. This allows for further surface modification to PDMS via the tethering of various functionalised and hydrophilic groups. Within the paper published by Brook et al the surface-bound thiols underwent thiol-ene click reactions using maleic anhydride and an acrylate-terminated silicone surfactant (ACR) [111] (Figure 1.14A). The thiol surfaces that underwent click chemistry with maleic anhydride, once maleic anhydride was successfully located at the surface of the PDMS, ring opening reactions of the maleic anhydride took place to attach polyethylene glycol (PEG) and chitosan ligands to the surface (Figures 1.14C, 1.14D and 1.14E).

The hydrophilicity and durability of the modified surface were measured using water contact angles. The results show that all four modifications improve the hydrophilicity of the material due to the introduction of hydrophilic functional groups such as carboxylic acid, amino and hydroxyl groups.
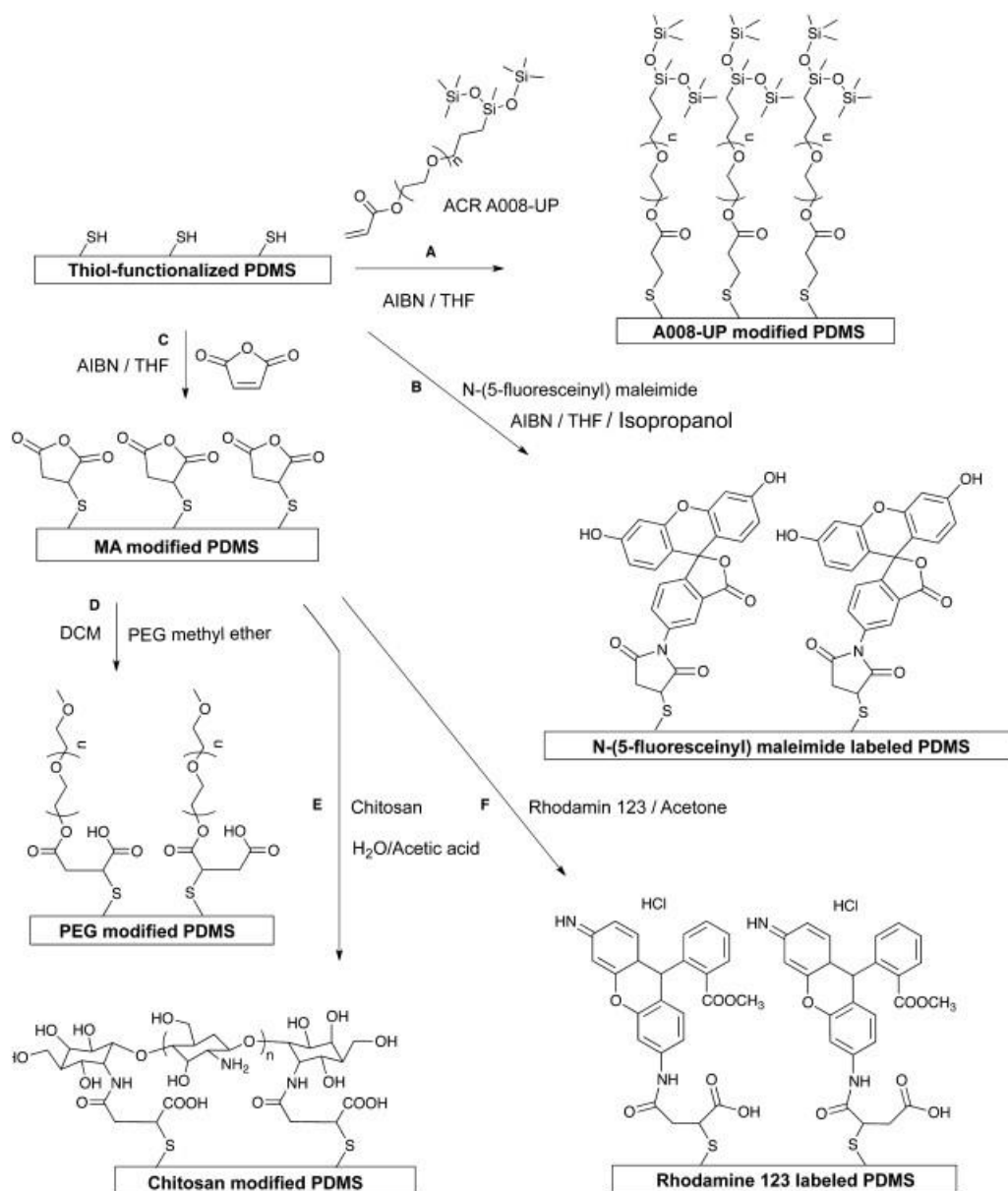
Figure 1.14: Surface modification of thiol-silicones: Surface thiol–ene reactions with (A) ACR A008-UP, (B) N-(5-fluoresceinyl)maleimide, and (C) maleic anhydride, followed in the latter case by ring-opening of the surface anhydride with (D) M-PEG, (E) chitosan, or (F) rhodamine 123 [104].

The hydrophilic durability of the modified PDMS materials were analysed within this experiment by examining how the water contact angles at the surface changed when stored in ambient air for 6 months (Table 1.7). Similarly to other hydrophilic modified PDMS surfaces, it was found that recovery of the hydrophobic silicones to the surface of the material was apparent in a matter of hours. However, the group regenerated the hydrophilic surface by soaking the material in a complimentary solvent for silicones. In this case, the solvent used was water. All four materials showed improved hydrophilicity after equilibration in water for three days, but only PDMS-S-MA-CH and PDMS-S-MA showed total recovery of the hydrophilic surface. Alternatively, PDMS-SH was stored at 2°C in a methanol solution for over 4 months and did not show total hydrophobic recovery while maintaining 25% thiol concentration at the surface.

Table 1.7: Contact angle measurements of modified PDMS [111].

	PDMS-S-ACR			PDMS-S-MA			PDMS-S-MA-PEG			PDMS-S-MA-CH		
		Old	Old		Old	Old		Old	Old		Old	Old
	New	Air	H$_2$O	New	Air	H$_2$O	New	Air	H$_2$O	New	Air	H$_2$O
Contact angle (°)	74	92	82	84	89	78	73	92	82	71	86	75
Error (°)	4	3	1	6	3	5	2	1	3	7	5	6

When comparing plasma, UV and chemical modifications to PDMS, each achieve reduced contact angle values indicating oxidation at the surface of the PDMS. However, the hydrophilicity in each modification is limited by the regeneration of the hydrophobic surface as the oligomers replace the newly oxidised polymer chains at the surface of the material. This regeneration process can be reduced by using appropriate storage, such as storing the samples in water. Furthermore, it has been shown that partial recovery of the oxidised surface can be achieved after the regeneration of the hydrophobic surface.

1.10.4 Small Molecule Encapsulation

A rarely documented form of PDMS modification is through encapsulation of small molecules. PDMS encapsulation manipulates the polymer's ability to swell in various organic solvents to capture small molecules in the matrix of the material. Opposed to the surface modification techniques previously described, this bulk modification was demonstrated by the Crick research group [112]. The research found that large concentrations of nanoparticles can be found at the surface of the material with lower concentration located within the bulk. PDMS was placed in a nanoparticle/hexane mixture where the hexane swelled the polymer material. This swelling generated space between the polymer chains in the matrix. Over-time the nanoparticles are adsorbed by the material, locating themselves across the surface of the material and within the gaps created by the swelling agent. PDMS was then removed from the nanoparticle/hexane mixture, rinsed and left to dry. It was this drying process which removed all the hexane solution, allowing the PDMS to shrink back to its original size and leaving the nanoparticles throughout the polymer (Figure 1.15).
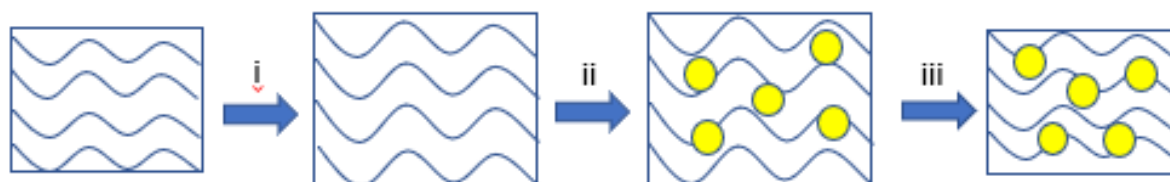
Figure 1.15: (i) PDMS placed in organic solvent, that leads to swelling; (ii) nanoparticles penetrate the PDMS, locating themselves in the matrix; (iii) PDMS dried of organic solvent, leaving the nanoparticles within the PDMS matrix.

1.11 Commercial Needs & Project Aims

The overall requirement from an industrial perspective is to develop a new sorbent phase to expand on the current HiSorb product portfolio. At this moment in time, HiSorb is available in a single PDMS phase and as such is limited to the extraction of analytes which adsorb to this siloxane surface. The category of analytes which adsorb to the surface of PDMS are primarily hydrophobic (LogP > 3). This limited analyte extraction range inhibits the HiSorb

competitiveness within the current market, as other products such as SPME showcasing a vast range of phases for different applications (Section 1.7).

Therefore, the aim of this study is to apply various modification techniques to PDMS, in-order to improve HiSorb adsorptive capabilities towards a larger range of organic compounds in aqueous solutions via immersive sampling.

It is expected that supplementing the PDMS with polar compounds or various other types of sorbents would alter the PDMS sorptive extraction performance.

This report will assess 3 different PDMS modification techniques and how each of these new sorbent materials perform at extracting organic compounds from aqueous solutions as measured by thermal desorption–gas chromatography–mass spectrometry (TD-GC-MS). Furthermore, each sample's physical and chemical properties will be measured after each thermal desorption cycle via techniques such as Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and contact angle measurements.

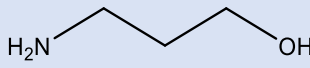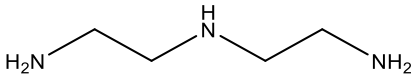# Chapter 2: Materials & Methodology
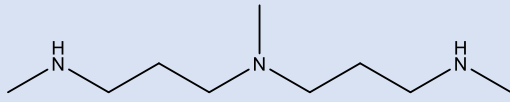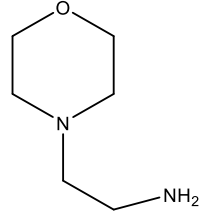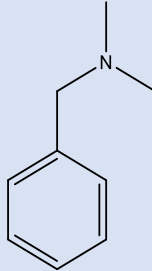
2.1   Material Preparation
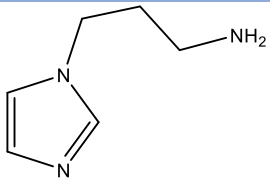
2.1.1 HiSorb Conditioning

Conditioning of the HiSorb probes within thermal desorption (TD) tubes was conducted on a Markes International TC20 for 2 hours 20 minutes at 300 °C under N_2 as recommended within the instructions. Upon completion, the probes were left to cool for 15 minutes at room temperature before being sealed with brass cap locks. The brass cap locks ensure that the HiSorb probes are not exposed to the environment, reducing contamination and ensuring sample integrity.

2.1.2 Amine Encapsulation

After the PDMS was conditioned on the TC20 (Section 2.1.1), a 10% concentrated encapsulation solution of total volume 7.5 mL was prepared by adding 0.75 mL of 3-aminopropan-1-ol to 6.75 mL of acetone (swelling agent) in a 10 mL flask. This process was then repeated for amines; diethylenetriamine, N,N-Bis[3-(methylamino)propyl]methylamine, 4-(2-aminoethyl)morpholine, N,N-dimethylbenzylamine and 1-(3-aminopropyl)imidazole (Table 2.1). Conditioned PDMS HiSorb probes were then added to each of corresponding encapsulation solutions, clamp sealed (to avoid evaporation of solution) and left for 24 hours under ambient conditions. After soaking the PDMS materials in their encapsulation amine solution for 24 hours, each probe was washed with acetone to remove any residual solution and left for 1 hour to dry under ambient conditions.

Table 2.1: Amines used for encapsulation and their relative polarity, boiling point and chemical structure.

Compound	LogP	Boiling Point (°C)	Chemical Structure
3-aminopropan-1-ol [113]	-1.12	187.5	
Diethylenetriamine [114]	-2.1	207	
N,N-Bis[3-(methylamino)propyl] methylamine [115]	-0.9	232.5	
4-(2-aminoethyl)morpholine [116]	-1.1	205	
N,N-dimethylbenzylamine [117]	1.98	183	
1-(3-aminopropyl)imidazole [118]	0.6	296	

2.1.3 Epoxy-terminated PDMS Crosslinking

Epoxy-terminated PDMS (250 µL) was mixed at a 10:1 ratio with each of the corresponding amines; diethylenetriamine (25 µL) and N,N-Bis[3-(methylamino)propyl]methylamine (25 µL). HiSorb tips were placed into NMR tubes (Figure 2.1a). NMR tubes were used because they had the correct diameter for making the tubular sorbent shape, inertness to ensure no side-reaction and high thermal stability for the crosslinking process. Once the pre-crosslinked polymer mixture was placed into the NMR tube to approximately 11 mm (same length of

current PDMS material), the tube was placed in an oven to cure at 180 °C for 120 hours (Figure 2.1b). Once cured and cooled under ambient conditions, the outer glass mould was removed from the newly formed PDMS-based sorbent material (Figure 2.1c). The HiSorb tip and phase were then screwed in the main body of the HiSorb probe (Figure 2.1d).
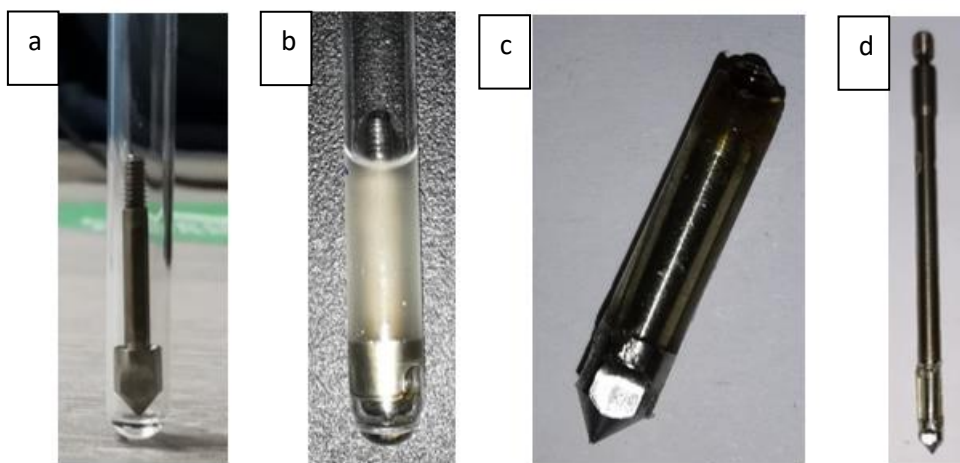
Figure 2.1: (a) HiSorb tip (without sorbent phase) was placed in the NMR tube. (b) The NMR tube was filled with the PDMS-based pre-crosslinked mixture to a length of approximately 11 mm and placed in oven at 180 °C for 120 hours. (c) Removed and left to cool before carefully removing the glass NMR tube mould. (d) Screwed onto the main body of the HiSorb ready for analysis.

2.1.4 Multi-phase PDMS

Various types of commercially available sorbents were provided by Markes International to cure in PDMS. However, within this study Carboxen 1016 (graphitised carbon) and Tenax GR (molecular sieve) were successfully synthesized into a cylindrical PDMS-based biphasic sorbent material. The PDMS used in this chapter was purchased from DOW. SYLGARD 184 is a 2-part PDMS curing kit. Part 1 is the PDMS pre-polymer and part 2 is the crosslinking agent. These structures were proprietary to DOW.

Carboxen 1016 (45 mg) and Tenax GR (45 mg) were weighed into individual 20 mL vials containing hexane (0.9 mL). As per the methodology described by the Jiang research group, each flask was vortexed for 1 minute, followed by 30 minutes sonication [119]. These steps

were taken to ensure a homogeneous distribution of particles. After mixing, high-density Sylgard PDMS pre-polymer (225 mg) was weighed into each vial. The vials were then further vortexed for 2 minutes each prior to 1 hour of sonication. Hexane was then removed from the mixture by placing the mixture in an oven at 85°C for 30 minutes before being left to cool to ambient temperatures. 30 minutes was found to be the optimum time to allow all hexane to evaporate. As per the DOW instructions of a 10:1 ratio of prepolymer : crosslinking agent, the crosslinking agent (22.5 mg) was then added to each vial and vortexed for a further 2 minutes. NMR tubes were then placed upright in a rack with HiSorb tips facing downwards at the bottom (Figure 2.1a). Each mixture was then placed into each of the corresponding glass NMR tubes (Figure 2.1b). Following these steps, the PDMS mixtures were left under vacuum for 24 hours prior to being placed in an oven at 80°C for 24 hours followed by a further 24 hours at 120°C. The vacuum step was to remove any trapped air within the mixture from the several mixing steps in the preparation steps. Over this period, the viscous PDMS-based sorbent was in a viscous liquid state. When exposed to the higher temperatures the PDMS underwent crosslinking and set as a rubber polymer. Once set, the PDMS-based sorbent was removed from the glass sleeve and attached to HiSorb probe bodies (Figures 2.1c & d). Prior to extraction, each HiSorb probe was placed in a Markes International TC20 at 300°C for 36 hours under N_2.

2.2   Material Characterisation

2.2.1   Thermal Desorption-Gas Chromatography-Mass Spectrometry

2.2.1.1   Preparation of Calibration Standards

Two sets of 5000 µg/mL concentrated calibration solutions were prepared. The first set was made by adding the quantities of each organic compound in Table 2.2 to a 10 mL volumetric flask and this mixture was to be used for the extraction testing via TD-GC-MS for the materials prepared via amine encapsulation (Section 2.1.2) and epoxy-terminated PDMS crosslinking (Section 2.1.3). For the multi-phase PDMS materials that were synthesized with the commercially available sorbent (Section 2.1.4) the quantities of organic compounds in Table

2.3 were add to a 10 mL volumetric flask. Each of the 5000 μg/mL solutions were made by then filling the volumetric flask with dichloromethane (DCM) up to the 10 mL line. Each solution was diluted with methanol to various concentration levels from 1 to 250 μg/mL (Table 2.4).

Table 2.2: The quantity of each organic compound added to the 5000 μg/mL stock solution for PDMS sorbents that underwent amine encapsulation and epoxy-terminated PDMS crosslinking.

Compound	Log P	Density (g/mL)	Volume Added (μL)	Quant Ion (m/z)	Boiling Point
Pyridine	0.71	0.98	51	79	115
Ethyl Acetate	0.73	0.89	56	43	77
Butanol	0.88	0.81	62	56	118
Hexanal	1.78	0.81	62	44	130
Toluene-d8	2.73	0.87	58	98	110
Cyclohexane	3.44	0.77	65	56	81
Isobornyl Methacrylate	4.30	0.98	51	69	129
Heptane	4.66	0.68	74	43	98

Table 2.3: The quantity of each organic compound added to the 5000 μg/mL stock solution for the PDMS materials moulded with commercially available sorbents, Tenax GR and Carboxen 1016.

Compound	Log P	Density (g/mL)	Volume Added (μL)	Quant Ion (m/z)	Boiling Point
Acrylonitrile	0.20	0.80	61	53	77
Pyridine	0.71	0.98	51	79	115
Ethyl Acetate	0.73	0.89	56	43	77
Butanol	0.88	0.81	62	56	118
Hexanal	1.78	0.81	62	44	130
Toluene-d8	2.73	0.87	58	98	110
Styrene	2.90	0.91	55	104	145
Cyclohexane	3.44	0.77	65	56	81
Heptane	4.66	0.68	74	43	98

Table 2.4: Dilution table that shows the ratio of 5000 µg/mL stock solution to methanol required to generate each known concentration level.

Required Concentration (µg/mL)	Volume of 5000 µg/mL stock solution (µL)	Volume of MeOH (µL)
250	50	950
100	20	980
75	15	985
50	10	990
25	5	995
10	2	998
5	1	999
1	0.2	999.8

Markes International stainless steel Tenax TA thermal desorption (TD) tube (C1-AAXX-5003) was placed under a flow of nitrogen gas and spiked with 1 µL of 250 µg/mL directly onto the gauze and left to purge under nitrogen at 100 mL/min for 3 minutes as per Markes internal protocol (Figure 2.2). This process was repeated for each known concentration level with 2 repeats for each concentration.

Figure 2.2: Stainless steel Tenax TA thermal desorption tubes used for spiking with calibration standards ranging from 250 - 1 µg/mL.

2.2.1.2　　　Preparation of Extraction Mixture and Extraction with HiSorb

A 10 ppb aqueous extraction mixture was prepared by half filling a 500 mL volumetric flask with Ultra-High Performance Liquid Chromatography (UHPLC) grade water and methanol (25 mL). 50 µL of 100 µg/mL standard in methanol was added to the volumetric flask prior to filling up to the 500 mL line with the UHPLC grade water and shaking. 7.5 mL of the 10 ppb solution was added to each of the 10 mL flasks prior to clamp sealing and insertion of the HiSorb probes via septum. Each flask was placed in an agitator at 30 °C and 200 rpm for 2 hours. After agitation, HiSorb probes were washed with UHPLC water and dried with tissue prior. The final step comprised of the probes being placed in empty inert coated thermal desorption tubes (C0-CXXX-0000) and sealed with inert DiffLok caps.
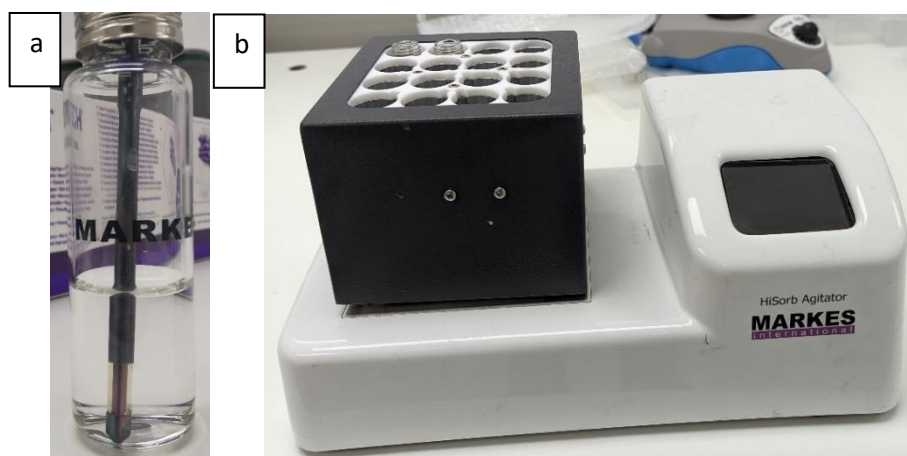
Figure 2.3: (a) HiSorb probe immersed in 7.5 mL 10 ppb extraction mixture. (b) Markes International HiSorb agitator.

2.2.1.3　　　Calibration

Each of the Tenax tubes which were spiked with varying levels of known concentration were analysed in the TD-GC-MS. The calibration sequence was set from the lowest to the highest concentration with each of the organic compounds adsorbed at the Tenax surface desorbed and analysed via thermal desorption gas chromatograph-mass spectrometry (TD-GC-MS).

The calibration analysis parameters were as follows:

Thermal Desorption

Instrument: Centri (Markes International)

Sorbent Tube: Tenax TA stainless steel sorbent tube (C1-AAXX-5003)

Tube Desorption: 300 °C (8 min)

Flow Path: 190 °C

Focusing Trap: General Purpose Trap - U-T2GPH-2S (10mm Quartz Wool, 25mm Tenax TA, 25mm Carbograph 1TD)

Purge Flow: 50 mL/min (1 min)

Trap Low: 20 °C

Trap High: 300 °C (8 min)

Split Flow: 5 mL/min

Gas Chromatography – Mass Spectrometry

Column: DB-624 UI, 60 m x 0.32 mm x 1.80 µm

Constant flow: Helium, 2 mL/min

Oven program: 45 °C (5 min), then 10 °C/min to 250 °C, then 35 °C/min to 300 °C (2.5 min)

Transfer line: 310 °C

Ion source: 250 °C

Quad: 200 °C

Mass range: m/z 25 – 300

The spiked Tenax TA thermal desorption tubes were used to quantitatively calculate how much of each organic compound was extracted. The spiked Tenax TA thermal desorption tubes also allowed for the calculation of retention times, which is the time at which each organic compound elutes from the GC and detected by the mass spectrometer (Tables 2.5 & 2.6). To identify these analytes the mass spectrometry data was compared to a customised library generated from spectra in the NIST MS Search 2.0 database.
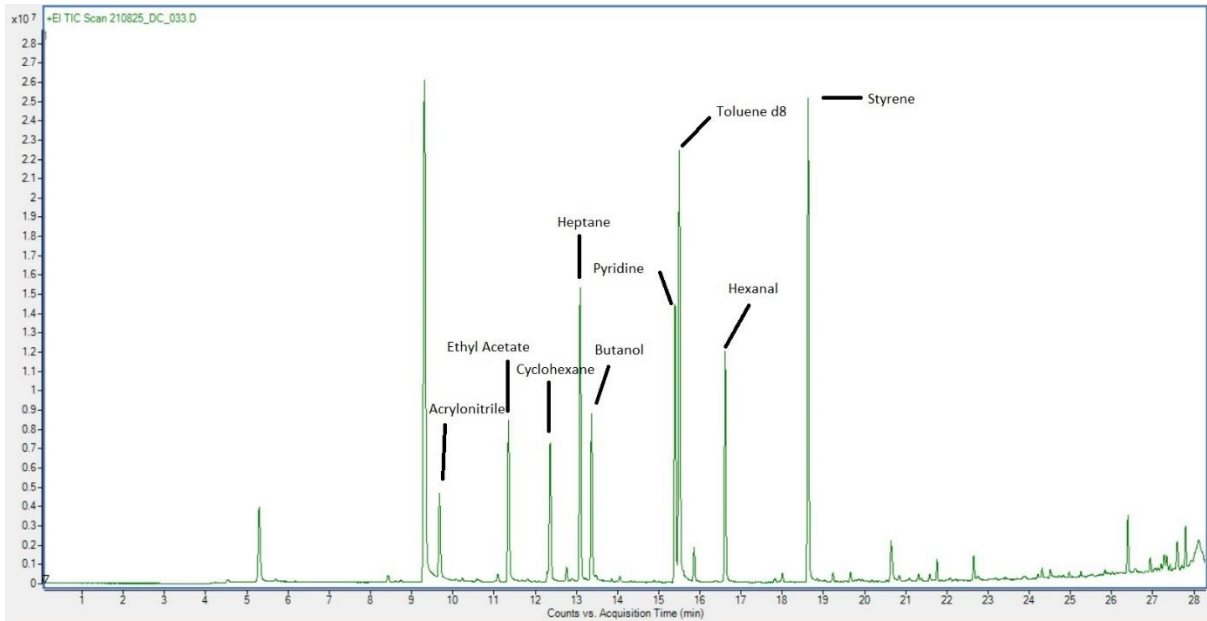
Retention times (RT) for each organic compound were located on the chromatogram depending on m/z value (Figure 2.4) and concentrations calculated by measuring peak area (Figure 2.5). A calibration curve for each compound was formed of concentration on the x axis and peak area on the y (Figure 2.6).

Table 2.5: Retention times for each organic compound used in the amine encapsulation and epoxy-terminated bonding PDMS experiments. The table shows the corresponding mass to charge ratios (m/z) used to identify each compound on the spectra.
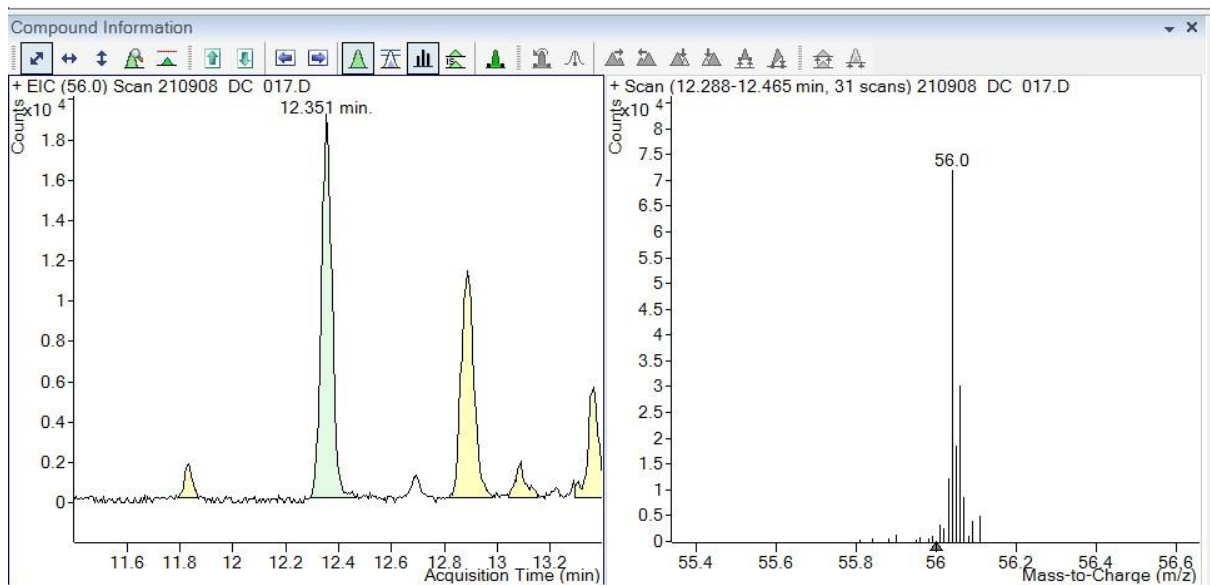
Compound	Retention Time (min)	Mass to Charge Ratio (m/z)
Ethyl Acetate	8.9	70
Cyclohexane	9.6	84
Heptane	10.2	57
Butanol	10.5	56
Pyridine	11.9	79
Toluene - d8	11.9	98
Hexanal	12.7	44
Isobornyl Methacrylate	21.4	136

Table 2.6: Retention times for each organic compound within the extraction mixture for the PDMS and commercially available experiments. The table shows the corresponding mass to charge ratios (m/z) used to identify each compound on the spectra.

Compound	Retention Time (min)	Mass to Charge Ratio (m/z)
Acrylonitrile	9.7	53
Ethyl Acetate	11.4	43
Cyclohexane	12.4	56
Heptane	13.1	43
Butanol	13.4	56
Pyridine	15.4	79
Toluene-d8	15.5	98
Hexanal	16.6	44
Styrene	18.6	104

Figure 2.4: Spectra from 250 ng concentrated spiked Tenax TA tube which clearly identifies the retention times of each organic compound in the extraction mixture.

Figure 2.5: (a) Peak area at retention time 12.4 min for cyclohexane. (b) Shows that within the peak at 12.4 min, 56 was the most common mass-to-charge ratio (m/z).

2.2.1.4   Desorption of Organic Compounds from HiSorb Probes

After each HiSorb probe had undergone organic compound extraction (Section 2.2.1.2), each of the probes were placed in the Markes International Centri, ready for analysis. TD-GC-MS parameters were based off the Markes International protocol and were as follows:

Thermal Desorption

Instrument: Centri (Markes International)

Probe: Standard-length stainless steel HiSorb probes – phase varied on on experiment.

Control phase: PDMS (H1-XXAAC)

Sorbent Tube: Empty inert sorbent tube (C0-CXXX-0000)

Tube Desorption: 160 °C (12 min)

Flow Path: 190 °C

Focusing Trap: General Purpose Trap - U-T2GPH-2S (10mm Quartz Wool, 25mm Tenax TA, 25mm Carbograph 1TD)

Purge Flow: 50 mL/min (1 min)

Trap Low: 20 °C

Trap High: 300 °C (8 min)

Split Flow: 5 mL/min

Gas Chromatography – Mass Spectrometry

Column: DB-624 UI, 60 m x 0.32 mm x 1.80 µm

Constant flow: Helium, 2 mL/min

Oven program: 45 °C (5 min), then 10 °C/min to 250 °C, then 35 °C/min to 300 °C (2.5 min)

Transfer line: 310 °C

Ion source: 250 °C

Quad: 200 °C

Mass range: m/z 25 – 300

The TD-GC-MS results obtained provided both qualitative (were the compounds extracted) and quantitative (how much was extracted) information about how each HiSorb probe performed at extracting organic compounds from aqueous mixtures. Furthermore, result of each modified HiSorb probe's extraction performance was directly compared to that of the non-modified PDMS HiSorb probes (H1-XXAAC).

After each thermal desorption cycle, the HiSorb probes underwent a secondary extraction using the same protocol described in section 2.2.1.2 prior to further TD-GC-MS analysis. This process was repeated 6 times for each of the modified and non-modified HiSorb probe to test the durability of each type of sorptive polymer. In the first run there were 6 replicates, however after each TD-cycle, one probe of each type was removed for qualitative analysis of the material.

2.2.2 Quantification of Encapsulated Amines

The PDMS HiSorb probes were weighed prior to the encapsulation of amines as described in Section 2.1.2. A control group was also included where the probes were left in 100% concentrated acetone solution (swelling agent). The materials were left for a defined period of time, prior to being removed from solution and dried under ambient conditions. The amine encapsulated PDMS and the control group samples were then re-weighed, and the mass difference calculated. This process was repeated across various encapsulation time lengths that ranged from 10 minutes to 7 days. The reason for this was to experiment at what time was the optimum concentration of amines encapsulated within each of the PDMS materials.

2.2.3 Fourier-Transform Infrared Spectroscopy (FTIR)

Fourier-transform infrared (FTIR) spectroscopy is an analytical technique used to identify various organic compounds at the surface of a material [120]. The FTIR applies a range of lights that vary in frequency to the surface of the material. The wavenumbers within the infrared spectrum that are absorbed by organic compounds at the surface of both the modified and non-modified PDMS samples indicates the bond characteristics present. The corresponding wavenumbers of light absorbed by the organic bonds was cross-referenced to literature to determine the type of bond [121].

A sample size of approximately 0.5cm x 0.5cm was cut from each of the modified and non-modified PDMS samples. Each sample was then clamped into position on to FTIR machine (Shimadzu IRAffinity-1S) and analysed. Each sample was then formatted into a graphical representation and material bond types characterised.

2.2.4 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) (1540X from Carl Zeiss, Germany) produced an image of each PDMS sample surface via scanning the surface with a focused beam of electrons [122]. Each modified and non-modified PDMS sample was cut into semi-cylindrical shapes to provide a flat, stable surface on the slide. Due to the non-conductive nature of the polymer, each surface was sprayed with a gold/platinum coating. Samples were then analysed by taking photos in 3 different areas of each sample. This was repeated across 3 different magnifications 500 x, 1000 x and 2000 x. All samples were analysed prior to extraction and TD-GC-MS analysis, as well as after each run thereafter (Runs 1-6). The purpose of applying this technique within the experimental was to provide a microscopic view of any physical or chemical changes to the surface compared to PDMS over time, such as cracking or blistering.

2.2.5 Contact Angle Measurements

Measuring the contact angle of droplets at the surface of modified and unmodified PDMS samples allowed for comparison in-terms of surface energies [123]. Surface energies have an impact on how the sorbent material interacts with the external environment [124]. Flat PDMS samples were used to encapsulate the amines as described in Sections 2.1.1 and 2.1.2. Whereas other modification techniques followed the protocols as described in Sections 2.1.3 and 2.1.4 but cured on a flat surface rather than in a tubular construct that was required for HiSorb extraction. Each sample had individual 5µL droplets of water, ethylene glycol and octan-1-ol placed at the surface. These 3 solvents were chosen due to their variety in polarity, with ethylene glycol being the most hydrophilic and octan-1-ol being the most hydrophobic [125]. Taking an up-close video and screenshots of the surface allowed for the measurements of the angles between each polymer surface and corresponding liquid (Figure 2.6). If contact angle θ of the water droplet is greater than 90° the surface is described as hydrophobic. If this value exceeds 150° then it is described a superhydrophobic. However, if the contact angle is less than 90° the surface is described as hydrophilic with superhydrophilicity being achieved lower than 5°.

Each liquid was placed at 3 different areas of each sample with 4 replicates of each, totalling 12 contact angle measurements per modified and non-modified sample. To measure the

surface energies of each material gave in-sight into how the surface of each material interacts with a range of hydrophilic and hydrophobic VOCs during the extraction process.
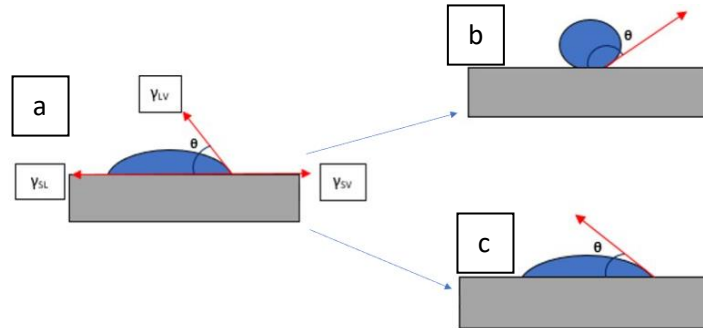
Figure 2.6: Character drawing that demonstrates (a) the various surface energy values: liquid/vapour γ_{LV}, solid/vapour γ_{SV}, solid/liquid γ_{SL}. In which angle θ between SL and LV determines the wettability of the surface (b) water droplet at hydrophobic surface (c) water droplet at hydrophilic surface.

Chapter 3: Amine Encapsulated PDMS Sorbent Materials

3.1   Abstract

The main limitation of Polydimethylsiloxane (PDMS) as a sorbent is the inability of the material to extract compounds of logP < 3 [126]. The first results chapter of this thesis explored how applying an encapsulated technique to PDMS enabled amines to be encapsulated within the matrix of the polymer sorbent. Each modified PDMS sorbent's ability to extract a range of organic compounds was compared to that of PDMS. It was found that encapsulating amines within the PDMS matrix influenced the uptake of organic compounds. The quantity of each organic compound extracted was independent to each amine modified sorbent. To deduce the extent of which the amines penetrated the PDMS matrix, various techniques including fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and contact angle (CA) measurements were conducted. The main limitation of this modification technique was the loss of amine concentration after each thermal desorption cycle. After several thermal desorption cycles the modification was reversed and each sample extracted the same quantity of organic compounds as that of PDMS.

3.2   Introduction

Polydimethylsiloxane (PDMS) is a widely used sorbent for the extraction of volatile and semi-volatile organic compounds (VOC and SVOC) due to characteristics such as sorbent capacity, chemical inertness and relatively cheap costs of production [127]. A further characteristic is the hydrophobic nature of these silicone polymers, with a partition coefficient (logP) value of 3[128]. The low surface energy of the polymer resists the wetting while maintain the extraction of VOCs for chemical analysis. There is extensive literature into increasing the surface energy of PDMS with the main techniques being plasma treatment[105], UV treatment [108], sol-gel coatings [129] and layer-by-layer depositions[130]. Applying such modification techniques to PDMS to improve the extraction and analysis of VOCs has drawbacks such as thermal instability, chemical fouling or includes a multi-step expensive procedure that could not be easily replicated on an industrial level. Instead of the above approaches, the development of a bulk modified PDMS sorbent for the analysis of VOCs could potentially offer prolonged modification properties with simple preparation. Modification of the bulk of PDMS has been a less explored approach to PDMS modification. What has been

reported was the presence of nanoparticles within the bulk of PDMS through an encapsulation technique, as detailed in Section 1.9.4 [86].

In this chapter, a technique modelled on this encapsulation technique was investigated. Whereby manipulating the ability of PDMS to swell in organic solvents was used to encapsulate 6 amines of various hydrophilicity, chemical structure and volatility. The effects embedded amines had on the ability of each material to extract trace levels of organic compounds was analysed and compared to unmodified PDMS. It was hypothesized that incorporating hydrophilic compounds into the matrix of the PDMS polymer material, there would be an improvement in the uptake of relative hydrophilic VOCs. The extraction efficiency and durability of the modification was tested using thermal desorption-gas chromatography mass spectrometry (TD-GC-MS) equipment (Section 2.2.1.3). Each material was analysed before and after each TD-GC-MS cycle through Fourier-Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope (SEM) and Contact Angle Measurements (Sections 2.2.3 – 2.2.5). Furthermore, the weighted quantity of each amine within piece of PDMS sorbent material was measured (Section 2.2.2).

3.3   Results

Results discuss the overall effect of encapsulating amines within PDMS had on the uptake of VOCs. The chosen method used to measure these uptakes was Thermal Desorption-Gas Chromatography-Mass Spectrometry (TD-GC-MS), in-which VOCs were measured through qualitative and quantitative design. Fourier-transform infrared (FTIR), Scanning Electron Microscopy (SEM) and Contact Angle measurements were taken as a means of characterising each modified and non-modified PDMS sample's surface. The data obtained from these characterising techniques was cross referenced with each other and the TD-GC-MS results. Results showed that the method of swelling PDMS in organic solvent does allow the incorporation of amines at both the surface and bulk of the polymer matrix, independent of polarity and chemical structure. This was best supported within the data that showed mass differences between PDMS and encapsulated PDMS samples in the uptake of the amines. Furthermore, the data demonstrated that the encapsulation of amines within the bulk of PDMS influenced VOC uptake with no modification to the surface of the material.

3.3.1 Thermal Desorption-Gas Chromatography-Mass Spectrometry

The results of the Thermal Desorption-Gas Chromatography-Mass Spectrometry (TD-GC-MS) analysis demonstrated that applying an encapsulation technique, where amines were incorporated into the polydimethylsiloxane (PDMS) polymer, influenced the extraction capabilities of the sorbent material. It was found that the chemical structure of the amine had a significant effect on the extraction of Volatile Organic Compounds (VOCs). This was best described in the results for the uptake of pyridine (Figure 3.1).
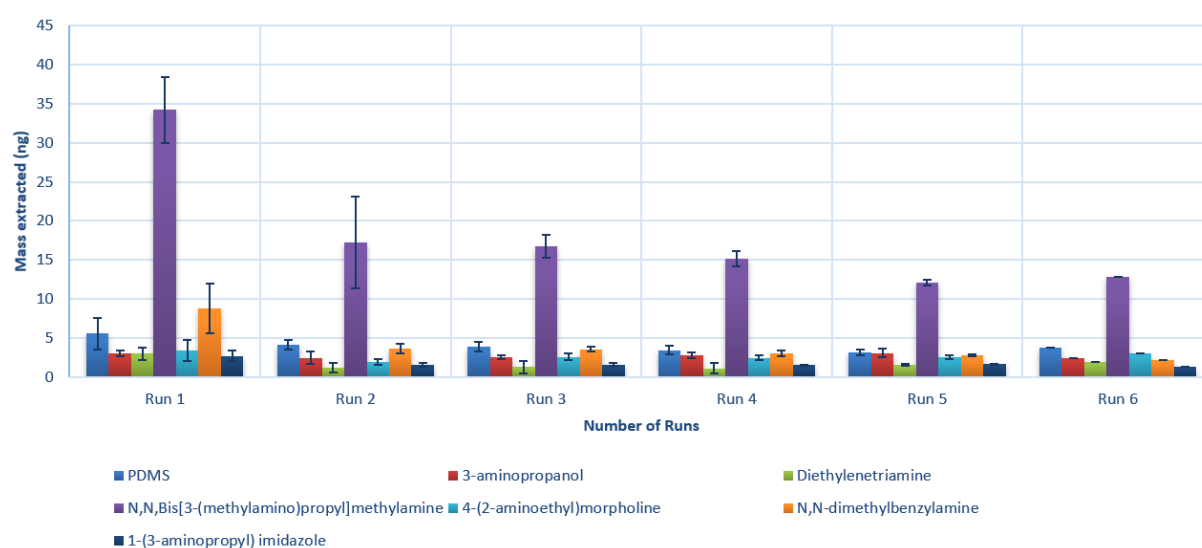

Figure 3.1: Graphical representation that measures the uptake of pyridine in PDMS compared to PDMS samples that underwent amine encapsulation.

In Run 1, N,N-Bis[3-(methylamino)propyl]methylamine encapsulated samples extracted 34 ng of pyridine on average, compared to PDMS which extracted 5.5 ng on average. The most noticeable result was the dramatic drop from 34 ng in Run 1 to an average of 17 ng in Run 2. From Run 2 through to Run 5, there was a less dramatic drop in quantity of pyridine extracted. Where it seems after Run 5 the drop seems to level off. However, after 6 extractions and thermal desorption cycles, the PDMS material that encapsulated N,N-Bis[3-(methylamino)propyl]methylamine maintained an extraction average of 12.5 ng of pyridine compared to PDMS which averaged 4 ng on Run 6.

The extraction of hexanal was another example of how encapsulating amines in PDMS improves uptake of VOCs. 4-(2-aminoethyl)morpholine encapsulated PDMS samples extracted an average of 55 ng of hexanal on Run 1 (Figure 3.2). Similarly to the extraction of pyridine, this quantity of hexanal extracted by the modified polymer material dropped between Runs 1-3, before steadying between Runs 4-6 at an extraction average of approximately 12 ng.
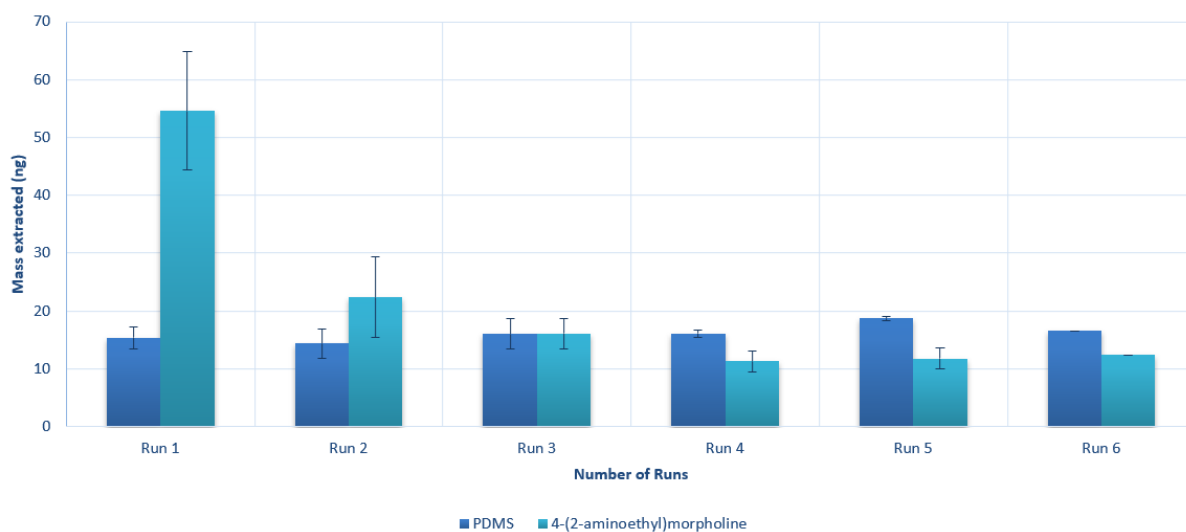
Figure 3.2: Comparison between PDMS and 4-(2-aminoethyl)morpholine encapsulated PDMS in the extraction of hexanal.

The TD-GC-MS results of this experiment highlighted not just improved extraction due to amine encapsulation, but also how encapsulating amines can have the opposite effect and reduce the uptake of each VOC compared to PDMS. The extraction of butanol best demonstrated how the type of amine encapsulated into the extraction efficiency of a VOC. In this case, it was found that encapsulating 3-aminopropanol in PDMS gave the largest uptake of butanol, while encapsulated diethylenetriamine failed to uptake any butanol until Run 3 (Figure 3.3).
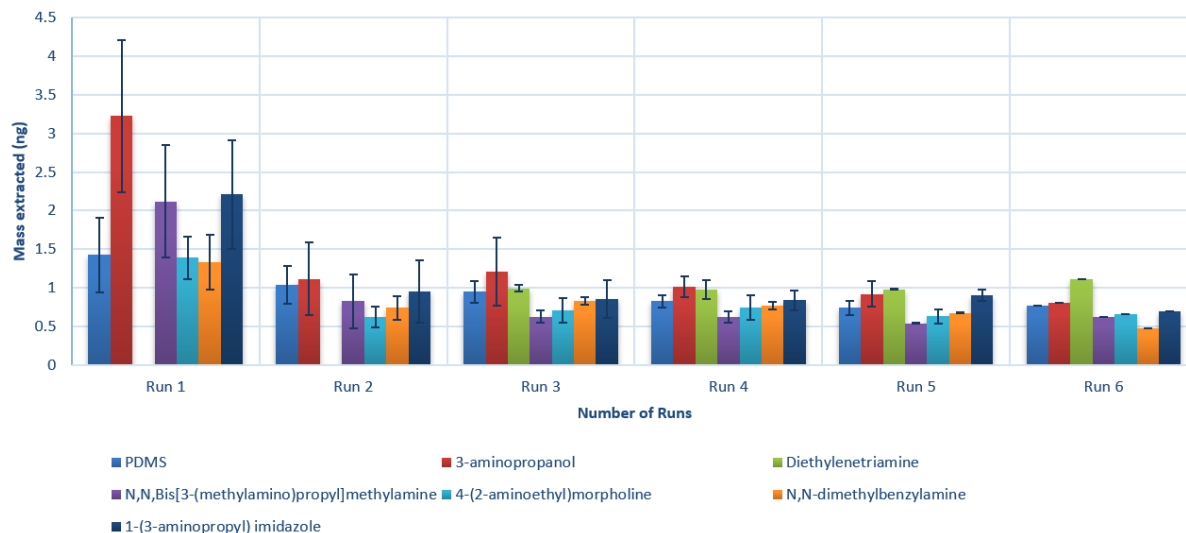
Figure 3.3: Graphical representation that measures the uptake of butanol in PDMS compared to PDMS samples that underwent amine encapsulation.

Interestingly, the 3-aminopropanol encapsulated PDMS shows similar extraction efficiency as that of PDMS after 1 Run. However, the diethylenetriamine encapsulated PDMS does not show any extraction of butanol until Run 3. Ethyl acetate and isobornyl methacrylate further demonstrated how varying the encapsulated amines within the PDMS reduced the uptake of VOCs.

Ethyl acetate uptake had the smallest number of samples which extracted the VOC. PDMS proved to be the greatest sample, with an average uptake of 3 ng in Run 1 (Figure 3.4). The only other sample to uptake any ethyl acetate in Run 1 was N,N-dimethylbenzylamine encapsulated PDMS which had an average uptake of 0.5 ng. 3-aminopropanol showed a slight uptake of ethyl acetate in Run 2, with N,N-dimethylbenzylamine showing an increase of ethyl acetate uptake by almost 2-fold. This increase towards a value to that of PDMS demonstrated the reversal of the modification. By Run 4, all samples showed an affinity for the extraction of ethyl acetate.
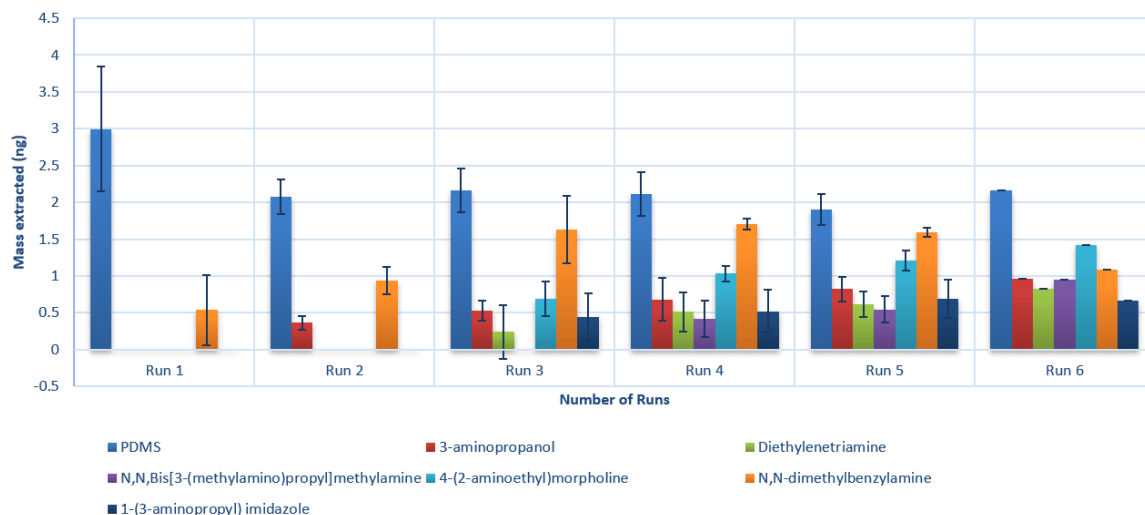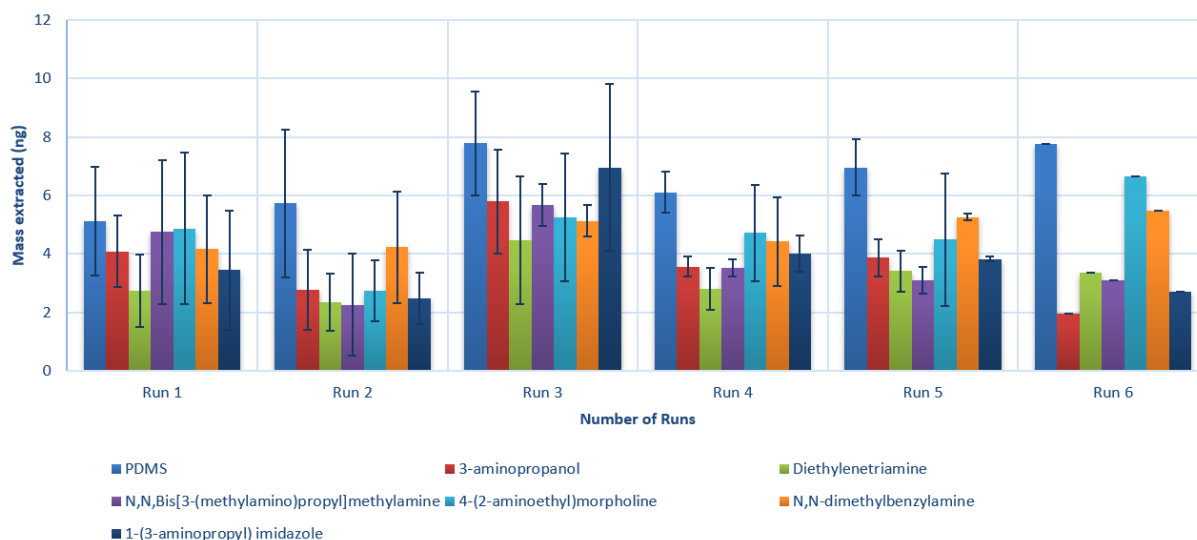
Figure 3.4: Graphical representation that measures the uptake of ethyl acetate in PDMS compared to PDMS samples that underwent amine encapsulation.

In the extraction of isobornyl methacrylate, all amine encapsulated samples extracted the VOC except 1-(3-aminopropyl)imidazole (Figure 3.5). Run 4 was the first time isobornyl methacrylate was extracted by the PDMS with 1-(3-aminopropyl)imidazole encapsulated. However, not all samples which had 1-(3-aminopropyl)imidazole encapsulated in Run 4 did extract this VOC, explaining the large standard deviation. Samples with amines 3-aminopropanol, diethylenetriamine and N,N-Bis[3-(methylamino)propyl]methylamine encapsulated showed little change in extraction efficiency across all 6 runs. This data showed that over 6 TD cycles, any change to the degree of modification to each of these samples did not influence the extraction of isobornyl methacrylate.

Not all VOCs extracted from the extraction mixture were affected by the amine encapsulation modification technique. The extraction of cyclohexane was an example of how encapsulating amines had no effect on the extraction efficiency (Figure 3.6).
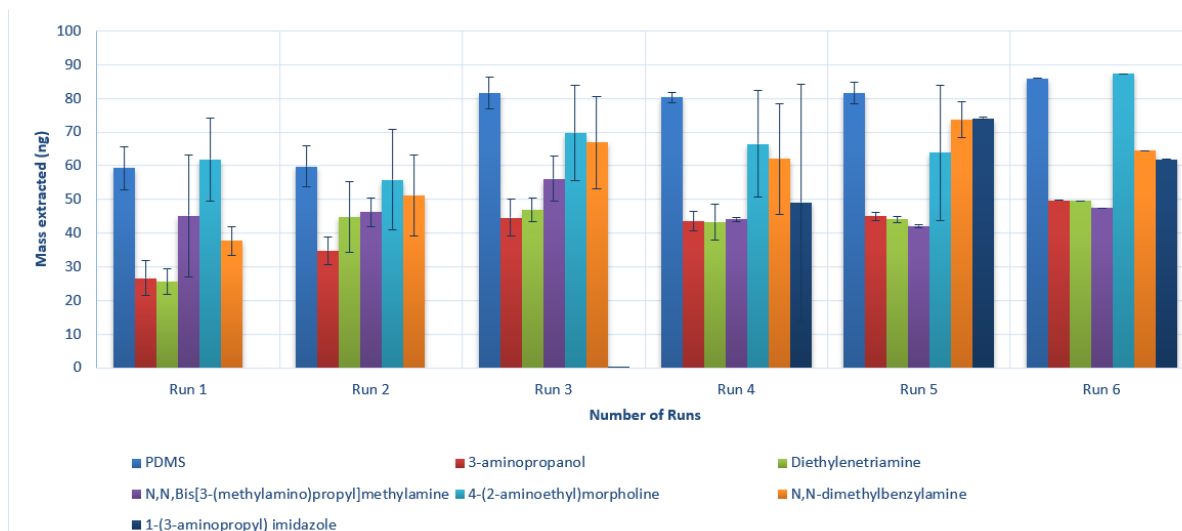
Figure 3.5: Graphical representation that measures the uptake of isobornyl methacrylate in PDMS compared to PDMS samples that underwent amine encapsulation.

Figure 3.6: Graphical representation that measures the uptake of cyclohexane in PDMS compared to PDMS samples that underwent amine encapsulation.

To conclude, the TD-GC-MS data showed that encapsulating amines in PDMS did influence organic compound extraction from aqueous matrices. It was hypothesised prior to the analysis that incorporating amines, which have polar characteristics, would improve the sorbent materials ability to attract and extract the polar organic compounds in the mixture.

This was however shown to be incorrect, in which there was no correlation between polarity of amine encapsulated and polarity of organic analyte.

3.3.2 Fourier-Transform Infrared Spectroscopy

Fourier-transform infrared spectroscopy (FTIR) data for PDMS displayed 4 significant bond characterisations that represent the 4 bonds which make up the PDMS monomer (Table 3.1). These 4 bond characterisations coincide with the literature (Table 3.2). When plotted graphically, the 4 bonds are shown by a drop in transmittance as the bonds absorb the light of discrete wavelengths (Figure 3.7).
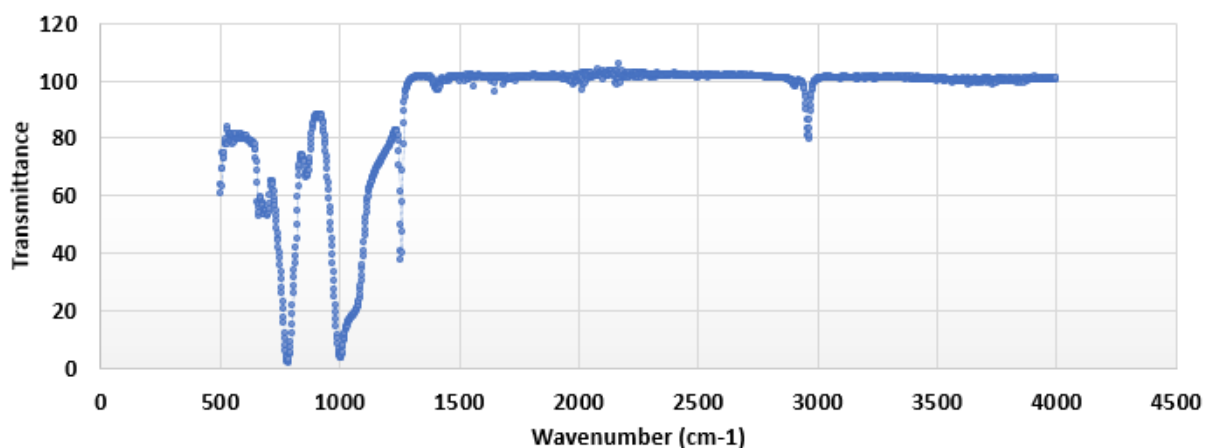
Figure 3.7: Graphical demonstration of FTIR data for PDMS that shows how the transmittance of the IR light changes as wavenumber increases.

Table 3.1: PDMS FTIR peaks with corresponding bond characterisations.

Wavenumber (cm^{-1})	Bond Characterisation
785	CH$_3$ rocking and Si-C stretching in Si-CH$_3$
1005	Si-O-Si stretching
1257	CH$_3$ deformation in Si-CH$_3$
2963	Asymmetric CH$_3$ stretching in Si-CH$_3$

Table 3.2: PDMS FTIR peaks from literature [131].

Wavenumber (cm^{-1})	Bond Characterisation
789 – 796	CH$_3$ rocking and Si-C stretching in Si-CH$_3$
1020 – 1074	Si-O-Si stretching
1260 – 1269	CH$_3$ deformation in Si-CH$_3$
2950 – 2960	Asymmetric CH$_3$ stretching in Si-CH$_3$

Superimposing the data from the amine encapsulated PDMS samples on top of unmodified PDMS samples, it was found that there was a difference in chemical composition at the surface of the material (Figure 3.8). This was best demonstrated when comparing PDMS samples that underwent encapsulation of 1-(3-aminopropyl)imidazole to that of PDMS. The data showed additional peaks, indicating the presence of the amine at the surface of the material (Figure 3.8). The 5 additional peaks found within the FTIR spectra of the 1-(3-aminoproyl)imidazole were each characterised and associated with bonds in found in 1-(3-aminopropyl)imidazole including C-C bonds in ring formation and N-H bond (Table 3.3).
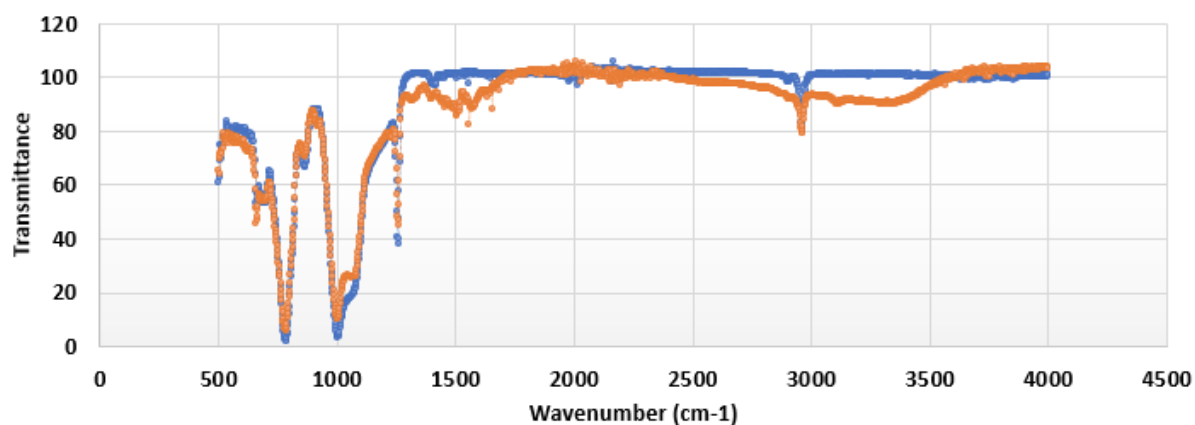

*Figure 3.8:* Comparison of PDMS (blue) and PDMS with encapsulated 1-(3-aminopropyl)imidazole (orange) FTIR data.

Table 3.3: PDMS with encapsulated 1-(3-aminopropyl)imidazole FTIR peaks with corresponding bond characterisations [132].

Wavenumber (cm^{-1})	Bond Characterisation
785	CH$_3$ rocking and Si-C stretching in Si-CH$_3$
1005	Si-O-Si stretching
1257	CH$_3$ deformation in Si-CH$_3$
1370	C-H rock
1506	C-C stretch (in-ring)
1570	C-C stretch (in-ring)
2963	Asymmetric CH$_3$ stretching in Si-CH$_3$
3113	C-H stretch
3298	N-H stretch

Comparing FTIR spectra of 3-aminopropanol encapsulated PDMS before and after the first TD cycle showed the loss of the broad peak at 3207cm^{-1} which corresponded to an N-H bond (Figure 3.9a). The FTIR spectra for 3-aminopropanol after the first TD cycle was complimentary to unmodified PDMS (Figure 3.9b). This indicated that 3-aminopropanol was present at or just below the surface of the material after the encapsulation process however after the first thermal desorption cycle, the amine was lost. The same trend was apparent with diethylenetriamine, 4-(2-aminoethyl)morpholine and 1-(3-aminopropyl)imidazole. Where prior to any TD cycles, the peaks which represented the various bond characteristics corresponding to the encapsulated amine were present, however after the first thermal desorption cycle these peaks were lost from the chromatogram. The FTIR data for samples which were encapsulated with N,N-Bis[3-(methylamino)propyl]methylamine and N,N-dimethylbenzylamine showed no difference in FTIR peaks compared to that of unmodified PDMS. This indicated that none, or a very low concentration of these amines were present at the surface of the PDMS material after encapsulation.
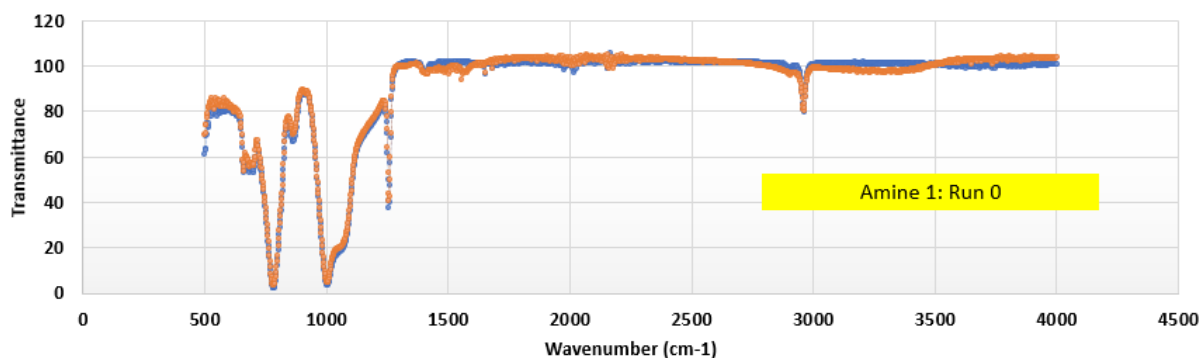
Figure 3.9: (a) Showed the difference in FTIR peaks of PDMS (blue) and 3-aminopropan-1-ol (orange) before the first TD-GC-MS cycle.
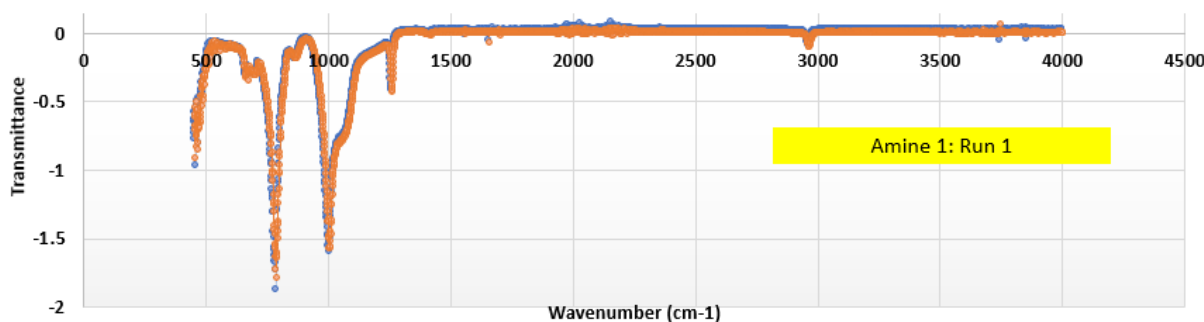
Figure 3.9: (b) Showed the difference in FTIR peaks of PDMS (blue) and 3-aminopropan-1-ol (orange) after the first TD-GC-MS cycle.

To summarise, the FTIR data showed that after the encapsulation method that amines were present at the surface of the PDMS material. However, after the first thermal desorption cycle each modified material showed no difference in surface chemical profile compared to that of unmodified PDMS. It was however assumed that amines were still located within the PDMS material after the first thermal desorption cycle due to varying extraction performance in the TD-GC-MS data compared to that of the PDMS (Section 3.3.1).

3.3.3 Scanning Electron Microscopy

Scanning electron microscopy (SEM) images were taken to deduce if there was any physical damage such as cracking or blistering to the PDMS or amine encapsulated PDMS samples after several thermal desorption cycles (Section 2.2.4). It was an important test as any physical damage to the surface of the polymer could affect extraction performance or contribute to large background peaks on the chromatogram.

The PDMS samples showed a smooth, flawless surface prior to any thermal desorption exposure (Figure 3.10a). However, after being heated via thermal desorption the surface showed significant cracking and blistering at the surface (Figure 3.10b).
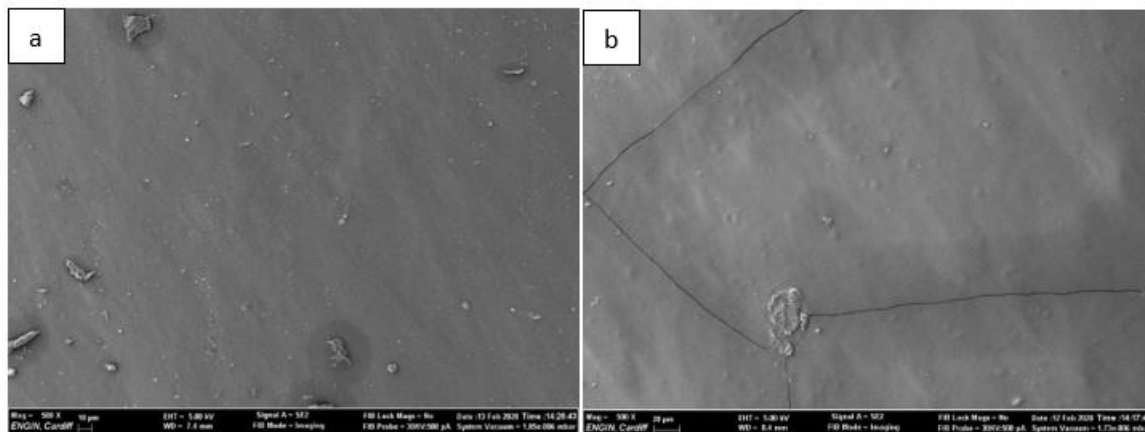

Figure 3.10: (a) SEM image of PDMS surface prior to TD-GC-MS exposure. (b) After exposure to TD-GC-MS in which there is a clear network of cracking and blistering.

SEM images recorded physical differences in the surfaces of 3-aminopropan-1-ol, diethylenetriamine, N,N-Bis[3-methylamino)propyl]methylamine and 1-(3-aminopropyl)imidazole encapsulated PDMS samples compared to PDMS after the encapsulation process (Figure 3.11). This change in the physical appearance was particularly present in N,N-Bis[3-methylamino)propyl]methylamine encapsulation where SEM images showed a blistering effect at the surface (Figure 3.11c). Whereas the other materials showed a mixture of blistering and amine droplets at the surface. However, over the several thermal desorption cycles each material was exposed to, the blistering at the surface was removed leaving a smooth surface (Figure 3.12). This contrasted with the cracked PDMS material that did not undergo any encapsulation modification (Figure 3.10). An explanation as to why the material surface physically changed after thermal desorption was degradation of the polymer under the heat of the thermal desorption machine. During each cycle a small layer of PDMS will be removed.
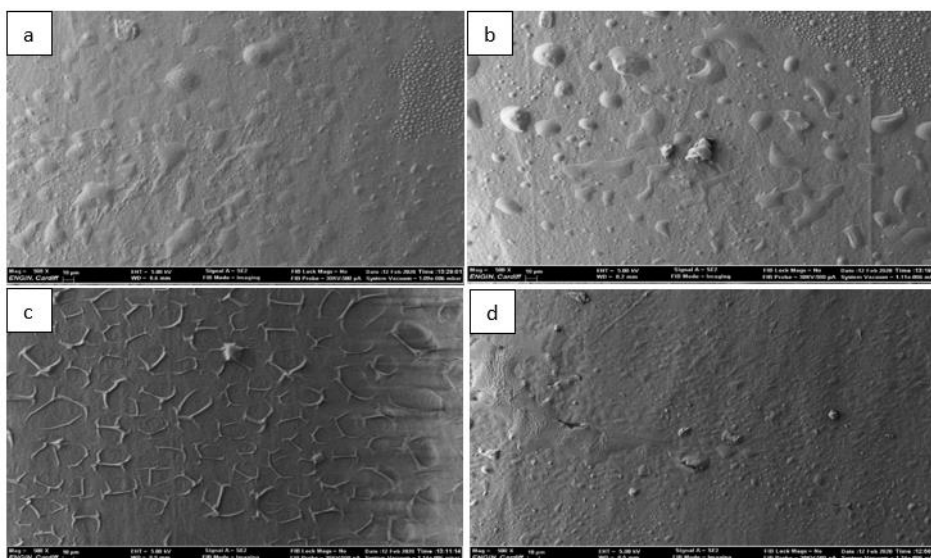
Figure 3.11: Surface of each amine encapsulated PDMS material after the encapsulation modification process prior to TD-GC-MS where (a) 3-aminopropan-1-ol (b)diethylenetriamine (c) N,N-Bis[3-methylamino)propyl]methylamine (d) 1-(3-aminopropyl)imidazole.
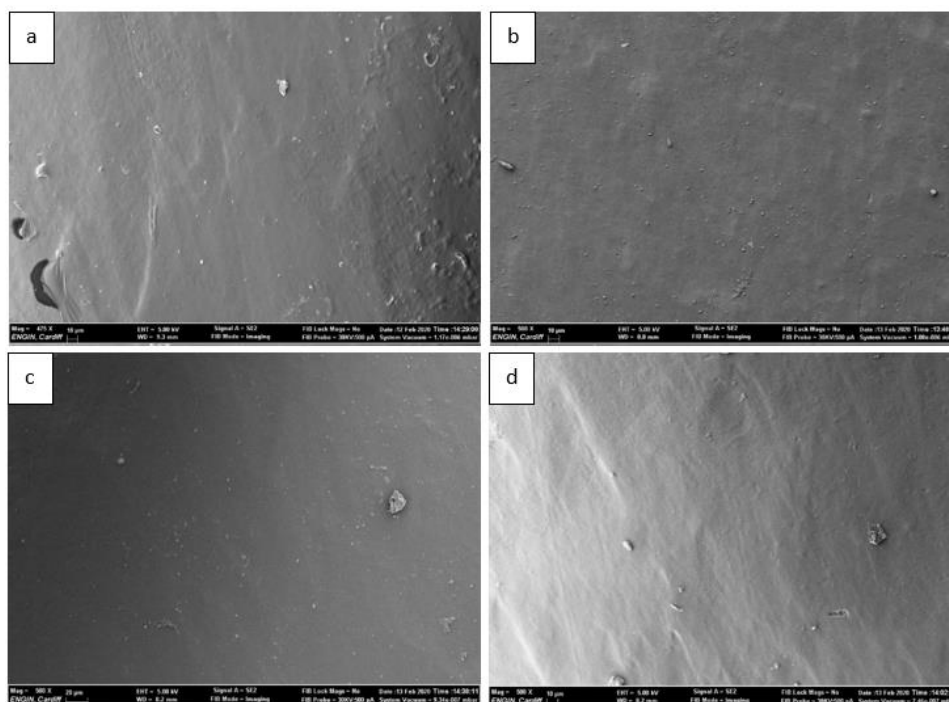
Figure 3.12: Encapsulated PDMS samples after TD-GC-MS (a) 3-aminopropan-1-ol (b)diethylenetriamine (c) N,N-Bis[3-methylamino)propyl]methylamine (d) 1-(3-aminopropyl)imidazole.

3.3.4 Contact Angle Measurements

The contact angles of deionised water, ethylene glycol and octan-1-ol droplets at the surface of each modified and non-modified PDMS material samples were measured as per the methodology set out in Section 2.2.5. For PDMS, the water droplets generated the largest average contact angles with an average angle of 110.2° recorded (Table 3.4). This repulsion of water at the surface indicated that the surface energy is low and therefore hydrophobic. In contrast to this, each of the modified PDMS samples had an average water contact angle lower than that of PDMS with values that ranged between 42.2° to 98.2°. This indicated that encapsulating amines in PDMS increased the surface energy of the material inducing a more hydrophilic material compared to the unmodified PDMS. Octan-1-ol was the least polar solvent used and the average contact angles supported the data from the water droplets. The results for PDMS showed the lowest average contact angle with a value of 45.1° with each of the modified materials having a larger average contact angle. Within this experiment there was a larger standard deviation on the octan-1-ol measurements due to the liquid being absorbed into the PDMS over time. Due to this adsorption, measuring the droplet was a lot more difficult and therefore lead to greater deviation in the results.

Table 3.4: Average calculated contact angle measurements for water, ethylene glycol and octan-1-ol droplets at the surface of both modified and unmodified PDMS samples.

Solvent	PDMS	Amine 1[a]	Amine 2[b]	Amine 3[c]	Amine 4[d]	Amine 5[e]	Amine 6[f]
Water	110.2 ± 0.6	76.3 ± 0.4	46.9 ± 0.2	42.2 ± 0.2	43.1 ± 0.4	98.2 ± 0.3	61.7 ± 0.3
Ethylene Glycol	105.1 ± 0.5	65.3 ± 0.4	62.5 ± 0.3	45.4 ± 0.2	57.2 ± 0.1	93.1 ± 0.7	68.9 ± 0.6
Octan-1-ol	45.1 ± 1.5	55.2 ± 2.0	55.3 ± 1.3	57.1 ± 1.5	52.2 ± 0.8	50.7 ± 0.9	52.5 ± 1.1

Note: a. 3-aminopropan-1-ol, b. Diethylenetriamine, c. N,N-Bis[3-(methylamino)propyl]methylamine, d. 4-(2-aminoethyl)morpholine, e. N,N-dimethylbenzylamine, f. 1-(3-aminopropyl)imidazole.

The method of encapsulating amines increased the surface energy of the material as represented in the lower contact angle values for the water droplets. The increased surface energy was due to the presence of the amines at the surface of the material with N,N-Bis[3-(methylamino)propyl]methylamine demonstrating the greatest surface energy and N,N-dimethylbenzylamine showing the lowest change in surface energy compared to the unmodified PDMS. Results were not obtained for samples that had undergone to thermal desorption or VOC extraction due to the tubular shape of the PDMS material. In-order to accurately measure the surface contact angles of liquids at a surface, the surface must be flat.

3.3.5 Quantification of Encapsulated Amines

The quantity of amines retained by PDMS through encapsulation was investigated via mass measurements. Furthermore, a control group of PDMS in the swelling agent (acetone) was also recorded (Section 2.2.2). Results showed a decrease in the mass of PDMS when left in acetone over time (Figure 3.14). This result was explained by the loss of impurities that could have been picked up by the material during manufacturing or manual handling. Alternatively, this mass loss could account for the removal of any unreacted PDMS monomer units contained within the PDMS prior to the experiment. Swelling the PDMS in acetone, allowed for the removal of these impurities into the solution. Assuming each 11 mm piece of PDMS tubing contained the same quantity of impurities, the graph can be adjusted to take the impurities into consideration (Figure 3.15). The amended graph demonstrated that each of the PDMS samples that underwent amine encapsulation presented with an increase in mass. When the PDMS samples were exposed to longer encapsulation times, the data showed an increase in the uptake of amines. This increased uptake was continuous until 6 hours where the maximum uptake of amines was recorded. This uptake then reduced between 6 and 24 hours before levelling out. Of the amines that were encapsulated in PDMS, N,N-Bis[3-(methylamino)propyl]methylamine was the most readily encapsulated with an average of 4.1 mg of amine recorded after 6 hours. However, after 7 days of encapsulation all encapsulated PDMS samples showed similar quantity of uptake with values ranging from 1.2 mg to 1.9 mg.
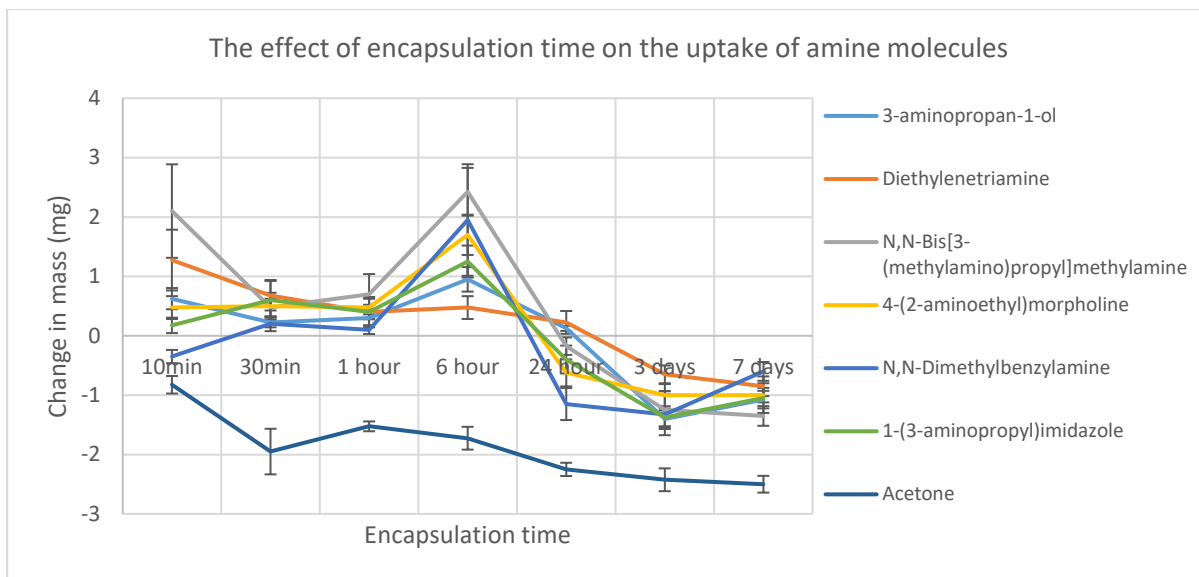
Figure 3.14: A graphical representation of the uptake of each amine by PDMS via an encapsulation technique.
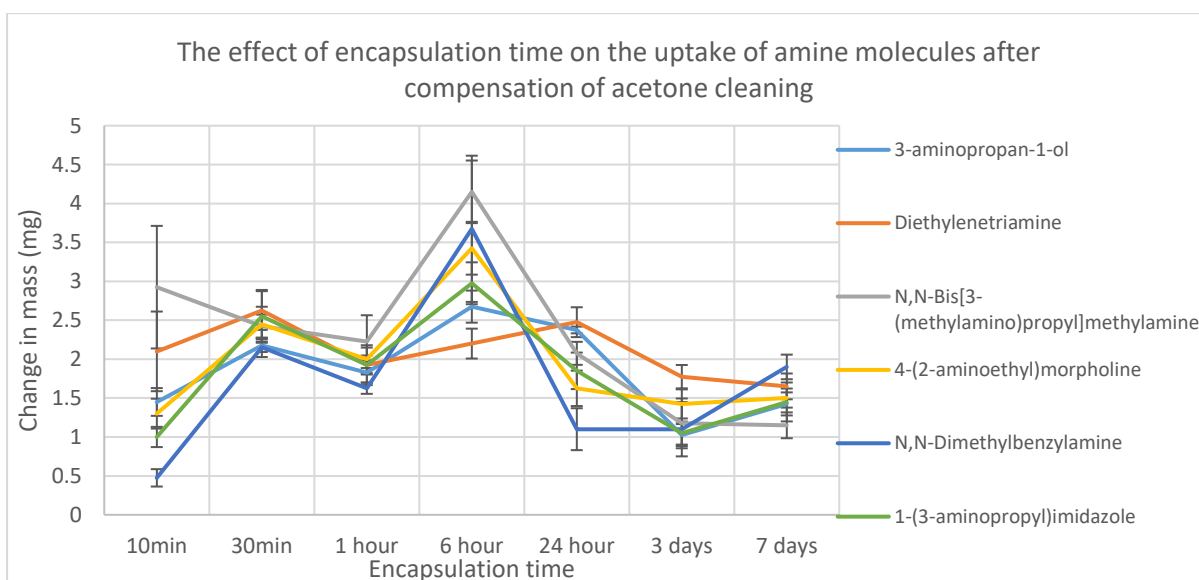
Figure 3.15: A graphical representation of the uptake of each amine by PDMS via an encapsulation technique after taking impurities into consideration.

3.4   Discussion

The results within this chapter evaluated the effectiveness of an encapsulation modification technique on the extraction of VOCs of varying polarity and chemical structure. The TD-GC-MS data showed that encapsulating amines within the bulk of the PDMS did influence VOC extraction. Prior to these results, it was known that PDMS sufficiently extracted VOCs with a logP > 3 [127]. Therefore, it was hypothesized that the modified PDMS samples would extract larger quantities of VOCs with a logP < 3 due to the incorporation of the polar amine within the bulk of the PDMS material. This was best demonstrated in the extraction of the most polar VOC, pyridine. Within the TD-GC-MS results for the extraction of pyridine, significant (P value < 0.05) quantities of the VOC were extracted by N,N-Bis[3-(methylamino)propyl]methylamine encapsulated PDMS material compared to unmodified PDMS samples (Figure 3.1). With the introduction of polar amines within the polymer it was expected that each modified material would uptake greater amounts of pyridine compared to PDMS. The results however, showed that the other 5 amine encapsulated PDMS samples exhibited no increased uptake of pyridine compared to PDMS. In-fact, N,N-Bis[3-(methylamino)propyl]methylamine was ranked as the fourth most polar amine and extracted more of the highly polar pyridine compared to the PDMS encapsulated sorbents that contained amines which were more polar. This led to the assumption that addition of polar amine compounds to PDMS did not always increase the uptake of polar analytes. This was further demonstrated in the uptake of ethyl acetate, the second most polar analyte in the extraction mixture. Where the extraction data verified that five of the six encapsulated PDMS polymers did not extract any ethyl acetate with PDMS extracting the most of any sample (Figure 3.4).

This evaluation of the TD-GC-MS data suggested that the polarity of the amine encapsulated within the PDMS did not necessarily influence the uptake of polar analytes, as first hypothesized. Therefore, understanding this left the scientific question to "what does influence the extraction of VOCs when using encapsulated sorbent materials?"

There were very few variables to consider during the experimental. The only difference between the encapsulated samples to that of PDMS would be the presence of amines. The group of amines were selected on their relatively high boiling points, polarity and small molecular size (Table 2.1). However, each amine differentiated in polarity and chemical structure. One theory as to why each amine encapsulated PDMS sample extracted at various

quantities was due to the unique chemical structure of each amine, as this was the main differential between each sorbent. When understanding how extraction works there are two types of interaction to consider, intermolecular and intramolecular bonding. Intramolecular bonding is described as the forces that hold the atoms together such as covalent bonds [133]. While intermolecular bonding describes how different molecules interact with each other, such as hydrogen bonding [134]. The outcome for this series of experiments was to extract organic compounds from an aqueous solution into the PDMS-based sorbent via various intermolecular bonds such as hydrogen bonding or electrostatic interactions [99]. It was hypothesized that the individual chemical structure of each amine determined which intermolecular bonds were formed through the extraction process and in-turn how well the encapsulated material performed in extracting VOCs. The TD-GC-MS results best supported this theory, particularly in the case of pyridine extraction.

N,N-Bis[3-(methylamino)propyl]methylamine encapsulated PDMS samples had the largest average extraction of pyridine compared to PDMS or any other modified sample (Figure 3.1). When looking at the structure of the encapsulated amine to that of the pyridine, it could be assumed that the intermolecular bonding responsible for the uptake would be the formation of a hydrogen bond between the lone pair of electrons on the nitrogen of pyridine and the hydrogens of either the amine or methyl functional groups on the N,N-Bis[3-(methylamino)propyl]methylamine (Figures 3.16a and 3.16b). Structurally, it was hypothesized that the methyl groups play a larger part in the intermolecular bonding. As when comparing to the diethylenetriamine structure which when encapsulated showed much less uptake values for pyridine, N,N-Bis[3-(methylamino)propyl]methylamine contained an extra CH_2 group at either end of the backbone as well as a methyl group replacing the hydrogen at the nitrogen in the middle of the backbone (Figures 3.16b and 3.16c). Therefore, concluding that an additional hydrogen on present on the N,N—Bis[3-(methylamino)propyl]methylamine greatly influenced the uptake of the pyridine VOC. Furthermore, the presence of methyl groups in replace of hydrogen may have provided more shielding from the lone pair of electrons on each of the nitrogen within the structure.
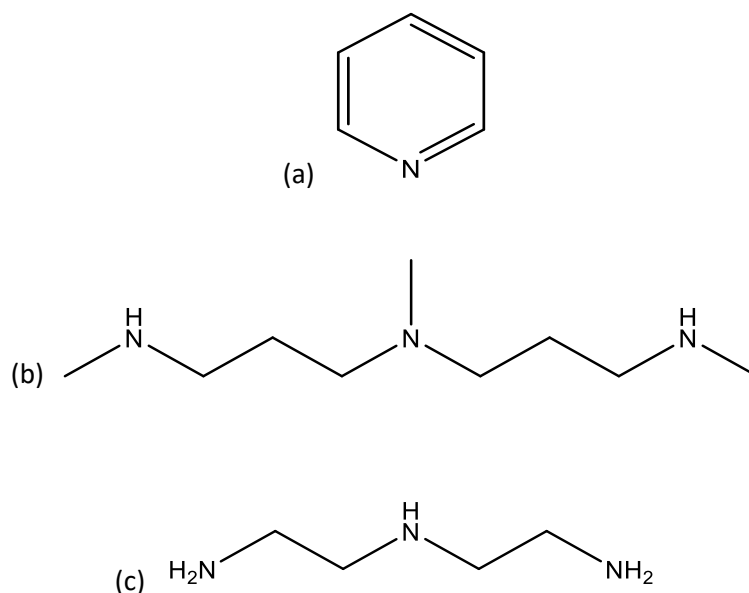
Figure 3.16: Structures of (a) Pyridine and (b) N,N-Bis[3-(methylamino)propyl]methylamine (c) Diethylenetriamine

It was expected that hexanal would be readily extracted by the amine encapsulated PDMS samples. However, the data showed that PDMS samples when encapsulated with amines showed little uptake of hexanal. This could be explained by insufficient intermolecular interactions between the amines and hexanal, but another possibility was that the amines may have reacted with the aldehyde. Amines are a reactive species of molecule, and this could be the cause of why few modified PDMS samples extracted the aldehyde, hexanal (Figure 3.17).
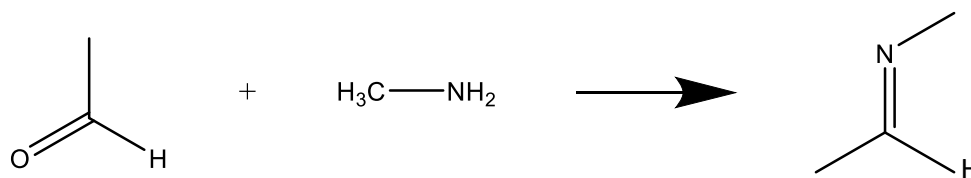
Figure 3.17: Possible reaction of primary amine with aldehyde forming an imine [136].

Further to the reactive nature of amines and this interference with VOCs in the extraction media, there were several other limitations to the encapsulation process as a method for new

sorbent materials. One such limitation within the encapsulation process was the drop in extraction performance over several thermal desorption cycles. The thermal desorption temperature was set at 160°C as this temperature was below that of any amine's boiling point and above that of the boiling point of all VOCs used in the extraction mixture (Tables 2.5 and 2.6). The set temperature intended to minimise the loss of amines during each thermal desorption cycle. Unfortunately, as all amines used were liquid and possessed a degree of volatility. Heating the encapsulated probes to 160°C led to some of the amines desorbing from the PDMS, particularly at the surface, alongside the VOCs during each thermal desorption cycle. This reduced concentration of amines within the PDMS encapsulated PDMS samples after each thermal desorption cycle led to the change in extraction efficiency. Over the 6 runs, the extraction performance of each modified sample shifted towards the extraction efficiency of PDMS. The rate at which this change took place was dependent on which VOC was being extracted. Some samples demonstrated similar extraction capabilities to PDMS after very few desorption cycles, while others did not completely revert to that of PDMS after 6 runs. It would however be expected that if more than 6 thermal desorption runs were carried out on the same sample, that eventually the modified PDMS samples would have the same extraction performance of PDMS. Simply explained, the thermal desorption process would reverse the modification.

FTIR and SEM data which showed that amines were present at the surface of the material before the first thermal desorption cycle. After this thermal desorption cycle the FTIR data showed no amines present and SEM images showed no physical difference between that of the modified samples and PDMS. This did not imply that all amines were lost during the first thermal desorption step as the extraction data from Runs 2-6 show there was still a difference in uptake between the encapsulated samples compared to PDMS. Therefore, it can be assumed that for Runs 2-6, amines located within the bulk of the PDMS were not lost through the first thermal desorption cycle and were responsible for any differentials within the extraction data compared to PDMS.

This was well demonstrated through the FTIR data for of N,N-Bis[3-(methylamino)propyl]methylamine and N,N-dimethylbenzylamine. Where after the encapsulation process showed no chemical differences to that of PDMS, indicating no amines present at the surface. The TD-GC-MS data concluded however that amines were

encapsulated within the bulk to the polymer sorbent. Where the data showed that both materials extract VOCs at differing quantities to PDMS due to the presence of amines within the bulk. Much literature on sorbent materials in relation to extraction of VOCs focus on surface chemistry modification [97], [99], [111], [130], [137]. This data however presents a strong argument to that of the literature, in that modifying the bulk of PDMS does impact the extraction capabilities of the polymer.

Another limitation of swelling PDMS in acetone to incorporate amines within the bulk of the polymer is that the quantity of amine encapsulated will differ slightly from sample to sample. This was carried out experimentally where the quantity of amine was measured through mass. The results showed that there were slight mass differences between samples and this difference may have had an impact on the VOC extraction. A possible solution for this would be generate the polymer from raw materials. PDMS is a "honey-like" liquid prior to polymerisation. To add discrete volumes of each amine to the PDMS liquid prior to polymerisation would allow known and repeatable quantities from sample to sample.

Another key issue with encapsulation as a modification technique to improve the extraction capabilities of PDMS towards VOCs was the background on the gas chromatogram. Due to the thermal instability of the amines within the polymer, large quantities of amines were passed through the GC column and detected on the mass spectrometer detector. This left large peaks covering the whole chromatogram, making it difficult to see the peaks associated with the extraction VOCs (Figure 3.18). Fortunately, the software allowed for the extraction of peaks with particular M/Z values, allowing for the detection of VOCs behind the amine peak.
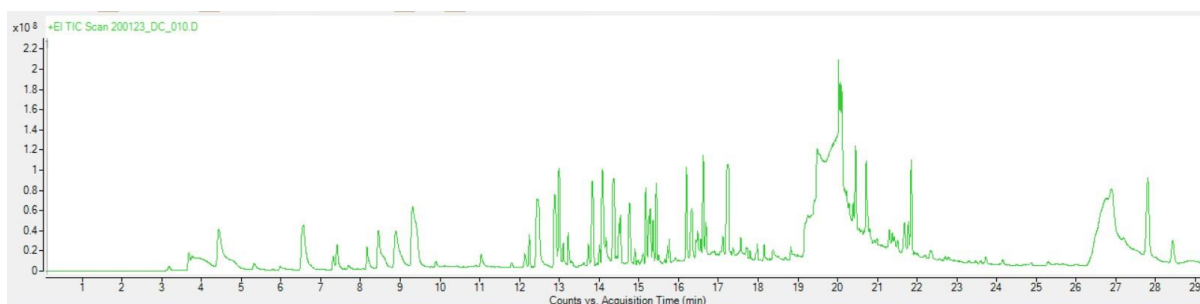
Figure 3.18: Gas chromatogram that demonstrates the background peaks of amine encapsulated PDMS samples.

3.5 Conclusion

- Method of encapsulating amines within PDMS was achieved.

- Encapsulating amines did influence the type and quantity of organic compounds extracted from the aqueous mixture.

- Study found that modification to the bulk of PDMS influenced extraction performance.

- The main issue with this modification technique was the thermal instability of the modification.

- **Issues to address:** reproducibility in extraction quantity over several runs and to reduce the background given off by the modified samples on the chromatogram

- **Next Step:** Covalently bond amines to PDMS monomer chains to improve the thermal stability of the modification and compare to PDMS through TD-GC-MS and qualitative techniques.

# Chapter 4: Epoxy-Terminated PDMS with Amine Crosslinking

4.1 Abstract

The results in this chapter explore whether covalently bonding amines to the PDMS monomer units would demonstrate the same organic compound extraction as demonstrated in the previous chapter but with improved thermal stability and repeatability. Two of the six amines were successfully synthesized with PDMS and used for the extraction of organic compounds as described in Table 2.5. Each of the amines when crosslinked with PDMS demonstrated varying extraction capabilities when compared to each other and the currently used PDMS material, as displayed through TD-GC-MS. Furthermore, the newly modified materials showed improved thermal stability with excellent reproducibility from run to run and a reduced background to that of the encapsulated modified samples.

4.2 Introduction

The results demonstrated in Chapter 3 showed how polydimethylsiloxane (PDMS) sorbent tubing can be modified to extract more polar volatile organic compounds (VOCs) via an encapsulation technique. 6 amines that varied in structure, volatility and polarity were individually encapsulated into PDMS sorbent tubing (Table 2.1). From this, the results showed that encapsulating amines within the matrix of the PDMS sorbent tubing increased the uptake of polar VOCs while maintaining the uptake of non-polar VOCs. Furthermore, it was found that the structure of the amine encapsulated within the PDMS sorbent's polymer matrix influenced the quantity of each VOC extracted from the extraction mixture. This was described as a structure/extraction relationship, best described by the extraction of pyridine with N,N-Bis[3-(methylamino)propyl]methylamine encapsulated PDMS (Section 3.4). The main limitation of the encapsulation method as a modification technique was the material's thermal instability throughout the thermal desorption cycle. As the sorbent underwent several extractions followed by thermal desorption cycles, the modification slowly reversed. The decrease in amine concentration within the PDMS material from the thermal desorption step led to a continual drop extraction of VOCs (Figures 3.1 – 3.6).

It has been reported in the literature that amines can covalently bond to PDMS at low curing temperatures to generate gel-based networks [103]. The methodology demonstrated how primary amines can be used to crosslink with epoxy-terminated PDMS monomers via covalent

bonds to generate a new PDMS polymer network (Scheme 4.1). Amine compounds are vastly researched for their epoxy curing capabilities due to the formation of resins with high thermal and chemical resistant properties [139]. The mechanism behind the curing process occurs via a nucleophilic attack. This involves the lone pair of electrons on the nitrogen of the amine attacking the terminal carbon of the epoxy-terminated PDMS monomer, generating an intermediate species with a delocalised area of electrons. This temporarily generates a positive charge on the nitrogen group and a negative charge at the oxygen on the epoxy. As such, the hydrogen of the amine relocates to form a new hydroxy group and stabilizing the nitrogen functionality in a term called proton transfer. This S_N2 type reaction mechanism demonstrates how a single primary amine can directly bond with two different epoxy-terminated PDMS monomers while secondary amines can react just once (Scheme 4.1) [140].
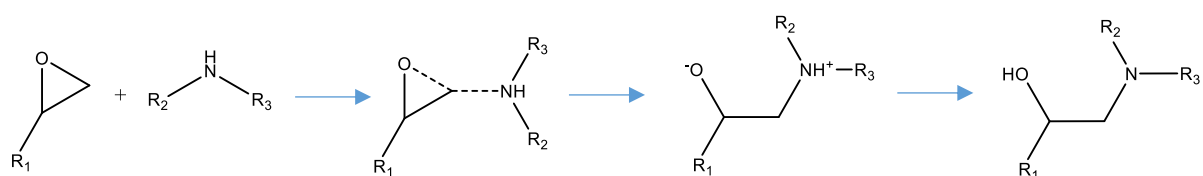

Scheme 4.1: S_N2 mechanism for a secondary amine/epoxy curing. Where the first step is assumed to be the rate determining step (rds) as the rate of proton transfer is greater than that of nucleophilic attack [140].

This chapter investigated whether covalently bonding amines to epoxy-terminated PDMS monomers produced thermally stable sorbent materials (Section 2.1.3). Where each material's extraction capability towards organic compounds was analysed via thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS) (Section 2.2.1.3). These results were compared to that of the currently used PDMS sorbent tubing as the control group. Characterisation of the surface chemistry was performed via Fourier-transform infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) after each thermal desorption cycle with Contact Angle Measurements taken to determine surface energies (Sections 2.2.3 – 2.2.5).

4.3   Results

### 4.3.1 Thermal Desorption-Gas Chromatography-Mass Spectrometry

The method of covalently bonding amines to epoxy-terminated PDMS as polymer crosslinkers had previously been established within the literature [138]. However, there were no reports of their sorptive extraction properties within the literature. It was therefore decided that the best method of measuring the epoxy-terminated PDMS would be through thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS). The results of the TD-GC-MS data showed that the epoxy-terminated PDMS materials had sorptive extraction characteristics towards VOCs of various functionality and polarity when crosslinked with each of the two types of amines, N,N-Bis[3-(methylamino)propyl]methylamine and diethylenetriamine.   With the amine crosslinkers within the PDMS mixture, it was hypothesized that this would encourage the uptake of more polar (LogP <3) VOCs compared to that of the platinum cured PDMS material. This was clearly demonstrated when looking at the extraction of butanol (Figure 4.1)
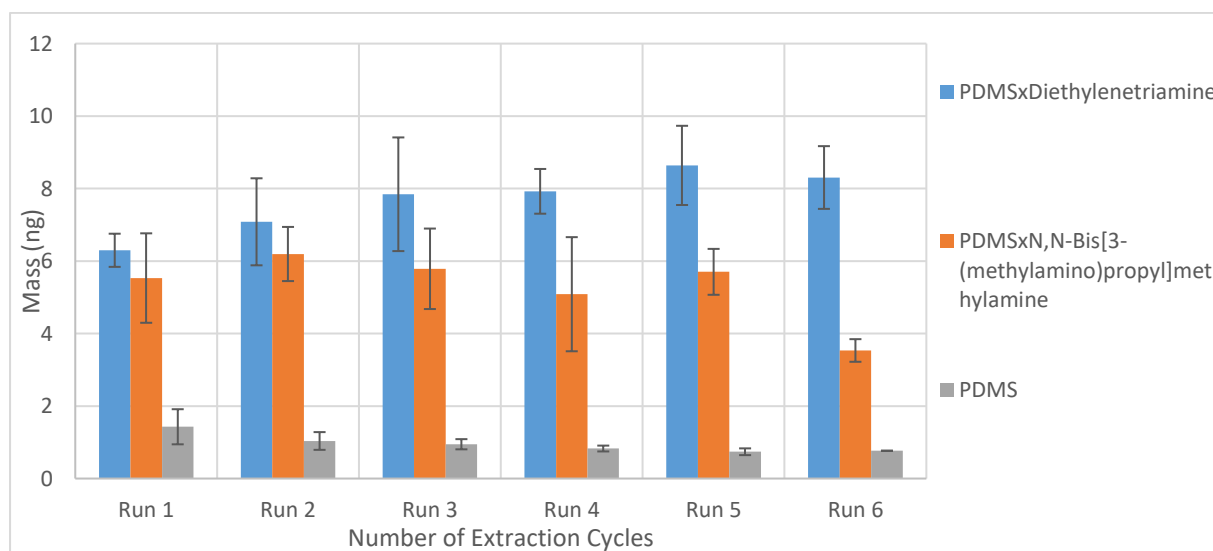
Figure 4.1: Graphical representation that measures the uptake of butanol in platinum-cured PDMS compared to PDMS samples that underwent amine crosslinking.

The result show that the PDMS monomers that were crosslinked with amines N,N-Bis[3-(methylamino)propyl]methylamine and diethylenetriamine, respectively showed increase uptake of butanol. Where diethylenetriamine extracted the largest quantity of butanol on average over 6 extractions.

Butanol was the third most polar compound within the extraction mixture with a LogP value of 0.88 (Table 2.2). The two most polar organic compounds in the extraction mixture were ethyl acetate and pyridine, which has logP values of 0.73 and 0.71, respectively (Table 2.2). The TD-GC-MS data from this showed that diethylenetriamine crosslinked PDMS did not extract as much pyridine as platinum-cured PDMS or the PDMS crosslinked with N,N-Bis[3-(methylamino)propyl]methylamine (Figure 4.2). Furthermore, diethylenetriamine crosslinked PDMS showed no extraction capability towards ethyl acetate over any of the 6 extractions (Figure 4.3). Within the same set of data, it was found that N,N-Bis[3-(methylamino)propyl]methylamine extracted the most ethyl acetate on average over the 6 runs compared to the other two sorbent materials.
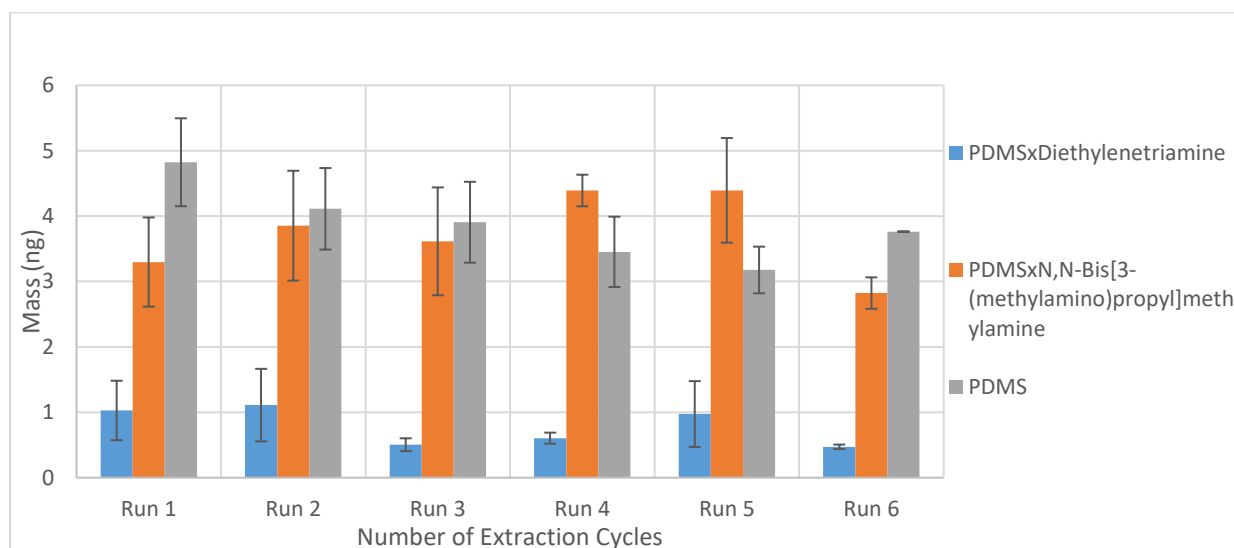
Figure 4.2: Graphical representation that measures the uptake of pyridine in platinum-cured PDMS compared to PDMS samples that underwent amine crosslinking.
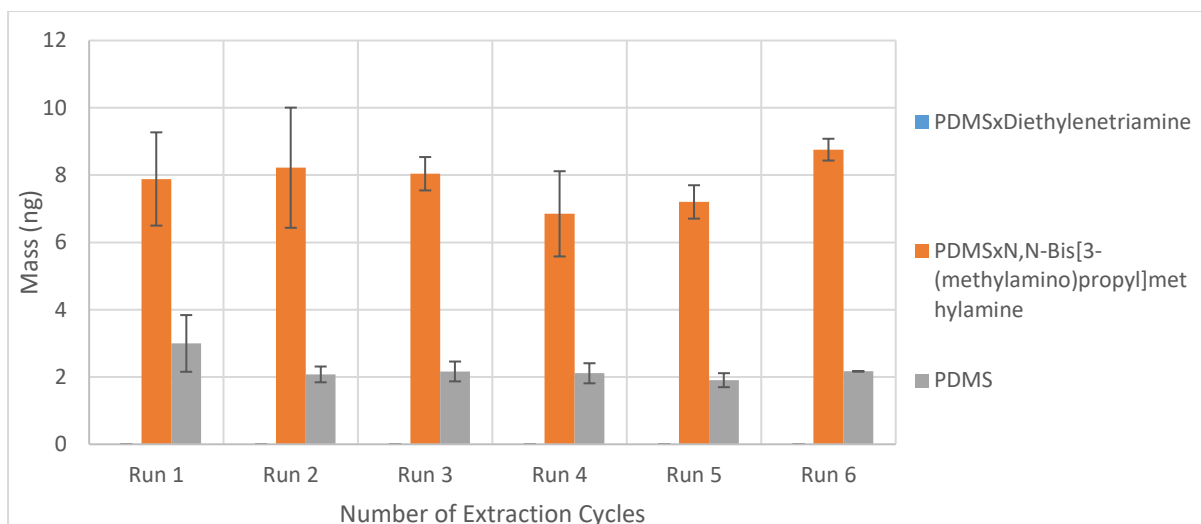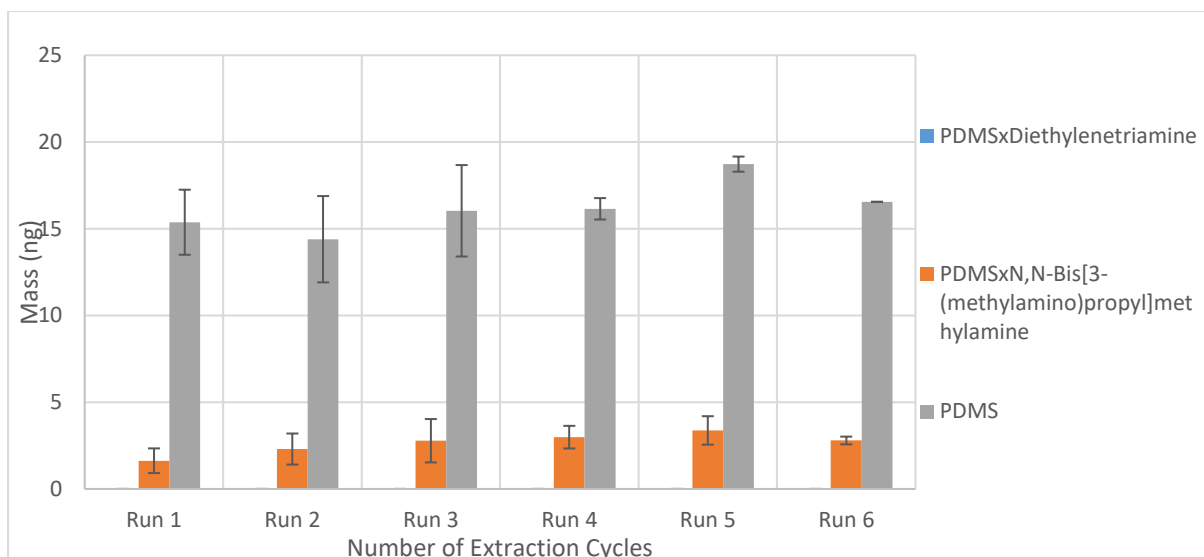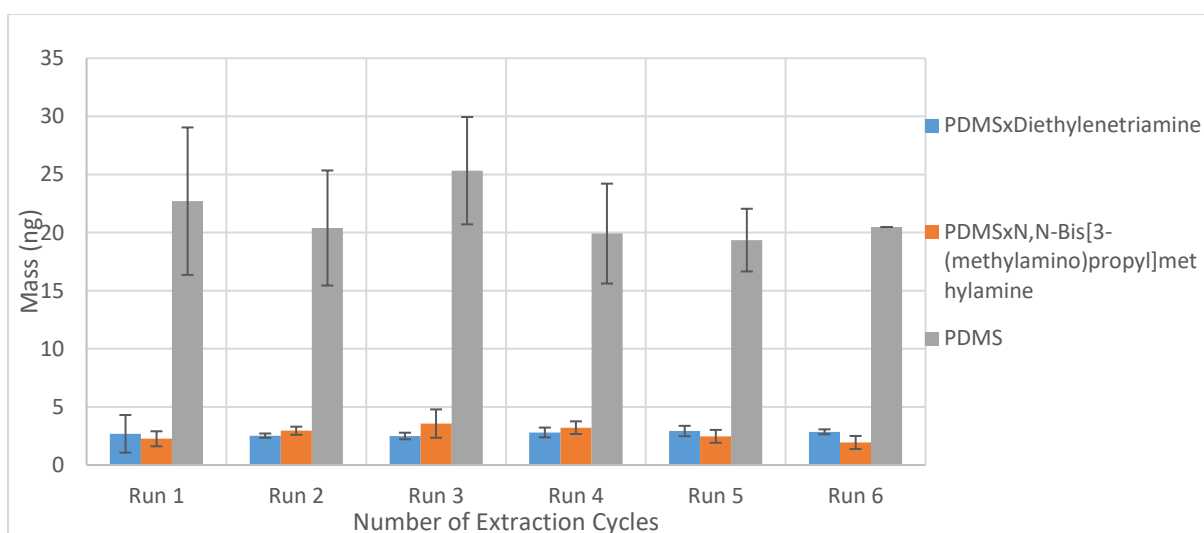
Figure 4.3: Graphical representation that measures the uptake of ethyl acetate in platinum-cured PDMS compared to PDMS samples that underwent amine crosslinking.

It is reported in literature that PDMS efficiently extracts VOCs with a LogP of greater than 3[141]. Therefore, the other VOC in the extraction mixture which falls below this threshold was hexanal, with a logP value of 1.78 (Table 2.2). Similarly to the extraction of ethyl acetate, diethylenetriamine crosslinked PDMS did not show any extraction of the VOC across 6 extractions and thermal desorption cycles (Figure 4.4). However, platinum-cured PDMS showed the greatest recovery of hexanal compared to the other materials. Across all the polar compounds tested against in the extraction mixture, N,N-Bis[3-(methylamino)propyl]methylamine was the most consistent with an average recovery between 3 – 10ng for all polar VOCs. Whereas diethylenetriamine was less consistent with no recovery of VOCs ethyl acetate and hexanal but the greatest recovery of butanol.

As for the extraction of the more non-polar compounds, it was expected that the platinum-cured PDMS tubing would perform better than that PDMS polymers that were crosslinked with amines. This was evident in the extraction of toluene-d8, cyclohexane and isobornyl methacrylate which have LogP values of 2.73, 3.44 and 4.30, respectively (Table 2.2) (Figures 4.5 – 4.7).

Figure 4.4: Graphical representation that measures the uptake of hexanal in platinum-cured PDMS compared to PDMS samples that underwent amine crosslinking.

Figure 4.5: Graphical representation that measures the uptake of toluene-d8 in platinum-cured PDMS compared to PDMS samples that underwent amine crosslinking.
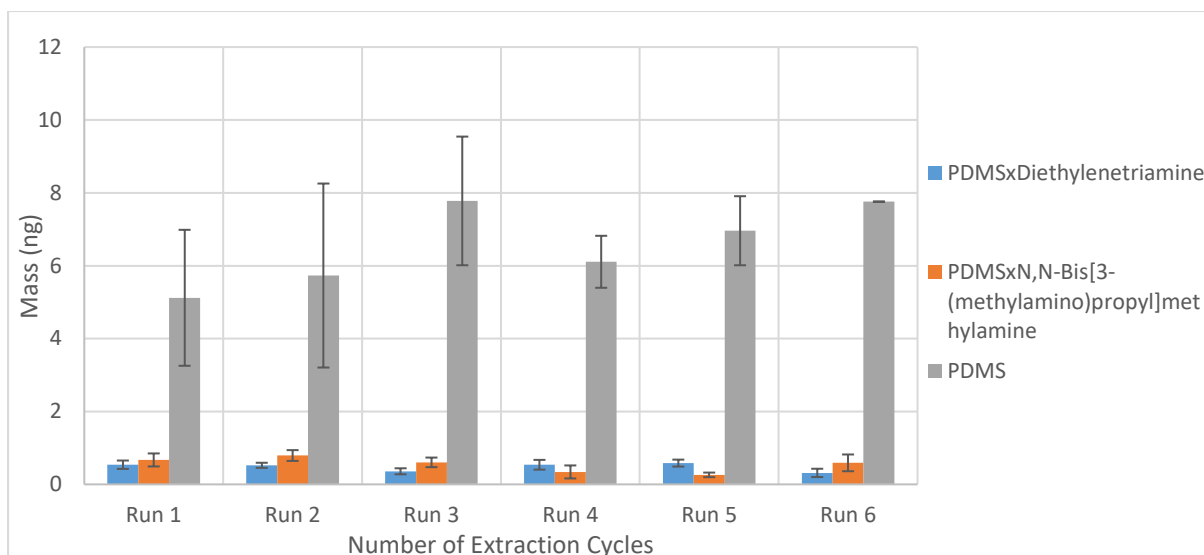
Figure 4.6: Graphical representation that measures the uptake of cyclohexane in platinum-cured PDMS compared to PDMS samples that underwent amine crosslinking.

Figure 4.7: Graphical representation that measures the uptake of isobornyl methacrylate in platinum-cured PDMS compared to PDMS samples that underwent amine crosslinking.

However, when extracting the most non-polar VOC in the extraction mixture, heptane. There were very low recovery levels for PDMS with extraction quantities averaging less than 1 ng over 6 runs. Furthermore, there PDMS-based sorbent which showed the greatest recovery

over the 6 runs was N,N-Bis[3-(methylamino)propyl]methylamine crosslinked PDMS and the diethylenetriamine crosslinked PDMS material showed zero recovery (Figure 4.8).

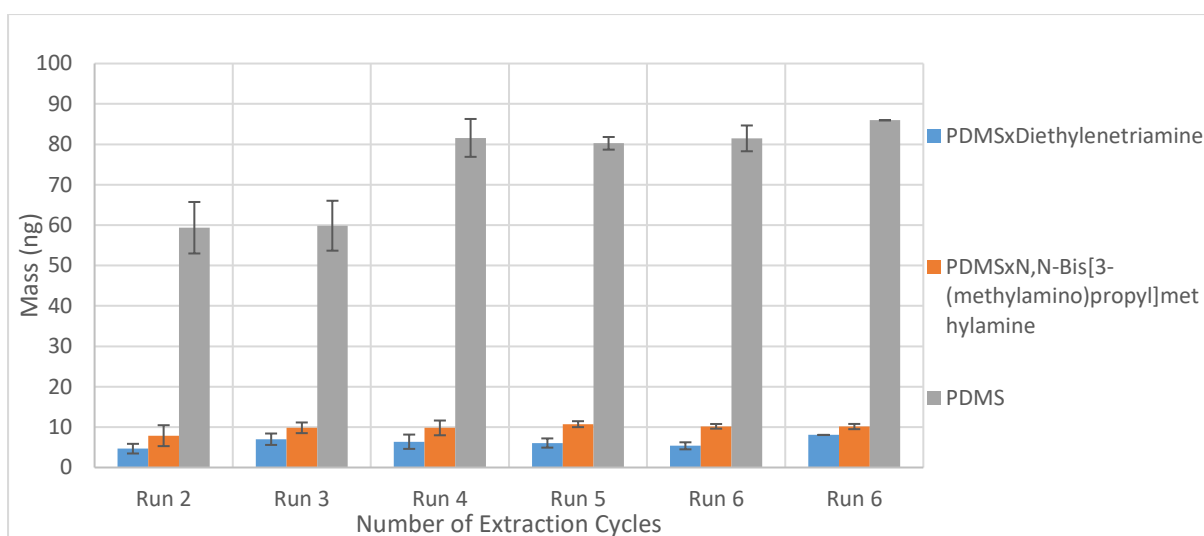*Figure 4.8:* Graphical representation that measures the uptake of heptane in platinum-cured PDMS compared to PDMS samples that underwent amine crosslinking.
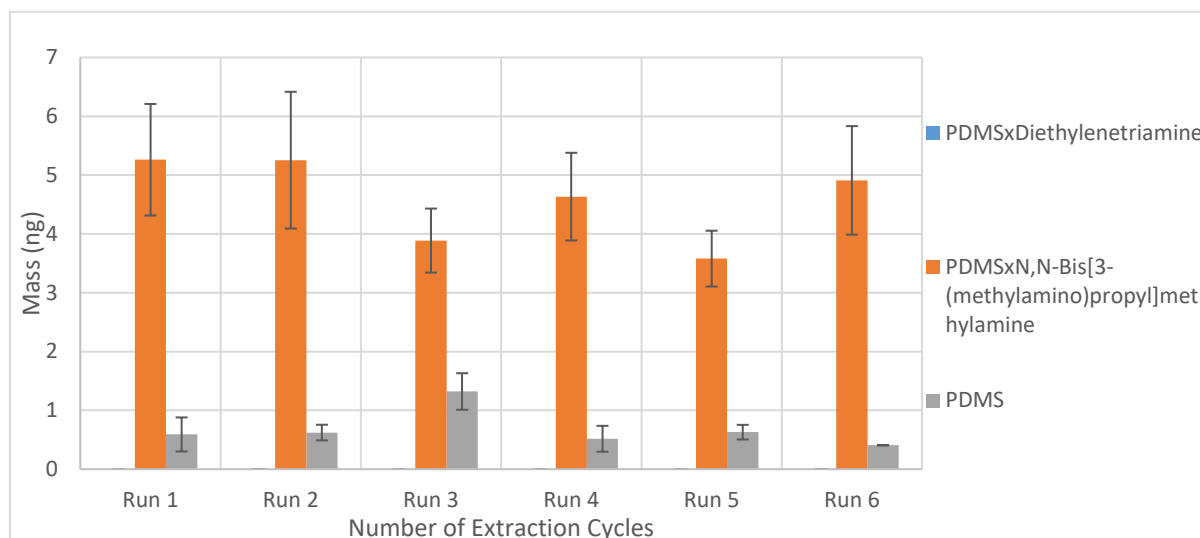
When assessing all the data, it was observed that the quantity extracted by all three types of PDMS-based materials was consistent across 6 runs. This suggests that all materials were thermally stable up to 160°C (thermal desorption temperature) and that the exposure to heat did not influence extraction performance.

4.3.2 Fourier-Transform Infrared Spectroscopy

Fourier-transform infrared spectroscopy was carried out to assess whether any of the amines added for crosslinking were present at the surface of the PDMS material (Section 2.2.3). The presence of these amines at the material would polarise the surface, drawing in more polar VOC species during extraction.

As previously demonstrated PDMS had 4 FTIR peaks associated with different bond characteristics. These peaks were present at wavenumbers 758 cm^{-1}, 1004 cm^{-1}, 1257 cm^{-1} and 2962 cm^{-1} (Figure 3.7 and Table 3.1). For the epoxy terminated PDMS samples crosslinked

with amines diethylenetriamine and N,N-Bis[3-(methylamino)propyl]methylamine showed similar FTIR characterisation to the platinum-cured PDMS (Figures 4.9 and 4.10). When compared to that of the PDMS FTIR, there was similar results with 4 bond characteristic peaks. PDMS samples that were crosslinked with diethylenetriamine showed FTIR spectra showed peaks at 788 cm^{-1}, 1015 cm^{-1}, 1257 cm^{-1} and 2961 cm^{-1} (Table 4.1).

Table 4.1: PDMS crosslinked with diethylenetriamine FTIR peaks with corresponding bond characterisations.

Wavenumber (cm^{-1})	Bond Characterisation
788	CH$_3$ rocking and Si-C stretching in Si-CH$_3$
1015	Si-O-Si stretching
1257	CH$_3$ deformation in Si-CH$_3$
2961	Asymmetric CH$_3$ stretching in Si-CH$_3$
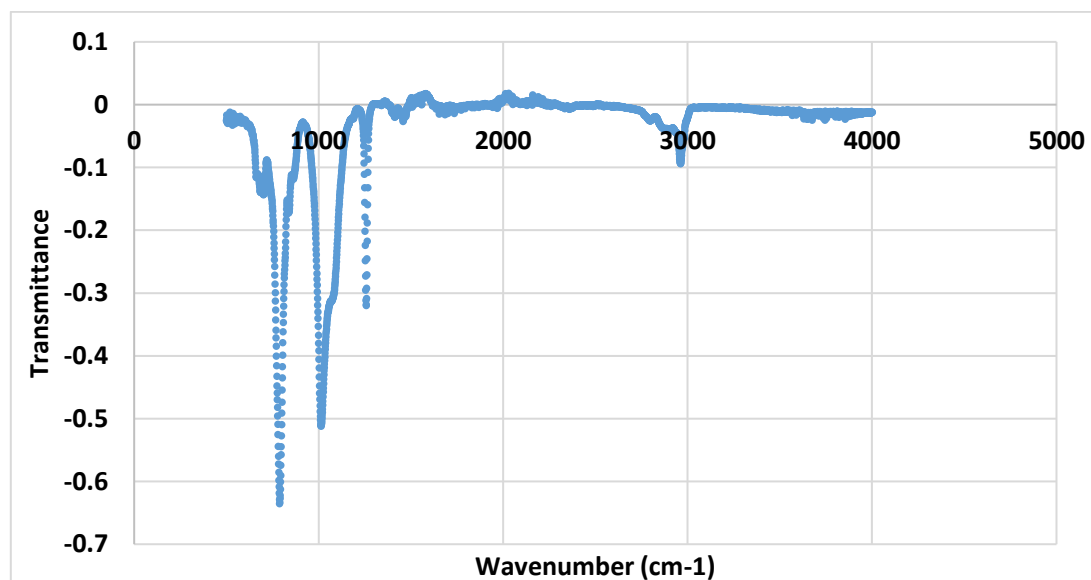
Figure 4.9: Graphical demonstration of FTIR data for PDMS crosslinked with diethylenetriamine.

The data showed a similar pattern for the PDMS samples which were crosslinked with N,N-Bis[3-(methylamino)propyl]methylamine. The data showed 4 FTIR bond characterisation peaks which were present at wavenumbers 789 cm^{-1}, 1013 cm^{-1}, 1257 cm^{-1} and 2961 cm^{-1}, similarly to that of both the platinum-cured PDMS and diethylenetriamine crosslinked PDMS (Table 4.2).

Table 4.2 PDMS crosslinked with N,N-Bis[3-(methylamino)propyl]methylamine FTIR peaks with corresponding bond characterisations.

Wavenumber (cm^{-1})	Bond Characterisation
789	CH$_3$ rocking and Si-C stretching in Si-CH$_3$
1013	Si-O-Si stretching
1257	CH$_3$ deformation in Si-CH$_3$
2961	Asymmetric CH$_3$ stretching in Si-CH$_3$

Figure 4.10: Graphical demonstration of FTIR data for PDMS crosslinked with N,N-Bis[3-(methylamino)propyl]methylamine.

The FTIR data for the amine crosslinked PDMS samples showed no difference in chemical structure at the surface of the material to that of the platinum-cured PDMS samples. Therefore, it would be assumed that during the crosslinking reaction that all the amines were reacted and bonded to the PDMS monomer chain. This would explain why no amine bond characteristics were present at the surface, just that of the PDMS.

4.3.3 Scanning Electron Microscopy

Scanning electron microscopy (SEM) was utilised to deduce whether there were any physical changes to the polymer material. Using the power of the microscope each material was measured at 3 different magnifications 500x, 1000x and 2000x (Section 2.2.4).

The platinum cured PDMS demonstrated cracking across the surface after each thermal desorption cycle (Figure 3.10a and 3.10b). This similar cracking was apparent in the samples which had undergone crosslinking with amines diethylenetriamine and N,N-Bis[3-(methylamino)propyl]methylamine. The samples which were crosslinked with diethylenetriamine showed a vast, interconnected range of cracking across the whole surface after just 1 thermal desorption cycle (Figures 4.11a and 4.11b). Over several thermal desorption cycles, this cracking remained prevalent at the surface of the PDMS material that was crosslinked with diethylenetriamine (Figures 4.11c and 4.11d).

There was a similar result in the SEM images taken of PDMS crosslinked with N,N-Bis[3-(methylamino)propyl]methylamine. Where after the first thermal desorption, cracks appeared to show at the surface (Figures 4.12a and 4.12b). However, the amount of cracking at the surface was greater than that of the PDMS crosslinked with diethylenetriamine. As the thermal desorption cycles continued the cracking became more prominent across the whole surface of the material (Figures 4.12c and 4.12d).
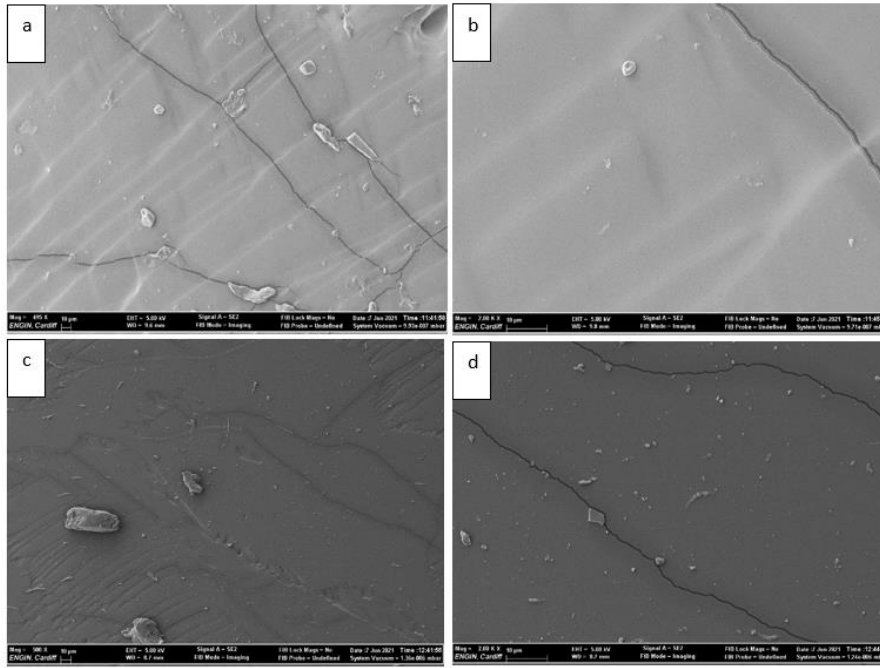
Figure 4.11: SEM images of PDMS material crosslinked with diethylenetriamine. After 1 thermal desorption cycle a) 500x magnification b) 2000x magnification. After 6 thermal desorption cycles c) 500x magnification d) 2000x magnification.
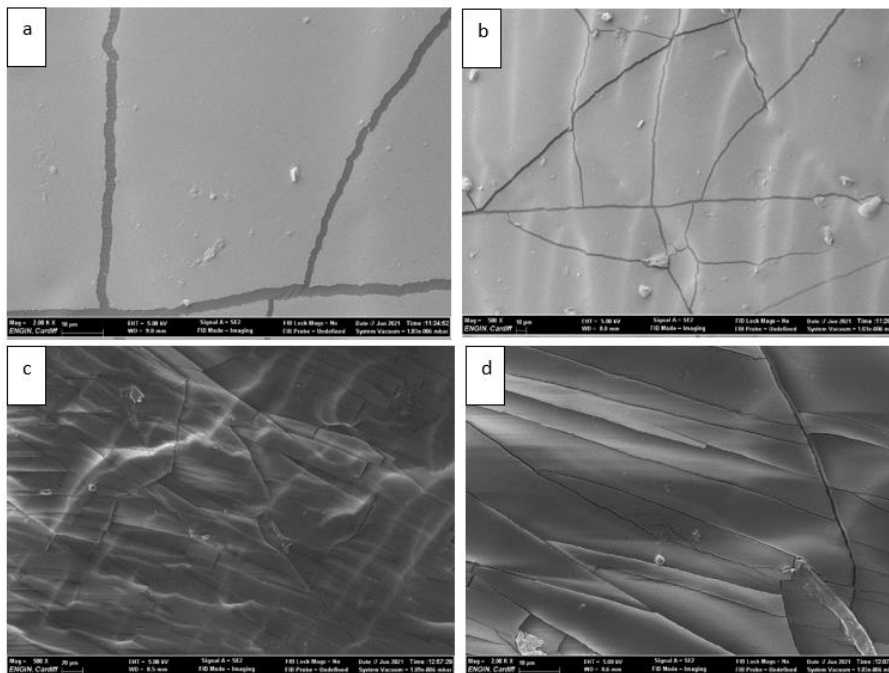
Figure 4.12: SEM images of PDMS material crosslinked with N,N-Bis[3-(methylamino)propyl]methylamine. After 1 thermal desorption cycle a) 500x magnification b) 2000x magnification. After 6 thermal desorption cycles c) 500x magnification d) 2000x magnification.

4.3.4 Contact Angle Measurements

The contact angle measurements of the diethylenetriamine and N,N-Bis[3-(methylamino)propyl]methylamine crosslinked PDMS samples were undertaken (Section 2.2.5). 3 different solvents were used of varying polarity and the angles between the surface and droplets were taken. The 3 different solvents used deionised water, ethylene glycol and octan-1-ol, in which the deionised water was the most polar and octan-1-ol being most non-polar. The data in Table 3.4 showed that PDMS has an average contact angle of 110.2°, 105.1° and 45.1° for deionised water, ethylene glycol and octan-1-ol, respectively. When comparing these values to the contact angles of the PDMS-based sorbents crosslinked with the amines, there was strong similarity. This suggested that at the surface energies of the three different types of PDMS were approximately the same and that there were no amines at the surface of the material, influencing surface polarity.

Table 4.3: Average calculated contact angle measurements for water, ethylene glycol and octan-1-ol droplets at the surfaces of diethylenetriamine and N,N-Bis[3-(methylamino)propyl]methylamine crosslinked PDMS samples compared to that of platinum-cured PDMS.

Solvent	PDMS	Diethylenetriamine	N,N-Bis[3-(methylamino)propyl]methylamine
Water	110.2 ± 0.6	108.4 ± 0.6	109.1 ± 0.8
Ethylene Glycol	105.1 ± 0.5	103.8 ± 0.9	104.3 ± 0.5
Octan-1-ol	45.1 ± 1.5	44.6 ± 1.9	46.4 ± 1.8

4.4   Discussion

This chapter explored whether covalently bonding amines to PDMS monomer chains influenced the uptake of VOCs from aqueous mixtures. Of the 6 amines that were used in Chapter 3, only 2 were successfully crosslinked with PDMS for the extraction and thermal desorption process. These were diethylenetriamine and N,N-Bis[3-(methylamino)propyl]methylamine, respectively. Such issues surrounding the other amines for crosslinking were unsuccessful crosslinking and adhering to the side of the glass tubes which was used for moulding and as such taring the polymer phase. The protocol of bonding amines to epoxy-terminated PDMS chains was based on a previously documented report [142]. However, there were notable differences between this published article and this chapter's results.

One such difference was the type of amines used. Of the 6 amines recorded for encapsulation in Chapter 3, only one amine (diethylenetriamine) was used for crosslinking with epoxy-terminated PDMS in the published article. Therefore, in the prior to the research there was uncertainty as to which amines would successfully synthesize. Diethylenetriamine and N,N-Bis[3-(methylamino)propyl]methylamine amines were independently crosslinked to epoxy-terminated PDMS.

However, the resulting PDMS-based polymer materials thermal stability and extraction capabilities were not reported in the literature. This was experimentally carried out using thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS) (Section 4.3.1). The overall results showed that these two PDMS-based polymer materials had the characteristics to extract VOCs from an aqueous matrix while showing variable extraction performance towards each of the organic compounds used in the extraction mixture.

It was originally hypothesized that the when the amines were crosslinked to the PDMS monomers, that these polar characteristics may induce polarity in the structure and improve the extraction of polar VOC compounds compared to that of the platinum-cured PDMS. Upon evaluation of the results there was no relationship between polarity of VOC and the PDMS materials that were synthesized with amines. Interestingly, the results of the FTIR demonstrated that in-fact there were no amines at the surface of the material with similar peak profile to that of PDMS (Section 4.3.2). This therefore would hinder the adsorption of

polar VOCs from the extraction mixture during extraction as the surface of the material showed a PDMS chemical portfolio, which was hydrophobic due to the presence of the methyl functional groups.

Furthermore, it was investigated as to the effect that covalently bonding the amines to the PDMS chains had on VOC extraction compared to that of PDMS material that has undertaken encapsulation. In Chapter 3 it was reported that encapsulating amines within the platinum-cured PDMS matrix did influence the uptake of VOCs in the extraction mixture (Section 3.3.1). Interestingly, the data showed that covalently bonding the amine to the PDMS to the polymer chain induced different extraction results compared to when encapsulated, as tested via TD-GC-MS. The best example of this was the difference in pyridine extraction between covalently bonded or encapsulated N,N-Bis[3-(methylamino)propyl]methylamine with PDMS. The PDMS material that was encapsulated with N,N-Bis[3-(methylamino)propyl]methylamine showed an average extraction quantity of 39 ng in Run 1 (Figure 3.1), whereas when covalently bonded an average extraction quantity of just 3.2 ng was observed (Figure 4.2). Overall, there were no trends in the extraction data between PDMS sorbents when the same type of amine was encapsulated compared to covalently bonded.

The main issue with the encapsulated amine sorbents was their thermal instability. This caused two issues:

1. Overloading of amines into the column and detector led to large background peaks on the spectra.
2. After each thermal desorption, the extraction performance of the encapsulated PDMS would reduce from run to run as the concentration of amines dropped from the thermal desorption process.

When looking at how thermal stability induced more repeatable results in the extraction of the organic compounds. It is a fair assessment to say that towards each organic compound extracted, over 6 runs there was very little difference in average mass extracted. That tells us that these covalently bonded PDMS/amine materials were a lot more stable than the encapsulated under the thermal desorption conditions.

When assessing the thermal stability of the material on chromatogram background, covalently bonding the amines to PDMS improved the thermal stability of the PDMS materials

during the thermal desorption process (Figure 4.13) compared to the encapsulated PDMS materials (Figure 3.18). Notably, it was found that bonding the amines to the PDMS did reduce the quantity of amine lost during thermal desorption. The largest peak heights in the background peaks of the encapsulated PDMS samples were recorded at $x10^8$, whereas the largest peak within the background of the covalently bonded PDMS peak was at $x10^7$. However, given the peak height of the target compounds was around $x10^5$ this was deemed an unacceptable level.
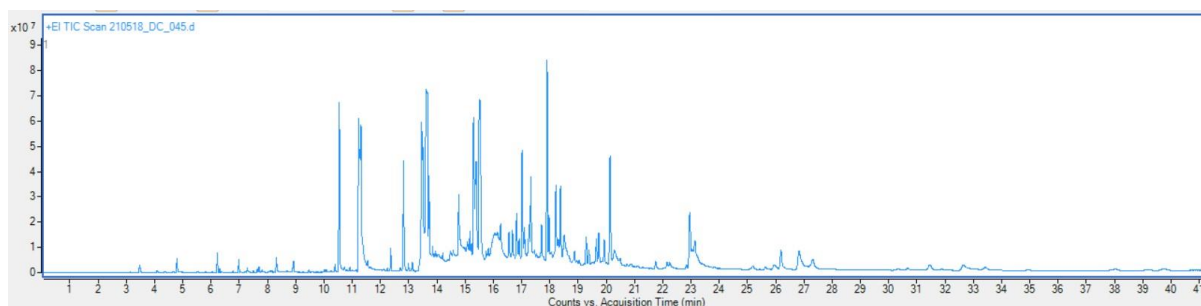
Figure 4.13: The background TD-GC-MS spectra of the diethylenetriamine crosslinked PDMS material.

The other main disadvantage to this covalently bonded amine/PDMS material was its brittle physicality. The polymer material was soft to touch and ripped when placed through the custom septum (Figure 4.14). From a commercial perspective, the lack of strength around the sorbent material was non-negotiable. It was an essentially quality for the HiSorb probe in-order to align with the automated process of Centri (Section 1.8.1) and stand-alone HiSorb (1.8.2) processes in-which the septum is used.

Figure 4.14: Custom clamped brass caps with the purple septum which the HiSorb penetrates prior to extraction.

4.5   Conclusion

- Covalently bonding amines to the PDMS monomer chains via epoxy-terminal groups did influence the uptake of polar VOC compared to that of the commercially used PDMS.

- When compared to the encapsulation modification method, equivalent amines did not show the same extraction proficiency as measured by TD-GC-MS.

- FTIR, SEM and contact angle measurements showed no chemical or physical variance to the PDMS.

- The modified epoxy PDMS samples demonstrated improved thermal stability with extraction reproducibility.

- However, background showed that each of the modified polymer materials did not fall within the specification of the product. Furthermore, physically they were in-compatible with the HiSorb septum.

- Future work will look to embed more thermally stable materials within the matrix of the PDMS material, similarly to that of the encapsulation technique as this modification technique showed the greatest extraction data as measured by TD-GC-MS.

- There is a range of commercially available sorbents (provided by Markes International) that have established thermal stability and sorptive properties. The largest task would be developing a method that embeds these sorbents into the PDMS material.

Chapter 5: Commercially available Sorbent Materials within PDMS

5.1 Abstract

This chapter looked at how mixing two commercially available sorbents, Tenax GR and Carboxen 1016, with PDMS into cylindrical moulds generated two novel sorbent materials. These bi-phasic PDMS mixtures were then compared to a laboratory synthesized PDMS and commercially available platinum-cured PDMS. Results looked at how each of the novel sorbents performed in the extraction of a range of organic compounds from an aqueous matrix and compared to both the laboratory synthesized and commercially available PDMS. The results showed that PDMS/Tenax GR improved the uptake of most of the organic compounds from the extraction mixture over several extractions whilst maintaining thermal stability over several thermal desorption cycles.

5.2. Introduction

Sorbent materials are vastly used within analytical studies for the adsorption of both volatile and semi-volatile organic compounds (VOCs & SVOCs) to the surface, with chemical inertness being the most important physical characteristic of each type. Sorbent materials are primarily classified under 3 main groups: graphitised carbon black, porous polymer and carbonised molecular sieve[143] [144] [145]. The determination of whether or how strongly VOCs or SVOCs adhere to the surface of a sorbent material varies from sorbent to sorbent, where for example Tenax readily adsorbs molecules to its surface therefore being described as a strong sorbent material. Within thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS) equipment, the sorbent materials are primarily found in thermal desorption (TD) tubes or focusing traps. Where heat is applied to desorb organic compounds from their surfaces.

Commercially available sorbent materials for the extraction of analytes from solid, liquid or gaseous samples has been vastly employed within the solid-phase microextraction (SPME) technique for many years [146], [147]. SPME does however suffer from the limited number of commercially available phases as optimization has been achieved through various combinations and thicknesses of the little number of phases available. At the centre of each coating tends to be PDMS. PDMS provides the structure of each fibre while being easy to mix and handle with other sorbents. This allows for the extraction of both more polar and volatile

compounds, compared to a sorbent material consisting of just PDMS. For example, the combination of PDMS with divinylbenzene (DVB) allows for the extraction of polar analytes while carbon wide range (CWR) extracts more volatiles [148], [149].

This chapter showed how PDMS was synthesized with commercially available materials, Tenax GR and Carboxen 1016 to improve the extraction of organic analytes from aqueous matrices (Section 2.1.4). Each synthesized PDMS-based material was be tested against two types of PDMS, currently used commercially available PDMS and the PDMS synthesized in the laboratory. Each HiSorb probe extraction efficiency was analysed on TD-GC-MS equipment and qualitatively analysed through fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and contact angle measurements.

5.3   Results

5.3.1 Thermal Desorption-Gas Chromatography-Mass Spectrometry

The ability of each PDMS-based polymer material at extracting organic compounds from aqueous immersive sampling was tested and analysed through thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS). The control group in this study was the currently used, commercially available, platinum-cured PDMS. The extraction results of this material were then compared to that of the laboratory synthesized single-phase PDMS and two biphasic PDMS-based materials that contained Tenax GR and Carboxen 1016, respectively.

Overall, each of the material's showed sorptive capabilities towards each organic compound with extraction of each maintained throughout the experiment. Of each of the organic compounds extracted, the largest quantity extracted was by the PDMS/Tenax GR biphasic polymer towards styrene (Figure 5.1). The PDMS/Tenax GR sorbent extracted an average of approximately 50 ng per extraction over 6 independent extractions. This quantity of uptake was much different to each of the other materials, who over each extraction showed little differentiation. As such, it could be assumed that the addition of Tenax GR to the PDMS, improved the uptake of styrene.

PDMS/Tenax GR showed similar results in the extraction of toluene d8 and hexanal compared to that of the other sorbent materials. For the extraction of toluene d8, PDMS/Tenax GR extracted an average of approximately 36 ng over the 6 extractions. Whereas the other sorbent materials extracted an average of 19 ng (Figure 5.2).
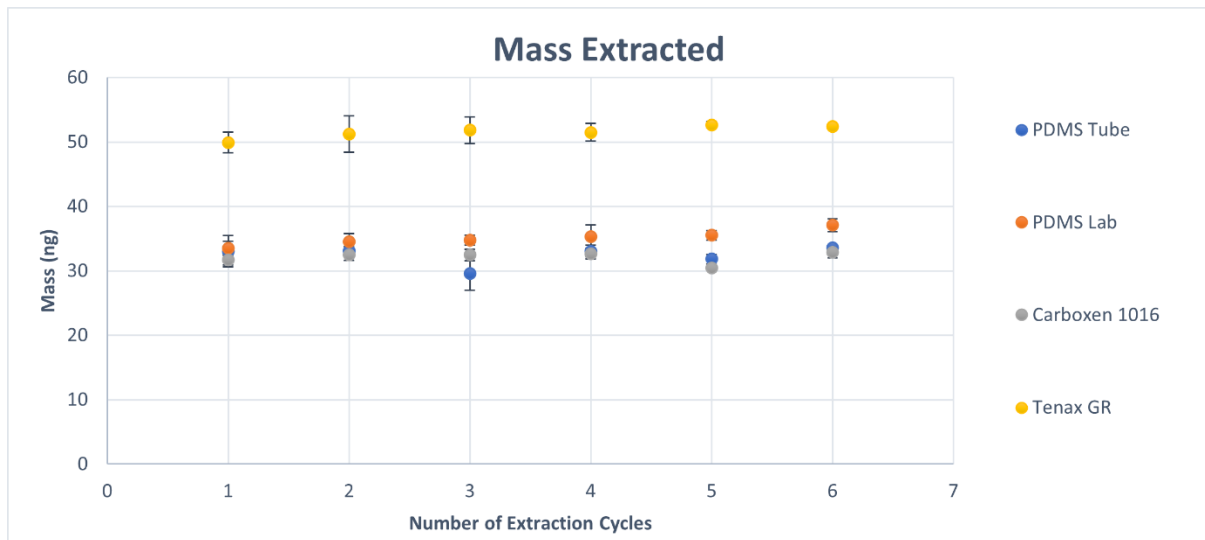
Figure 5.1: Graphical representation of the uptake of styrene in commercially available platinum-cured PDMS tubing compared to laboratory synthesized PDMS, PDMS/Tenax GR and PDMS/Carboxen 1016 samples.
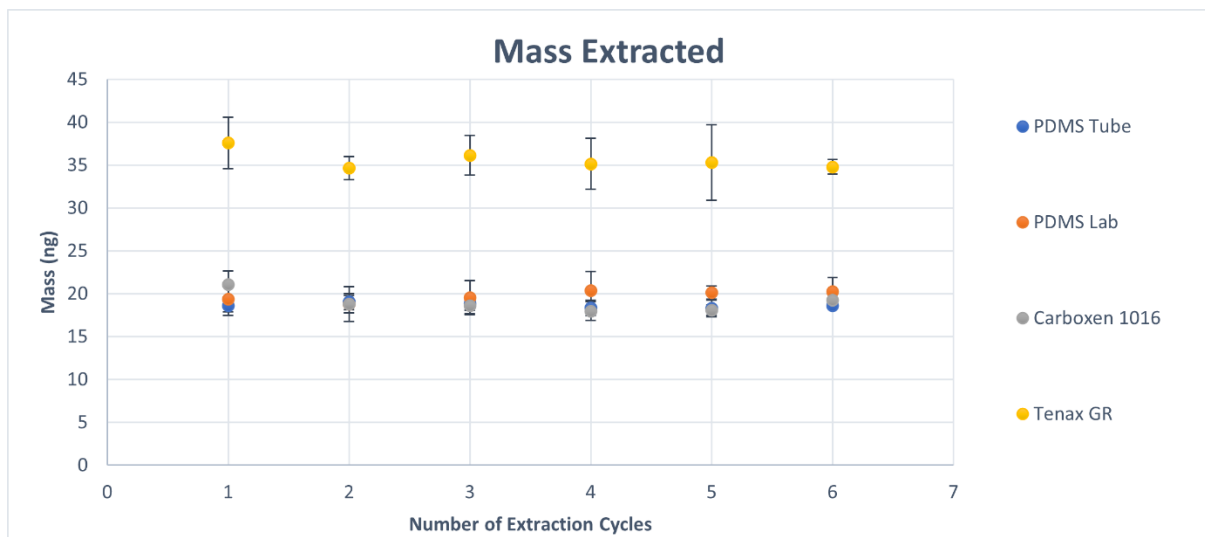
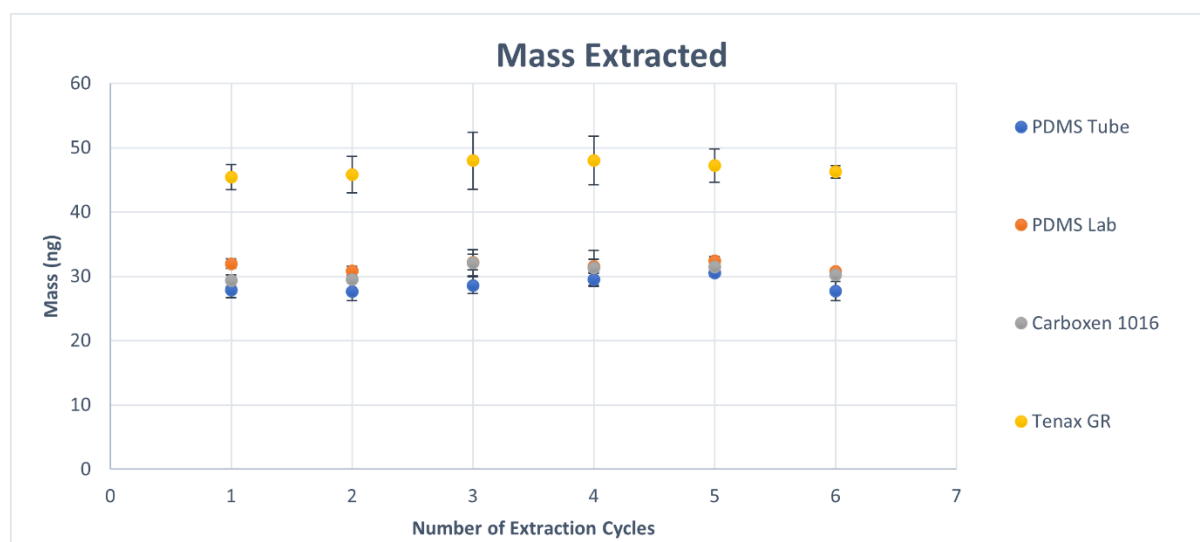**Figure 5.2:** Graphical representation of the uptake of toluene d8 in commercially available platinum-cured PDMS tubing compared to laboratory synthesized PDMS, PDMS/Tenax GR and PDMS/Carboxen 1016 samples.

As previously mentioned, there was the same trend in the extraction of hexanal in which the PDMS/Tenax GR extracted approximately 50% more hexanal to the other sorbents which showed little differentiation in extracting around 30 ng of compound per probe on average (Figure 5.3).

PDMS/Tenax GR showed the greatest uptake for ethyl acetate compared to the other 3 sorbent materials (Figure 5.4). However, for the extraction of this organic compound PDMS/Carboxen 1016 extracted less than both the commercial and synthesized PDMS materials. This was an example of how adding different commercially sorbents to PDMS can induce contrasting effects of sorptive capabilities.

For the extraction of heptane, the commercially available PDMS and PDMS/Tenax GR performed similarly on average over 6 extractions (Figure 5.5). Interestingly, the heptane extraction data could be used to differentiate between the PDMS synthesized in the laboratory and the commercially available PDMS. The data showed distinctive differences in mass extracted of heptane, with the commercially bought PDMS extracting approximately twice the amount of heptane compared to that of the laboratory synthesized PDMS. Furthermore, the material which extracted the lowest quantity of heptane was the PDMS/Carboxen 1016 material.

Figure 5.3: Graphical representation of the uptake of hexanal in commercially available platinum-cured PDMS tubing compared to laboratory synthesized PDMS, PDMS/Tenax GR and PDMS/Carboxen 1016 samples.
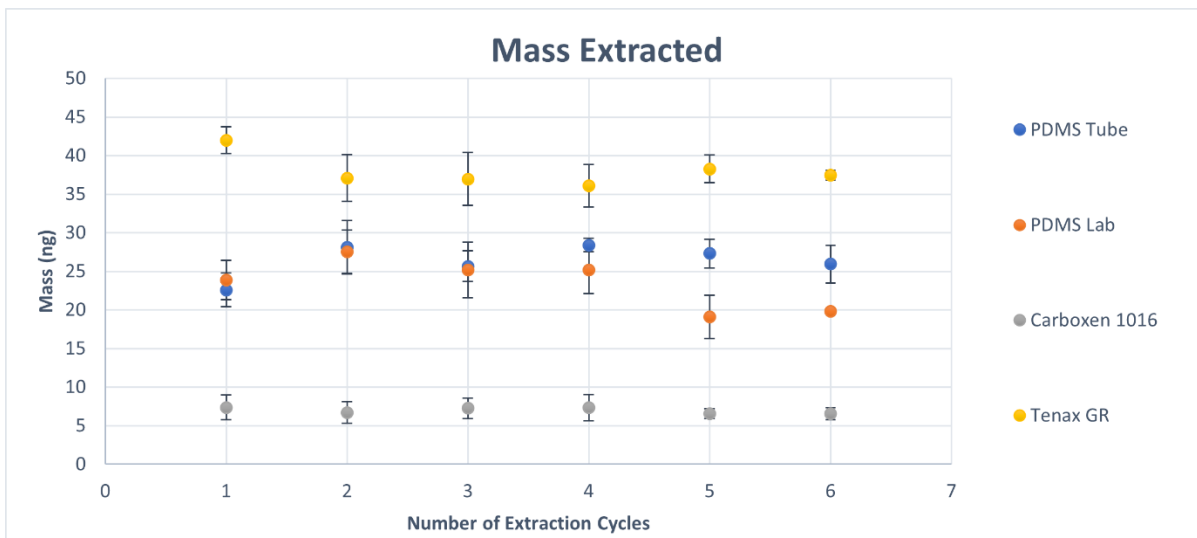
Figure 5.4: Graphical representation of the uptake of ethyl acetate in commercially available platinum-cured PDMS tubing compared to laboratory synthesized PDMS, PDMS/Tenax GR and PDMS/Carboxen 1016 samples.
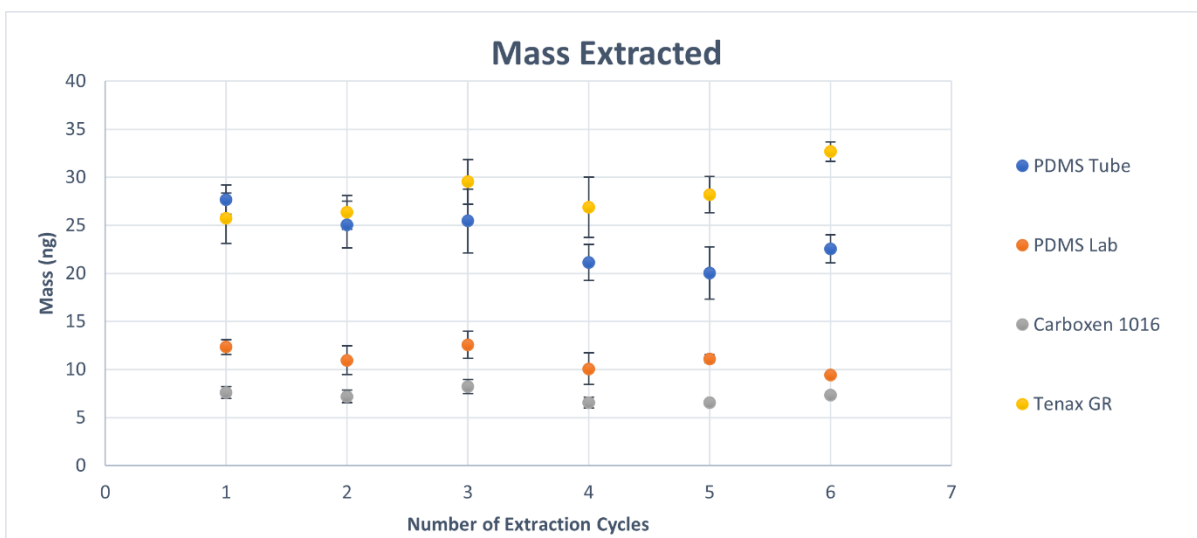
Figure 5.5: Graphical representation of the uptake of heptane in commercially available platinum-cured PDMS tubing compared to laboratory synthesized PDMS, PDMS/Tenax GR and PDMS/Carboxen 1016 samples.

As for the extraction of acrylonitrile and cyclohexane, PDMS/Tenax GR showed the largest uptake quantities (Figures 5.6 & 5.7). Whereas the commercially available PDMS tubing showed the greatest uptake of pyridine (Figure 5.8). Although there are some differences in the uptake of each of these organic compounds, the mass extracted was much lower than that of the other organic compounds in the extraction mixture.

Of all the organic compounds in the extraction mixture, butanol was the only extraction compound to show the least difference in uptake values across all 4 materials (Figure 5.9). Similarly to the results for the extraction of acrylonitrile the quantity of butanol extracted was very low implying neither sorbent were specifically effective at extracting this organic compound.

Figure 5.6: Graphical representation of the uptake of acrylonitrile in commercially available platinum-cured PDMS tubing compared to laboratory synthesized PDMS, PDMS/Tenax GR and PDMS/Carboxen 1016 samples.
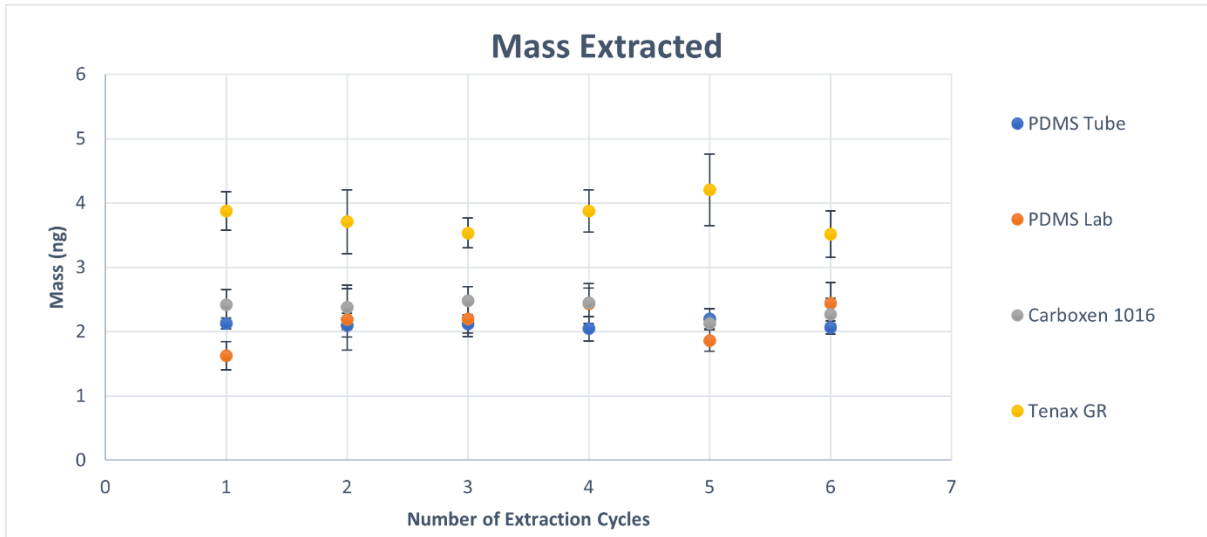
Figure 5.7: Graphical representation of the uptake of cyclohexane in commercially available platinum-cured PDMS tubing compared to laboratory synthesized PDMS, PDMS/Tenax GR and PDMS/Carboxen 1016 samples.
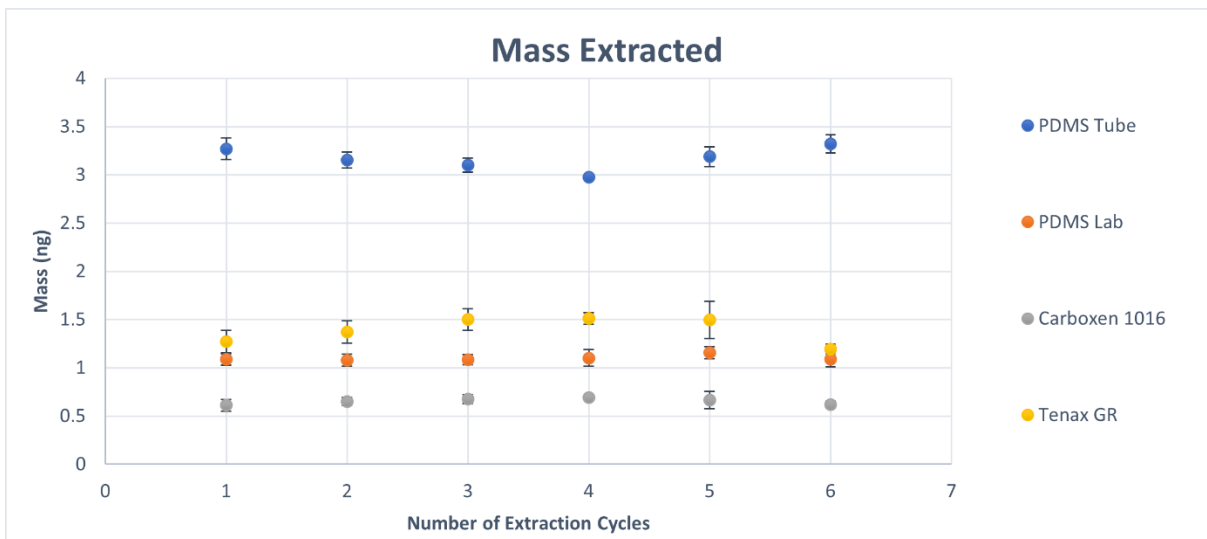
Figure 5.8: Graphical representation of the uptake of pyridine in commercially available platinum-cured PDMS tubing compared to laboratory synthesized PDMS, PDMS/Tenax GR and PDMS/Carboxen 1016 samples.
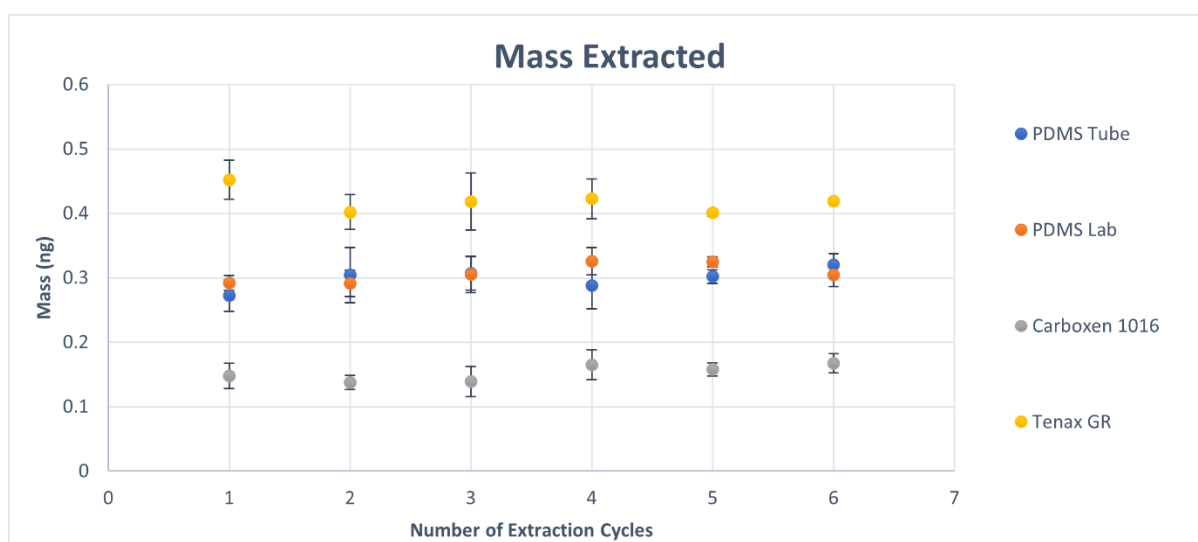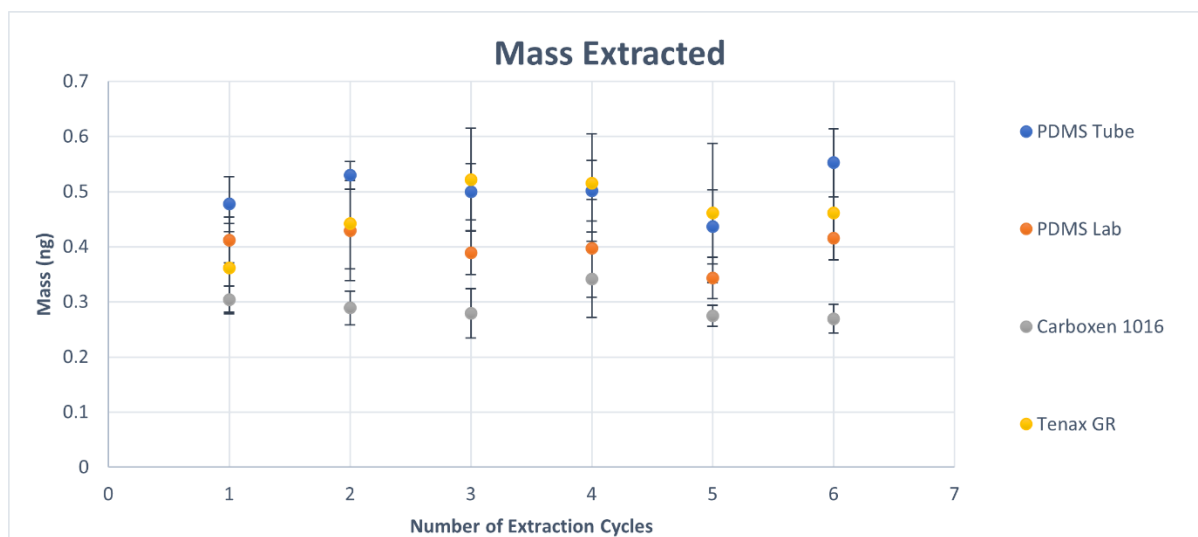
Figure 5.9: Graphical representation of the uptake of butanol in commercially available platinum-cured PDMS tubing compared to laboratory synthesized PDMS, PDMS/Tenax GR and PDMS/Carboxen 1016 samples.

A further observation of the TD-GC-MS data showed great reproducibility between each sample in the same batch in-terms of extraction efficiency. The consistent extraction volumes of each material, towards each organic compounds would indicate that each material showed impressive thermal resistance and little degradation over 6 thermal desorption cycles.

5.3.2 Fourier-Transform Infrared Spectroscopy

Fourier-transform infrared spectroscopy (FTIR) was used to characterise the chemical bonds at or near to the surface of each material. As previously shown in the earlier chapters PDMS has 4 known characteristic FTIR bonds (Table 3.1 & Figure 3.7). When comparing the FTIR data of the two types of PDMS used in the analysis, there is strong overlap in the 4 peaks that characterise PDMS at wavelengths 701 cm^{-1}, 786 cm^{-1}, 1258 cm^{-1} and 2961 cm^{-1} (Figure 5.10). FTIR was also used to deduce any chemical changes at the surface of each material after extraction and thermal desorption. For the commercially available PDMS there was no change to the chemical profile after extraction and thermal desorption cycles, consistent with the results recorded in previous chapters (Figure 3.10b).
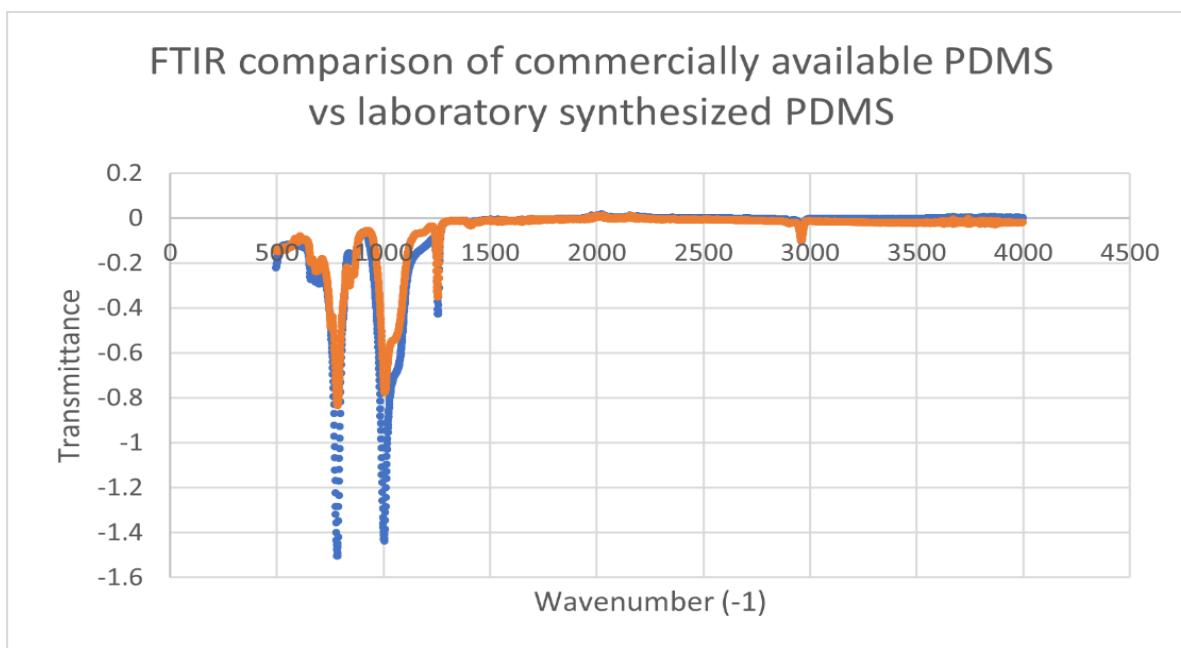
Figure 5.10: FTIR spectra compares the surface bond characteristics of commercially available platinum-cured PDMS (blue) and laboratory synthesized PDMS (orange).

The PDMS was synthesized in the laboratory was also tested for chemical inertness and stability after extraction and thermal desorption cycles. Similarly to that of the commercially available PDMS, it was also unaffected by the TD-GC-MS analysis. Where the spectra showed similar overlap and to one another but most importantly the 4 bond characteristics associated with PDMS (Figure 5.11).

The FTIR data for the bi-phasic sorbent materials PDMS/Tenax GR and PDMS/Carboxen 1016 surprisingly showed no additional bond characteristics to that of the PDMS FTIR data (Figure 5.12 & Figure 5.13).

Similarly to that of the PDMS FTIR data, FTIR was used to deduce any chemical changes at the surface of each material after extraction and thermal desorption cycles. For two biphasic material's that were synthesized PDMS/Tenax GR and PDMS/Carboxen 1016, there appeared to be no change to the surface chemistry after TD-GC-MS analysis (Figure 5.14 & 5.15).
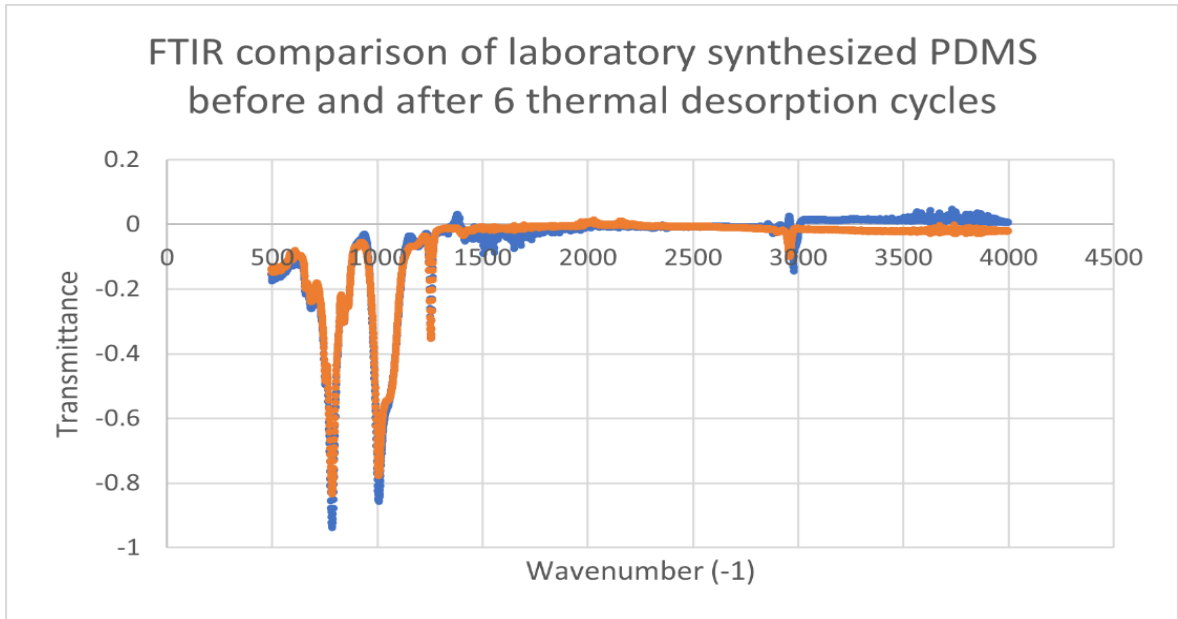
Figure 5.11: FTIR spectra compares the surface bond characteristics of the laboratory synthesized PDMS before (orange) and after TD-GC-MS analysis (blue).
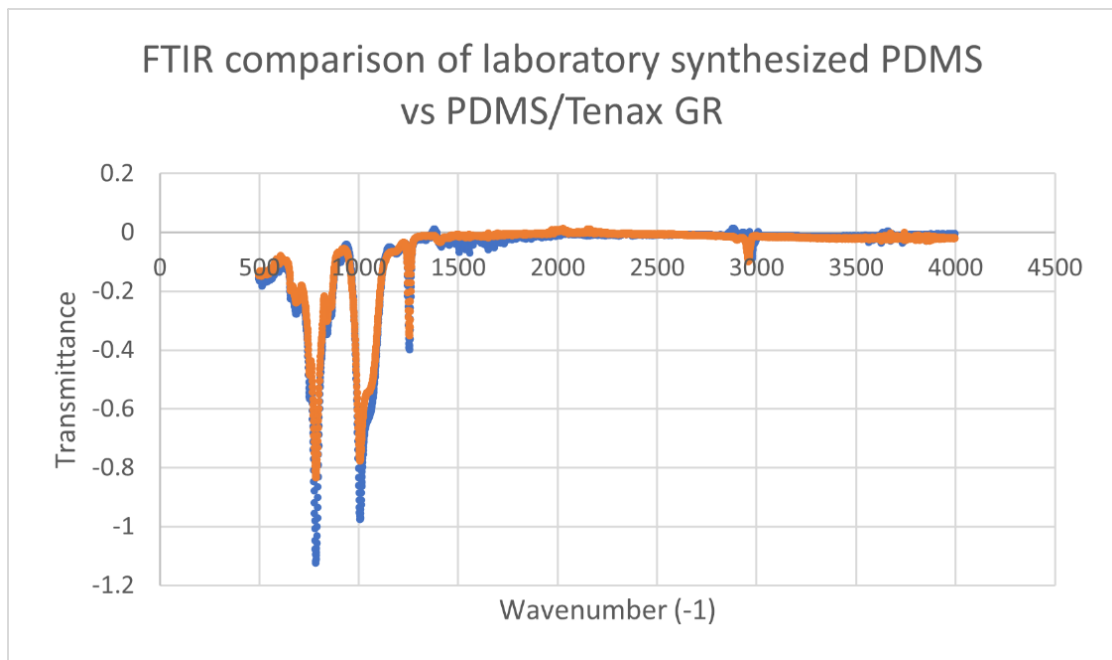
Figure 5.12: FTIR spectra compares the surface bond characteristics of the laboratory synthesized PDMS before (orange) and PDMS/Tenax GR (blue).
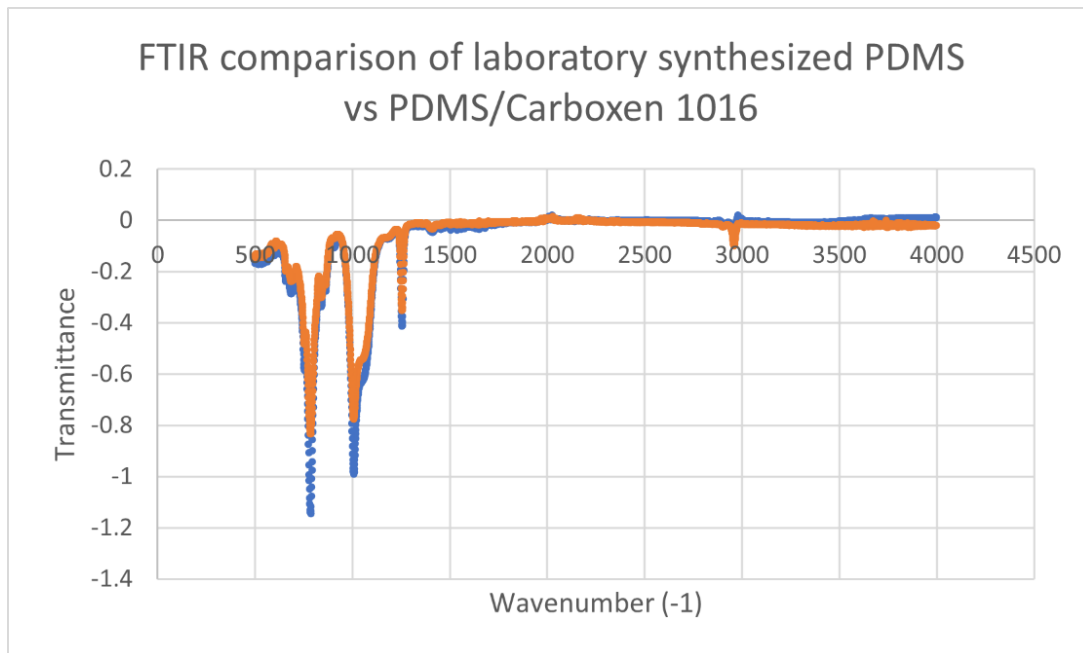
Figure 5.13: FTIR spectra compares the surface bond characteristics of the laboratory synthesized PDMS before (orange) and PDMS/Carboxen 1016 (blue).
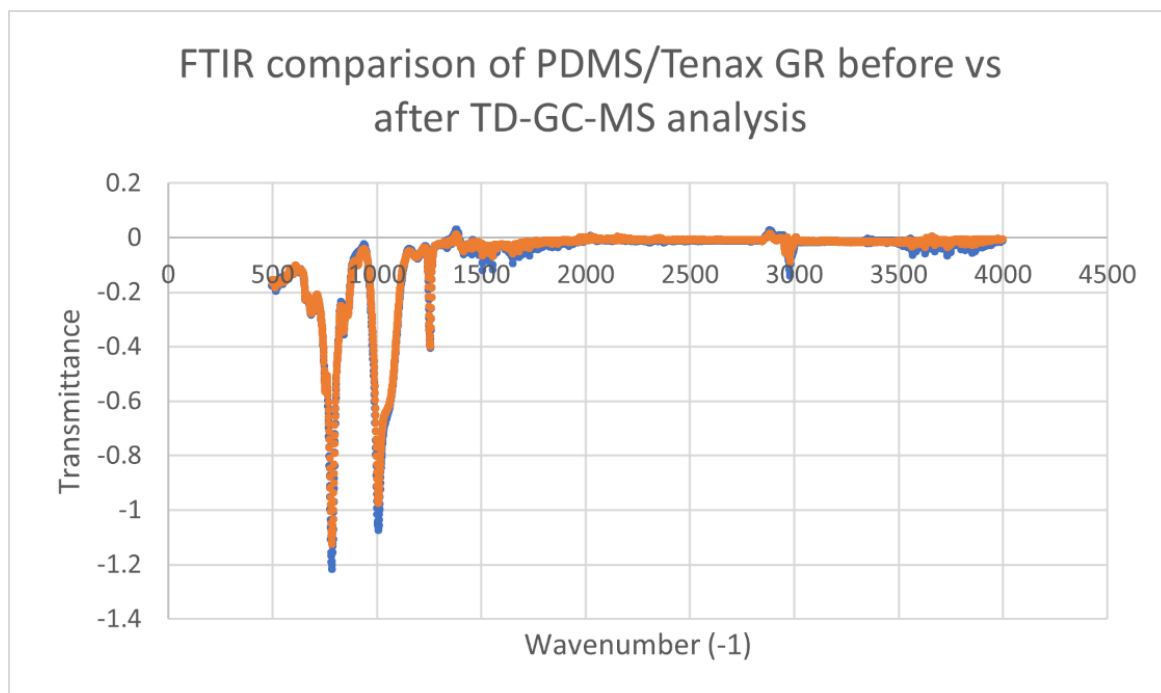
Figure 5.14: FTIR spectra compares the surface bond characteristics of the laboratory synthesized PDMS/Tenax GR before (orange) and after TD-GC-MS analysis (blue).
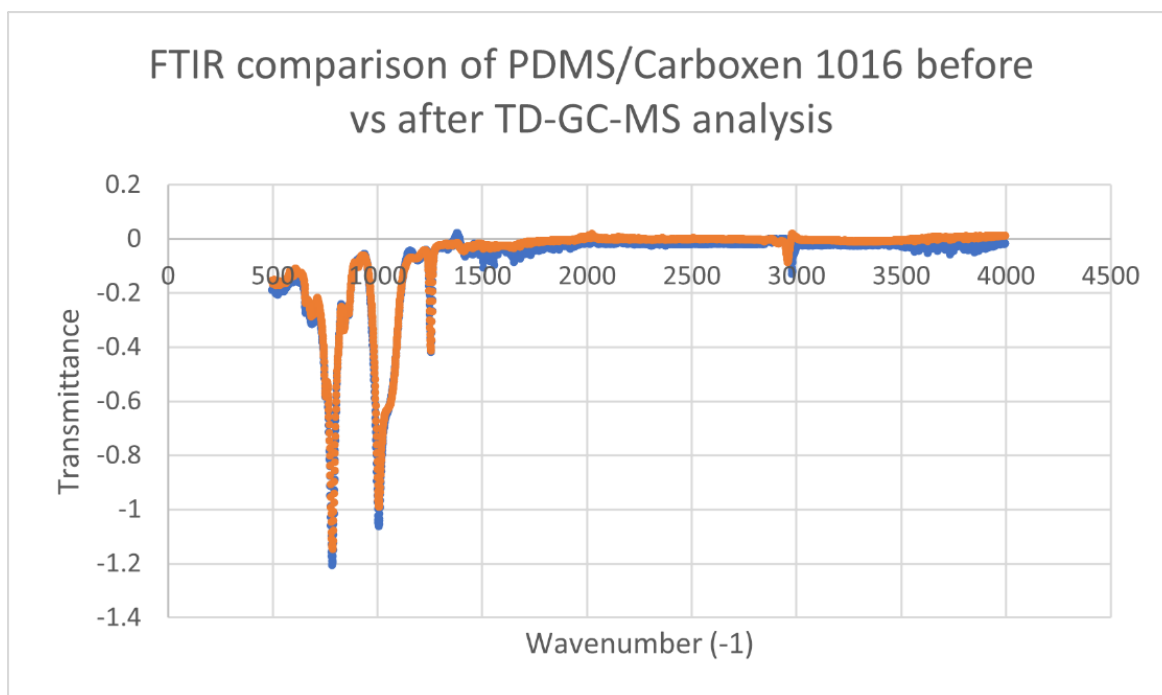
Figure 5.15: FTIR spectra compares the surface bond characteristics of the laboratory synthesized PDMS/Carboxen 1016 before (orange) and after TD-GC-MS analysis (blue).

5.3.3 Scanning Electron Microscopy

Scanning electron microscopy (SEM) was used to deduce any physical changes to the surface of each material. Each material's surface was analysed before and after each TD-GC-MS cycle. The commercially available PDMS showed a smooth, undamaged surface prior to any extraction or TD-GC-MS exposure (Figures 5.16a&b). However, after TD-GC-MS cycles the surface started to show signs of blistering (Figures 5.16c&d). The likely cause of the blistering was due thermal exposure when the organic compounds were desorbed from the material prior to GC injection.

There were distinct differences when comparing the SEM images of the commercially available PDMS to that of the laboratory synthesized PDMS. The laboratory synthesized PDMS showed a range of interconnected cracks (Figures 5.17a&b) after synthesis. However, these cracks smoothed out after the first TD-GC-MS cycle (Figures 5.17c&d). As you increased the number of TD-GC-MS cycles, the laboratory synthesized material started to show signs of blistering similarly to that of the commercially available PDMS (Figures 5.16e&f). However, this was only apparent as you increased the magnification of the microscope.
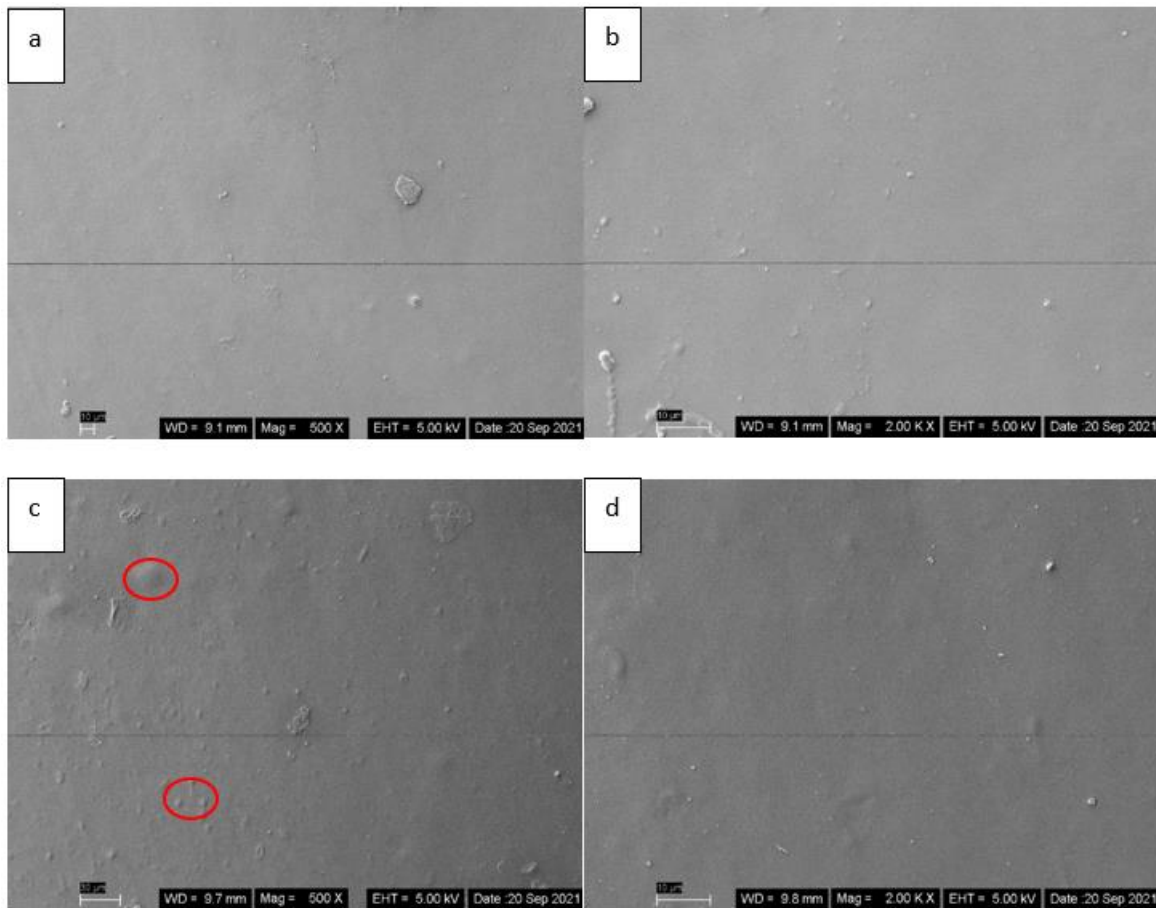
Figure 5.16: SEM images of commercially available PDMS material before TD-GC-MS a) 500x magnification b) 2000x magnification. After 6 TD-GC-MS cycles c) 500x magnification d) 2000x magnification. Red circles highlight the areas of blistering from TD-GC-MS process.

PDMS/Tenax GR surface also showed a range of cracking similarly to that of the laboratory synthesized PDMS indicating that the addition of Tenax GR did not provide any physical strength to the material (5.18a&b). The similarity of the two different materials did not end there as the PDMS/Tenax GR surface cracking was also lost after the first TD-GC-MS cycle (Figures 5.18c&d). There was also noticeable roughness to the surface of PDMS/Tenax GR before and after the primary TD-GC-MS cycle, which over several TD-GC-MS cycles appear to be removed (Figures 5.18e&f).

The PDMS/Carboxen 1016 SEM images showed cracking at the surface prior to TD-GC-MS analysis (Figures 5.19a&b). However, compared to that of the PDMS/Tenax GR there was very little induced surface roughness after TD-GC-MS on the surface of the PDMS/Carboxen 1016 (Figures 5.19c-f).
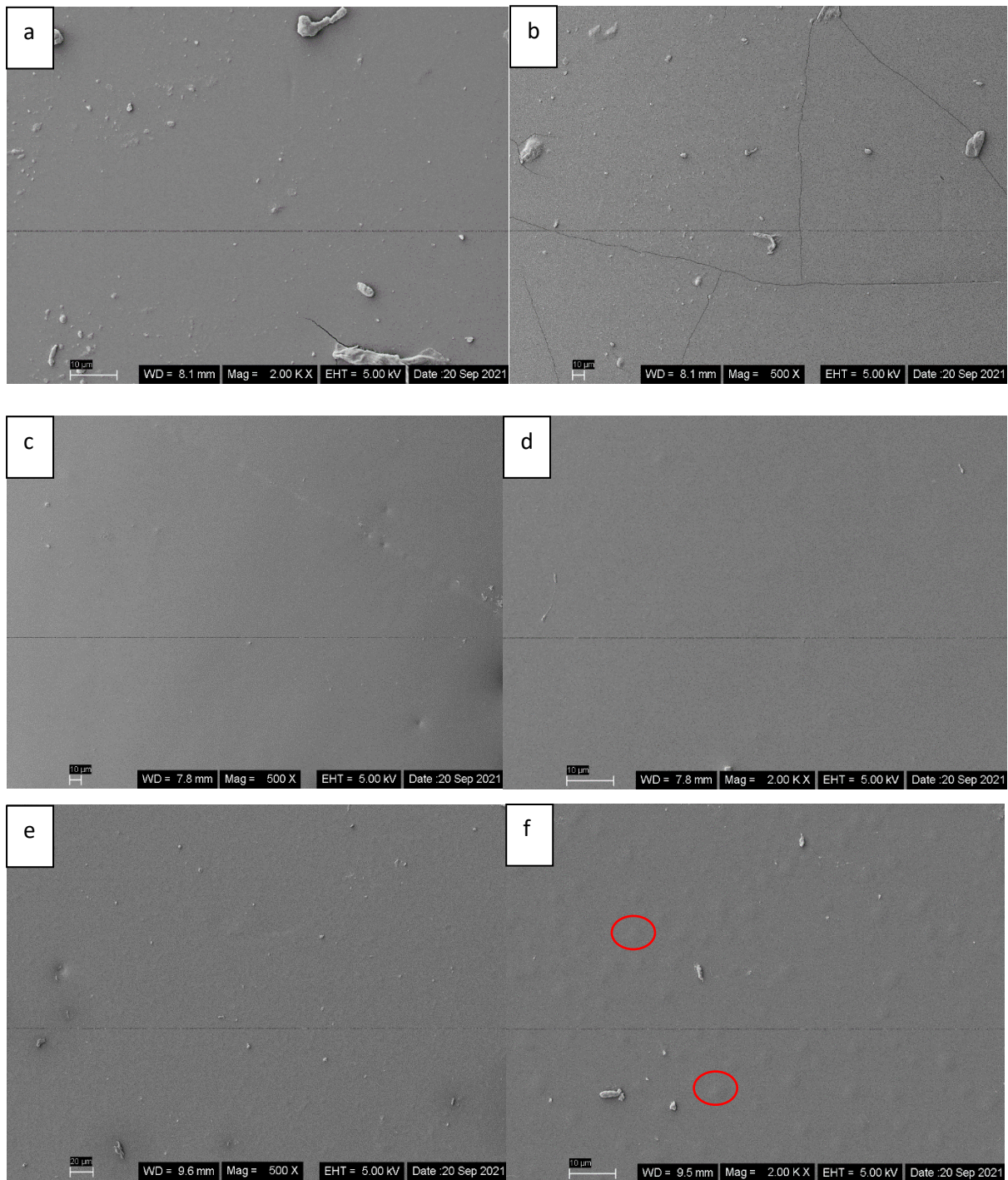
Figure 5.17: SEM images of the laboratory synthesized PDMS material before TD-GC-MS a) 500x magnification b) 2000x magnification. After the first TD-GC-MS cycle c) 500x magnification d) 2000x magnification. After 6 TD-GC-MS cycles e) 500x magnification f) 2000x magnification. Red circles highlight the areas of blistering from TD-GC-MS process.
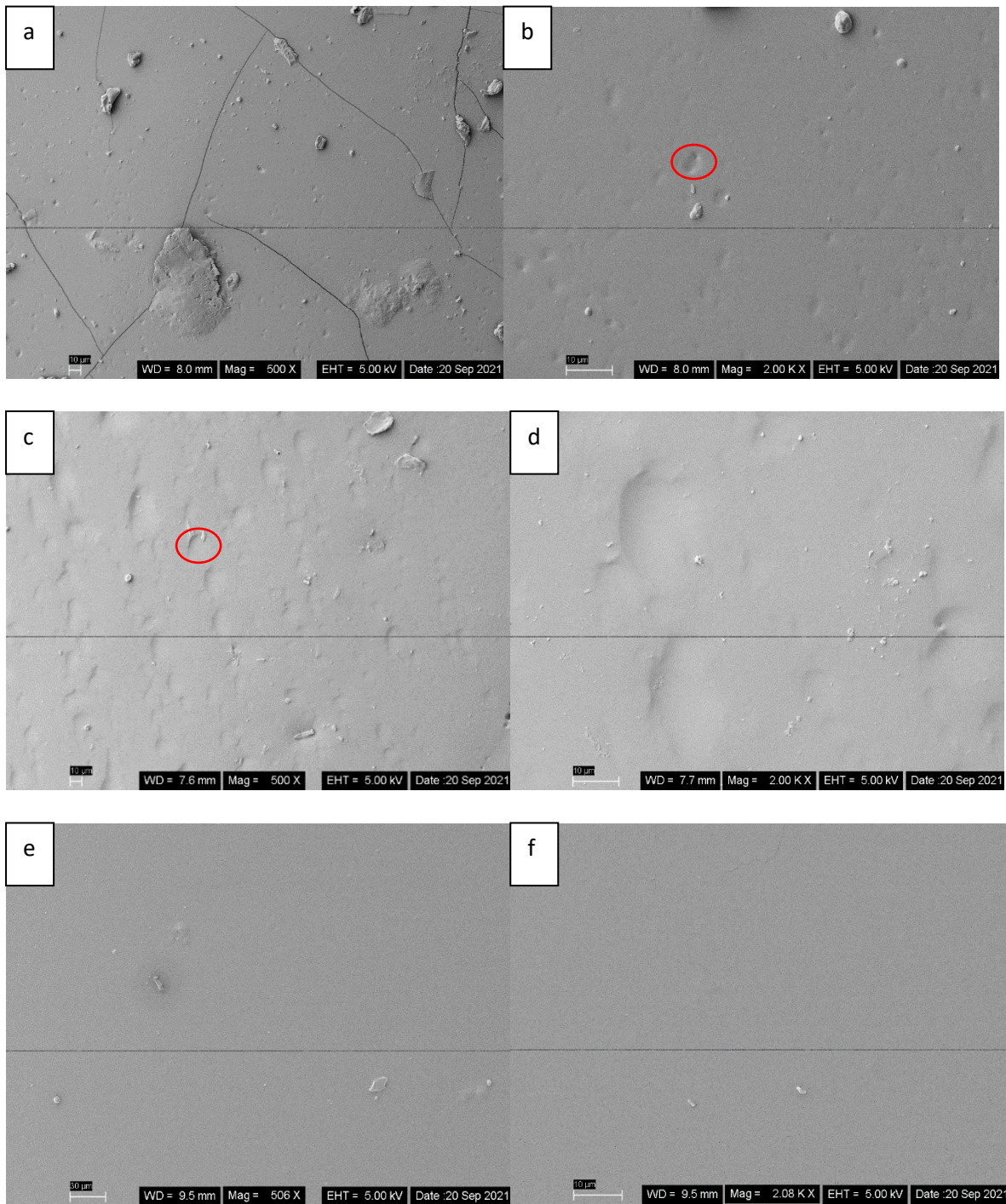
Figure 5.18: SEM images of the PDMS/Tenax GR material before TD-GC-MS a) 500x magnification b) 2000x magnification. After the first TD-GC-MS cycle c) 500x magnification d) 2000x magnification. After 6 TD-GC-MS cycles e) 500x magnification f) 2000x magnification. Red circles highlight the areas of surface roughness.
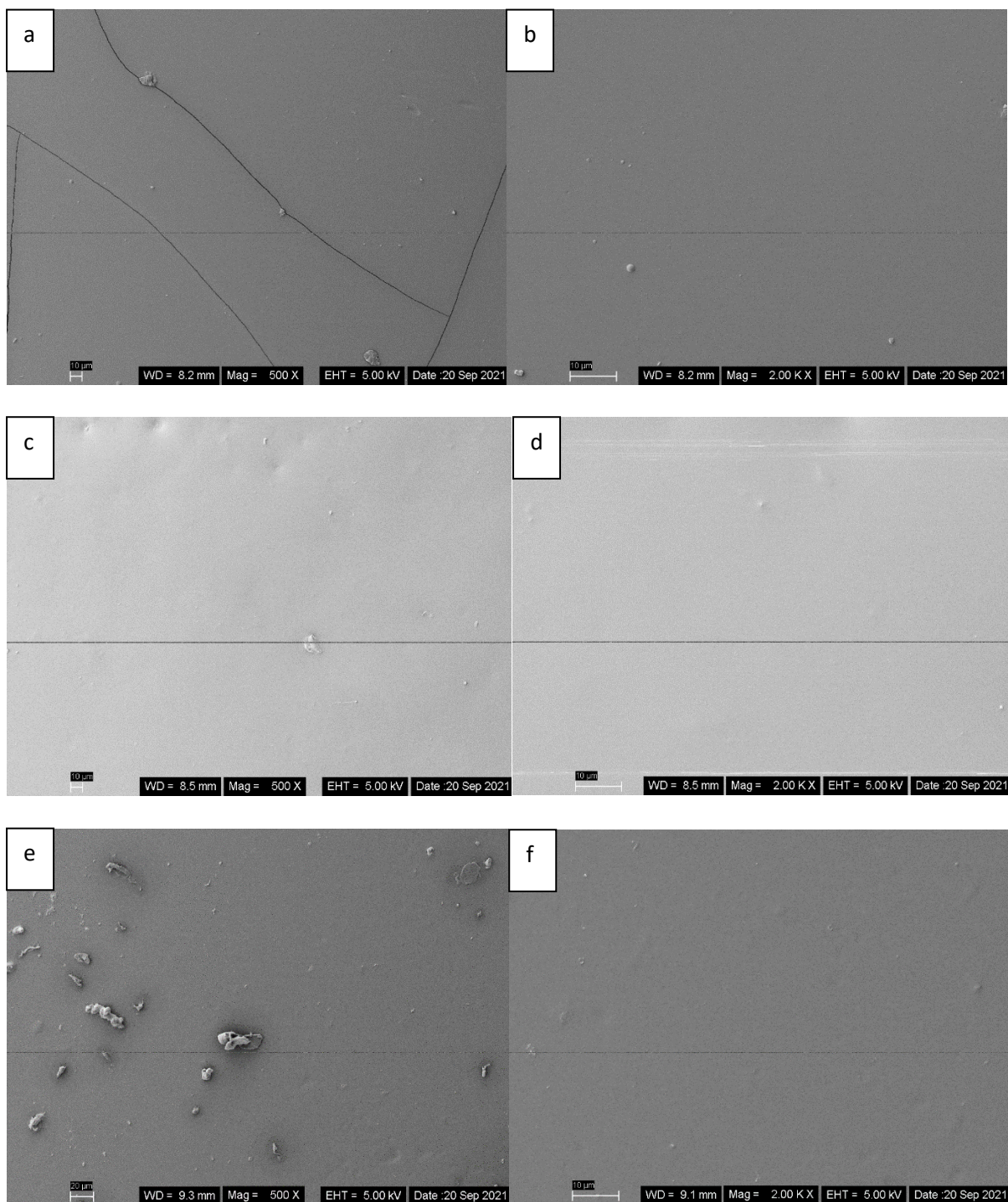
Figure 5.19: SEM images of the PDMS/Carboxen 1016 material before TD-GC-MS a) 500x magnification b) 2000x magnification. After the first TD-GC-MS cycle c) 500x magnification d) 2000x magnification. After 6 TD-GC-MS cycles e) 500x magnification f) 2000x magnification.

5.3.4 Contact Angle Measurements

Contact angle measurements were taken at the surface of each material prior to TD-GC-MS analysis. It was earlier recorded the commercially available PDMS had average contact angle measurements of 110.2, 105.1 and 45.1 degrees for water, ethylene glycol and octan-1-ol, respectively (Table 3.4). Contact angle measurements were taken with each of these 3 solvents at the surface of each material and compared to that of the commercially available PDMS. It was found that all 3 materials had similar surface contact angle measurements to that of the commercial PDMS.

Table 5.1: Average calculated contact angle measurements for water, ethylene glycol and octan-1-ol droplets at the surface of commercially available PDMS, laboratory synthesized PDMS, PDMS/Tenax GR and PDMS/Carboxen 1016.

Solvent	PDMS (Commercial)	PDMS (Lab)	PDMS/Tenax GR	PDMS/Carboxen 1016
Water	110.2 ± 0.6	110.4 ± 0.2	108.9 ± 0.2	111.1 ± 0.6
Ethylene Glycol	105.1 ± 0.5	105.7 ± 0.3	103.3 ± 0.8	106.1 ± 0.3
Octan-1-ol	45.1 ± 1.5	45.3 ± 0.9	44.1 ± 1.1	46.1 ± 1.3

5.4 Discussion

Within this chapter PDMS was synthesized in the laboratory and compared to commercially available PDMS. Furthermore, two novel PDMS-based sorbents were synthesized in tubular form and applied to HiSorb technology. Each material underwent TD-GC-MS analysis to deduce how each performed at extracting organic compounds from aqueous solutions that varied in polarity, molecular weight and chemical functionality.

It was found that of the 9 organic compounds in the extraction mixture, PDMS/Tenax GR extracted the most from each sample for 8/9 compounds (Table 5.2). Given that the PDMS

aspect of the PDMS/Tenax GR was the same PDMS of the laboratory synthesized material. The data clearly showed how adding the Tenax GR to the PDMS polymer material improved uptake of organic compounds from aqueous samples. Tenax GR is a mixture of Tenax TA and 30% graphitised carbon. It falls under the group of porous polymers and is described as a weak sorbent material. In-terms of the strength of sorbent, the stronger the sorbent the better it is at retaining smaller, more volatile compounds. Therefore, a weak sorbent retains heavier compounds from n-C_7 to n-C_{30} (BP $100 - 450^oC$). The TD-GC-MS data however showed that in combination with PDMS, Tenax GR improved the uptake of organic compounds with carbon chains and boiling points outside of this range. The reasoning behind this would be the addition of the graphitised carbon. Graphitised carbon is a slightly stronger sorbent material and therefore better than the Tenax TA at extracting the more volatile organic compounds. With a 30% concentration of graphitised carbon in the Tenax aspect of the PDMS/Tenax GR sorbent, it was expected that the more volatile organic compounds within the extraction mixture could be extracted. For the extraction of butanol there was little difference between each of the PDMS-based materials (Figure 5.9). Therefore, the only organic compound in which PDMS/Tenax GR did not extract the greatest mass of was pyridine (Figure 5.8). Pyridine was one of the most polar compounds in the extraction mixture with a value of 0.71 (Table 2.3). This lower extraction performance of the PDMS/Tenax GR therefore would be explained by the hydrophobic nature of the Tenax TA within the sorbent phase. As such, the Tenax TA would inhibit the extraction of the more polar compounds such as pyridine.

The sorbent Carboxen 1016 falls under the category of carbonised molecular sieve [145]. Carbonised molecular sieve sorbent materials are relatively strong sorbent materials and are used to extract more volatile compounds (n-C_2 to n-C_6). Therefore, the organic compounds in the extraction mixture from this study would fall outside of this range. The TD-GC-MS data from this chapter well supported this with the PDMS/Carboxen 1016 being the worst performing sorbent in extracting 4/9 organic compounds within the mixture. Furthermore, unlike the PDMS or Tenax GR, the carboxen 1016 slightly hydrophilic and therefore could retain water and introduce this into your GC. The main surprise in the data was that the PDMS/Carboxen 1016 did not extract the most pyridine or acrylonitrile, the two most polar compounds in the mixture. With the carboxen 1016 being the most hydrophilic sorbent in the

study, it was hypothesized that the PDMS/Carboxen 1016 would extract the greatest quantities of these compounds.

Table 5.2: Ranking of how each material did at extracting each of the corresponding organic compounds, with 1 = most and 4 = least.

Organic Compound	Commercial PDMS	Laboratory PDMS	PDMS/Tenax GR	PDMS/Carboxen 1016
Acrylonitrile	2	2	1	4
Butanol	1	1	1	1
Cyclohexane	2	2	1	2
Ethyl Acetate	2	2	1	4
Heptane	2	3	1	4
Hexanal	2	2	1	2
Pyridine	1	3	2	4
Styrene	2	2	1	2
Toluene d8	2	2	1	2

The other comparison to discuss from the TD-GC-MS data was how synthesizing PDMS in the laboratory varied extraction compared to that of the commercially available PDMS. For most of the organic compounds in the extraction mixture, there was very little to differentiate between the two PDMS materials. The main compound which showed the greatest variance was the extraction of pyridine in which the commercially available PDMS extracted the most (Figure 5.8). Each of the PDMS materials consisted of the same chemical make-up in which was supported by the FTIR data (Figure 5.11). Therefore, the extraction difference between the two materials towards pyridine would most likely be due a physical characteristic such as elasticity. However, to conclude this as the reason each material would have to undergo further tests such as Atomic Force Microscopy (AFM).

Within the experiment 3 different PDMS-based sorbent materials were synthesized PDMS, PDMS/Tenax GR and PDMS/Carboxen 1016, with 7 samples required per material (Section 2.1.4). Rather than synthesizing each material in one singular batch, the 7 samples were made independent of each other. The TD-GC-MS data showed little variance in the average uptake

of organic compounds from sample to sample as demonstrated by the small standard deviation values. Therefore, it can be said that the novel method of producing each material from batch to batch is reproducible for this application. Another piece of important information that consistent average uptake tells us over several TD-GC-MS cycles is that the synthesized materials were thermally stable throughout the experiment. This was best demonstrated by looking at the chromatograms of all the materials compared to that of the PDMS. When comparing the background of the commercially available PDMS to that of the laboratory synthesized the data shows that the laboratory-based PDMS was showed slightly more background than the commercially available PDMS, but this fell within the acceptable range of Markes International as the two chromatograms were almost equivalent (Figure 5.20).
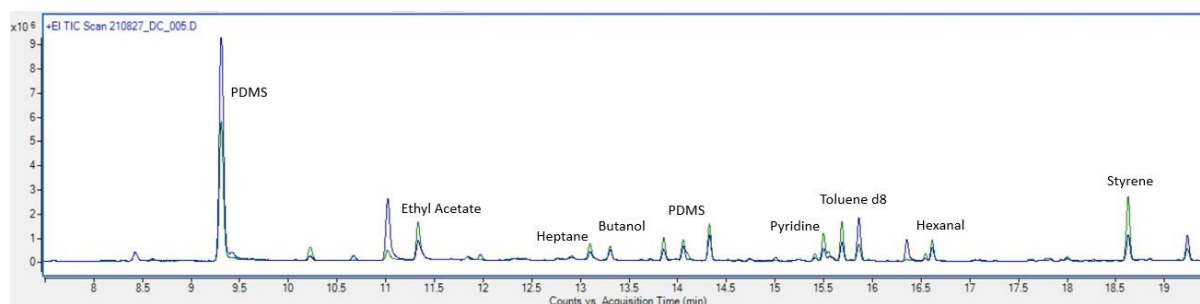
Figure 5.20: Overlapped chromatogram of commercially available PDMS (green) compared to the PDMS that was synthesized in the laboratory (blue).

As for the PDMS/Carboxen 1016 compared to the commercially available PDMS, the TD-GC-MS data showed that the Carboxen 1016 did not increase the background on the chromatogram (Figure 5.21). This told us that the Carboxen 1016 was thermally stable in the PDMS mould and was not released during the thermal desorption cycle. However, the PDMS/Tenax GR showed the largest background results on the TD-GC-MS data (Figure 5.22). Overall, all the chromatograms fell within the acceptable specifications laid out by Markes International. As you can see from Figures 5.20 – 5.22, all the peaks that represent the organic compounds from the extraction mixture are clearly visible with little overlap from the PDMS-based sorbent materials.
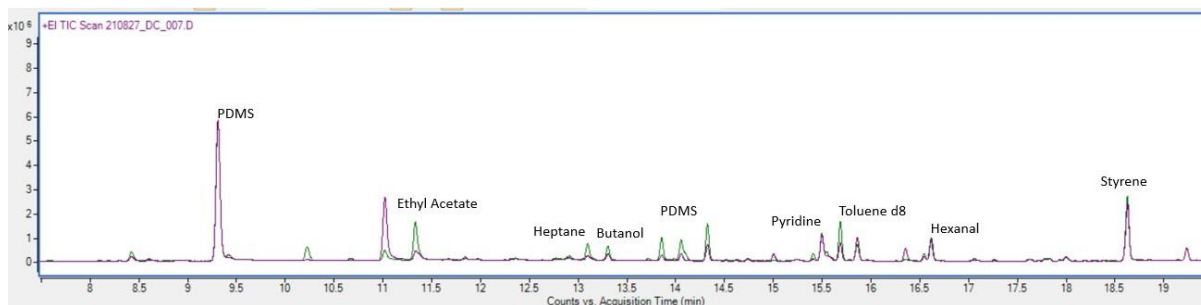
Figure 5.21: Overlapped chromatogram of commercially available PDMS (green) compared to the PDMS/Carboxen 1016 (purple).
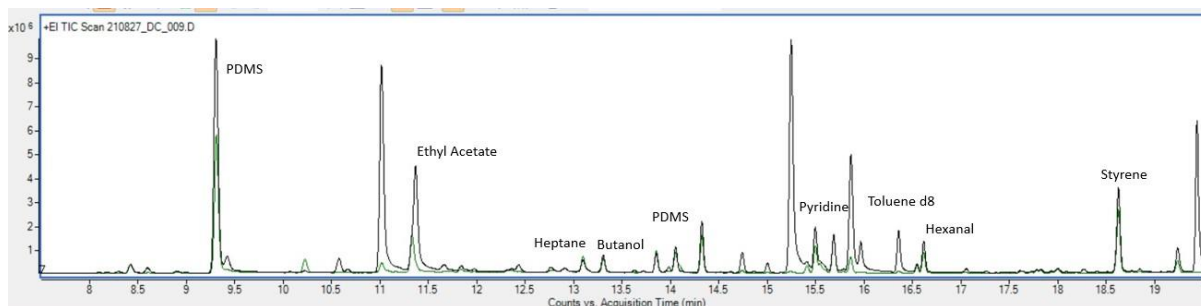
Figure 5.22: Overlapped chromatogram of commercially available PDMS (green) compared to the PDMS/Tenax GR (black).

As well as quantitatively measuring the uptakes of each organic compound in the extraction mixture. FTIR, SEM and contact angle measurements were taken after each extraction and TD-GC-MS cycle. This allowed for the measurement of any physical or chemical changes to each material from the TD-GC-MS process. The FTIR and SEM data showed no change in the surface chemistry of the materials throughout the experiment. However, this was not surprising given no noticeable difference in extraction data between run 1 and 6 but furthermore, the fact that all materials were inert. The most surprising discovery from the SEM data was blistering at the surface of both types of PDMS after the TD-GC-MS process (Figures 5.16 and 5.17). This physical change would explain the presence of PDMS peaks as background on the chromatogram. Each time the material was heated to desorb the organic compounds a fine layer of PDMS is converted to the gas phase and carried with the organic compounds into the GC-MS. There were physical differences between the two types of PDMS prior to TD-GC-MS in which the PDMS that was synthesized in the lab displayed cracking across the surface (Figures 5.17a&b). This was also present in the PDMS/Tenax GR and

PDMS/Carboxen 1016 samples at the same stage (Figures 5.18a&b and 5.19a&b). A possible explanation for this would be stretching of the material when being removed from the glass sleeves after crosslinking. Similarly to the PDMS, this surface cracking was removed after the first TD-GC-MS cycle for each material and once again this would be apparent in the GC chromatogram in the form of background.

5.5   Conclusion

To conclude, this chapter demonstrated how adding two different types of sorbents, Tenax GR and Carboxen 1016 to PDMS influenced each material's ability to organic compounds from aqueous samples. Each of the materials were compared to two different PDMS materials, one synthesized in the laboratory and the other the current PDMS material used in HiSorb technology. Of all the materials used in this chapter, the TD-GC-MS results showed that the PDMS/Tenax GR had the greatest success at extracting the organic compounds. However, all the sorbents showed both chemical and physical robustness with excellent thermal stability and inertness. The novel method used to synthesize these PDMS-based materials was analysed to show inter-batch reproducibility and the foundations for developing a greater range of sorbent materials.

Chapter 6: Conclusion and Future Works

6.1　Conclusion

This project looked at how different methods of PDMS modification influenced how each polymer sorbent performed at extracting organic compounds with varying polarity, chemical structure and volatility from an aqueous solution. The primary aim of the project was to modify the currently used PDMS sorbent material to improve organic compound extraction as measured by TD-GC-MS. This was achieved by swelling the material in an organic solvent and spiking the mixture with various amines that differed in polarity. As such, the currently used PDMS material was modified with amines encapsulated both within the matrix and at the surface. This novel method of PDMS modification to improve organic compound extraction was best demonstrated through the variable quantities of each organic compound extracted from the extraction mixture compared to that of the original PDMS material. Unfortunately, after the first thermal desorption cycle this modification dramatically dropped as the amines were desorbed from the material and into the GC-MS as supported by the large background peaks on each chromatogram. However, the most notable recording from this data set was that the amine encapsulated PDMS materials differentiated from that of unmodified PDMS when no amines were present at the surface. This indicated that when amine molecules were embedded in the matrix of the PDMS material, rather than at the surface, variable levels of organic compounds were extracted. In previous studies recorded in the literature, the focus was how modifying the surface of a sorbent material with various compounds or other sorbent materials influenced the extraction performance. Furthermore, there were no found studies in the literature that showed how modification to the matrix of a PDMS polymer material influenced extraction until this study.

With the thermal instability of the encapsulated PDMS materials not meeting the requirements of the funding company. The next logical step was to investigate whether the improved extraction characteristics governed by the amines in the PDMS material could be sustained throughout the thermal desorption process by chemically bonding them to the PDMS monomers. As such, it was at this point of the project that the intentions of modifying the current PDMS material disintegrated and instead all PDMS-based samples were made from their monomer components within the laboratory. To chemically bond the amines to PDMS, epoxy-terminated PDMS was used. These new PDMS-based materials were then compared to that of the currently used PDMS. It was found that chemically bonding the

amines to PDMS did not yield the same extraction results as when encapsulated. However, the amine bonded PDMS materials proved to be more thermally stable than the encapsulated equivalents with greater reproducibility of each organic compound extracted by each material over several thermal desorption cycles with lower background on each chromatogram.

The final chapter looked towards how known, well-established sorbent materials could be embedded into the PDMS to improve organic compound extraction. The sorbent materials used in this section were currently used in thermal desorption tubes with adsorption capabilities along with chemical inertness, thermal stability and large surface area. Each of these chemical and physical properties allowed for the extraction of various organic compounds with sample integrity. However, there was no reported literature or methodologies associated with incorporating these sorbents in PDMS. Two different types of sorbents were successfully synthesized in PDMS and moulded to HiSorb specificity. Tenax GR which was a hybrid of porous polymer and graphitised carbon black, and Carboxen 1016 which was a carbonised molecular sieve. Of the PDMS-based materials used in this study the PDMS-Tenax GR had the greatest extraction ability, outperforming the currently used platinum-cured PDMS and PDMS/Carboxen 1016. Furthermore, all the sorbents synthesized in this chapter had acceptable levels of background on the chromatogram. A result which up to this point, had not been achieved but was of great importance to the funding company and any prospective customers.

Overall, each of the three methods used to develop alternative sorbent materials showed extraction capabilities towards organic compounds in aqueous solutions with the commercially embedded sorbent materials showing the most promise. As this was an industrial-focused project, this TD-GC-MS data showed great potential for a new sorbent product range within the sample extraction market. However, the method of making the tubular shaped material using glass tubes as a vessel could not be replicated on a manufacturing level. Alternatively, it would have to be extruded by a large-scale manufacturer and bought in large quantities. Given that only 11 mm of material is used per probe, buying many meters of this product would therefore include a large up-front cost which could prove a long time to pay off.

There were many study limitations to overcome during this study, mainly being equipment availability. All the analytical equipment used such as TD-GC-MS, SEM and FTIR had to be

booked out when available from 3rd parties. This had huge bearings on the project as this did not allow for the running of simple tests prior the main analysis which was extraction. As I prepared each material in the laboratory for analysis, I only had one opportunity to get the results from that material. If the material did not work in the equipment, I would have to go make more and wait weeks or even months for the equipment to be available again. The sample run time on the TD-GC-MS was approximately 45 minutes per sample. Therefore, to run several samples meant the equipment was running for days and the company would need the equipment back shortly after I finished to carry out their research on site. I believe with more equipment at my disposal I would have been able to test a greater range of samples and techniques as discussed in the future works section. Another time limiting factor was the impact of COVID-19 on my research. Lockdown occurred exactly halfway through my studies. Eventually, I was allowed to use the university facilities in my building however all the testing equipment was operational external to this. This delay in accessing these facilities also meant obtaining fewer types of samples as I planned.

However, to conclude I believe I have provided the funding company a solid basis for future research and investment into various PDMS-based materials and phases for HiSorb technology. Prior to this study, there was no data or ideas on how to develop these materials and what impact the various sorbents have on organic compound extraction. Since finishing the company have dedicated a specialist team to carry on the research based off my findings and consultancy throughout the project and beyond. As such, in the last 12 months Markes International have used the data demonstrated in Chapter 5 to release three new HiSorb phases. Two bi-phasic sorbents, PDMS/Carbon Wide Range (PDMS/CWR) and PDMS/Divinylbenzene (PDMS/DVB). As well as a triple phase PDMS/CWR/DVB. I was fortunate enough to be offered the role as Product Manager at the sponsor company upon completion of the practical aspect of my PhD, for which HiSorb was one of many products I managed. As such, I was able to learn more about how these new phases were produced on an industrial scale using specialist equipment as well as see how this met the needs of the consumer whether through sales with various industries or working with university departments on collaborations. Overall, I still believe that this area of material science can offer further benefits to various academia and industrial applications, ranging from medical devices to water purification analysis to name a few.

6.2   Future Works

The results from this thesis have laid the foundation for a new range of HiSorb phases. The results detailed different methods of modification and how each method has an impact on properties such as extraction and thermal stability. The most successful result from the thesis was the combination of PDMS and pre-existing sorbent materials, PDMS-Tenax GR due to the improved extraction results compared to PDMS with an acceptable level of background (Section 5.3). However, the results only showed how well this sorbent performed towards a small range of semi-volatile organic compounds (SVOCs) in an aqueous solution. Furthermore, the material was only made using one mesh size (particle size) and concentration. In-order to optimise the material, future works should investigate varying ratios of PDMS to Tenax GR and how this impacts extraction of the organic compounds as well as seeing if increasing or decreasing the sorbent particle size influenced VOC extraction.

PDMS-Carboxen 1016 was also used in this study. However, did not extract the organic compounds selected within this extraction mixture as well as PDMS or PDMS/Tenax GR. This was later explained in the literature which showed that Carboxen 1016 is more effective towards more volatile compounds. HiSorb technology can also be used in headspace analysis. This is when the gases above a liquid or solid is analysed via adsorption to the HiSorb sorbent phase, oppose to immersive as studied in this thesis. Typically, the lower weight (less than n-C_7), more volatile compounds would be located here and an experiment to see whether the PDMS-Carboxen 1016 outperforms the PDMS and PDMS-Tenax GR would be of great interest and value to the industry. The reason I say value to the industry is because PDMS is so good extracting the heavier organic compounds, there is still scope for a HiSorb probe to extract organic compounds that fall under the more volatile range. Unfortunately, due to limited equipment time and facilities I was constrained to picking just one extraction mixture.

There are also many other sorbents within each of these categories that could be successfully embedded into PDMS using this novel preparation method. As with Tenax-GR and Carboxen 1016, information as to which organic compounds adsorb to the surface of each sorbent is already known but the key scientific question here would be how does each of these sorbents perform towards these groups of compounds when embedded within a PDMS matrix? My approach to answering this would be to perform a series of experiments with a range of PDMS-based sorbent materials that have commercially available sorbents embedded,

similarly to how I conducted the experiments in Chapter 5. However, with unlimited access to the TD-GC-MS equipment, I would do independent, custom extraction mixtures based on the literature that supports these commercially available sorbent materials.

This research only looked a bi-phasic samples (samples made of just 2 phases). A next step would be to investigate the extraction of PDMS-based materials with more than 1 other sorbent in the matrix. This has been well documented in SPME materials and increases the range of molecules extracted in-terms of polarity and volatility compared to just PDMS (Section 1.7).

When assessing the methods of bonding vs encapsulation of amines in PDMS, both had advantages and disadvantages. The encapsulation of amines in PDMS increased the extraction efficiency towards select organic molecules. The best example of this being the encapsulation of N,N-Bis[3-(methylamino)propyl]methylamine in PDMS and how that material improved on the extraction of pyridine compared to that of PDMS. However, these amines encapsulated sorbent materials showed unacceptable levels of thermal stability and reproducibility over several extractions. The opposite occurred for when the amines were bonded to PDMS. All-be-it more thermally stable and demonstrating consistent extraction capabilities, when bonded to the PDMS it did not demonstrate as significant increases in organic compound uptake. If to continue this area of research, my suggested ideas would be to encapsulate much more stable compounds such as nanoparticles or zeolites in the PDMS matrix. This was discussed during this thesis however incurred a cost greater than what the product was worth. As for bonding to PDMS, the next logical step would be to bond compounds to the surface of the material. Much literature shows how you can functionalise the surface of PDMS with various types of compounds but little, if not any, research into how these materials perform as sorbents with TD-GC-MS application.

One area of data that was not obtained for this research was robustness testing. One such advantage HiSorb has over competitive products is its robustness. Whether this is how many uses you get per probe or how long the material physically lasts before ripping or dropping in performance. Such tests should include elasticity and stress resistance and even open the opportunity to deduce the effects of elasticity on analyte extraction and how this could be optimised.

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