Novel materials for VOC analysis

by
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Thesis presented in partial fulfilment of the requirements for the degree Master of Science in Polymer Science at the University of Stellenbosch

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December 2012

Declaration

By submitting this dissertation, I declare that the entirety of the work contained therein is my own, original work, that I am the owner of the copyright thereof (unless to the extent explicitly otherwise stated) and that I have not previously in its entirety or in part submitted it for obtaining any qualification.

Date: December 2012

Abstract

The need to analyse and detect volatile organic compounds (VOCs) at trace levels has led to the development of specialized sample preparation techniques. The requirement for trace analysis of VOCs stems from the negative effects they have on the environmental and human health. Methods for the analysis of non-polar VOCs commonly found as trace contaminants in water and analysis of more polar oxygenated compounds commonly found in zero-VOC water-based paints were developed. Solid phase micro extraction (SPME) was employed and extraction of the majority of the target analytes could be achieved at levels below 0.3 $\mu g.l^{-1}$. In an attempt to further improve the detection of these two target analyte groups, novel materials based on poly(dimethyl siloxane) (PDMS) were investigated as possible extraction phases for VOCs, with the focus specifically on the analysis of the polar analytes in paint. Conventional free radical polymerization was used to synthesize poly(methyl methacrylate-graft-poly(dimethyl siloxane) (PMMA-g-PDMS), poly(methacrylic acid)-graft-poly(dimethyl siloxane) (PMAA-g-PDMS), polystyrene-graft-poly(dimethyl siloxane) (PSty-g-PDMS) and poly(butyl acrylate)-graft–poly(dimethyl siloxane) (PBA-g-PDMS). These polymers have a copolymer functionality which presents a series of different polarities. The MMA-g-PDMS and MAA-g-PDMS as well as the homopolymers were electrospun into nanofibers. The low glass transition temperature and molecular weight of the PBA-g-PDMS meant that this polymer could not be electrospun. Scanning electron microscopy (SEM) was used to study the fiber morphology of the electrospun fibers and the non-beaded fibers were further investigated. Polyacrylonitrile-graft-poly(dimethyl siloxane) (PAN-g-PDMS) previously synthesized and electrospun by another member of the group were also investigated for use as possible extraction material in volatile analysis. The thermal stability of the nanofibers at 200°C was studied using thermal gravimetric analysis (TGA). This property is important since after the target analytes are extracted using the nanofibers, elevated temperatures are used to thermally desorp the volatile analytes from the extraction materials prior to GC analysis. The PAN-g-PDMS, MMA-g-PDMS and PMMA showed no significant weight loss during thermal evaluation, however, it was observed that the PMMA and PMMA-g-PDMS nanofibers looses their nanostructure and that the PAN-g-PDMS nanofibers changes colour from white to yellow to rust brown. The polymers based on MAA showed weight losses of more than 10% after one hour of exposure to the elevated temperatures, but the nanostructure remained intact. The PAN-g-PDMS, PMAA-g-PDMS and PMAA nanofibers were evaluated as possible extraction materials for VOC analysis. The nanofibers were evaluated using a similar approach to that of stir bar sorptive extraction (SBSE). Headspace sorptive extraction (HSSE) using a commercially available PDMS stir bar and the novel materials were used to evaluate the extraction efficiency of the different materials. The optimized

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extraction method developed using SPME were employed for the extraction using the nanofibers and PDMS stir bar. It was noted that the nanofibers lose their extraction capabilities during the first extraction/desorption cycle possibly due to thermal degradation therefore each of the materials can only be used in a single extraction. The majority of the non-polar analytes were extracted using the nanofibers at levels of 500 $\mu g.l^{-1}$, however it was noted that the commercially available SPME extraction materials and the PDMS stir bar had superior extraction efficiencies for the specific target analytes. In the evaluation of the nanofibers for extraction of the more polar oxygenated analytes it was noted that 2-Ethylhexylacrylate was the only analyte to be extracted by all of the materials. The PAN-g-PDMS extracted three of the four analytes at levels of 100 $\mu g.l^{-1}$. At lower analyte concentrations of 10 $\mu g.l^{-1}$ only two of the four acrylate compounds were detected using the PAN-g-PDMS nanofibers. Ethyl acrylate was not extracted by any of the novel materials, whereas in SPME using the CAR/PDMS fiber, the LOD was determined to be below 1 $\mu g.l^{-1}$. Although these materials were not superior to the commercially available phases, this is only the case for the specific target analytes analyzed.

Opsomming

Die behoefte vir die analiese van vlugtige organiese verbindings (VOS) op spoorvlak, het gelei tot die ontwikkeling van gespesialiseerde monster voorbereidingstegnieke. Die vereiste vir die spoor analiese van die VOS het ontstaan uit die negatiewe uitwerking wat hierdie stowwe het op die omgewing en menslike gesondheid. Metodes vir die analiese van nie-polêre VOS wat algemeen voorkom as spoorkontaminante in water en polêre suurstofryke verbindings wat algemeen voorkom in nul-VOS water-gebaseerde verf was ontwikkel. Soliede fase mikro-ekstraksie (SFME) was gebruik, en die ekstraksie van die meerderheid van die teikenstowwe kon gedoen word op vlakke laer as 0,3 $\mu g.l^{-1}$. In 'n poging om die opsporing van hierdie twee teiken analietgroepe verder te verbeter, is nuwe materiale gebaseer op polidimetielsiloksaan (PDMS), ondersoek as moontlik ekstraksiefases vir VOS, met die fokus spesifiek op die analiese van die polêre stowwe in verf. ’n Konvensionele vrye radikaal polimerisasieproses was gebruik om poli (metiel- metakrilaat)-ent-poli(dimetielsiloksaan) (PMMA-g-PDMS), poli(metakrilaatsuur)-ent–poli (dimetielsiloksaan) (PMAA-g-PDMS), polistireen-ent-poli(dimetielsiloksaan) (PSty-g-PDMS) en poli(butielakrilaat)-ent-poli(dimetielsiloksaan) (PBA-g-PDMS) te sintetiseer. Hierdie ko-polimere het 'n kopolimeer funksionaliteit wat 'n reeks van verskillende polariteite bied. Die MMA-g-PDMS en MAA-g-PDMS sowel as die homopolimere was ge-elektrospin in orde om nanovesels te vorm. Die lae glasoorgangstemperatuur en molekulêre gewig van die PBA-g-PDMS het beteken dat hierdie polimeer nie elektrospin kon word nie. Skandeerelektronmikroskopie (SEM) was gebruik om die veselmorfologie van die ge-elektrospinde vesels te bestudeer en die nanovesels wat ’n eweredige oppervlak gehad het, was verder ondersoek. Poliakrilonitriel-ent-poli(dimetielsiloksaan) (PAN-g-PDMS) wat voorheen gesintetiseer en ge-elektrospin was deur 'n ander lid van die groep is ook ondersoek vir gebruik as moontlik ekstraksiemateriaal vir die analiese van vlugtige stowwe. Die termiese stabiliteit van die nanovesels was by 200°C bestudeer met behulp van ‘n termiese gravimetriese analiese (TGA) instrument. Hierdie eienskap is belangrik, aangesien die teikenstowwe by hoë temperature van die nanovesels gedesorbeer word voor die GC-analiese. Die PAN-g-PDMS, MMA-g-PDMS en PMMA het geen beduidende gewigsverlies tydens termiese evaluering gehad nie, alhoewel dit egter waargeneem was dat die PMMA en PMMA-g-PDMS nanovesels hulle nanostruktuur verloor en dat die PAN-g-PDMS nanovesels se kleur verander van wit na geel na roesbruin gedurende die termiese analiese. Die polimere wat gebaseer was op MAA het ’n gewigs-verlies van meer as 10% getoon na 'n uur van blootstelling aan die verhoogde temperature, maar die nanostruktuur het ongeskonde gebly. Die PAN-g-PDMS, PMAA-g-PDMS en PMAA nanovesels was geëvalueer as moontlike ekstraksiemateriale vir VOS-analiese. Die nanovesels was geëvalueer met 'n soortgelyke benadering tot dié van “stir bar“ sorpsie ekstraksie

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(SBSE). Bo-ruimte sorpsie ekstrasie is gebruik om die ekstraksie-doeltreffendheid van die verskillende materiale (kommersiële PDMS en nanovesels) te evalueer. Die geoptimaliseerde ekstraksiemetode ontwikkel in SFME was gebruik vir die ekstraksie van die VOS met die nanovesels en die PDMS "stir bar". Dit was waargeneem dat die nanovesels hul ekstraksievermoë verloor tydens die eerste ekstraksie/desorpsie siklus, moontlik as gevolg van termiese degradasie dus, kon die materiale slegs 'n enkele maal gebruik word vir die ekstraksie. Die meerderheid van die nie-polêre stowwe was ge-ëkstraeer deur gebruik te maak van die nanovesels op vlakke van 500 $\mu g.l^{-1}$, maar die kommersieel beskikbare SFME ekstraksie materiale en die PDMS "stir bar" se ekstraksie-doeltreffendheid vir die spesifieke stowwe was beter. In die evaluering van die nanovesels vir die ekstraksie van die meer polêre suurstofryke stowwe was daar waargeneem dat 2-etielheksielakrilaat die enigste analiet was wat ge-ëkstraeer was deur al die materiale. Die PAN-g-PDMS kon drie van die vier polêre stowwe op vlakke van 100 $\mu g.l^{-1}$ opspoor. By laer analietkonsentrasies van 10 $\mu g.l^{-1}$ kon slegs twee van die vier akrilaat verbindings opgespoor word deur gebruik te maak van hierdie nanovesels. Etielakrilaat was nie ge-ëkstraeer deur enige van die nuwe materiale nie, terwyl in SFME met die gebruik van die CAR/ PDMS vesel, die analiet op vlakke onder 1 $\mu g.l^{-1}$ opgespoor kon word. Alhoewel hierdie nuwe materiale nie beter is as die kommersieel beskikbare ekstraksiemateriale nie is dit net die geval vir die spesifieke teiken analietgroepe wat ondersoek was in hierdie studie.

Acknowledgements

I would like to express my gratitude for the guidance that Prof Mallon and Dr de Villiers gave me throughout this thesis. Thank you for all your patience. Thank you to Gareth, Wael and Andreas for taking the time to teach me everything I needed to know in the lab. Thank you to everyone else in the chemistry and polymer chemistry department that assisted me throughout this project.

A very special thanks to Dr Mcleary and the rest of my colleagues at Plascon for all your encouragement, words of wisdom and all the good times I had working here in Stellenbosch. Angela, thanks for all lunch breaks and good wine that we shared during the past three years, it was a real pleasure having such a good friend at work. I also want to thank Plascon for giving me the opportunity to do my Masters.

For my parents, brother and sister, thank you for all the support, love, prayers and good times. Thank you for giving me the opportunity to come and study in such a beautiful place.

To all my friends, especially Anneli and Shani, for listening and supporting me when times were tough.

Finally, to my heavenly Father for walking beside me every day of my life. “Trust in the Lord with all your heart and lean not on your own understandings, in all your ways acknowledge him and he will make your path straight”.

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Glossary

Abbreviations

2-EHA:	2-ethylhexylacrylate
AIBN:	2,2'-azobis(isobutyronitrile)
ASTM:	American society for testing and materials
ATRP:	Atom transfer radical polymerization
BA:	Butyl acrylate
CW/DVB:	Carbowax/Divinylbenzene
CAR/PDMS:	Carboxen/Polydimethylsiloxane
$CDCl_3$:	Deuterated chloroform
CNT:	Carbon nano tubes
CRP:	Controlled radical polymerization
DMAc:	Dimethyacetimide
DMSO-D_6:	Deuterated dimethyl sulfoxide
EDS:	Energy dispersive detector
EPA:	Environmental Protection Agency
EU:	European Union
FRP:	Free radical polymerization
GC:	Gas chromatography
GC-MS:	Gas chromatography mass spectrometry
HVOC:	Halogenated volatile organic compound
HPLC:	High performance liquid chromatography
HSSE:	Headspace sorptive extraction
ISO:	International organization for standardization
KOH:	Potassium hydroxide
LLE:	Liquid-liquid extraction
LOD:	Limit of detection
LOQ:	Limit of quantitation
MAA:	Methacrylic acid
MMA:	Methyl methacrylate
NIST:	National institute of science and technology
NMR:	Nuclear magnetic resonance

MMD:	Molar mass distribution
MS:	Mass spectrometer
Ni-Ti:	Nickel-Titanium
PA:	Polyacrylate
PAN:	Polyacrylonitrile
PDMS:	Polydimethylsiloxane
PDMS/DVB:	Polydimethylsiloxane/divinylbenzene
PBA:	Polybutyl acrylate
PEG:	Polyethylene glycol
PMAA:	Polymethacrylic acid
PMMA:	Polymethyl methacrylate
PSty:	Polystyrene
ppb:	parts per billion
ppm:	parts per million
ppt:	parts per trillion
PSTY:	Polystyrene
PS-DVB:	Polystyrene-divinylbenzene
PTV:	Programmed temperature vaporizing injector
PVA:	Polyvinyl alcohol
RAFT:	Radical addition fragmentation chain transfer
RI:	Refractive index
RSD:	Relative standard deviation
SBSE:	Stir bar sorptive extraction
SEC:	Size exclusion chromatography
SEM:	Scanning electron microscope
SFRP:	Stable free radical polymerization
SPE:	Solid phase extraction
SPME:	Solid phase micro extraction
Sty:	Styrene monomer
SWNTs:	Single walled carbon nanotubes
TDS:	Thermal desorption system
TEMPO:	2,2,6,6-Tetramethyl(piperidin-1-yl)oxyl
TIC:	Total ion chromatogram
TGA:	Thermal gravimetric analysis
THF:	Tetrahydrofuran

UV:	Ultraviolet
VOCs:	Volatile organic compounds

Notations

n:	the amount of analyte extracted in SPME
δ:	Chemical shift in NMR
Đ:	Dispersity of the molecular weight distribution of a polymer
M_n:	Number average molecular weight
M_w:	Weight average molecular weight
β:	Phase ratio in SBSE
K_{fs}:	Fiber/sample distribution coefficient in SPME
V_f:	Fiber coating/phase volume in SPME
V_s:	Sample volume in SPME
C_0:	Initial concentration of the internal standard
K_{hs}:	Headspace/sample distribution coefficient
V_f:	Headspace volume
K_{PDMS}:	Distribution coefficient between the PDMS phase and the water in SBSE
$K_{(o/w)}$:	Octanol/water distribution coefficient
μm:	Micron meters
C_{PDMS}:	Analyte concentration in the PDMS phase at equilibrium
C_w:	Analyte concentration in the water/sample at equilibrium
m_{PDMS}:	Analyte mass in PDMS phase
m_w:	Analyte mass in the water/sample
V_w:	Volume of the water/sample
V_{PDMS}:	Volume of the PDMS extraction phase
ε_r:	Dielectric constant
ΔH:	Change in the enthalpy of the analyte when moving from the sample to the extraction material
R:	The ideal gas constant
K_0:	The distribution coefficient at temperature T_0
T:	The extraction temperature

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Chapter 1

Introduction and Objectives

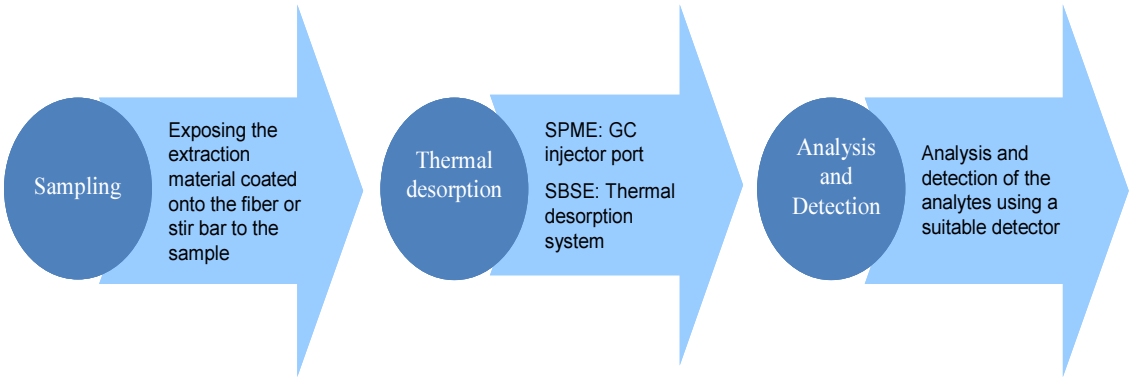
The importance of volatile analysis and the current available techniques for the analysis of these compounds will be briefly discussed in this chapter. Subsequently the synthesis, electrospinning and characterization of novel materials for volatile analysis are also discussed. At the end of this chapter the objectives of the study are summarized.

1.1 Introduction

Volatile organic compounds (VOCs) are the cause of much concern amongst environmental bodies and health organizations. This is a group of compounds that contaminate the environment (air, water, soil) due to their continual use in numerous products, some of which include pesticides, detergents, coatings, gasoline, paraffin etc[1-3]. Strict regulations have therefore been put in place regarding the use of and monitoring of VOCs[4]. Growing concerns about the adverse effects these compounds have, even when present at trace levels, has resulted in ever stricter legislation being introduced[5]. One group of VOCs that is of concern is VOCs found in water-based paints, which has an influence on the quality of indoor air. With the new directive of finding greener alternatives to ensure environmental sustainability, paint companies have put efforts into developing zero-VOC coatings. Water-based coatings usually contain a number of different solvents, including aliphatic compounds, glycols and alcohols used as coalescing agents i.e. materials that assist in film formation. The Environmental Protection Agency (EPA) and the European Union (EU) both classify zero-VOC coatings as paints containing less than 5 $g.l^{-1}$ VOCs. Without the addition of a coalescing agent, the VOCs present in the paints originate from a number of different sources. The most common contributor to the VOCs in zero-VOC paint is residual monomers (mostly acrylates) originating from the emulsions used. Companies have therefore again put focus on the reduction of the levels of residual monomers. This can be achieved by optimizing a number of different parameters. The most effective way of getting rid of these compounds are by steam-stripping, which leaves almost no trace of these compounds. With the decrease in the concentration of these compounds in the coatings, current analytical methods available are no longer able to detect these compounds. The analysis of VOCs is mostly done using gas chromatography mass spectrometry (GC-MS), which allows for rapid identification and quantitation[6-7]. The requirement for specialized and intensive sample preparation techniques to enable the detection of these compounds at extremely low levels, has led to extensive research focusing on the analysis of VOCs at trace levels.

Sample preparation techniques like solid phase extraction (SPE), solid phase micro extraction (SPME) and stir bar sorptive extraction (SBSE) were introduced in the 1990's and early 2000's. All of these sample preparation techniques works on the principle of extracting VOCs using a polymeric or porous material/coating followed by desorption of the VOCs from the extraction material and subsequent analysis by GC[6]. The use of these sample preparation techniques has become widespread. However, only a small number of extraction materials are commercially available, which limits the range of compounds that can be extracted and analyzed at trace levels in a single analysis[8]. SPE is best utilized in this sense as it is the only extraction technique where materials for the analysis of diverse target analytes are available. However, the use of solvents is

still required which makes other techniques worth looking at for the environmental benefit that they represent[9]. This study focuses on the availability of extraction materials for use in completely solvent free techniques. SBSE and SPME are non-exhaustive, solvent free extraction techniques based on diffusion of analytes onto a fiber or stir bar coating[10]. This can either be an absorptive or adsorptive process. SPME has the advantage that less complicated instrumentation is used, whereas SBSE either needs an extra solvent extraction step or a thermal desorption system for the transfer of analytes into the analytical instrument. Scheme 1.1 illustrates the process followed for VOC analyses using SPME and SBSE.



Scheme 1.1: Process followed in the analyses of VOCs using SPME and SBSE.

A number of extraction phases are commercially available for VOC analysis using SPME, whereas the commercially available coatings for SBSE are more limited. The extraction and analysis of commonly found VOCs in waste water (non-polar) and in acrylic latexes used in water-based paints (medium polar to polar) will be optimized using SPME, as this technique present the largest range of commercial coatings available for extraction. The extraction of these VOCs will be done using headspace sampling, as the matrices in which these compounds usually occur are dirty and of no interest. Headspace sorptive extraction (HSSE) using a polydimethyl siloxane (PDMS) stir bar will also be evaluated, however, a special interface is needed to thermally desorb the VOCs. Effective analysis of certain analytes has previously been challenging due to the lack of availability of target specific coatings. The focus of research has therefore shifted to the development of novel coatings for the extraction of volatile organic compounds at trace levels[11].

PDMS based materials are the most widely used material for the extraction of volatile organic compounds at trace levels[12]. SPME and SBSE use PDMS and PDMS hybrid materials as absorbtive/sorptive coatings. In this study, PDMS based hybrid materials will be synthesized using conventional free radical polymerization. These hybrid materials are combinations of organic and inorganic segments, which give these materials their unique properties[13]. The polymers were

produced using the grafting through techniques making use of a PDMS macromonomer and a low molecular weight monomer. In this project, the following hybrid graft polymers based on PDMS were synthesized: Polymethyl methacrylate graft polydimethyl siloxane (PMMA-g-PDMS), polystyrene graft polydimethyl siloxane (PSTY-g-PDMS), polybutyl acrylate graft polydimethyl siloxane (PBA-g-PDMS) and polymethacrylic acid graft polydimethyl siloxane (PMAA-g-PDMS). These polymers have a copolymer functionality which presents a series of different polarities. The combination of the PMDS with another polymer of different properties leads to a hybrid material often showing characteristics superior to that of the individual homopolymer[14]. In this study the electrospinning technique was used to create nanofibers of the synthesized hybrid materials. An image of the surface morphology of these nanofibers obtained by scanning electron microscopy (SEM) is shown in Figure 1.1. Electrospinning is a relatively simple technique that can be used to create nanofibers from a polymer solution. The suitability of the nanofibers prepared in this study will be evaluated as possible solvent free extraction medium for VOC analysis. Recently Qi et al.[15] prepared nanofibers as extraction material in SPE for the analysis of six trace pollutants in water.

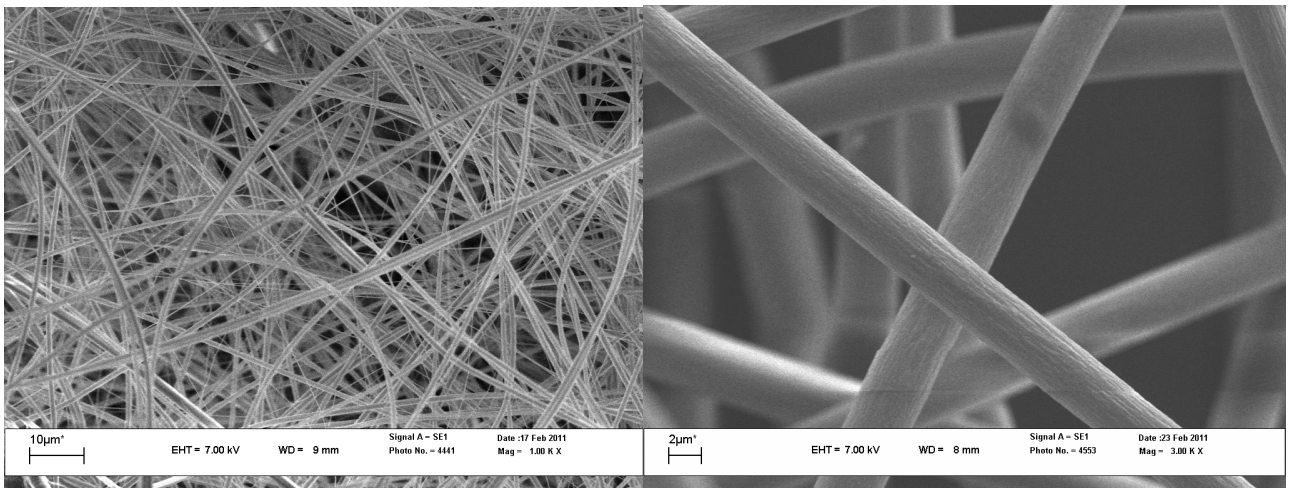


Figure 1.1: Nanofibers created through the process known as electrospinning

However, no reports could be found where nanofibers have been employed as extraction phase in solvent free techniques, with the current focus being more on the introduction of sol-gel novel coatings[8,16-17]. Nanofibers provide a large surface area for the volatiles to absorb onto which may make nanofibers a viable extraction medium in volatile analysis. One of the most important properties that will be evaluated is the thermal stability of these fibers. This property is important due to the high temperatures at which the VOC's are desorped from the material after extraction. The high temperature ensures that total desorption of the volatiles takes place, limits peak broadening and peak tailing and ensures total vaporization of all the analytes. The nanofibers were evaluated using a similar approach to that of SBSE. HSSE of the two groups of target analytes were

performed using the novel fibers as an extraction phase. The fibers were then removed from the headspace vial and placed in a thermal desorption system (TDS) coupled to a GC-MS. Due to long desorption times (ca.10 minutes) the analytes were cryogenically trapped using a programmed temperature vaporizer (PTV) prior to being introduced into the chromatography instrument[6].

1.2 Objectives

The study had the following objectives

- Optimizing the extraction and analysis of 15 non-polar volatile pollutants commonly found in waste water using SPME. This includes the optimization of the fiber, temperature, time and salt addition.
- Optimizing the extraction and analysis of 4 acrylate monomers, which are common indoor air contaminants due to their use in acrylic paints. The following parameters will be optimized for the SPME analysis: type of fiber, temperature, time and salt addition.
- Determining the limit of detection, limit of quantitation and precision for each of the groups of analytes using the optimized methods.
- Evaluate the extraction of the analytes using SBSE.
- Synthesize PMMA-g-PDMS, PBA-g-PDMS, PSTY-g-PDMS and PMAA-g-PDMS copolymers with a PDMS macromonomer using the "grafting through" technique.
- Characterize the copolymers synthesized.
- Develop an electrospinning process that produces nanofibers for each of the PDMS containing hybrid copolymers as well as for the homopolymers.
- Evaluation of the nanofiber morphology using scanning electron microscopy
- Evaluate the thermal stability of each of the graft-copolymers. Both the nanofibers and the polymer before electrospinning were evaluated in order to determine if the change in the morphology of the polymer had an influence on its thermal stability.
- Evaluate of the nanofibers as extraction medium in volatile analysis and compare this to the currently available micro extraction techniques evaluated in this study.

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Chapter 2

Historical and Literature Review

This chapter gives an overview of the micro extraction techniques available for volatile analysis. The focus will be on research that has been done and that is currently being done on different extraction materials for use in these techniques. An introduction to hybrid materials, their synthesis and electrospinning will also be given.

2.0 Introduction

In this chapter different extraction techniques for volatile organic compounds will be discussed. These include solid phase extraction (SPE), solid phase micro extraction (SPME) and stir bar sorptive extraction (SBSE). All of these techniques make use of an extraction material or phase for the extraction of volatile organic compounds (VOCs) and most of the materials are polymeric in nature. Emphasis will be placed on the commercially available materials and on the novel materials that are being developed for the extraction of VOCs. The synthesis and electrospinning of organic-inorganic hybrid graft copolymers based on polydimethyl siloxane (PDMS) will also briefly be discussed.

2.1 Volatile organic compounds

VOCs are prevalent in numerous synthetic, biological and natural products[1-5]. Their widespread abundance has led to a growing interest amongst scientists in the analysis of these compounds during the last decade, especially because of the negative impact they have on the environment and human health[5-6]. One of the important issues in this regard is the analysis of these compounds with greater accuracy and precision. There are different definitions of how to classify a compound as a VOC. Commonly, a VOC is referred to as an organic compound that evaporates spontaneously when in contact with the atmosphere[7]. Some of the most general definitions are based on the vapour pressure and boiling point of a compound. According to the European Union, VOCs can be classified as organic compounds with a vapour pressure above 10Pa at 20°C[5].

2.1.1 Analysis of volatile organic compounds

The monitoring and analysis of VOCs has become of paramount importance due to legislation being put in place for environmental and health protection[8]. This legislation makes way for a safer, cleaner and greener planet. For this purpose reliable assessment has become important and the need for appropriate analytical techniques eminent. Since the introduction of gas chromatography mass spectrometry (GC-MS), the technique has become a routine tool for analyzing and identifying VOCs. Some of the first and most commonly used techniques for the analyses of VOCs are direct injection of the sample and static headspace analysis, a slightly more sensitive, solvent free technique. Both these methods are limited by sensitivity, usually to the part per million (ppm) levels. With the requirement to identify VOCs at much lower levels, the development of techniques to extract and quantify compounds at lower levels have become important[9].

Sample extraction and enrichment techniques are usually an extremely time consuming process and often use large amounts of toxic solvents, which are hazardous for the operator as well as the environment[10]. The most commonly known extraction technique is liquid-liquid extraction (LLE). Drawbacks of LLE include the large sample and solvent volumes needed, as well as being labour intensive and time consuming[11-12]. In fact, typically more than two thirds of the total analysis time is spent on sample preparation and often numerous steps are involved, which usually means the margin of error in the analysis increases[10]. Over the past few decades, different solvent free sample preparation techniques have emerged. These include SPME, a micro extraction technique developed by Pawliszyn et al. in 1984 and SBSE, developed in the late 1990s by Sandra et al[13-15]. These sorptive extraction techniques works on the principle that the analytes partition between the sample matrix and a polymeric/sorptive phase. After the extraction step, the analytes are introduced into the GC or high performance liquid chromatography (HPLC) via either thermal or liquid desorption for further separation and analysis[15]. Other extraction techniques include solid phase extraction (SPE), membrane assisted extraction and single drop micro extraction. Compared to extraction techniques like LLE and soxhlet extraction, these micro-extraction techniques have the advantage that they are simpler to use, less time consuming and more environmentally friendly. The use of these techniques leads to a reduction in organic solvent consumption (SPE) or the complete elimination of solvents (SPME and SBSE). One drawback of these techniques is the limited number of materials commercially available for the selective analysis of certain classes of analytes[8]. In the following section the analysis of VOCs in drinking water and in water-based coatings will briefly be discussed.

2.1.2 Analysis of VOCs in aqueous media

Continual monitoring of organic micro pollutants in drinking water is required by environmental laws due to their toxicological properties[11-12,16]. These environmental pollutants include compounds like organochloro pesticides and polyaromatic hydrocarbons, which are contaminants from waste water streams and industrial effluent[8]. For quality control at trace levels, cheap, fast, highly sensitive and reliable analytical methods are needed. The low analyte concentrations present in the water means that SPME or SBSE are generally used as pre-concentration techniques. Numerous papers have been published on the trace analysis of hydrophobic or non-polar VOCs in water. On the other hand, little effort has gone into the trace analysis of VOCs from architectural coatings. Architectural coatings together with other building materials are one of the major contributors to indoor air pollutants, especially in newly constructed buildings. In the 1980s the World Health Organization (WHO) defined “sick building syndrome” after a number of health related complaints were made[17]. Paint systems can usually be categorized into solvent-borne and water-borne coatings.

Solvent-borne and industrial coatings contain a vast number of VOCs due to the paraffin waxes and mineral spirits used in these paints, which are usually complex mixtures of sometimes hundreds of organic components[18]. Advanced analysis techniques like 2-dimensional GC and/or HPLC are needed to separate and identify these compounds. The water-based systems on the other hand usually only contain a few solvents. These solvents are typically a combination of high boiling coalescing agents, glycol type solvents, smaller quantities of residual monomers and other impurities. Other components that might be present in smaller quantities and contribute to the total VOC content, include certain additives, surfactants and biocides[19]. Even though water-borne coatings have a lower VOC content than solvent-borne systems, they still influence the quality of indoor air due to the toxicity of some of the solvents used[19-21]. Legislation had been set in place to eliminate the hazardous effects some of these solvents can have on human health. The newest trends are to develop VOC-free and solvent free water-borne paint systems. For this reason it has become important to look at alternative ways of determining low levels of VOCs in paints[19].

Table 2.1: Common VOCs found in water-borne paint systems

Volatile organic compound	Boiling Point (°C)
Propylene Glycol	188.2
Ethylene glycol	197.3
Propylene glycol monomethyl ether	117.0
Tripropylene glycol	265
n-Butanol	118
Butoxyethanol	171
Butoxyethoxyethanol	231
Butyl acrylate	144
Styrene	145
Vinyl acetate	72.7
Methylmethacrylate	101
Isopropyl Alcohol	82.5

It is important for the paint industry to have analytical techniques available to monitor the levels and types of VOCs present in paint systems. Gas chromatography (GC) is the most popular technique used to analyze VOCs in coatings[21]. Different approaches can be followed for the analysis of VOCs present at trace levels and at higher concentrations. Direct injection gas chromatography for VOC analysis is commonly used in the coatings industry with both ISO11890-2 and ASTM method D6886 being widely accepted. Both these methods are direct-injection gas chromatography techniques following dissolution or extraction of the coating, which is needed due

to the complex nature of a paint system. However, a number of problems are associated with these methods. Solvents of different polarities are needed for complete extraction of the analytes, which usually uses multiple extractions. This is not always possible due to the sample matrix becoming gel-like after the initial extraction, thus limiting the extraction efficiency. All non-volatiles and polymeric compounds should be removed prior to analysis. The introduction of non-volatiles can cause a decrease in the lifetime of the analytical column, which means that only diluting the coating is not sufficient. Direct injection also results in limited sensitivity and is most commonly used for highly concentrated samples. Static headspace GC eliminates some of the matrix associated concerns and is commonly used in coating analysis, with well established methods like ISO17895 available. The sensitivity of this technique is limited to the high ppb/low ppm levels[22]. It was shown by Censullu et al.[18] that SPME can be used to determine the levels of certain VOCs in waterbased paint systems. However, the limits of detection are still restricted when using SPME due to most volatiles found in coatings being polar oxygenated compounds. The available coatings for SPME are well suited for the analysis of non-polar compounds, but few coatings are available for the analysis of polar compounds. In this study a group of non-polar VOCs commonly found as water pollutants and a group of more polar oxygenated compounds found in water-based paints will be analyzed at trace levels using novel materials and comparing it to commercially available coatings in SPME and SBSE. In the next section SPE, SPME and SBSE and the polymeric phases available for extraction of VOCs will be discussed in more detail.

2.2 SPE, SPME and SBSE

2.2.1 Solid Phase extraction

2.2.1.1 General overview

Solid phase extraction (SPE) is one of the first techniques to replace LLE. It is mostly used for environmental and biological samples with complex matrices to purify. In addition, SPE is also used for concentrating and extracting volatile organic compounds before analysis on the GC. It is a less time consuming extraction technique than LLE, and requires less solvent. However, when compared to other micro extraction techniques it is still more time consuming due to the numerous steps required for the successful extraction of analytes[23]. These steps include the conditioning of the polymeric phase, sample application and the extraction of the analytes from the SPE column using small amounts of solvent. One of the advantages of solid phase extraction over other micro extraction techniques is its ability to effectively extract polar analytes. As is the case with SPME and SBSE, the sorbent phase is the significant factor in the extraction capabilities of the technique.

There are numerous sorbent phases available for SPE, the most common are silica-based carbons (C2, C8 and C18), carbon based sorbents and macroporous polymeric sorbents like poly-(styrene-divinylbenzene). Other sorbents include hydrophilic polymers which are especially suitable for the analyses of polar analytes. The use of polymeric sorbents is preferred due to their high chemical stability[9,24]. Innovative coatings have been developed in recent years to broaden the field of application. In the next section current and new coatings available for SPE will be discussed.

2.2.1.2 Extraction materials

Extraction materials developed for SPE can generally be categorized as hydrophobic polymer sorbents, hydrophilic polymeric sorbents and mixed-mode ion-exchange sorbents. Although these are the most popular sorbents available, the introduction of monolithic technology and carbon nano tubes (CNT) for SPE applications has also been reported[9]. Monolith technology is rapidly being introduced into numerous separation fields and can be separated into two categories, polymer and silica based materials[9,11]. Polymeric monoliths are macroporous polymers prepared in a mould using direct polymerization. These macroporous polymers can be prepared with different pore sizes, the smaller pore sizes giving larger surface areas. One of the drawbacks of polymeric based monoliths is their shrinking/swelling behaviour when exposed to elevated temperatures or certain solvents, whereas silica-based monoliths show an increase in mechanical strength and organic solvent resistance[25]. A hydrophobic organic-inorganic silica monolith functionalized with octyl and thiol groups was developed by Zheng et al.[25] through a two step catalytic sol-gel process and was used as sorbent in micro-SPE. This monolith had strong cation-exchange sites due to sulfonic acid functionalities synthesized via an oxidative reaction with hydrogen peroxide and was used for the extraction of sulfonamides. Good extraction efficiencies and relative standard deviations were reported for this acid functionalized hybrid monolith[25]. Xie et al.[26] prepared porous monoliths based on a 2-hydroxyethyl methacrylate monomer. The incorporation of this polar monomer into the divinylbenzene backbone resulted in higher extraction of polar analytes[11]. Despite the successful application of monolithic materials to extract the polar compounds, no intensive studies have since been done with monoliths in solid phase extraction. Multiwalled carbon nano tubes have, however, been proven successful in early studies when used as a sorbent in SPE. The reason for this might be that the carbon nano tubes have strong surface interactions with other molecules[27].

One of the most commonly used hydrophobic sorbents for SPE is macroporous polystyrene-divinyl benzene (PS-DVB). Sorbents based on PS-DVB with different surface areas are commercially available from Rohm & Haas (XAD series), Polymer Labs (PLRP-S-10/30) and Phenomenex (Strata SBD-L), with hyper-cross linked sorbents available from Purolite Int. (Styrosorb series).

The most important characteristic of these sorbents are the surface area especially in the extraction of highly polar analytes. The higher the surface area, the more sites for interaction with the analytes are available, and the higher the extraction efficiency. To increase the extraction efficiency of polar analytes several hydrophilic sorbents are commercially available some of which include the Amberlite XAD series (Rohm&Haas) and the Oasis HLB (Waters, Milford, MA, USA). The sorbents from Rohm&Haas are methacrylate-divinylbenzene copolymer derivatives. The more polar methacrylate increases the interaction between polar analytes and the sorbent. The Oasis HLB is a macroporous poly (N-vinylpyrrolidone-divinylbenzene) copolymer and is one of the most commonly used hydrophilic sorbents for solid phase extraction. Even though there is already a vast number of SPE sorbents available for the extraction of highly polar analytes new sorbents are still being developed due to the challenges presented by these analytes[24]. Polymers with a high crosslinking density have been introduced as sorbents for the extraction of the more polar analytes in SPE. These materials offer high surface areas and micropore content giving them superior sorption properties. Fontanals et al.[24] synthesized a novel monodisperse hypercrosslinked polymer microsphere and showed its successful application for the extraction of polar pollutants from water. Nanofibers have also been introduced as sorbent phases to extract volatile compounds. Qi et al.[12] prepared three nanofibers based on polystyrene for the extraction of trace pollutants in environmental water. They investigated nanofibers of polystyrene, poly(styrene-co-methacrylic acid) and poly(styrene-co-p-styrene sulfonate) and showed that these nanofibers could successfully be used to analyze extract VOCs in water at trace levels[12]. Nanofibers have the advantage of a much larger surface area compared to commercially available microfibers.

2.2.2 Solid phase micro extraction

2.2.2.1 General overview

SPME is an extraction technique based on analytes partitioning between the sample and sorbent and presents the advantage that simultaneous extraction and enrichment of the target analytes takes place[28-29]. It can be used for liquid, solid and gas samples and is extremely valuable when the matrix of the samples is of no interest or very complex. Extremely complex volatile mixtures, pre-concentrated by SPME, can be separated with high efficiency and sensitivity by gas chromatography coupled with mass spectrometry (GC-MS)[29].

Since SPME fibers and instrumentation became commercially available in the early 1990's, there has been a growing interest in the technique. SPME provides a lot of advantages over other sampling techniques as it is an organic solvent free, non-laborious, relatively cheaper and a less

time consuming technique which provides good analytical performance and sensitivity in the parts per billion (ppb) and trillion (ppt) ranges[30]. SPME has been successfully applied for the determination of volatiles in a lot of different sample matrices such as waste water, soil, honey, asphalt and has even been applied in indoor air quality control[31-38].

2.2.2.2 Instrumentation and experimental techniques

In SPME a fused-silica fiber coated with a polymeric phase is used to extract low concentrations of analytes from the matrix[28]. The construction of a SPME device is shown in figure 2.1.

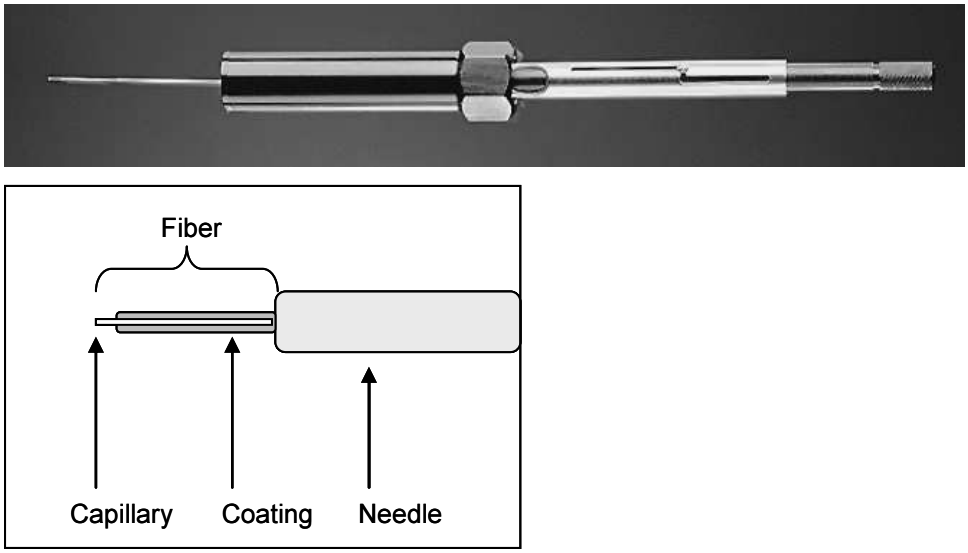

Figure 2.1: Manual SPME holder (above) with retractable coated fiber in needle (bottom).

A SPME device consists of a sample holder that resembles a micro syringe, a stainless steel plunger and a fused-silica fiber coated with a polymer. After the fused-silica fiber is coated and attached to a needle, it is mounted onto the holder so that the coated fiber is retractable inside the needle and a plunger is then used to expose and retract the fiber[10,14]. The holder also has a variable depth gauge that allows the user control of how far the needle penetrates into the sample. Upon exposure of the fiber to the sample the device gets locked at the z-shaped slot which prevents any movement of the plunger. Commercial devices for both manual sampling and adaptable with autosamplers are available from Supelco, Inc (Bellefonte, PA).

2.2.2.3 Procedure

Sampling can either be done by direct immersion of the fiber into the sample or by exposure of the fiber to the sample headspace. The method of sampling will be based on the volatility of the analytes of interest and on the nature of the sample matrix[11]. The first step is extraction of the

analytes which is illustrated in Figure 2.2. The coated SPME fiber tip is exposed to the gaseous headspace of the sample or directly immersed into the sample matrix for a certain amount of time and the volatiles partition into the fiber via an equilibrium process[10]. The fiber should be retracted inside the needle as to protect the fragile fiber. The fiber is only exposed to the sample after the septum is pierced. Typical extraction times are between 2 and 30 minutes but can be as short as 30 seconds. This depends on the volatility of the analytes, the type of fiber used, the concentration of the analytes in the matrix and whether equilibrium sampling is taking place or not. After sampling, the fiber is retracted inside the needle before removing the holder.

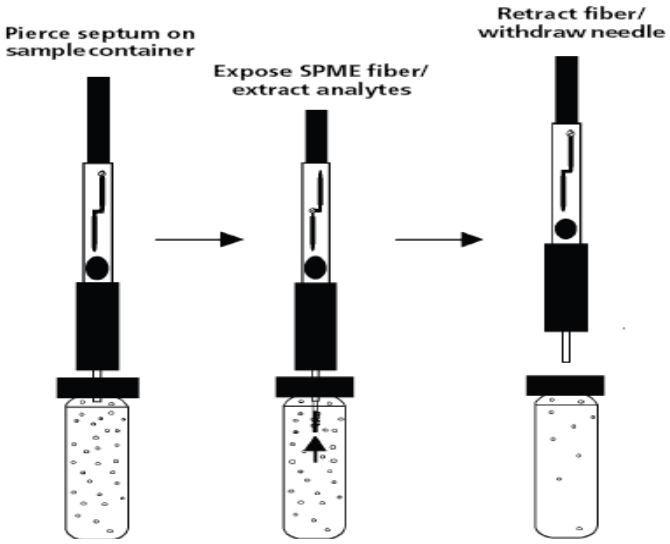

Figure 2.2: Extraction of analytes using a SPME fiber[10].

The second step is desorption of the trapped analytes as illustrated in Figure 2.3.The fiber tip was developed in such a way that after extraction the fiber can be exposed inside the heated GC injection port. Here the analytes are thermally desorbed into a splitless injection liner and transferred onto the analytical column[10].

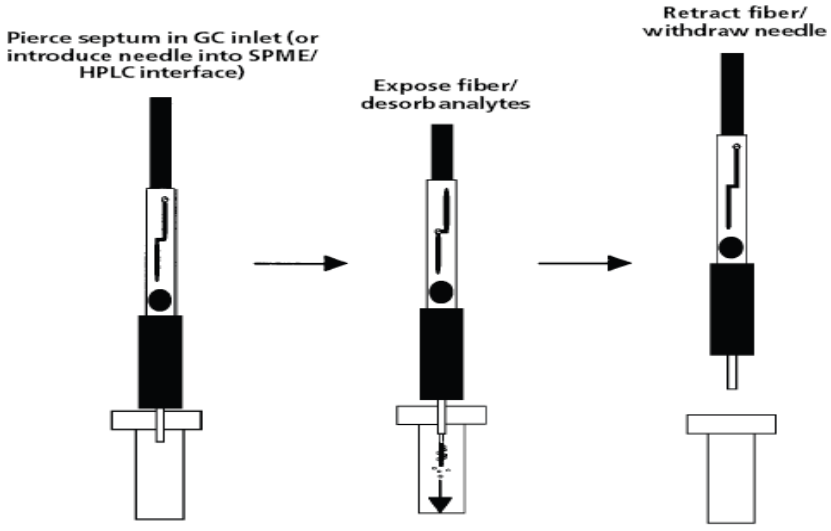

Figure 2.3: Thermal desorption of the analytes from the SPME fiber in the GC injection port[10].

When doing headspace SPME, the temperature of the matrix can be increased to force more of the analytes into the gaseous phase, thereby decreasing the sampling time and increasing the sensitivity. For reproducible results, sampling must be done at a constant temperature. However, temperatures used for the liquid-phase coatings are typically not as high as used for static headspace, to avoid evaporation of the analytes from the fiber. There are different approaches that can be used to force more of the analytes into the headspace and assure better analyte recovery. Salting out, adjusting the pH and agitation of the samples are just some of the examples[14]. When using any of these techniques it is important to be consistent. The theory of how SPME works will be discussed in the following section.

2.2.2.4 Theory of extraction mechanism

There are different types of extraction modes which include direct extraction, where the coated fiber is inserted into the liquid sample, headspace sampling, where the fiber is exposed to the headspace above the aqueous sample and the membrane protection mode where the fiber is protected against non-volatiles in the sample matrix[14]. This thesis will mainly focus on extraction of analytes in the headspace mode, as the relevant sample matrices often contain non-volatile compounds and are therefore of no concern. The extraction of the analytes from the headspace is dependant on two mass transfer mechanisms. The mass transfer at the liquid/gas interphase and the mass transfer at the headspace/fiber interface[39].

In the instant that the coated fiber is exposed to the gaseous headspace the diffusion of analytes onto the coating begins. The extraction is complete only when the gas-liquid phase equilibrium between the matrix and headspace has been reached[11]. The equilibrium for liquid phase coatings (sorption mechanism) can be described by the following equation:

$$n = \frac{K_{fs} V_f V_s C_0}{K_{fs} V_f + V_s + K_{hs} V_h}$$

where n is the amount of analyte extracted by the fiber, K_{fs} is the fiber/matrix distribution coefficient, V_f is the fiber coating/phase volume, V_s the sample volume, C_0 is the initial concentration of the internal standard in the sample, K_{hs} is the headspace/sample distribution coefficient and V_f is the headspace volume.

From this equation it is observed that the sample concentration is directly proportional to the amount of analyte extracted from the sample matrix and independent of the fiber location if the fiber coating, sample and headspace volumes are kept constant. The equation describes the

equilibrium process when absorption is the extraction mechanism. However the principle for analysis remains the same when using porous particle blends (i.e. an adsorption mechanism) if the assumption is true that the coating volume and surface area available for analytes to adsorp onto is proportional to each other[39].

SPME is a multiphase equilibrium process (illustrated in Figure 2.4) and this is the basis for analyte quantitation[14]. At equilibrium conditions the amount of analyte extracted is reliant on the partition coefficient of the analyte. Extraction can also be performed at non-equilibrium conditions to shorten the extraction time. In this case, the time of each extraction must be precise as the amount of analyte extracted at a specific time is directly proportional to the concentration of the analyte in the sample, this is especially important when doing quantitative analysis[10,14,39]. It is, therefore, always better to do sampling at a time close to equilibrium for quantitative purposes; and there are numerous ways to decrease the time it takes to reach equilibrium.

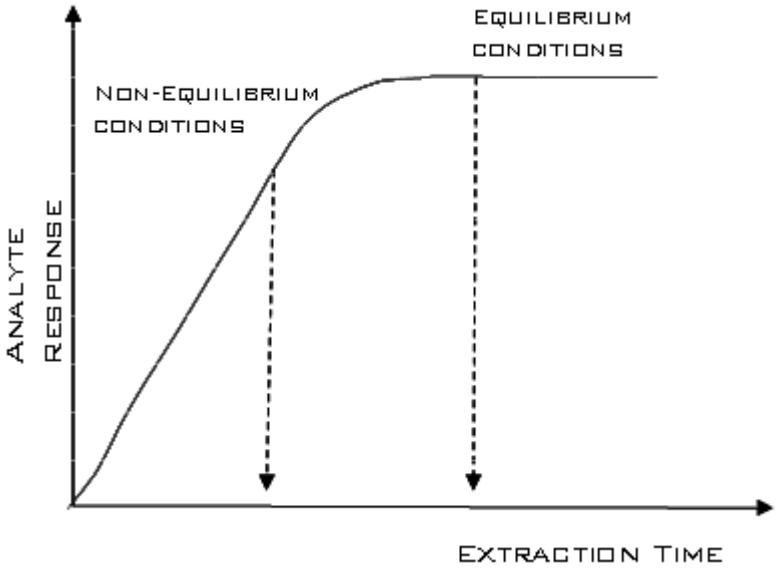

Figure 2.4: SPME at non-equilibrium and equilibrium conditions.

Stirring during sampling decreases the time it takes to reach equilibrium. Other agitation techniques like sonification and vibration can also be used to reach equilibrium faster and thus yield faster extraction times and assure better precision and accuracy. Since each of the different operating parameters will have an effect on the extraction of the analytes from the sample matrix, it is important to optimize these which can include: time and temperature of extraction, the type of extraction phase, the pH and salt modifiers and the desorption time and temperature[14].

2.2.2.5 Extraction phases for SPME

Choosing the correct extraction phase or fiber for a spesific analysis is extremely important. Similar to selection of an analytical column, a fiber is chosen based on its polarity and film thickness. The fiber must have high efficiency for extraction, high selectivity, good durability and reproducibility. The efficiency of the fiber is dependant on the film thickness of the stationary phase and on the distribution coefficients of the analytes in the fiber. With an increase in boiling point and molecular weight, the distribution coefficient of the analyte in question will also increase, meaning that a thinner extraction phase will be sufficient for less volatile compounds. The correct fiber will be selective towards the analyte of interest whilst not letting the matrix interfere; a non-polar fiber will be more selective toward non-polar analytes, whilst a polar coated fiber will be more selective towards polar analytes[14]. It is very important to take both the chemical and physical properties of the fiber into consideration. Various commercial fibers are available for different applications. For very fast extractions a fiber with a thin film will be chosen, for longer extraction times a thicker film thickness will be preferred. The thickness of the film coating influences both the speed of the extraction and the capacity of the fiber. Thicker coatings provide higher capacities (i.e. the amount of analyte absorbed by the fiber). In industry the general rule applies that the faster the analysis, the better, thus the thinner coated fiber will be the preferred choice. One of the first generations of commercially available fibers were non-polar PDMS coated fibers. The silica fibers were coated by dipping them into a PDMS solution. After the fiber is coated, the solvent is evaporated leaving behind a thin coating of cross-linked polymer. A second method of coating the fiber is by using electron deposition. This allows for the formation of uniform films on the fibers with specific film thicknesses[28].

Fused silica fibers are usually coated with a polymeric liquid or solid sorbent with film thickness of between 10 and a 100 µm, as this allows for very short extraction times[14,39]. SPME is successfully used for the analysis of trace impurities in water; however, the use of SMPE has been broadened into the pharmaceutical, food, forensic and many other industries. The most commonly used coatings are the non-polar PDMS fiber and PDMS derivatives like PDMS-DVB. There are currently 7 commercially available fibers from Supelco (Bellefonte, PA, USA), which are available in film thicknesses ranging from 100 µm to 7 µm. A summary of these fibers can be found in Table 2.2. The available phases are either liquid phases, where the analytes gets absorbed in the liquid phase, or porous particle blends with pore sizes ranging from micropores to macropores, where the extraction mechanism is based on the competitive adsorption process[10].

Table 2.2: Commercially available SPME fiber coatings from Supelco

Fiber Coating	Film Thickness	Working pH range	Maximum Temperature (°C)	Recommended Operating Temperature (°C)
PDMS	100 µm	2-10	280	200-280
PDMS	30 µm	2-11	280	200-280
PDMS	7 µm	2-11	340	220-320
PA	85 µm	2-11	320	220-300
PDMS/DVB	65 µm	2-11	270	200-270
Carboxen/PDMS	75 µm	2-11	320	250-310
Carbowax/DVB	70 µm	2-9	250	200-240
DVB/CAR/PDMS	50/30 µm	2-11	270	230-270
PEG	60 µm	2-9	250	200-250

*Supelco, Bellefonte, CA

Polydimethyl siloxane (PDMS) and polyacrylate (PA) coated fibers are prepared by physical deposition in the liquid phases, which means that the analytes are extracted by a non-competitive absorption process. This means that once all the binding sites are saturated, no further absorption can take place[40]**.** Blended phase cross-linked polymers like polydimethyl siloxane – divinylbenzene (PDMS/DVB), carboxen-polydimethyl siloxane (CAR/PDMS), carbowax-divinylbenzene (CW/DVB) and divinylbenzene-carboxen-polydimethyl siloxane (DVB/CAR/PDMS) are available and hold the advantage over liquid phases in that analytes with a higher affinity for the coating are preferentially extracted[10].

2.2.2.6 Novel extraction phases

Although there are already fibers of different polarities commercially available, there is a trend in developing coatings with increased affinity towards certain types of analytes[29,41]. Both SPME and SBSE are limited in the analysis of polar analytes, which has led to an increase in new materials with greater affinities for polar compounds. Even though more polar polymeric phases like PA and Carbowax polymeric blends like CW-DVB are available, the hydrophilic sorbents available for SPE are still more efficient. One of the main disadvantages of a phase like polyacrylate is the limited surface area, which means the extraction of polar compounds is limited. With this limitation in mind an increasing number of research groups have focused on the development of phases which are more suitable for analysis of polar solutes. When developing a novel extraction material, it is important to keep in mind the thermal and chemical stability of the sorbent phase. Thermal desorption of the analytes from the extraction materials is more beneficial than liquid desorption therefore, it is important that the extraction material are thermally stable. One of the most commonly used techniques of creating new sorbents is by sol-gel technology. This technique works

on the principle of depositing the sorbent phase on the fiber and also provides the possibility for multiple functionalities. The most common coatings developed by this process are based on polysiloxanes and alkoxysilanes[29]. Chong et al.[42] described a novel method to prepare sol-gel SPME fibers, where they removed part of the polyimide coating from a fused-silica fiber and coated it with a bonded sol-gel layer of PDMS. This fiber enabled them to efficiently analyze a number of target analyte groups some of which included alcohols, phenolic compounds and polycyclic aromatic hydrocarbons. A significant increase in the thermal stability of the sol-gel PDMS coating was noted when compared to the conventional PDMS fibers[42]. The covalent bonding between the film and the substrate of these sorbents resulted in higher stability of the coating at elevated temperatures and increased resistance to organic solvents. A further improvement on the sol-gel technology was shown by Azenha et al[29]. They used a UV-curable sol-gel layer to attach functionalized silica particles to a Ni-Ti wire. The functionalized silica particles provided an enhanced extraction profile when compared to the sol-gel layer on its own. The use of the Ni-Ti wire instead of the silica fiber provided additional mechanical strength and decreased the possibility of fiber breakage[29,43-44]. A number of other research groups have investigated alternatives for the fragile silica fiber, some of which include pencil lead and anodized zirconium[45-46]. Another approach involves the development of novel sol-gel polymer functionalized single walled carbon nanotubes (SWNTs) as SPME sorbent. Zhang et al.[30] functionalized SWNTs with hydroxyl-terminated silicone oil and used this to prepare novel sol-gel coatings as an extraction medium for polybrominated diphenyl ethers in water samples[30]. This material exhibited higher thermal stability and increased lifetime when compared to commercially available fibers. Li et al.[28] developed a polythiophene film for analysis of organochlorine pesticides in water. They used cyclic voltammetry and electrodeposited the film onto a stainless steel wire using a boron trifluoride diethyl etherate solution[28]. A number of other novel coatings including conducting polymers like polyaniline and polypyrrole have been developed and successfully used to extract analytes from a various number of different sample matrices[47-48]. The focus of this study will be on the preparation and evaluation of novel coatings based on PDMS nanofibers. Commercially available SPME fibers will be evaluated and the extraction optimized for the analysis of a number non-polar and more polar compounds. The same analytes will then be analysed using the novel materials in an attempt to improve the extraction of these analytes; especially that of the more polar compounds.

2.2.3 Stir bar sorptive extraction

2.2.3.1 General overview

Stir bar sorptive extraction (SBSE) is a micro extraction technique developed in the late 1990's by the Research Institute of Chromatography (Kortrijk, Belgium) for the pre-concentration and extraction of volatile organic compounds in aqueous matrices[41]. SBSE is a solventless technique based on sorptive extraction where a magnetic stirrer is encapsulated in a glass jacket and coated with a polymeric material like PDMS[15]. These stir bars are commercially known as "Twister" and available from Gerstel (Mulheim, Germany) as 1 or 2 cm rods with a non-polar PDMS coating with a thickness of 0.5 or 1.0mm[41,49] (figure 2.5). The coated stir bar is used to stir the sample of interest extracting the analytes into the coating.

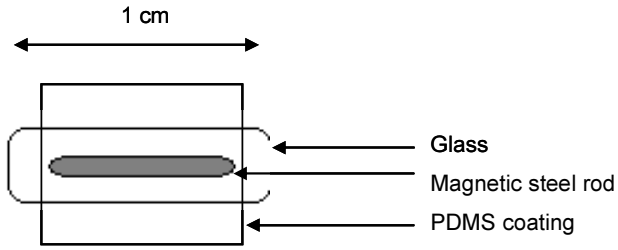

Figure 2.5: Typical construction of a PDMS stir bar.

2.2.3.2 Theory of extraction mechanism

The extraction mechanism is an equilibrium process which is controlled by the partitioning coefficient of the analytes between the aqueous phase and the polymer coating[50]. This is similar to the equilibrium process of SPME, but the higher volume of the coating results in much greater sensitivity and longer extraction kinetics.

The following equation describes the extraction process:

$$K_{PDMS/w} = \frac{C_{PDMS}}{C_w} = \frac{m_{PDMS}}{m_w}\frac{V_w}{V_{PDMS}} = \frac{m_{PDMS}}{m_w}\beta$$

Where K_{PDMS} is the distribution coefficient between the PDMS phase and the water. This coefficient is based on the octanol/water distribution coefficient ($K_{o/w}$) which is used to give an indication for the extraction efficiency of SBSE[15]. C_{PDMS} and C_w are the equilibration concentrations of the analyte in the polymer phase and water phase, respectively. This is in turn equal to the ratio between the mass of analyte in the PDMS, m_{PDMS}, and mass of analyte in the

water, m_w, taking into account the phase ratio, β. β is the ratio between the volume of water, V_w, and polymer coating, V_{PDMS} [51].

The theoretical amount of analyte extracted at equilibrium conditions can now be determined by the following equation:

$$\frac{m_{PDMS}}{M_0} = \frac{K_{PDMS/w} / \beta}{1 + (K_{PDMS/w} / \beta)}$$

where m_0 is the original amount of analyte present in the aqueous phase. From this equation it is obvious that there will be an increase in extraction efficiency with a higher coating amount and lower phase ratio. This will be crucial when deciding on extraction efficiency vs. time of extraction. When using a higher amount of coating the time to reach equilibrium will increase. Depending on what is to be analyzed, a compromise will have to be made between extraction efficiency and time of extraction. Extraction using SBSE can also be done using pre-equilibrium conditions.

2.2.3.3 Procedure

SBSE is used primarily for the extraction of trace volatile compounds from aqueous samples. SBSE can be performed either by directly adding the stir bar to the liquid sample or by headspace sorptive extraction (HSSE) through mounting the stir bar into a device exposed to the sample headspace[15]. This is especially useful when working with highly volatile compounds or dirty sample matrixes. Extraction typically takes place until equilibrium is reached, the time required for equilibrium can range from anything between 30 and 240 minutes[51]. The extraction time of the analytes can be optimized by plotting the detector response of a certain analyte against the extraction time. In this manner, it can be established when equilibrium is reached. The time in which equilibrium is reached is kinetically dependant on the sample volume, speed of agitation and amount of coating used on the stir bar[15]. To decrease the analysis time, the analytes can be extracted at non-equilibrium conditions. Working at non-equilibrium conditions will usually still provide good sensitivity and reduce the time of the analysis, although care has to be take to ensure reproducible extraction under these conditions.

Once the analytes are sorbed into the polymeric coating, they have to be transferred into the chromatograph instrument for analysis. Unlike SPME, where the split/splitless injection port of the gas chromatograph is used for desorption, SBSE requires other approaches. Liquid desorption can

be used to extract the analytes from the coating. For VOCs, a non-polar solvent like hexane is used, followed by injection of this solvent for analysis by gas chromatography. This technique has limitations, most notably the efficiency of extraction is much lower than when thermal desorption is used. In addition solvent impurities can interfere with the analytes. The use of liquid extraction is also more time consuming and labour intensive, and is therefore mostly used when analysis is done by liquid chromatography. Thermal desorption on the other hand allows for the complete transfer of the analytes into the gas chromatograph. Dedicated thermal desorption systems are available from Gerstel GmbH in Germany. This thermal desorption system (TDS) works together with a programmed temperature vaporizing (PTV) injector, where the volatiles are cryotrapped at temperatures below -100°C using liquid nitrogen. This allows for focusing and concentration of the thermally desorbed analytes. The trapped analytes are then transferred to the analytical system for analysis in either the split or splitless mode by rapidly increasing the temperature of the PTV. This approach ensures that loss of analytes doesn't occur and that complete transfer of the extracted volatiles take place without additional band broadening due to injection[15]. Depending on the type of analyte and the amount of extraction phase, the desorption temperature and flow as well as the cryotrap temperature can be adjusted[51]. Typical times for complete desorption to take place is around ten minutes at temperatures between 150 - 300°C.

One of the disadvantages of SBSE is that automation of the whole process is not possible. The desorption of the analytes from the stir bar can be automated but all the steps prior to that needs to be done manually. Fortunately, this drawback of SBSE does not over shadow all the advantages of this technique[16].

2.2.3.4 Extraction phases for SBSE

One of the advantages of SBSE over SPME is the larger volume of the extraction material or extraction phase that is available. Generally in SPME a 100µm PDMS coated fiber contains around 0.5µl of extraction phase, whereas in SBSE the volume of the extraction phase is up to 250 times larger[9,41,52]. This results in higher recoveries of analytes from the aqueous matrix and higher sensitivity but slower extraction kinetics[41,52]. PDMS is the most commonly used sorptive extraction phase due to its high thermal stability and good diffusion properties[15,51]. SBSE is mostly used for the extraction of medium to non-polar analytes from aqueous samples. Due to the non-polar character of PDMS the recovery of polar analytes is usually poor[53-54]. A number of approaches have been followed to overcome this limitation. The use of in-situ derivatization can be used to overcome this. Polar analytes like phenols, aldehydes, ketones and amines can be derivatized in the aqueous solution. Two commonly used derivatization techniques include acetylation and in-port silylation.

The former is mostly used for the derivatization of phenol containing compounds like hydroxyl polyaromatic hydrocarbons[55]. An increase in the hydrophobicity of polar compounds through derivatization improves the detectability of these analytes and results in better recoveries when using the commercially available PDMS coating[51]. Although derivatization can be successfully applied, this requires a lot of extra sample preparation and introduces an additional source of error. Different novel materials have, therefore, been introduced. In the next section, recent developments on extraction materials for SBSE will be discussed in detail[41].

2.2.3.5 Novel extraction phases

As mentioned in the previous section, the main drive toward developing new extraction phases is to overcome the poor detectability of polar compounds when using the commercially available PDMS twister. Successful extraction of polar analytes using a PDMS coating as extraction phase requires chemical derivatization. Derivatization is, however, not always possible and the detectability of some polar analytes remains problematic[41]. For this reason research teams have put their efforts into the development of new extraction phases for SBSE. As previously mentioned one of the most common ways of preparing novel phases is by the sol-gel technique, which was first used by Chong et al.[42] to create cross-linked PDMS fibers. One of the first SBSE sol-gel phases was developed by Yu et al.[52] when they prepared a novel Carbowax/PDMS/PVA phase. This was compared to a commercial PDMS coated stir bar and CAR/PDMS SPME fiber for the analysis of volatile organic sulphur compounds. The carbowax and poly(vinylalcohol) (PVA) increased the polarity of the extraction phase, thereby increasing the detectability of polar analytes at lower concentrations. The novel material had a better performance than the PDMS stir bar, but only slightly better performance than the SPME fiber. The latter, however, had a smaller linear range, most likely due to the limited number of active sites available when using the SPME fiber[52]. Other extraction phases developed to improve the detection of polar compounds include the coating of a glass fiber with a poly(acrylate) phase, and novel phases based on polyurethane foams[50,56-57]. The polyurethane materials are more robust and are suitable for use as extraction phase in the analysis of more polar analytes[15]. One of the more recent developments by Bicchi et al.[33,58] was the use of a dual phase twister, which is now also available from Gerstel. This is an empty PDMS tube which can be filled with any other sorbent material. To date only carbon-based materials have been tested and these showed improved recoveries of polar analytes compared to the conventional PDMS coated stir bar[41]. The use of two different phases dramatically expands the extraction capabilities of the stir bar and increases the applicability of the technique. The development of polar phases for SBSE has increased extraction efficiency for polar analytes and leads the way for future developments for coatings with enhanced extraction capabilities.

2.3 Electrospinning

2.3.1 An overview

Nanotechnology is a diverse and fascinating field that has taken the science world by storm. The concept of "nanotechnology" was first introduced in 1959 by the physicist Richard Feynman when he talked about manipulating matter at an atomic and molecular level. With so many things in the world becoming bigger and better, at the same time a world of new possibilities was created, where it is now possible to work on scales which are one billionth of a meter. In this study, the focus will be on creating nanofibers via electrospinning to be used as extraction materials for VOCs. The appeal of these phases are the increased surface area to volume ratio which might lead to increased adsorption of VOCs from matrices like air and water, as well as the flexibility and increased mechanical stability of polymer nanofibers, as compared to microfibers[12,59-60].

Electrospinning is the most commonly used method for the formation of continuous sub-micron fibers typically in the range of 100 nm – 1 μm[61-63]. Electrospinning has been around for many years, but this technique has only attracted attention in the past two decades. The initial setup invented was where an electrical charge was used to spray liquids and was patented by Colley and Morten in 1902/1903. Later the electrostatic spinning of polymers, as it was known then, was patented by Anton Formals in 1934 through to 1944[59,64]. Different types of materials have been subjected to this technique of creating nanofibers, some of which include natural and synthetic polymers, composites, ceramics, and metals[64]. The first commercial fibers that were produced in this way, were filters that were used in the nonwovens industry[63]. The simplicity and efficiency of this method for creating fibrous materials led to applications being found in a number of different technological areas. These include biomedicine and biotechnology application[65], drug delivery and tissue engineering applications[66-69], and energy and environmental applications[60]. By using specialized methods and setups, it is even possible to produce hollow fibers and fibers in ordered and stacked arrangements, which can be used for more specific applications[62-63].

The focus of this study will be on the electrospinning of polymers, where the polymer is typically dissolved in a solvent and this solution is then used to create the nanofibers. The morphology and structure of these nanofibers can be manipulated by simply changing one of the various processing parameters of the electrospinning setup or by adjusting the polymer solution properties. This seems quite simple, but the number of different technical and process parameters is quite vast[63].

2.3.2 The process

Electrospinning is a fairly simple technique, although to create nanofibers of certain morphology and structure a lot of different process parameters need to be taken into account[60]. A typical laboratory setup for electrospinning consists of a high voltage power supply, syringe with a metallic needle of narrow diameter (spinneret), a syringe pump that provides a controlled flow rate, a metallic collector plate and the polymer solution[59,62]. The positive electrode from the power supply is attached to the needle or spinneret through which the polymer solution flows to create fibers and the counter electrode is attached to the metallic collector. The polymer solution can either be gravity fed in a vertical setup or the feed can be controlled by a syringe pump when using a horizontal setup. When a voltage of between 5-30kV is applied, the polymer solution becomes highly charged and these charges are distributed evenly across the surface. The electrostatic forces induce a liquid pendant drop in the shape of what's known as a Taylor cone[60,62]. When the electrostatic forces reach a critical level and overcome the surface tension of the polymer solution, a liquid jet is ejected from the needle in a straight line, where after it bends in a complex path. This electrified liquid jet is continuously elongated to form ultra thin nanofibers[70]. The elongation or thinning of the electrified jet is due to bending instability associated with such a jet[62-63,71]. As the solvent evaporates, these fibers are collected on the metallic collector plate[62,71]. A number of different mathematical models have been developed to investigate the process of electrospinning. Using the Maxwell equation, the Reneker group gave a good idea of the three dimensional trajectory of the jet[71-72], where as the Rutledge group developed a model based on a jet that is elongated and thin[70]. They showed that electrospinning involves the whipping of a liquid jet which is mainly due to electrostatic interactions. This model can be used to predict the diameter of the nanofibers[62]. These models give a better understanding about the electrospinning mechanism and can assist in the experimental design of an electrospinning setup. Figure 2.6 is a representation of a typical experimental setup for electrospinning. While the setup is quite simple, the process of electrospinning is actually complex and relies on a number of different process parameters. Some of these include the concentration, viscosity and electrical conductivity of the polymer solution, the molecular weight and solubility of the polymer in the solvent, the surface tension and polarity of the solvent, the feed rate of the solution through the electrode, the tip-to-collector distance and the amount of voltage applied[62-63]. Other factors not directly related to the setup that can have an influence on the diameter and morphology of the fibers, include the temperature and humidity of the surroundings[62].

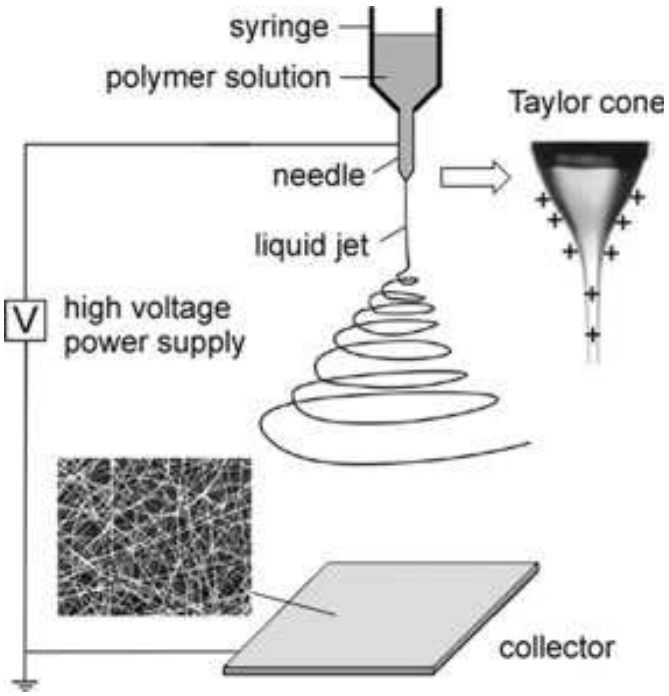

Figure 2.6: Typical electrospinning setup for creating nanofibers[62].

One of the phenomena influenced by these parameters is the formation of beads during electrospinning. As mentioned, the processing parameters play a role in the morphology and structure of the nanofibers, therefore to prevent the formation of beads the different parameters can be varied until an optimal setup is found[59,73]. The key factors in bead formation were identified by the Reneker group as the viscoelasticity and surface tension of the solution and the charged density from the liquid jet. Further manipulation using different experimental setup can be done to design certain types of nanostructures. Figure 2.7 shows how the experimental setup can be manipulated to obtain uniaxial, random or aligned fibers.

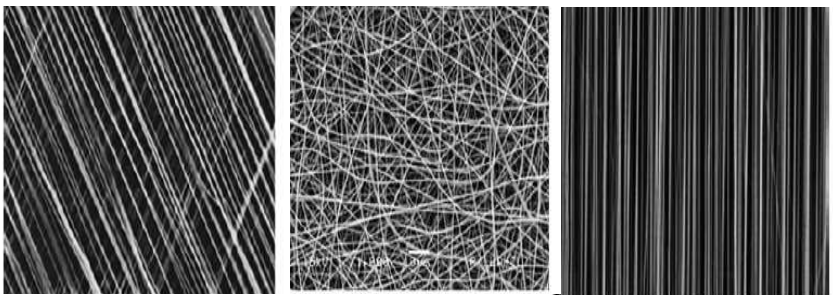

Figure 2.7: Different nanofiber mats obtained by electrospinning by changing the experimental setup[60].

Usually non-woven nanofiber mats are produced when using the experimental setup as described previously, however by collecting the fibers on a rotating disc, aligned and uniaxial fiber bundles can also be formed[60]. An in-depth discussion of these diffent parameter that influence fiber

formation can be found in a number of review papers and scientific journals and will not be further discussed in this study[61-62,73-78].

2.4 Hybrid Materials

The development of hybrid materials has grown considerably in recent years due to the superior properties these materials exhibit when compared to their pure counterparts. The introduction of hybrid materials fills the gap created by technological advancements and requirements that cannot be filled by materials currently available on the market[79]. Like many other fields of science, the science of hybrid materials originates from nature[80]. Natural materials like bone consist of inorganic and organic building blocks where the inorganic part provides structure and strength and the organic part bonding between the bone and soft tissue. The synthesis and creation of hybrid materials have been around for many centuries, but the unique properties that these materials possess and endless possibilities that these materials provide were only discovered recently[79]. Some of the most successful hybrid materials were introduced as composites, an example being inorganic fiber-reinforced polymers. These types of materials are heterogeneous in composition due to the size distribution of the inorganic building blocks. By incorporation of the inorganic segment at molecular level the materials developed were more homogeneous. The development of homogenous materials with di-phasic morphologies make it possible to fine-tune properties of the hybrid material on the molecular and nanoscale[81]. These hybrid materials are a combination of two classes of materials that either show properties in between the two classes or completely new properties[79]. The interest in hybrid materials was also fuelled by the availability of different analytical techniques that enabled the physico-chemical characterization of these materials. Understanding the properties these materials exhibits, enables the scientist to the design hybrid materials with novel properties[79]. Currently the synthesis of hybrid materials can be categorized into four sections: 1. molecular engineering, 2. nano- and micrometer sized organization (nanocomposites), 3. functional to multifunctional hybrids and 4. combining of bio-active components. One of the most important processes introduced for the synthesis of organic-inorganic hybrid materials was the sol-gel process in the 1930s, where an organic polymer is attached to an inorganic copolymer. The sol-gel process, especially the silicon-based sol-gel process, set the tone for creation of inorganic-organic hybrid material. However, multiple other synthetic routes such as “living” anionic polymerization, free radical polymerization and controlled polymerization techniques such as atom transfer radical polymerization and reversible addition-fragmentation also exists that enables the design of hybrid materials with specific properties, morphologies, shapes and topologies[80-82]. Figure 2.8 shows examples of some of these different hybrid materials that can be designed via different synthetic routes.

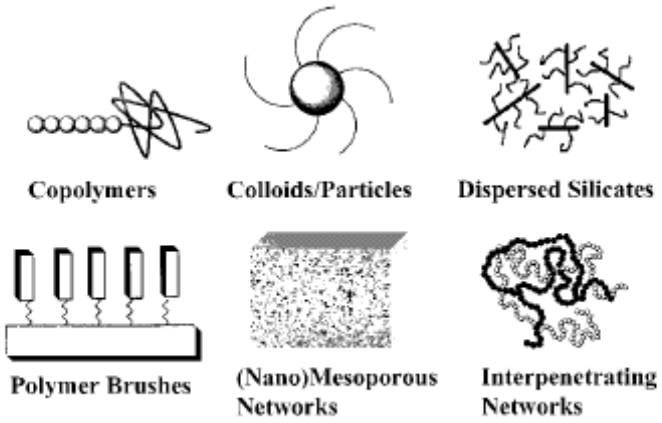

Figure 2.8: Different morphologies and shapes of hybrid materials[80].

Some of the most popular hybrid materials are silicon-based due to the good stability and processability of these materials. Some recent developments of inorganic-organic hybrid materials include polyorganosiloxane based materials and will be discussed in the next section.

2.4.1 PDMS based hybrid materials

Polyorgano siloxanes like polydimethyl siloxane (PDMS) exhibit properties that make them suitable for development as part of hybrid materials, mostly due to the Si-O-Si bond characteristics of the backbone. Polyorganosiloxanes are compounds with glass transition temperatures below zero and exist as viscous liquids at room temperature partly due to the high bond angle of the Si-O-Si bond and longer bond lengths of the Si-O bonds, which allows for torsional motion of the backbone[83]. In this study the focus will be on synthesis, characterization and electrospinning of PDMS hybrid materials for the subsequent use in volatile extraction. As discussed in the previous sections, PDMS coatings are commonly used for the extraction of volatile organic materials. One of the challenges in analytical chemistry remains the development of coatings for more selective analysis of target compounds. Even though hybrid materials based on PDMS (PDMS-DVB and Carboxen-PDMS) are already available for volatile extraction, the unique characteristics of PDMS allows for further investigations and developments in this field of science.

PDMS is one of the most commonly used polyorgano siloxanes in developing hybrid copolymers. On its own PDMS is a hydrophobic, rubbery material and has good thermal and mechanical stability. By using PDMS together with an organic copolymer for the synthesis of hybrid materials, a material with a thermoplastic segment that has completely different properties to that of the elastomeric PDMS segment can be created[84]. These unique combinations of organic and inorganic segments provide numerous possibilities for applications in various fields. Copolymers of various molecular architectures can be produced, some of these include block-, star- and graft copolymers[80].

In this study the focus will be on developing graft PDMS copolymers using the "grafting through" technique.

Various PDMS hybrid materials have been developed in recent years. Some of the graft and block copolymers previously synthesized using PDMS as the inorganic segment includes: Polymethyl methacrylate-block-PDMS-block-polymethyl methacrylate (PMMA-*b*-PDMS-*b*-PMMA), Polystyrene-block-PDMS-block-PDMS (PS-*b*-PDMS-*b*-PDMS), PDMS-*g*-PSTY[80], PDMS-graft-poly(acetic acid) (PDMS-*g*-PAA), PMMA-*g*-PDMS and PDMS-graft-poly(acrylo nitrile) (PDMS-*g*-PAN). One of the dominating factors that contribute to the unique properties of these materials is the difference in surface energy between the PDMS and organic segment, which allows for the preferential surface segregation of the PDMS. To incorporate PDMS into the polymer structure, it is often functionalized with polymerizable moieties prior to polymerization[80]. In the next section the polymerization of graft polymers will be discussed.

2.5 Polymerization

Different polymerization techniques exist which enables the synthesis of PDMS based copolymers. Anionic polymerization, free radical polymerization and controlled radical polymerization techniques like RAFT (radical addition fragmentation chain transfer) and ATRP (atom transfer radical polymerization) are some of the methods that have been used to synthesize these materials[80,84]. In this study the focus will be on conventional free radical copolymerization, specifically that of graft copolymers. Most of the work on graft and block copolymers containing PDMS were done by Graiver et al.[84] using a PDMS macro initiator. Graft copolymers consists of two different polymeric segments, in this case an inorganic PDMS segment as the side chain and an organic segment as the main chain. Graft polymers have a branched structure which usually means that there is a large concentration of terminal end groups, which gives the polymer unique properties when compared to the linear polymer counterparts. Graft polymers can be synthesised via three mechanisms, grafting through, grafting onto and grafting from. Figure 2.9 illustrates the different routes that can be followed.

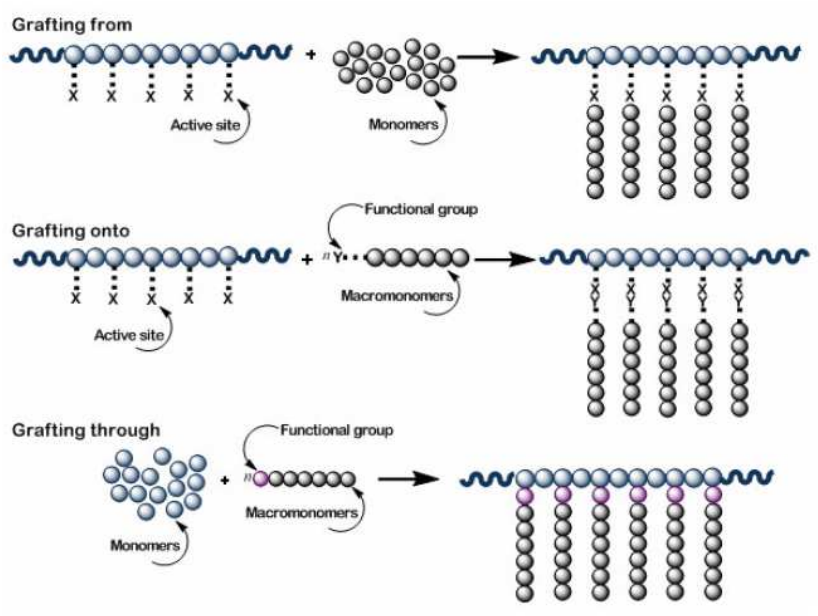

Figure 2.9: Illustration of different routes graft copolymers can be synthesized[85-86].

This can be done from either macromonomers or monomers. One of the main limitations of graft polymerization is steric hindrance of the reactive centre, which affects the efficiency of the grafting techniques[85].

2.5.1 "Grafting through"

The "grafting through" method is the easiest synthetic route to follow for the synthesis of graft copolymers. It is also known as the "macromonomer method", where an acrylate/methacrylate or any other functionalized macromonomer is copolymerized with a low molecular weight monomer via free radical polymerization. The acrylate/methacrylate functionality at the terminal end of the macromonomer serves as the copolymerizable moiety[85]. The macromonomer can be incorporated into the backbone which has been prepared by free radical polymerization; this polymerization is done "through" the macromonomers terminal functionality. Macromonomers can be prepared by various controlled polymerization processes and subsequently be used in copolymer synthesis. Using the "grafting through" procedure, well defined graft polymers can be designed as is shown in Figure 2.10. The composition of the copolymer is greatly dependant on the reaction conditions and the type of radical polymerization used. It is possible to control properties like copolymer composition, backbone and branch length, dispersity and functionality of these graft copolymers by using a combination of controlled radical polymerization processes. Different polymerization techniques will lead to different distributions of chain lengths and composition.

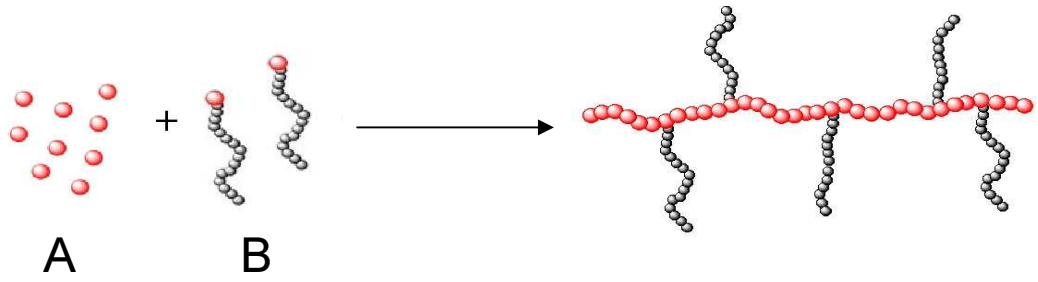

Figure 2.10: Schematic illustration of the reaction between the low molecular weight monomer (A) with a terminally functionalized PDMS macromonomer (B) to form a well-defined graft copolymer.

By controlling the ratio of the molar concentrations of the low molecular weight monomer and macromonomer, the degree of branching on the back bone can be controlled. The branching can be either homogeneously or heterogeneously distributed along the back bone depending on the reactivity ratio between the monomer and terminal end groups of the macromonomer. Figure 2.11 shows the difference between these two graft distributions. The density and distribution of branching will have a significant effect on the physical properties of the copolymer as well as the degree of polymerization of the back bone.

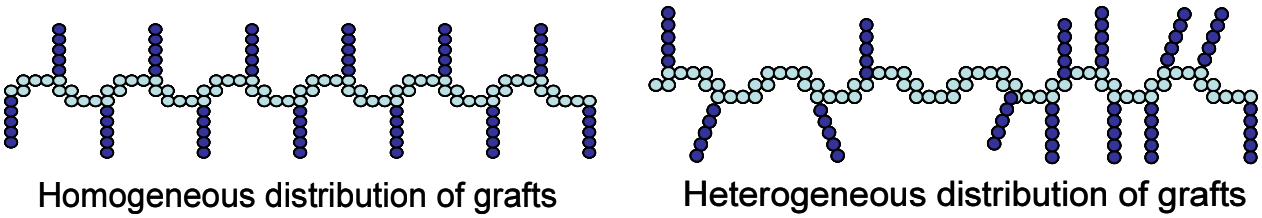

Figure 2.11: Different distributions of branches that can be achieved using different polymerization techniques

Shinoda et al.[87] illustrated the influence different radical polymerization techniques had on the microstructure of a copolymer by copolymerization of MMA with a polydimethyl siloxane-methacrylate macromonomer (figure 2.12). Using conventional free radical polymerization, copolymers with a broad distribution in chain length and composition were prepared. This is mostly due to the continuous initiation/growth/termination of the polymerization throughout the reaction. When using a different radical polymerization technique like ATRP, copolymers with a uniform chain length distribution were prepared.

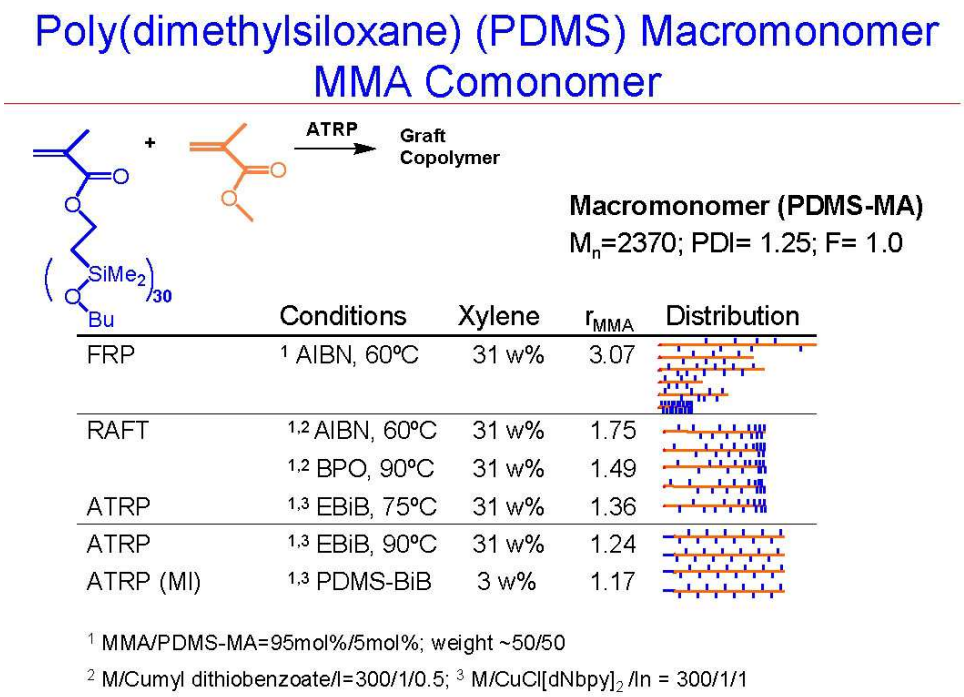

Figure 2.12: Different distributions of grafts achieved as a function of which copolymerization technique was used[87].

The use of controlled polymerization techniques have become popular for synthesizing copolymers due to the ability of controlling certain properties of the copolymer. However, like any other technique there are certain drawbacks of using the "grafting through" technique. This polymerization technique often leads to side products and residual macromonomers, which then requires further processing of the copolymer to remove the residual macromonomers.

2.5.2 "Grafting onto"

The "grafting onto" technique uses an organic polymer that has been terminally functionalized with an organic moiety. Qin et al.[88] prepared polystyrene with an azido end group which was then grafted to single-walled carbon nanotubes. This method is different to other techniques in the sense that the backbone and the side chains are synthesized independently, where after the prepared precursor are reacted together to form a graft copolymer[89]. Figure 2.13 shows the routes followed to prepare graft copolymers using the "grafting from" and "grafting onto" methods.

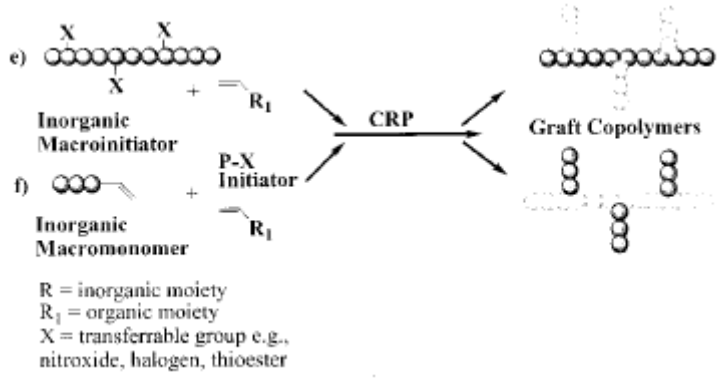

Figure 2.13: Scheme of "Grafting from" (e) and "grafting to" (f) methods using controlled radical processes to synthesize graft copolymers[80].

This technique can be used to prepare graft copolymers with a well defined structure.

2.5.3 "Grafting from"

The "grafting from" technique utilizes a polymeric backbone with polymerizable reactive groups that serve as the initiating functionality. Contrary to the other two techniques, the "grafting from" technique does not require the use of a macromonomer but rather a macro initiator[80,90]. This minimizes the resulting steric hindrance seen in grafting techniques. In the "grafting from" technique a monomer is introduced into the system and the reactive functionalities on the backbone will initiate polymerization and chain growth will occur at these sites[85]. Graft polymers with high densities known as bottle-brush copolymers can be obtained via this technique by controlling the active sites generated along the backbone. Steric hindrances between the chains cause molecules to take on unusual conformations due to the close packing of the side chains or the molecules can take on a linear conformation due to congested structure. A popular method for synthesizing graft copolymers where the molecules have unique or unusual conformations is through controlled radical polymerization (CRP) where the molecular weight, composition of the backbone and side chains can be controlled. Hawker et al.[91] used stable free radical polymerization (SFRP) after establishing that a unimolecular 2,2,6,6-Tetramethyl(piperidin-1-yl)oxyl-based (TEMPO) initiator can be used to control the polymerization of styrene. TEMPO is a stable nitroxide radical commonly used in SFRP. After preparing a macroinitiator through a copolymerization of styrene and a vinyl benzene TEMPO derivative, the macroinitiator was heated in the presence of styrene, which led to the activation of the TEMPO bond and polymerization of the graft copolymer. Nakagawa et al.[90] used atom transfer radical polymerization to successfully synthesize graft polymers of polystyrene (PSTY) from a PDMS backbone using a macrointiator[80,90]. The macroinitiator was synthesized by reaction of hydrosilyl or vinylsilyl attachable initiators with a difunctional PDMS with a corresponding functional end group. Using this technique, polymers with

well-defined structures and low polydispersities ($1.05<M_w/M_n<1.05$) could be developed[90]. This technique is however not limited to PDMS functional initiators but has also been used to functionalize polystyrene with single walled carbon nanotubes (SWNT). Qin et al.[88] achieved this through ATRP of styrene with SWNT which was functionalized with 2-bromopropionate groups. The successful preparation of graft copolymers using the "grafting from" technique has led to a variety of other materials being prepared via CRP. "Grafting from" reactions from polyethylene, polyisobutylene, polypropylene and polyvinylchloride have since been successfully prepared.

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Chapter 3

Experimental setup and methods

This chapter describes the synthesis of the homopolymers and graft copolymers as well as the setup used to electrospin these polymers into nanofibers. The analysis of two groups of volatile organic compounds using both the novel materials as well as commercially avialable materials as extraction phases will also be discussed.

3.0 Introduction

This chapter will give an overview of the routes followed to synthesize, electrospin and characterize the various novel materials to be used in VOC extraction. The different parameters optimized and the analysis conditions used in the extraction of VOCs using the commercially available and the novel polymeric materials will also be discussed.

3.1 Synthesis of homo polymers and graft copolymers

The following section will describe the synthesis of the different hybrid graft copolymers and homopolymers. The "grafting through" method which utilizes a functionalized macromonomer was used to prepare the copolymers[1].

3.1.1 Materials

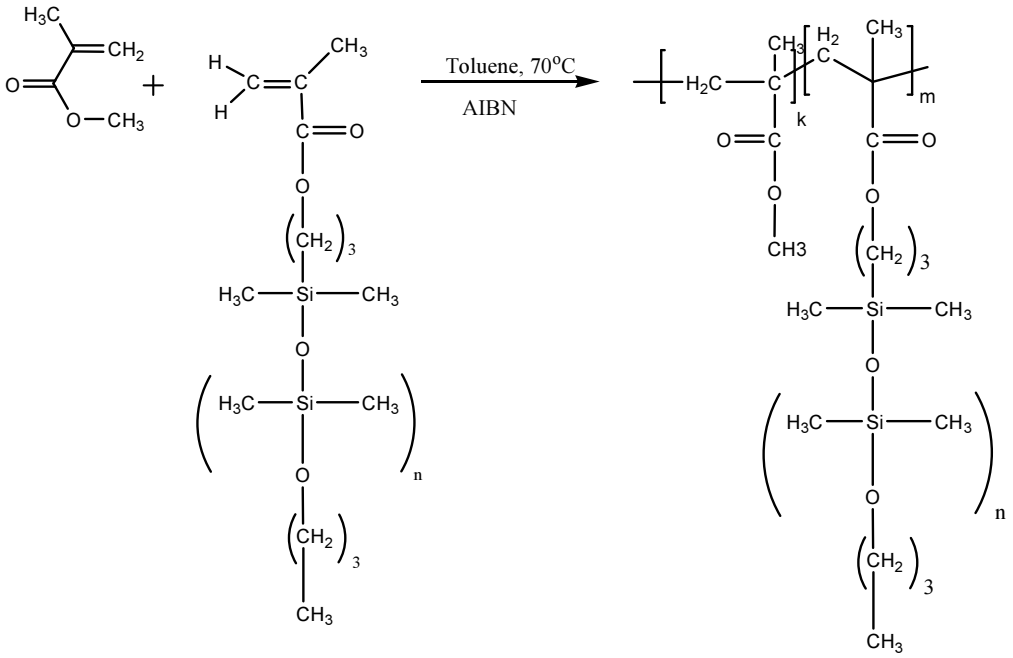
The following materials were used for the synthesis, electrospinning and characterization of the polymers: Methylmethacrylate (Plascon SA), butyl acrylate (Plascon SA), styrene (Plascon SA), methacrylic acid (Plascon SA), 2,2'-azobis(isobutyronitrile) (AIBN) (Plascon SA), monomethacryloxypropyl terminated polydimethylsiloxane (Gelest INC), toluene (Sigma-Aldrich), methanol (Sigma-Aldrich), n-hexane (Sigma-Aldrich), chloroform (Sigma-Aldrich), dimethyl-formamide (DMF) (Sigma Aldrich), potassium hydroxide (KOH) (Associated Chemical Enterprises, 85%), nitrogen (Afrox Scientific UHP Cyl 11 kg N5.0, 99.999%), deuterated chloroform, $CDCl_3$, (Cambridge Isotope Laboratories), deuterated dimethyl sulfoxide (DMSO-D_6) (Merck, 99.9%), tetrahydrofuran (THF) and dimethylacetimide (DMAc) (Sigma-Aldrich, 99.9%). All chemicals received from Plascon were further purified whilst the rest were used as received. The AIBN was recrystallized from methanol. All glassware used in this project was thoroughly cleaned and dried in a glassware oven before use.

3.1.2 Purification of monomers

To insure that all the inhibitor is removed from the monomers, a 0.3M KOH solution was used to wash the methyl methacrylate (MMA), butyl acrylate (BA) and styrene (Sty). A separating funnel was used to retrieve the washed monomer. This was repeated three times using a 1:1 volume ratio. The monomers were then stored on molecular sieves to remove any water that might be present[2-4]. The MAA monomer could not be washed using a KOH solution due to its miscibility with water. The MAA monomer was filtered through a disposable inhibitor removing column from Sigma Aldrich. Vacuum distillation was used to purify the monomers. The distillation was done under

vacuum in order to prevent thermal auto-polymerization of the monomers. The first fraction collected was discarded and the purified monomers were then collected in a round bottom flask, molecular sieves were added and the monomers were stored in the fridge at -8°C until use, with the exception of the MAA monomer which was stored in a dark cupboard at room temperature.

3.1.3 Synthesis of PSty-g-PDMS, PBA-g-PDMS, PMMA-g-PDMS and PMAA-g-PDMS



Scheme 3.1: Synthesis of PMMA-g-PDMS by conventional free radical polymerization[2].

Conventional free radical polymerization was used to synthesize the different graft polydimethyl siloxane copolymers. The same procedure was used for synthesizing all four graft copolymers. The monomer (1.4g), monomethacryloxypropyl terminated polydimethyl siloxane (0.6g) and Azobis(isobutyronitrile) (AIBN) (0.0014g) were added together with toluene (10g) to a 100mL round bottom flask. A magnetic stirrer was added and the round bottom flask was covered with a rubber septum. The flask was purged with nitrogen for 10 minutes to remove any oxygen that might be present before placing it in a 70°C oil bath. The flask was removed from the oil bath after allowing the reaction to take place for 48 hours. Methanol was used to precipitate the PSTY-g-PDMS and PMMA-g-PDMS, whereafter the polymers were retrieved with filtration and allowed to dry for 24 hours under vacuum at 50°C to remove any excess solvent or unreacted monomers. The low glass transition temperature of both the BA and PDMS meant that this graft copolymer could not be recovered using precipitation. Rota-vaporization was used to remove the solvent and recover

the polymer. There was, however, still some unreacted BA monomer present which could not be removed. Precipitation of the PMAA-g-PDMS was not necessary as the polymer was already present as a precipitate in the reaction flask. The precipitate/powder was removed from the round-bottom flask and dried in the vacuum oven overnight. Table 3.1 gives a summary of the graft polymers synthesized via conventional free radical polymerization.

Table 3.1: Formulation of hybrid graft copolymers prepared

Polymer	Mono-Methyacryloxypropyl terminated PDMS	Monomer	AIBN
	(g)	(g)	(mg)
PMMA-g-PDMS (10cSt)	0.603	1.400	1.5
PSTY-g-PDMS (10cSt)	0.600	1.399	1.4
PBA-g-PDMS (10cSt)	0.603	1.409	1.7
PMAA-g-PDMS (10cSt)	1.207	2.799	3.4
PMAA-g-PDMS (50-80cSt)	1.213	2.807	3.8
PMAA-g-PDMS (150-200cSt)	1.197	2.802	3.0
PMMA-g-PMDS (150-200cSt)	1.198	2.807	3.2

3.1.4 Synthesis of the homopolymers

Homopolymers were prepared using the same process as described in 3.1.3. MMA, MAA, BA and Styrene were polymerized using AIBN (0.1%wt on monomer weight) as initiator. The polymerization took place over a 48 hour period. The product was recovered by precipitation using methanol, whereafter it was filtered and dried in a vacuum oven for 24 hours. Table 3.2 summarizes the formulations of the homopolymers prepared via conventional free radical polymerization.

Table 3.2: Formulation of homopolymers prepared

Sample	Monomer	AIBN
	(g)	(mg)
PMMA	4.12	4.2
PSTY	3.99	4.0
PBA	3.99	4.1
PMAA	4.02	3.9

3.2 Electrospinning

This section will give an overview on the conditions used to prepare the nanofibers of the synthesized novel PDMS polymers and homopolymers.

3.2.1 Preparation of the polymer solutions

The synthesized graft copolymers and homo-polymers were used to create nanofibers using electrospinning. Electrospinning requires the polymer to be in solution[5]. Consequently each of the polymers was dissolved in a 2:3 Chloroform: Dimethylformamide solution over a 24 hour period. 10-12 wt% solutions of the polymers were used for the electrospinning.

3.2.2 Procedure and setup

A 10 - 25kV, 400 micro ampere output high voltage supply equipped with two electrodes was used for electrospinning. Electrospinning was done by placing the polymer solution in a reservoir which consisted of a glass syringe and syringe pump. A high electric potential/voltage was applied to the viscous polymer solution by attaching the positive electrode to the tip of the syringe needle and attaching a grounded electrode to the collector plate. The high voltage insures that the polymer solution becomes charged, that the surface tension of the liquid is counteracted by electrostatic repulsion and that the polymer solution is ejected through the capillary tip. Due to the dangers presented by using high voltages safety precautions was taken. Non-conducting materials were used as far as possible and conducting materials were isolated to prevent build up of static electricity[3].

3.2.3 Collection of the nanofibers

The polymer solution was fed through the glass syringe with a syringe pump at a constant flow rate. The collector plate consisted of a glass plate covered in aluminium foil. The grounded electrode was attached to the aluminium foil and the fibers were collected on the foil for ease of removal. For each of the different polymers the voltage and tip-to-collector distance was adjusted for optimal

formation of the nanofibers. The electrospinning of all the polymers were done at ambient temperatures. The final conditions used for electrospinning is summarized in Table 3.3.

Table 3.3: Electrospinning conditions for creating nanofibers

	Distance (cm)	**Voltage (kV)**	**Concentration (wt%)**	**Feedrate (ml/min)**	**Temperature (°C)**	**Humidity (%)**
MMA-g-PDMS	20	10	12	0.02	23.6	55.9
MAA	20	15	10	0.02	25.0	46.5
MMA	20	20	10	0.02	24.1	55.1
MAA-g-PDMS	20	15	10	0.02	24.4	52.9
STY	15	15	12	0.007	22.8	59.1

3.3 Characterization of polymers and nanofibers

Size exclusion chromatography (SEC) and nuclear magnetic resonance (NMR) were used to confirm the formation of the graft copolymers and homopolymers. SEM-EDS were used as an additional tool to confirm the presence of the silicon from the PDMS macromonomer in the formed graft copolymers. The morphology of the nanofibers was studied using scanning electron microscopy (SEM). SEM images were used to determine the average fiber diameter. The thermal stability of the synthesized polymers and the nanofibers was evaluated using thermal gravimetric analysis (TGA).

3.3.1 Size exclusion chromatography

SEC is a chromatographic technique used to separate molecules in solution based on their hydrodynamic volume, i.e. the size of the polymer in solution. It is one of the most commonly used techniques for determining the molecular weight of polymers.

The PBA-g-PDMS, PBA, PSty-g-PDMS, PSty, PMMA-g-PDMS and PMMA samples were dissolved in THF stabilized with 0.125% BHT at a concentration of approximately 1mg/ml. The solution was filtered using 0.45µm nylon filters whereafter 100µl of the polymer solution was injected. A flow rate of 1mL/min and a mobile phase of THF stabilized with 0.125% BHT were used. A calibration curve constructed from narrow polystyrene standards (Polymer Laboratories) was used to determine the molecular weight of all the polymers relative to that of styrene. A Waters HPLC equipped with a 1515 isocratic HPLC pump, 717 plus Autosampler, 2487 Dual λ Absorbance detector and 2414 Refractive index (RI) detector was used. For the separation the

following columns were used from Polymer Laboratories: Two PLgel 5µm mixed-C.300 × 7.5mm columns with a PLgel 3µm 50 × 7.5mm guard column. All samples were analyzed at 30°C. The total run time of the method was 30 minutes.

The MAA and MAA-g-PDMS were dissolved in dimethylacetimide (DMAc) stabilized with 0.05% BHT and 0.03% LiCl (w/v). The samples were filtered with 0.45µm glass membrane filters whereafter 100 µl of the polymer solution was injected. A flow rate of 1 mL/min and a mobile phase of DMAc stabilized with 0.05% BHT and 0.03% LiCl (w/v) were used. For the MAA based polymers methyl methacrylate standards (Polymer Laboratories) were used to determine the relative molecular weight of these polymers. The analysis was performed on a Shimadzu LC-10AT equipped with an isocratic HPLC pump, Waters 717 plus Autosampler and Waters 410 differential refractometer. For the separation the following columns were used: Three PSS GRAM 10µm 300 ×8mm (2 × 3000Å, 1× 100Å) columns with a PLgel 5µm 50 × 7.5mm guard column. All samples were analyzed at 40°C. The total run time of the method was 30 minutes.

3.3.2 Nuclear magnetic resonance

^{1}H-NMR analysis was used for characterization of the copolymers. A Varian VXR 300 MHz NMR Spectrometer was used. The samples were prepared by dissolving 30-50mg of polymer in 2mL deuterated chloroform ($CDCl_3$) (Merck, 99.8%) in a NMR borosilicate tube. The MAA and MAA-g-PDMS was not soluble in chloroform and deuterated dimethyl sulfoxide (DMSO-D_6) (Merck, 99.9%) was used instead. All of the monomers and macromonomers used in the preparation for the polymers were also analyzed via H^1-NMR for reference purposes. Approximately 80mg of monomer and 110mg of macromononomer were dissolved in 2mL deuterated solvent for the analysis.

3.3.3 Scanning electron microscopy

Scanning electron microscopy (SEM) was used to study the surface structure of the electrospun nanofibers and to determine the average diameter of the fibers. The fibers were mounted onto SEM stubs using double sided tape where after it was sputter coated with a thin layer of gold. The gold coat improves the electric conductivity of the sample surface. High resolution images were produced through electron backscattering from the sample surface. A LEO® 1430VP SEM fitted with backscatter, cathodoluminescence, variable pressure and energy dispersive detectors (EDS) were used to analyze the samples. The acceleration voltage of 7kV was used, with a beamcurrent of 60µA. INCA software was used for the analysis of EDS data.

3.3.4 Thermal gravimetric analysis

The thermal stability of the polymers before and after electrospinning was determined using a Perkin Elmer TGA-7. Approximately 5mg of each material were weighed of into ceramic pans. The samples were evaluated isothermically in 2 cycles at 200°C for 1 hour under an inert N_2 atmosphere. This was done in order to determine the loss in mass over time, at a selected operating temperature.

3.3.5 Optical Microscopy

An Olympus ZSX12 optical microscope was used to take images of the nanofibers before and after thermal analysis. The microscope is equipped with a binocular observation tube with an eyepiece with 10 × magnification, a 12 × zoom microscope body, 1.0 × and 1.6 × lenses and an Intralux 5000^{-1} external light source. The sample is placed on the optical stage, over the aperture, and a light source illuminates the sample from either above or below. The sample absorbs or reflects the light and the magnified image is directed through a series of lenses to an eyepiece and the image is captured using a colourview soft imaging camera. The images were analyzed using Analysis software.

3.4 Extraction of VOCs

The analysis of VOCs in the headspace at trace levels were evaluated using two different micro extraction techniques. Solid phase micro extraction (SPME) and Stir bar sorptive extraction (SBSE) were used for the extraction of selected non-polar volatile compounds commonly found in waste water and selected oxygenated volatile analytes commonly found in water-based latexes. Evaluation of the novel materials was done using a similar approach of extraction and desorption used in SBSE. Extraction efficiency of these compounds using the commercially available coatings will be compared with the novel coatings prepared, using similar extraction conditions.

3.4.1 Sample preparation

A 1g/L stock solution with different volatile organic compounds commonly found in waste water was prepared in HPLC grade methanol (Merck). The following chemicals were used: trichloroethlylene, tetrachloroethylene, tert-butyl benzene, o-dichlorobenzene, dibromomethane, chloroform, chlorobenzene, benzene, 1,2-dibromoethane, 1-bromo-3-chloropropane, bromoform, 1-bromo-4-fluorobenzene, mesitylene, 1,3-dichlorobenzene, trichlorobenzene. All the chemicals were acquired from Sigma Aldrich or Merck and have a purity of at least 99%. Each of the individual analytes were also analysed using GC-MS to evaluate the purity.

A 1g/L stock solution with different volatile organic compound commonly found in water based paint systems were prepared in HPLC grade methanol (Merck). The following chemicals were used: ethyl acrylate, methyl methacrylate, butyl acrylate and 2-hexylethyl acrylate.

For the method optimization in SPME and SBSE, 10ppb solutions were prepared by diluting the stock solutions with deionised water. Fresh samples were prepared from the stock solution every day. The stock solutions were stored in the freezer at -8°C.

3.4.2 Solid phase micro extraction

A SPME holder was acquired from Supelco (Bellefonte, PA, USA) together with the following fibers: 85µm polyacrylate (PA), 65µm polydimethylsiloxane-divinylbenzene (PDMS/DVB) and 75µm carboxen-polydimethylsiloxane (CAR/PDMS). The fibers were conditioned in the GC injector according to the instructions of the supplier. 22ml Headspace vials were used and filled with 10ml of the volatile mixture. The vials were capped with PTFE-Silica septa form Supelco (Bellefonte, PA, USA). The following parameters were evaluated to find the optimum extraction conditions: selection of coating; extraction temperature, addition of salt; extraction time; desorption time and desorption temperature[6].

3.4.2.1 Parameters evaluated

1. Coating selection: Extractions at room temperature (22°C) were done for 45 minutes to determine the fiber with the largest response for the greatest number of analytes. The fiber of choice was determined to be Carboxen-PDMS for both groups of analytes. This phase consists of solid particles of carbon molecular sieves that is embedded in the PMDS phase[7].

2. Extraction temperature: Increasing the temperature will speed up the time it takes to reach equilibrium between the sample and the headspace. Extraction temperatures between 40°C and 80°C were evaluated[8].

3. Salt addition: Adding salt can reduce the solvating power of a solution and force more of the analytes into the headspace. Salt was added to saturation level (3.4g/10ml) to evaluate whether improved extraction can be achieved.

4. Extraction time: The following extraction times were evaluated: 5 minutes, 15 minutes, 30 minutes, 45 minutes, 60 minutes and 75 minutes. Curves of time vs. analyte reponse can be constructed in order to determine when equilibrium is reached.

5. Desorption temperature: Must be high enough to desorp all the analytes from the fiber whilst keeping in mind the thermal stability of the fibre and the analytes. A desorption temperature of 250°C and 280°C were evaluated.

6. Desorption time: To avoid carry over of analytes between analysis, desorption times of 3 minutes and 5 minutes were evaluated. The analytes were injected in the splitless injection mode for 1.5 minutes where after the purge valve was opened. A 0.88mm (i.d) SPME liner was used to assure a faster flow of analytes from the injector to the column

3.4.2.2 GC-MS analysis

The analyses of the VOCs were done using a focus gas chromatograph hyphenated with a Dual System Quadropole mass spectrometer (Thermo Finnigan, Austin, TX, USA). A BPX5 30m × 250µm i.d., 0.25µm analytical column was used for chromatographic separation and helium was used as the inert carrier gas at a constant flow of 1.5ml/min. The following GC – oven conditions were used: Initial temperature of 40°C (hold 3 minutes), ramp at 10°C/min to 100°C, ramp at 20°C/min to 250°C. The MS transfer line temperature was set at 260°C. The mass range scanned was from m/z 40-350. Positive electron ionization was used at an electron impact energy of 70eV. For the analysis of the samples a solvent delay of 1.5 minutes was used. All the chromatograms and mass spectra were processed with XCalibur software and compounds were identified using the US National Institute of Science and Technology (NIST) mass spectral library.

3.4.3 Stir bar sorptive extraction

A PDMS stir bar commercially known as “Twister” and available from Gerstel (Mulheim, Germany) was used for the extraction. The PDMS coated stir bar was conditioned for 1 hour at 250°C before use. Headspace sorptive extraction (HSSE) was used[6,9]. The volume of coating in SBSE is much higher than the volume of coating used in SPME, therefore very long extraction times might be necessary to reach equilibrium[10]. In order to keep the time it takes to do one analysis reasonable the same sampling conditions used in SPME were used in the stir bar extraction. Agitation via stirring with a magnetic stirrer was evaluated as an additional parameter due to the SBSE being a manual process vs. the automated process of the SPME. Table 3.4 summarize these conditions.

Table 3.4: SBSE sampling conditions

Parameters	Non - polar analytes	Polar analytes
Extraction temperature	60°C	60°C
Extraction time	60 minutes	45 minutes
Salt addition	No salt added	Salt added
Stirring	Stirring at 600rpm	Stirring at 600rpm

3.4.4 Extraction of VOCs using novel materials

The following novel materials were evaluated as possible extraction media for VOC analysis: PMAA-g-PDMS, PAN-g-PDMS and PMAA. These nanofibers were chosen based on the fiber morphology and thermal stability. Although the MAA based polymers showed weight loss during thermal analysis they were still evaluated. The weight of the nanofibers used in a single extraction was recorded in order to make comparisons in the extraction efficiency between the commercial coatings and novel coatings used. The sampling conditions used were similar to the conditions used for the extraction using SPME and SBSE.

3.4.5 Thermal desorption conditions

Unlike SPME where the fiber can be directly introduced into the GC injector port, SBSE requires the use of an integrated thermal desorption system to desorb the analytes. A Gerstel TDS 3 thermal desorption system and a Gerstel 505 pressure controller coupled with liquid nitrogen supplied by Affrox were used. The desorption time of VOCs is usually in the range of 10 minutes using SBSE. To refocus the VOCs prior to chromatographic analysis they were cryogenically trapped using liquid nitrogen. The cryotrap is then heated up using a PTV injector and the analytes are introduced into the GC[6]. Table 3.5 summarizes the conditions of the thermal desorption system.

Table 3.5: Desorption, trapping of analytes and introduction

	CIS conditions	Sample conditions
Start temperature	-100°C	40°C
Start time	0.10 minutes	0 minutes
Heating rate	12°C/minute	20°C/minute
End temperature	200°C	200°C
Hold time	2 minutes	5 minutes
Equilibrium time	0.5 minutes	N/A
Flow mode	Splitless for 1.5 minutes	Splitless
Transfer temperature	N/A	220°C

Similar conditions were used for the desorption of the VOCs from the novel materials, with the exception of MAA-g-PDMS where a desorption temperature of 150°C were used to reduce background peaks from impurities present in the material.

3.4.6 GC-MS analysis

The analyses of the VOCs after thermal desorption were done using a HP6850 series gas chromatograph system hyphenated with a 59873 network mass selective detector from Agilent technologies. A BPX5 30m × 250µm i.d., 0.25µm analytical column was used for chromatographic separation and helium was used as the inert carrier gas at a constant flow of 1.5ml/min. The following GC – oven conditions were used: Initial temperature of 40°C (hold 5 minutes), ramp at 10°C/min to 220°C. The MS transfer line temperature was set at 230°C. The mass range scanned was from m/z 40-350. Positive electron ionization was used at an electron impact energy of 70eV. A solvent delay of 1.5 minutes was used. All the chromatograms and mass spectra were processed with chemstation software and compounds were identified using the US National Institute of Science and Technology (NIST) mass spectral library.

3.5 References

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Chapter 4

Results and Discussion

This chapter describes the results obtained for the SPME method optimization for the extraction of the target VOCs. The characteristics of the polymers, and subsequently the morphology and thermal stability of the nanofibers is also discussed. Finally, the application of the nanofibers for the use as VOC extraction materials is discussed.

4.0 Extraction and analysis of VOCs

As previously discussed in Chapter 2, different parameters will influence the efficiency of extraction of analytes from a matrix. One of the most important parameters is the type of extraction phase used for the extraction; usually an extraction phase with the greatest affinity for the largest number of analytes is selected[1]. Other factors that influence the extraction include extraction time, extraction temperature, agitation, desorption time and desorption temperature[2]. To develop a method for the extraction of the target analytes, a number of these variables were evaluated. Standard solutions of 10µg.l^{-1} were used for the headspace extraction optimization.

4.1 Selection of extraction mode

The two sampling modes available for SPME are headspace solid phase micro extraction (HS-SPME) and direct immersion solid phase micro extraction (DI-SPME). DI-SPME requires the fiber to be inserted directly into the liquid sample, therefore a decrease in the fiber lifetime is seen, especially when the sample matrix is complex. In HS-SPME a sample vial is filled only partially with the sample and the fiber is exposed to the vapour phase or headspace above the sample. In this mode a 2-part equilibrium takes place, firstly between the sample liquid phase and vapour phase and secondly between the fiber and the headspace. With headspace extraction the fiber has no direct contact with the sample, which ensures that the fiber lifetime is extended. For the analysis of volatile compounds in complex matrices HS-SPME is generally the best sampling mode. In this study the focus will be on HS-SPME as real life samples are generally complex and may contain numerous non-volatile compounds.

4.2 Optimization for the SPME extraction of non-polar VOCs in water

Halogenated volatile organic compounds (HVOCs) and benzene derivatives are organic pollutants that can be found in various environmental samples some of which include water, soil and air. These VOCs need to be monitored due to their high toxicity. Organohalogen solvents are used as cleaning agents, solvents, disinfectants and pesticides and can enter the environment by wastewater contamination. A number of challenges are faced when analyzing these compounds in the environment, including the high volatility of the compounds, low concentrations present in environmental samples and poor stability of the samples, as well as complex matrices[3]. Isolating these compounds from the matrix is time consuming and requires the use of large quantities of solvents. With new solvent-free techniques available, the analysis of these compounds has become

simpler. The extraction of these HVOCs and benzene derivative compounds from water using SPME was investigated and the limits of detection determined.

4.2.1 Fiber selection

Fiber selection plays the most important role in the extraction of these analytes[4]. Using the correct fiber will yield better recoveries of the analytes from the matrix and will result in shorter analysis times. The target analytes extracted have different polarities (Table 4.1) and this will influence the selection of the fiber. All the compounds have a dielectric constant of less than 15 and are considered non-polar. The three different fibers evaluated were 85 µm polyacrylate (PA), 65 µm polydimethyl siloxane-divinylbenzene (PDMS/DVB) and 75 µm carboxen-polydimethyl siloxane (CAR/PDMS). Figure 4.1 shows the different properties that these extraction phases possess and from this CAR/PDMS seems to be the most suited fiber for the analysis of the non-polar halogenated compounds.

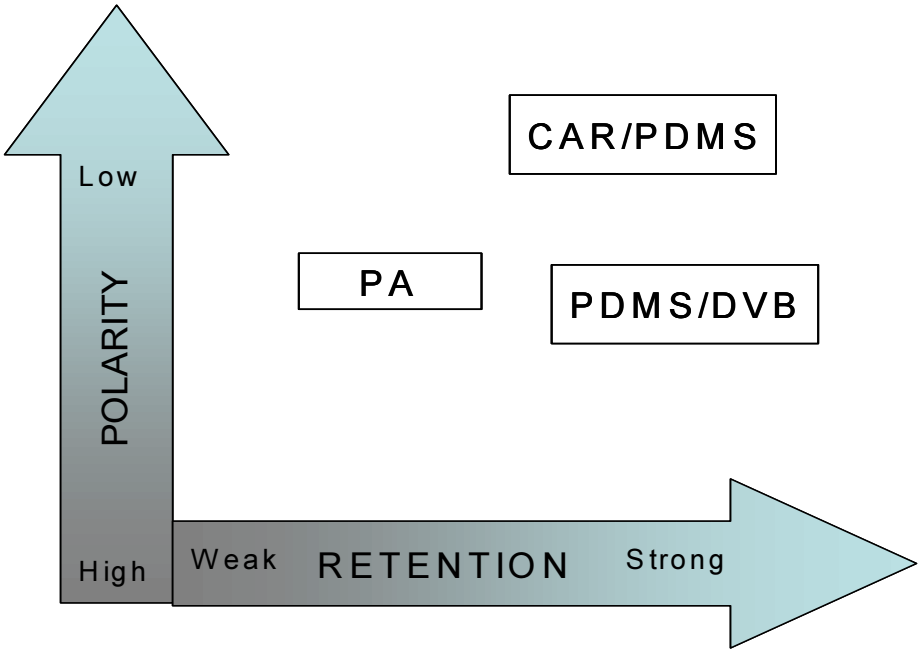


Figure 4.1: The properties of the three coatings evaluated for the extraction of the analytes of interest[5].

Extractions were done at room temperature for 45 minutes using a 10 µg.l^{-1} solution of the analytes of interest in water. Figure 4.2 shows the detector response for each of the different fibers for the selected analytes. The fiber that has the greatest affinity for the highest number of compounds was selected and used for further optimization for the extraction of these compounds.

Table 4.1: Properties and concentration of analytes of interest

Compound	Vapour pressure hPA @ 20°C	Boiling point (°C)	Dielectric constant[a] ε_r (20°C)	Concentration ($\mu g.l^{-1}$)
chloroform	213	61	4.81	10.06
benzene	101	80	2.3	10.10
tetrachlorethylene	19	121	2.5 (21°C)	10.20
1,2-dibromoethane[b]	14.7	132	NA	10.14
chlorobenzene	12	132	5.6	10.03
1-bromo-3-chloropropane[b]	7.5	141-143	NA	10.11
bromoform	7.5	149.5	4.4 (10°)	10.13
1-bromo-4-fluorbenzene[b]	25	151-163	NA	10.03
bromobenzene	4	156	5.4	10.16
mesitylene	2.8	163-165	2.4	10.07
tert.butyl benzene	1.33	64	2.34	10.12
1,3-dichlorobenzene	3	173	5	10.40
1,2-dichlorobenzene	1.33	180	9.9	10.31
1,2,4-trichlorobenzene	1.3	213.5	2.24 (25°C)	10.03

[a] The dielectric constants are reported for 20°C unless otherwise indicated

[b]Dielectric contants not available

It is evident from Figure 4.2 that the polyacrylate fiber had the poorest affinity for the volatiles of interest. The most volatile compounds, chloroform, benzene, trichloroethylene, tetrachloroethylene and 1,2-dibromoethane were not detected at all when using the PA fiber as extraction material. All of these compounds are non-polar in nature, whilst the PA fiber is more suitable for the extraction of polar compounds[2]. The diffusion coefficients of the analytes in PA are also lower when compared to the PDMS phases. Extraction of the analytes occurs via an absorption process.

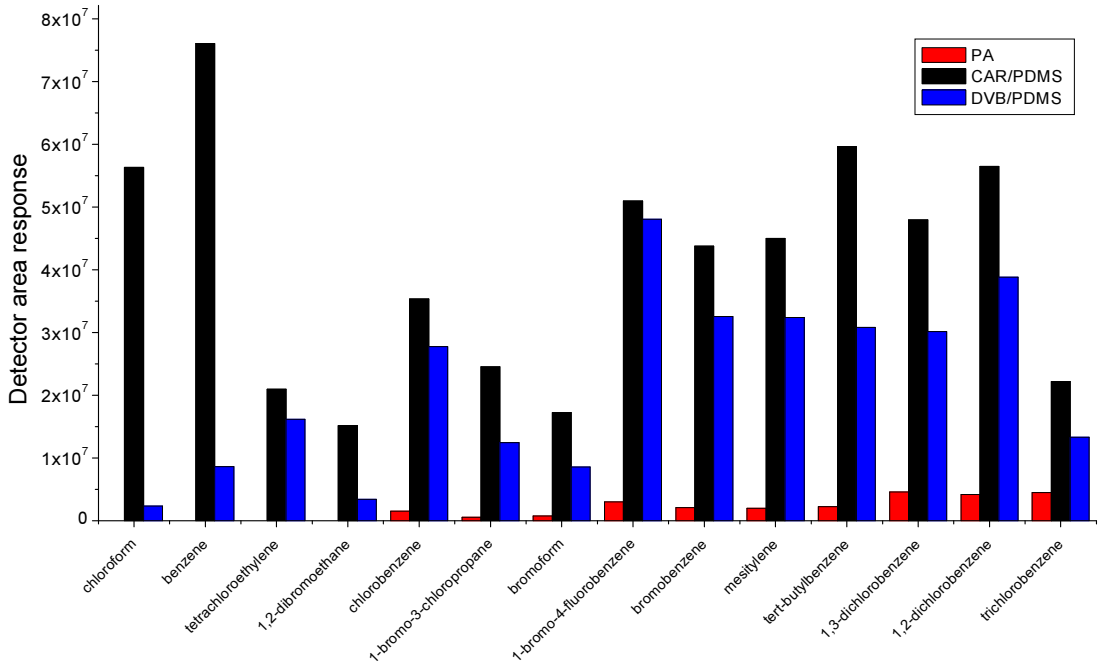


Figure 4.2: Selection of the fiber coating with optimal extraction efficiency. Fibers evaluated: 85 µm PA, 65 µm PDMS/DVB and 75 µm CAR/PDMS. Experimental conditions: 10 ml distilled water containing approximately 10 µg.l^{-1} of all the compounds; extraction time, 45 minutes; extraction temperature, 30°C; desorption temperature 250°C; desorption temperature, 5 minutes.

The mixed DVB/PDMS and CAR/PDMS phases extracted all of the volatiles and are, therefore, more suitable for the extraction of highly volatile compounds. Both these phases work on the principle of adsorption and usually the only drawback with these phases is the displacement effect, where analytes with a higher affinity for the extraction phase replaces analytes with a lower affinity. These phases usually also have a smaller linear dynamic range due to their adsorptive properties[2]. In this case the CAR/PDMS fiber outperformed the DVB/PDMS for all the compounds and especially for the extraction of the more volatile compounds. The best fiber was, therefore, determined to be the 75 μm carboxen-polydimethylsiloxane (CAR/PDMS) fiber.

4.2.2 Extraction temperature

The sampling conditions for the extraction were further optimized using the previously selected CAR/PDMS fiber. Different sampling temperatures were used to determine the effect that temperature has on the extraction process; usually an increase in extraction efficiency is observed at higher temperatures. Increasing the temperature forces more of the volatiles into the headspace. At first the SPME headspace extraction was evaluated at room temperature (22°), 40°C and 50°C for 45 minutes. Figure 4.3 show an increase in the amount of analytes extracted when using elevated extraction temperatures up to 50°C

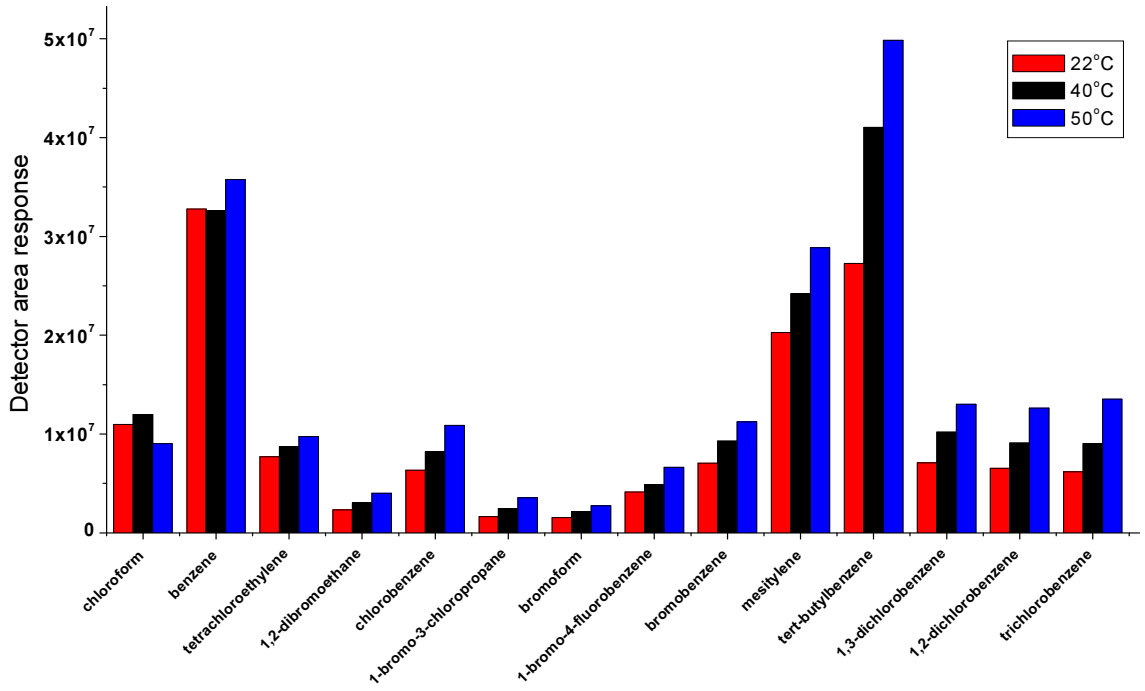


Figure 4.3: Extraction profile of non-polar compounds at extraction temperature of 22°C, 40°C, 50°C. Fiber evaluated, 75 µm CAR/PDMS; Experimental conditions: 10 ml distilled water containing approximately 10 µg.l^{-1} of all the analytes; extraction time, 45 minutes; desorption temperature 250°C; desorption temperature, 5 minutes.

Temperatures from 50°C to 80°C were evaluated to determine if the extraction efficiency can be further improved. Extraction at such high temperatures results in the generation of significant amounts of water vapour, which might lead to a decrease in the lifetime of the coating and sample losses. However, even at temperatures of 80°C improvement in the extraction efficiency is still seen for most compounds. This increase in extraction efficiency is due to an increase in the distribution coefficient of the analytes between the sample and the headspace when the temperature is increased[2]. The relationship between the sample temperature and the distribution coefficient, $K_{fs,}$ is illustrated by the following equation:

$$K_{fs} = K_0 \exp \frac{-\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T_0}\right]$$

where K_0 is the distribution coefficient at temperature T_0 (initial extraction temperature), T_1 is the new extraction temperature, ΔH is the change in the enthalpy of the analyte when moving from the sample to the extraction material and R is the ideal gas constant. From Figure 4.3 and Figure 4.4 it is evident that the temperature is an important parameter for the optimization of extraction efficiency.

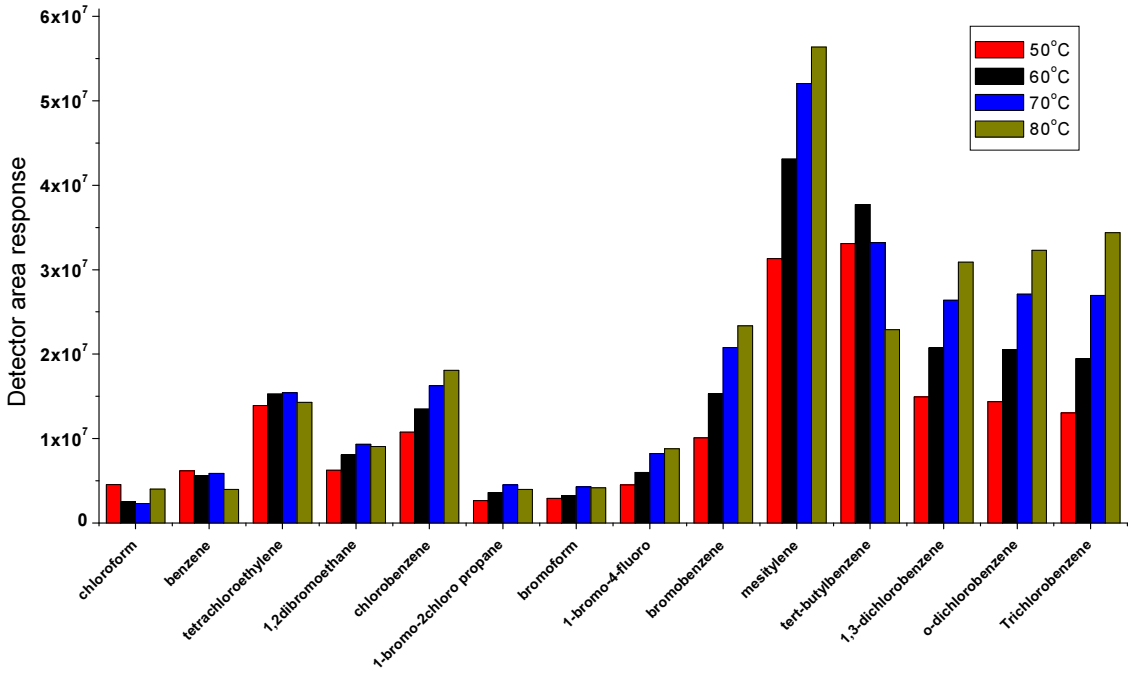


Figure 4.4: Extraction profile of non-polar compounds at extraction temperatures of 50°C, 60°C, 70°C and 80°C. Fiber evaluated, 75 µm CAR/PDMS; Experimental conditions: 10 ml distilled water containing approximately 10 µg.l^{-1} of all the analytes; extraction time, 45 minutes; desorption temperature 250°C; desorption temperature, 5 minutes.

All further sampling and method optimization was done at an extraction temperature of 60°C. This temperature was chosen to avoid sample losses for highly volatile compounds like benzene and chloroform while still maintaining good sensitivity for all the other analytes.

4.2.3 Salt addition

The addition of salt or any other pH modifier can greatly increase or decrease the extraction of the VOCs. This is dependent on the type of analytes and on the concentration of the analyte solution, extraction of more polar analytes have generally been seen to benefit from the salting effect. No theoretical studies have been done to explain the salting effect in SPME and thus far, has only been determined experimentally[2]. Figure 4.5 illustrates the effect on the extraction when NaCl was added at saturation level to the aqueous sample at an extraction temperature of 60°C.

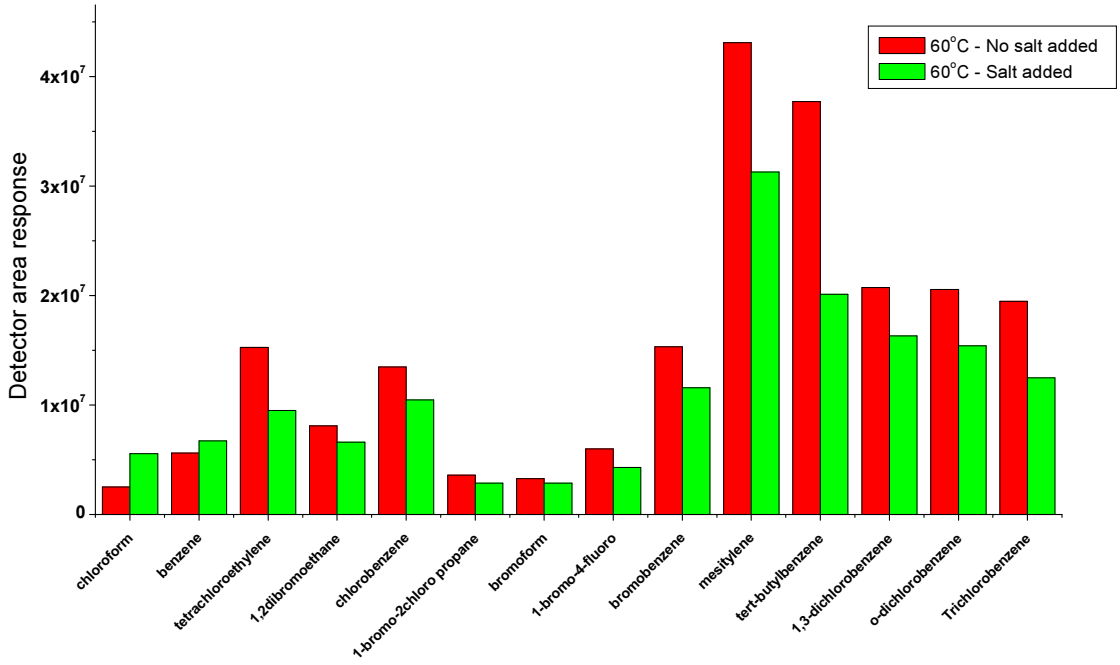


Figure 4.5: Extraction profile of non-polar compounds with and without the addition of salt at levels of 340 mg.ml^{-1}. Fiber evaluated, 75 µm CAR/PDMS; Experimental conditions: 10 ml distilled water containing approximately 10 µg.l^{-1} of all the analytes; extraction time, 45 minutes; extraction temperature, 60°C; desorption temperature, 250°C; desorption temperature, 5 minutes.

When using the optimized temperature of 60°C a decrease in the extraction efficiency is seen when salt is added to the sample matrix. The exception for this was the improved extraction of chloroform and benzene with the addition of salt at 60°C. Based on these results salt addition was not used during the rest of the method development.

4.2.4 Extraction time

Figure 4.6 shows the total extraction profile of all the analytes at room temperature when using the PA fiber. In the first few minutes, an exponential increase in the amount of analytes extracted is observed, where after the slope decreases as equilibrium is reached. Distribution equilibrium is reached when no further increase in the detector response is noted with an increase in the extraction time[2]. Working at equilibrium conditions reduces variations in the mass transfer. Extraction times from 5 to 75 minutes were evaluated for the CAR/PDMS fiber.

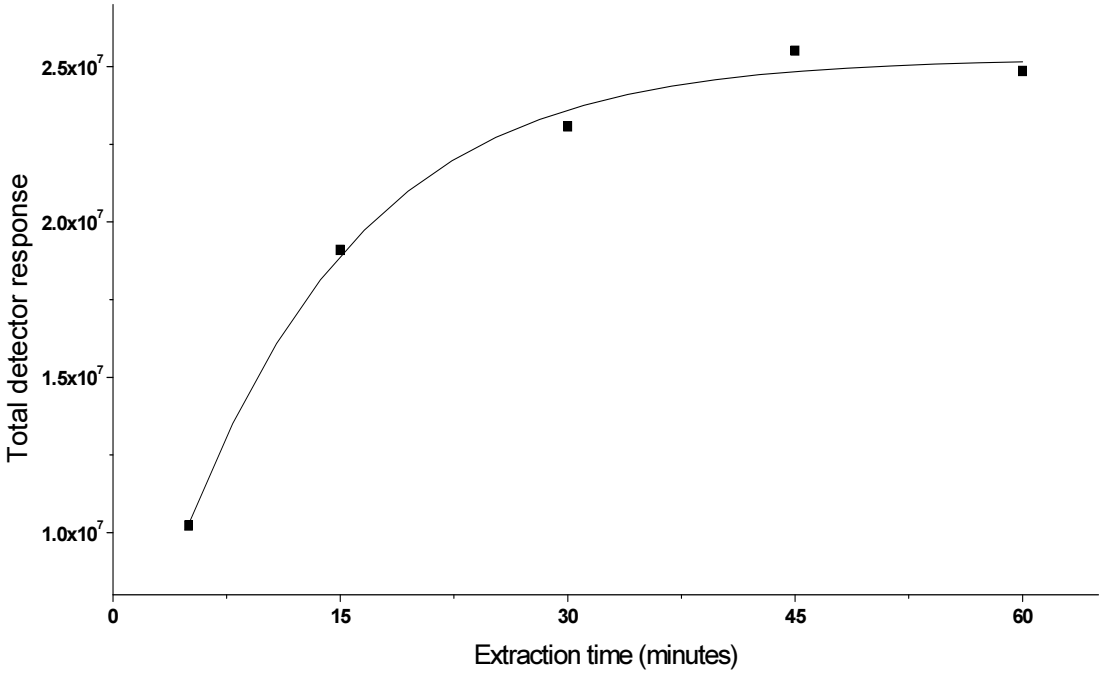


Figure 4.6: Total extraction time profile for the 85 µm PA fiber. Experimental conditions: 10 ml distilled water containing approximately 10 $\mu g.l^{-1}$ of all the compounds; extraction temperature, 30°C; desorption temperature 250°C; desorption temperature, 5 minutes.

Figure 4.7 shows the extraction profiles for bromobenzene, o-dichlorobenzene, m-dichlorobenzene and trichlorobenzene. During the first 30 minutes no major increase is observed in the amount of analytes extracted. From 30 minutes to 60 minutes a notable increase is seen in the detector response, whereafter the incline of the slopes starts to decrease. Bromobenzene shows no significant increase in the amount extracted between 60 and 75 minutes, an indication that equilibrium conditions have been reached. However, for the other three compounds, the amount extracted after 75 minutes is still increasing. In general longer extraction times are needed for compounds with a higher affinity to the extraction phase[6]. To maintain reasonable experimental times, longer extraction times weren't evaluated. This would eliminate any displacement effects that might start taking place. All of the compounds were evaluated up to 75 minutes and the total detector response for all the analytes in the sample was calculated. The extraction was efficient for all the target analytes in the entire time profile. The total extraction yield of the sample is shown in Figure 4.8 for different extraction times.

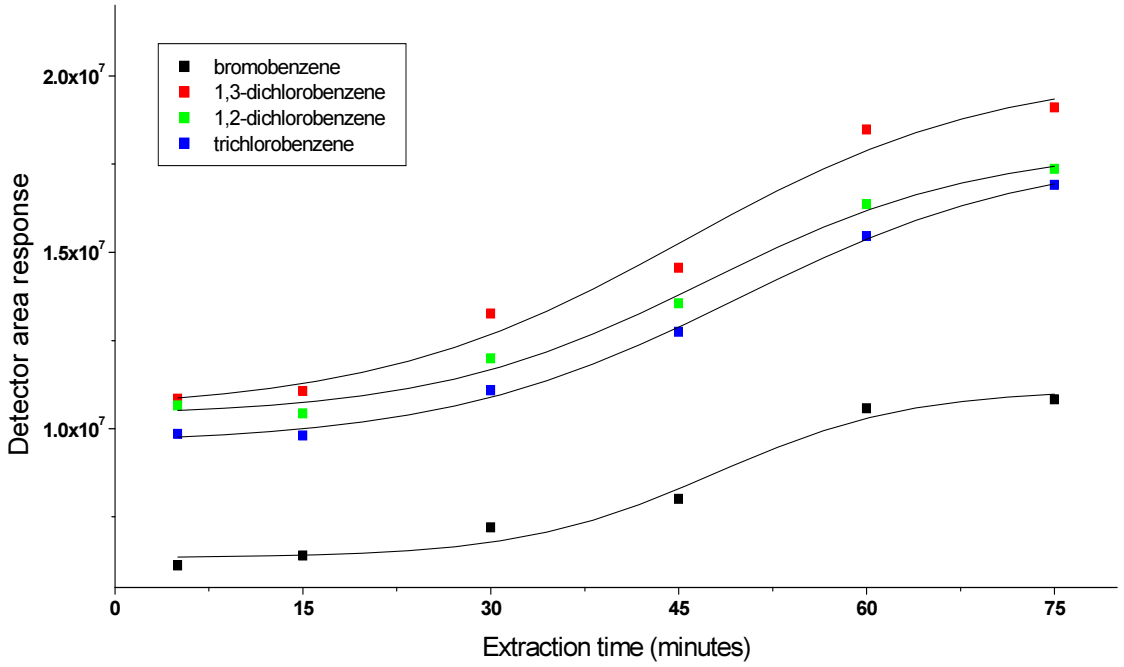


Figure 4.7: Time profile at 60°C without salt addition for bromobenzene, 1,3-dichlorobenzene, 1,2-dichlorobenzene and trichlorobenzene. Fiber evaluated: 75 µm CAR/PDMS. Experimental conditions: 10mL distilled water containing approximately 10 ug.l^{-1} of all the compounds; extraction temperature, 60°C; desorption temperature 250°C; desorption temperature, 5 minutes.

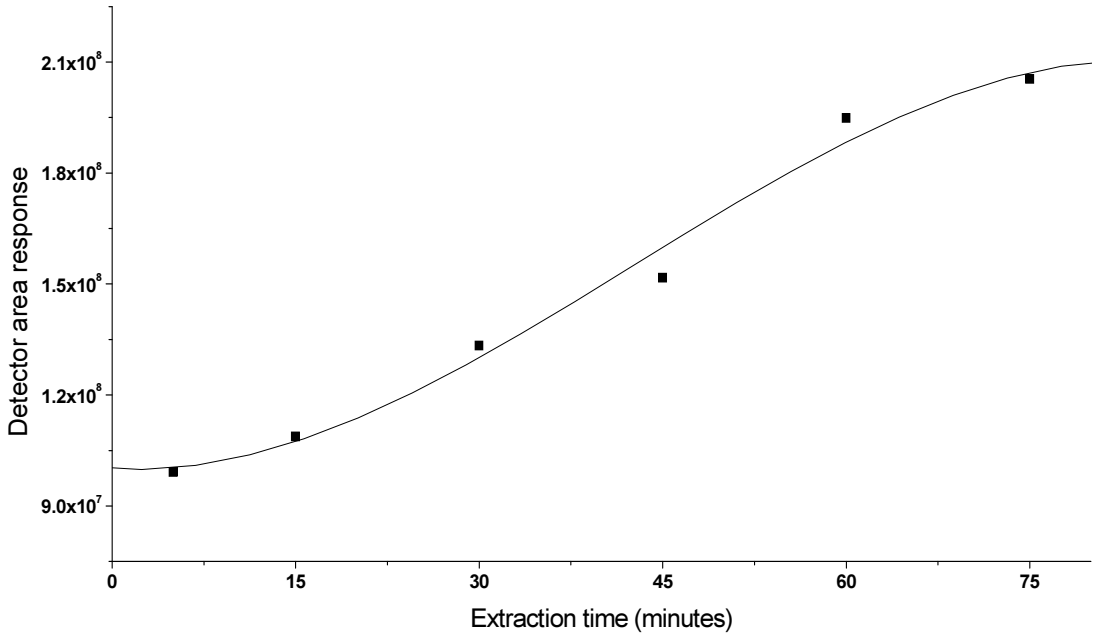


Figure 4.8: The total extraction time profile without salt addition for the 75 µm CAR/PDMS fiber. Experimental conditions: 10 ml distilled water containing approximately 10 µg.l^{-1} of all the compounds; extraction temperature, 60°C; desorption temperature 250°C; desorption temperature, 5 minutes.

The total extraction yield follows the same behaviour as the selected compounds in Figure 4.7. The total analyte profile indicates that equilibrium has not been reached after 75 minutes. There was, however, only a small increase in the amount extracted from 60 to 75 minutes. An optimized extraction time of 60 minutes was chosen as a compromise and therefore all analyses were done in the pre-equilibrium state.

4.2.5 Desorption conditions

The desorption temperature must be high enough to desorp all the analytes from the fiber, whilst taking into account the recommended and maximum operation temperature defined by the supplier. The recommended operating temperature for the 75 µm CAR/PDMS fiber is defined as between 250°C and 310°C. A desorption temperature of 250°C and 280°C were evaluated, both temperatures being within the range defined for the fibers. No significant difference was observed between the two desorption temperatures and the desorption temperature was therefore chosen as 250°C. Working at a lowest recommended temperature of the fiber increases the lifetime of the fiber and decreases the presence of thermal degradation products in the chromatogram. Desorption times of 2 minutes and 5 minutes were evaluated. At 2 minutes the compounds with higher boiling points are not completely desorbed, resulting in carry over (analytes from one extraction is still present on the fiber in the next extraction leading to incorrect GC results). After 5 minutes all of the compounds were desorbed from the fiber and transferred to the analytical column using a splitless time of 1.5 minutes.

4.2.6 Limit of detection, limit of quantitation and precision

The following optimized conditions were used to determine the limit of detection (LOD), limit of quantitation (LOQ) and precision (%RSD): Extraction were done using a 75 µm Carboxen/PDMS fiber at 60°C for 60 minutes for a 10 ml sample in a 22 ml headspace vial without the addition of salt. The agitator installed with the autosampler was switched on during all extractions. The analytes were desorbed from the fiber for 5 minutes at a temperature of 250°C.

The LOD and LOQ of the SPME analysis was determined by evaluating the total ion chromatogram (TIC) obtained in scan mode for the extraction of the target analytes over a range of 0.01 $\mu g.l^{-1}$ to 1000 $\mu g.l^{-1}$. The LOD and LOQs were determined at a signal to noice (S/N) ratio of 3:1 and 5:1 respectively. Figure 4.9 show the total ion chromatogram (TIC) of these compounds extracted by SPME at 10 $\mu g.l^{-1}$.

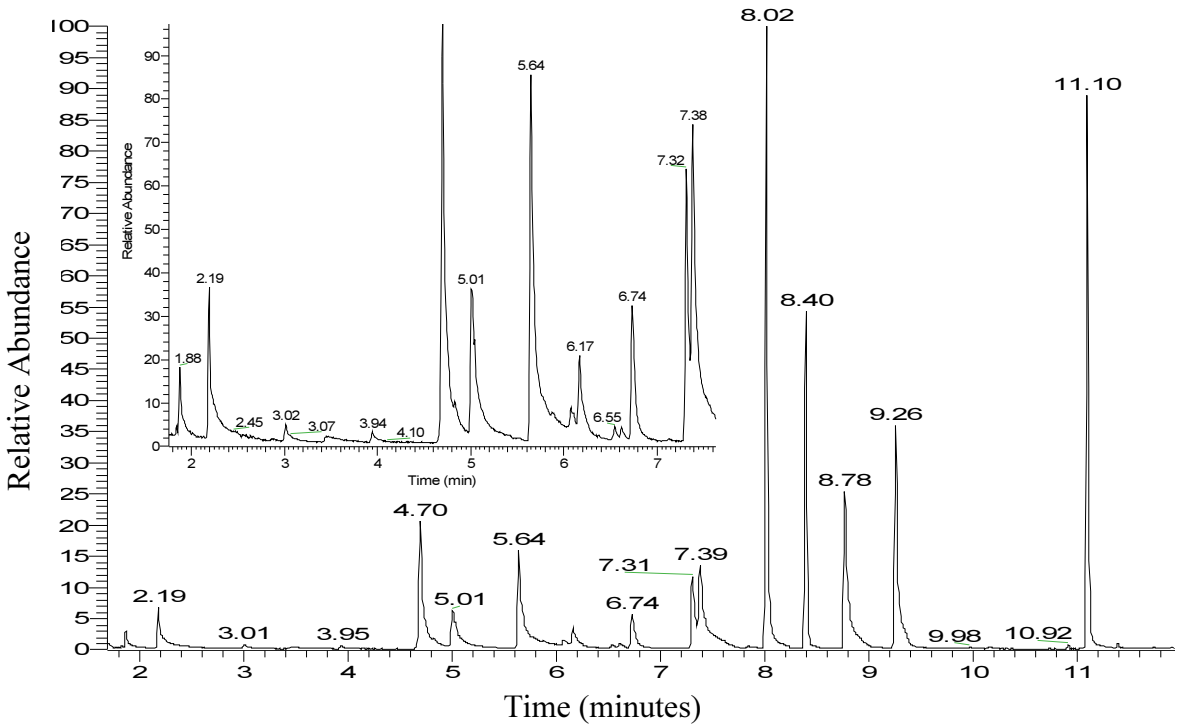


Figure 4.9: TIC of the non-polar compounds extracted using the CAR/PDMS fiber at 60°C for 60 minutes.

Baseline separation of all the compounds is achieved except for the bromobenzene and 1-bromo-4-fluorobenzene. Changing the temperature profile of the GC does not improve the separation and most likely the only way to achieve baseline separation of these two compounds is by using a column with a different stationary phase. The BPX5 stationary phase column which was used is non-polar in nature. A boiling point separation is seen, with the most volatile compounds eluding first (chloroform and benzene) and the least volatile compounds eluding last.

Table 4.2 shows the determined detection and quantitation limits, as well as the precision of the optimized SPME method.

Table 4.2: Detection and quantitation limits and precision (%RSD)

Compound	Retention time (minutes)	LOD (µg l^{-1})[a]	LOQ (µg l^{-1})[b]	Precision (%RSD)[c]
chloroform	1.87	1.111	1.850	7.4
benzene	2.19	0.230	0.384	6.6
tetrachlorethylene	4.70	0.002	0.029	9.3
1,2-dibromoethane	5.01	0.166	0.329	12.6
chlorobenzene	5.64	0.095	0.158	12.7
1-bromo-3-chloropropane	6.17	1.088	1.813	8.5
bromoform	6.74	0.188	0.242	8.9
1-bromo-4-fluorbenzene	7.31	0.155	0.297	1.7
bromobenzene	7.39	0.123	0.249	4.3
mesitylene	8.02	0.003	0.066	8.6
tert.butyl benzene	8.40	0.002	0.030	2.2
1,3-dichlorobenzene	8.78	0.153	0.256	3.0
1,2-dichlorobenzene	9.26	0.001	0.007	6.0
trichlorobenzene	11.10	0.024	0.040	4.4

[a] The limit of detection was calculated as the point where the signal-to-noise-ratio is 3:1

[b] The limit of quantitation was calculated as the point where the signal-to-noise-ratio is 5:1

[c] $n = 3$

It is evident from these results that the majority of the non-polar compounds can effectively be analyzed using SPME at levels below 1 µg l^{-1}. In the next section the SPME analysis of more polar oxygenated compounds present as VOCs in water-based paints will be discussed.

4.3 Optimization for the SPME extraction of acrylate VOCs commonly found in zero VOC water-based paints

VOCs found in water-based paints are some of the most common contributors affecting the quality of indoor air. Numerous volatile compounds are present in these materials therefore different methods are necessary to evaluate these VOCs. Using the same methodology as for the non-polar compounds an optimized SPME method was developed for the analysis of the following analytes: ethyl acrylate (EA), methyl methacrylate (MMA), butyl acrylate (BA) and 2-ethylhexyl acrylate (2-EHA), where EA is the most polar compound and 2-EHA the most non-polar. These compounds are just one group of volatiles found in paint. Other volatile compounds include alcohols, ketones, esters and glycols. Initial screening of a 10 µg.l^{-1} solution containing butanol as well as propylene

glycol, ethyl glycol and diethylene glycol mono butyl ether was done. However none of these compounds was extracted by any of the available SPME fibers, even though there boiling points are below 200°C. The evaluation of these compounds did not form part of this study.

Table 4.3 list the properties of the four acrylate analytes evaluated.

Table 4.3: Properties and concentration of analytes of interest

Compound	Vapour pressure hPA @ 20°C	Boiling point (°C)	Concentration ($\mu g.l^{-1}$)
EA	39	100	9.74
MMA	53	101	9.97
BA	5.3	147-148	10.02
2-EHA	0.12	229	10.49

4.3.1 Fiber selection

The target analytes are more polar in nature than the VOCs analysed in the previous section due to the presence of ester functionalities. Currently there are not a lot of extraction phases available for the extraction of more polar compounds. The PA phase is usually more suited for the extraction of polar compounds than the other commercially available absorption fibers, and have for example successfully been used in the extraction of phenols[2]. Analytes have very low diffusion coefficients for the PA phase and therefore the adsorption phases often yield improved extraction compared to the PA phase. The three different fibers evaluated were 85 µm polyacrylate (PA), 65 µm polydimethylsiloxane-divinylbenzene (PDMS/DVB) and 75 µm carboxen-polydimethylsiloxane (CAR/PDMS). Figure 4.10 plots the detector response for each of the different analytes when extracted with the three different fibers.

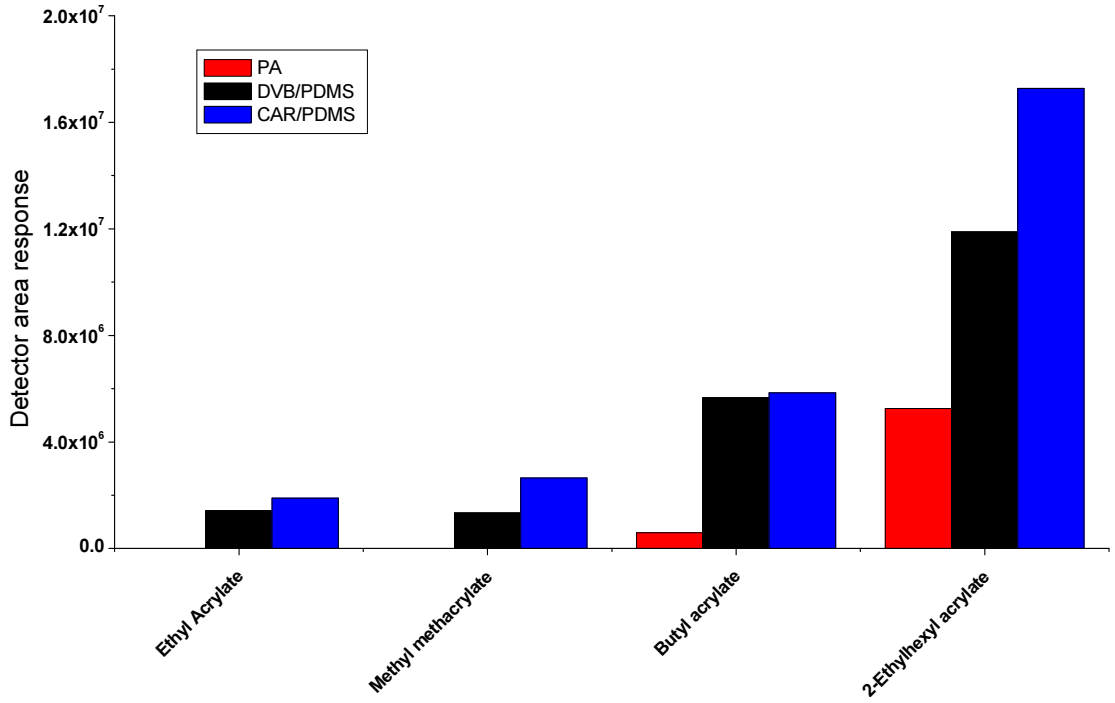


Figure 4.10: Selection of the fiber coating with optimal extraction efficiency. Fibers evaluated: 85 µm PA, 65 µm PDMS/DVB and 75 µm CAR/PDMS. Experimental conditions: 10 ml distilled water containing 12.18 $\mu g.l^{-1}$ EA, 12.47 $\mu g.l^{-1}$ MMA, 12.76 $\mu g.l^{-1}$ BA and 13.12 $\mu g.l^{-1}$ 2-EHA; extraction time, 45 minutes; extraction temperature, 30°C; desorption temperature 250°C; desorption temperature, 5 minutes.

The extraction efficiency using the 85µm PA was very poor with only very small amounts of the BA and 2-EHA extracted. The adsorptive phases were more effective for the extraction of these compounds. The 65 µm PDMS/DVB fiber efficiently extracted BA and showed good performance when compared to the 75 µm CAR/PDMS fiber. The CAR/PDMS fiber had superior performance with the extraction of EA, MMA and 2-ethylhexyl acrylate. Therefore, it was determined that the only fiber that yielded significant response for all the analytes was the CAR/PDMS coating, and this fiber was hence forth used for the optimization of the sampling conditions.

4.3.2 Extraction temperature

The target analytes all have boiling points well above100°C. The extraction temperatures evaluated were room temperature (22°C), 40°C, 60°C and 80°C. Evaluating at these higher temperatures force more of the analytes into the headspace by increasing their vapour pressures therefore accelerating the equilibrium process and improving the extraction efficiency for short extraction times.

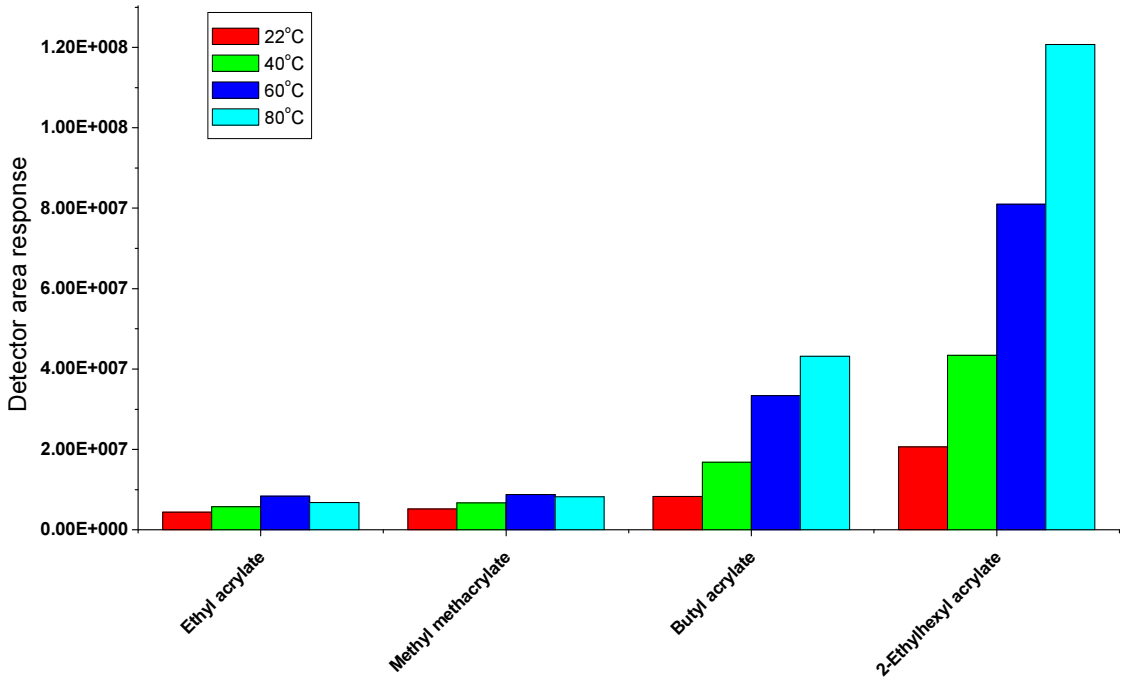


Figure 4.11: Extraction profile of EA, MMA, BA and 2-EHA at 22°C, 40°C, 60°C and 80°C. Fiber evaluated, 75µm CAR/PDMS; Experimental conditions: 10 ml distilled water containing 12.18 µg.l^{-1} EA, 12.47 µg.l^{-1} MMA, 12.76 µg.l^{-1} BA and 13.12 µg.l^{-1} 2-EHA; extraction time, 45 minutes; desorption temperature 250°C; desorption temperature, 5 minutes.

Figure 4.11 show an increase in the amount of analytes extracted when using higher extraction temperatures. This increase is expected due to the higher boiling points that these analytes possess. An increase in the extraction of all the compounds is seen up to 60°C; increasing up to 80°C leads to a slight decrease in the extraction of EA and MMA, although the extraction of both BA and 2-EHA improves. A significant increase is noted for BA and 2-EHA when increasing the temperature from room temperature to 80°C, with almost six times more extracted at the higher temperature. All further sampling and method optimization was therefore done at an extraction temperature of 80°C.

4.3.3 Salt addition

Figure 4.12 illustrates the effect on the extraction when NaCl was added at saturation level to the aqueous sample containing the analytes of interest.

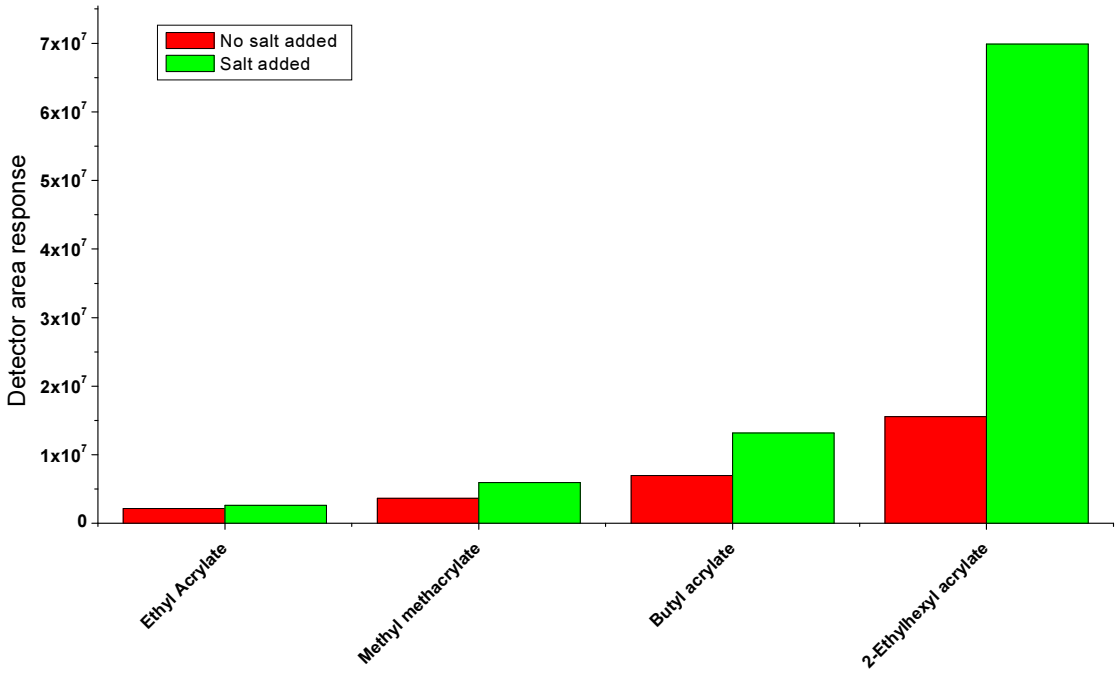


Figure 4.12: Extraction profile of EA, MMA, BA and 2-EHA with and without the addition of NaCl. Fiber evaluated, 75 µm CAR/PDMS; Experimental conditions: 10mL distilled water containing 12.18 $\mu g.l^{-1}$ EA, 12.47 $\mu g.l^{-1}$ MMA, 12.76 $\mu g.l^{-1}$ BA and 13.12 $\mu g.l^{-1}$ 2-EHA; extraction temperature, 80°C; extraction time, 45 minutes; desorption temperature 250°C; desorption temperature, 5 minutes.

The addition of salt increases the extraction of all the analytes. Therefore all further method optimization was done with the addition of salt to the analyte solution.

4.3.4 Extraction time

Extraction times from 5 minutes up to 60 minutes were evaluated for the 75 µm CAR/PDMS fiber. Figure 4.13 shows the total extraction profile of all the analytes as well as the individual profiles of the analytes. A clear decline in the slope is seen at around 30 minutes indicating that equilibrium conditions have been reached. At 45 minutes no distinct increase in the amount of analytes extracted is seen. Increasing the extraction time to 60 minutes results in a small decline in the amount of analytes extracted, sample loss evidently starts occurring when extracting at such high temperature for a long period of time. Therefore an extraction time of 45 minutes was used in the extraction of the target analytes.

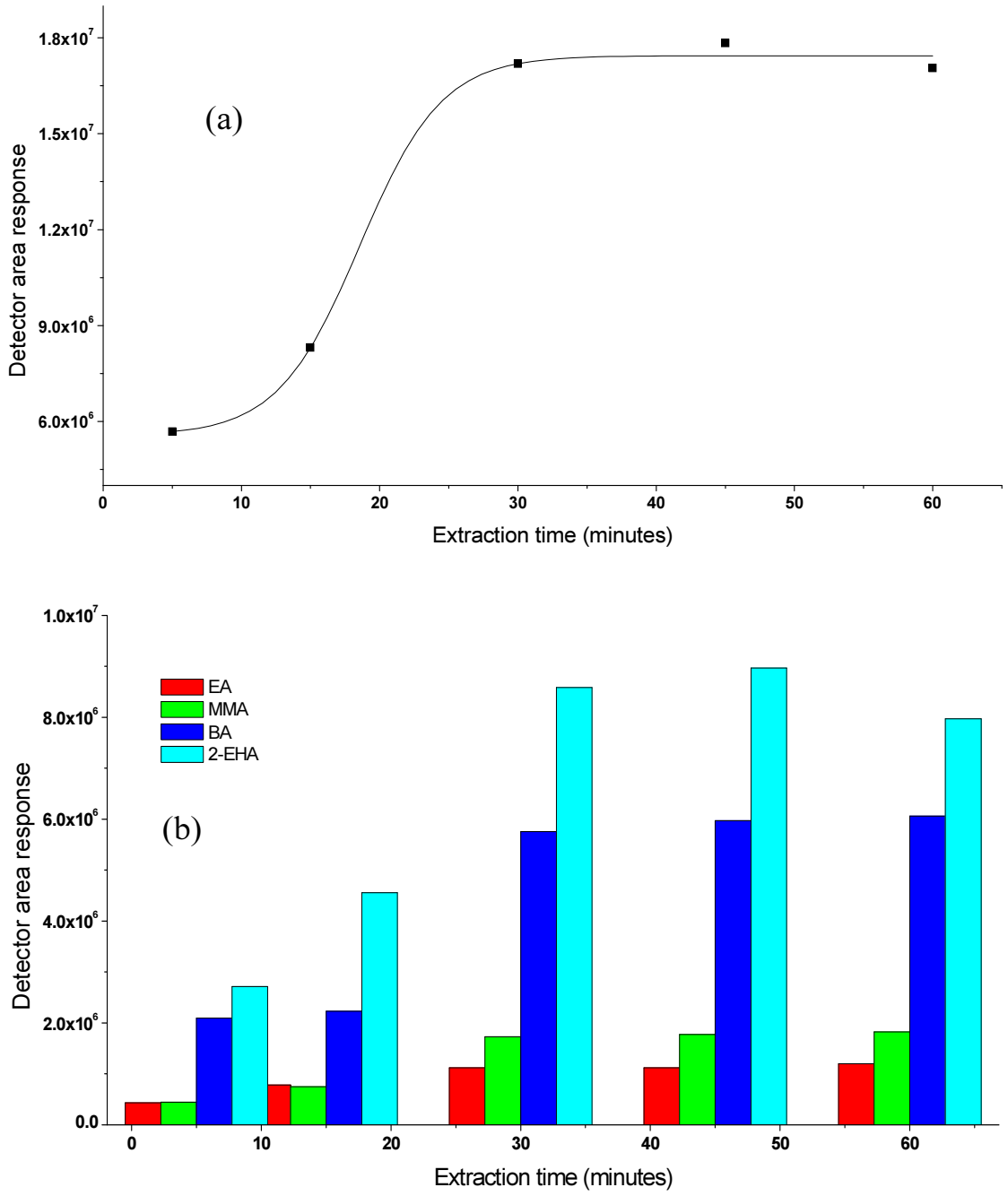


Figure 4.13 a,b: The total and individual extraction time profiles of EA, MMA, BA and 2-EHA. Fiber evaluated, 75 µm CAR/PDMS; Experimental conditions: 10 ml distilled water containing 12.18 µg.l^{-1} EA, 12.47 µg.l^{-1} MMA, 12.76 µg.l^{-1} BA, 13.12 µg.l^{-1} 2-EHA and 340 ug.l^{-1} NaCl; extraction temperature, 80°C; desorption temperature 250°C; desorption temperature, 5 minutes.

4.3.5 Limit of detection, limit of quantitation and precision

The optimum extraction of these acrylate monomeric compounds from water can be done using a 75 µm Carboxen/PDMS fiber at 80°C for 45 minutes for a 10 ml sample in a 22 ml headspace vial with the addition of 340 µg.ml^{-1} NaCl. The agitator installed with the autosampler was switched on

during all extractions. The analytes were desorbed from the fiber for 5 minutes at a temperature of 250°C. The LOD and LOQ of the SPME analysis was determined by evaluating the total ion chromatogram (TIC) obtained in scan mode for the extraction of the target analytes over a range of 0.01 µg.l^{-1} to 1000 µg.l^{-1}. The LOD and LOQs were determined at a signal to noise (S/N) ratio of 3:1 and 5:1 respectively. Figure 4.14 show the total ion chromatogram for the four acrylate analytes obtained using the optimized method for extraction of a 10 µg.l^{-1} solution.

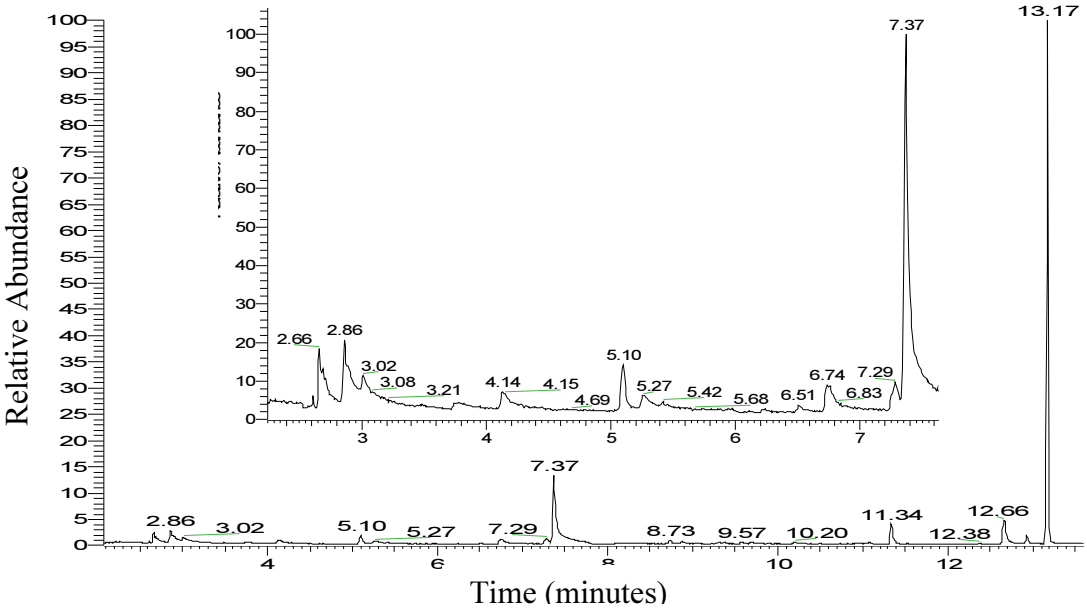


Figure 4.14: TIC of the acrylate analytes extracted using the CAR/PDMS fiber at 80°C for 45 minutes.

Table 4.4 shows the determined detection and quantitation limits, as well as the precision of the optimized SPME method[7].

Table 4.4: Detection and quantitation limits and precision (%RSD)

Compound	Retention time (minutes)	LOD (µg l^{-1})[a]	LOQ (µg l^{-1})[b]	Precision (%RSD)[c]
EA	2.66	0.817	1.362	25.3
MMA	2.86	0.104	0.174	9.0
BA	7.37	0.015	0.025	7.3
2-EHA	13.17	0.008	0.013	9.8

[a] The limit of detection was calculated as the point where the signal-to-noise-ratio is 3:1

[b] The limit of quantitation was calculated as the point where the signal-to-noise-ratio is 5:1

[c] $n = 3$

The extraction of acrylate monomers can successfully be done using a CAR/PDMS fiber. At levels below 0.8 µg.l^{-1} only the ethyl acrylate could no longer be extracted, due to the high polarity of this analyte. Unlike with non-polar analytes, there are not a lot of extraction materials available for the

analyses of polar analytes and only recently has the focus of research groups shifted to these compounds. The trend is also to develop extraction materials for specific groups of analytes. In an effort to further improve the extraction efficiency of these analytes, novel materials based on PDMS were synthesized and electrospun nanofibers were created to be used in the extraction of the analytes. In the next section the synthesis, characterization and electrospinning of these materials will be discussed.

4.4 Synthesis, characterization and electrospinning of novel materials

4.4.1 Introduction

In Chapter 2 it was mentioned that PDMS based materials are popular for the use in volatile extraction. Inorganic-organic hybrid graft copolymers based on PDMS can easily be polymerized using conventional free radical polymerization[8]. A PDMS macromonomer and low molecular weight monomers were used to synthesize a variety of novel PDMS based materials for use as extraction media in volatile analysis. PSty–g–PDMS, PMMA-g-PMDS, PBA-g-PDMS and PMAA-g-PDMS were synthesized and electrospun into nanofibers. Additionally a PAN-g-PDMS polymer synthesized by another member of the group was evaluated[9]. Homopolymers of styrene, methyl methacrylate, butyl acrylate and methacrylic acid were also prepared via conventional polymerization techniques, electrospun and investigated as possible extraction media. The homo-polymers, hybrid copolymers and nanofibers were characterized using nuclear magnetic resonance (NMR), size exclusion chromatography (SEC), scanning electron microscope (SEM), SEM with energy dispersive X-rays (SEM-EDS) and thermal gravimetric analysis (TGA).

4.4.2 Polymerization

Commercial mono-methacyloxypropyl terminated PDMS from Gelest,inc. with a viscosity of 10 Pa.s and molecular weight of approximately 1000g/mol was used in the synthesis of the graft copolymers. This short chain PDMS macromonomer was preferred in order to keep the polarity of the copolymers high and at the same time achieve relatively high PDMS content polymers. In a previous study it was shown that the molecular weight of the PMMA-g-PDMS copolymer increases with increasing wt% PDMS charged, therefore a relatively high wt% PDMS was used in the preparation of the graft copolymers[8]. A constant weight ratio of 30 wt% PDMS and 70 wt% monomer were used in the synthesis of all the graft copolymers. The polymers were synthesized in toluene and precipitated using methanol with the exception of the MAA based polymers. Both the PDMS macromonomer and the MAA monomer were soluble in the toluene however during

polymerization precipitation of the polymer occurs. The precipitates were recovered using filtration and dried overnight in a vacuum oven. The effect that the incorporation of longer chain PDMS macromonomers (a higher molecular weight) has on the thermal stability and molecular weight of the polymers was also investigated. Two additional PDMS macromonomers with molecular weights of 5000g/mol and 10000g/mol were used. These polymers were, however, not used for the preparation of nanofibers.

4.4.3 Determination of molar mass via SEC

The aim of this study was to synthesize novel PDMS based hybrid materials and to electrospin nanofibers to be used as extraction phases for analysis of VOCs. One of the prerequisites for spinning nanofibers is that the polymer solution must have a high enough viscosity and the polymer molar mass must be high enough so that chain entanglement is sufficient[8]. Size exclusion chromatography with dual refractive index (RI) and ultra violet (UV) detectors were used to determine the molecular weight of the homopolymers and copolymers. The homo-PDMS data could not be included in this data due to the similar refractive index of the PDMS macromonomers to that of the THF mobile phase. PMAA and PMAA-*g*-PDMS did not dissolve in THF and were therefore analyzed using dimethylacetimide (DMAc) as mobile phase. The molecular weight determined for the copolymers and homopolymers is relative to the polystyrene calibration standards used in the THF system and to the polymethylmethacrylate calibration standards used in the DMAc system. A summary of all the molecular weight data can be seen in Table 4.5.

Table 4.5: Molar mass of the prepared homopolymers and copolymers

Sample	M_n ($\times 10^4$)	M_w ($\times 10^4$)	Đ	wt% PDMS
PMMA	10.76	18.81	1.7	-
Short[a] PMMA-*g*-PDMS	8.45	13.06	1.5	13.7
PMAA	2.58	14.45	5.6	-
Short[a] PMAA-*g*-PDMS	6.09	17.60	2.8	10.7
Medium[b] PMAA-*g*-PDMS	4.19	16.67	3.9	-
Long[c] PMAA-*g*-PDMS	5.74	21.85	3.8	-
PSTY	5.64	9.59	1.7	-
Short[a] PSTY-*g*-PDMS	3.18	5.74	1.8	8.7
PBA	3.11	6.45	2.1	-
Short[a] PBA-*g*-PDMS	0.06	0.10	1.7	-

Note 1. These data exclude the contribution from any homo-PDMS that might be present due to the similar refractive index of the PDMS to that of THF and DMF. The wt% PDMS were determined from the NMR results for the short PDMS graft copolymers.

[a]1000g/mol, [b]5000g/mol, [c]10000g/mol

With the exception of the MAA based polymers, all of the homopolymers and copolymers had a relatively narrow dispersity for conventional free radical polymerization. The dispersities reported were in the range of 1.5 to 2.1. The use of conventional free radical polymerization results in random incorporation of the graft chains which can lead to the formation of the homopolymer as well as causing some in unreacted PDMS macromonomer to remain behind[10]. Conventional free radical polymerization usually yields polymers with broad molecular weight distributions as can be seen for the polymethacrylic acid. The homopolymer had a dispersity of 5.6, whilst the copolymers had slightly narrower dispersities with the copolymer based on the short PDMS having the narrowest distribution.

Figure 4.15 shows the normalized molecular weight distribution graphs obtained for PSty-*g*-PMDS, PMMA-*g*-PDMS, PBA-*g*-PDMS and PMAA-*g*-PDMS using the short PDMS macromonomer.

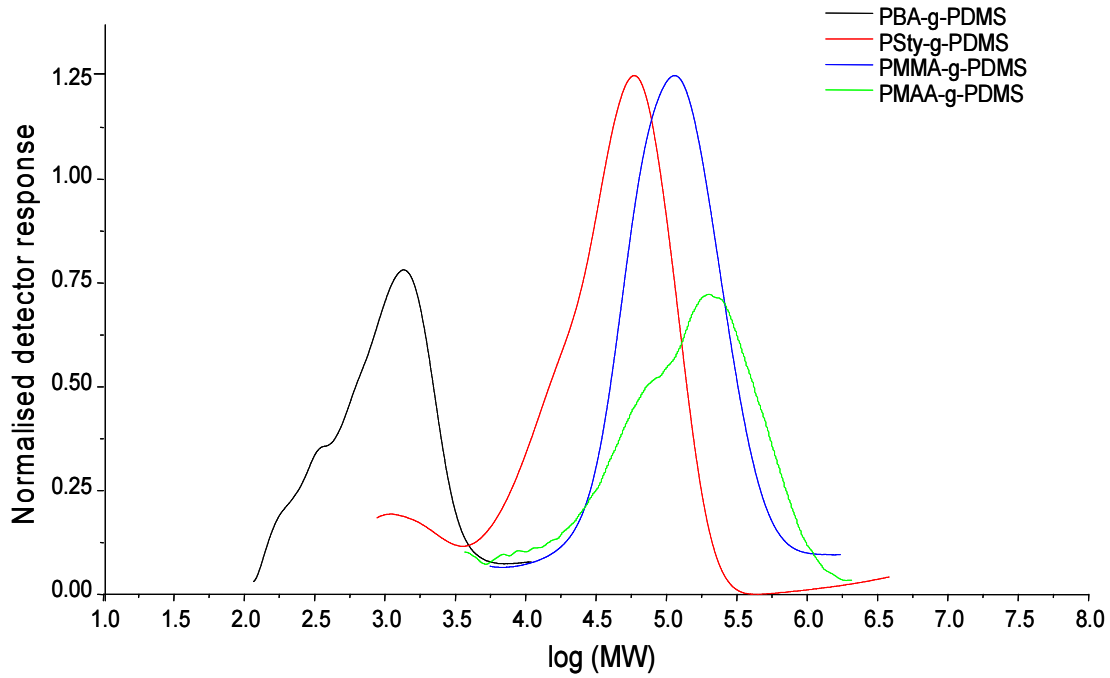


Figure 4.15: SEC chromatograph obtained for PBA-*g*-PDMS, PSty-*g*-PDMS, PMMA-*g*-PDMS and PMAA-*g*-PDMS using the short PDMS macromonomer.

The SEC chromatograms of the PSty-*g*-PDMS and PMMA-*g*-PDMS show a gaussian distribution for each of these samples. The low molecular weight of the PBA-g-PDMS indicates that the polymerization of the graft copolymer was unsuccessful. The low molecular weight of the PBA-g-PDMS, as well as the low T_g of the polymer which might prevent electrospinning of the polymer, means that this polymer is no longer a candidate to be used as a novel extraction phase for VOC analysis. In the SEC chromatogram of the PMAA-g-PDMS polymer a shoulder is observed. In

figure 4.16 overlays of the PMAA-*g*-PDMS with the different chain length PDMS macromonomers can be seen.

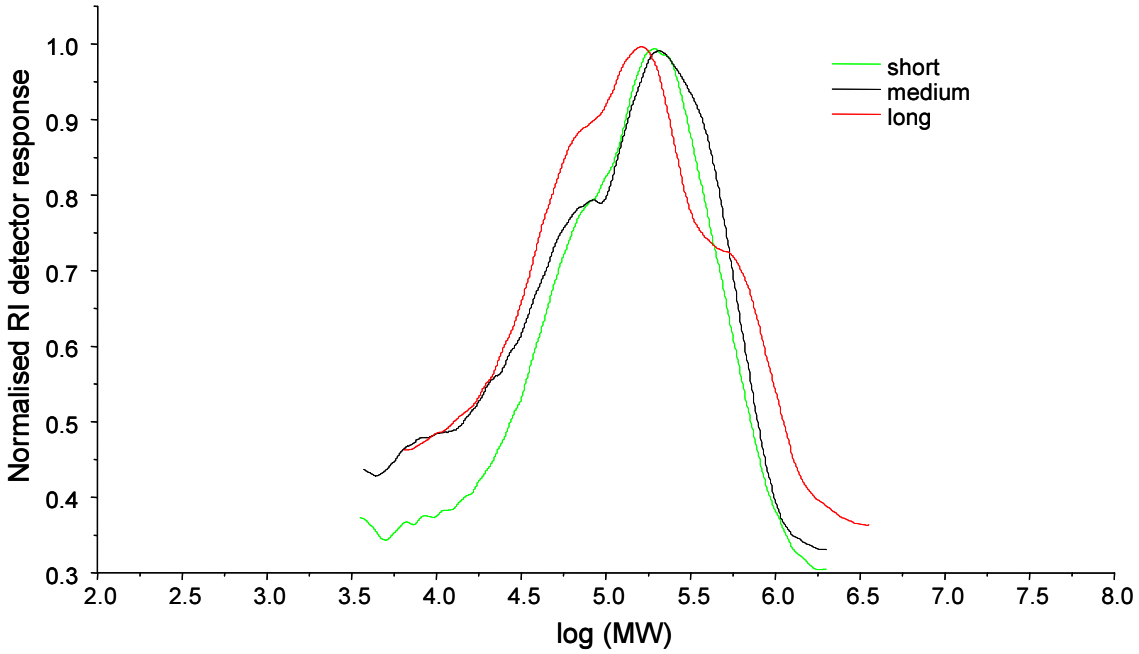


Figure 4.16: Overlays of the SEC graphs of the short, medium and long MAA-*g*-PDMS.

Different branch length macromonomers results in different molecular weight distributions as can be seen from Figure 4.16. From this curve it is also evident that all of the PMAA-*g*-PDMS polymers have a very broad molecular weight distribution. A shoulder is noted in all three the polymers at a lower molecular weight, whilst an additional shoulder is noted for the long chain PDMS at a higher molecular weight. The shoulder may indicate the presence of homopolymer as well as graft copolymer. This is possibly due to the insolubility of the PMAA in the polymerization solvent.

4.4.4 Characterization of graft copolymers with NMR

The PDMS graft copolymers were analysed by ^{1}H NMR. Figure 4.17 shows the ^{1}H NMR spectra obtained for the short chain mono-methacyloxypropyl terminated PDMS. The chemical shifts noted at δ 6.12 ppm (a) and δ 5.56 ppm (b) are assigned to the two protons from the vinyl group present in the PDMS macromonomer. When the PDMS macromonomer is incorporated into the polymer chain a clear diminishing of these peaks is seen.

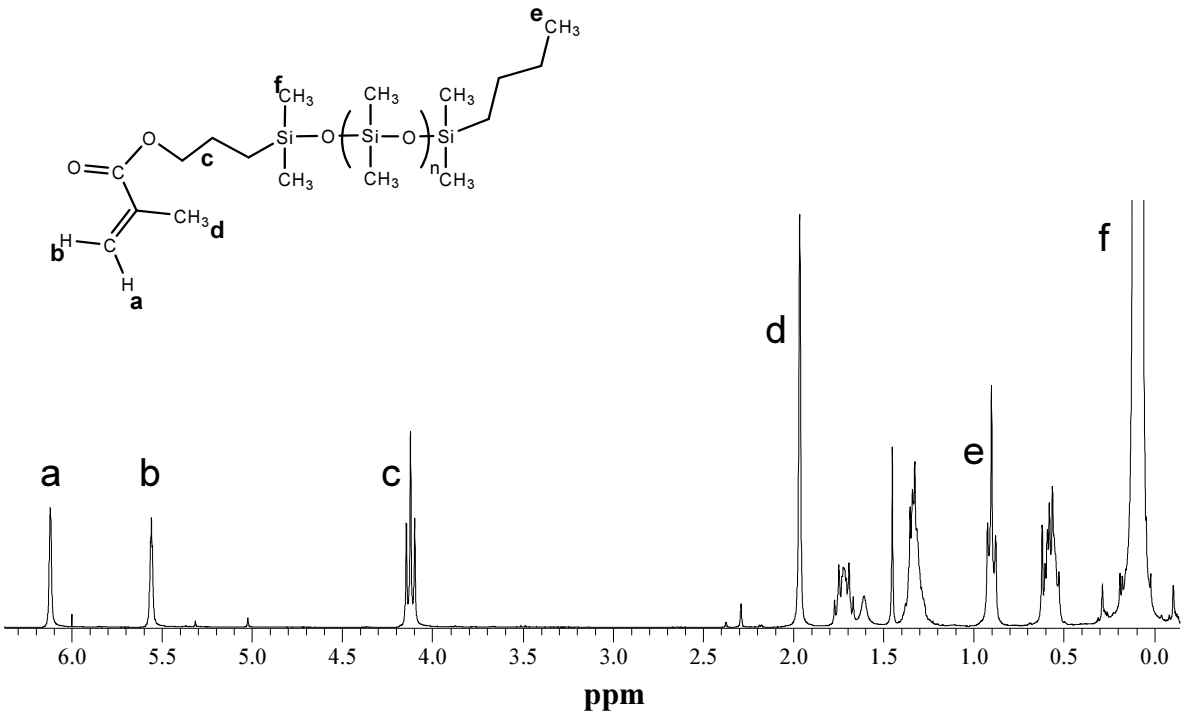


Figure 4.17 : ^{1}H-NMR spectra of 10 cSt mono-methacyloxypropyl PDMS.

Figure 4.18 shows the ^{1}H NMR spectra for the MMA monomer(a) and the short PMMA-g-PDMS(b).

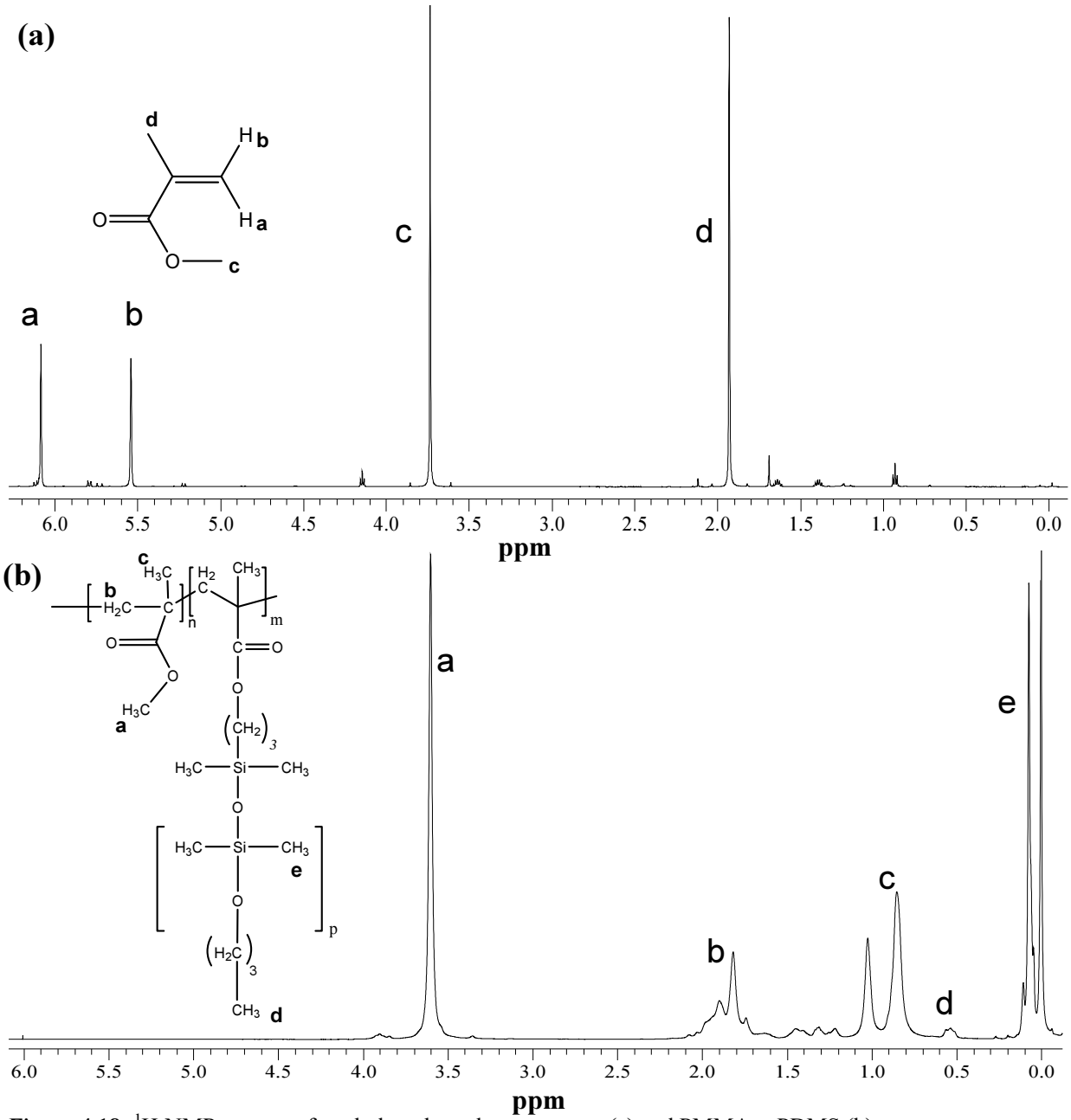


Figure 4.18: [1]H-NMR spectra of methyl methacrylate monomer (a) and PMMA-g-PDMS (b).

The MMA monomer ^{1}H NMR spectra has sharp defined peaks and the methyl groups from the O-CH_3 group can be observed at a chemical shift of δ 3.7 ppm; upon formation of the polymer this peak as well as the other peaks from the methyl groups broaden as can be seen in Figure 4.18 b. There is also a clear disappearance of the vinyl groups observed at a chemical shift of δ 6.1ppm and 5.5ppm in both the PDMS macromonomer spectra (figure 4.17) and the MMA (figure 14.18a) upon formation of the polymer. The ^{1}H NMR spectra of the homo-polymer and the PMMA-*g*-PDMS are very similar. The incorporation of a Si-CH_3 peak from the PDMS silicon back bone is observed at a chemical shift of δ 0.1 ppm

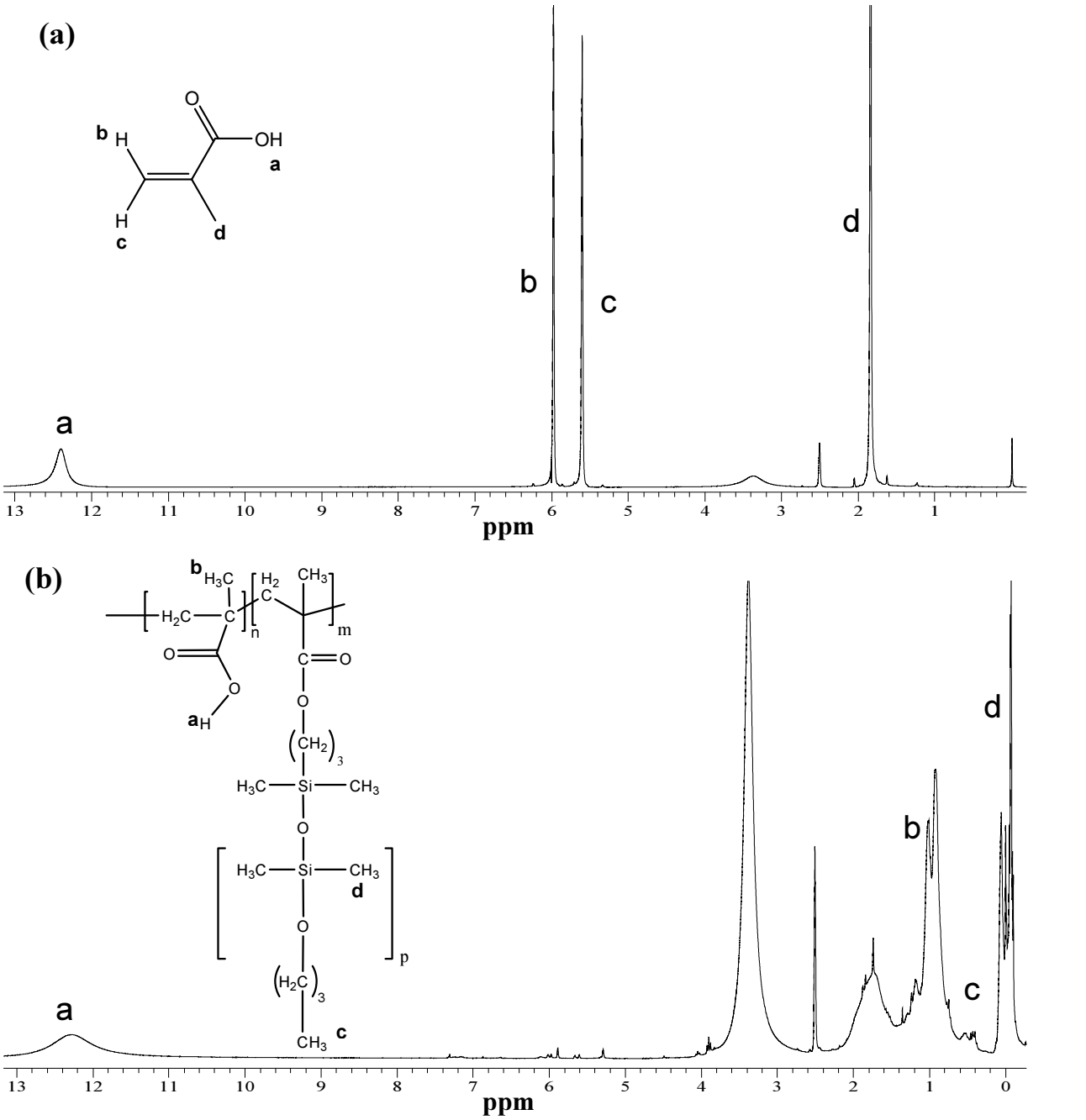


Figure 4.19 (a), (b): ^{1}H-NMR spectra of the methacrylic acid monomer and PMAA-*g*-PDMS respectively, obtained in DMSO.

In figure 4.19 the broadening of the peak at δ 12.2 ppm and diminishing of the vinyl peaks at δ 6.0 ppm and δ 5.6 ppm indicates the formation of the MAA based copolymer. The presence of the extra Si-CH_3 peak from the PDMS silicon backbone at a chemical shift of δ 0.08 ppm is also noted. The presence of the peak at a chemical shift of δ 3.4 ppm is most likely due to a contaminant compound present in the sample and cannot be assigned to one of the hydrogens from the graft copolymer. The incorporation of the PDMS into the MAA and MMA backbone was confirmed by SEM-EDS analysis.

4.4.5 Characterization of graft copolymers with SEM-EDS

Energy dispersive X-ray spectrometry coupled to a scanning electron microscope was used to identify the surface elemental composition of the graft copolymers. In SEM-EDS a material is excited by bombarding its surface with high-energy beam of charged particles or a beam of X-rays. The incident beam excites an electron in one of the inner shells, ejecting it from the shell. Outer shell electrons then fall into the vacancy left by the displaced electron. In doing so, the difference in energy between the two shells is released in the form of x-ray radiation, which is characteristic of a specific element. SEM-EDS is a surface analysis technique, therefore it was ensured that a representative sample was selected and multiple analyses were performed. Figure 4.20 shows the EDS spectra of the Short PMAA-*g*-PDMS and PMMA-g-PDMS co-polymers.

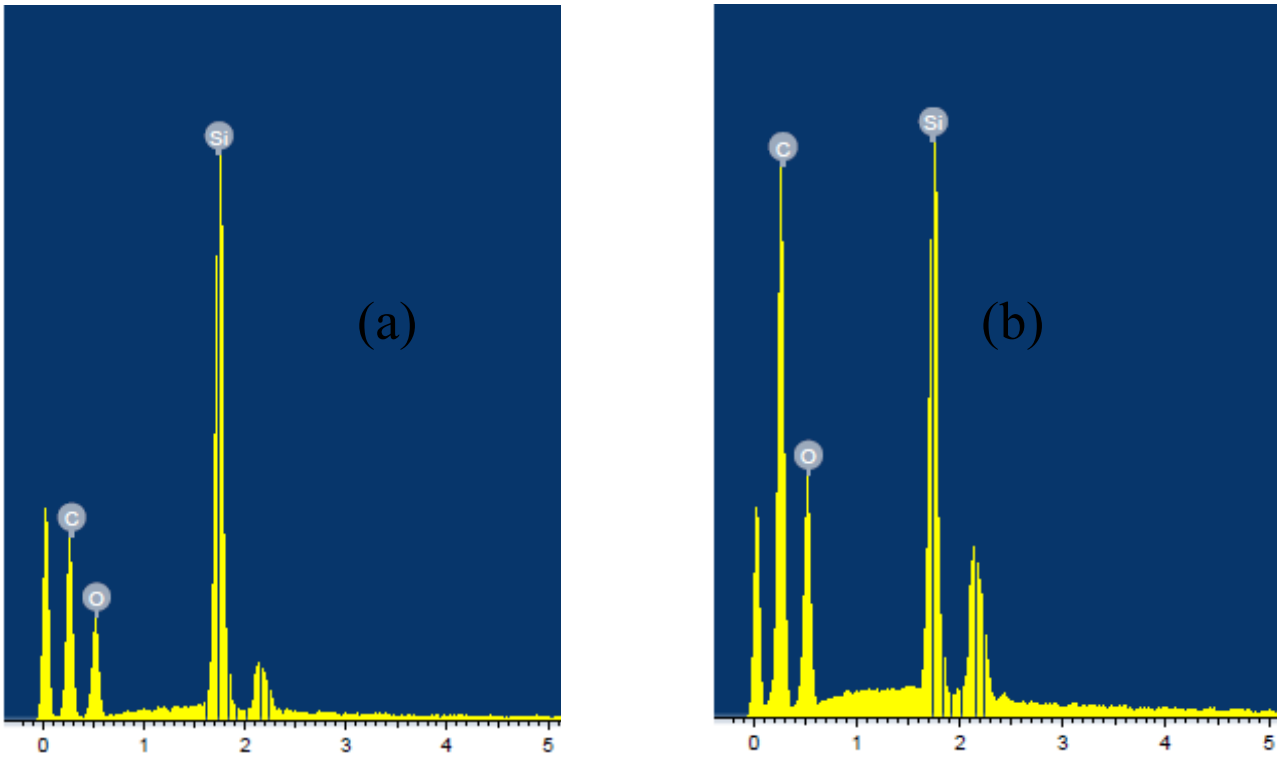


Figure 4.20: SEM-EDS spectra of the short PMAA-g-PDMS (a) and PMMA-g-PDMS (b) to indicate the grafting of the PDMS onto the polymer backbone.

The SEM-EDS analysis confirms the incorporation of the silicon in the PMAA-*g*-PDMS and PMMA-g-PDMS copolymers.

4.5 Electospun Nanofibers

The morphology of the nanofibers is influenced by a number of different parameters, some of which include the applied voltage, the tip-to-collector distance and the concentration of the polymer solution[11]. Scanning electron microscopy (SEM) was used to study the fiber morphology. These

fibers will be evaluated for the extraction of VOCs, therefore the thermal stability of these fibers were studied as the VOCs are usually desorbed from the extraction medium at temperatures of 200°C and above. The thermal stability of the fibers was investigated using thermal gravimetric analysis (TGA). PAN-*g*-PDMS nanofibers synthesized via conventional free radical polymerization using a 1000g/mol PDMS macromonomer were also investigated. This polymer was previously synthesized and electospun by G.M Bayley[9].

4.5.1 Fiber morphology

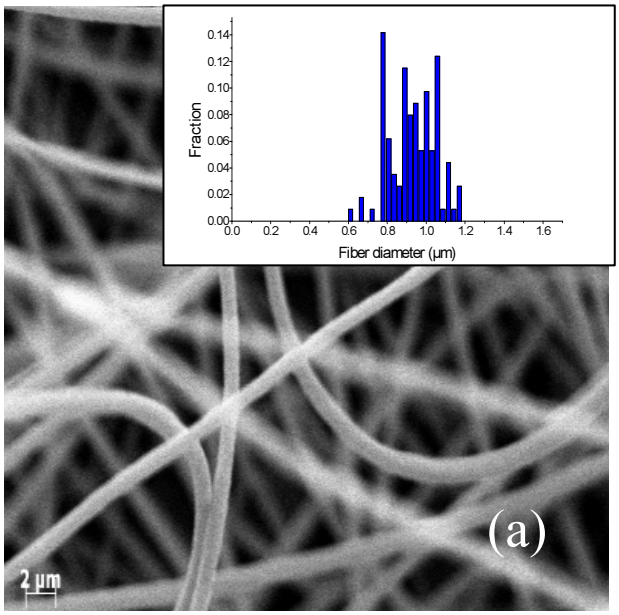
Figure 4.21 shows the SEM images of the different graft copolymers as well as the homopolymers. Different conditions were used to electrospin the PDMS hybrid polymers, which led to different fiber morphologies. Some of the samples are electrospun more readily whilst others did not form nanofibers at all. A detailed summary of the parameters used to spin these fibers can be found in Chapter 3. Table 4.6 gives a summary of the properties of the electrospun nanofibers.

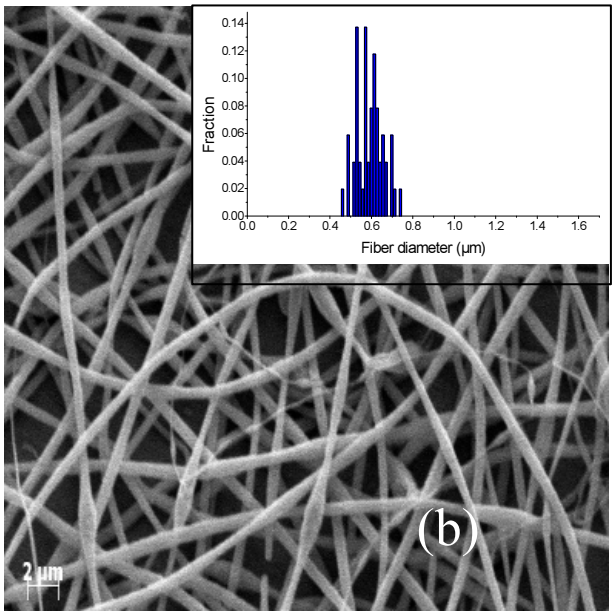
Table 4.6: The average fiber diameter and appearance of the nanofibers

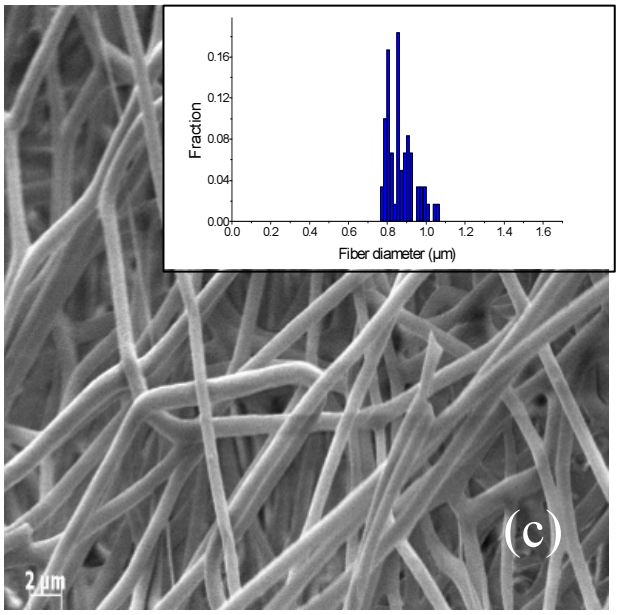
[a]Sample	Avg. Fiber diameter (nm)	Appearance
[#]PMMA-*g*-PDMS (a)	700 - 1100	Smooth
PMMA-*g*-PDMS (b)	460 – 740	Slightly beaded
[#]PMMA (c)	700 - 1000	Smooth
PSTY (d)	150-400	Highly beaded
PSTY-*g*-PDMS (e)	NA	Highly beaded – no nanofibers
[#]PAN-*g*-PDMS (f)	1200 - 1800	Smooth
[#]PMAA (g)	200 - 400	Smooth
[#]PMAA-*g*-PDMS (h)	100 – 300 and 800 - 1200	Smooth, thin and thick fibers

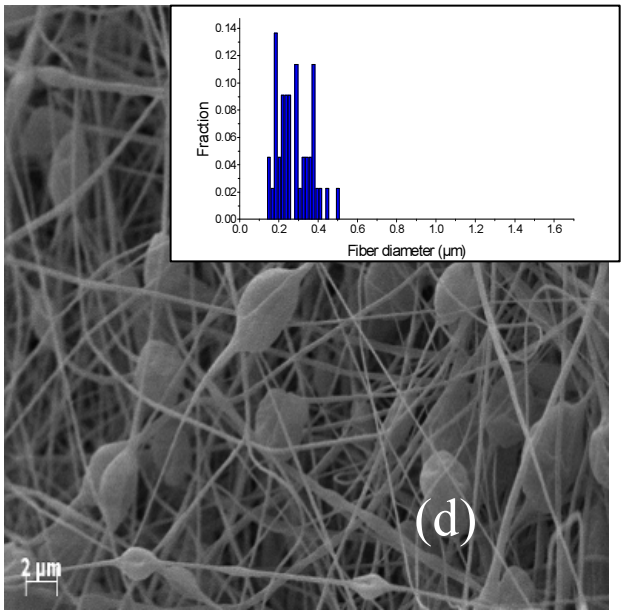
[a]All the graft polymer nanofibers are based on the short PDMS – 1000g/mol

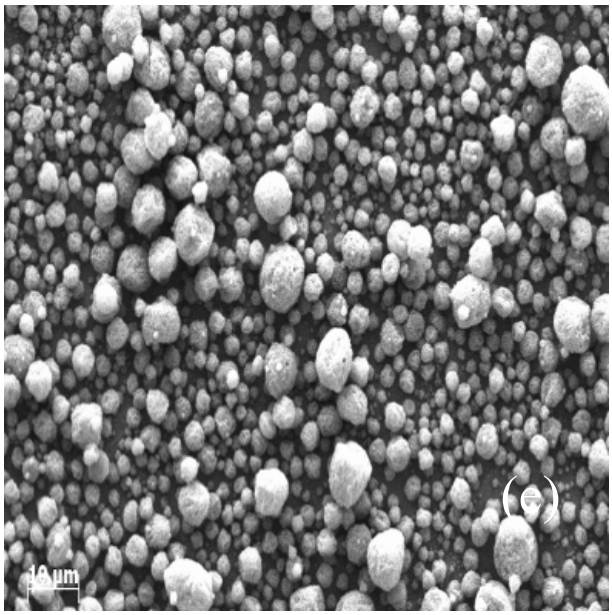
[#] Nanofibers evaluated as possible extraction materials for VOC analysis

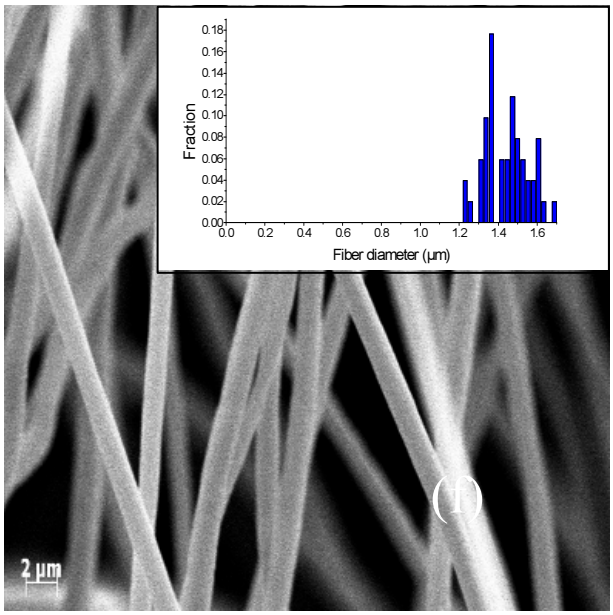












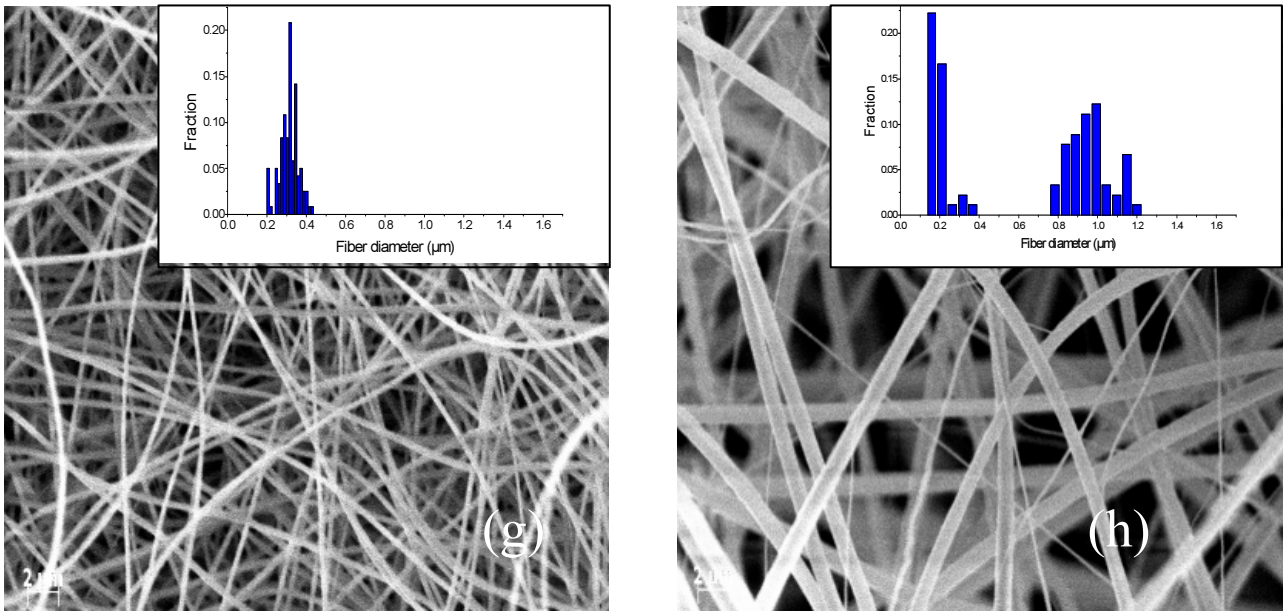


Figure 4.21: SEM images of the different surface morphologies and fiber diameter distributions of the homo-and copolymers. (a) PMMA-g-PDMS, 10-12kV, 15cm; , (b) PMMA-g-PDMS, 15kV, 25cm; (c) PMMA, 10-12kV, 8cm (d) PSty, 15kV, 15cm; (e) PSty-g-PDMS, 15kV, 25cm; (f) PAN-g-PDMS, 12.5kV, 18cm (g) PMAA, 15kV, 20cm; (h) PMAA-g-PDMS, 15kV, 20cm

Figure 4.21 shows the morphologies of the homo and graft copolymer fibers acquired via electrospinning as well as the fiber diameter distributions. The fiber diameters differ when using different spinning parameters as can be seen by Figure 4.21 (a)-(b). Smooth fiber morphologies were achieved for the PMMA-g-PDMS spun at tip-to-collector (TCD) distance of 15cm, whilst the PMMA-g-PDMS with a TCD of 25cm shows elongated bead morphology. Beaded structures are also observed for the PSTY (d). Electrospinning of the PSTY-g-PDMS could not be achieved at all and the formation of small bead-like particles was observed (e). The PMAA-g-PDMS had fibers of different diameters whilst using the same spinning conditions throughout the process; this might be due to the presence of both the graft and homopolymer. Figure 4.21 (h) shows the bimodal distribution of the PMAA-g-PDMS nanofibers. The distribution at the lower end of the scale is in the same range as the fiber distribution of the pure PMAA fibers (g).

4.5.2 Thermal stability of the nanofibers

The thermal stability of the nanofibers was evaluated using TGA in order to determine whether the fibers are suitable for use as extraction media in volatile analysis. All of the homo-polymers and graft copolymers that formed unbeaded nanofibers were evaluated before and after electrospinning. This was done in order to determine whether the thermal stability of the samples was altered upon formation of nanofibers. The PMAA-g-PDMS with the long and medium chain PDMS were also

evaluated in the powder form to study the influence of PDMS on the thermal stability of the polymers.

PDMS is commonly used as extraction medium in the analysis of volatile compounds due to its high thermal stability. A PDMS polymer was analyzed at 200°C to show that the PDMS polymer is thermally stable with a weight loss of less than 3% when kept at 200° (for 1 hour). Figure 4.22 shows that the bulk of the weight loss happens in the first 30 minutes, where after the rate of weight loss decreases. The maximum amount of time that the nanofibers will be exposed to elevated temperatures during thermal desorption is 10 minutes, therefore the fibers were conditioned before use.

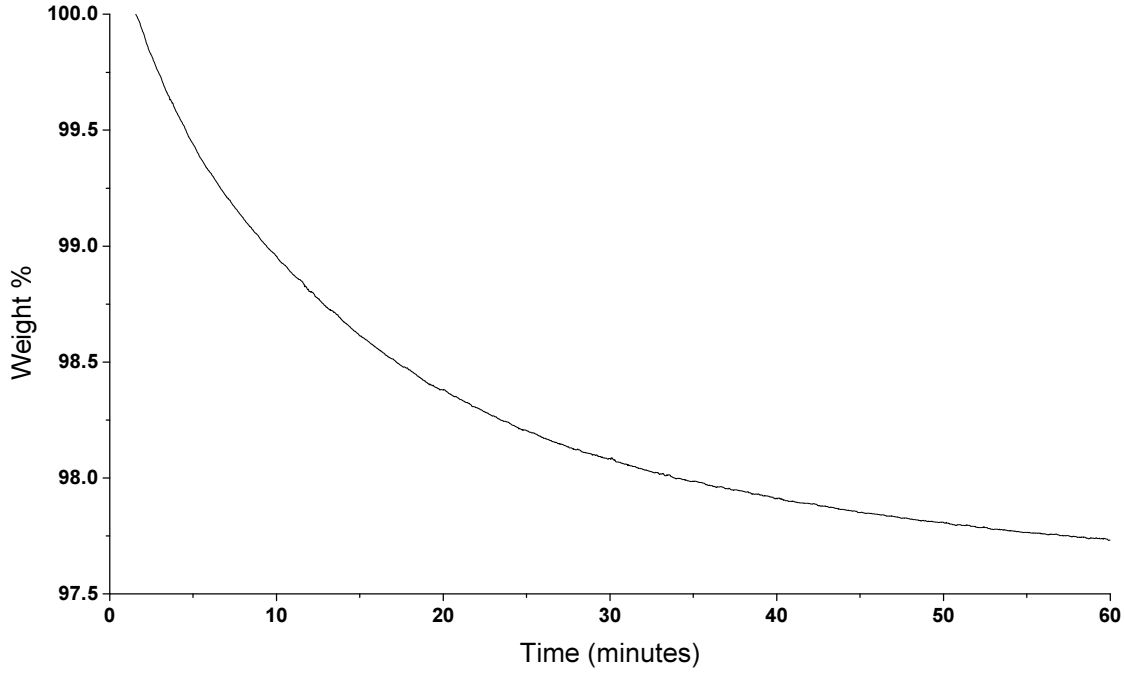


Figure 4.22: Isothermal profile of the PDMS polymer at 200°C for a time of 1 hour.

Figure 4.23 shows the isothermal profile of the PMAA-g-PDMS polymers with different chain length PDMS macromonomers. As the chain length of the PDMS increases so does the thermal stability of the polymer. The medium and long chain PMAA-g-PDMS showed superior performance compared to the graft polymer with the short chain PDMS.

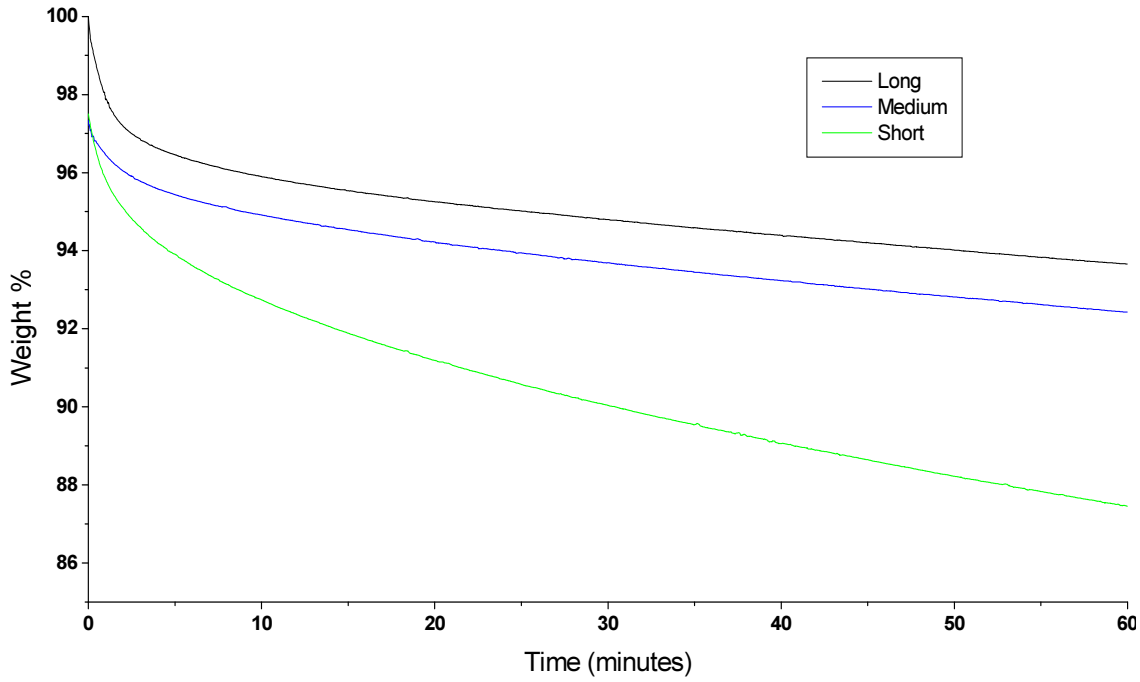


Figure 4.23: Isothermal profile of the powder PMAA-g-PDMS polymers with short, medium and long chain PDMS macromonomers at 200°.

All three of these polymers still experienced weight loss after 60 minutes. These polymers were evaluated for a second isothermal cycle, since the initial weight loss might be due to volatile contaminants, unreacted monomer or water that was absorbed by the polymers. The MAA based polymers still showed significant weight loss during the second isothermal cycle. This weight loss is not necessarily attributed to polymer degradation and the PMAA and short PMAA-g-PDMS were still evaluated as possible extraction materials for volatile analysis. Blank analyses were done of the extraction materials prior to the volatile analysis to evaluate whether any major contaminant or degradation peaks were present.

Table 4.7 summarizes the thermal stability of all the polymers in their powder and nanofiber forms. Like mentioned before, the PAN-g-PDMS were synthesized and electrospun by another member of the group, therefore thermal stability studies were only performed on the nanofibers received.

Table 4.7: Weight loss of graft and homopolymers for two one hour cycles at 200°C.

Sample	% Weight loss Cycle 1	% Weight loss Cycle 2
PDMS	2.26	0.43
PMAA	13.04	6.55
Short MAA-g-PDMS	13.78	3.93
Medium MAA-g-PDMS	9.08	2.39
Long MAA-g-PDMS	6.34	5.16
PMMA	4.12	0.42
Short MMA-g-PDMS	0.96	0.38
Nanofibers		
PMMA	2.47	1.18
PMMA-g-PDMS	1.76	0.79
PAN-g-PDMS	4.73	0.60
PMAA	13.04	6.55
PMAA-g-PDMS	13.81	3.57

Figure 4.24 shows the thermal profiles at 200°C for the short PMAA-g-PDMS in its powder and nanofiber forms. No significant change is observed in the thermal profile of the PMAA-g-PDMS copolymers after formation of the nanofibers.

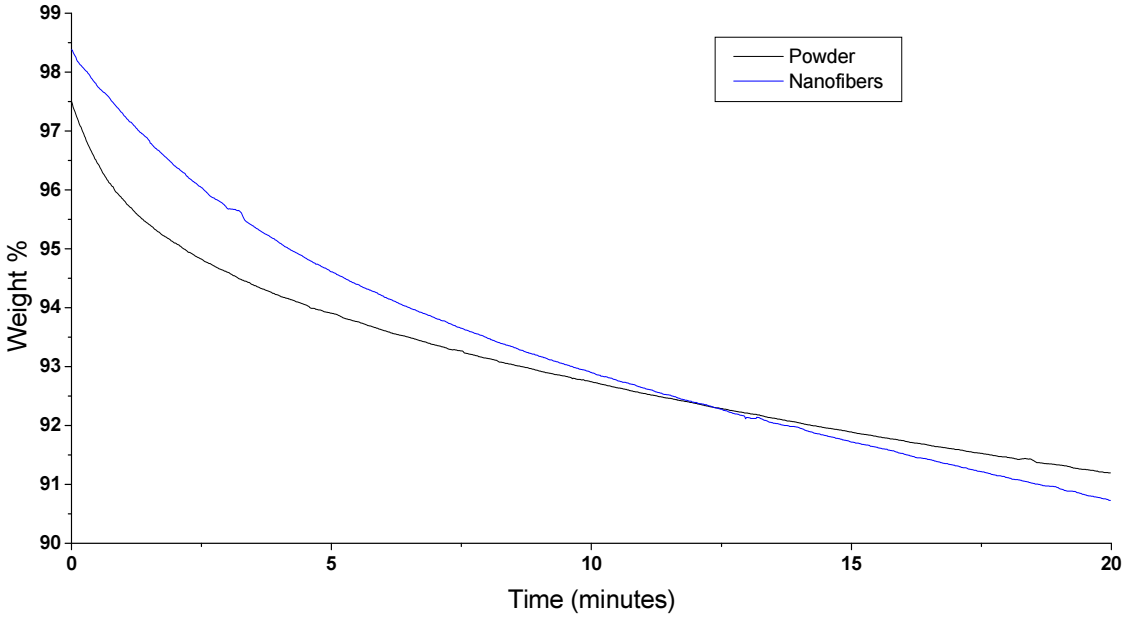


Figure 4.24: Isothermal profile over 20 mintues at 200° of the short PMAA-g-PDMS powder polymer and its nanofibers.

The PMMA, PMMA-g-PDMS and PAN-g-PDMS polymers showed good thermal stability and were characterized to have weight losses of less than 1.5% during the second isothermal cycle. The

PMAA and PMAA-g-PDMS had weight losses of above 13% during the first cycle; however during the 2nd cycle the weight loss was significantly lower. Even though weight loss occurred during the thermal evaluation of the MAA based polymers, the nanofibers were still evaluated as extraction materials for VOC analysis. Upon inspection of the fibers after the isothermal evaluation it was noted that the PMMA and PMMA-g-PDMS lost their nanostructure and upon heating the PAN-g-PDMS changed colour from white to light yellow to brown. This change in colour is due to pyrolysis of the polyacrylonitrile (PAN) part of the copolymer[12,13]. PAN is commonly used in the manufacturing of carbon fibers where cyclization of the PAN occurs upon heating. Optical microscopy images were taken to illustrate this phenomenon. Only the PMAA and PMAA-g-PDMS nanofibers remained intact during the thermal evaluation and no visual difference was noted even though the weight losses for these polymers upon heating were more severe.

4.5.3 Optical microscopy to evaluate visual changes observed during thermal analysis

Optical microscopy was used to examine the change in the fiber morphology after heating the nanofibers at 200°C for 2 cycles of 60 minutes. Figure 4.25 shows the disintegration of the nanostructure when heating the PMMA-g-PDMS graft copolymer nanofibers.

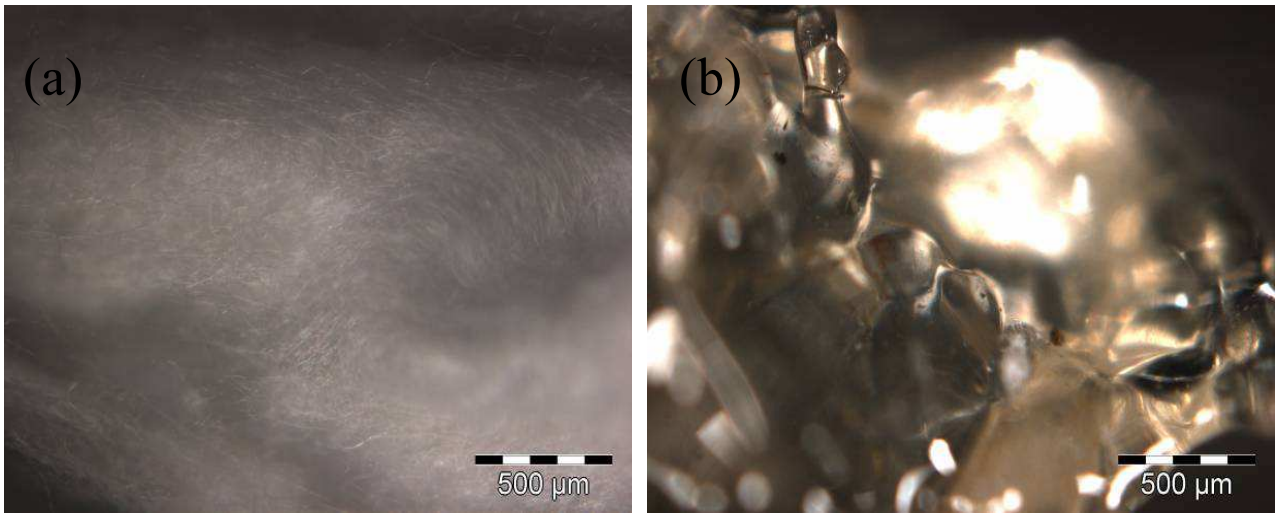


Figure 4.25: The change in the appearance of the PMMA-g-PDMS that is noted. Image (a) is before isothermal heating took place and Image (b) is after.

It is clear from Figure 4.25 that the PMMA-g-PDMS loses its nanostructure when it is exposed to elevated temperatures, most likely due to the glass transition temperature of this material being below the isothermal evaluation temperature. The use of the PMMA-g-PDMS nanofibers in volatile analysis is not feasible as desorption of VOCs from the extraction materials usually takes place at temperatures of 200°C and above. The PAN-g-PDMS nanofibers had no significant weight loss

during isothermal heating and the nanofiber structure remained intact, however, a difference in the colour of the fibers was noted when heating the nanofibers at 200°C for 2 cycles of 60 minutes. Figure 4.26 illustrates this change.

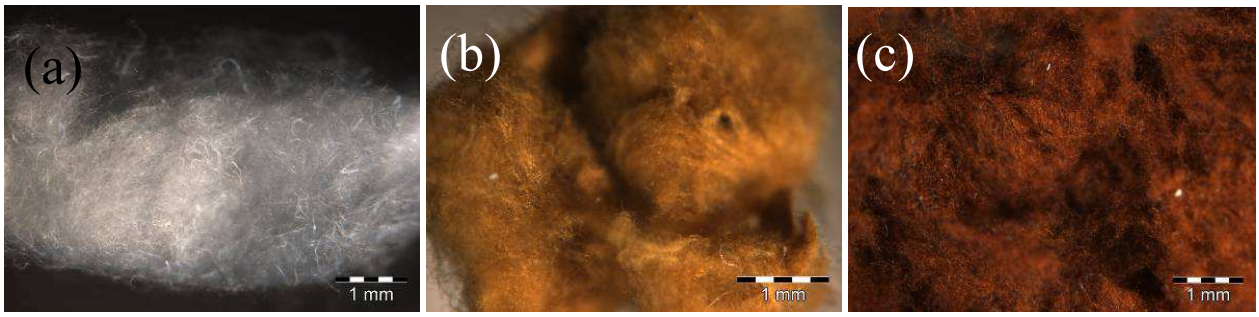


Figure 4.26: Optical microscopy images of the PAN-g-PDMS nanofibers before isothermal heating (a), after the 1st cycle at 200°C (b) and after the 2nd cycle at 200°C for 60 minutes (c).

Although pyrolysis of the PAN-g-PDMS takes place upon heating, the nanofibers were still evaluated as possible extraction material for volatile analysis. In the last section of this chapter, the evaluation of the nanofibers as volatile extraction material are discussed and compared to the current available coatings.

4.6 Headspace sorptive extraction using the PDMS stir bar and novel materials

The following nanofibers were evaluated as possible volatile extraction materials: PAN-g-PDMS, PMAA-g-PDMS and PMAA. The nanofibers and PDMS stir bar were placed in a glass insert that fits into a headspace vial to enable headspace extraction. Figure 4.27 illustrates this setup. The extraction and desorption of the nanofibers is similar to stir bar sorptive extraction (SBSE), therefore, any additional extraction optimization was done using a commercially available PDMS stir bar. SPME cannot directly be compared to the nanofibers therefore the PDMS stir bar was also evaluated. Comparisons between the nanofibers, SPME and SBSE were drawn on the basis of detection limits, whilst keeping the amount of extraction phase used in mind. The extraction times were kept identical to the extraction times used in SPME, in order to draw comparisons on the efficiency of extraction for the same extraction time. Other conditions that were kept the same were the addition of salt for the extraction of the polar compounds. The conditions used for the evaluation of the novel materials as well as the PDMS stir bar are summarized in Table 4.8.

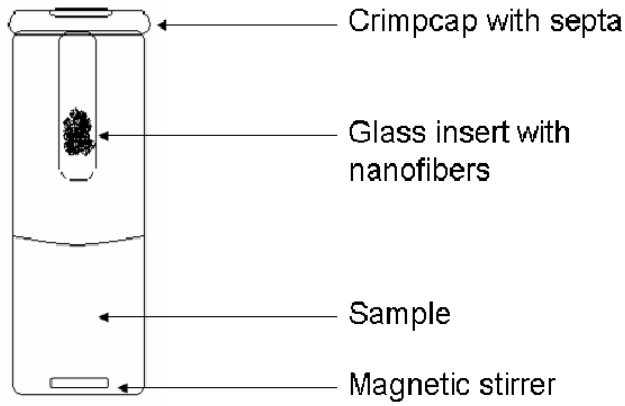


Figure 4.27: Headspace vial with glass insert for the nanofibers to be placed in.

Table 4.8: Summary of the extraction conditions for the headspace sorptive extraction.

Extraction condition	Non-polar analytes	Polar analytes
Temperature	60°C	80°C
Time	60 minutes	45 minutes
Salt addition	No salt added	Salt added to saturation
Stirring	600 rpm	600 rpm

The desorption of the VOCs from the PDMS stir bar and novel materials were done using a thermal desorption system (TDS). The nanofibers or PDMS stir bar was placed in a glass transfer tube, which gets heated up in order for the VOCs to be desorbed. To refocus the VOCs prior to chromatographic analysis they were cryogenically trapped using liquid nitrogen. The cryotrap was then heated up using a PTV injector and the analytes introduced into the GC. The experimental conditions of the TDS are summarized in chapter 3.

4.6.1 Extraction of volatile analytes using SBSE

As an additional extraction parameter, the agitation of the samples by stirring at 600 rpm was evaluated. Figure 4.28 show that agitation of the sample improves the extraction efficiency for the vast majority of the analytes. Extraction of the highly volatile compounds was insufficient at a concentration of 1 $\mu g.l^{-1}$. This may be a result of analyte losses taking place during the transfer of the stir bar from the sample vial to the thermal desorption system. This problem was not encountered with the higher boiling point analytes and extraction of these analytes was sufficient even at levels below 0.1 $\mu g.l^{-1}$.

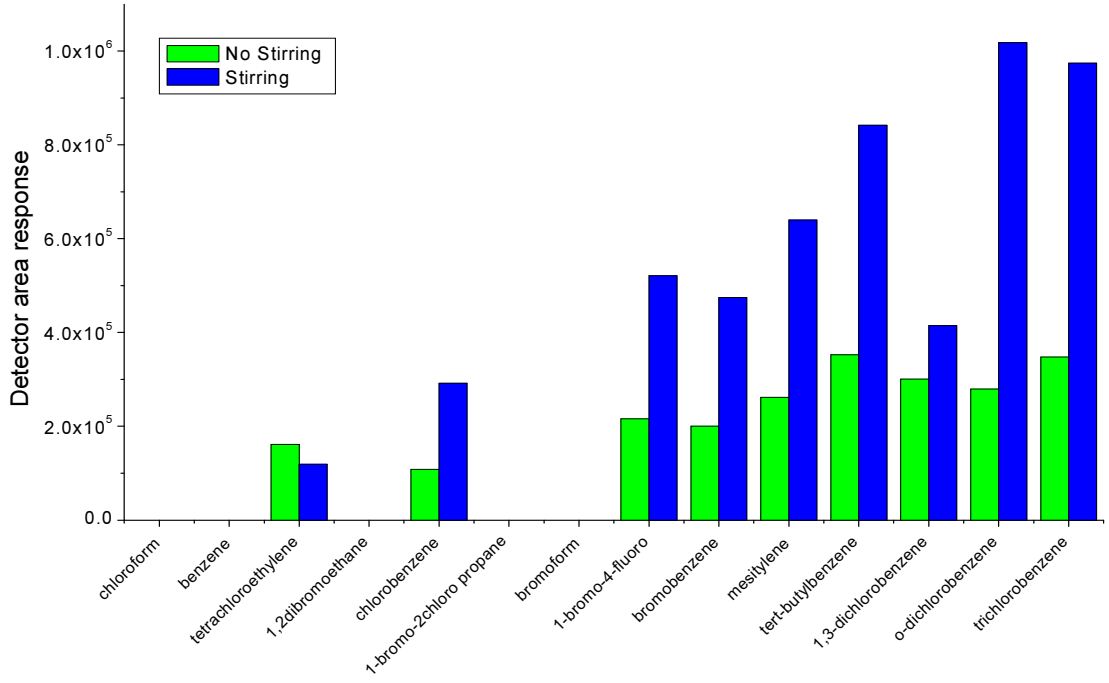


Figure 4.28: Extraction profile for non-polar compounds obtained by HSSE with and without stirring at 600 rpm using the PDMS stir bar. Experimental conditions: 10 ml distilled water containing approximately 1 µg.l^{-1} of all the analytes; extraction time, 60 minutes; extraction temperature 60°C.

Figure 4.29 shows the total ion chromatograms (TICs) obtained for HSSE-GC-MS of the non-polar analytes at 1 µg.l^{-1} and polar analytes at 10 µg.l^{-1}. Baseline separation for the majority of the non-polar compounds was achieved, with the exception of the bromoform and 1-bromo-2-chloropropane at 6.9 minutes and the bromobenzene and 1-bromo-4-fluorobenzene at 7.9 minutes. Peak broadening was also observed in the first 4 minutes of the analysis, which is due to poor cryofocussing of the highly volatile compounds despite using a trapping temperature of -100°C. This resulted in high LODs for these compounds. At levels below 1 µg.l^{-1}, chloroform, benzene and 1,2-dibromoethane could no longer be detected. The majority of the other analytes could still be detected at levels below 0.01 µg.l^{-1}. Complete baseline separation of EA (3.17 minutes) and MMA (3.37 minutes) in the analysis of the polar analytes was also not achieved due to severe peak broadening. Peak broadening, poor extraction due to the more polar character of the analytes and relatively high volatility of the EA and MMA led to much higher LODs for these compounds compared to the other two acrylate analytes. An increase in the detector response is seen as the boiling point of the analytes increases and polarity decreases. The detector response for the BA (8.22 minutes) and the 2-EHA (14.70 minutes) is much larger; therefore LODs below 0.1 µg.l^{-1} could be achieved, whereas the LODs for the EA and MMA were between 0.5 and 1 µg.l^{-1}.

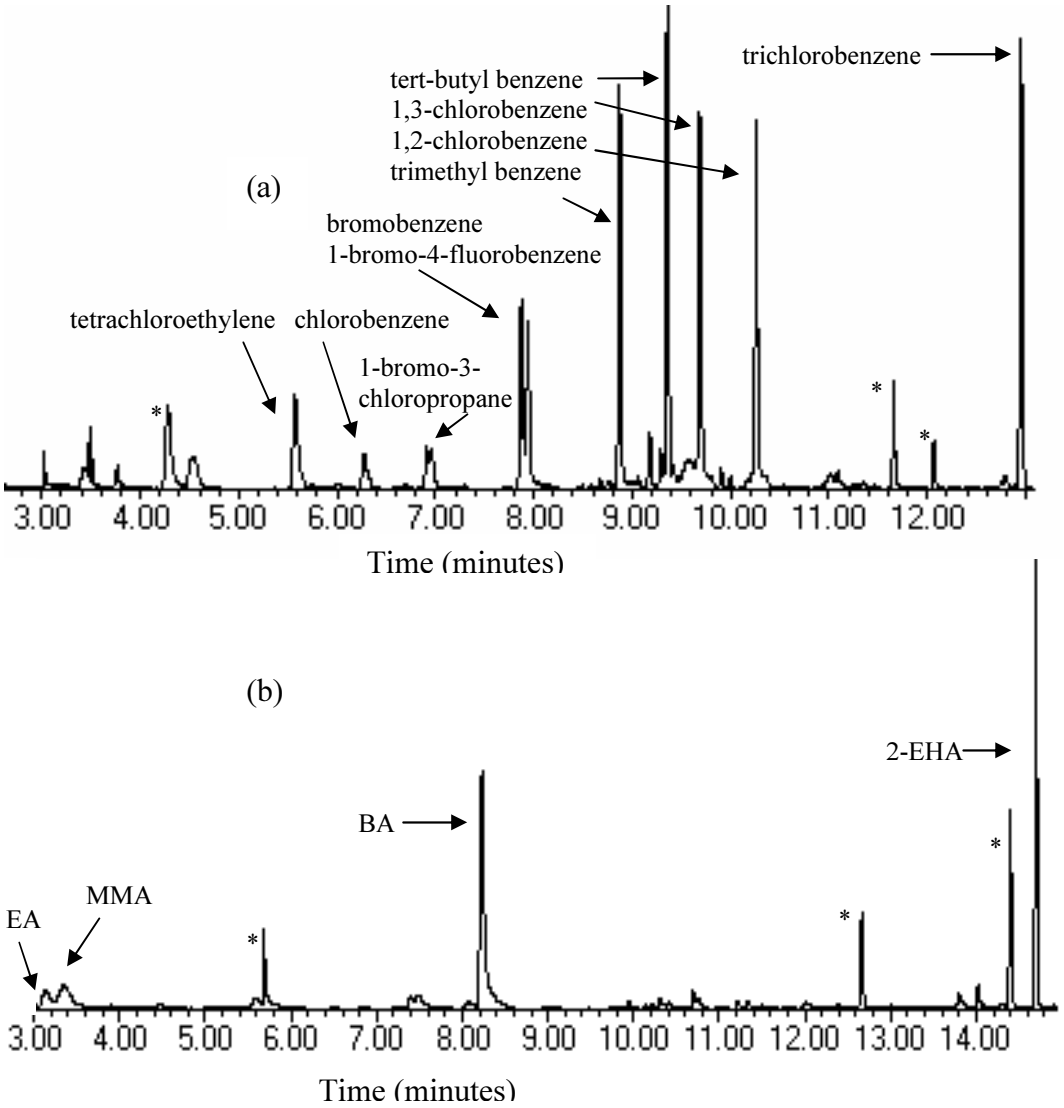


Figure 4.29: TIC obtained for the non-polar analytes (a) and polar analytes (b) using the PDMS stir bar for extraction. Blank peaks are indicated by an asterisk.

4.6.2 Extraction of non-polar compounds using the novel materials

For the extraction of the non-polar volatiles, approximately 4.0 mg of nanofiber material was used. This is approximately eight times the amount of extraction material used with SPME, and about ten times less than the amount of extraction material used in SBSE. PAN-g-PDMS and PMAA-g-PDMS were tested for extraction of the non-polar analytes using a 500 $\mu g.l^{-1}$ analyte solution. All analytes were extracted with the PAN-g-PDMS fibers; while benzene, chloroform and 1-bromo-3-chloropropane were not detected when using the PMAA-g-PDMS fibers. However, the extraction efficiency for the analytes extracted by the PMAA-g-PDMS fibers, was an order of magnitude higher than for the PAN-g-PDMS fibers. Figure 4.30 shows the TIC for the non-polar compounds extracted using the PMAA-g-PDMS fibers. Several blank peaks were noted for the PMAA-g-PDMS fibers. At a concentration of 500 $\mu g.l^{-1}$ the blank peaks were of approximately, the same intensity as the analyte peaks. The major blank peaks were identified as DMF at 6.55 minutes, this

is most likely still some residual solvent from the electospinning, (trimethyl silyl) acetic acid at 7.5 minutes, ethyl dimethyl silanol at 7.8 minutes and octa methyl cyclotetra siloxane at 10.15 minutes. The latter three blank peaks are possible degradation products from the PMAA-g-PDMS. The octa methyl cyclotetra siloxane is a common degradation product found in degradation of the PDMS stationary phase from the column; however this peak was not observed when doing a blank analysis for the PAN-g-PDMS, it was therefore assumed that degradation of the extraction material occurs during thermal desorption.

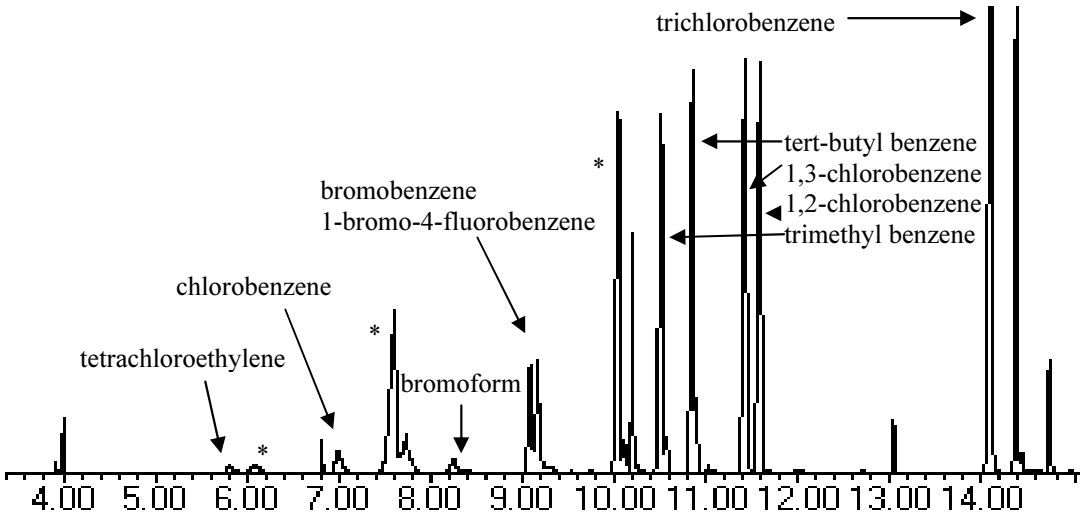


Figure 4.30 TIC obtained for the non-polar analytes extracted at 500 µg.l^{-1} using the PMAA-g-PDMS nanofibers. Blank peaks originating from the PMAA-g-PDMS fibers are indicated by an asterisk

Upon doing a second extraction in order to determine the precision of the nanofibers, a dramatic decrease in the extraction efficiency of the nanofibers was seen. Figure 4.31and Figure 4.32 illustrates the difference in efficiency between the first and second extraction using the same nanofibers.

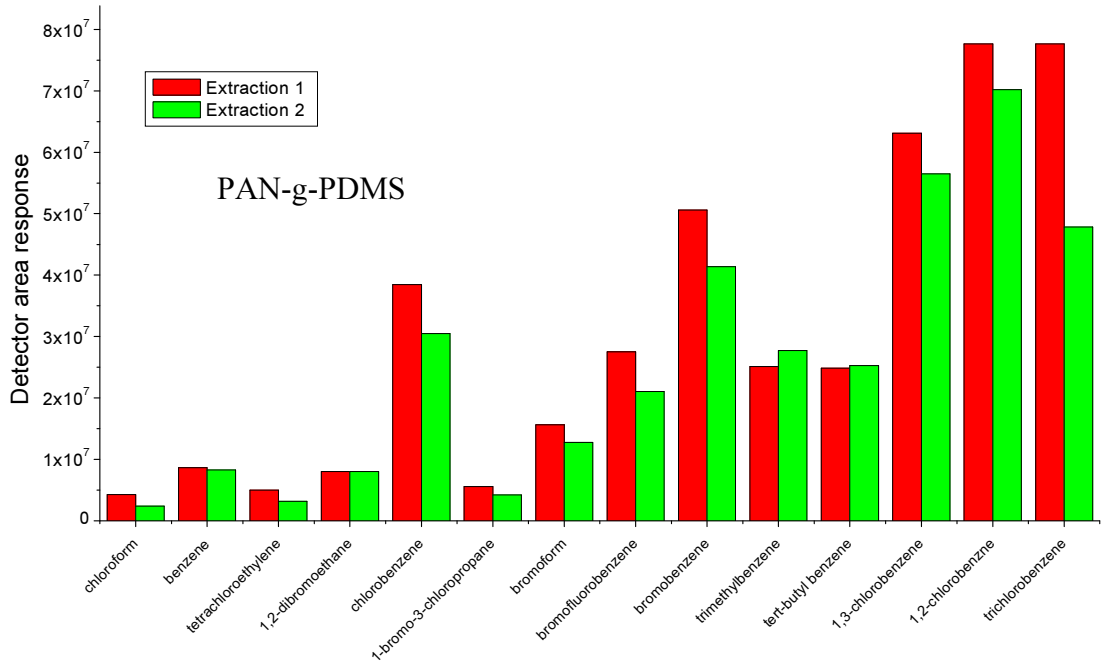


Figure 4.31: Extraction profile of non-polar compounds using 4.0 mg of PAN-g-PDMS. Experimental conditions: 10 ml distilled water containing approximately 500 µg.l^{-1} of all the analytes; extraction time, 60 minutes; extraction temperature 60°C, agitation at 600 rpm.

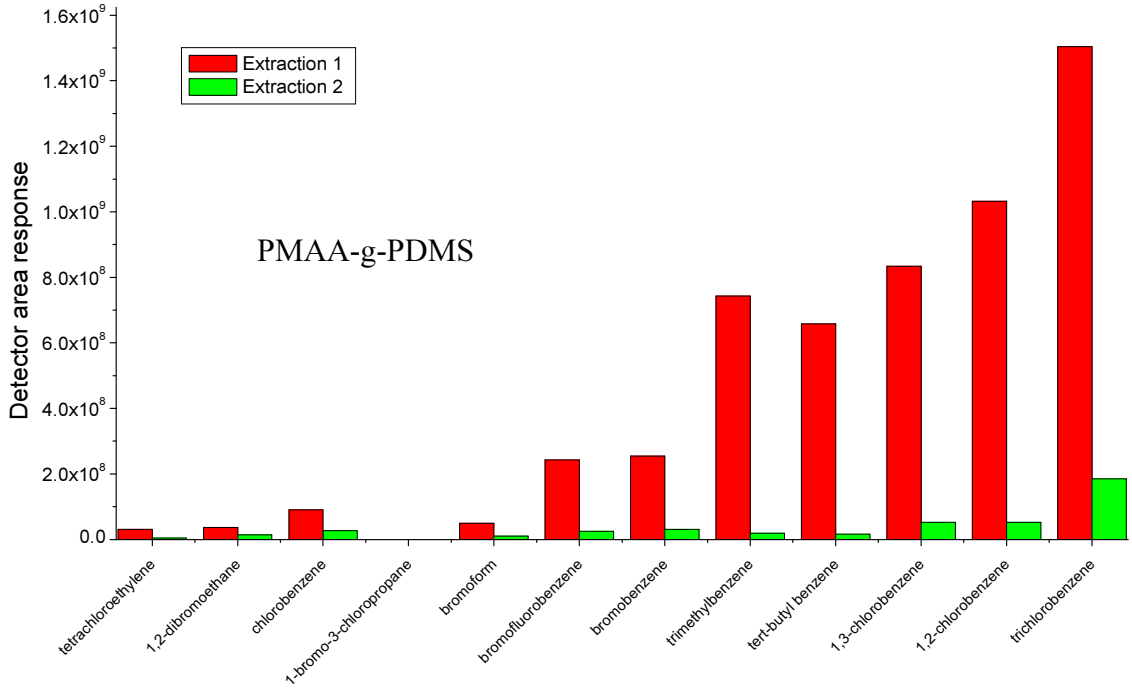


Figure 4.32: Extraction profile of non-polar compounds using 3.9 mg of PMAA-g-PDMS. Experimental conditions: 10 ml distilled water containing approximately 500 µg.l^{-1} of all the analytes; extraction time, 60minutes; extraction temperature 60°C, agitation at 600 rpm.

The PAN-g-PDMS shows a slight decrease in the extraction efficiency for the second extraction. The PMAA-g-PDMS almost completely loses the ability to extract volatile analytes and a severe

decrease in the amount of analytes extracted was seen, this is most likely due to chemical and thermal degradation taking place during the first extraction cycle. Chemical degradation of the fiber might possibly be due to uptake/absorption of water vapor and the exposure to the volatile analytes. The inability to extract the analytes more than once using the nanofibers leads to very high relative standard deviations and therefore, poor confidence levels for the re-use of the fibers.

At concentration levels of 1 $\mu g.l^{-1}$ the non-polar compounds using the PAN-g-PDMS fibers were not detected at all and at levels of 10 $\mu g.l^{-1}$ only extraction of the higher boiling compounds take place as is shown in Figure 4.33.

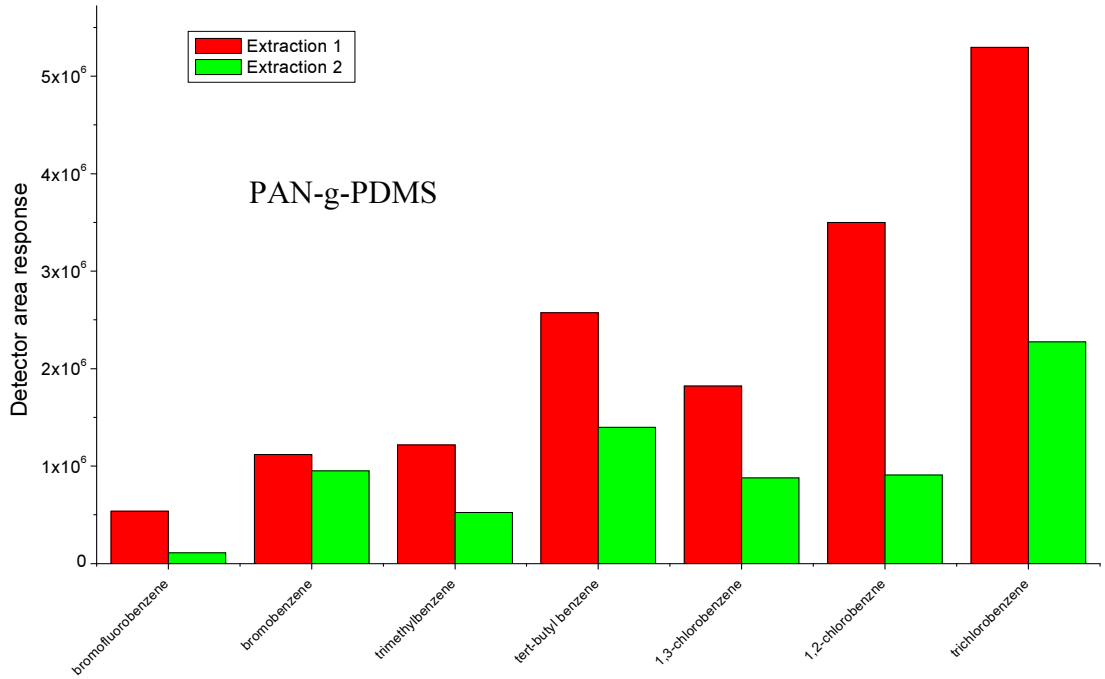


Figure 4.33: Extraction profile of non-polar compounds using 4.0 mg of PAN-g-PDMS. Experimental conditions: 10ml distilled water containing approximately 10 $\mu g.l^{-1}$ of all the analytes; extraction time, 60minutes; extraction temperature 60°C, agitation at 600 rpm.

This graph also shows that for the PAN-g-PDMS fibers extraction efficiency decreases after the initial extraction; this may be due to the thermal degradation of the fibers taking place, as discussed in the previous section. Although extraction of the volatiles with the PAN-g-PDMS fibers do take place, the extraction materials used in SPME are superior in both precision and detection limits. The LODs was determined to be less than 0.5 $\mu g.l^{-1}$ for the vast majority of the compounds using SPME. The use of the PDMS stir bar in HSSE is superior for the higher boiling non-polar compounds when compared to SPME, with LODs below 0.001 $\mu g.l^{-1}$ obtained for some of the

compounds. However this is due to the much higher volume of the extraction material used in SBSE.

The PMAA-g-PDMS and PMAA fibers were evaluated using a 10 µg.l^{-1} solution in order to determine if the PMAA is a better extraction material than the PMAA-g-PDMS. The commercially available PDMS stir bar was also evaluated and the results normalized to give an indication of the extraction efficiency for a specific amount of coating used.

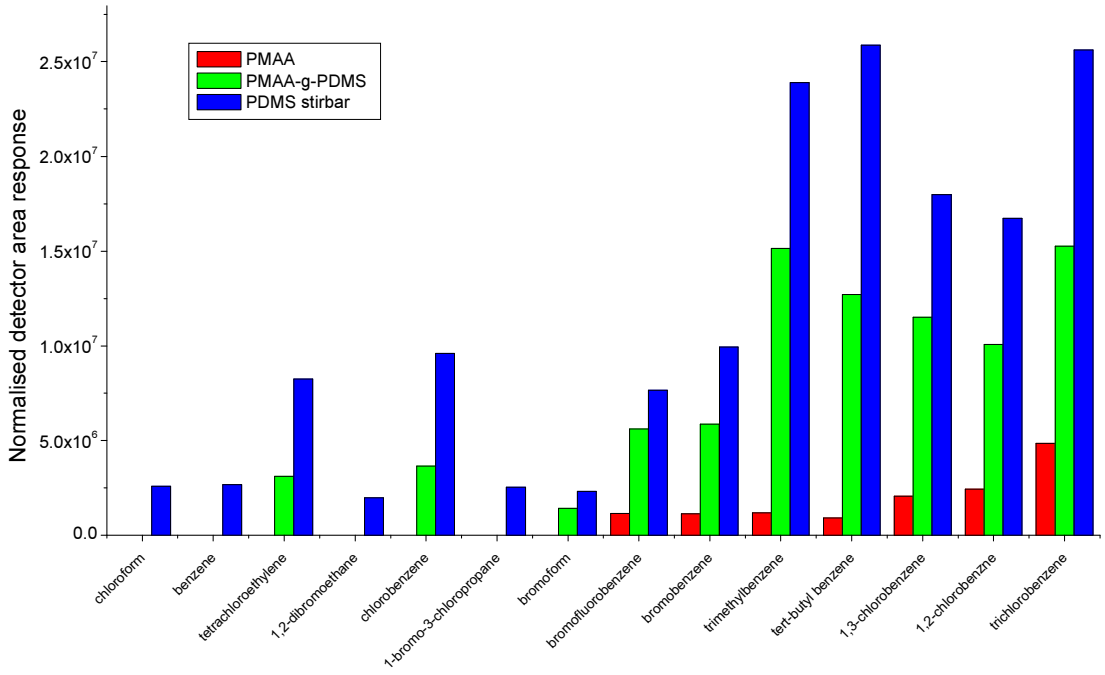


Figure 4.34: Extraction profile of non-polar compounds using the PMAA and PMAA-g-PDMS nanofibers as well as the commercially available PDMS stir bar. Experimental conditions: 10 ml distilled water containing approximately 10 µg.l^{-1} of all the analytes; extraction time, 60 minutes; extraction temperature 60°C, agitation at 600 rpm.

The PMAA-g-PDMS extraction efficiency is far superior to that of the PMAA nanofibers as is illustrated in Figure 4.34. The extraction of the lower boiling point compounds using the nanofibers is still insufficient and only the higher boiling point analytes are extracted. However, the normalised graph of the extraction profile shows that using the commercially available PDMS stir bar is superior compared to both of the MAA-based nanofibers.

The PAN-g-PDMS, PMAA and PMAA-g-PDMS nanofibers were used to evaluate the extraction of the polar compounds even though the precision of the fibers cannot be determined. As discussed in previous sections a lot of emphasis has been placed in the past two decades on the development of extraction materials for non-polar analytes. There are sufficient coatings for SPME and SBSE available to extract these types of analytes at trace levels with good precision.

4.6.3 Extraction of polar analytes using the novel materials

Extraction of the four acrylate analytes was also evaluated with the commercially available PDMS stir bar and the PAN-g-PDMS, PMAA-g-PDMS and PMAA nanofibers. Figure 4.35 was normalized in order to compare the extraction efficiencies of the nanofibers to the stir bar for a specific amount of coating.

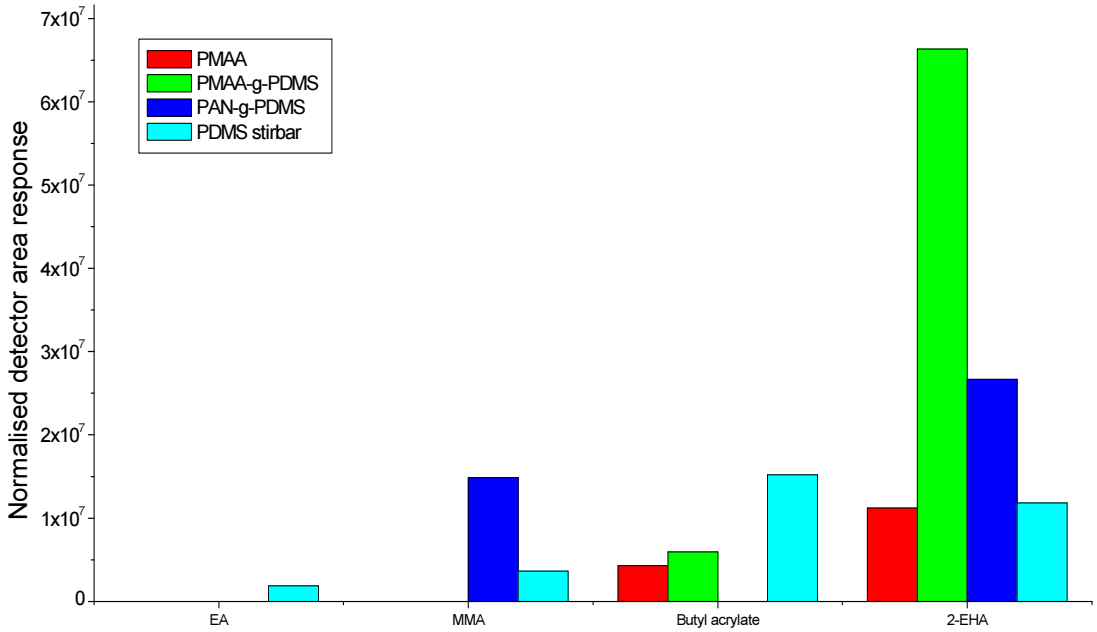


Figure 4.35: Extraction of the polar compounds using the PAN-g-PDMS, PMAA-g-PDMS and PMAA nanofibers as well as the commercially available PDMS stir bar. Experimental conditions: 10ml distilled water containing approximately 10 $\mu g.l^{-1}$ of all the analytes; extraction time, 45 minutes; extraction temperature 80°C, salt addition, agitation at 600rpm.

2-Ethylhexylacrylate was the only analyte to be extracted by all of the materials. Previously, in SPME, the extraction of 2-EHA was also far better compared to the other analytes, this is most likely due to a much higher boiling point and a longer carbon backbone, which makes this analyte more non-polar. Figure 4.36 shows the TIC for the extraction of the polar analytes using the PAN-g-PDMS and PMAA-g-PDMS nanofibers at a concentration level of 100 $\mu g.l^{-1}$. Numerous blank peaks are observed on the TIC where the PMAA-g-PDMS nanofibers were used, and at lower levels the analyte peaks are obscured by these blank peaks. The PMAA and PMAA-g-PDMS fibers were not suitable for extraction of the analytes with higher volatility. The only compound extracted with good efficiency using the PMAA-g-PDMS was 2-EHA. On the other hand, the PAN-g-PDMS extracted three of the four analytes at levels of 100 $\mu g.l^{-1}$. At lower analyte concentrations of 10 $\mu g.l^{-1}$only MMA and 2-EHA were detected. From figure 4.35 it is evident that the PAN-g-PDMS

fibers have superior extraction efficiency for MMA compared to the PDMS stir bar for an equivalent amount of extraction phase used.

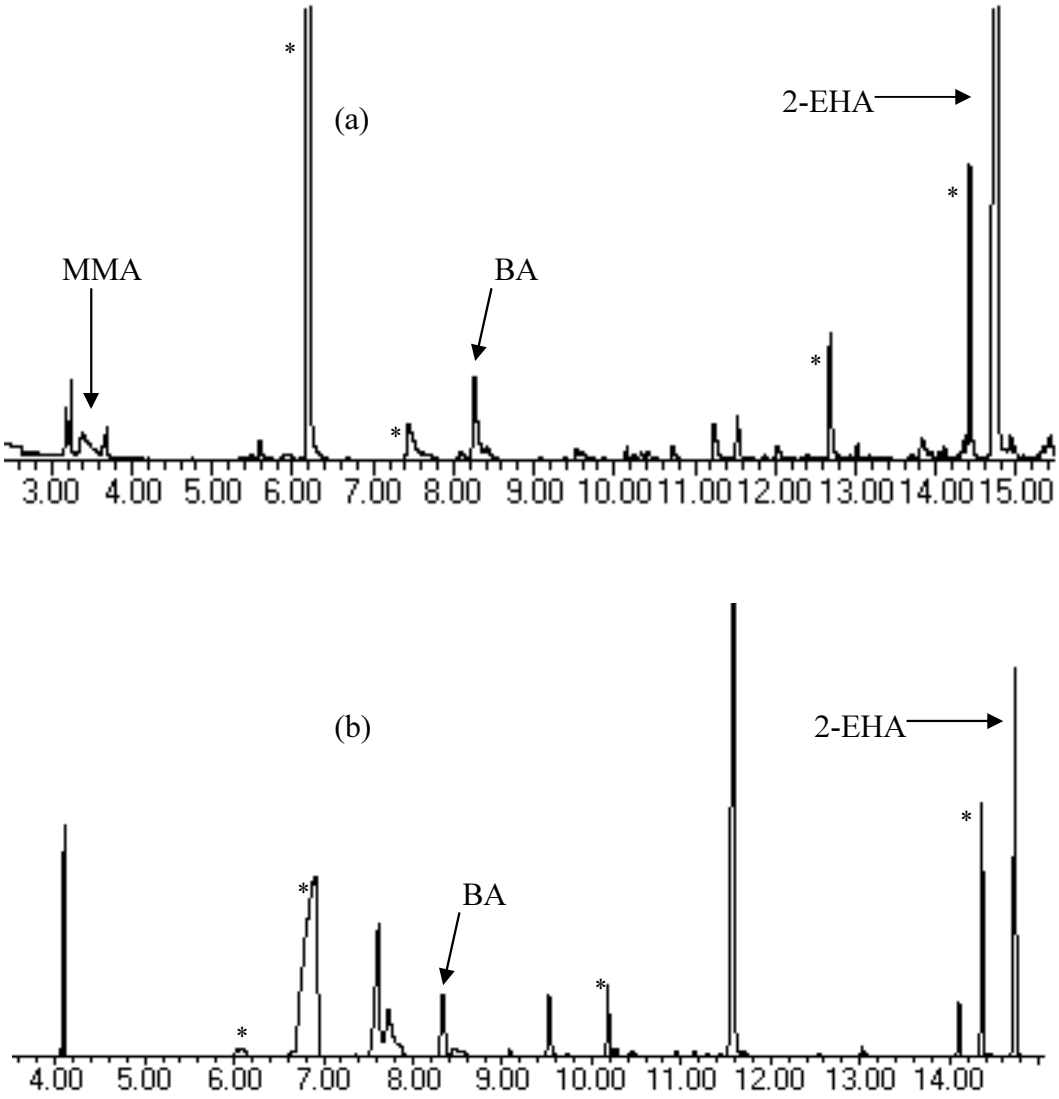


Figure 4.36: TIC obtained for the polar analytes extracted at 100 µg.l^{-1} using a) PAN-g-PDMS and b) PMAA-g-PDMS nanofibers. Blank peaks are indicated by an asterisk.

EA was not extracted by any of the novel materials, whereas for SPME using the CAR/PDMS fiber, the LOD was determined to be below 1 µg.l^{-1}. The LOD of EA determined using the PDMS stir bar was approximately 1 µg.l^{-1}, however the amount of extraction material in SBSE is approximately a 100 times more than in SPME. The chromatographic separation of EA using the stir bar was also extremely poor and the peaks could only be seen at levels of 1 µg.l^{-1} when the mass ions were extracted. Improved trapping of the more volatile analytes might reduce peak broadening and improve the analysis of these compounds. This is a consequence of using thermal desorption with cryofocusing, which is not efficient for highly volatile analytes. The extraction of the MMA using SPME was also superior, with a LOD of approximately 0.1 µg.l^{-1}. It is clear from these results that

SPME is superior in the extraction of highly volatile materials. Although the novel materials showed some affinity to extract certain of the acrylate analytes, the main drawback of using these materials was the thermal instability of the polymers and the inability to do multiple extractions using the same nanofibers in order to determine the precision of an analysis. The commercially available extraction materials were superior in the extraction of these spesific target analyte but the novel fibers still showed some promise to be used as extraction materials for polar analytes. If the manufacturing of these nanofibers are consistent it would be possible to use these nanofibers as cheap, disposable extraction phases in volatile analysis. Where the thermal degradation peaks are problematic in the chromatogram alternative ways of using these nanofibers as extraction phases can be investigated.

4.7 References

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Chapter 5

Conclusions and Recommendations

This chapter briefly discusses the conclusions that can be made from the study. Finally some recommendations for future work will be made.

5.1 Conclusions

The analyses of VOCs at trace levels have become increasingly important due to health and environmental concerns and different techniques are available for their extraction and analysis. An optimized SPME extraction method was developed for a group of non-polar halogenated compounds and benzene derivatives, as well as for more polar oxygenated analytes commonly present as VOCs in water-based paints. Only a few extraction materials are currently commercially available for the extraction of VOCs at trace levels. In an attempt to improve the extraction of the target VOCs, novel materials based on PDMS were prepared. Hybrid PDMS graft copolymers, prepared with different monomers were successfully synthesized using the grafting through technique. Nanofibers of the PMMA-g-PDMS and PMAA-g-PDMS organic-inorganic hybrid polymers were successfully prepared using the electrospinning technique. Electrospinning of PMMA-g-PDMS have previously been reported, however, this is the first documented case where PMAA-g-PDMS was synthesized and electrospun into nanofibers. Homopolymers of PMMA and PMAA were also "spun" into nanofibers and evaluated as possible extraction materials for VOCs. PAN-g-PDMS nanofibers previously prepared by G.Bayley were also included in the study.

The nanofiber morphology was studied using SEM analysis. Nanofibers with elongated beaded morphology were observed for the PMMA-g-PDMS when using very long tip-to-collector distances. In the PMAA-g-PDMS nanofibers, both thick and thin nanofibers were obtained whilst using the same electrospinning conditions. This is most likely due to the presence of the both the graft and homopolymer. Only nanofibers with non-beaded morphology were considered for the use as extraction materials for VOCs. VOCs are desorped at temperatures of 200° and above, therefore, one of the most important properties of the nanofibers that needed to be evaluated is their thermal stability. The TGA analysis indicated that the weight loss of the PMMA-g-PDMS, PMMA and PAN-g-PDMS was the least; however upon closer inspection it was observed that the PMMA and PMMA-g-PDMS lost their nanostructure after exposure to elevated temperatures. A change in the colour of the PAN-g-PDMS was observed although no weight loss occured. Exposing this polymer to elevated temperatures resulted in a change in the chemical nature of the polymer. The MAA based polymers showed weighed loss during the TGA analysis, but the nanofiber structure remained in tact. The PAN-g-PDMS and the MAA based polymers were evaluated as possible extraction phases for VOC analysis. At high concentration levels, the PAN-g-PDMS successfully extracted all of the non-polar analytes, whereas the extraction of the highly volatile compounds using MAA-g-PDMS and MAA did not occur. Numerous blank peaks were also observed in the PMAA-g-PDMS chromatograms, which can most likely be attributed to degradation compounds. The use of the commercially available extraction materials for the analysis of non-polar compounds at trace levels

are superior to the use of the novel materials prepared in this study. Most non-polar analytes can effectively be extracted using the commercially available extraction phases. The focus in recent years has been on the development of extraction phases for more polar compounds and for the extraction of specific target analyte groups. Employing the same methodology as for the non-polar compounds, the nanofibers were evaluated as extraction materials for the acrylate analytes and compared to the commercially available extraction phases. The novel materials could be used to extract certain of the acrylate analytes at concentration levels of 10 $\mu g.l^{-1}$ and above. The EA could not be extracted by any of the novel materials and using the commercially available phases resulted in relatively high LODs and low precision. The 2-EHA is the only analyte that was effectively extracted by all of the nanofibers, as well as the commercially available extraction materials, most likely due to the high boiling point and low polarity of this analyte compared to the other acrylate analytes.

There are a number of draw backs of using the electrospun materials. Firstly, the thermal instability of certain of the polymers means that thermal desorption is not the best process to be used for these materials. Secondly, it is clear that each of the materials can only be used in a single extraction, due to the changes/degradation of the material during the thermal desorption process. This inability to do multiple extractions with the same material means that it is not possible to determine the precision of an analysis. However the reproducibility could still be determined in future with a series of samples. Generally it was found that there is poor extraction of the highly volatile and polar compounds evaluated in this study. Although these materials were not superior to the commercially available phases, this is only the case for the specific target analytes analyzed. The possibility to use these phases successfully as extraction materials for other polar analytes should be further investigated. These materials have the potential to be used as a cheap alternative for the extraction of VOCs and multiple analyses would be possible if the manufacturing of these nanofiber materials are consistent. Where the thermal stability of the fibers is insufficient alternative ways for using the nanofibers as extraction materials can be investigated.

5.2 Recommendations

The synthesis of novel materials using a higher molecular weight PDMS macromonomer has shown some improvements in the thermal stability of the graft copolymers. Further investigations should be made into the electrospinning of these copolymers and into the effectiveness of the nanofibers as extraction phase in VOC analysis. Application of these the novel materials as extraction phase in SPE should be evaluated. The thermal stability of the materials will not play an influence using this extraction technique; however, the chemical stability of the fibers when in direct contact with

solvents and water should be considered. The acrylate analytes can be extracted to some extend using the commercially available techniques. There are, however, numerous other classes of compounds where the extraction is extremely poor. Initial screening in the study of VOCs in paints showed that the extraction and analysis of many alcohol and glycol type analytes found in water-based paints does not occur at all. The development of novel extraction materials for the analysis of these types of polar VOCs should continue.