Development of Poly(dimethylsiloxane)-co-diphenylsiloxane(5%)-coated and Poly(ethylene glycol)-coated Stir Bars for use in Stir Bar Sorptive Extraction

by

Helen M. Prochazka, B.Sc.

A Thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfillment of
the requirements for the degree of

Master of Science

Department of Chemistry

Carleton University
Ottawa, Ontario
May 26, 2006

Your file Votre référence
ISBN: 978-0-494-18372-4
Our file Notre référence
ISBN: 978-0-494-18372-4

Abstract

Sol-Gel Technology was used to produce novel stir bar coatings to be used for Stir Bar Sorptive Extraction of analytes of different polarities and partition coefficients. Naphthalene, 3,3',4,4'-tetrachlorobiphenyl and pentachlorophenol were extracted using stir bars (HPBars) coated with poly(dimethylsiloxane) (PDMS), poly(dimethylsiloxane)-co-diphenylsiloxane(5%) (PDMS-co-DPS(5%)) and poly(ethylene glycol) (PEG).

Limits of detection for naphthalene were found to be 0.680 μg/mL, 0.770 μg/mL, and 3.70 μg/mL for the PDMS, PDMS-co-DPS(5%), and PEG-coated HPBars, respectively. Limits of detection for 3,3',4,4'-tetrachlorobiphenyl were found to be 0.72 ng/mL, 0.89 ng/mL, and 2.50 ng/mL for the PDMS, PDMS-co-DPS(5%), and PEG-coated HPBars, respectively. Limits of detection for pentachlorophenol were found to be 7.20 ng/mL, 5.40 ng/mL, and 0.54 ng/mL for the PDMS, PDMS-co-DPS(5%), and PEG-coated HPBars, respectively. Therefore, the polar PEG coating had the greatest extraction efficiency and sensitivity for pentachlorophenol.

The Linear Dynamic Ranges for naphthalene using the PDMS-coated HPbar, for 3,3',4,4'-tetrachlorobiphenyl using the PDMS-do-DPS(5%)-coated HPBar, and for PCP using the PEG-coated HPBar were 0.7 μg/mL – 5 μg/mL, 0.9 ng/mL – 174 ng/mL, and 0.5 ng/mL – 1000 ng/mL, respectively.

Competition and interference effects were analyzed by extraction from a multianalyte solution, and a solution made with water obtained from the Rideau River. It was found that the presence of other analytes and organic compounds decreased the partition coefficients of the analytes of interest, but the general trends remained the same.

Acknowledgements

Bob – Thanks for all the help and support throughout the years. Your patience was much appreciated and the compliments about my writing always gave me a boost. Thanks for everything.

Barb, Mohamed, Dave, Rana – thanks for being patient with me, sharing the lab with me, discussing science with me, and making me laugh. I couldn't find a better group of people to work with.

Christina – you are my homie, fo' shizzle. Thanks for still living just down the street from me and thanks for putting up me the last 24 years or so.

Jacques – Finally, someone who understands what's going on in this brain of mine. Thanks for not letting your eyes glaze over every time I talked/complained about my thesis. I, in return, promise to never let mine glaze over when you talk about yours. Thanks for being my other half.

Caroline and Veronica – we are the fabulous Prochazka sisters. Never forget that you're a part of this special club that no one else is allowed to join. I call 'President'!

Most of all, Antonin and Jitka – If I could write something that showed you just how much I appreciate all your help and guidance throughout the years it would fill enough pages to reach from the Czech Republic to Canada. So, I will just say that without you I really don't know where I'd be. You guys are the best parents a gal could have, I love you, and I dedicate this thesis to you both.

And thanks to all my friends who have supported me in the years leading up to this. Thanks to all of you who could pronounce my last name properly...and of course, from henceforth, I give you all permission to refer to me as 'Stir Bar' Prochazka.

TABLE OF CONTENTS

LIST OF FIGURES

List of Figures in Appendix

LIST OF TABLES

1. INTRODUCTION

1.1 Chemicals: Good or Bad?

A large portion of the chemicals released in to the environment are pesticides. Pesticides (consisting of herbicides and insecticides) are applied to plants to maximize the product output of a farm. After being applied to the plants, the pesticides will have three fates: *sorption, transfer,* and *degradation*:

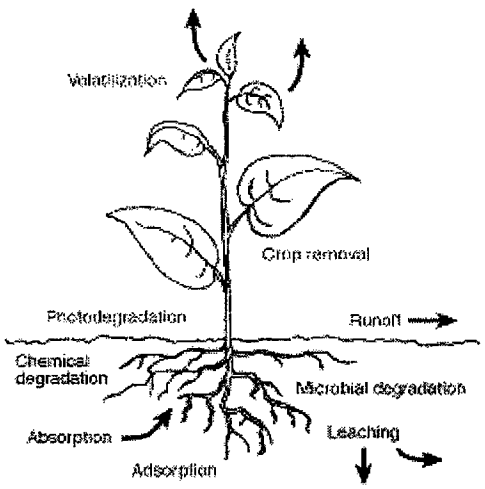


Figure 1.1: Fates of a pesticide

[Brown et al, 1997]

Since chemicals applied to plants need to have some sort of stability so that they are effective, the main fate is *transfer('runoff' in Figure 1.1)* in which the chemical will be moved to different areas by water.

One of the most widely known pesticides is the insecticide dichlorodiphenyltrichloroethane (DDT). Its development occurred during World War II

so that soldiers could work without the distraction of mosquitoes, lice and other insects. The LD_{50} of DDT is 87 mg/kg body weight in rats making its toxicity to mammals approximately the same as the toxicity of the nicotine in cigarettes [Kruus et al, 1991]. Due to certain insects becoming immune to its effects, and it being toxic to non-target species (such as frogs and fish), the use of DDT was banned from the United States by 1973 [Kruus et al, 1991]. However, DDT is just one example of a chemical that was used in vast amounts and then banned because of the risk which resulted from its use.

Two major groups of pesticides are the organochlorine and organophosphate compounds. Organochlorine compounds are persistent, relatively insoluble in water, and are consequently very soluble in lipids (such as fatty tissue in fish). They include DDT, polychlorinated biphenyls (PCBs) and dioxins. Organophosphate compounds are less persistant in that they are more soluble in water (due to the polar phosphate groups) and less soluble in lipids [Kruus et al, 1991]. Organophosphate compounds include the common pesticide named Malathione. Also, organophosphate compounds are more likely to biodegrade than organochlorine compounds because of the oxygen atoms. The presence of oxygen allows for sites where water can hydrolyze the molecule, breaking it up into smaller molecules which are not as toxic.

1.1.1 Important Chemicals of Current Study

A large group of compounds called the Dioxins and Furans have become the focus of much research. Dioxins and Furans are toxic in low concentrations. The LD_{50} of the most harmful dioxin, 2,3,7,8-tetrachlorodibenzo-p-dioxin or TCDD, is 275 μg/kg in rabbits [PI, 2006]. In Guinea Pigs, the LD_{50} is 500.0, ng/kg [PI, 2006]

Dioxins and Furans are formed by the incineration of chlorinated compounds like Poly(chlorinated) Biphenyls (PCBs) or chlorinated phenols. Therefore, chlorinated compounds like PCBs and Phenols are also of great interest and their analysis can help develop new techniques for dioxins and furans

PCBs are a family of 209 congeners, the naming of which depends upon the number of chlorine atoms and where they are situated. PCBs which are coplanar can form furans by incineration. PCB77, the industrial name for 3,3',4,4'-tetrachlorobiphenyl, is a coplanar PCB congener [Bemis, 2005]. A coplanar PCB may have similar behaviour as a dioxin or furan, therefore, it will be analyzed in this research project. Also, pentachlorophenol will be analyzed due to its role as a dioxin precursor and because it is a polar compound which makes it more difficult to extract from water.

The three compounds being analyzed, Naphthalene, 3,3',4,4'-Tetrachlorobiphenyl and Pentachlorophenol have the structures seen in Figure 1.2.

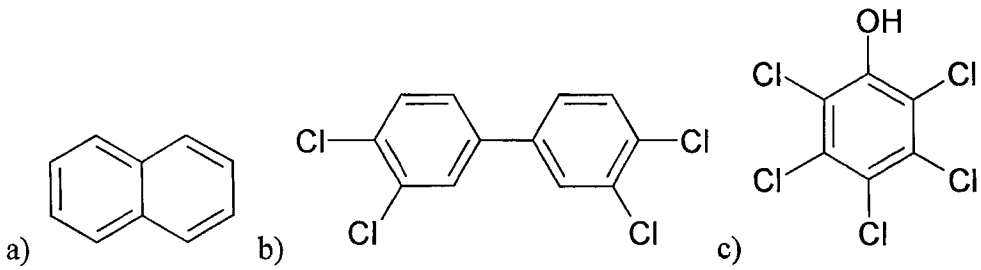


Figure 1.2: Structures of Analytes to be Analyzed: a) Naphthalene; b) 3,3'4,4'-Tetrachlorobiphenyl (PCB77); c) Pentachlorophenol (PCP)

Naphthalene is being analyzed because it is a nonpolar, aromatic compound with a relatively low Octanol-Water partition coefficient (to be described in a later section). As previously mentioned, PCB77 and PCP will be analyzed because of their similarities to dioxins and furans, as well as their differences in Octanol-Water partition coefficient.

1.2 Water in the Environment

The Environmental Protection Agency estimated in 1989 that approximately 2.4 billion pounds of chemicals were intentionally released into the atmosphere, and 1.9 billion pounds were released into the water system (in North America alone) [EPA, 1989].

Water is the Earth's most valuable resource. Every living thing needs water and yet humans are dumping tonnes of pollutants into the lakes, rivers, and oceans even though they eventually end up leading back to us. Chemicals are released into the environment (whether it is accidental or intentional) and the rain water moves them so that they enter the water system, thus affecting the water and the aquatic life. As humans drink the water and consume fish (or other animals that have consumed fish), they are

exposed to these chemicals. Therefore, the chemicals that are released into the environment by humans ultimately affect the health of humans. From the previous statement, it is evident that a growing concern is the movement of chemicals in groundwater.

1.3 Why the need for new methods in water analysis?

Since our health is at risk, an analytical method that is cheap, fast, can effectively analyze a large range of analytes and is simple to use is required. Essentially, it is important to know how polluted a sample of water is so that it can be deemed drinkable or undrinkable. Also, some pollutants are toxic at extremely low concentrations; therefore, a method with a low detection limit is desirable.

Current methods (which will be described in the following section) have been proven to be effective at analyzing water samples. However, there is always room for improvement in terms of speed, cost, limits of detection and robustness of the methods.

1.4 Current Methods in Water Analysis

Methods that are currently being used for water analysis include liquid-liquid extraction, solid-phase extraction (SPE), and solid-phase microextraction (SPME).

1.4.1 Liquid-Liquid Extraction

Liquid-Liquid extraction is an old technique that depends upon the immiscibility of different organic solvents with water. When the extraction of an analyte from water is desired, one simply adds a small portion of an immiscible organic solvent to the aqueous sample. The vial containing the aqueous and organic phases is shaken, and the phases are allowed to separate. The polarity of the analyte will dictate the ratio of the concentration of the analyte in the organic phase and the concentration of the analyte in the aqueous phase. Typically, one would choose an organic solvent which is immiscible with water and that is of similar polarity of the analyte because *like dissolves like*. One such solvent is hexane.

1.4.2 Solid-Phase Extraction (SPE)

Solid-phase extraction is a relatively old technique involving the use of a solid phase in a vial. A liquid sample is passed through the solid phase and compounds of similar polarity to the solid phase will be sorbed, allowing the analytes of the opposite polarity to remain in the solution. Figure 1.3 shows a schematic diagram of solid-phase extraction.

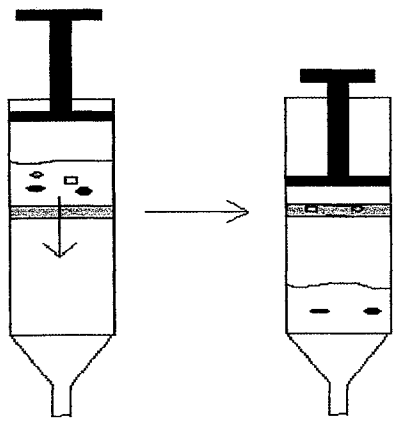


Figure 1.3: Schematic Diagram of a Solid-Phase Extraction cartridge. As the liquid is forced through the solid phase disc, analytes of similar polarity are adsorbed and the remaining analytes in solution are of opposite polarity.

Some typical problems that occur with SPE are incomplete analyte removal, low recovery of analytes, and high variability (large relative standard deviation) [Levin, 2006].

1.4.3 Solid-Phase Microextraction (SPME)

Solid-Phase Microextraction is a derivative of SPE. The main difference between the two methods is the amount of solid-phase. Therefore, since SPME involves the use of much smaller amounts of solid phase, it can extract much smaller amounts of analyte. The instrument used for SPME is a syringe-like fiber which is coated with approximately 0.5 μL of solid-phase. The coatings range in composition. Some well-known coatings are poly(dimethylsiloxane), divinylbenzene, poly(ethylene glycol), and mixtures of the three. Figure 1.4 shows a diagram of an SPME syringe.

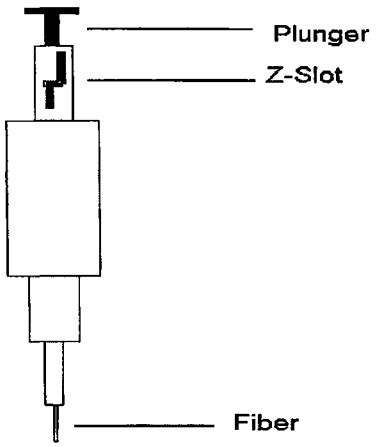


Figure 1.4: Solid-Phase Microextraction Fiber

Solid-Phase Extraction and Solid-Phase Microextraction are both based on the equilibrium reached between the concentration of the analyte in the aqueous phase and the concentration of the analyte in the solid phase. Therefore, the partition coefficient, or $K_{O/W}$, of a compound needs to be taken into consideration when choosing an appropriate solid phase.

The partition coefficient is a ratio of the solubility of a compound in an organic phase to that of it in an aqueous phase. From the previous statement, in the term $K_{O/W}$, the 'o' represents the organic phase and the 'w' represents the water phase. The higher the partition coefficient, the more soluble the compound is in the organic phase and the less polar it is. The lower the partition coefficient, the more soluble the compound is in the aqueous phase and the more polar it is [Prochazka, 2004].

The process of SPME involves the fiber being exposed to either a liquid or gaseous sample, ad/absorbing the analyte for a specified time, and then inserting the fiber

into the injection port of a gas chromatograph. The injection port will be heated to high temperatures, therefore, the analyte will desorb thermally.

Solid-phase microextraction is a method that is portable, has low detection limits, and is simple to use, but the small amount of solid phase limits the amount of analyte that the fiber can extract. SPME also relies on the equilibrium of the analyte between the fiber and the liquid or gaseous sample remaining the same in different matrices. However, this is not usually the case. The small amount of solid phase will not allow for an exhaustive extraction of the analyte since at trace levels the amount extracted will be limited by the amount of solid phase. Therefore, the same principle of SPME is used, but a magnetic, glass-encased stir bar replaces the SPME fiber. A larger volume of solid phase coats the stir bar, resulting in an exhaustive method which allows for the extraction of larger amounts of analyte. This method is called Stir Bar Sorptive Extraction, or SBSE.

1.5 Stir Bar Sorptive Extraction (SBSE)

1.5.1 Conventional SBSE

To date, various research has been done using Stir Bar Sorptive Extraction and the Twister ® stir bars produced by Gerstel in Germany. Nearly 200 publications involve some use of the stir bar sorptive extraction method. However, this is not a large amount.

Stir Bar Sorptive Extraction was initially developed by Erik Baltussen and his colleagues in Belgium in 1999. Initially, the method was used as a sample enrichment step to pre-concentrate liquid or gaseous samples. By stirring the coated stir bar in an

aqueous sample, the compounds would adsorb onto or absorb into (the process of both is called 'sorption') the polydimethylsiloxane coating. For example, if one were analyzing a 10 mL sample of water, and was using a 10 mm long stir bar with 25 μL of coating, there would be a preconcentration of approximately 400 times. Therefore, though the analytical instrument such as a gas chromatograph (GC) may have a detector with a moderate detection limit, one could potentially analyze very dilute aqueous samples since this preconcentration step would drastically lower the method detection limit. Application notes on the Gerstel website indicate that sub-ppb or ppt detection limits have been found for the analysis of polycyclic aromatic hydrocarbons, pesticides, drugs, off-odours, flavours and fragrances [Pfannkoch et al, 2003]. Also, SBSE has been used to extract analytes from many different matrices such as wine, urine, sperm, fruit pulp, and blood. The most notable analyses are described below.

1.5.1.1 Thermal Desorption SBSE

Popp et al discussed the analysis of polycyclic aromatic hydrocarbons using GC-MS. Detection limits were found to be between 0.05 and 1.0 ng/L. With High Performance Liquid Chromatography (HPLC), the detection limits were found to be between 0.3 to 2.0 ng/L [Popp et al, 2003].

Compounds such as 2-methylisoborneol (MIB), geosmin, and certain haloanisoles cause drinking water to have a bad taste or odour. Benanou et al analyzed the off-flavours found in the aquatic environment using SBSE-thermal desorption(TD)-capillary GC-mass

spectrometry (MS)-olfactometry. Quantification limits were found to be 0.1-0.2 ng/L for the haloanisoles, 0.5 ng/L for the geosmin, and 1 ng/L for MIB [Benanou et al, 2003].

Pesticides used on fruits and vegetables may increase the output of a farm, but residues ingested by humans may be harmful. Therefore, analysis of pesticides in fruit and vegetables is of increasing importance. Bicchi and his colleagues used SBSE to extract from pear pulp, a heterogenous phase, which was spiked with ppb (ng/g) of chlorpyriphos methyl and ethyl, parathion methyl, and α and β-endosulfan. Juan-Garcia and her colleagues obtained lettuce, tomatoes, grapes, and strawberries and used SBSE with TD and GC-MS to analyze acrinathrin, bitertanol, cyproconazole and several other pesticides. Bicchi found recoveries ranging from 23.9% to 82.6% [Bicchi et al, 2002]. Juan-Garcia found that when compared to solid-phase extraction, SBSE had higher limits of quantification, but proved to be advantageous in that it used no organic solvent and had cleaner extracts [Juan-Garcia et al, 2004].

Standler et al investigated the presence of insect repellent Bayrepel® in pool and lake water using SBSE with TD and GC-MS. The limit of detection for this analysis was 25 ng/L. Again, SBSE was compared to SPE and SBSE was chosen due to the simplicity of the method as well as the low detection limit [Standler et al, 2004].

Wine aromas were analyzed using SBSE by Alves et al. Compounds such as esters, carboxylic acids, alcohols, aldehydes, pyrans, lactones, and monoterpenes were quantified in Madeira wine. From these analyses, one could determine the chemical differences between dry/medium dry and sweet/medium sweet young wines [Alves et al, 2005].

Many analytes are not extractable by SBSE using the commercial stir bars because of the lack of polarity of the solid phase. Therefore, more polar compounds must be derivatized pre-extraction so that they are more easily extracted from aqueous samples. Kawaguchi et al describe the in situ derivatization of bisphenol A in river water and body fluid samples. The compound was treated with acetic acid anhydride and then extracted using SBSE-TD-GC-MS. The detection limits in river water, urine, plasma and saliva samples were found to be 1-5 pg/mL, 20 pg/mL, 100 pg/mL, and 20 pg/mL, respectively [Kawaguchi et al, 2004]. Nakamura et al did the same with bisphenol A as well as some alkylphenols, obtaining detection limits ranging from 0.1 to 3.2 pg/mL [Nakamura et al, 2004]

Hormonal compounds make their way into the aquatic system and result in mutations in frogs and fish. Kawaguchi et al have analyzed phenolic xenoestrogens in water by in situ derivatization and SBSE-TD-GC-MS. They found that the detection limits of 2,4-dichlorophenol, 4-tert-butylphenol, 4-tert-octylphenol, 4-nonylphenol, and pentachlorophenol were 2 pg/mL, 1 pg/mL, 0.5 pg/mL, 5 pg/mL and 2 pg/mL, respectively [Kawaguchi et al, 2004].

A method for rapid diagnosis of pulmonary tuberculosis was developed by Stopforth et al. Tuberculostearic acid (TBSA) was taken from sputum samples with the disease. The mycobacterial lipids were hydrolyzed and then derivatized with ethyl chloroformate so that they would be more easily extractable by the non-polar poly(dimethylsiloxane) solid phase. The limit of detection for the mycobacterial lipids was found to be 0.2 ng/mL [Stopforth et al, 2005].

1.5.1.2 SBSE Using Liquid Desorption

Though there have been many documents describing the use of SBSE with TD and GC-MS, there have been very few detailing the use of SBSE with liquid desorption (LD) and GC-MS or HPLC.

Endocrine disruptors in environmental water samples were analyzed by Brossa et al. [Brossa et al, 2004]. However, instead of thermal desorption, liquid desorption was used by placing the stir bar in a small volume of isooctane after stirring the aqueous sample. After this step, the liquid sample was injected into a GC/MS for analysis. Limits of detection were found to be between 0.005 and 0.02 μg/L for river water samples.

As previously stated, polycyclic aromatic hydrocarbons were analyzed using SBSE-TD-GC-MS. However, Zuin et al used LD as well as HPLC with fluorescence detection. 160 μL of Acetonitrile was used as the organic solvent and the 15 PAHs were obtained from Mate ™ herbal teas. The limits of detection were found to be between 0.1 ng/mL and 8.9 ng/mL [Zuin et al, 2005].

Overall, the low detection limits, high volumes of stable solid phase and ease of use of the stir bar are the main advantages of this method. Also, since one can use the stir bar in different matrices, the method seems to be free from interferences.

1.5.2 The Facts and Principles behind SBSE

As previously stated, the amount of solid phase will determine the amount of analyte that is extractable. Therefore, depending on the size of the stir bar, SBSE will allow for much more solid phase, and thus extractable analyte, than SPME.

Gerstel, a company in Germany, produces coated stir bars commercially. They range from 10 mm to 40 mm in length, and usually have a coating that is 0.5 mm thick. Therefore, the coated stir bar can have anywhere from 25 μL to 300 μL of solid phase. The stir bar consists of a magnetic metal rod, a glass encasement, and a tube of poly(dimethylsiloxane) with 40% (v/v) fumed silica. Figure 1.5 shows a schematic diagram of the Gerstel Twister® Stir bar.

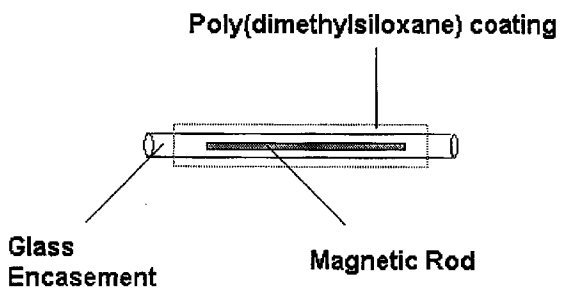


Figure 1.5: Schematic Diagram of Twister® Stir Bar, glass ends are melted closed

The principle behind SBSE is very similar to that of SPE and SPME. As the coated stir bar is stirred in a sample, the analyte will adsorb onto and absorb into the polymer. In other words, it will dissolve into the solid phase. The partition coefficient, $K_{o/w}$, can be equated to the partition coefficient of the concentration of the analyte in the

PDMS solid phase and the concentration of the analyte in the aqueous phase. The two can be equated because PDMS is a very non-polar phase much like octanol, causing analytes to dissolve to a similar degree in both.

After the analyte in the aqueous sample has been sorbed onto the stationary phase of the coated stir bar, one can either perform thermal desorption (TD) or liquid desorption (LD). Thermal desorption involves the heating of the stir bar so that analytes will become gaseous and desorb directly into the gas chromatograph. Liquid desorption involves the use of a small amount of organic solvent into which the analyte can desorb since there will be an increase in entropy when moving from a solid to a liquid (as is the case here with the stationary phase and the organic solvent). Because of the latter method of desorption, one can call SBSE a pre-concentration method since one can begin with a large volume of aqueous sample and finish with a small volume of organic sample [Prochazka, 2004]. In the case of thermal desorption, the preconcentration is even larger, since the analytes are desorbed into the gas phase, and usually concentrated at the head of a GC column without the use of any liquid solvent.

1.5.3 Optimization Factors of the SBSE Method

Using the approximation that the $K_{o/w}$ is proportional to the $K_{PDMS/W}$, the relationship between the mass of analyte in the water and PDMS phases at equilibrium can be derived as follows:

$$K_{O/W} \approx K_{PDMS/W} = \frac{C_{PDMS}}{C_W} = \left(\frac{M_{PDMS}}{M_W}\right) \times \left(\frac{V_W}{V_{PDMS}}\right)$$

And, $$\frac{V_W}{V_{PDMS}} = \beta \qquad [1]$$

Then, $$\frac{K_{O/W}}{\beta} = \frac{M_{PDMS}}{M_W} = \frac{M_{PDMS}}{(M_O - M_{PDMS})}$$

And finally, $$\frac{m_{PDMS}}{m_O} = \frac{\frac{K_{PDMS/W}}{\beta}}{1 + \frac{K_{PDMS/W}}{\beta}} \qquad [2]$$

[Baltussen et al, 1999]

In the above equations, PDMS can represent a general solid-phase, then C_{PDMS} is the concentration of analyte in the solid phase, C_W is the concentration of analyte in water at equilibrium, M_{PDMS} is the mass of analyte in the solid-phase, M_W is the mass of analyte in water at equilibrium, V_W is the volume of aqueous sample, V_{PDMS} is the volume of solid-phase, β is the phase ratio between the volume of aqueous sample and the volume of solidp-phase, and M_o is the original mass of analyte in the aqueous solution.

From equation 2, one can see that the recovery (m_{PDMS}/m_o) is affected by three main factors: the partition coefficient, which is a function of the analyte and the type of solid phase, and the phase ratio which includes both the volume of sample and the volume of solid phase. As the partition coefficient increases, so will the recovery. As the volume of sample increases, the phase ratio will increase and the recovery will decrease. As the volume of solid phase increases, the phase ratio will decrease and the recovery will increase. Other minor factors that will affect the recovery of the analyte are the temperature of the environment in which the stir bar is stirring, the volatility of the analyte and the speed at which the stir bar is stirring (rotations per minute).

By comparing to the amount of solid phase on an SPME fiber (see section 1.4.3), the amount of solid-phase on the stir bar is up to 600 times greater. Even the smaller stir bars which have 25 μL of coating allow SBSE to be an exhaustive method, meaning if enough time is allowed for equilibrium to be reached, one can obtain approximately 100% recovery. Also, Gerstel currently only produces the poly(dimethylsiloxane) coating, which will have its own range of recoveries depending on the partition coefficient. However, the more coatings that are available, the broader the range of extractable analytes. Therefore, it would be beneficial to be able to produce stir bars that have different coatings. One of the main objectives of this work was therefore to produce novel SBSE solid phases. To do this, one can use sol-gel technology.

1.6 Sol-Gel Technology

Sol-Gel technology is mainly used for the production of ceramic and glass products at the nanometer size level. However, sol-gel can also be used for making thin films and dip-coating. Basically, a solution in the liquid form will transform into a gel-like solid form due to polymerization of the chemicals in the solution [Sol-Gel Technology, 2005]. In this research project, sol-gel technology was being used to coat a small glass-encased stir bar with polymeric phases appropriate for extraction of various classes of analytes from water.

The are several papers dealing with the use of sol-gel for items such as non-reflective coatings on rear-view mirrors, solar-reflecting coatings, and many other coatings that are made of SiO_2 and TiO_2 [Dislich, 1988]. The most interesting and closely

related articles are described in the next three paragraphs. However, there are only 2 publications to date dealing with the actual process of coating a stir bar using sol-gel technology and using that coated stir bar for SBSE.

Dongxin Wang et al used sol-gel technology to coat the inner wall of a Gas Chromatography Capillary Column. They found many advantages to using Sol-Gel such as thermal stability, the ability to separate compound of a wide polarity range, and a 10 fold reduction in column preparation time. Primarily, using sol-gel technology to coat a capillary column simultaneously takes care of surface treatment, deactivation, coating, and immobilization [Wang et al, 1997].

Chetan Shende et al also coated the inner wall of a GC capillary column using a sol-gel process, but with poly(ethylene glycol) (PEG) instead of PDMS. This is of interest because commercial Carbowax columns (or PEG columns) are known to have lower thermal stability of about 240-250 °C. Shende found that coating the column using Sol-Gel technology would give a thermal stability of up to 320 °C [Shende et al, 2003].

Fernandes De Oliveira et al developed a method to coat SPME fibers using Sol-Gel technology. In addition to using a fused silica base that is used in commercial SPME fibers, De Oliveira used a thin glass-ceramic rod. They compared coating thickness and absorption capacity and found that one could obtain a thicker coating using the glass-ceramic rod. In fact the thickness of the coating on the glass-ceramic rod was approximately 7 times thicker that the coating on the fused silica fiber. They also found the detections limits for a BTEX (benzene, toluene, ethylbenzene and xylene) mixture to be below 0.8 μg/L. De Oliveira also compared the results obtained to those of a commercially made 100 μm thickness PDMS SPME fiber. They found that when

analyzing toluene and xylene, the fused silica base gave the lowest GC peak area, the glass-ceramic base fiber gave a higher peak area, and the commercially made PDMS SPME fiber gave the highest peak area. This can be attributed to the thickness of coating (fused silica fiber coating thickness = ~6 μm, glass-ceramic rod coating thickness= ~44 μm) [de Oliveira, 2004]. The greater the thickness of coating, the more analyte that can be extracted, resulting in a higher sensitivity for the analyte.

Wenmin Liu et al used Sol-Gel technology to coat a glass-encased stir bar. By using an object that has a greater surface area than an SPME fiber, one will naturally obtain a coating that is more voluminous. If one obtains a greater amount of coating, one can potentially obtain greater peak areas, and consequently, great recoveries. Hydroxyl-terminated PDMS was used in order to make a PDMS sol-gel coating. Aqueous samples were spiked with *n*-alkanes, polycyclic aromatic hydrocarbons, straight-chain hydrocarbons, and organophosphorous pesticides and GC-FID was used for analysis. Detection limits were found to be between 0.18 pg/mL and 20 pg/mL [Liu et al, 2004].

Liu and his colleagues also used the Sol-Gel PDMS coated stir bar for analysis of organophosphorous pesticides in cucumber and potato. Sample extraction efficiencies were tested based on extraction temperature, percent salt added, extraction time. Detections limits of ≤ 0.15 ng/g were obtained showing that more coating does indeed lead to greater recoveries [Liu et al, 2005].

In this research project, Shende's method of coating the inner wall of glass-capillary GC columns with a poly(ethylene glycol) coating was used to coat stir bars. By doing this, more polar analytes could be extracted.

1.6.1 Bonding the Coating to the Glass-Encasement

One can easily form a polymer around a stir bar. However, depending on the polarity of the coating, organic solvents may result in the swelling of the polymer. If the polymer is not bonded to the glass, the stir bar mar slip out of the coating when it swells in organic solvent.

In order for the coating to bond to the glass-encasement of the stir bar, the bar must be placed in a 1 M solution of sodium hydroxide (NaOH). This initial step is considered the pre-conditioning of the stir bar so that $Si\text{-}O_2$ groups are opened up to form $Si\text{-}O^-$, allowing for the attachment of the sol-gel polymer.

1.6.2 Poly(dimethylsiloxane) Coating

The polymer-precursor used in preliminary experiments was a hydroxy-terminated polydimethylsiloxane (ht-PDMS) as seen in Figure 1.6.

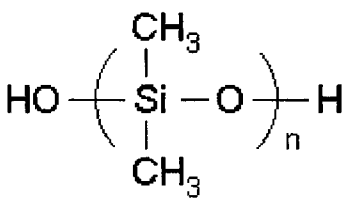


Figure 1.6: Structural Diagram of hydroxy-terminated Poly(dimethylsiloxane)

The ht-PDMS is partially bonded to the surface of the glass, at the silanol groups. The partial bonding is due to the large size of the molecules. A loose network is created

when the ht-PDMS is added, but the addition of a catalyst, Trifluoroacetic Acid, will allow for further polymerization of the ht-PDMS. Poly(methylhydrosiloxane) (PMHS) is added to the solution for deactivation, or end-capping, of extra silanol groups and to terminate the formation of the network of ht-PDMS [Liu et al, 2004]. The stir bar is removed from the sol solution and conditioned in a nitrogen environment at high temperature, promoting further drying and crosslinking. After conditioning, the stir bar can then be used to extract analytes from an aqueous solution. Figure 1.7 shows the schematic diagram of the sol-gel polymer network. Essentially, a polycondensation reaction produces the polymer.

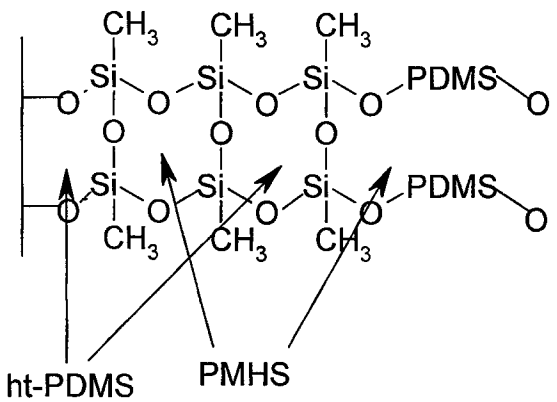


Figure 1.7: Schematic Diagram of ht-PDMS polymer network
[Liu et al, 2004]

A coating made from this precursor is chemically equivalent to commercial GC Column Stationary Phases such as DB-1 (made by J and W Scientific).

1.6.3 Poly(dimethylsiloxane)-co-Diphenylsiloxane(5%) Coating

The scheme explained above will work with many other polymers as long as the monomer is hydroxy-terminated. For example, hydroxy-terminated polydimethylsiloxane-co-diphenylsiloxane (5%) (dt-PDMS-co-DPS) will work in the same manner, giving the structure seen in Figure 1.8.

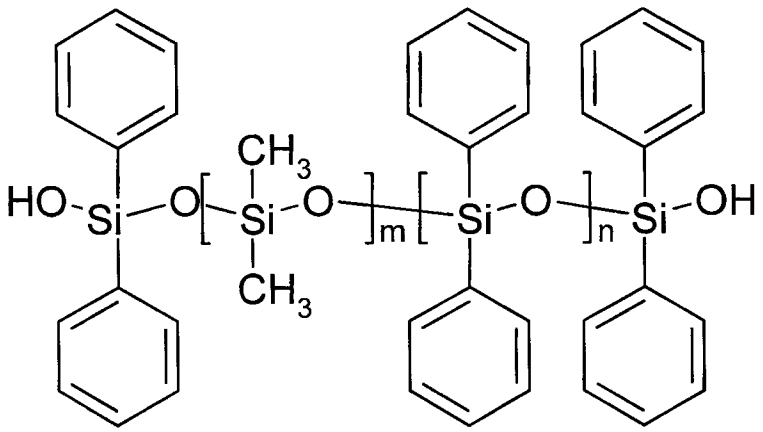


Figure 1.8: Structural Diagram of hydroxy-terminated polydimethylsiloxane-co-diphenylsiloxane (5%)

A coating made from this precursor is chemically equivalent to commercial GC Column Stationary Phases such as DB-5 (made by J and W Scientific).

1.6.4 Poly(ethylene Glycol) Coating

As stated in the previous section, the sol-gel method will work with a precursor that is terminated at each end with a hydroxy group. Therefore, one would assume that one could replace poly(dimethylsiloxane) by poly(ethylene glycol) which is depicted in Figure 1.9.

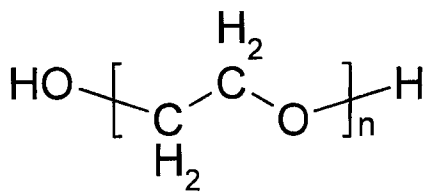


Figure 1.9: Structural Diagram of Poly(ethylene glycol)

However, due to the polar nature of PEG, the coating resulting from this sol-gel polymerization dissolves in water and is consequently, not useful for extractions from aqueous phases.

To remedy this problem, other precursors are used in order to obtain the same (or a very similar) end result. In the following explanation, three precursors are used to make the PEG coating. Two of the three precursors are derivatives of PEG, and the third helps to cross-link the polymer. Figure 1.10 shows diagrams of the three precursors of PEG Sol-Gel Synthesis.

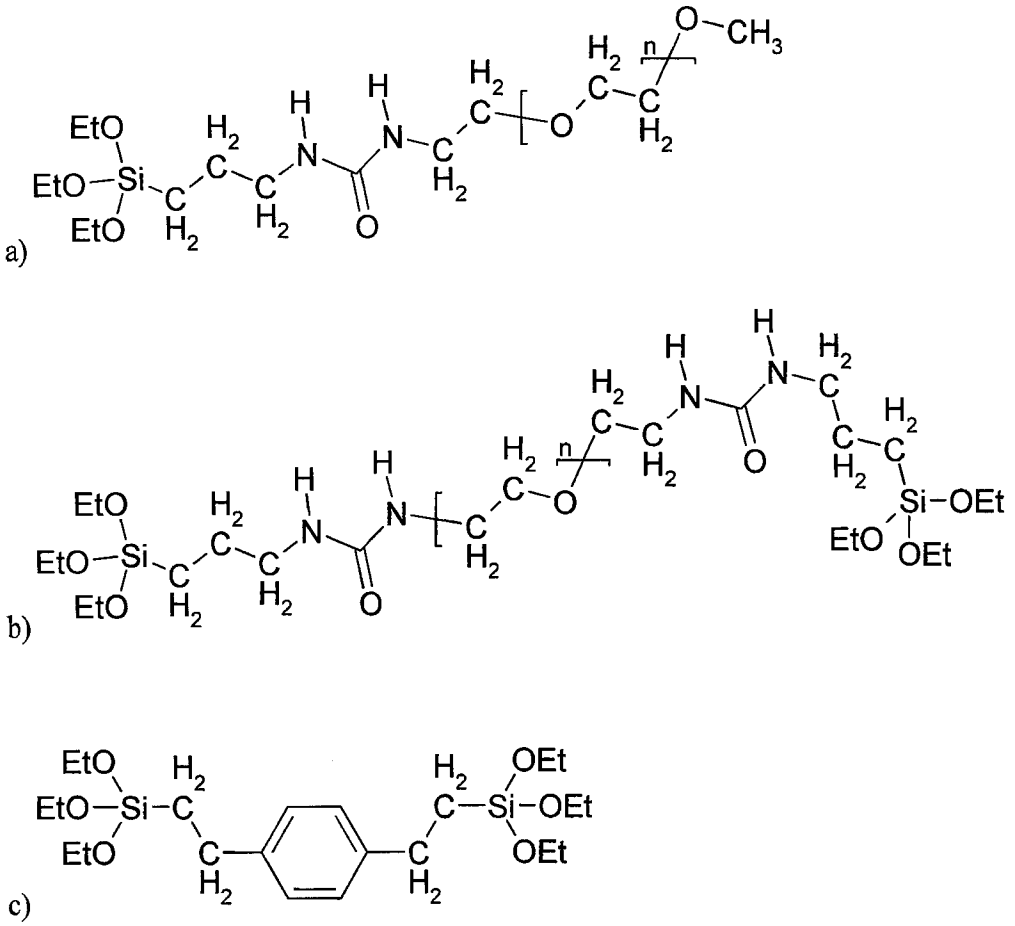


Figure 1.10: Structural Diagrams of three PEG Sol-Gel Ingredients: a) PEG1 Derivative with one 'bondable' silane end; b) PEG2 Derivative with two 'bondable' silane ends; c) bis(Trimethoxysilylethyl)benzene (bis-TMSEB)

When the two PEG derivatives, called PEG1 and PEG2, are interwoven by a polycondensation reaction with the bis-TMSEB, one obtains a flexible coating that is thermally stable. This is due to the presence of the phenyl ring in the backbone of the network. There is steric hindrance that serves to halt unwanted rearrangement reactions that could lead to stationary phase degredation [Shende at al, 2003]. For example, if

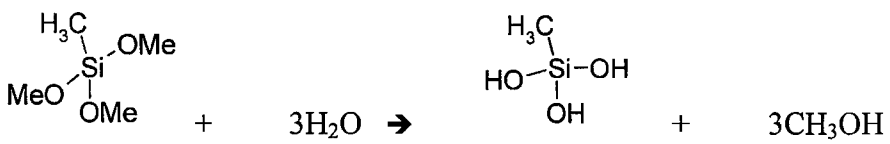
rearrangement reactions occur in an aqueous phase, water molecules could find vacant areas and work to dissolve the coating.

As with the PDMS and PDMS-co-DPS(5%) coatings, TFA (containing 5% water) is used as the catalyst. However, with the PEG method, Ammonium Fluoride is used as a secondary catalyst.

Figures 1.11 and 1.12 show the schematic formation of the PEG Sol-Gel polymer.

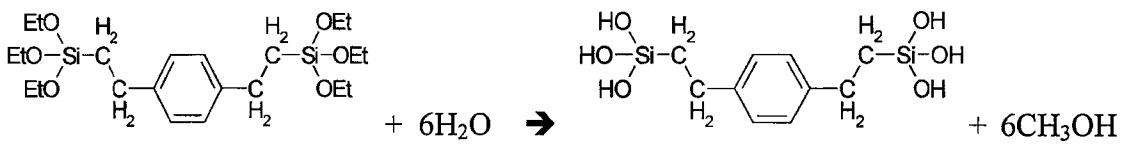
STEP 1:

a)



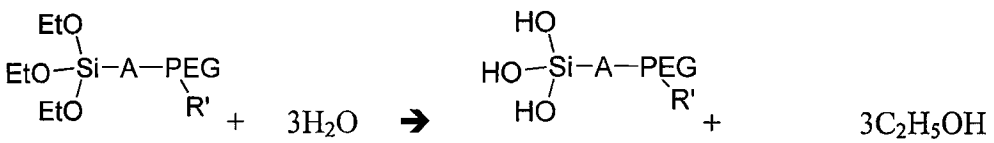
(with presence of a catalyst)

b)



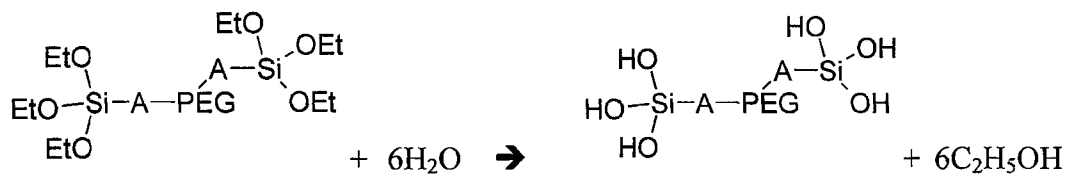
(with presence of a catalyst)

c)



(Where A is the NH-CO-NH grouping, and R' is the inactive end group, and PEG is the CH_2CH_2O repeating structure) (with presence of a catalyst)

d)

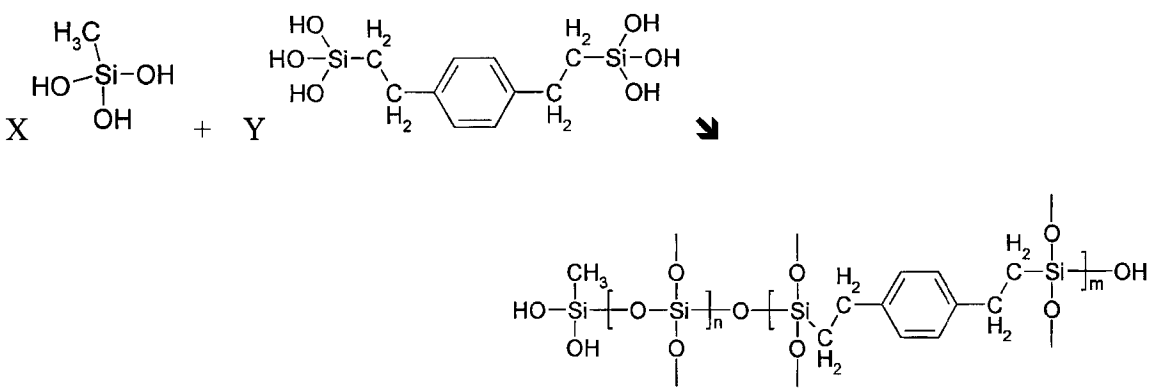


(with presence of a catalyst)

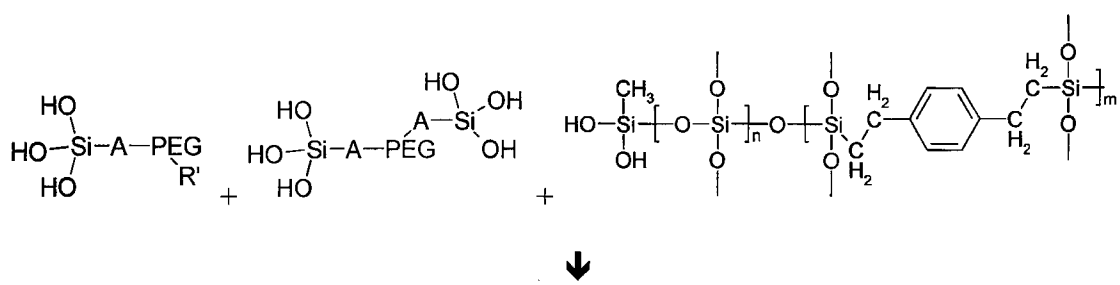
Figure 1.11: Step1: Hydrolysis of a) methyltrimethoxysilane; b) bis(trimethoxysilylethyl)benzene; c) PEG1 derivative; and d) PEG2 derivative

STEP 2:

a)



b)



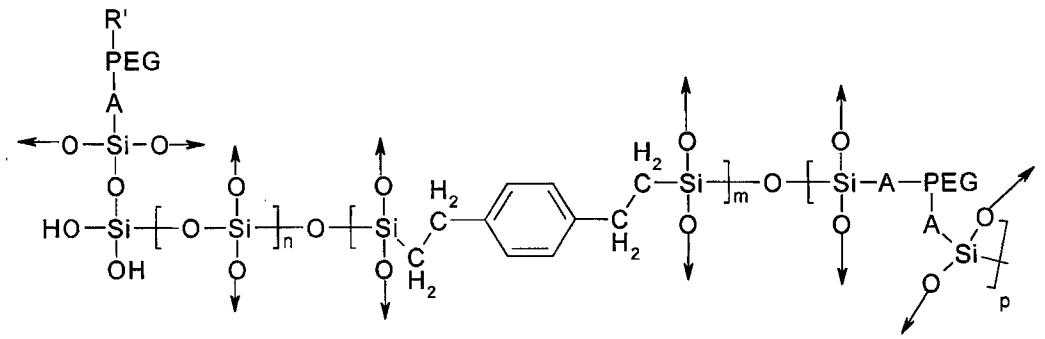


Figure 1.12: Step 2: a) and b) Formation of Sol-Gel PEG polymer by polycondensation [Shende et al, 2003]

A coating made from these precursors is very similar to a DBWax commercial GC Column.

One can see that this PEG polymer, containing hydroxy, amino, and carbonyl groups will be more polar than the other coatings mentioned. This will allow it to be better at extracting polar analytes since *like dissolves like.*

1.7 Derivatization of Polar Analytes

Derivatization of an analyte is sometimes required in order to reduce polarity, which alleviates problems of poor peak shape and poor sensitivity in GC analysis. Derivatization may also result in lower solubility of the analyte in water and higher solubility in organic phases, which leads to higher recoveries and hence lower detection limits. In this research project, PCP will be extracted by three different coatings.

Figure 1.13 shows a diagram of Pentachlorophenol and how it becomes hydrolyzed in water:

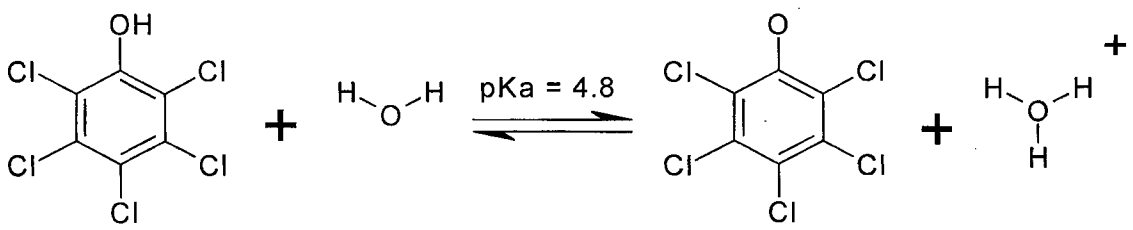


Figure 1.13: Pentachlorophenol in Water at equilibrium producing the deprotonated form of PCP and the hydronium ion

Since PCP loses a proton, this can make it very difficult to extract from water. Lowering the pH keeps the molecule in the protonated form, and makes it possible to extract it into an organic phase, but the analyte is still quite polar and analysis by GC is problematic. Therefore, if one can add a functional group to PCP so that it remains neutral in water, it will be extractable to a greater extent. Normally, one would derivatize the PCP before extraction, but in this research study, the extraction of PCP in its native form will be tested by different coatings; one polar and two non-polar. Then it will be derivatized post-extraction in order to prevent peak tailing in the GC column.

After extraction by the stir bar, the analyte will be in an organic solvent. In the case of PCP, acetone will be used. To derivatize PCP, one must first create a basic environment. One can achieve this by adding enough of a 5% $K_2CO_{3(aq)}$ solution to make the solution basic. By making the solution basic, the hydroxyl group of the PCP will be deprotonated, resulting in a negatively charged PCP molecule. After the PCP has been deprotonated, one can add Acetic Anhydride in excess. This will allow for the acetylation of PCP as seen in Figure 1.14:

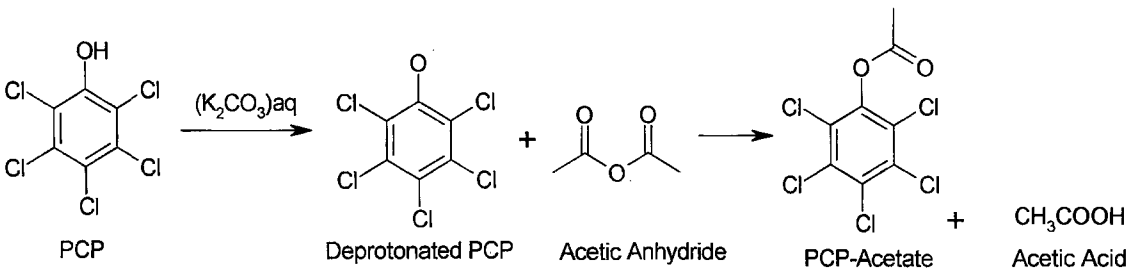


Figure 1.14: Derivatization Scheme of Pentachlorophenol

1.8 Partition Coefficients

As previously mentioned, the partition coefficient ($K_{o/w}$) is a ratio of the solubility of a compound in an organic phase to that of it in an aqueous phase. The higher the partition coefficient, the more soluble the compound is in the organic phase and the less polar it is. The lower the partition coefficient, the more soluble the compound is in the aqueous phase and the more polar it is [Prochazka, 2004]. One can use the following equation to calculate the partition coefficient:

$$K_{COATING\,/\,WATER} = \frac{\left(\frac{M_{analyte_{coating}}}{V_{coating}}\right)}{([Analyte]_{H_2O,\,equilibrium})} \qquad [3]$$

Where $K_{COATING/WATER}$ is the partition coeffient of a specific analyte in a specific coating, $M_{ANALYTEcoating}$ is the mass of the analyte in the coating, $V_{coating}$ is the volume of solid-phase, and $[ANALYTE]_{H2O}$ is the concentration of analyte in water at equilibrium.

One would therefore think that a polar compound automatically has a lower partition coefficient. However, this is not always the case. PCP has $K_{o/w} = 10^{5.12}$, and it is a polar compound [EPA, 2006]. Naphthalene has $K_{o/w} = 10^{3.01}$ and PCB77 has $K_{o/w}$ $10^{6.21}$

and these are both non-polar compounds [EPA, 2006]. Therefore, it is possible for a compound to be polar and have relatively low solubility in water. The idea of 'polarity' is a bit misleading. Yes, PCP has a hydroxy group, making one side of it more electronegative than the other. However, for the most part, the molecule is non-polar, giving it a rather low solubility in water and a high partition coefficient.

The Gas Chromatograph detectors being used are an Ion-trap Mass Spectrometor, Flame Ionisation Detector, and Electron Capture Detector. The instrumental detection limits for these detectors are approximately 1 ng/μL, 1 ng/μL and 1 pg/μL, respectively. Therefore, per injection, one would need approximately 1 ng of analyte present in the solution to be injected. For GC-FID, one can back-calculate the amount of analyte needed in solution in order to be able to detect with a certain confidence. By using the equation in section 1.5.2, if one has a 2 mL sample of Naphthalene ($K_{o/w} = 10^{3.01}$) in water, being concentrated into 2 mL of organic solvent, and 10 uL of coating, one would need to begin with a solution of 1.2 ppm (or 1.2 μg/mL). The following shows the calculation:

$$\text{From: } \frac{m_{PDMS}}{m_O} = \frac{\frac{K_{PDMS/W}}{\beta}}{1+\frac{K_{PDMS/W}}{\beta}} \quad \text{and} \quad \frac{V_W}{V_{PDMS}} = \beta$$

$$\text{Where: } \beta = \frac{V_W}{V_{PDMS}} = \frac{2000\mu L}{10\mu L} = 200 \quad \text{and} \quad K_{PDMS/WATER} = 10^{3.01} \quad \text{and}$$

$$m_{PDMS} = 1\mu g$$

$$\text{Therefore: } \frac{1\mu g}{m_O} = \frac{\frac{K_{PDMS/W}}{\beta}}{1+\frac{K_{PDMS/W}}{\beta}} = \frac{\frac{10^{3.01}}{200}}{(1+\frac{10^{3.01}}{200})} = 1.2\mu g/mL$$

If PCP were the analyte, one would need to begin with a concentration of 1 ppm using the same calculation. However, the partition coefficient stated for PCP is for the neutral form. The $K_{o/w}$ of the negatively charged PCP (which is 50% present at pH equal to the pKa at 4.8) would be much lower, resulting in a decreased percent recovery. If the $K_{o/w}$ of negatively charged PCP were as low as $10^{1.5}$ one would need to begin with a concentration of approximately 7.3 μg/mL.

The equation used for the calculations in the previous paragraph is from prior analysis using the Gerstel Twister ® Stir Bars which have a non-polar coating of PDMS [Baltussen et al, 1999]. This means that one can equate (at least quanlitatively) the literature partition coefficient (or $K_{O/W}$) to the method partition coefficient (ie: $K_{PDMS/W}$) since both octanol and PDMS are relatively non-polar compounds when compared to water. Therefore, if one were to use a coating that is polar for the extraction of PCP, the partition coefficient (ie: $K_{PEG/W}$) would be drastically different. In fact, one may be able to begin with a concentration that is much lower than 7.3 μg/mL, in the case of PCP.

1.9 Competition of Analytes

The extraction efficiency of a coated stir bar can be estimated according to equation 2 in section 1.5.2. However, this is only a valid estimate of what the extraction would be with only one analyte in solution. The presence of other analytes will result in competition for vacant sites within the solid phase. Competition would interfere with the extraction of the analyte of interest, most likely decreasing the partition coefficient since the recovery would be lower.

A method that is trustworthy will be able to efficiently extract the analyte of interest whether there are other analytes present or not. Therefore, competitive experimental partition coefficients must be calculated and compared to non-competitive partition coefficients in order to see whether interference occurs.

1.10 Interference Effects of Fulvic and Humic Acids in Rideau River Water

As stated in the previous section, other analytes can interfere with the extraction of the analyte of interest. If one were to extract an analyte from River Water, one would also come across interference effects. However, these effects are from the organic acids which naturally occur in unpurified waters.

Fulvic and Humic acids are present in water obtained from the Rideau River. Figures 1.15 and 1.16 show partitial structures of Humic and Fulvic acid.

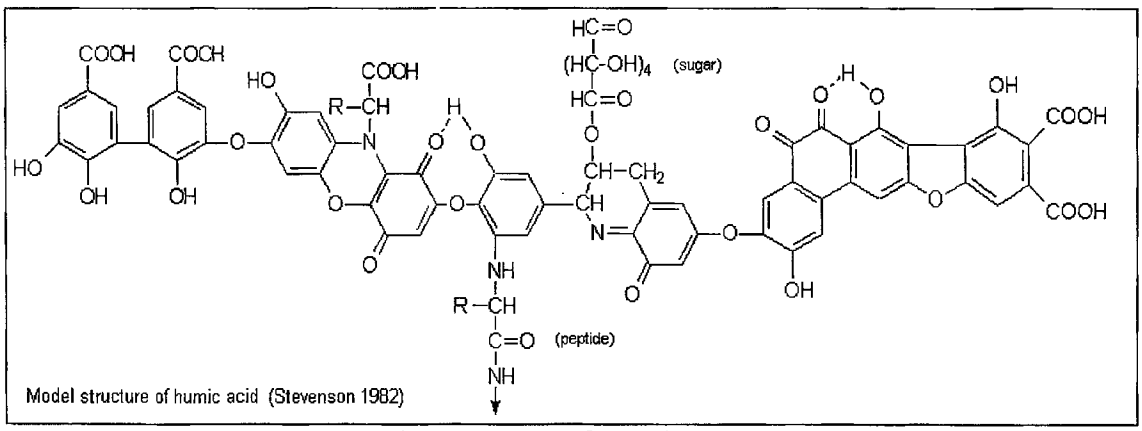


Figure 1.15: Partial Structure of Humic Acid [AUoW, 2006]

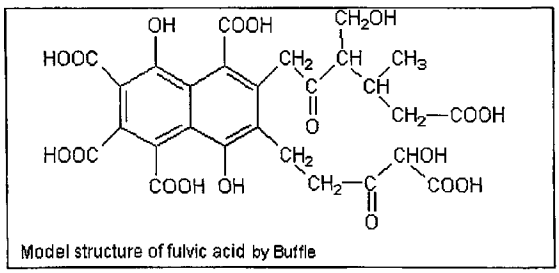


Figure 1.16: Partial Structure of Fulvic Acid [AUoW, 2006]

Humic Acids are are soluble at pH values higher than 2. They produce the black/brown colour in river water. Fulvic Acids are a portion of Humic Acids that are always soluble in water, no matter the pH. They produce the yellowish-brown colour in river water. [AUoW, 2006].

In both acids, there are phenyl groups along with many carboxylic acid and amino functional groups. Due to the aromatic nature of the aforementioned analytes, it is possible that they could adsorb onto these acids, resulting in a loss of analyte and lowered partition coefficient. The polarity of the acids could result in specific interference with the Poly(ethylene glycol) solid phase, since there are also polar groups present. However, in order to see these effects, one must once again calculate the experimental partition coefficients of the analyte in Rideau River water and compare them to the non-competitive partition coefficients.

1.11 Statement of Objectives

The objectives of this research project are as follows: to develop new solid-phases for SBSE (especially increasingly polar phases), to prove that they have a greater affinity for polar analytes, to test for durability, and to compare to already available technology.

2. EXPERIMENTAL

2.1 Coatings

2.1.1 Materials

Poly(dimethylsiloxane)-hydroxy terminated (ht-PDMS), Poly(dimethylsiloxane)-co-diphenylsiloxane(5%)-dihydroxy terminated (dt-PDMS-co-DPS(5%)), Dichloromethane (DCM), Methyltrimethoxysilane (MTMOS), Trifluoroacetic Acid (TFA), Poly(methylhydrosiloxane) (PMHS), 1,1,1,3,3,3-hexamethyldisilazane (HMDS), and Ammonium Fluoride (NH_4F) were purchased from Aldrich. PEG1 and PEG2 were obtained from Nektar Therapeutics (Huntsville, AL). Bis(trimethoxysilylethyl)benzene (bisTMSEB) was purchased from Gelest Inc. (Tullytown, PA). Porous Teflon tubing was obtained from International Polymer Engineering (Tempe, AZ).

Naphthalene (99%) was purchased from BDH Chemicals Ltd (Poole, England), 2,2'3,3'-Tetrachlorobiphenyl was purchased from Accustandard (New Haven, Connecticut), and Pentachlorophenol (99 +%) was purchased from Aldrich.

Solutions of 1mol/L $NaOH_{(aq)}$ and 0.1 mol/L $HCl_{(aq)}$ were produced by dissolving approximately 10g of solid NaOH in 250mL of distilled water, and diluting 2mL of 12.0 Molar HCl to 250 mL in two 250 mL volumetric flasks, respectively.

Small glass-encased stir bars were produced by breaking off the thin tube-end of a Pasteur Pipette. One end was melted shut with a Bunsen burner. A small piece of iron

was placed in the tube, and the other end was melted shut. The stir bars had an average length of approximately 1 centimetre.

A Conditioning Tube was made by taking a stainless steel tube, cleaning it out with water, and attaching a long piece of 1/8" O.D. copper tubing to one end. This copper tubing was attached to a regulator attached to a tank containing Ultrapure Nitrogen Gas. The other end of the conditioning tube was covered, but had a small hole through which gas could escape. A small piece of glass wool was pushed into the tube, and after the stir bars were placed in the tube for conditioning, another piece of glass wool would be added so that the conditioning liners would not move around freely within the conditioning tube.

Conditioning liners were produced by breaking off the ends of several Pasteur Pipette tubes. These liners were then used to guard the conditioning stir bars from the inner wall of the conditioning tube. Figure 2.1 shows a schematic diagram of the conditioning tube and liners.

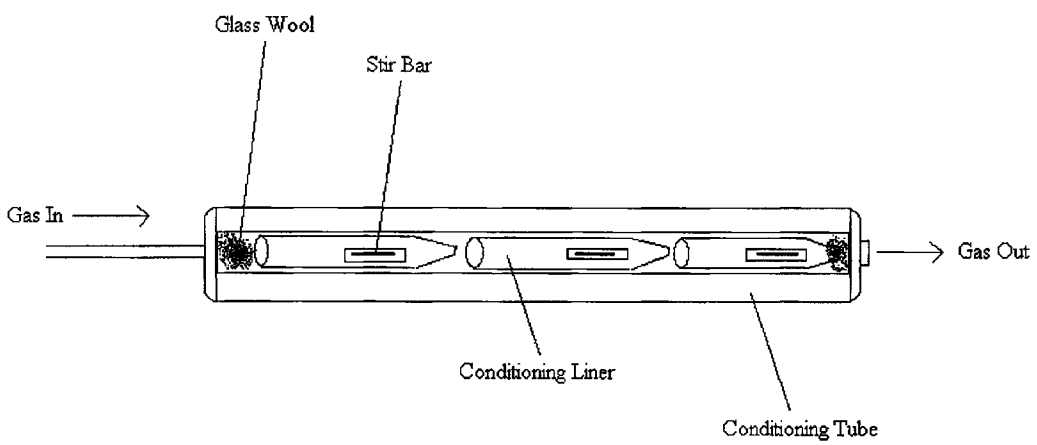


Figure 2.1: Schematic Diagram of Conditioning System

2.1.2 Sol-Gel Method

2.1.2.1 Pretreatment of Glass-encased Stir Bars

The glass-encased stir bars to be coated with Poly(dimethylsiloxane) and Poly(dimethylsiloxane)-co-Diphenylsiloxane(5%) were placed in approximately 5 mL of 1 mol/L $NaOH_{(aq)}$ for 5 hours. After this time, they were placed in approximately 5 mL of 0.1 mol/L HCl for 1 minute. This latter step was repeated several times until the supernatant solution was pH neutral. The stir bars were then dried under a stream of nitrogen and sealed in a nitrogen-filled glass vial.

The glass-encased stir bars to be coated with Poly(ethylene glycol) were pre-treated by washing with DCM and then drying under a stream of nitrogen gas.

2.1.2.2 Coating Stir bars with Poly(dimethylsiloxane) and Poly(dimethylsiloxane)-co-Diphenylsiloxane(5%)

The sol-solution was prepared by following the method described by Liu et al [Liu et al, 2004]. However, since the stir bars were small, some of the quantities were changed so as to not waste chemicals.

100 mg of the ht-PDMS was dissolved in 150 μL of DCM, in a 1.5 mL microcentrifuge vial. The vial was closed and mixed using a vortex for approximately 5 minutes. 25 μL of MTMOS and 25 mg of PMHS were added and again, the mixture was vortexed for 5 minutes. 25 μL of TFA (containing 5% water) was added to the vial and the mixture was vortexed for another 5 minutes to obtain a homogeneous mixture.

The sol-solution was poured into a larger vial and pre-weighed glass encased stir bars were placed in the solution. The solution was allowed to gel (a duration of approximately 30 minutes) and the stir bars were then removed, using a razor to trim the coating into an aesthetically pleasing shape.

The stir bars were placed in the pre-made conditioning liners and then placed into the conditioning tube. Ultrapure Nitrogen gas was allowed to slowly flow through the conditioning tube to prevent any oxidation. The tube was then placed in the oven of a Gas Chromatograph (GC).

The following GC temperature program (derived from the program used by Liu et al [Liu et al, 2004]) was used to condition the stir bars:

Initial Column Temperature:	40 °C
Temperature Ramp:	10 °C/min
Holding Temperature:	120 °C for 30 minutes
Temperature Ramp:	10 °C/min
Holding Temperature:	240 °C for 30 minutes
Temperature Ramp:	10 °C/min
Final Holding Temperature:	300 °C for 60 minutes

The stir bars were weighed and the amount of coating was calculated in grams. The volume of coating was determined by calculating the density of the solid-phase.

The coated stir bars were stirred in distilled water for 10 minute increments. After one 10 minute increment, the stir bar was removed, dried under nitrogen, and then weighed in order to determine the volume of coating, since some may have detached

during stirring. This process was repeated five more times, and then six more times in DCM. A graph of Volume of Coating versus Time Stirred in Water and Dichloromethane was plotted for the PDMS-coated HPBars.

The same procedure was used to coat stir bars with Poly(dimethylsiloxane)-co-diphenylsiloxane (5%), but 150 mg of the dihydroxy terminated-PDMS-co-DPS(5%) was used instead of 100 mg of ht-PDMS.

2.1.2.3 Coating Stir Bars with Poly(ethylene glycol)

The sol-solution was prepared by following the method described by Shende et al [Shende et al, 2003]. However, due to this being the coating of stir bars and not glass capillaries for GC, some steps were removed from the procedure.

35 mg of PEG1 and 15 mg of PEG2 were weighed and transferred to a 1.5 mL microcentrifuge vial. 600 μL of DCM was added and the mixture was vortexed for 5 minutes in order to dissolve all of the solid. 5 μL of MTMOS, 10 μL of bis-TMSEB, and 5 μL of HMDS were added to the vial and the mixture was vortexed again for 5 minutes. 50 μL of TFA (containing 5% water) was added to the solution and the mixture was vortexed again for 5 minutes. The solution was then allowed to sit for 10 minutes.

After the 10 minute waiting period, 20 μL of the NH_4F solution was added to the mixture. The solution was made up to 1000 μL with DCM and vortexed for another 5 minutes.

The microcentrifuge vial containing the solution was centrifuged for 5 minutes at approximately 4500 rpm. The supernatant was poured into a vial and pre-weighed, pre-

treated glass-encased stir bars were placed in the solution. The solution was allowed to gel overnight and the stir bars were then removed and trimmed with a razor. These PEG-coated HPBars were not conditioned due to the tendency of the solid-phase to crack during conditioning. The stir bars were weighed and the amount of coating was calculated in grams. The volume of coating was determined by calculating the density.

The coated stir bars were stirred in distilled water for 10 minute increments. After one 10 minute increment, the stir bar was removed, dried under nitrogen, and then weighed in order to determine the volume of coating, since some may have detached during stirring. This process was repeated five more times, and then six more times in Hexane.

Infrared Spectroscopy (IR) and Nuclear Magnetic Resonance (NMR) were used to characterize the coatings. For IR, a KBr pellet was produced for each coating. The spectra are located in the Appendix as Figure A.1. For NMR, All data was collected on a Bruker ASX 200 NMR spectrometer operating at 50.3 MHz for 13C.The samples were packed in 7 mm rotors using powdered alumina for balance. The rotors were spun at 4000 Hz. For all of the spectra a 4.5 microsecond 13C 90 degree pulse was used. The acquisition time was 108 milliseconds. NMR spectra are located in the Appendix as Figures A.2, A.3, and A.4.

2.1.2.4 Increasing the Volume of Coating on the Stir Bars

Small pieces of porous Teflon (Polytetrafluoroethylene (PTFE)) tubing were cut and placed around uncoated, glass-encased stir bars. These stir bars with PTFE tubing

were weighed and coated in the same fashion as the regular glass-encased stir bars. However, the stir bars covered with the PTFE tubing were not conditioned in $NaOH_{(aq)}$ and $HCl_{(aq)}$ prior to being coated since the coating would be mechanically bonded to the stir bar.

2.2 Extraction of Naphthalene using PDMS-, PDMS-co-DPS(5%)-, and PEG-coated HPBars

2.2.1 Calibration Procedures for Naphthalene using GC-Mass Spectrometry (MS) and GC-Flame Ionisation Detection (FID)

Naphthalene standards of 0.0, 0.5, 1.0, 1.5, 2.0, and 5.0 ppm were prepared and used to calibrate a Varian Saturn II GC-MS and a graph of Peak Area versus Concentration was plotted. The following temperature program was used:

Initial Temperature:	80°C, hold for 2 minutes
Temperature Ramp:	10°C/min
Final Temperature:	250°C, hold for 1 minute
Column:	DB5, 30 m x 0.25 mm ID x 0.25 μm film thickness
Carrier Gas:	Helium, 2.0 mL/min
Injection Volume:	1 μL
Mass Spectrometer:	SIM from 125-130 m/z

Standards of 0.0, 1.0, 5.0, and 10.0 ppm standards were used to calibrate a Varian 3300 GC-FID and a calibration curve of Peak Area versus Concentration was plotted. The GC temperature program used was the following:

Initial Temperature:	60°C, hold for 5 minutes
Temperature Ramp:	10°C/min
Final Temperature:	300°C, hold for 1 minute
Column:	DB5, 30 m x 0.25 mm ID x 0.25 μm film thickness
Carrier Gas:	Helium, 4.62 mL/min
Makeup Gas:	Nitrogen, 29 mL/min
FID Detector:	Compressed Air, 307 mL/min
	Hydrogen, 35 mL/min
Injection Volume:	1μL

See Figures A.5 and A.6 in the Appendix for the Naphthalene calibration curves.

2.2.2 Optimization of the Extraction Procedure -- Sorption and Desorption Times and Other Variables

A 25 ppm aqueous solution of Naphthalene was prepared and diluted with distilled water to 5 ppm in a 200 mL volumetric flask.

Prior to each extraction, the coated stir bar was weighed and the volume of the coating was determined. 2 mL of the 5 ppm aqueous Naphthalene solution was transferred to a 10 mL beaker. A PDMS-coated HPBar was added to the solution and the beaker was placed on a magnetic stirrer. The sorption times tested were 1, 10, 15, 30, 45, 60, 90, and 120 minutes. After the sorption time, the stir bar was removed from the solution, gently dried using a Kimwipe, and then placed in 2 mL of DCM in another 10 mL beaker. The solvent was stirred for 30 minutes (while changing the sorption time, the desorption time was kept constant at 30 minutes). Then the solvent containing the

extracted analyte was transferred to an autosampler vial and three 1μL aliquots were injected into a GC with Mass Spectrometry (MS).

After the optimal sorption time was determined, it was kept constant while the desorption time was changed. The desorption times tested were 1, 10, 15, 30, 45, 60, 90, and 120 minutes. The samples were analyzed using GC-MS.

The same two tests were performed on the PDMS-co-DPS(5%)-coated HPBars and similar optimal sorption and desorption times were determined. The optimal sorption and desorption times for the PDMS and PDMS-co-DPS(5%)-coated HPBars were 30 minutes and 15 minutes, respectively. Cleaning of the stir bars between extractions was done by placing the used stir bar in a small amount of DCM for 30 minutes. The cleaning solution was extracted to see if there was any analyte present.

Other variables such as stirring speed and sample volume were kept constant in order to obtain consistent extractions. However, changing these variables could affect the recovery of the analyte.

To determine the durability of the coating on the HPBar, the stir bar was used to perform 10 extractions of 2mL of the 5 ppm aqueous Naphthalene solution.

2.2.3 Partition Coefficients of Naphthalene

After each extraction, the exhausted water sample was transferred to a vial. The remaining naphthalene in the water was extracted by liquid-liquid extraction, using DCM as the solvent. The amount of naphthalene in the post-extraction water sample was

determined by GC-MS and this concentration was used to determine the partition coefficients of naphthalene in the PDMS coating.

The same procedure was used for the PDMS-co-DPS(5%)-coated HPBar and the PEG-coated HPBar, but GC-FID was used. Also, instead of DCM, hexane was used as the organic solvent for the PEG-coated HPBars due to dissolution of the coating in DCM.

2.3 Extraction of 3,3',4,4'-Tetrachlorobiphenyl (PCB77) using PDMS-, PDMS-co-DPS(5%)-, and PEG-coated HPBars

2.3.1 Calibration Procedure for 3,3',4,4'-Tetrachlorobiphenyl (PCB77) using GC-Electron Capture Detector (ECD)

PCB77 Standards of 50, 100, 200 and 500 ppb were prepared and used to calibrate a Varian 3600 GC-ECD and a calibration curve of peak area versus concentration was plotted. The GC temperature program used was as follows:

Initial Temperature:	70°C, hold for 0 minutes
Temperature Ramp:	15°C/min
Final Temperature:	280°C, hold for 2 minutes
Column:	DB5, 30 m x 0.25 mm ID x 0.25 μm film thickness
Carrier Gas:	Helium, 5 mL/min
Makeup Gas:	Nitrogen, 30 mL/min

See Figure A.7 in the Appendix for the PCB77 calibration curve.

2.3.2 Extraction Procedure for PCB77

An aqueous PCB77 solution of 174 ppb was prepared by taking approximately 10.9 μL of the 1600 ppm standard, transferring to a 100 mL volumetric flask and diluting to the mark with distilled water.

4 mL of the aqueous solution was extracted with 1 mL of hexane, a total of three times to make a final extract of approximately 3 mL of hexane. The extract was analyzed in triplicate using the GC-ECD.

2 mL of the 174 ppb PCB77 aqueous solution was transferred to a 10 mL beaker. The weight of the PDMS-coated HPBar was recorded and the stir bar was then dropped into the beaker and the solution was stirred for 30 minutes. After this time, the stir bar was removed from the solution, dried using a Kimwipe, and placed in another 10 mL beaker containing 1 mL of Hexane. The solution was stirred for 15 minutes after which the extract was evaporated transferred to an autosampler vial. Three 1 μL portions of the sample were injected into the GC-ECD for analysis.

The same procedure was followed using the PDMS-co-DPS(5%)-coated HPBar and the PEG-coated HPBar.

The peak areas obtained for the extracts were compared to the standard calibration curve and percent recoveries were calculated as well as the partition coefficients for PCB77 in each of the solid phases.

2.4 Extraction of Pentachlorophenol (PCP) using PDMS-, PDMS-co-DPS(5%)-, and PEG-coated HPBars

2.4.1 Calibration Procedure for PCP using GC-ECD

PCP Standards of 0, 5.0, 10.0, 50.0, 100.0, 200.0, and 500.0 ppb were prepared and used to calibrate the Varian 3600 GC-ECD. A standard calibration curve of peak area versus concentration was produced. The temperature program used was as follows:

Initial Temperature:	80°C, hold for 2 minutes
Temperature Ramp:	10°C/min
Final Temperature:	300°C, hold for 2 minutes
Column:	DB5, m x 0.25 mm ID x 0.25 μm film thickness
Carrier Gas:	Helium, 5 mL/min
Makeup Gas:	Nitrogen, 30 mL/min

See Figure A.8 in the Appendix for the PCP calibration curve.

2.4.2 Extraction Procedure for PCP

A 1 ppm aqueous solution of PCP was prepared by taking approximately 47.6 μL of the 2100 ppm PCP standard, transferring to a 100 mL volumetric flask and diluting to the mark with distilled water.

0.5 mL of the 1 ppm aqueous PCP solution was transferred to a 10 mL beaker. The PDMS-coated HPBar was weighed and then dropped into the solution. The solution was stirred for 30 minutes, after which the stir bar was removed from the beaker, gently

dried using a Kimwipe, and then transferred to another beaker containing 1 mL of acetone. The remaining aqueous solution was transferred to a 1-1/2 Dram Screw Cap Vial. The acetone was stirred for 15 minutes, after which the stir bar was removed and the extract was transferred to another 1-1/2 Dram screw cap vial.

2.4.3 Post-Extraction Derivatization Procedure

Approximately 2 mL of 5% $K_2CO_{3(aq)}$ was added to each of the vials and the vials were shaken for approximately 1 minute. 0.5 mL of Acetic Anhydride was added to each vial and the solutions were mixed, pausing every ten seconds to vent any gas that had been produced. This continued until the solutions became clear. 1 mL of hexane was added to the vials and the analyte was extracted through liquid-liquid extraction. The extract was then transferred to an autosampler vial. The extract was then evaporated to dryness with Nitrogen gas, and then made up to 1 mL with hexane. Each sample was analyzed in triplicate using the GC-ECD.

The same procedure was followed using the PDMS-co-DPS(5%)-coated HPBar and the PEG-coated HPBar.

The peak areas obtained for the extracts were compared to the standard calibration curve and percent recoveries were calculated as well as the partition coefficients for PCP in each of the solid phases.

A straight derivatization and liquid extraction of 0.5 mL of the nominally 1 ppm aqueous solution was performed and analyzed using GC-ECD to obtain the actual concentration.

A 100 ppb aqueous PCP solution was made by transferring 4.7 μL of the 2100 ppm PCP standard to a 100 mL volumetric flask and diluting to the mark with distilled water. 1 mL of the 100 ppb aqueous solution was transferred to another 100 mL volumetric flask and diluted to the mark to make a 1 ppb aqueous PCP solution. Both of these solutions were extracted and analyzed using the HPBars. For the 100 ppb PCP solution, 0.5 mL was sampled and the final volume was made to 1 mL with hexane. For the 1 ppb PCP solution, 1 mL was sampled and the final volume was made to 0.5 mL with hexane.

2.5 Simultaneous Extraction of Naphthalene, PCB77 and PCP using PDMS-, PDMS-co-DPS(5%)-, and PEG-coated HPBars

An aqueous solution containing Naphthalene, PCB77 and PCP was prepared by taking approximately 350 μL of a standard containing approximately 200 ppm of Naphthalene, 50 ppm of PCB77, and 50 ppm of PCP.

2 mL of the tri-analyte aqueous solution was transferred to a 10 mL beaker with an automatic pipette. Sorption and desorption took place for 30 minutes and 15 minutes, respectively. The same post-extraction procedure used for the extraction of PCP in section 2.4.3 was used for this experiment. However, instead of evaporating to dryness under N_2, the extract was evaporated down to approximately 0.1 mL, and then refilled to 1 mL. The reason for this is that there was a loss of naphthalene when evaporating to dryness. Therefore, as long as a small portion of solvent was left remaining, there was no loss of naphthalene. This was repeated once more, resulting in a final hexane volume of 1

mL. The reason for the repeat was to ensure that all the acetic anhydride had been evaporated so as to not derivatize the coating in the GC column.

The extract was divided into two portions of approximately 0.5 mL in two autosampler vials and analyzed by GC-FID for Naphthalene and GC-ECD for PCB77 and PCP. The procedure was repeated for each type of coated HPBar.

A 2 mL portion of the aqueous solution was put through the same procedure as above, but the analytes were not extracted by HPBar. This extract was also analyzed for Naphthalene by GC-FID and PCB77 and PCP by GC-ECD. Peak areas were compared to those obtained from the calibration curves and concentrations of the extracts were calculated.

2.6 Extraction from Rideau River Water spiked with PCB77

Water obtained from the Rideau River near Carleton University was filtered through filter paper to remove any large, solid particles. A 174 ppb solution of PCB77 was prepared by transferring approximately 25 μL of a 700 ppm PCB77 standard to a 100 mL volumetric flask and diluting to the mark with Rideau River water.

2 mL of the Rideau River water solution was transferred to a 10 mL beaker and the PDMS-coated HPbar was added. Stirring took place for 30 minutes, after which the stir bar was removed from solution and gently dried using a Kimwipe. The stir bar was then transferred to a beaker containing 1 mL of hexane and stirring took place for 15 minutes. The extract was transferred to an autosampler vial and analysis was done in

triplicate using GC-ECD. Concentrations of the extracts were calculated using the calibration curve.

3. RESULTS AND DISCUSSION

One will note that the terms *stir bar* and *HPBar* (Helen Prochazka Bar) will be used, hereafter, interchangeably.

3.1 Characterization of the Coatings

Characterization of the coatings was performed for two reasons. First, since an objective was to produce coatings more capable of extracting polar analytes, it was necessary to chemically characterize the coatings so that extraction efficiency could be correlated with these chemistries. These chemical characterizations were done using Infrared (IR) spectroscopy and Solid-State Nuclear Magnetic Resonance (NMR). Second, mechanical and chemical stabilities of the coating were established (section 3.2).

IR spectra of the three coatings show many functional groups. Table 3.1 shows a summary of the peaks identified for each coating.

Coating	Peak (1/cm)	Functional Group
PDMS	2966	C-H
	2164	Si-H
	1262	$Si-CH_3$
	1101/1021	Si-O-Si
	802	$Si-CH_3$
PDMS-co-DPS(5%)	2965	C-H
	2169	Si-H
	1431	Si-ph
	1262	$Si-CH_3$
	1091/1020	Si-O-Si
	804	$Si-CH_3$
	717/699	Si-ph
PEG	2961	C-H
	2880	Aromatic C=C
	1783	C-NH-CO-
	1345/1173	R-ph-R
	1101	Si-O-Si
	846	Si-OH

Table 3.1: Infrared Spectrum Analysis of HPBars Coatings
Infrared Spectra are in the Appendix as Figure A.1

It is evident that the peaks identified match the structures of all three coatings. Therefore, the PDMS coating is indeed the least polar and PDMS-co-DPS(5%) has some aromatic rings, making it more polarizable than PDMS. The PEG solid-phase only seems to have a small amount of aromatics, but it also has amino groups and Si-OH groups, making this coating the most polar of the three, as expected.

As stated in the introduction, the structure of the PEG postulated by Shende et al is:

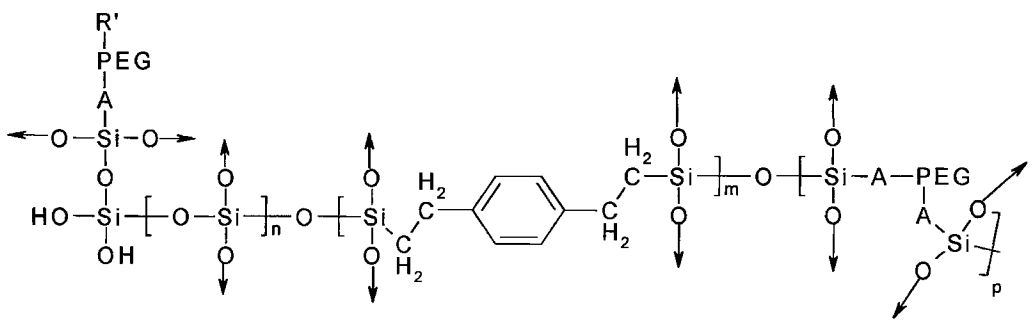


Figure 3.1: structure of PEG-solid phase

From Figure 3.1, one can see three main groupings in the molecule having the numbers or repeating units n, m, and p. However, Shende states that these three components will interact in different ways each time the sol-solution is made [Shende et al, 2003]. Therefore, it is possible that the values of n and p are much greater than m. If this occurred, then there would be minimal aromatic functional groups in the polymer. However, as previously stated, the PEG polymer has many polar amino and hydroxyl groupings, resulting in a very polar solid-phase.

The Solid-State Nuclear Magnetic Resonance (NMR) analysis showed similar results. NMR spectra of the three coatings can be found in the Appendix as Figures A.2 through A.4.

The NMR spectrum for PDMS showed a strong peak at 1.294 ppm, indicating a large amount of R-CH_3 groupings, which is expected since the main functional groups are –CH_3. From this, one can deduct that the PDMS phase is indeed non-polar and not very polarizable.

The NMR spectrum from PDMS-co-DPS(5%) showed a strong peak at 1.3362 ppm and a grouping of peaks around 130 ppm. The first peak is, again, the CH_3 groupings. The other set of peaks indicates that aromatic rings are present. A ratio of the integration of the peaks shows that approximately 14% of the constituents are aromatic. Therefore, NMR analysis also predicts that the PDMS-co-DPS(5%) coating is slightly more polarizable than the PDMS coating due to the presence of aromatic rings.

The NMR spectrum of PEG shows a large peak at 70.3 ppm, a small grouping of peaks from 107 to 124 ppm, and another small grouping of peaks from 158 to 160 ppm. The large peak at 70.3 ppm indicates the presence of carbon bonded to oxygen (C-O).

The small grouping from 107 to 124 ppm indicates the presence of Trifluoroacetic Acid (the catalyst used in the experiment) and the small grouping from 158 to 160 ppm indicates the presence of R-CO-NH_2. The presence of both the C-O groups and the R-CO-NH_2 groups is expected in the structure suggested by Shende. Also, there was no grouping of peaks at approximately 130 ppm, indicating very little to no aromatic rings. Therefore, the suggestion that the values on n and p are much greater than m is possible, having seen the IR and NMR analyses. The presence of the C-O groups and the R-CO-NH_2 groups would nevertheless make the PEG structure quite polar.

3.2 Durability of the Coatings

As advantageous as would be a stir bar with a large volume of coating, it would also be advantageous to have a coated stir bar which can be used repeatedly without much coating loss. Therefore, the stir bars produced from this project were tested for coating loss in water and organic solvent, when made with and without the porous poly(tetrafluoroethylene) (PTFE) tubing.

When stirred in water for six 10 minute increments, the PDMS-coated HPBars (with and without PTFE tubing) had minimal coating loss. The total percentage of PDMS coating lost was found to be 3.2% and 0.8%, respectively. When stirred in dichloromethane (DCM) for six 10 minute increments, the total percentage of PDMS-coating lost was found to be 1.3% and 6.9%. The data obtained for these experiments can be seen in Table 3.2.

Stir Bar (coating)	Liquid Medium	Density of Coating (g/mL)	Initial Coating Volume (uL)	Final Coating Volume (uL)	Percent Loss (%)
PDMS	Water	0.73	8.49	8.22	3.2
	DCM	0.73	10.82	10.69	1.3
PDMS w/ PTFE	Water	0.73	33.01	32.74	0.8
	DCM	0.73	46.44	43.29	6.8
PDMS-co-DPS(5%)	Water	0.74	9.19	9.05	1.5
	DCM	0.74	43.38	42.97	0.9
PDMS-co-DPS(5%) w/ PTFE	Water	0.74	9.189	9.189	0.0
	DCM	0.74	31.76	24.32	23.4
PEG w/ PTFE	Water	0.80	35.90	17.24	52.0
	Water	0.80	20.50	14.32	30.1
	Hexane	0.80	9.70	6.87	29.2

Table 3.2: Change in Volume of Coating as a function of Time Stirred in Water for PDMS-, PDMS-co-DPS(5%)- and PEG-coated HPBars, with and without porous PTFE tubing

Figures 3.2 and 3.3 show the loss of PDMS coating for the stir bars with and without PTFE tubing, in both water and dichloromethane.

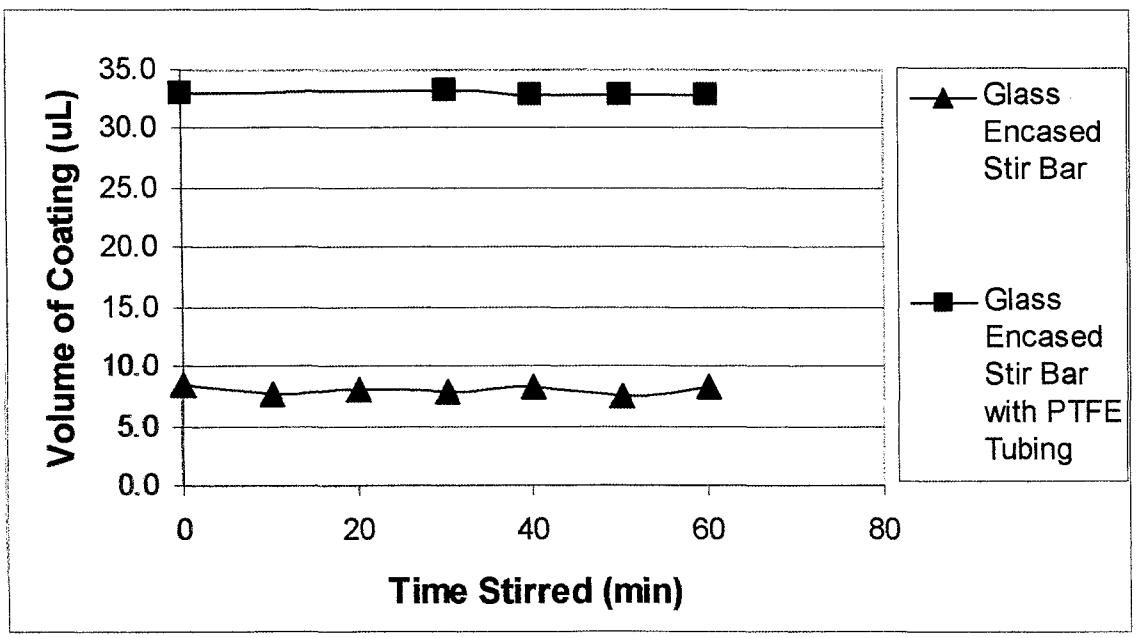


Figure 3.2: Volume of Coating versus Time Stirred in Water for PDMS-coated HPBar, with and without PTFE tubing

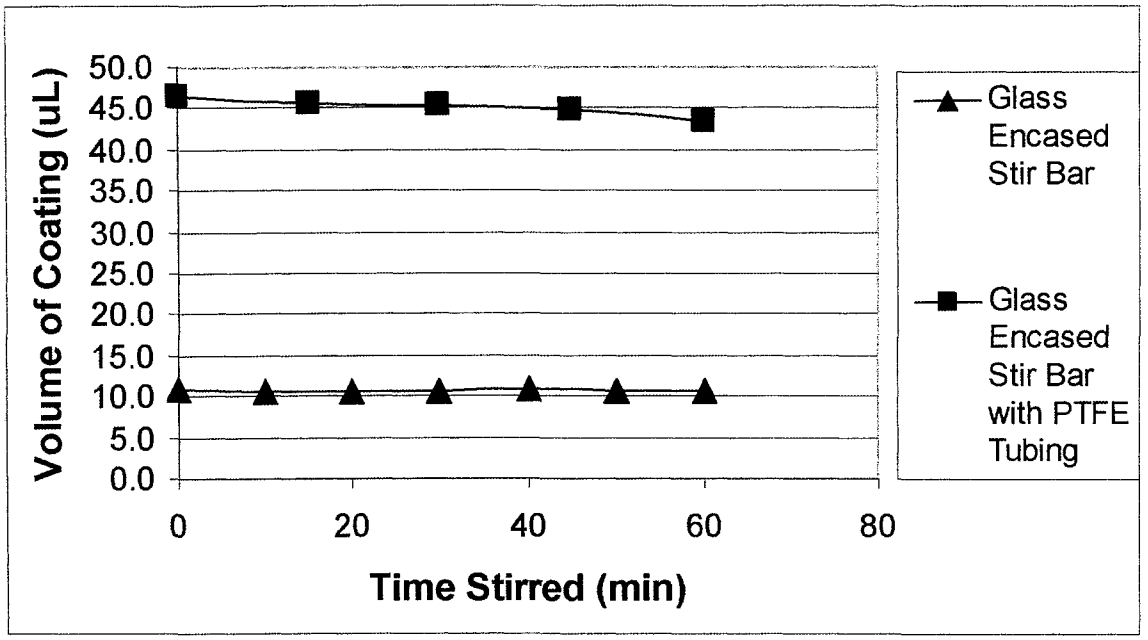


Figure 3.3: Volume of Coating versus Time Stirred in Dichloromethane for PDMS-coated HPBar, with and without PTFE tubing

PDMS is a non-polar substance that has a high degree of hydrophobicity, resulting in a stable coating-volume over the course of the six 10 minute intervals in water.

The PDMS-coated HPBar with PTFE tubing that was stirred in the DCM had a greater loss of coating when compared to the other PDMS-coated HPBars. This is due to the fact that PDMS swelled in DCM which enhanced cracks that were present in the coating, resulting in coating loss. There would naturally be more cracks present since there was a greater volume of coating.

After the stir bars were coated with PDMS, there was a conditioning step during which the stir bars would be heated in nitrogen up to 300 °C. The main reason for this was to evaporate any leftover solvent and promote further crosslinkage within the coating. Therefore, if the remaining solvent evaporated too quickly, the coating would shrink and crack under the stress of the high temperature. When placed in DCM, the

coating swelled and since the PDMS was only mechanically bonded to the PTFE tubing (instead of chemically bonded to the glass-encasement), the swelling greatly magnified any cracks in the coating. Cracks then resulted in small pieces of PDMS breaking off of the stir bar. However, once all the loosely bound pieces (or pieces containing a lot of cracks) had fallen off, the coating-volume stabilized.

The same analysis was done using the PDMS-co-DPS(5%)-coated HPBars that were produced with and without PTFE tubing. The percent loss when stirred in water was 0.9% and 1.5%, respectively. The percent loss when stirred in dichloromethane was 23.6% and 0.0%, respectively. Figure 3.4 and Figure 3.5 show the change in coating volume over the course of the six 10 minute intervals in both water and DCM.

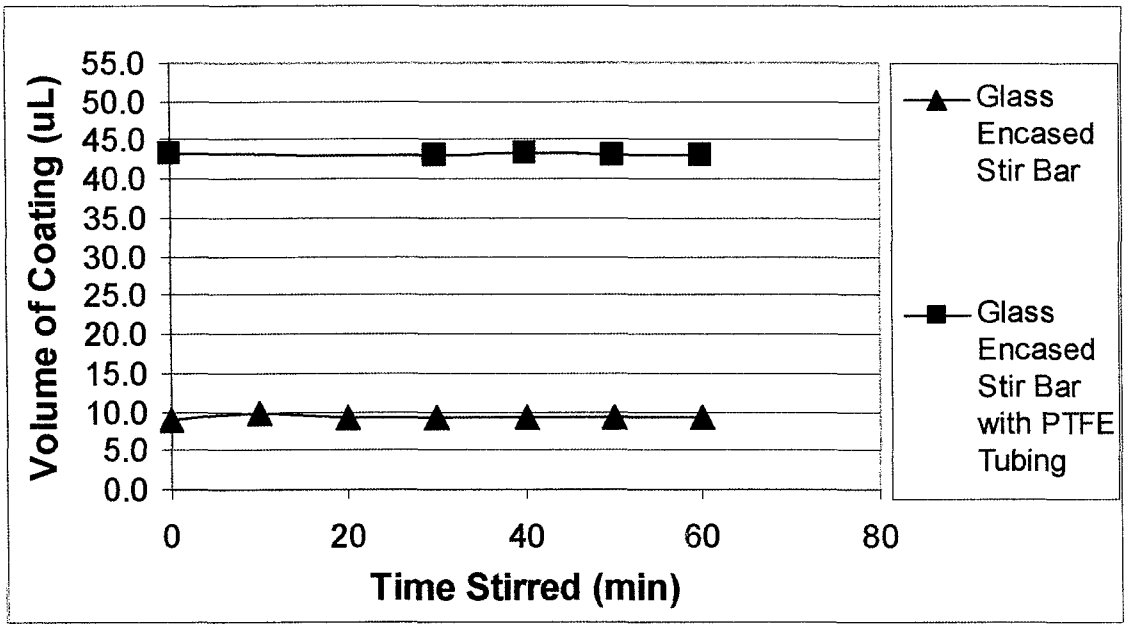


Figure 3.4: Volume of Coating versus Time Stirred in Water for PDMS-co-DPS(5%)-coated HPBar, with and without PTFE tubing

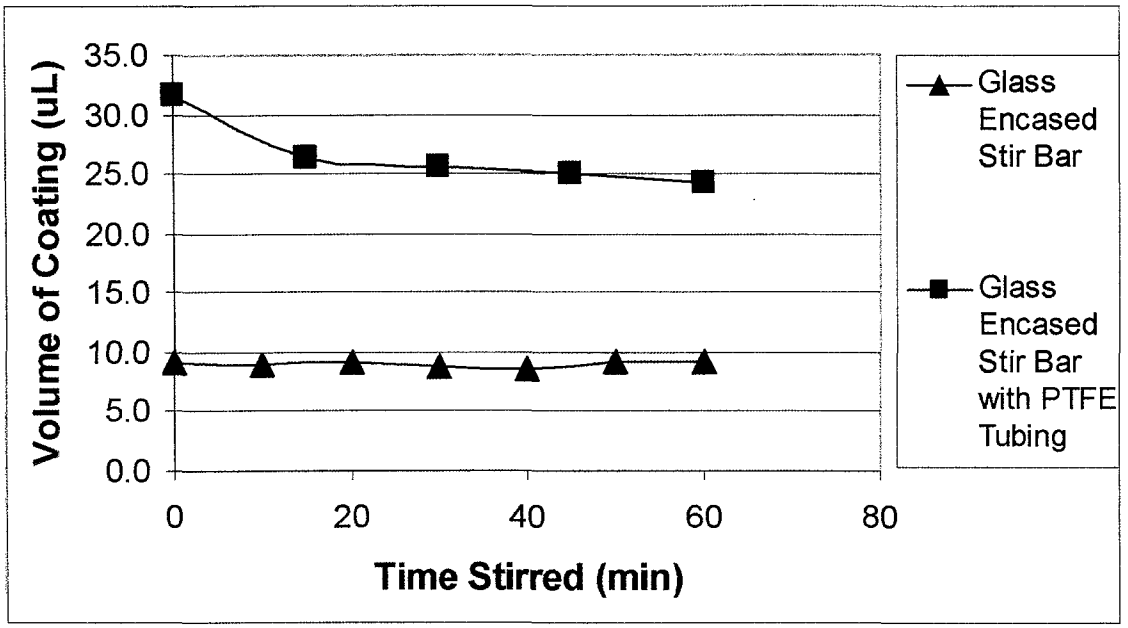


Figure 3.5: Volume of Coating versus Time Stirred in Dichloromethane for PDMS-co-DP(5%)-coated HPBar, with and without PTFE tubing

Again, while the coating-volume is relatively stable when stirred in water, the volume seems to initially drop when stirred in DCM and then stabilize. This occurred due to the same reasons: PDMS-co-DPS(5%) is also fairly non-polar and is hydrophobic. It swells in DCM and any cracks present are magnified, resulting in loss of coating.

From Figure 3.5, one can see that the coated stir bars with PTFE tubing have the largest percent loss of coating. This is again due to the initial high volume of coating and the fact that mechanical bonding has taken the place of chemical bonding. However, it is more important to obtain higher volumes of solid phase, whether there is a large loss of coating or not. Therefore, the stir bars with PTFE tubing were advantageous because after stabilization, the volume on these stir bars was greater than the volumes on the stir bars without PTFE tubing.

The PEG-coated HPBars made with PTFE tubing had a percent loss of 52.0% and 30.1%, respectively, when stirred in water and 29.2% when stirred in hexane. This is a

trend that is opposite to that of the PDMS and PDMS-co-DPS(5%)-coated HPBars since there was a greater percent loss when stirred in water, rather than organic solvent. The loss of coating when stirred in hexane is very close to the loss of coating for the stir bar without PTFE tubing that was stirred in water. In Figure 3.5, one can see that the initial loss of coating occurred in the first 10 minute increment, therefore, a large piece of coating that was loosely attached most likely broke away from the rest of the coating. After this occurred, one can see that the coating-volume stabilized.

The PEG-coating is soluble in dichloromethane (note that DCM was used as the solvent during the sol-gel process) and it is for this reason that hexane was used as the organic solvent for the PEG-coated HPBars. PEG, however, is a polar coating when compared to PDMS and PDMS-co-DPS(5%). This is due to the presence of Si-OH and R-NH-CO groups, leading to strong differences in electronegativity, and consequently, polarity. Therefore, the PEG-coating will swell in a polar phase like water instead of an organic solvent since *like dissolves like*. In other words, there is a strong affinity of water for such a polar phase. Figure 3.6 and 3.7 show the change in volume of PEG-coating as a function of time stirred in both water and hexane.

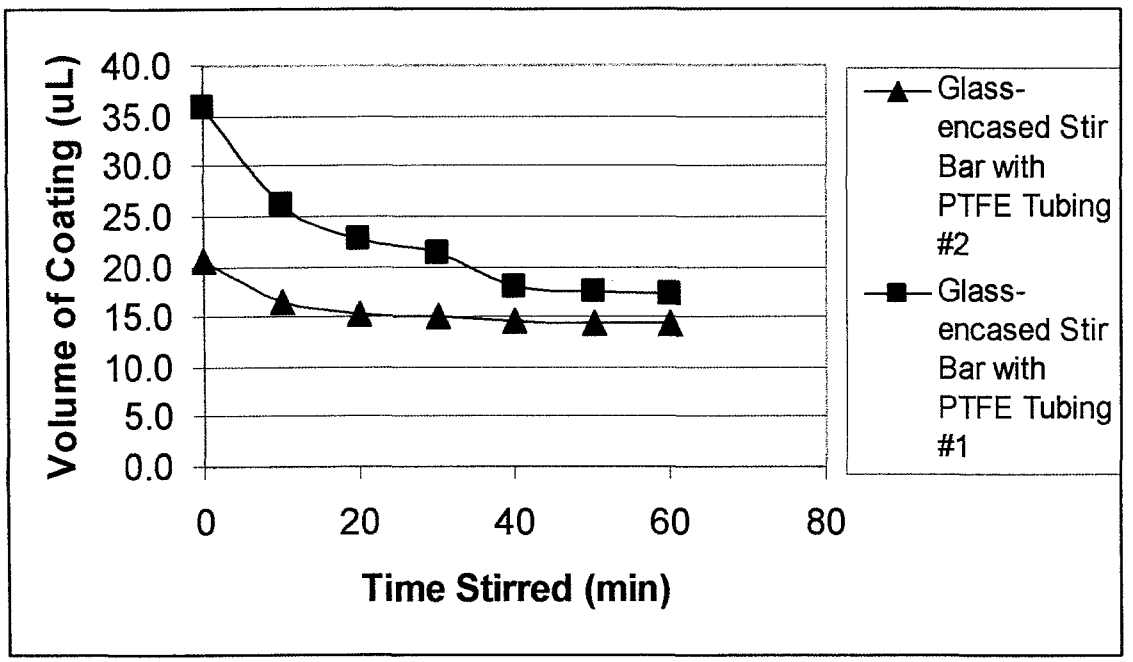


Figure 3.6: Volume of Coating versus Time Stirred in Water for PEG-coated HPBar

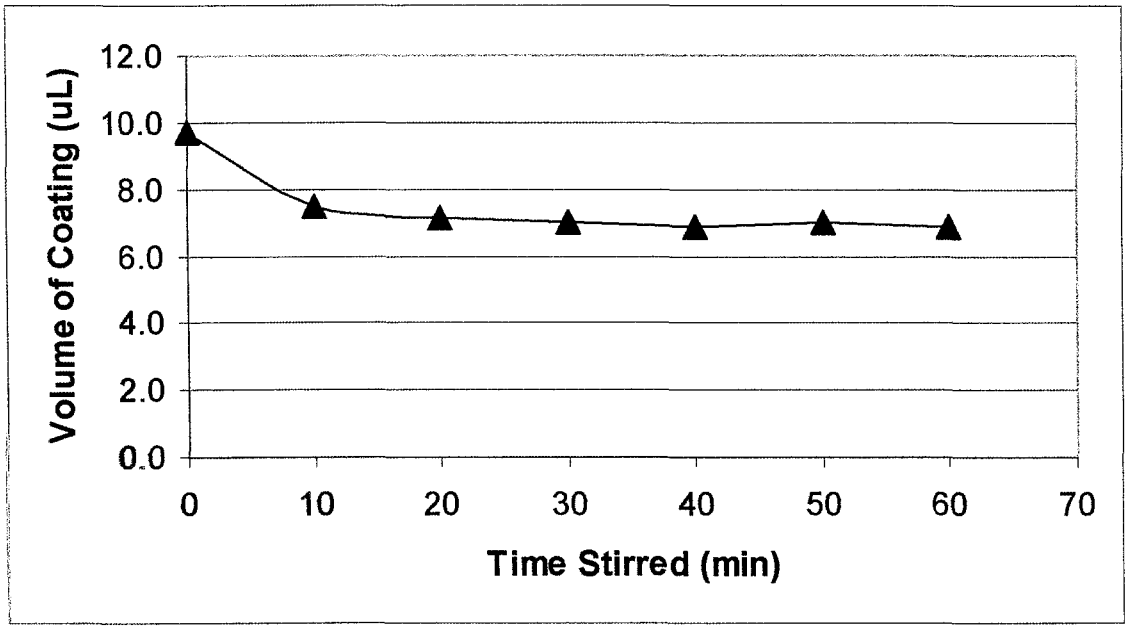


Figure 3.7: Volume of Coating versus Time Stirred in Hexane for PEG-coated HPBar

Another reason for the increased loss of PEG-coating is the lack of a conditioning step. Poly(ethylene glycol) is known to melt at relatively low temperatures [Aldrich, 2006], resulting in decomposition when conditioning was attempted. However, since thermal desorption was not being used in the experimental procedure, the conditioning step was overlooked for the PEG-coated HPBars. Essentially, if the stir bars need not withstand high temperatures, why have a conditioning step at all?

Because of this missing step, the coating may not have crosslinked to completion, resulting in a loss of coating during the first couple stirring-time intervals. However, after about 30 minutes of stirring, the coating-volume seemed to stabilize. Therefore, even without the presence of the conditioning step, the coating volume stabilized after the first 30 minutes of stirring.

To summarize, all the coated stir bars seemed to lose some coating. Also, the greatest loss occurred in the solvent which was similar in polarity to the coating. For example, the non-polar stir bars lost the most coating in the non-polar solvent (DCM) and the polar stir bars lost the most coating in the polar solvent (water). However, after the initial 3 time intervals, the coating-volumes all stabilized. Because of this stabilization, the stir bars could then be used to perform multiple extractions. In fact, stir bars with PTFE tubing that had been tested in water and organic solvent were used for the extraction of the three analytes.

3.3 Extraction of Naphthalene using HPBars

3.3.1 Standard Calibration Curve for Naphthalene in DCM with GC-MS and GC-FID

The standard calibration curves for Naphthalene in Dichloromethane using GC-MS and GC-FID showed linear regression coefficients of 0.9976 and 0.9931, respectively. These values indicate good linearity. The standard calibration curves for Naphthalene are located in the Appendix as Figures A.5 and A.6.

3.3.2 Optimization of Naphthalene Extraction using Sorption/Desorption Times

The minimum sorption and desorption times needed for maximum recovery of the analytes need to be determined. For the extraction of a 5 ppm aqueous solution of Naphthalene using the PDMS-coated HPBar, the sorption time in which maximum recovery of Naphthalene from the aqueous sample was obtained was 30 minutes. The desorption time needed for maximum desorption was found to be less than 5 minutes. However, for the sake of being thorough, the optimal desorption time was set to 15 minutes. Figures 3.8 and 3.9 show plots of percent recovery versus Sorption time and Desorption time for the PDMS-coated HPBar.

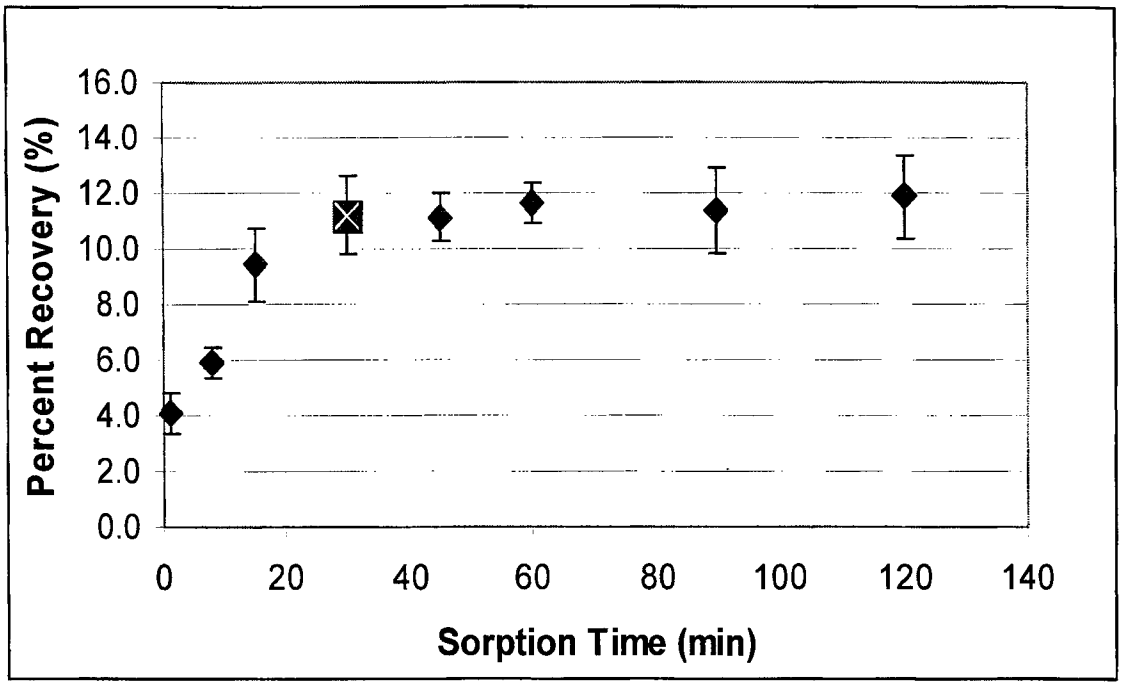


Figure 3.8: Percent Recovery of Naphthalene versus Sorption Time using PDMS-coated HPBar. Symbol at 30 minutes indicates minimal sorption time needed.

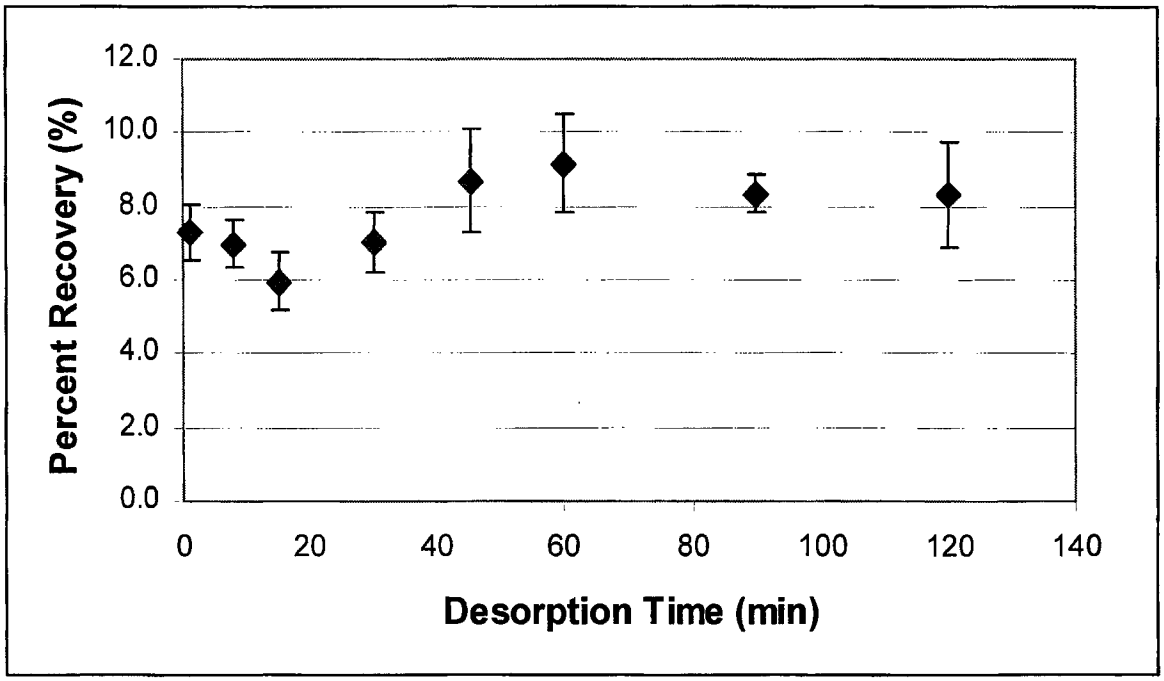


Figure 3.9: Percent Recovery of Naphthalene versus Desorption Time using PDMS-coated HPBar

The recovery with this phase was less than 12%. This is very low, and can be explained by the low theoretical partition coefficient of log $K_{O/W}$ of 3.01 [EPA, 2006]. This value indicates that naphthalene has a lower solubility in a nonpolar phase when compared to an analyte that has a high partition coefficient. Since the PDMS-phase is the least polar out of the three coatings, one could expect a slightly lower recovery.

In Figure 3.8, the slope of the curve begins to flatten around the 30 minute mark, nearing a slope of zero. Since the slope is more or less zero between 30 minutes and 60 minutes, one would obtain similar recoveries at both sorption times. Therefore, 30 minutes is the quickest time in which equilibrium can be reached, and consequently the optimal sorption time.

The optimal sorption of Naphthalene onto the PDMS-co-DPS(5%)-coated HPBar was found to be approximately 15 minutes and the optimal desorption time was found to be again, less than 5 minutes. However, for simplicity, the sorption and desorption times were set equal to those of the PDMS-coated HPBar. The plots of percent recovery versus sorption and desorption time of naphthalene using the PDMS-co-DPS(5%)-coated HPBars can be seen in Figures 3.10 and 3.11.

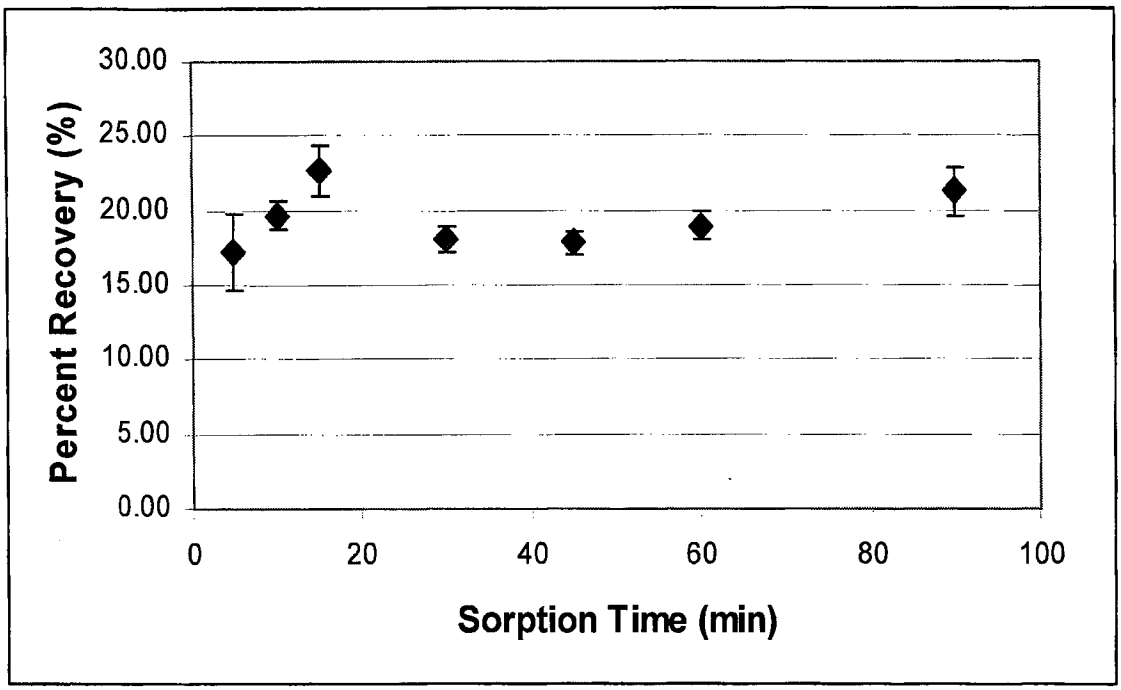


Figure 3.10: Percent Recovery of Naphthalene versus Sorption Time for PDMS-co-DPS(5%)-coated HPBar

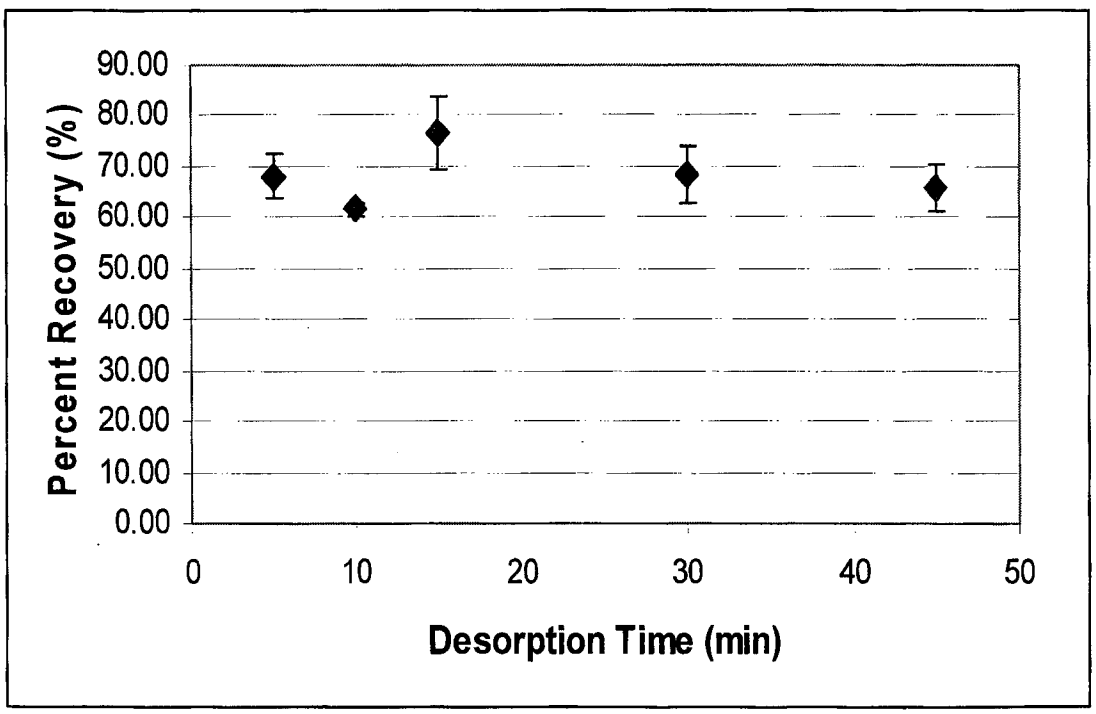


Figure 3.11: Percent Recovery of Naphthalene versus Desorption Time using PDMS-co-DPS(5%)-coated HPBar

As previously stated, the optimal sorption and desorption times for the PDMS-co-DPS(5%)-coated HPBars were shorter than for the PDMS-coated HPBars. One must note that this is for the extraction of naphthalene which is a polycyclic aromatic hydrocarbon. The PDMS-co-DPS(5%)-coated HPBar also contains aromatic rings. The interaction of naphthalene with the PDMS-co-DPS(5%) phase results in strong π-π interactions between the aromatic rings, allowing more naphthalene to be extracted by this phase when compared to the amount extracted by the PDMS phase.

3.3.3 Extraction Reproducibility of the PDMS-coated HPBar

To verify that the coated stir bar gives reproducible recoveries for each extraction, several extractions were performed under identical conditions. The amount of naphthalene recovered was calculated to see whether the extraction efficiency decreased over time. Figure 3.12 shows how the extraction efficiency stays constant over the course of 10 extractions.

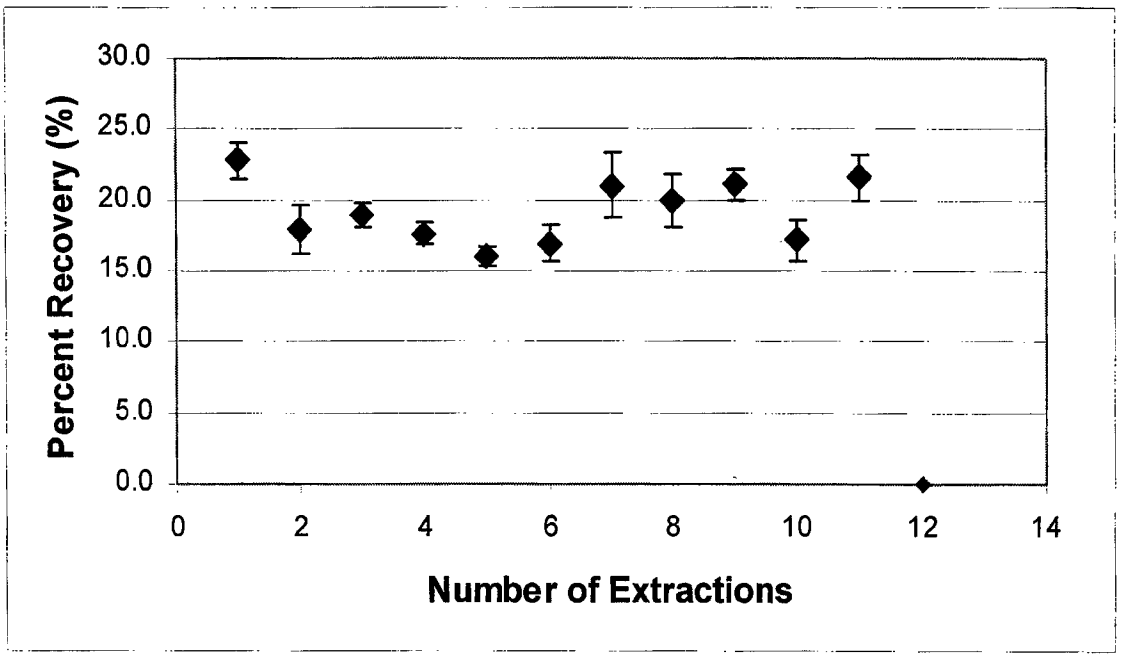


Figure 3.12: Percent Recovery of Naphthalene versus Number of Extractions using Poly(dimethylsiloxane)-coated HPBar, Standardized for any loss of coating, 2 mL of 5 ppm Aqueous Sample

From Figure 3.12, the average percent recovery seems to be approximately 20 % when taking into consideration the standard deviations of the separate extractions. Therefore, one obtains relatively reproducible recoveries with the PDMS-coated HPBar. This test was not performed on the PDMS-co-DPS(5%)- or PEG-coated HPBars, however, so long as there is not a substantial loss of coating, then the extractions should be similar in efficiency.

3.3.4 Experimental Partition Coefficients for Naphthalene for PDMS-, PDMS-co-DPS(5%)-, and PEG-coated HPBars

Partition coefficients of naphthalene from water to each of the three coatings were calculated.

To calculate the partition coefficient, equation 3 from section 1.8 was used:

$$K_{COATING\,/\,WATER} = \frac{\left(\frac{M_{analyte_{coating}}}{V_{coating}}\right)}{([Analyte]_{H_2O,\,equilibrium})} \qquad [3]$$

Essentially, the concentration of analyte in the extract was compared to the concentration of analyte leftover in the aqueous sample in order to obtain a ratio.

Table 3.3 summarizes the calculated partition coefficients for naphthalene for each of the coatings.

Stir Bar (Coating)	Partition Coefficient (K coating/w)	log Partition Coefficient (log K coating/w)
PDMS	229	2.36
PDMS-co-DPS(5%)	309	2.49
PEG	31	1.49

Table 3.3: Experimental Partition Coefficients for Naphthalene using PDMS-, PDMS-co-DPS(5%)-, and PEG-coated HPBars

Figure 3.13 shows the logarithmic partition coefficients of naphthalene when compared to each other.

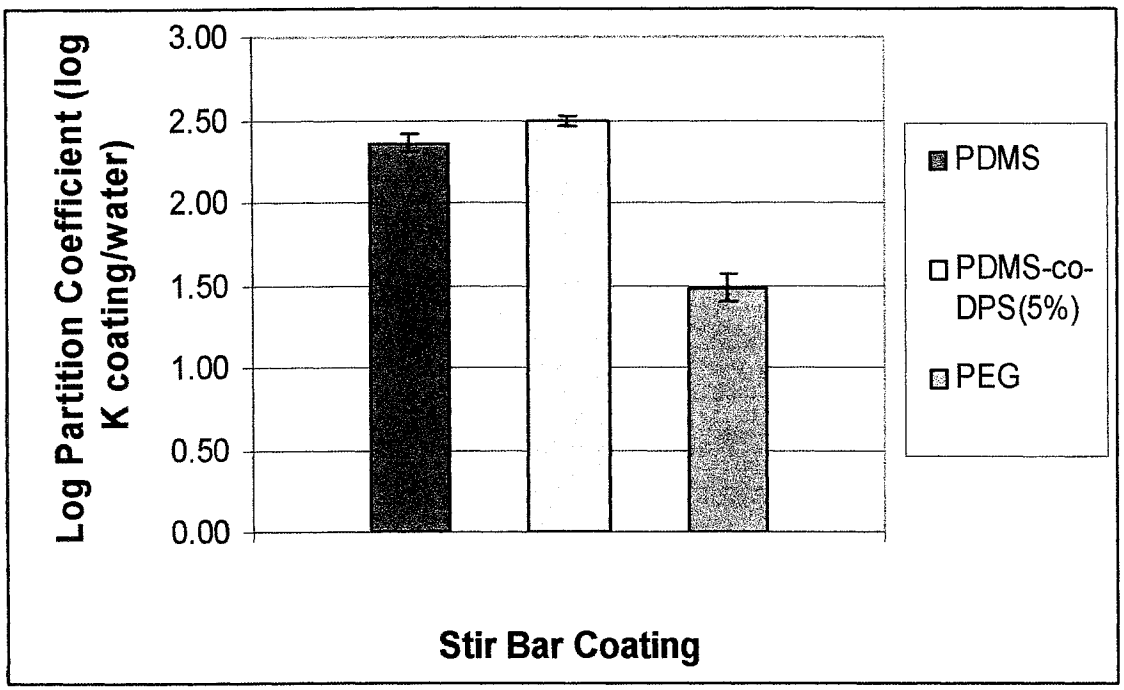


Figure 3.13: Log Partition Coefficients of Naphthalene for PDMS-, PDMS-co-DPS(5%)-, and PEG-coated HPBars

From Table 3.3 and Figure 3.13, one can see that the partition coefficient was the greatest when extracting with the PDMS-co-DPS(5%)-coated HPBar. Also, since this is a logarithmic comparison, one must note that the difference in partition coefficient between the PDMS-co-DPS(5%)-coated HPBar and the PEG-coated HPBar is roughly ten times. Therefore, the PEG-coated HPBar has an extraction efficiency that is approximately ten times less efficient then that of the other two stir bars. This is expected since Naphthalene is a nonpolar compound and would have low solubility in a polar solid phase.

The PDMS-co-DPS(5%) coating is made with dihydroxy-terminated poly(dimethylsiloxane)-co-diphenylsiloxane with the diphenylsiloxane making up approximately 5 % of the weight of the compound. Therefore, one would expect the partition coefficient of naphthalene for the PDMS-co-DPS(5%)-coated HPBar to be greater than for the PDMS coating. Since naphthalene is an aromatic compound, it

interacts to a greater degree with the phenyl groups in the coating, resulting in a higher amount extracted and a higher partition coefficient.

From characterization of the coatings with solid-state Nuclear Magnetic Resonance, the PEG coating has only a small amount of aromatic carbons compared to the PDMS-co-DPS(5%) phase. Also, in addition to the lack of aromaticity, the naphthalene is not efficiently extracted due to the polar nature of the coating. Therefore, it is the combination of both the polarity of the coating and the amount of aromatic carbons that dictates how high the partition coefficient will be.

The literature logarithmic partition coefficient (log $K_{O/W}$) of naphthalene is 3.01 [EPA, 2006]. This is higher than any of the experimental partition coefficients listed in Table 3.3. Whether the experimental partition coefficient is higher or lower than the literature partition coefficient, any difference is expected since these experiments involved the equilibrium between the coating and water, not octanol and water. Also, the literature partition coefficient of naphthalene is lower than that of PCB77 (log $K_{O/W}$ = 6.12 [EPA, 2006]) therefore, naphthalene is more soluble in a polar phase eventhough it is a nonpolar molecule. Though octanol in the $K_{O/W}$ is considered to be nonpolar, it is actually slightly polar due to the hydroxy group at the end of the molecule. Therefore, when comparing octanol to the phases we see here, the naphthalene may partition to a greater degree in the octanol rather than the solid-phases in these experiments. This would mean lower partition coefficients for the solid-phases, as is the case here.

3.4 Extraction of 3,3',4,4'-Tetrachlorobiphenyl using HPBars

3.4.1 Standard Calibration Curve for PCB77 in hexane with GC-ECD

The standard calibration curve for 3,3',4,4'-tetrachlorobiphenyl in hexane using GC-ECD showsed a linear regression coefficient of 0.9846. The standard calibration curve for 3,3',4,4'-tetrachlorobiphenyl is located in the Appendix as Figure A.7.

3.4.2 Experimental Partition Coefficients of PCB77 using PDMS-, PDMS-co-DPS(5%)-, and PEG-coated HPBars

The partition coefficients for 3,3',4,4'-tetrachlorobiphenyl were calculated and Table 3.4 summarizes the results.

Stir Bar (Coating)	Partition Coefficient (K coating/w)	log Partition Coefficient (log K coating/w)
PDMS	179	2.25
PDMS-co-DPS(5%)	216	2.33
PEG	51	1.71

Table 3.4: Experimental Partition Coefficients for 3,3',4,4'-tetrachlorobiphenyl using PDMS-, PDMS-co-DPS(5%)-, and PEG-coated HPBars

Figure 3.14 shows the logarithmic partition coefficients of PCB77 compared to each other.

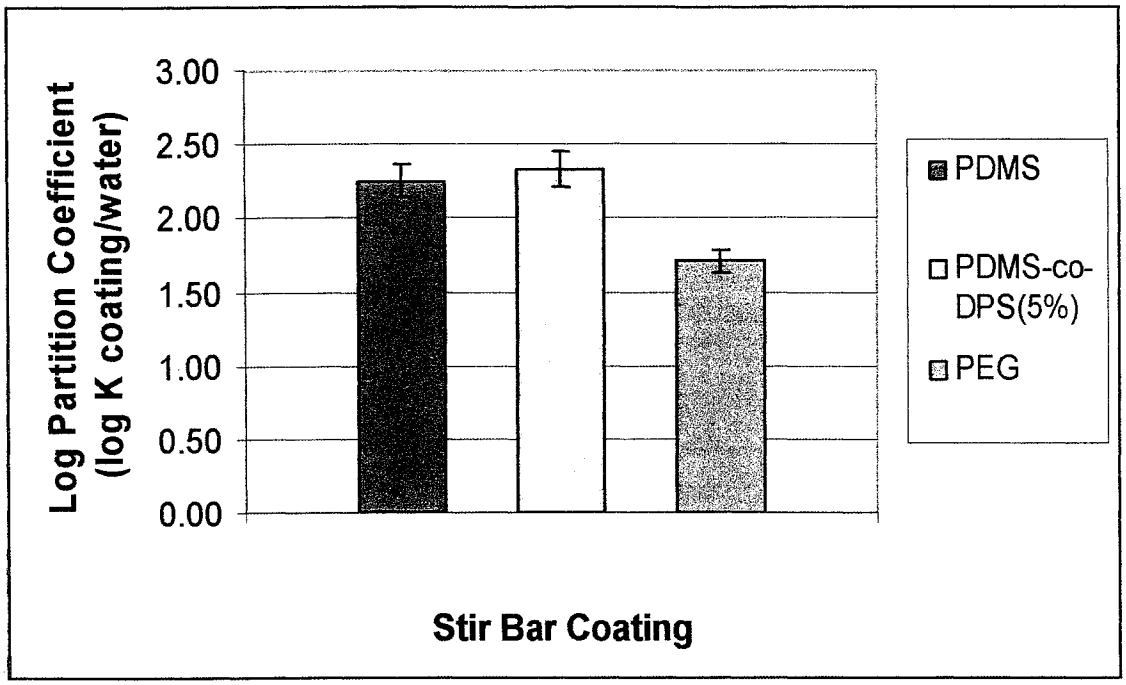


Figure 3.14: Log Partition Coefficients of 3,3',4,4'-Tetrachlorobiphenyl for PDMS-, PDMS-co-DPS(5%)-, and PEG-coated HPBars

As with naphthalene, the PDMS-co-DPS(5%)-coated HPBar had the highest partition coefficient. This is again due to the aromatic nature of PCB77 and the phenyl groups within the coating. Also, the PEG-coated stir bar gave the lowest partition coefficient again, due to the nonpolar nature of the analyte.

3.5 Extraction of Pentachlorophenol using HPBars

3.5.1 Standard Calibration Curve for PCP in hexane with GC-ECD

The standard calibration curve for pentachlorophenol in hexane using GC-ECD showed a linear regression coefficient of 0.9859. The standard calibration curve for pentachlorophenol is located in the Appendix as Figure A.8.

3.5.2 Experimental Partition Coefficients of PCP using PDMS-, PDMS-co-DPS(5%)-, and PEG-coated HPBars

For a solid phase to give reproducible results, there must be a constant partition coefficient for a given anlyte, regardless of the concentration of the analyte in the water sample. To test this, the concentration of PCP in water was varied in order to see whether the partition coefficients were dependent or independent of concentration.

The partition coefficients for pentachlorophenol were calculated and Table 3.5 summarizes the results.

Concentration (PCP in water)	Stir Bar (Coating)	Partition Coefficient (K coating/w)	log Partition Coefficient (log K coating/w)
~100 ppb	PDMS	6	0.75
	PDMS-co-DPS(5%)	17	1.24
	PEG	2138	3.33
~ 1ppb	PDMS	218	2.34
	PDMS-co-DPS(5%)	696	2.84
	PEG	2611	3.42

Table 3.5: Experimental Partition Coefficients of Pentachlorophenol for PDMS-, PDMS-co-DPS(5%)-, and PEG-coated HPBars. Calculated for higher and lower PCP concentrations in water

Figure 3.15 shows the logarithmic partition coefficients of high concentration PCP compared to each other.

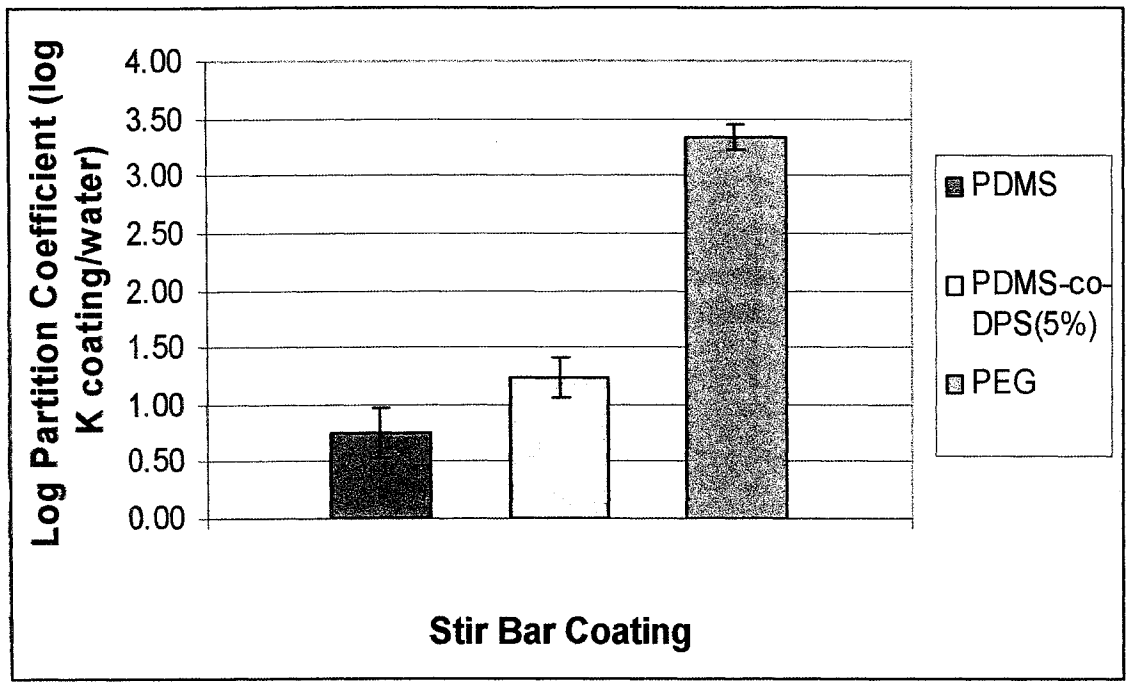


Figure 3.15: Log Partition Coefficients of high concentration of Pentachlorophenol for PDMS-, PDMS-co-DPS(5%)-, and PEG-coated HPBars

From Table 3.5 and Figure 3.15, the partition coefficients increase as the polarity of the coating increases. Therefore, PCP is better extracted with a polar solid phase. PCP was also extracted at lower concentrations (1 ppb as opposed to 100 ppb) to see whether the partition coefficients would be dependent or independent of the concentration. Figure 3.16 shows the results from these experiments compared to the results in Figure 3.15.

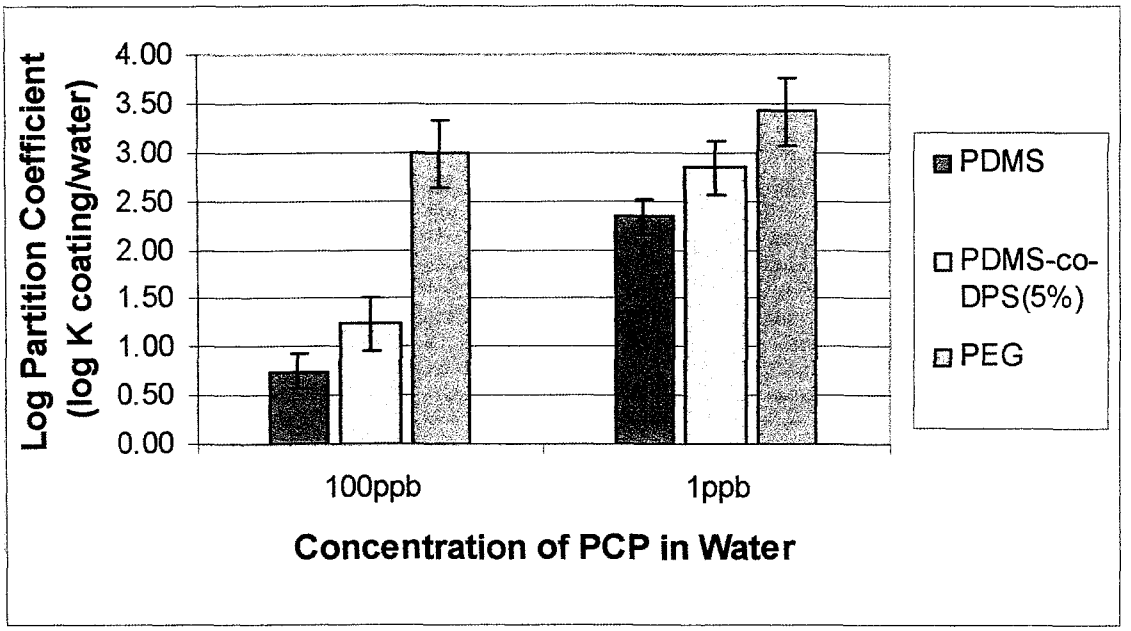


Figure 3.16: Log Partition Coefficients of Pentachlorophenol for PDMS-, PDMS-co-DPS(5%), and PEG-coated HPBars, concentration decreasing.

From Figure 3.16, the partition coefficients for the PDMS- and PDMS-co-DPS(5%)-coated HPBars increased as the concentration of PCP in water decreased. From this trend, it would seem that the lower the concentration, the greater efficiency of extraction. However, one must note that the partition coefficient is a ratio of the concentration of analyte extracted by the solid-phase compared to the concentration of analyte remaining in the water at equilibrium. It should be independent of initial concentration. Therefore, an increase of efficiency with decreasing concentration is not the case.

If the PDMS- and PDMS-co-DPS(5%)-coated HPBars actually have a very low efficiency and are simply saturated with PCP to the same degree after every extraction, then one would obtain the same trend seen in Figure 3.16. At high concentrations, the ratio of extracted PCP to remaining aqueous PCP would be very low since most of the PCP would be in the aqueous phase. At low concentrations, the same amount of extracted

PCP would be in the aqueous phase. At low concentrations, the same amount of extracted PCP would be compared to the already 100-fold less amount of PCP in water, so the calculated partition coefficient would appear larger. In fact, at concentrations lower than 1 ppb, the PDMS- and PDMS-co-DPS(5%)-coated HPBars might have calculated partition coefficients equal to that of the PEG-coated HPbar. These are not, however, accurate representations of the partition coefficients for those two coated stir bars since the coatings are saturated with PCP. Though the equilibrium has been reached, the concentration of PCP in water is most likely outside of the linear dynamic range for the nonpolar solid-phases and the extraction of PCP has simply reached its limit, causing the partition coefficient to become dependent on the concentration.

From equation 3,

$$K_{COATING\ /\ WATER} = \frac{\left(\frac{M_{analyte_{coating}}}{V_{coating}}\right)}{([Analyte]_{H2O,\ equilibrium})}$$

the above reasoning can be explained. One could first make the numerator (the concentration of analyte on the solid-phase) a constant. Then, as the denominator decreases in concentration, the ratio will increase since the fraction is becoming larger. Therefore, when the coating is saturated to its limit, the partition coefficient will be dependent on the concentration.

3.6 Simultaneous Extraction of Naphthalene, 3,3',4,4'-Tetrachlorobiphenyl (PCB77) and Pentachlorophenol (PCP) using PDMS-, PDMS-co-DPS(5%)-coated, and PEG-coated HPBars

When extracting from a real water source, one might unknowingly come across the presence of other compounds, even if they are not the analyte of interest. This might cause some of the analytes to compete for vacancies in the solid phase. Competition or interference between analytes could result in the decrease in extraction efficiency, leading to decreased partition coefficients. By comparing the partition coefficients of each analyte with and without the possible interference of other analytes, any decrease in extraction efficiency can be seen. Figure 3.17 shows the competitive (three analytes) and non-competitive (single analyte) experimental partition coefficients of Naphthalene using all three coated HPBars.

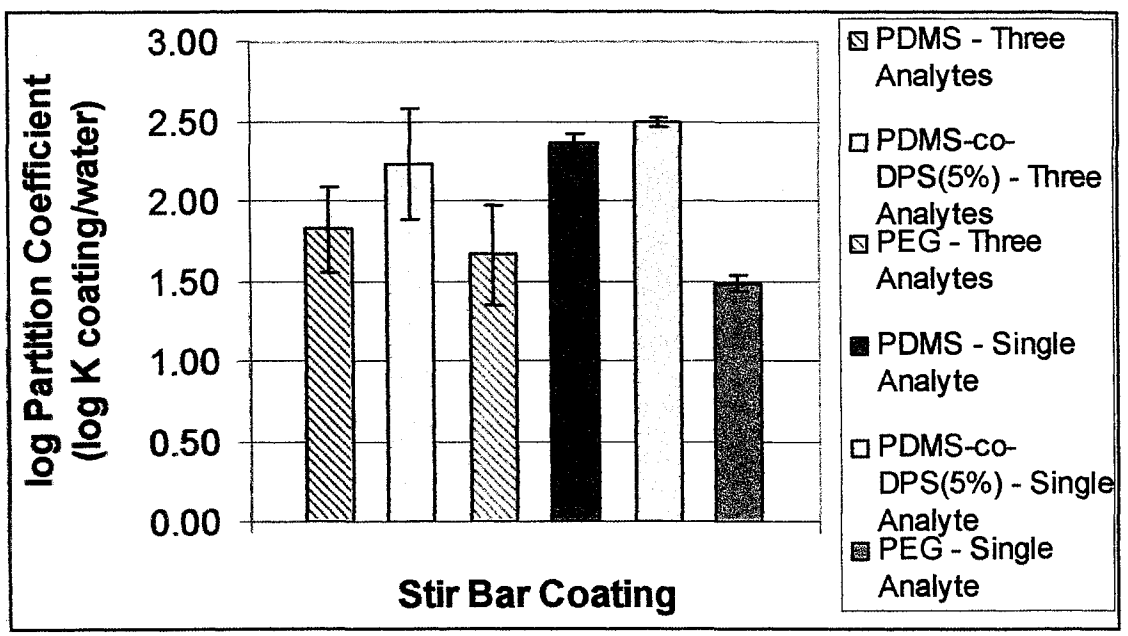


Figure 3.17: Comparison of Experimental Log Paritition Coefficients for Naphthalene for PDMS-, PDMS-co-DPS(5%)-, and PEG-coated HPBars, with and without competition from the other analytes

From Figure 3.17, it is evident that the competitive partition coefficients for all three coated stir bars are not significantly different from each other since the standard deviations (1 σ) overlap. When compared to the non-competitive partition coefficients, there is no significant difference in the K values between the PDMS-co-DPS(5%) and PEG-coated HPBars. The PDMS-coated HPBar has the only significant difference between the competitive and non-competitive partition coefficients. The log Octanol-Water partition coefficients (log $K_{O/W}$) for Naphthalene and PCB77 are 3.01 and 6.12, respectively. Therefore, PCB77 should be more soluble in a non-polar phase. This would mean that if both analytes are present in solution, the PDMS solid phase should have a greater extraction efficiency for PCB77, lowering the amount of naphthalene that is extractable. One can see the same trend in the PDMS-co-DPS(5%)-coated HPBar in Figure 3.18.

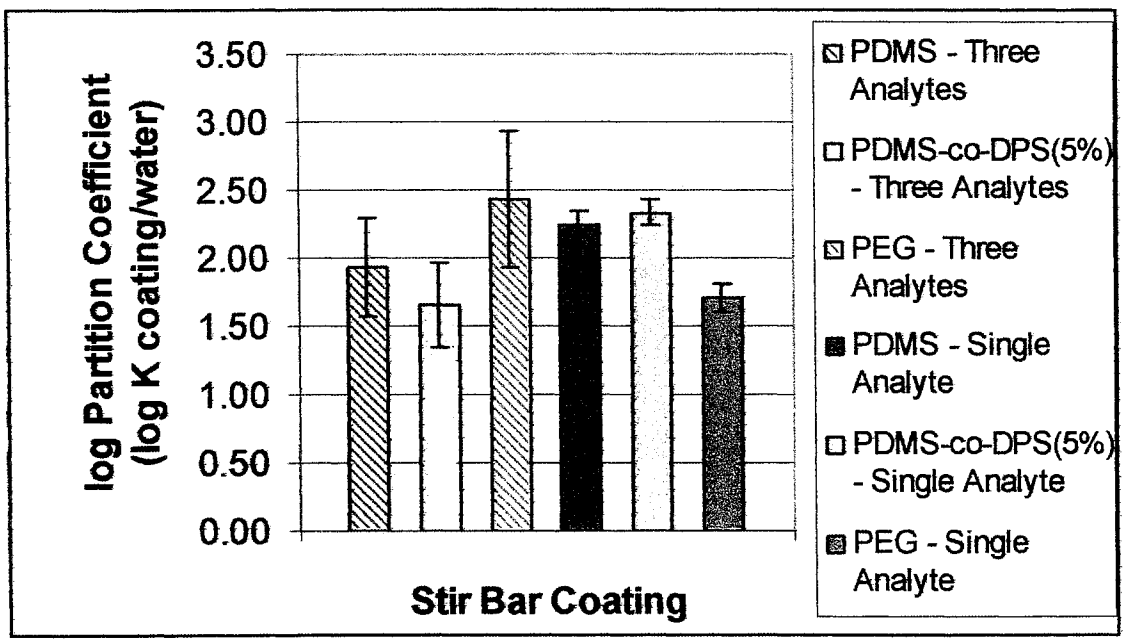


Figure 3.18: Comparison of Experimental Log Paritition Coefficients for 3,3',4,4'-Tetrachlorobiphenyl for PDMS-, PDMS-co-DPS(5%)-, and PEG-coated HPBars, with and without competition from the other analytes

The competitive partition coefficients are relatively indistinguishable from each owing to the large standard deviations. However, when compared to the non-competitive partition coefficients, there is a clear difference between the partition coefficients calculated for the PDMS-co-DPS(5%)-coated HPBar. This is due to the fact that the PDMS-co-DPS(5%) solid phase was best at extracting naphthalene, lowering the extraction efficiency of PCB77. The $K_{O/W}$'s previously stated for naphthalene and PCB77 indicate that though non-polar, naphthalene is more soluble in a polar phase. PDMS-co-DPS(5%) has a small degree of polarity owing to the 5% quantity of phenyl groups. Therefore, more naphthalene would be extracted, decreasing the extraction efficiency of the solid phase for PCB77.

An entirely different trend was seen when the competitive and non-competitive parrition coefficients for PCP were compared in Figure 3.19.

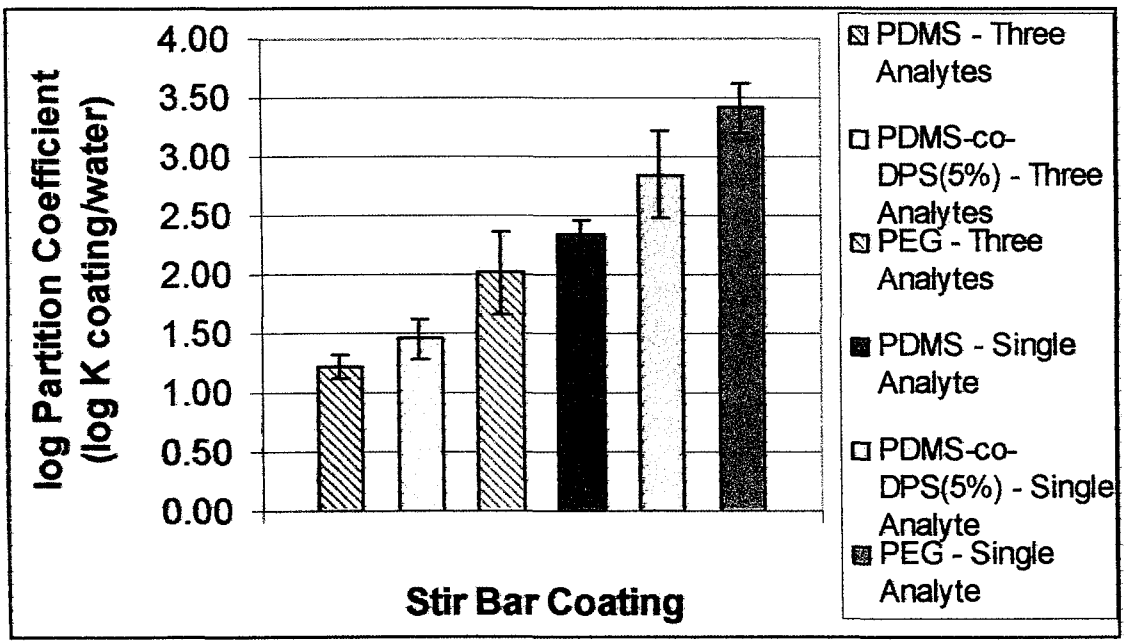


Figure 3.19: Comparison of Experimental Log Paritition Coefficients for Pentachlorophenol for PDMS-, PDMS-co-DPS(5%)-, and PEG-coated HPBars, with and without competition from the other analytes

In Figure 3.19, there is a clear decrease in all partition coefficients for PCP when competing analytes are introduced into the same aqueous solution. Within the competitive and non-competitive groupings, the trends do not differ. The PEG-coated HPBar is still the most efficient at extracting PCP from water, whether there are interfering analytes present or not. However when comparing the specific coatings in the competitive and non-competitive experiments, one can see that the extraction efficiency for PCP decreased in all coatings with the presence of other analytes. The PDMS- and PDMS-co-DPS(5%)-coated HPBars have a greater affinity for naphthalene and PCB77, meaning they would readily extract those two analytes as opposed to PCP. Therefore, the partition coefficient for PCP decreases in those two phases when naphthalene and PCB77 are present. As for the PEG-coated HPBar, the presence of other analytes will naturally result in some vacant sites being occupied, leading to a decreased extraction of PCP. Also, it is possible that the naphthalene and PCB77 were merely adsorbed onto the surface of the solid-phase, sterically hindering the absorption of PCP into the phase. This would result in less PCP being extracted, decreasing the partition coefficient. Therefore, even though PEG had the greatest affinity for PCP, its partition coefficient was still decreased when competing analytes were present. A more indepth explanation of these phenomena follows.

When discussing the competition effects of multiple analytes in solution, one must also consider whether one is using the process of adsorption or absorption. If the analyte is only adsorbed onto the solid-phase, then the total surface area of the solid-phase will dictate how much can be extracted and that value will be the saturation limit.

If the analyte is absorbed, then the amount extracted would be greater than what would fit on the surface area of the coating.

Figure 3.20 shows the molecular measurements for the analytes using PC Spartan Software.

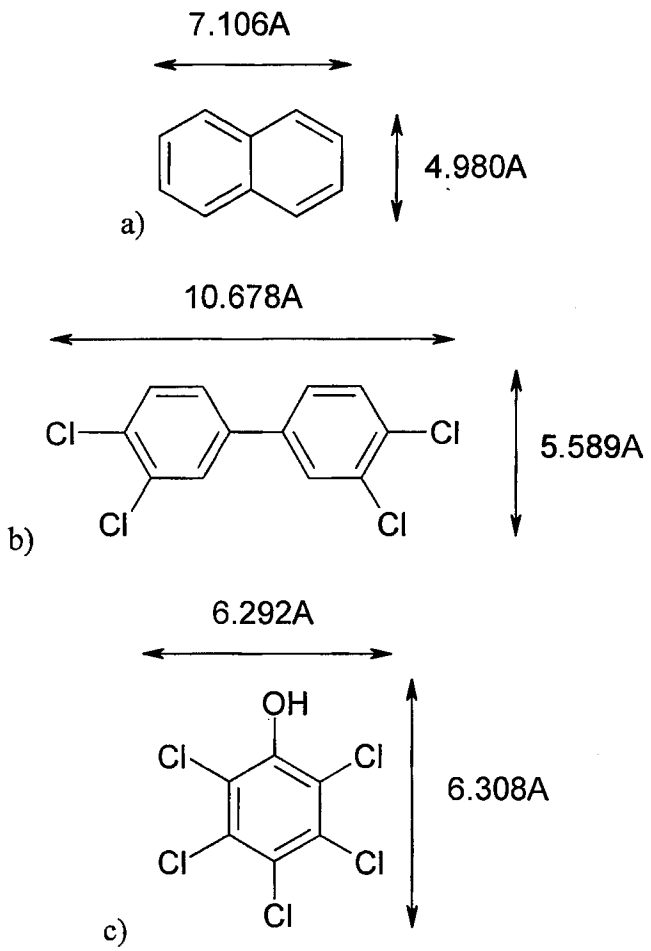


Figure 3.20: Molecular Measurements of a) Naphthalene; b) 3,3',4,4'-Tetrachlorobiphenyl; and c) Pentanchlorophenol using PC Spartan Software

From the above measurements, the approximate area can be calculated:

Firstly: $Area = length \times width$ and $1A = 1 \times 10^{-10} m$

Then: for Naphthalene, Area= (7.106×10^{-10})m x (4.980×10^{-10})m

$= 35.4 \times 10^{-20} m^2$

$= 35.4 \times 10^{-14} mm^2$

Total Stir Bar Surface Area can be equated with the surface area of the PTFE tubing which is in the form of a cylinder:

$$SA_{cylinder} = 2\pi r^2 + 2\pi rh$$ Where r = radius = 2mm

h = height = 8 mm

Therefore, $SA_{cylinder} = 2\pi 2^2 + 2\pi(2)(8) = 125.6\ mm^2$

The total amount of naphthalene that can cover the surface of the stir bar is:

$$Molecules_{naphthalene} = \frac{SA_{stirbar}}{A_{naphthalene}} = \frac{125.6}{(35.4 \times 10^{-14})} = 3.55 \times 10^{14}\ molecules$$

Then, to get the number of moles of naphthalene, divide by Avogadro's Number:

$$Moles_{naphthalene} = \frac{Molecules}{Avogadro's Number} = \frac{3.55 \times 10^{14}\ molecules}{6.022 \times 10^{23}\ molecules/mole} = 5.89 \times 10^{-10}\ mol$$

Then, to get the mass of naphthalene, multiply by the molecular weight:

$$Moles_{naphthalene} = \frac{mol}{g/mol} = \frac{5.89 \times 10^{-10}\ mol}{128 g/mol} = 7.5 \times 10^{-8}\ g = 75 ng$$

Therefore, approximately 75 ng of naphthalene can cover the surface area of the stir bar if only adsorption occurs. Similarly, approximately 102 ng of 3,3',4,4'-tetrachlorobiphenyl and 140 ng of pentachlorophenol can fill the surface area of the stir bar when only adsorption occurs.

By comparing these values to the actual amounts of analyte that were extracted, one can determine whether only adsorption occurred, or whether

absorption was also involved. To calculate the area of the amount of analyte extraction, one must simply reverse the calculation above.

Table 3.6 shows the amount of analyte extracted by each stir bar and their respective areas.

Amount Extracted	Unit	PCP – 266 g/mol	PCB77 – 292 g/mol	Naphthalene – 128 g/mol	Total Area of All Analytes
PDMS	g	6.48E-08	1.96E-08	3.00E-07	
	moles	2.44E-10	6.71E-11	2.34E-09	
	molecules	1.47E+14	4.04E+13	1.41E+15	
Total Area	mm^2	**58.2**	**24.1**	**499.6**	**582.0**
PDMS-co-DPS	g	5.70E-08	7.80E-09	2.96E-07	
	moles	2.14E-10	2.67E-11	2.31E-09	
	molecules	1.29E+14	1.61E+13	1.39E+15	
Total Area	mm^2	**51.2**	**9.6**	**493.0**	**553.8**
PEG	g	8.00E-08	1.82E-08	1.70E-07	
	moles	3.01E-10	6.23E-11	1.33E-09	
	molecules	1.81E+14	3.75E+13	8.00E+14	
Total Area	mm^2	**71.9**	**22.4**	**283.1**	**377.4**
Total Surface Area of Stir bar	mm^2				**125.6**

Table 3.6: Total Area of Analytes for Multianalyte Extraction for PDMS-, PDMS-co-DPS(5%)-, and PEG-coated HPBars

From Table 3.6, the total area of analytes in each phase is higher than that of the stir bar surface area limit of 125.6 mm^2. Therefore, the analytes were absorbed into the coating as well as adsorbing onto the surface.

The values from Table 3.6 must be compared to the amount of analyte extracted when there was only a single analyte in solution. This will show whether the amounts have decreased due to the presence of other analytes. As expected, the amounts of analyte extracted by each stir bar decreased when other analytes were present. Table 3.7 shows the amounts of analyte extracted and their respective areas for a typical single analyte extraction.

Amount Extracted	Unit	Single Analyte - PCP	Single Analyte - PCB77	Single Analyte - Naphthalene
PDMS	g	7.00E-08	1.30E-07	2.70E-06
	moles	2.63E-10	4.47E-10	2.11E-08
	molecules	1.58E+14	2.69E+14	1.27E+16
Total Area	mm^2	**62.9**	**160.5**	**4496.7**
PDMS-co-DPS	g	9.15E-08	1.57E-07	3.20E-06
	moles	3.44E-10	5.37E-10	2.50E-08
	molecules	2.07E+14	3.23E+14	1.51E+16
Total Area	mm^2	**82.2**	**193.1**	**5329.5**
PEG	g	1.90E-07	4.80E-08	3.70E-07
	moles	7.14E-10	1.64E-10	2.89E-09
	molecules	4.30E+14	9.90E+13	1.74E+15
Total Area	mm^2	**170.8**	**59.1**	**616.2**
Total Surface Area of Stir bar	mm^2			**125.6**

Table 3.7: Total Area of Analytes for Single-analyte Extraction for PDMS-, PDMS-co-DPS(5%)-, and PEG-coated HPBars

From Table 3.7, in some instances the area of analyte extracted for the single analyte extraction was greater than the total area of analyte that would fill the surface area of the stir bar. In other cases, the area of analyte is lower than the stir bar area limit. In these cases, the low result was from the stir bar coating that had the least affinity for that specific analyte. For example, in Table 3.7, one can see that the total area for PCB77 extracted by the PEG-coated HPBar was approximately 59.1 mm^2, which is much lower than the 125.6 mm^2 limit set by the stir bar itself. Also, one must note that the analyte-areas extracted by the PDMS-coated and PDMS-co-DPS(5%)-coated HPBars are well above the limit at 160.5 and 193.1 mm2, respectively. This is as expected since these two coatings do not have a great affinity for PCP.

Since one is able to obtain amounts of analyte that result in areas greater than the surface area of the stir bar, one can assume that both adsorption and absorption are occurring during extraction. Therefore, the decrease in partition coefficients for an

analyte competing with another may be a result of more than just the occupancy of vacant sites in the entire solid-phase. The partition coefficient is actually the activity of an analyte in one phase compared to its activity in another. When the activity coefficients are equal to 1, then the ratio simply depends on the concentration of analyte in each phase.

The trend in Figure 3.19 was different than the trend seen in Figures 3.17 and 3.18. This can be explained by a change in the activity of pentachlorophenol. When other analytes are present, it is possible that the activity of pentachlorophenol changed since it becomes a charged species in water. This would result in the decrease in partition coefficient seen in Figure 3.19.

Another reason for a change in partition coefficient is steric hindrance. Since it has been proven that both adsorption and absorption are occurring, it is possible that the portion of analyte adsorbing onto the surface of the stir bar could sterically hinder the extraction of other analytes. In Figures 3.17 and 3.18, there is a decrease in the partition coefficient obtained by the PDMS-coated HPBar and the PDMS-co-DPS(5%)-coated HPBar, respectively. For the PDMS phase, it was stated that since PCB77 has a larger Octanol-Water partition coefficient than naphthalene, it is more soluble in a nonpolar phase. Therefore, the PDMS phase has a greater affinity for PCB77. If some of the PCB77 adsorbs onto the surface, the naphthalene would encounter steric hinderance since the PCB77 is a larger molecule. Steric hinderance would decrease the amount of naphthalene that is able to both adsorb onto and absorb into the solid-phase, lowering the partition coefficient. Similarly, apart from the PDMS-co-DPS(5%) phase having a greater affinity for naphthalene due to it being

more aromatic than PCB77, there is a possibility that some of the naphthalene was adsorbed onto the surface. The would hinder the PCB77 from being either adsorbed or absorbed by the coating since it needs more area to be able to adsorb onto or absorb into the coating.

Another variable to mention is the initial concentration of all the analytes in the multianalyte extraction. The concentration of both PCP and PCB77 were approximately 174 ppb where as the concentration of naphthalene was approximately 696 ppb. The naphthalene was at a higher concentration than the other two analytes because GC-FID was used for its analysis. GC-FID is roughly 1000 times less sensitive than the ECD detector, requiring a sample that is more concentrated with the analyte of interest. This would mean that a large amount of analyte would initially bombard the surface of the stir bar, first adsorbing onto the surface and then being absorbed into the coating. If the stir bar was not in solution for a long period of time (sorption time was 30 minutes) then it is possible that the analyte did not absorb to a great degree into the coating. Therefore, two things can remedy this. Either the time can be lengthened to accommodate the time it takes for absorption to occur, or a lower concentration can be used so that the solid-phase is bombarded with less analyte and the adsorbed analyte can diffuse more quickly through the solid-phase.

From these explanations, it is evident that there indeed was competition between analytes in the same solution, resulting in steric hinderance, possible change in analyte activities, and build up of analyte on the surface of the stir bar. The ideal solution to these problems is to decrease the concentration of the analytes in solution so that competition effects are minimized.

3.7 Extraction from Rideau River Water spiked with 3,3',4,4'-Tetrachlorobiphenyl

As may occur with the presence of other analytes, fulvic and humic acids in Rideau River Water could also interfere with the extraction of a specific analyte. Figure 3.21 shows the experimental partition coefficients of PCB77 in Rideau River water compared to those in distilled water.

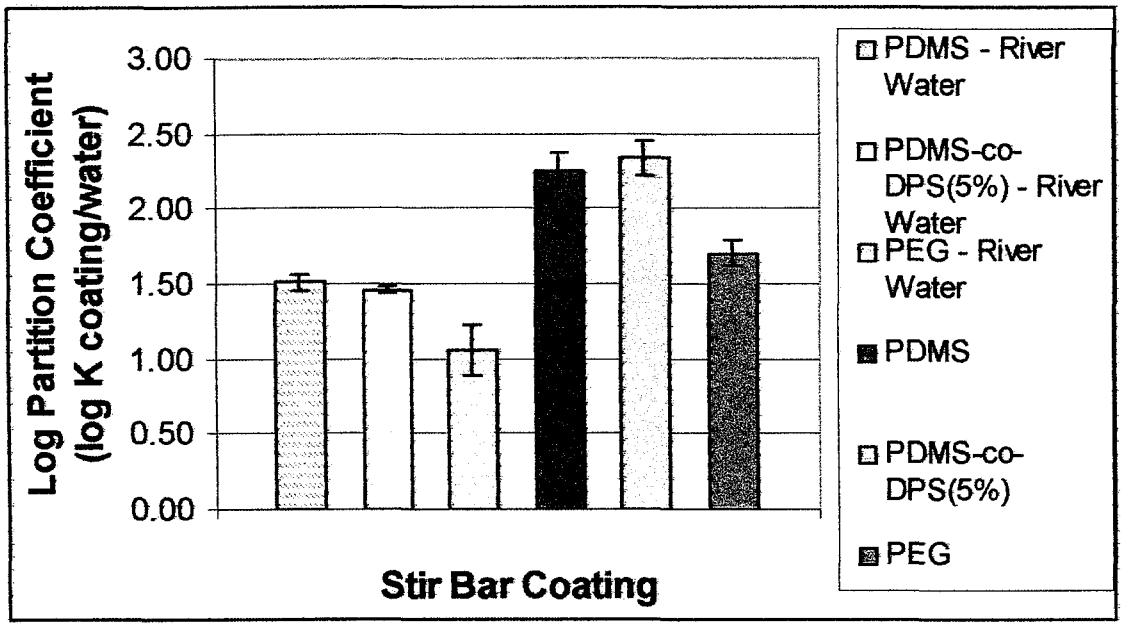


Figure 3.21: Experimental Partition Coefficients of 3,3',4,4'-Tetrachlorobiphenyl in Rideau River and distilled water

The experimental partition coefficients of PCB77 in Rideau River water were lower than those in distilled water. However, the calculated mass balance was not 100% in these experiments. Table 3.8 shows the percent loss (which indicates the difference between the total mass of analyte present before and after the extraction) of PCB77 for each coated stir bar.

Stir Bar (coating)	Percent Loss of Analyte		
	24 hours	72 hours	80 hours
PDMS	36.2	32.7	7.4
PDMS-co-DPS(5%)	42.6	19.8	14.4
PEG	56.0	46.1	15.7

Table 3.8: Percent Loss of PCB77 from Rideau River Water for PDMS-, PDMS-co-DPS(5%)- and PEG-coated HPBars

There are many reasons that this loss of analyte could occur. One of the most likely possibilities is that PCB77 adsorbs onto the fulvic and humic acids in the river water solution. By forming a complex with the acids, one obtains un-extractable PCB77, whether the extraction is done by coated stir bar, or organic solvent. Therefore, it looks as if some of the PCB77 has disappeared when in fact it still must still be in the aqueous solution. Another possibility is that the PCB77 adsorbs onto the fulvic and humic acids; fulvic/humic acid-adsorbed PCB77 and free-PCB77 are extracted by the coated stir bar, but only the free-PCB77 desorbes into the organic solvent. However, this should result in a constant decrease in partition coefficient over time, since the stir bar would become less and less effective at extracting the analyte. Figure 22 shows the partition coefficients of PCB77 in river water after three time periods.

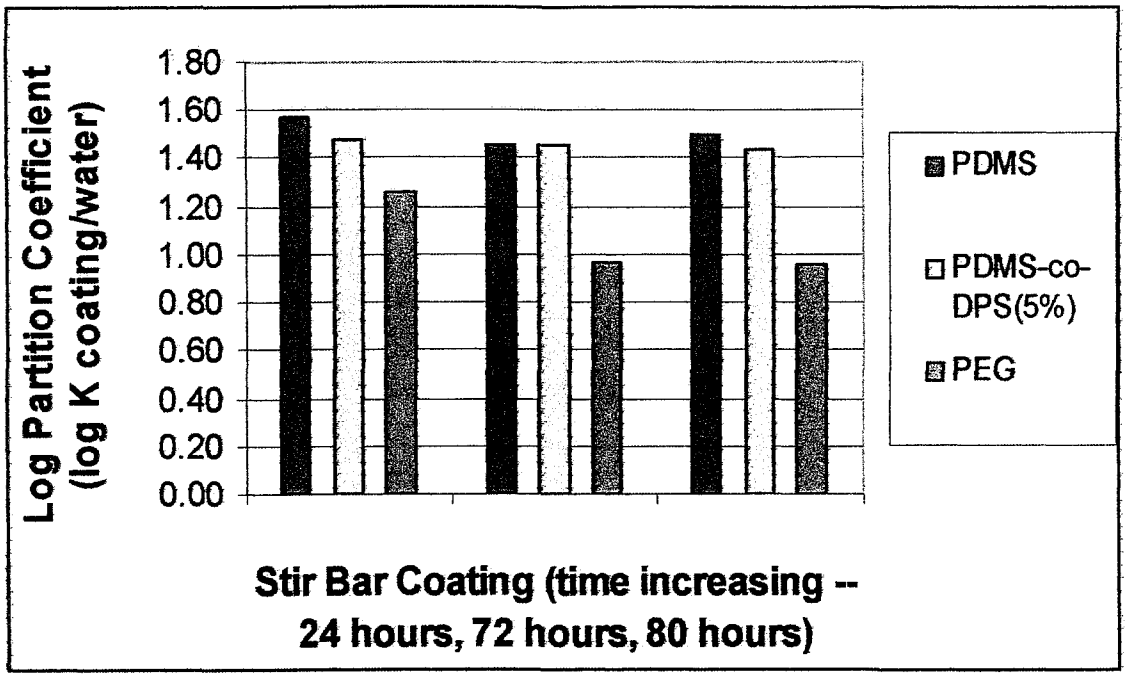


Figure 3.22: Experimental Partition Coefficients of PCB77 after extraction from spiked Rideau River water at 24 hours, 72 hours, and 80 hours after preparation of solution

From Figure 3.22, only the PEG-coated HPBar has a substantial decrease in partition coefficient, possibly because PEG is a polar phase and the acids are also polar. This would result in an increased adsorption of those acids over time, specifically in the PEG-coated HPBar.

To summarize, three situations could occur to affect the extraction outcome of an HPBar:

1. The surface of the solid-phase could be physically blocked by the fulvic and humic acids;
2. The solid-phase could change structurally because of the ad/absorption of the acids; and
3. Over time, more PCB77 is adsorbed on the fulvic and humic acids, resulting in time-dependent partition coefficients.

In situation 1, the fulvic and humic acids would adsorb onto the surface of the coating and since they are such large molecules, would hinder the PCB77 from coming in contact with the surface. This would result in a lower recovery of the analyte.

In situation 2, the adsorption of the acids onto the stir bar could change the polarity of the coating since the acids are polar compounds. This could, consequently, change the affinity of the coating for the analyte. One will recall that PCB77 is very soluble in a nonpolar phase. Therefore, if the phase was made more polar, the solubility of PCB77 in the coating would be compromised.

In situation 3, the adsorption of PCB77 onto the acids would result in the incorporation of PCB77 into extremely large molecules. Then, a combination of situation 1 and 2 would occur. Either the complexes adsorbed by the stir bar would create steric hindrance for other compounds, or the adsorption of these compounds would change the affinity of the coating for the non-adsorbed PCB77. If this is time-dependent, then the recovery would decrease as more PCB77 is adsorbed by the acids.

Whichever the situation, the partition coefficient would decrease when compared to the extraction of PCB77 free from interferences.

3.8 Limits of Detection for PDMS, PDMS-co-DPS(5%), and PEG Solid-Phases

As stated and illustrated in section 1.8, one can determine the actual limit of detection of the analytes of interest. The parameters have been changed to include the experimental partition coefficients and phase ratios. Table 3.9 shows the limits of detection for each coated-stir bar (not the coating on its own) and each analyte.

Stir Bar Coating	Analyte	Partition Coefficient	Phase Ratio (β)	Limit of Detection (ng)	LOD for 1mL of Aqueous Sample (ng)
PDMS	Naphthalene	229	80	1349	675
	PCB77	179	80	1.5	0.72
	PCP - low conc.	219	80	1.4	0.68
PDMS-co-DPS(5%)	Naphthalene	309	167	1539	770
	PCB77	216	167	1.8	0.89
	PCP - low conc.	692	167	1.2	0.62
PEG	Naphthalene	31	200	7451	3726
	PCB77	51	200	4.9	2.46
	PCP - low conc.	2291	200	1.1	0.54

Table 3.9: Limits of Detection (LOD) for PDMS-, PDMS-co-DPS(5%)- and PEG-coated HPBars for the extraction of Naphthalene, 3,3',4,4'-Tetrachlorobiphenyl, and Pentachlorophenol. Highlighted values show lowest LOD for that specific analyte, but not necessarily the coating that was best at extracting that analyte.

The solid-phase that was best at extracting Naphthalene was the PDMS-co-DPS(5%) phase, but the PDMS had a detection limit that was lower at 675 ng/mL. This is due to the fact that the PDMS-coated HPBar possessed approximately 25 μL of coating, roughly twice as much as the PDMS-co-DPS(5%)-coated HPBar. Therefore, the phase ratio because smaller for the PDMS-coating, resulting in a lower detection limit. If one could increase the amount of solid phase on the PDMS-co-DPS(5%)-coated HPBar, it would prove to be the best at extracting Naphthalene. This

could be done by changing the ratios of the precursors for the sol-gel reaction, or re-coating the stir bar twice or more to produce more layers of coating.

The solid-phase that was best at extracting PCB77 was also the PDMS-co-DPS(5%), but again, the PDMS-coated HPBar had a lower detection limit at 0.72 ng/mL. This is due to the same reasons stated above.

The solid-phase that was bext at extracting PCP was the PEG, which also had the lowest detection limit of 0.54 ng/mL.

Drinking water guidelines for the analytes are 500 ng/mL for Naphthalene, 3 ng/mL for PCB77, and 60 ng/mL for PCP [Health Canada, 2006]. From Table #, it is evident that the lowest detection limits for PCB77 and PCP prove to be less than the drinking water guidelines. However, for Naphthalene, the LOD was higher than the drinking water guideline. The experimental limits of detection could be decreased by increasing the volume of aqueous sample. If the volume of water (V_W) increased from 2 mL to 10 mL, then the LOD for the PDMS-coated HPBar would be as follows:

$$\text{From: } \frac{m_{PDMS}}{m_O} = \frac{\frac{K_{PDMS/W}}{\beta}}{1+\frac{K_{PDMS/W}}{\beta}} \quad \text{and}$$

$$\frac{1\mu g}{m_O} = \frac{\frac{K_{PDMS/W}}{\beta}}{1+\frac{K_{PDMS/W}}{\beta}} = \frac{\frac{10^{3.01}}{200}}{(1+\frac{10^{3.01}}{200})} = 1.2\mu g/mL \; \frac{V_W}{V_{PDMS}} = \beta$$

$$\text{Where: } \beta = \frac{10000\mu L}{25\mu L} = 400 \quad \text{and} \quad K_{PDMS/W} = 229 \quad \text{and} \quad m_{PDMS} = 1\mu g$$

$$\text{Therefore: } \frac{1\mu g}{m_o} = \frac{\frac{229}{400}}{(1+\frac{229}{400})} = 2.7\mu g \text{ in 10 mL}$$

New limit of Detection = 0.270 μg/mL = 270 ng/mL

This new limit of detection for Naphthalene is smaller than the drinking water guideline set by Health Canada. Therefore, by increasing the volume of aqueous phase, one can decrease the limit of detection and the method will be reliable for naphthalene detection.

Kolahgar et al did a study of polycyclic aromatic hydrocarbons using Stir Bar Sorptive Extraction and Thermal Desorption and the limit of detection obtained for naphthalene was 0.5 ng/L [Kolahgar et al, 2002] This is roughly 1000 times less than that obtained for this research project. What Kolahgar did was test the effects of the addition of methanol and hyamine to solution during extraction. This consequently aided increasing the extraction recoveries and lowering the detection limit because less analyte was adsorb onto the walls of the beaker. Therefore, it is possible that in this research the limits of detection could be decreased by adding a small amount of methanol.

Popp et al did a study of polychlorinated biphenyls using Stir Bar Sorptive Extraction and Thermal Desorption and the limit of detection obtained for PCB77 was 0.10 ng/L [Popp et al, 2005]. This is also less than the detection limit obtained for this research. Popp et all performed extractions with the addition of methanol, as did Kolahgar et al. PCBs are an extremely lipophilic group of congeners. When extracted from solution, it is possible that some of the analyte will adsorb onto the glass walls of the beaker. With the addition of methanol, the adhesion affects of water

are minimized, allowing for less PCB to adsorb onto the surface of the glass beaker, resulting in a greater extraction since there is a minimized loss of analyte [Popp et al, 2005].

Kawaguchi et al did a study of chlorinated phenols using Stir Bar Sorptive Extraction and Thermal Desorption and the limit of detection obtained for PCP was 2 pg/mL. Again, this is smaller than the LOD obtained for this research project. The difference here is that Kawaguchi et al first derivatized the pentachlorophenol and then extracted the acetylated-PCP from solution. By first derivatizing the compound, it is made neutral, allowing more to be extracted by the stir bar. This would then result in lower recoveries [Kawaguchi et al, 2005]. Therefore, to lower the limits of detection for PCP in the PEG-coated HPBar, the PCP could first be derivatized and then extracted. However, the objective was to find a method which could extract a large amount of PCP from water without pre-treatment. This objective was ultimately reached since the PEG-coated HPBar had the lowest detection limit out of the three coated stir bars.

Though the experimental limits of detection obtained for this research project were consistently higher than other studies conducted using the commercially available coated stir bars, all the LODs obtained were lower than the guidelines set by Health Canada. This is of great importance when having to deal with the question of whether a water source is safe and drinkable. By having detection limits lower than the guidelines, one can be sure that the results will be trustworthy whether there is a large margin of error or not.

In order to be able to tell whether this method is better than other available methods, one must compare certain aspects such as speed, limits of detection, cost, and robustness.

SPE and SBSE both have larges amounts of solid phase, resulting in similar limits of detection. As for speed, the extraction of analytes by SPE is much faster than SBSE. However, according to the analyte, one could have short SBSE sorption times. Also, both methods have the same degree of robustness.

Though SPE and SBSE seem relatively similar in terms of amount of solid-phase and robustness, a comparison of cost between SPE tubes and SBSE stir bars (commercially available from Gerstel) shows that SBSE stir bars are relatively inexpensive, and consequently more advantageous to use.

A package of 54 single-use C_{18} SPE tubes costs approximately $140 according to the Supelco catalogue, making the cost of a single tube approximately $2.50. A package of 10 multi-use Gerstel Twister® Stir Bars costs approximately $380, making the cost of a single stir bar approximately $3.80. Therefore, it is evident that the stir bars will be cheaper in the long run since one can use them for multiple extractions. Also, when using an SPE tube, one must use an organic solvent to remove the analyte from the solid phase. When using SBSE, one uses very little organic solvent for liquid desorption, or zero organic solvent for thermal desorption. Therefore, though SPE and SBSE are very similar in many aspects, there are some key elements which prove that SBSE is infact more advantageous than SPE.

3.9 Linear Dynamic Ranges for PDMS-, PDMS-co-DPS(5%)-, and PEG-coated HPBars

The linear dynamic ranges for each stir bar were determined from plots of peak area versus concentration. These ranges are important in that they will show at what concentrations the stir bars are most sensitive and at what particular concentration they begin to lose sensitivity. Graphs of peak area versus concentration of analyte in water were plotted for the extraction of naphthalene using the PDMS-coated HPBar, PCB77 using the PDMS-co-DPS(5%)-coated HPBar, and PCP using the PEG-coated HPBar.

Figures 3.23, 3.24, and 3.25, shows the graphs of peak area versus concentration in water.

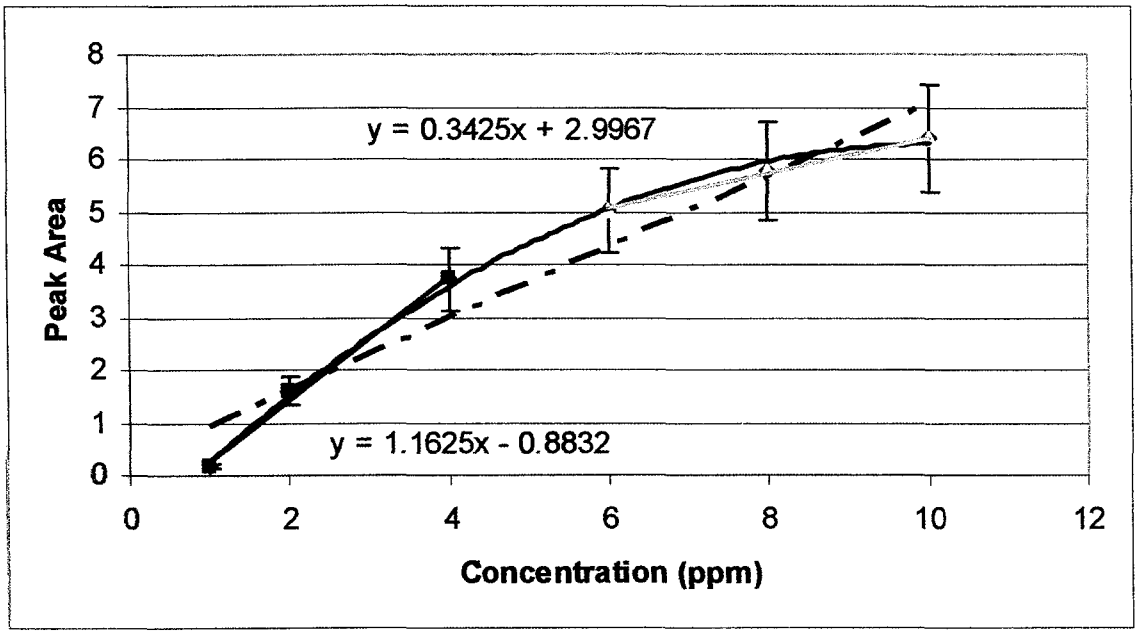


Figure 3.23: Peak area versus concentration of naphthalene in water using the PDMS-coated HPBar. Pink slope indicates approximate linear dynamic range, green slope indicates concentrations at which stir bar loses sensitivity.

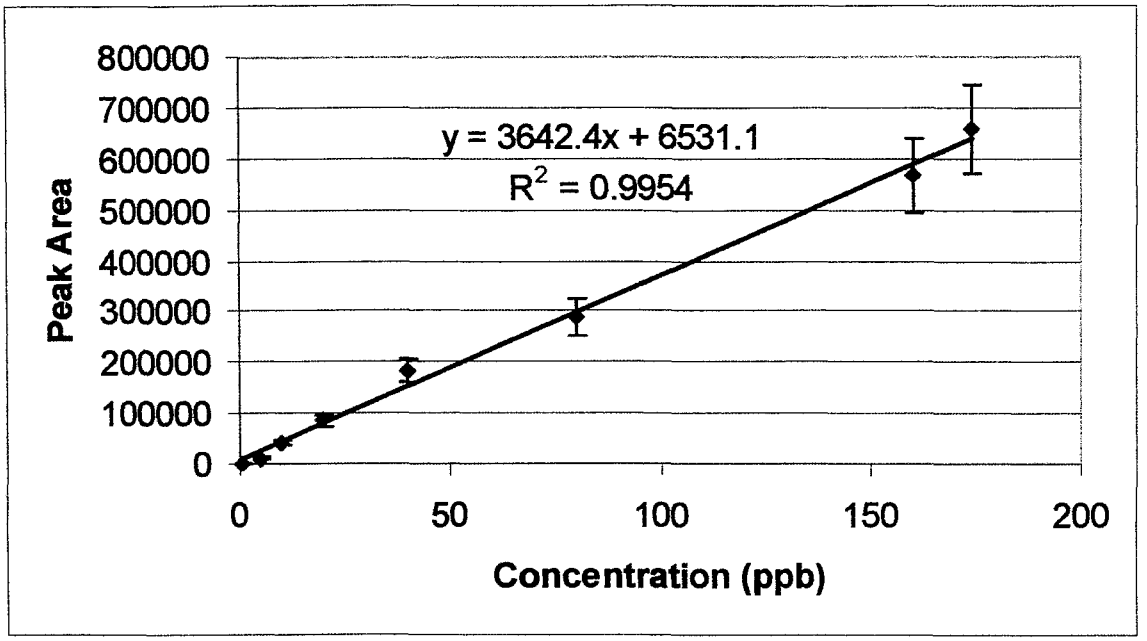


Figure 3.24: Peak area versus concentration of PCB77 in water using the PDMS-co-DPS(5%)-coated HPBar

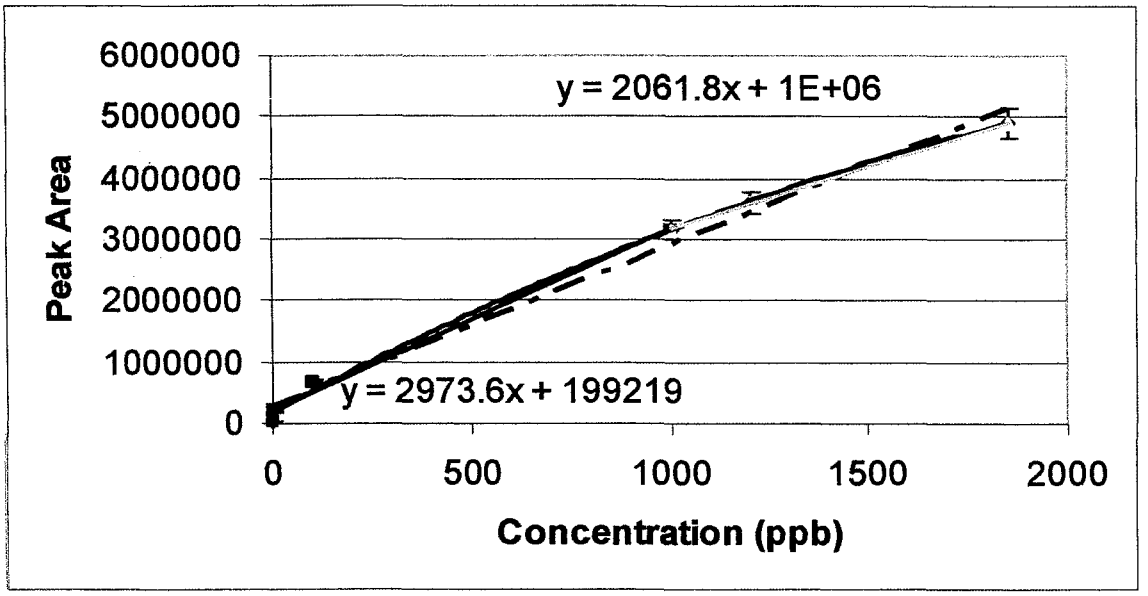


Figure 3.25: Peak Area versus Concentration of PCP in water using the PEG-coated HPBar. Pink slope indicates linear dynamic range, green slope indicates concentrations at which the stir bar loses sensitivity.

Therefore, the linear dynamic range (LDR) for naphthalene using the PDMS-coated HPBar is 0.7 μg/mL – 5 μg/mL. Similarly, the LDR for PCB77 using the PDMS-co-DPS(5%)-coated HPBar is 0.9 ng/mL – 174 ng/mL and for PCP using the PEG-coated HPBar is 0.5 ng/mL – 1000 ng/mL.

These ranges show that the analyses done all fall within the most sensitive concentration ranges for these stir bars, also indicating reliable results.

In Figure 3.24, the slope does not begin to approach zero. The reason for this is that the maximum solubility of PCB77 in water is approximately 174 ppb. Because of this, the upper limit of the linear dynamic range is automatically set to 174 ppb if the stir bar does not become less sensitive at lower concentrations. Therefore, the range is as stated above, from 0.9 ng/mL to 174 ng/mL.

4. CONCLUSION

Trends arose from the extraction of naphthalene, 3,3',4,4'-tetrachlorobiphenyl (PCB77), and pentachlorophenol (PCP) using all three coated stir bars. The order of increasing partition coefficients for naphthalene was: PEG < PDMS < PDMS-co-DPS(5%). For PCB77, the order of increasing partition coefficients was: PEG < PDMS < PDMS-co-DPS(5%). For PCP, the order of increasing partition coefficients was: PDMS < PDMS-co-DPS(5%) < PEG.

Limits of detection for naphthalene were found to be 0.680 μg/mL, 0.770 μg/mL, and 3.70 μg/mL for the PDMS, PDMS-co-DPS(5%), and PEG-coated HPBars, respectively. Limits of detection for 3,3',4,4'-tetrachlorobiphenyl were found to be 0.72 ng/mL, 0.89 ng/mL, and 2.50 ng/mL, respectively. Limits of detection for pentachlorophenol were found to be 7.20 ng/mL, 5.40 ng/mL, and 0.54 ng/mL, respectively.

The nonpolar coatings did not have reliable partition coefficients for PCP since they were dependent on the initial concentration in water, indicating concentrations that fell outside of the linear dynamic range for those stir bars. The PEG coating had the greatest extraction efficiency for the polar pentachlorophenol, supported by the fact that the partition coefficient remained independent of concentration.

The Linear Dynamic Ranges for naphthalene using the PDMS-coated HPbar, for 3,3',4,4'-tetrachlorobiphenyl using the PDMS-do-DPS(5%)-coated HPBar, and for PCP using the PEG-coated HPBar were 0.7 μg/mL – 5 μg/mL, 0.9 ng/mL – 174 ng/mL, and 0.5 ng/mL – 1000 ng/mL, respectively.

Competition and interference effects were analyzed by extraction from a solution containing all three analytes, as well as a sample of Rideau River water spiked with PCB77. Competition effects were seen between naphthalene and PCB77 due to their similarities in nonpolarity and aromaticity. Also, the presence of naphthalene and PCB77 lowered the amount of PCP that was extracted due to steric hindrance when those analytes were adsorbed onto the surface of the coatings. It was also found that the presence of organic acids in river water decreased the partition coefficients of PCB77, showing interference effects.

5. REFERENCES

Agricultural University of Worcraw, Properties of Humic Substances (**AUoW**), **2006**, http://www.ar.wroc.pl/~weber/kwasy2.htm

Alves, R.F., Nascimento, A.M.D., Nogueira, J.M.F., Characterization of the Aroma Profile of Madeira Wine by Sorptive Extraction Techniques, **2005**, Analytica Chimica Acta, 546 (11-21)

Baltussen, E., Sandra, P., David, F., Janssen, H-G., Cramers, C., Study into the Equilibrium Mechanism between Water and Poly(dimethylsiloxane) for Very Apolar Solutes: Adsorption or Sorption?, **1999**, 71(5213-5216)

Bemis, J.C., Nazarenko, D.A., Gasiewic, T.A., Coplanar Polychlorinated Biphenyls Activate the Aryl Hydrocarbon Receptor in Developing Tissues of Two TCDD-Responsive lacZ Mouse Lines, **2005**, Toxicological Sciences, 87 (529-536)

Benanou, D., Acrobas, F., de Roubin, M.R., David, F., Sandra, P., Analysis of Off-flavours in the Aquatic Environment by Stir Bar Sorptive Extraction-Thermal Desorption-Capillary GC/MS/Olfactometry, **2003**, Analytical and Bioanalytical Chemistry, 376 (69-77)

Bicchi, C., Iori, C., Rubiolo, P., Sandra, P., Headspace Sorptive Extraction (HSSE), Stir Bar Sorptive Extraction (SBSE), and Solid Phase Microextraction (SPME) Applied to the Analysis of Roasted Arabica Coffee and Coffee Brew, **2002**, Journal of Agricultural and Food Chemistry, 50 (449 – 459)

Brossa, L., Marce, R.M., Borrull, F., Pocurull, E., Determination of Endocrine Disruptors in Environmental Water Samples by Stir Bar Sorptive Extraction-Liquid Desorption-Large Volume Injection-Gas Chromatography, **2004**, Chromatographia, 61 (61-65)

Brown, C.L., Hock, W.K., Saunders, D.P., Jarman, J.H., Pesticides and the Environment, **1997**, University of Missouri, http://muextension.missouri.edu/explore/agguides/pests/g07520.htm

de Oliviera, F., A., Berto da Silveira, C., Denofre de Campos, S., Antonio de Campos, E., Carasek, E., The Use of a Thin Glass-Ceramic Rod as a Surface for Sol-Gel Coating in the Preparation of SPME Fibers, **2005**, Chromatographia, 61 (277-283)

Dislich, H., Klein, L.C., Sol-Gel Technology for Thin Films, Fibers, Preforms, Electronics and Specialty Shapes: Part II. Coatings, Thin Films and Surface Treatment, **1988**, William Andrew Publishing/Noyes

Environmental Protection Agency (**EPA**), **1989**, www.EPA.gov

Juan-Garcia, A., Manes, J., Font, G., Pico, Y., Evaluation of Solid-Phase Extraction and Stir-Bar Sorptive Extraction for the Determination of Fungicide Residues at Low-$\mu g\ kg^{-1}$ Levels in Grapes by Liquid Chromatography-Mass Spectrometry, **2004**, Journal of Chromatography A, 1050 (119-127)

Kawaguchi, M., Inoue, K., Sakui, N., Ito, R., Ixumi, S-I., Makino, T., Okanouchi, N., Nakazawa, H., Determination of Bisphenol A in River Water and Body Fluid Samples by Stir Bar Sorptive Extraction with In Situ Derivatization and Thermal Desorption-Gas Chromatography-Mass Spectrometry, **2004**, Journal of Chromatography B, 805 (41-48)

Kawaguchi, M., Inoue, K., Yoshimura, M., Sakui, N., Okanouchi, N., Ito, R., Yoshimura, Y., Nakazawa, H., Trace Analysis of Phenolic Xenoestrogens in Water Samples by Stir Bar Sorptive Extraction with In Situ Derivatization and Thermal Desorption-Gas Chromatography-Mass Spectrometry, **2004**, Journal of Chromatography A, 1041 (19-26)

Kawaguchi, M., Ishii, Y., Sakui, N., Okanouchi, N., Ito, R., Saito, K., Nakazawa, H., Stir Bar Sorptive Extraction with In Situ Derivatization and Thermal Desorption-Gas Chromatography-Mass Spectrometry for determination of Chlorophenols in Water and Body Fluid Samples, **2005**, Analytica Chimica Acta, 533 (57-65)

Kolahgar, B., Hoffmann, A., Heiden, A.C., Application of Stir Bar Sorptive Extraction to the Determination of Polycyclic Aromatic Hydrocarbons in Aqueous Samples, **2002**, Journal of Chromatography A, 963 (225-230)

Kruus, P., Demmer, M., McCaw, K., Chemicals in the Environment, **1991**, Polyscience Publications

Levin, Dr. Shulamit, Dr. Shulamit Levin, Sample Preparation using Solid-Phase Extraction, Medtechnica Analytical Department, **2006**, http://www.forumsci.co.il/HPLC/SPE_handouts.pdf

Liu, W., Wang, H., Guan, Y., Preparation of Stir Bars for Sorptive Extraction Using Sol-Gel Technology, **2004**, Journal of Chromatography A, 1045 (15-22)

Liu, W., Hu, Y., Hao, J., Xu, Y., Guan, Y., Determination of Organophosphorus Pesticides in Cucumber and Potato by Stir Bar Sorptive Extaction, **2005**, Journal of Chromatography A, 1095 (1-7)

Nakamura, S., Daishima, S., Simultaneous Determination of Alkylphenols and Bisphenol A in River Water by Stir Bar Sorptive Extraction with In Situ Acetylation and Thermal Desorption-Gas Chromatography-Mass Spectrometry, **2004**, Journal of Chromatography A, 1038 (291-294)

PAN Pesticides Database (**PI**), U.S. National Toxicology Program acute toxicity studies for Dioxin (2,3,7,8-TCDD), **2006**, www.pesticideinfo.org

Pfannkoch, E., Whitecavage, J.A., Kinton, V.R., Stir Bar Sorptive Extraction: Recovery of Organic Acids and Amines, **2003**, Gerstel (Application Note), www gerstelus.com

Popp, P., Bauer, C., Hauser, B., Keil, P., Wennrich, L., Extraction of Polycyclic Aromatic Hydrocarbons and Organochlorine Compounds from Water: A Comparison Between Solid-Phase Microextraction and Stir Bar Sorptive Extraction, **2003**, Journal of Separation Science, 26 (961-967)

Popp, P., Keil, P., Montero, L., Ruckert, M., Optimized Method for the Determination of 25 Polychlorinated Biphenyls in Water Samples using Stir Bar Sorptive Extraction followed by Thermodesorption-Gas Chromatography/Mass Spectrometry, **2005**, Journal of Chromatography A, 1071 (155-162)

Prochazka, H., Extraction of 2,2'-Dichlorobiphenyl, Naphthalene, and Atrazine using Stir Bar Soriton Extraction, **2004**, Carleton University

Shende, C., Kabir, A., Townsend, E., Malik, A., Sol-Gel Poly(ethylene glycol) Stationary Phase for High-Resolution Capillary Gas Chromatography, **2003**, Analytical Chemistry, 75 (3518-3530)

Sol-Gel Technology, **2005**, http://www.chemat.com/html/solgel.html

Standler, A., Schatzl, A., Klampfl, C.W., Buchberger, W., Determination of the Insect Repellent Bayrepel® in Pool and Lake Water by Gas Chromatography after Preconcentration with Solid-Phase Extraction and Stir-Bar-Sorptive Extraction, **2004**, Microchimica Acta, 148 (151-156)

Stopforth, A., Tredoux, A., Crouch, A., van Helden, P., Sandra, P., A Rapid Method of Diagnosing Pulmonary Tuberculosis using Stir Bar Sorptive Extraction-Thermal Desorption-Gas Chromatography-Mass Spectrometry, **2005**, Journal of Chromatography A, 1071 (135-139)

Wang, D., Chong, S.L., Malik, A., Sol-Gel Column Technology for Single-Step Deactivation, Coating, and Stationary-Phase Immobilization in High-Resolution Capillary Gas Chromatography, **1997**, Analytical Chemsitry, 69(4566-4576)

Zuin, V.G., Lopes, A.L., Yariwake, J.H., Augusto, F., Application of a Novel Sol-Gel Polydimethylsiloxane-Poly(vinyl alcohol) Solid-Phase Microextraction Fiber for Gas Chromatographic Determination of Pesticide Residues in Herbal Infusions, **2004**, Journal of Chromatography A, 1056 (21-26)

APPENDIX

Figure A.1 a) Infrared Spectrum of Poly(dimethylsiloxane) Solid-Phase

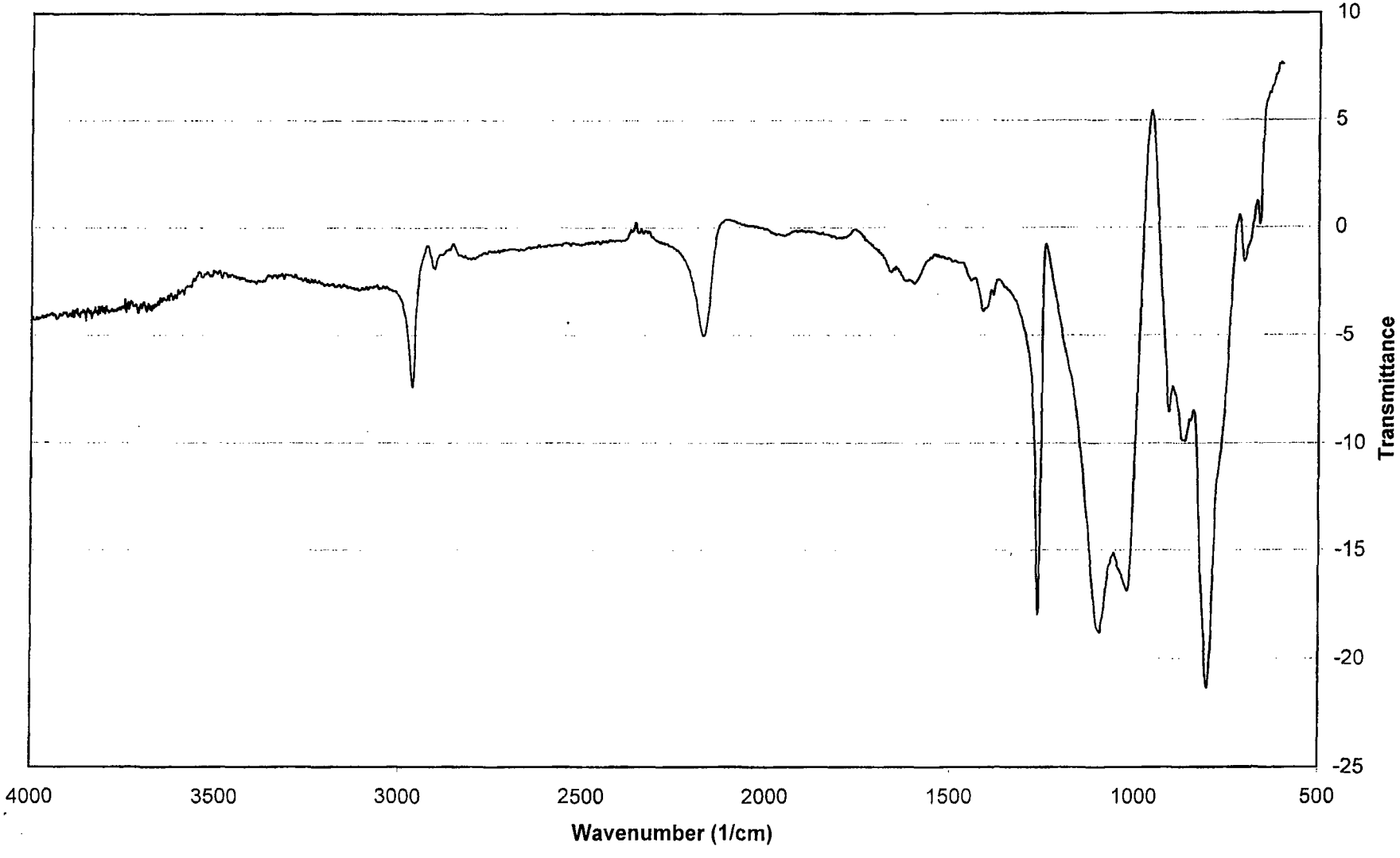
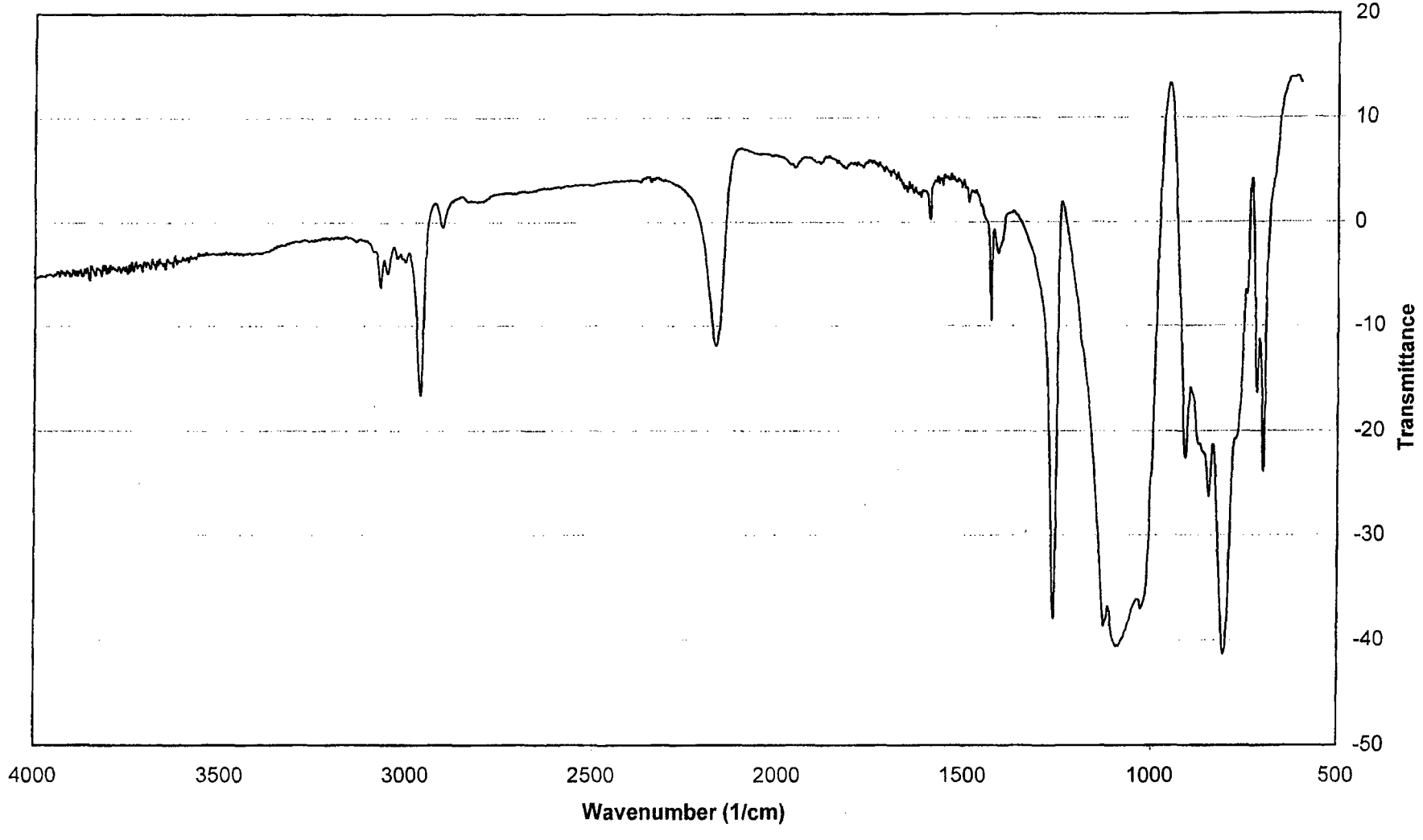


Figure A.1 b) Infrared Spectrum of Poly(dimethylsiloxane)-co-diphenylsiloxane(5%) Solid-Phase



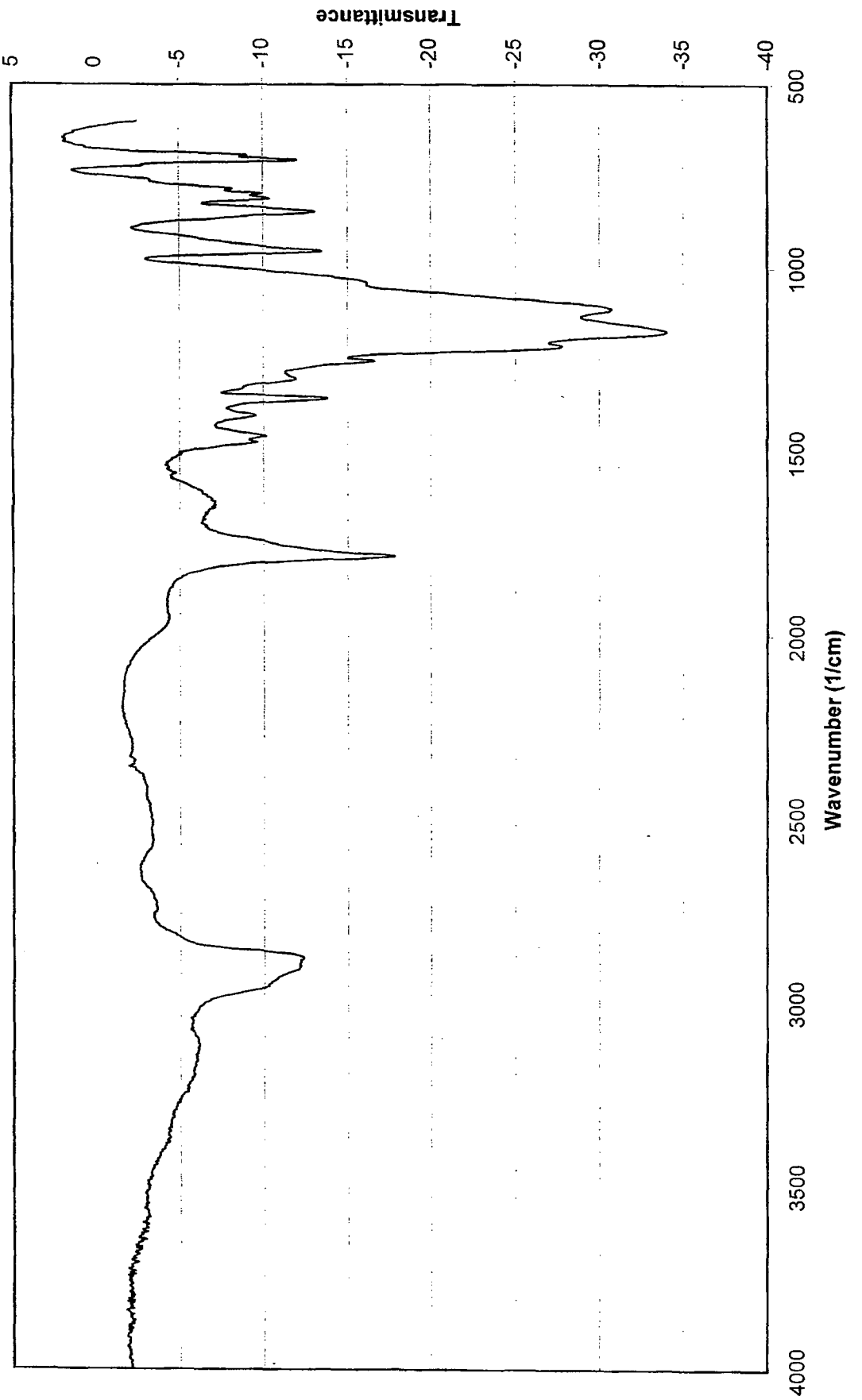


Figure A.1 c) Infrared Spectrum of Poly(ethylene glycol) Solid-Phase

Figure A.2: ^{13}C Nuclear Magnetic Resonance Spectrum of PDMS

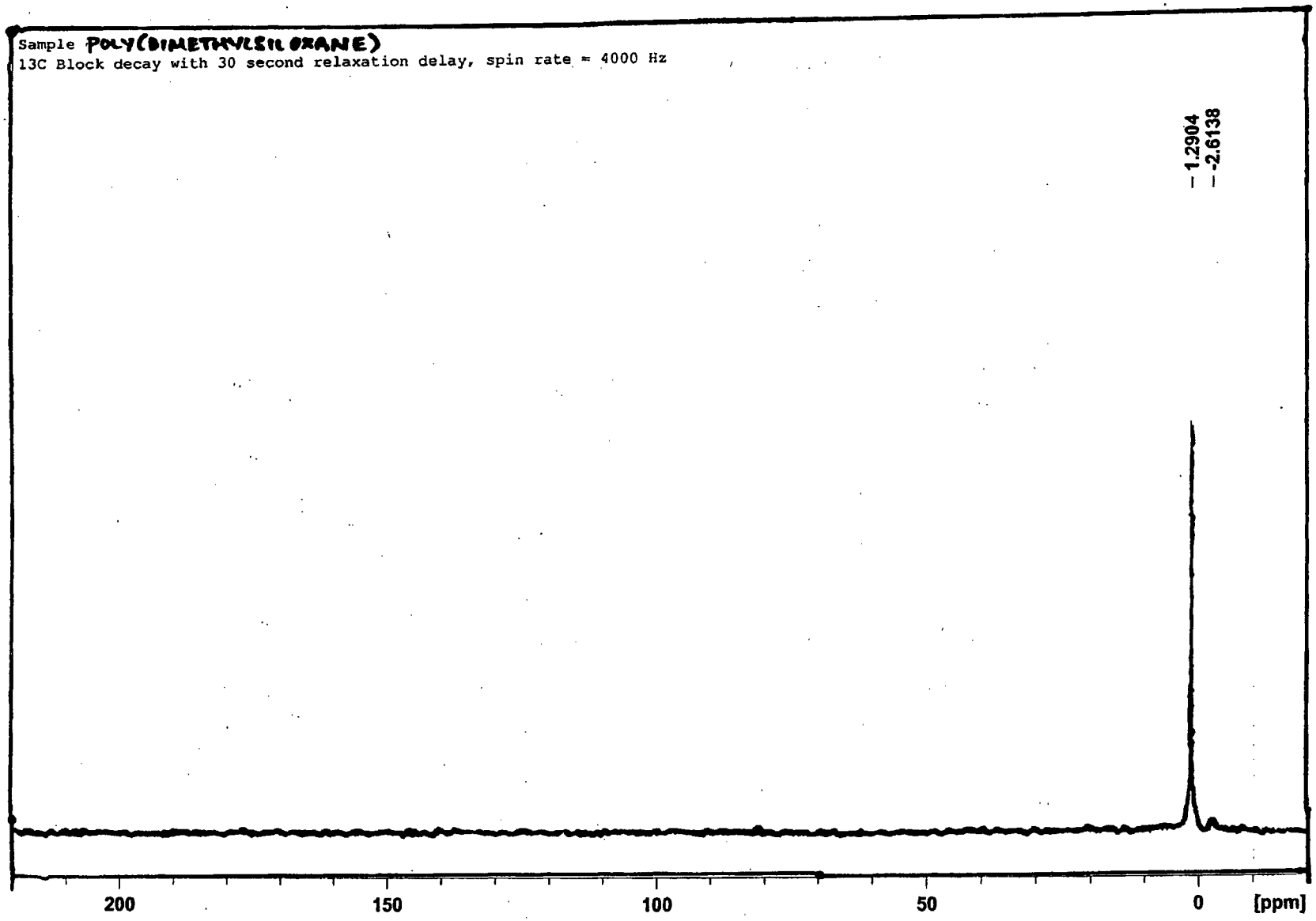


Figure A.3: ^{13}C Nuclear Magnetic Resonance Spectrum of PDMS-co-DPS(5%)

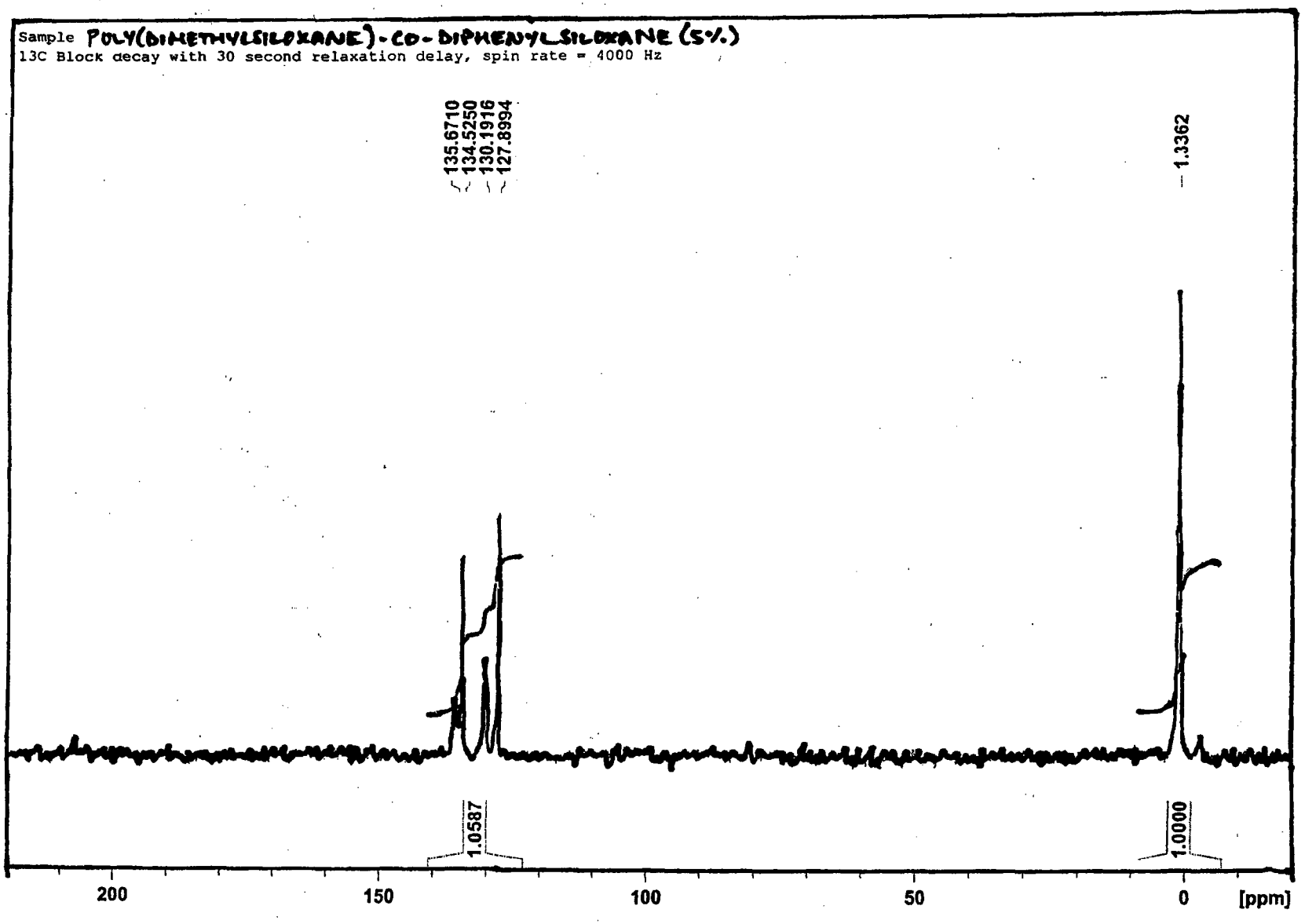


Figure A.4: ^{13}C Nuclear Magnetic Resonance Spectrum of PEG

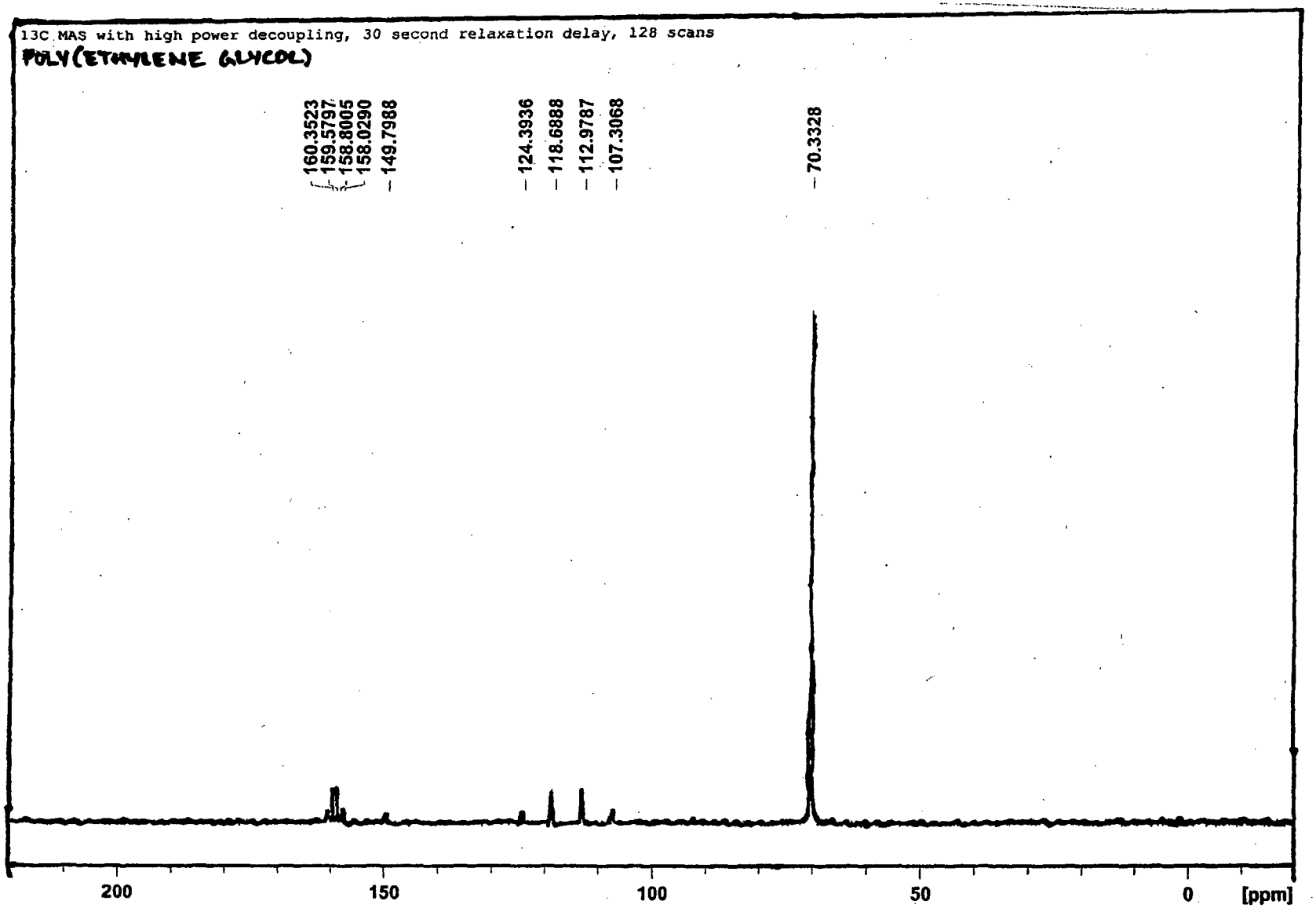


Figure A.5: Standard Calibration Curve for Naphthalene in Dichloromethane using GC-MS

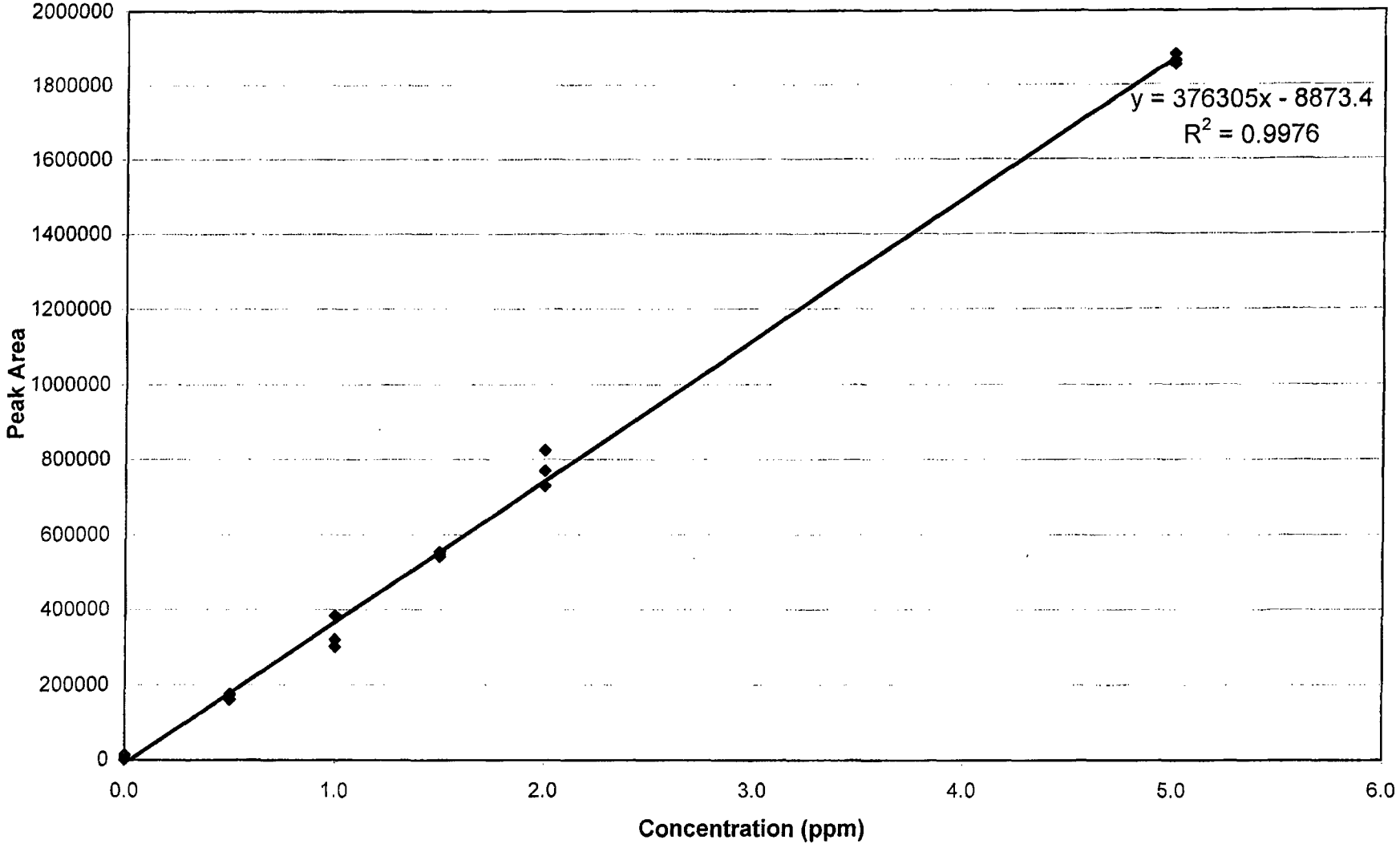


Figure A.6: Standard Calibration Curve of Naphthalene in Dichloromethane using GC-FID

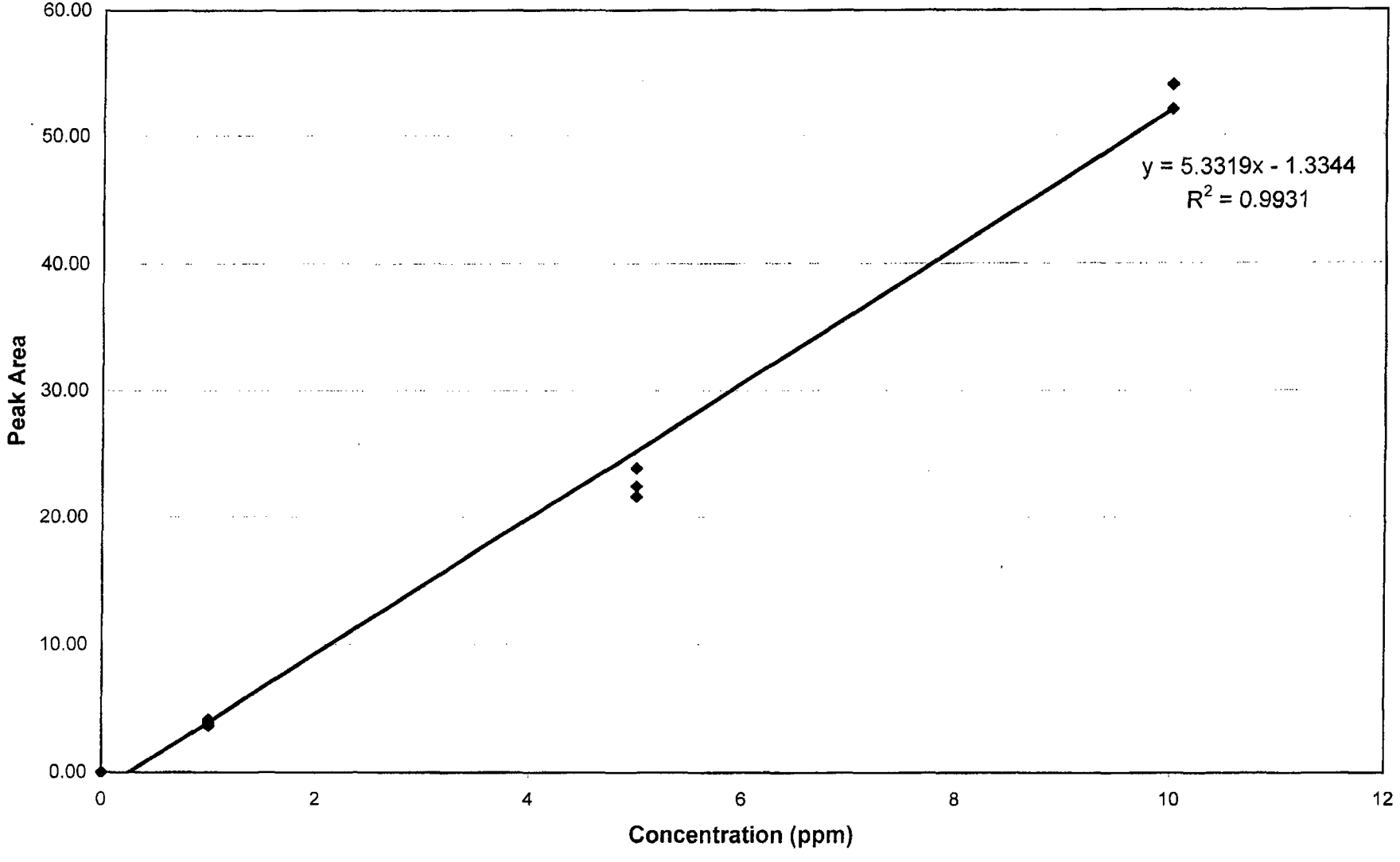


Figure A.7: Standard Calibration Curve for 3,3',4,4'-Tetrachlorobiphenyl in Hexane using GC-ECD

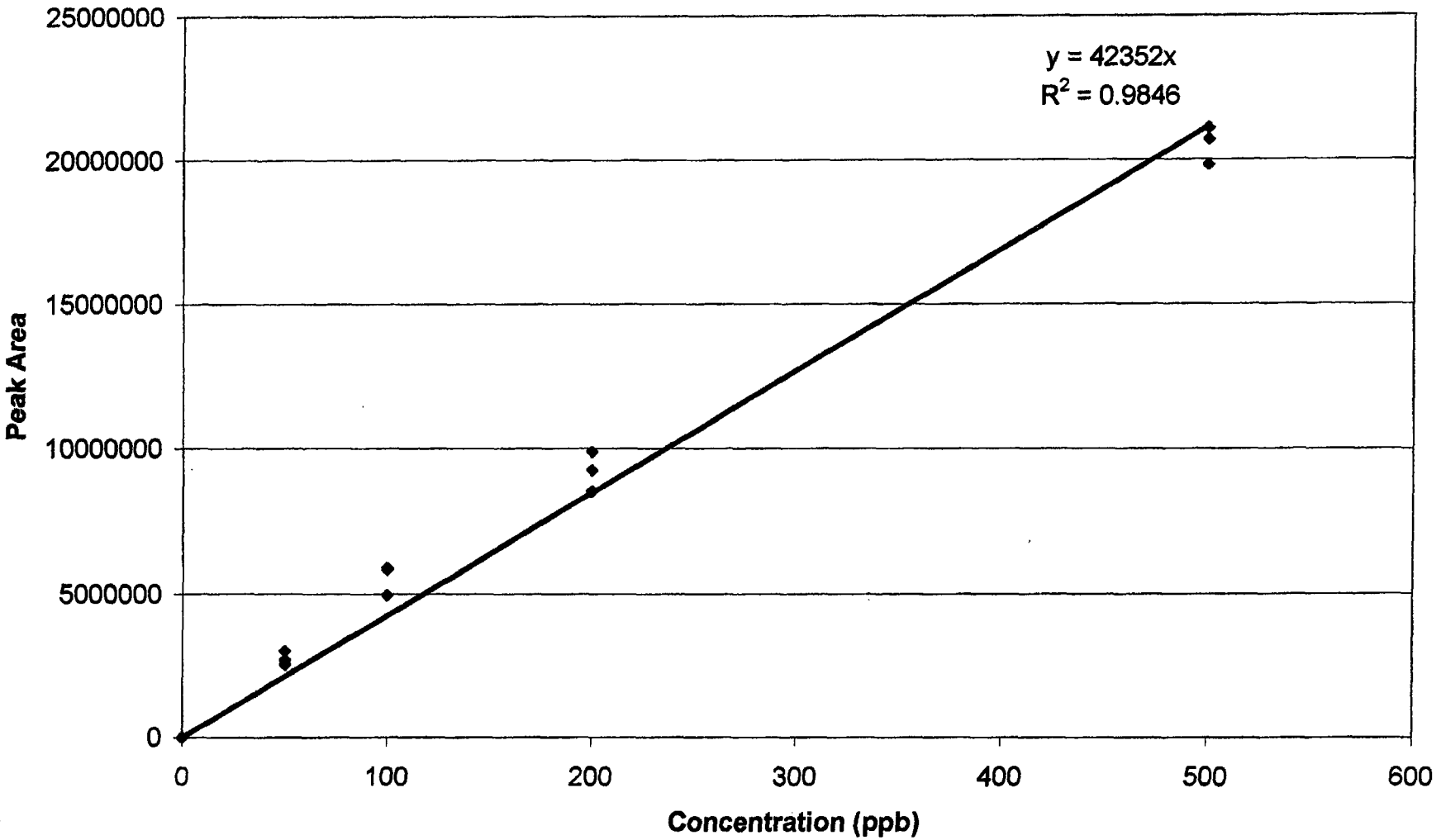


Figure A.8: Standard Calibration Curve for Pentachlorophenol in Hexane using GC-ECD