ABSTRACT

DEVELOPMENT OF MEMBRANE EXTRACTION TECHNIQUES FOR WATER QUALITY ANALYSIS

by
Dawen Kou

This research involved the development of membrane-based analytical techniques as applied to various aspects of water quality analysis. Gas injection membrane extraction was developed for fast on-line analysis of volatile organic compounds in water. Gas injection of aqueous samples increased the speed of membrane extraction. The aqueous boundary layer effects encountered during water elution was reduced. Axial mixing of the sample with a gaseous eluent was minimal, and this eliminated the tailing in the permeation profiles. The overall effect was significantly faster permeation. The overall diffusion coefficient during gas injection was found to be seven times the value during aqueous elution. The simulated permeation profile, using the calculated value, was in good agreement with the experimental results. The effects of system parameters on the analytical performance were investigated. Fast on-line analysis of water containing ppb level pollutants as listed in EPA method 602 was demonstrated.

Simultaneous extraction and concentration with membranes during on-line analysis of semivolatile organic compounds was studied. The influences of distribution coefficient, solvent polarity, solvent and water flow rates, as well as membrane material on enrichment factor and extraction efficiency were investigated. It was observed that solvent loss during extraction had significant impacts on enrichment factor and extraction efficiency. Continuous on-line monitoring of semivolatile organic compounds was demonstrated using this technique.

Haloacetic acids are a major group of harmful disinfection by-products in potable water generated during chlorination. A simple, economical, and highly efficient method was developed for the determination of all nine haloacetic acids in water. The extraction and preconcentration were accomplished using Supported Liquid Membrane Mircoextraction. Enrichment factor as high as 3000 was obtained with 60 minutes of extraction. The extract was directly analyzed, without derivatization, by a novel Ion-pair chromatographic method with flow programming. Low detection limits at ppb or sub-ppb level was obtained with relative standard deviation in the range of 3-12%. Various supported liquid membranes were tested. The extraction conditions were optimized by varying pH, ionic strength, stirring speed, and extraction time. This method was successfully applied to the analysis of tap water.

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FOR WATER QUALITY ANALYSIS

by
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A Dissertation
Submitted to the Faculty of
New Jersey Institute of Technology and
Rutgers, The State University of New Jersey - Newark
in Partial Fulfillment of the Requirements for the Degree of
Doctor of Philosophy in Environmental Science

Department of Chemistry and Environmental Science

August 2002

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   to be submitted to *Analytical Chemistry.*

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To my mother and father

ACKNOWLEDGMENT

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CHAPTER 1

INTRODUCTION

1.1 Water Quality Analysis

1.1.1 Water Quality

The importance of water to the lives on the planet cannot be too highly stated. On a global scale, water quality is being impaired or threatened by many factors. Industrial discharges, urban rainwater runoff, and agricultural activities (such as the use of pesticides) are the major sources of water pollution. Many pollutants in water are organic compounds. From an analytical perspective, they can be classified into two categories: Volatile Organic Compounds (VOCs) and Semivolatile Organic Compounds (SVOCs). VOCs are defined by the U.S. Environmental Protection Agency (USPEA) as organic compounds with vapor pressure over 0.01 kPa at 25 ^{0}C. They include alkyl, aromatic, as well as halogenated hydrocarbons, which are often used as solvents. SVOCs generally are larger molecules, such as pesticides and polychlorinated biphenyls (PCBs). These compounds can pose serious health and environmental threats even at trace concentrations (ppb or ppm). Therefore, all water resources, drinking water and wastewater discharges should be under constant watch. Pollutants need to be measured frequently so that contamination can be detected in a timely manner and remedial actions can be taken as quickly as necessary.

The United States Congress has passed several environmental laws to protect the nation's water resources. Clean Water Act (CWA) is aimed to protect surface water rivers, lakes, and reservoirs), and Safe Drinking Water Act (SWDA) to protect

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groundwater and drinking water. Today, water contamination is a serious problem in the United States. The USEPA stated in its 2000 Overview of Current Total Maximum Daily Load - TMDL - Program and Regulations: "Over 40% of our assessed waters still do not meet the water quality standards states, territories, and authorized tribes have set for them. This amounts to over 20,000 individual river segments, lakes, and estuaries. These impaired waters include approximately 300,000 miles of rivers and shorelines and approximately 5 million acres of lakes. An overwhelming majority of the population - 218 million - live within 10 miles of the impaired waters." Much work needs be done in cleaning up polluted waters. Before any clean-up actions can be taken, monitoring is needed to identify specific existing or emerging problems, and to gather information to design specific pollution prevention or remediation programs. However, EPA's 2002 Integrated Water Quality Monitoring and Assessment Report Guidance pointed out: "Today, the majority of the nation's waters remain unmonitored and unassessed. Yet Section 305(b) of the Clear Water Act requires that all waters be assessed every two years." Clearly, the goals set in CWA have yet to be attained.

Drinking water quality has a more direct impact on public health than any other water sources. The safety of drinking water relies heavily on the disinfection process to kill pathogens. Chlorination is the most widely used method for disinfection. However, it also generates harmful Disinfection By-Products (DBPs) [1]. Haloacetic Acids (HAAs) are the major components of non-volatile DBPs. All HAAs are toxic, and some of them have been identified as carcinogens. As required by the SWDA, EPA has set stringent rules to regulate HAA levels in water. Therefore, sensitive and reliable methods for measuring HAAs are needed to ensure drinking water quality.

1.1.2 Conventional Sample Preparation Techniques

Conventionally, water analysis involves several steps: sampling at site, transport to the lab, sample storage, sample preparation, and chemical or instrumental analysis. The whole process takes place in separate steps at different times and places. In other words, the analysis is not on-site, on-line, and takes a rather long time. Meanwhile, analytes are subject to evaporation, degradation, and cross-contamination, which can introduce errors into the analysis result. Secondly, those methods require expensive manual labor. The high cost of such techniques limits the number of samples that can be analyzed. This in turn limits the amount of data that can be obtained at reasonable expense. Moreover, the delay between sampling and analysis compromises the capacity of immediate response in emergency situations.

Sample preparation (or sometimes called sample treatment) is a key step in the overall analytical process. The gap between sampling and analysis is partly due to the need for sample preparation. In environmental applications, the analyte concentration can be very low, and the matrix can be very complex and contain a large number of compounds. The function of sample preparation is to convert the analytes into an appropriate form in a suitable matrix at a suitable concentration for analysis. In many cases, analytes are separated from the sample and transferred to another matrix. This is termed "extraction". The compounds that interfere with the determination of the target analytes may be removed or reduced prior to analysis. This is called "clean-up". It is often necessary to increase the analyte concentration in order to lower the method detection limit. This is known as "concentration" or "enrichment". The ideal sample

preparation technique should provide both enrichment and clean-up. It is also desirable if it can be directly coupled with an instrument such that the analysis can be automated, on-line, in real-time. The technique should also minimize the use of organic solvents, which are expensive to purchase and dispose of, and pose danger to the environment.

Different types of analytes require different sample preparation techniques. The conventional techniques for VOCs include Purge-and-Trap (P&T) and Headspace Analysis. Liquid-Liquid Extraction (LLE) and Solid-Phase Extraction (SPE) are the main techniques for SVOCs. In Headspace Analysis, the sample is placed in a vial and sealed with a cap. Due to their high volatility, VOCs in the water can easily vaporize into the headspace. After equilibrium is reached, the headspace air is drawn into a syringe, and injected into a GC for analysis.

Purge-and-trap is also known as Dynamic Headspace. In P&T, an inert gas stream such as nitrogen or helium is dispersed through the water sample. Volatile organics are purged out of water by the gas, and carried to a sorbent trap and concentrated there. The sample may be heated to increase purge efficiency. After purging for a preset time at a controlled temperature, the trap is heated to a certain temperature (typically 180 ^{0}C). The analytes are desorbed from the trap and released into the GC for analysis. P&T provides more efficient extraction than static headspace, because analytes are continuously removed from the headspace and this creates larger concentration gradient. Many EPA standard methods use P&T in VOC analysis. However, this technique is not suitable for compounds with high water solubility, such as alcohols, which are difficult to purge out of water.

Liquid-Liquid Extraction uses an immiscible phase, typically an organic solvent (or solvents), to extract organic compounds from water. Liquid-Liquid Extraction has been around for a few centuries, and is widely used in many standard procedures. It is a universal technique that can be applied to all types of samples. Good selectivity can be achieved based on the choice of solvents. Liquid-Liquid Extraction has several disadvantages. It uses a relatively large amount of solvents. The extract often needs to be concentrated via solvent evaporation. Sometimes emulsion occurs and makes the separation of two phases difficult. Liquid-Liquid Extraction is typically carried out in a separatory funnel. Continuous LLE systems are also available. However, it is difficult to directly couple conventional LLE with an analytical instrument for on-line use.

Solid-Phase Extraction was first used about five decades ago. It underwent significant development in the last ten to twenty years [2]. In SPE, organic compounds are adsorbed by a solid sorbent made of bonded silica or polymers. A typical SPE procedure involves several steps. First, the SPE disc or cartridge needs to be conditioned (activated) and then cleaned. Then the water sample is passed through the sorbent. The organic compounds in water are retained while water passes through. Then an eluent is used to wash out the interfering compounds. Lastly, the analytes are eluted using a solvent. The selectivity of SPE relies upon a variety of SPE materials. Recently, the developments of Imminoaffinity-based sorbents and molecularly imprinted polymers (MIP) provide very high selectivity towards specific compounds [2]. Solid-Phase Extraction uses relatively less solvent compared with LLE. It can be coupled with HPLC or GC for semi-continuous on-line analysis [3].

Sample preparation for very polar, water soluble organic compounds can be quite challenging, because they are more difficult to extract from water. The common approach is to utilize a derivatization step to convert polar analytes into less polar ones.

1.1.3 Alternative Sample Preparation Techniques

Solid-Phase Microextraction (SPME) has merged as a promising new technique [4-5]. It was invented by Pawliszyn and coworkers in 1990, and commercialized in 1993 by Supelco. In SPME, a fused silica fiber coated with a bonded organic phase serves as the sorbent for the analytes. The fiber is housed in a syringe needle and can be extended from or retracted into it. During extraction, the needle is inserted into a sample vial through the septum. The fiber is extended from the needle and exposed to the sample (or its headspace). Solid-Phase Microextraction is a one-step operation in which extraction and enrichment take place simultaneously. After extraction, the fiber is retracted into the needle and removed from the vial. Then the needle is inserted into an analytical instrument, where the fiber is exposed and the analytes are desorbed and analyzed.

Solid-Phase Microextraction is a solvent-less technique, and can be used for both VOCs and SVOCs. It works best for volatile, non-polar compounds. Derivatization is often necessary for the extraction of polar compounds with SPME. Selectivity can be achieved by varying the fiber material, which has different affinity to different types of analytes. Compared with LLE and SPE, SPME does not provide as much clean-up capacity.

Membrane-based separation has been recognized as a promising alternative to conventional techniques. It has been used in many industrial applications such as gas
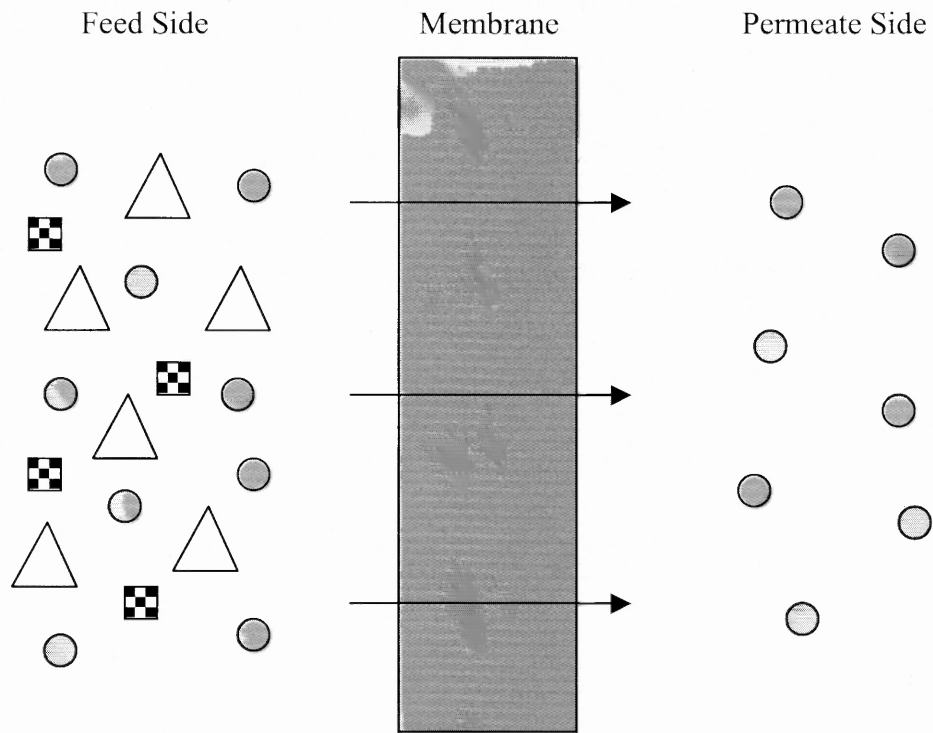
Figure 1.1 Concept of membrane separation.

separation, dehumidification, dialysis, ultrafiltration, osmosis, and reverse osmosis [6]. Figure 1.1 shows the concept of membrane separation. The mixture to be separated is in contact with one side of the membrane, which is called the feed (or donor) side. The membrane serves as a selective barrier. Some components of the mixture can pass through and go to the other side, called the permeate side. Sometimes, the permeated species are collected by another phase, called the acceptor. The types of membranes available can be classified as porous and non-porous membrane based on their structure, or as flat and hollow fiber membranes based on their geometry. Generally, hollow fibers provide larger surface to volume ratio and high packing density, because a large number of fibers can be packed into a small volume.

Four types of membrane-based techniques have been used in sample preparation [7]. They are dialysis, electrodialysis, membrane filtration, and membrane extraction. Dialysis is a membrane process in which microsolutes permeate through the membrane while macrosolutes are blocked. On the permeate side, an aqueous solution is used to receive the permeated microsolutes. The driving force for permeation is the concentration gradient between the two sides of the membrane. The mechanism for selectivity is sieving by membrane pores. Therefore, the pore dimensions are critical in deciding separation selectivity. This technique has been used mainly in biomedical and food analysis [8]. In electrodialysis, a pair of electrodes are placed on the two sides of the membrane, This creates an electrical potential difference, which together with a concentration gradient are the driving forces for separation. This technique is more complicated than dialysis because of the additional use of electrodes and power supplies.

Moreover, membrane fouling is more problematic in electrodialysis. Because of these drawbacks, its analytical applications are rare.

Table 1.1 Comparison of Various Membrane Separation Techniques

Technique	Dialysis	Electrodialysis	Filtration	Membrane extraction
Driving force	Concentration gradient	Concentration gradient and electrical potential difference	Pressure difference	Concentration gradient
Separation Mechanism	Sieving	Counter ion transport	Sieving	Solution-diffusion
Membrane Structure	Porous	Porous	Porous	Non-porous*

*Porous membranes are sometimes used as the support of non-porous membranes.

In membrane filtration, a pressure is applied on the feed side of a (porous) membrane. Macrosolutes in the feed solution are retained by the membrane, while the liquid phase together with microsolutes pass through. Membrane filtration can be further specified as microfiltration (MF) and ultrafiltration (UF). Both filtration and dialysis are based on size exclusion. One difference between them is that concentration gradient is the sole driving force for permeation in dialysis, while filtration relies upon pressure difference to achieve separation. Another difference is that filtration does not need an acceptor, since the bulk liquid phase of the feed solution ends up on the permeate side. The only analytical application of membrane filtration has been fermentation process monitoring, where cells and macromolecules are removed from the fermentation broth, and the filtrate is collected and analyzed [8].

Unlike the techniques mentioned above, membrane extraction is not based on size exclusion. The separation mechanism can be described by a Solution-Diffusion theory [9]. The solutes first dissolve into the membrane, and then diffuse through it. The extraction is driven by a concentration gradient between the two sides of the membrane. Membrane extraction can be used to separate a variety of volatile and semi-volatile analytes from the sample matrix, with high enrichment and selectivity. It is the most relevant technique to water quality analysis, and will be discussed in detail in the next section. Table 1.1 summaries the differences of the techniques discussed above.

1.2 Membrane Extraction

1.2.1 Extraction of VOCs

Volatile organic compounds can be extracted from water through membrane pervaporation. Pervaporation (permselective "evaporation" of liquid molecules) refers to the process organic solutes in a liquid diffuse through the membrane to a gas phase. Membranes used in pervaporation are generally non-porous solid silicon membranes. Composite membranes that have a thin siloxane layer deposited on a porous support can provide faster pervaporation [10].

Steady state permeation is governed by Fick's First Law.

$$J = - A D (dC/dx) = A D \Delta C/l \qquad (1.1)$$

Where J is flux, A is membrane surface, D is diffusion coefficient, C is solute concentration, x is the distance along the membrane wall, and l is membrane thickness. Unsteady state permeation can be described by Fick's Second Law.

$$dC(x,t)/dt = - D (d^2C(x,t)/dt^2) \qquad (1.2)$$
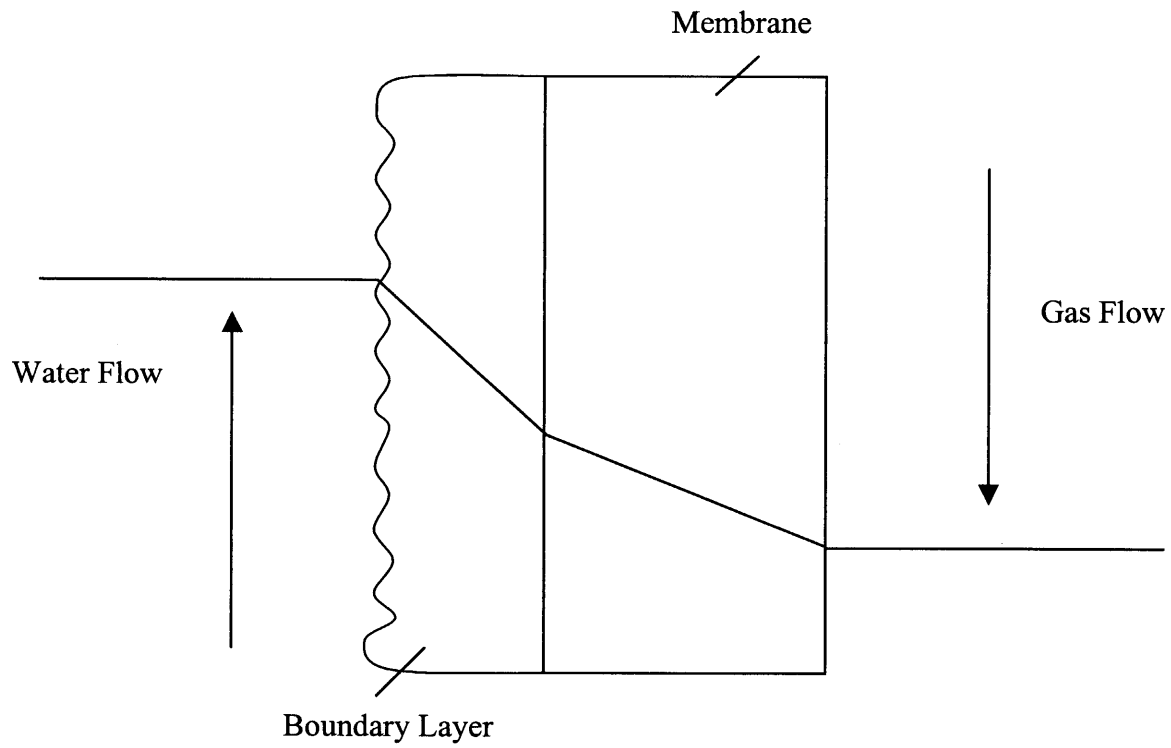
Figure 1.2 Boundary layer resistance during pervaporation.

where $C(x,t)$ is the solute concentration at position x and time t.

Membrane pervaporation can be used in conjunction with a mass spectrometer (MS) or a gas chromatograph (GC) for the on-line analysis of VOCs. The former is known as Membrane Introduction Mass Spectrometry (MIMS) [11-21]. In MIMS, the permeate side of the membrane is in the vacuum compartment of the MS. The vacuum provides a pressure gradient to facilitate fast permeation through the membrane. However, MS alone has limited capacity in simultaneous analysis of multiple species. Although a GC run takes a longer time than MS, it provides much needed separation power in dealing with a large number of analytes.

The hyphenation of membrane pervaporation with GC has been investigated in the recent few years [22-31]. The permeation is slower in a GC-membrane interface, as a positive pressure is required for carrier gas flow. This increased the sample process time. During pervaporation, with water flowing on one side of the membrane, a stagnant layer is formed between the membrane and water if the flow rate is not high enough to reach turbulent flow. In this layer, solutes soon dissolve into the membrane and become depleted. The concentration gradient is the driving force for pervaporation across the membrane. The analyte-depleted boundary layer reduces the effective concentration gradient for mass transfer [32-35]. Figure 1.2 shows a diagram of the formation of aqueous-membrane boundary layer.

The overall mass transfer resistance is the sum of the mass transfer coefficients of the aqueous boundary layer on the feed side, the membrane, and the gaseous boundary layer on the permeate side. In analytical applications where thin membranes, and relatively low sample flow rates are used, mass transfer through the aqueous boundary

layer is the rate-limiting step [32-35].

1.2.2 Extraction of SVOCs

Semivolatile Organic Compounds do not readily vaporize, so they cannot be extracted by pervaporation. For SVOCs, a microporous membrane can be used and an organic solvent is used as the acceptor. Water is introduced to the donor side. The two phases contact in the membrane pores. This membrane-based solvent extraction (MSE) has been studied in some engineering applications [36-39]. In analytical applications, the MSE system resembles a micro scale continuous LLE, with the membrane being the phase separator. The advantages of MSE are that emulsion formation can be avoided, and the system can be coupled with an on-line instrument.

There are two types of membrane available: hydrophobic and hydrophilic. If a hydrophobic membrane is used, the membrane pores are filled with the organic phase. If a hydrophilic membrane is used, the aqueous phase wets and fills the membrane pores. The overall mass transfer resistance for an organic compound is the sum of mass transfer resistance in the three individual phases. For hydrophobic membranes,

$$1/K = m/ k_w + 1/k_{mo} + 1/k_o \tag{1.3}$$

and for hydrophilic membranes,

$$1/K = m/ k_w + m/k_{mw} + 1/k_o \tag{1.4}$$

where K is overall mass transfer coefficient; m is distribution coefficient between the organic and aqueous phase; k_w is mass transfer coefficient in the bulk aqueous phase; k_{mo} and k_{mw} are mass transfer coefficients in the hydrophobic membrane and hydrophilic membrane; k_o is mass transfer coefficient in the bulk organic phase. If $m \gg 1$, which is

true for most non-polar and mid-polar organic compounds, the overall mass transfer coefficient is higher in a hydrophobic membrane. Therefore, in most cases, hydrophobic membranes should be used for the extraction of SVOCs.

When a hydrophobic membrane and an organic solvent are used to extract organic compounds from water, the water pressure needs to equal or higher than that of the organic phase, in order to prevent the organic phase coming out of the membrane pores. It was reported that mass transfer coefficient was not affected by the magnitude of pressure difference [36-39]. However, the excessive water pressure should not exceed a critical value, called the breakthrough pressure, ΔP_{cr}, otherwise, the organic phase in the pores can be displaced by water. Generally, ΔP_{cr} is higher for membranes with smaller pore sizes.

1.2.3 Extraction of Polar, Ionizable Compounds

Some polar compounds such as weak acids or bases can exist in water in two forms: dissociated and undissociated. Supported liquid membrane (SLM) can provide high enrichment and selectivity for the extraction of these compounds. Supported liquid membrane is a liquid film held in a porous support. A SLM can be easily made by impregnating a microporous membrane with an organic extractant known as the membrane liquid. The membrane liquid should be non-volatile, and insoluble in water. Typical membrane liquids are *n*-undecane and di-*n*-hexyl ether [40-41].

In SLM extraction, the donor (water sample) is adjusted to certain pH so that the analytes are in the undissociated molecular form and partition into the membrane liquid. On the other side, an acceptor solution at a different pH is used to receive the analytes

through acid-base reaction. The analytes in the acceptor are in the dissociated form and cannot reenter the membrane. Supported liquid membrane extraction resembles a two-step process: extraction (into an organic extractant) and backextraction (into an aqueous solution). However, the two processes take place simultaneously in SLM so that it is much more efficient than two separate steps.

K_D is the partition coefficient between the membrane and the donor, and K_A is the partition coefficient between the membrane and the acceptor.

$$K_D = C_M /(C_W * \alpha_D) \tag{1.2}$$

$$K_A = C_M /(C_A * \alpha_A) \tag{1.3}$$

K_D and K_A are of the same order, provided the ionic strength of the donor and the acceptor are not significantly different. C_W, C_M, and C_A are the equilibrium analyte concentrations in the extracted sample, in the membrane, and in the acceptor respectively. α_D and α_A are the fractions of analyte in the undissociated form in the donor and acceptor phase. Ideally, α_D should be close to one, and α_A a very small number. In the extraction of weak acids, the donor pH must be at least 2 pH units lower than the pKa value of the analyte in order to attain $\alpha_D > 0.99$. To achieve $\alpha_A < 0.0005$, the acceptor pH must be at least 3.3 pH units higher than the pKa value. In the extraction of weak bases, the donor pH must be at least 2 pH units higher than the pKa value of the analyte, and the acceptor pH must be at least 3.3 pH units lower than the pKa value to ensure $\alpha_D > 0.99$ and α_A < 0.0005 [42]. Under such conditions, enrichment of three to four orders of magnitude can be attained.

High selectivity is also characteristic of SLM extraction. Neutral compounds in the donor can partition into the membrane liquid, and then into the acceptor. However, the concentration in the donor is the same as that in the acceptor, i.e. no enrichment for the neutral compounds. In the extraction of acidic analytes, basic compounds in the sample are charged ions and cannot be extracted. Likewise, acidic compounds will be excluded in the extraction of basic analytes.

Supported liquid membrane extraction is also economical and environmental friendly, because except for a tiny amount (typically microliters) of non-volatile membrane liquid, no organic solvent is used during the entire extraction process.

Haloacetic acids (HAAs) are very polar and acidic compounds. They exist predominantly in dissociated form (anions) at the pH of drinking water. These compounds can be directly analyzed by liquid chromatography or ion chromatography, but the detection limits are high. GC analysis provides superior sensitivity, but requires the conversion of HAAs to esters. The current EPA standard method uses LLE, followed by derivatization. This procedure uses large amounts of organic solvents, and is lengthy and complicated. It appears that the high enrichment capacity of SLM extraction may be able to offset the lower sensitivity of LC methods. The possibility of combining SLM extraction with LC to provide a sensitive, yet simple and inexpensive method for HAA analysis is worth exploring.

CHAPTER 2

RESEARCH OBJECTIVE

The objective of this research was to develop membrane extraction techniques for the analysis of various types of organic compounds in water. Gas Injection Membrane Extraction (GIME) with GC was developed for fast on-line analysis of volatile organic compounds (VOCs). This technique was aimed to increase the speed of membrane extraction. It solved problems of boundary layer effect and dispersion, which had been the main causes of long lag time in membrane extraction.

Membrane Solvent Extraction (MSE) with HPLC was developed for on-line monitoring of Semivolatile Organic Compounds (SVOCs). Simultaneous extraction and concentration during on-line analysis was investigated. It significantly increased the enrichment factor of membrane extraction.

Supported Liquid Membrane Micro-Extraction (SLMME) with Ion-Pair Chromatography (IPC) was developed for the determination of all nine haloacetic acids (HAAs) in water. This technique is simple and inexpensive, without using complicated derivatization procedures. It used very little organic solvent, thus being economical and environmental friendly. The detection limits were lower than or comparable to the EPA methods. The SLMME technique could also be used to improve the sensitivity of other HAA analysis methods that use liquid chromatography or capillary electrophoresis.

In summary, the objective of this research was three fold:

- To develop the technique of Gas Injection Membrane Extraction (GIME) for fast on-line analysis of VOCs in water.

- To develop Membrane Solvent Extraction (MSE) for on-line monitoring SVOCs in water, and to study simultaneous extraction and concentration during on-line analysis.

- To develop a Supported Liquid Membrane Microextraction (SLMME) technique for the analysis of nine haloacetic acids (HAAs) in water.

CHAPTER 3

GAS INJECTION MEMBRANE EXTRACTION (GIME) FOR FAST ON-LINE ANALYSIS USING GC DETECTION

3.1 Introduction

In the determination of volatile organic compounds in water, the first step is usually separation of analytes from the matrix. Conventional sample preparation techniques, such as purge-and-trap and headspace analysis, are mainly used for laboratory analysis of discrete samples. Membrane separation has emerged as a promising alternative [10-31, 40, 43]. It offers high selectivity and high enrichment factors, and can be used for on-line, automated analysis. Membrane extraction has been used in conjunction with a mass spectrometer (MS) [11-21] or a gas chromatograph (GC) [10, 22-31]. The vacuum in an MS provides fast permeation through the membrane. The permeation is much slower in a GC or GC/MS interface, as a positive pressure is required for carrier gas flow. As instrumentation for faster GC becomes commonplace, there is a real need to develop faster membrane techniques that can speed up extraction.

Both hollow fiber and flat membranes have been used in developing GC interfaces [10, 22-31]. Generally, hollow fibers are preferable because they offer the advantage of larger surface area per unit volume and high packing density. A large number of parallel fibers can be packed into a small volume. All hollow fiber modules share a common feature, i.e., the sample contacts the membrane on the feed side, while a stripping gas flows on the permeate side to transport analytes to GC. Contact between the sample and the membrane can be done in two ways. The membrane can be introduced

into the sample (referred to as Membrane In Sample, or, MIS), or the sample can be introduced into the membrane (referred to as Sample In Membrane, or, SIM).

In the MIS configuration, the membrane is either directly submerged in the sample, or in its headspace, while the stripping gas flows inside the membrane [31]. At any point in time, only a small fraction of the sample directly contacts the membrane. The ratio of membrane surface area to sample volume is fairly low. The sample is usually stirred to enhance analytes diffusion through the aqueous phase. In the case of headspace extraction, analytes first vaporize and then permeate through the membrane. Diffusion in the gas phase and the gas-membrane interface is faster than in the aqueous phase and the liquid-membrane interface. However, slow mass transfer from the sample into headspace prolongs the overall process. It takes a rather long time to achieve high extraction efficiency. It was reported that quantitative extraction of a 2ml sample required 100 minutes to complete [31].

In the SIM configuration, the membrane modules have the classical shell and tube design [6]. The sample is either made to "flow through" or "flow over" the membrane. In both cases, the sample contact is dynamic, and the extraction is over once the sample has passed through. This allows multiple samples to be analyzed in quick succession. In either case, the contact surface to volume ratio is much higher than in the MIS extraction, and quantitative extraction can be achieved faster. It was reported that it took four minutes to extract 90% of analytes from a 2ml sample in the flow-through mode, although ten additional minutes were needed to complete permeation [26]. Between the flow-through and the flow-over mode, the former provides higher extraction efficiency, because the tube side volume is smaller than the shell side volume. Comparison studies

show that under similar experimental conditions, flow-through extraction provides the highest sensitivity among all available SIM and MIS configurations [31,44].

In the flow-through extraction, the sample can be introduced into the membrane continuously [10, 22-23]. Permeation may take a relatively long time to reach steady state, and any measurement during the transitional period provides erroneous results. To avoid this problem, a non-steady state membrane extraction method referred to as Pulse Introduction Membrane Extraction (PIME) was developed recently [24-27]. Deionized water (or an aqueous solution) has been used as the carrier stream to transport the sample to the membrane in PIME [25-27]. A static analyte-depleted boundary layer is formed between the membrane and the aqueous phase [32-35]. The overall mass transfer resistance is the sum of the mass transfer coefficients of the aqueous boundary layer on the feed side, the membrane, and the gaseous boundary layer on the permeate side. In analytical applications where thin membranes, and relatively low sample flow rates are used, mass transfer through the aqueous boundary layer is the rate-limiting step [31]. The concentration gradient is the driving force for the analyte permeation across the membrane. The analyte-depleted boundary layer reduces the effective concentration gradient for mass transfer [24]. In PIME, gas purging at a predetermined delay following the sample injection was used to break up the boundary layer. It improved extraction efficiency and shortened response time to a limited degree [25-27].

Sample dispersion is another cause of slow permeation in PIME [25-27] and other flow injection type techniques where an aqueous carrier stream is used [15]. The aqueous sample is diluted by axial mixing with the carrier stream. Dilution reduces the effective concentration on the feed side of the membrane, which is the driving force for diffusion.

Moreover, dispersion increases sample volume and sample residence time in the membrane. The overall effects are slower extraction and lower sensitivity.

In this study, Gas Injection Membrane Extraction (GIME) of aqueous samples is presented to address the issues of boundary layer effect and sample dispersion. The goal is to have fast extraction while maintaining high sensitivity. This can significantly increase sample throughput in laboratory analysis, and is highly desirable for on-line source water monitoring and process control.

3.2 Experimental

Figure 3.1 shows the schematic diagram of the GIME system. An aqueous sample is introduced into a N_2 stream by a pneumatically controlled 10-port valve (Valco Instruments Co. Inc., Houston, TX). The N_2 stream injects the sample into the membrane. The membrane serves as a selective barrier through which organic analytes permeate. On the permeate side, a counter-current gas stream strips the organics and transports them to a microsorbent trap (referred to as the microtrap). The microtrap concentrates and then desorbs the analytes into the GC. After the GC run, a chromatogram is obtained. The system can be used for the analysis of individual samples by discrete injections, or for continuous on-line monitoring by sequentially injecting a series of samples. A chromatogram is obtained corresponding to each injection.

The membrane module was constructed with three 50cm long membranes in a 0.318cm o.d. spiraled stainless steel tube. The membrane was a 0.260mm o.d. and 0.206mm i.d. composite hollow fiber (Applied Membrane Technology, Minnetonka, MN). It had a 1 μm thick homogeneous siloxane as the active layer deposited on a film
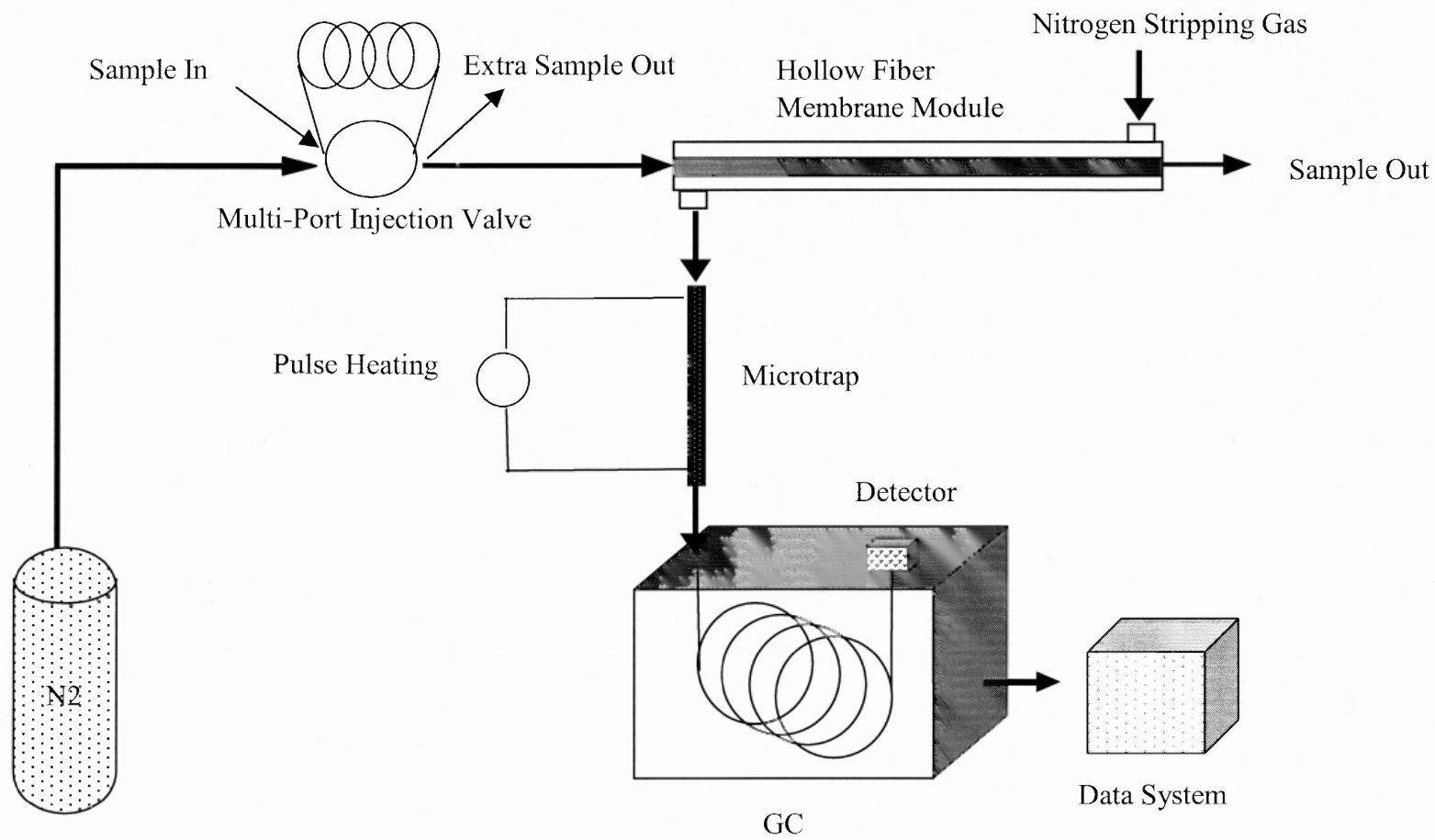
Figure 3.1 Schematic diagram of gas injection membrane extraction.

of microporous polypropylene as the support. A "T" unit (Components & Controls Inc. Carlstadt, NJ) was connected to each end of the tube, serving as the inlet and outlet for the elution gas and the stripping gas. The space between the membrane and the "T" units was sealed with epoxy to prevent mixing of the two countercurrent nitrogen streams.

The microtrap was a small diameter silica-lined metal tube packed with a small amount of adsorbent. It had low thermal mass and could be heated and cooled rapidly. As the permeate stream flowed through the microtrap, the organics were trapped and concentrated. The microtrap was then resistively heated to desorb the analytes into the GC column as a sharp injection. Thus, the microtrap served as a concentration-cum-injection device for GC. The details of the microtrap and its working principles have been presented in previous publications [45-47]. In this study, a 15cm long, 0.53mm o.d. silica-lined tube (Restek Corp., Bellefonte, PA) packed with 0.02g of Carbotrap C (Supelco, Supelco Park, PA) served as the microtrap. A 7-10A current was supplied from a 30 V AC power source to heat the microtrap. The duration and frequency of the heating were controlled by a microprocessor-controlled device fabricated in house.

The chemicals used in the experiments were analytical grade (Sigma Chemical Co. St. Louis, MO); the EPA 602 standard solution was purchased from Supelco (Supelco, Supelco Park, PA). Analysis was carried out with a portable SRI 8600 GC (SRI Instruments, Torrance, CA) equipped with a Photo Ionization Detector, and a 30m long, 0.53mm o.d. × 0.21mm i.d. DB-624 capillary column. Peaksimple for Windows 95 software (SRI Instruments, Torrance, CA) was used for data acquisition and analysis.

3.3 Results and Discussion

A major issue with membrane extraction has been the speed of analysis. Diffusion through the membrane and the boundary layer on its surface is a slow process [10, 22-27]. In order to prevent carryover, a sample cannot be analyzed until permeation from the previous injection is completed. The time required to complete permeation is referred to as lag time, which is defined as the time interval between the points corresponding to 10% of maximum response in the ascending and descending parts of the permeation profile [26].

Typical profiles of permeate flux through the membrane using aqueous elution, aqueous elution followed by gas purging, and GIME, are shown in Figure 3.2. The permeation profiles were obtained by injecting a 1ml sample into the membrane and then monitoring the output every ten seconds. Compared to aqueous elution, the lag time in membrane extraction reduced by 75%, from eight to two minutes with gas injection. In the case of aqueous elution with gas purging at the forth minute, the lag time was five minutes, and the reduction in lag time by gas injection was 60%.

The system response with GIME was 97% of that with aqueous elution; i.e. sensitivity remained the same. The profile during aqueous elution exhibits a long drawn out tailing, which increases the lag time but makes little contribution to sensitivity. The permeation profile during GIME generated a symmetric, Gaussian profile with no tailing. Therefore, gas elution offers the advantage of shorter lag time with practically no loss in sensitivity.

The advantage of GIME over aqueous elution can be realized from a theoretical standpoint as well. A mathematic model was previously reported for describing the
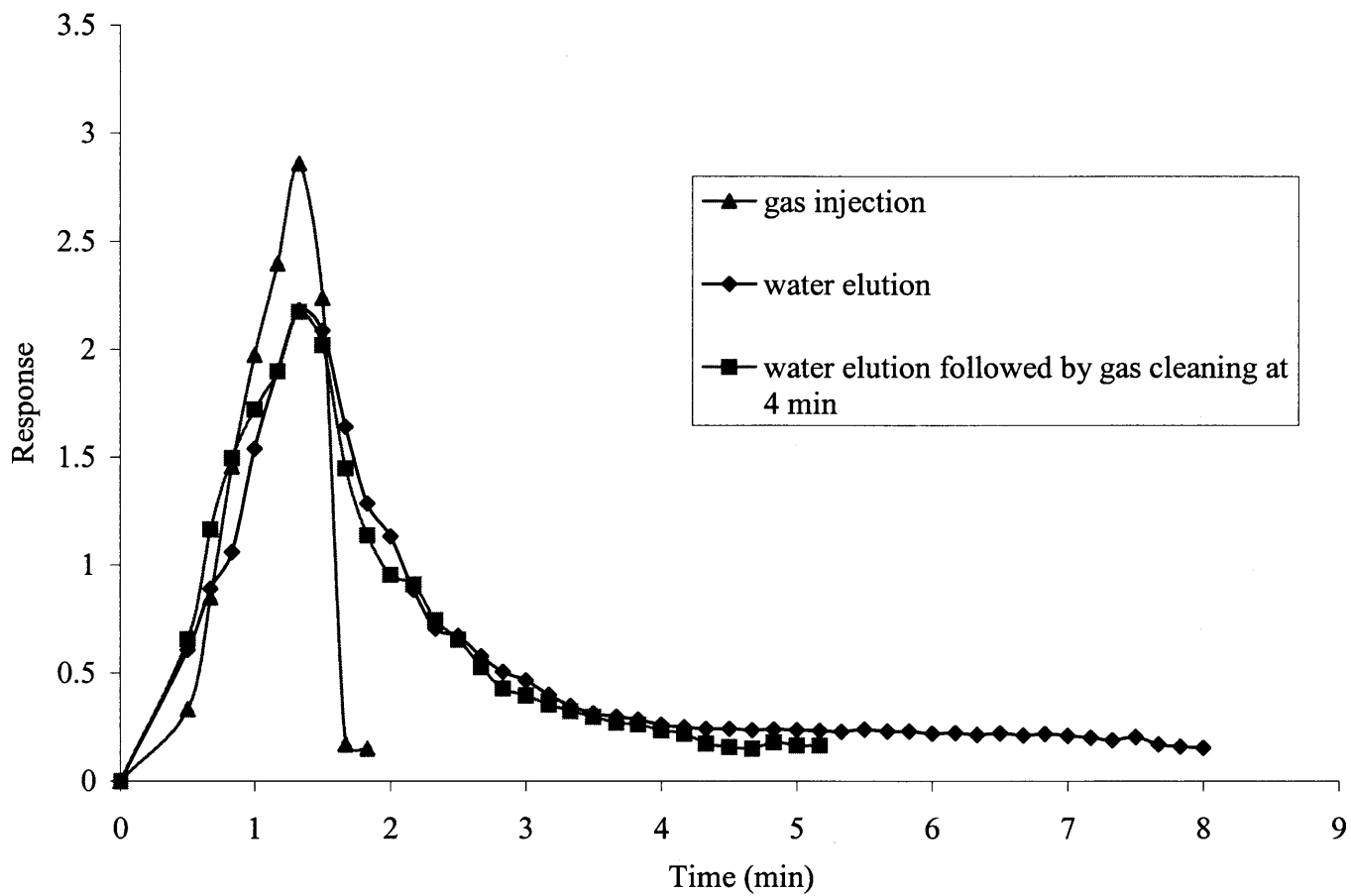
Figure 3.2 Permeation profiles for a 1ml 500ppb benzene sample at an eluent (gas or liquid) flow rate of 1ml/min.

permeation profile in non-steady state membrane extraction [32-48] using an aqueous eluent. The model is applicable to GIME because the only thing that changes by going from a liquid to a gas is the transport properties of the eluent [49]. This change is reflected as the change in the overall diffusion coefficient. The permeation rate at time t, is given as J (t):

$$J(t) = J_{ss} [f(D t /L^2) - \gamma f(D (t-\Delta t)/L^2)] \tag{3.1}$$

where Δt is the duration of the sample pulse, D is diffusion coefficient, L is membrane thickness, J_{ss} is the steady state permeation rate,

and $f(Dt/l^2) = 1 + 2 \sum\limits_{n=1}^{\infty} (-1)^n \exp [-D t (n\pi/L)^2]$.

$$\text{At } t<\Delta t, \gamma=0, J (t) = J_{ss}\{1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp [-D t (n\pi/L)^2]\}, \tag{3.2}$$

and at $t>\Delta t, \gamma=1$,

$$J (t) = J_{ss} \{2 \sum_{n=1}^{\infty} (-1)^n \exp [-D t (n\pi/L)^2] - 2 \sum_{n=1}^{\infty} (-1)^n \exp [-D (t-\Delta t)(n\pi/L)^2]\} \tag{3.3}$$

The overall diffusion coefficient D can be calculated from Equations 3.2 and 3.3 as follows [26]. At the maximum point in the permeation profile,

$$J_{max} = J_{ss}\{2 \sum_{n=1}^{\infty} (-1)^n \exp [-D t_{max} (n\pi/L)^2] - 2 \sum_{n=1}^{\infty} (-1)^n \exp [-D (t_{max}-\Delta t)(n\pi/L)^2]\} \tag{3.4}$$

where t_{max} is the time corresponding to J_{max}, the maximum permeation flux. By injecting two different volume samples at the same N_2 flow rate, two different t_{max} and J_{max} were obtained, and Equation 3.4 was solved numerically. The overall diffusion coefficient D

for benzene (using a 500ppb sample) was found to be 6.3×10^{-8} cm^2/s. This was seven times higher than that reported for benzene during aqueous elution [26]. Since the same membrane was used in both cases, the higher diffusion coefficient is attributed to the reduction of boundary layer effects in GIME. Permeation profile was computed using this value of D, and is plotted in Figure 3.3. Good agreement between experimental and computed results is seen.

Membrane extraction follows similar mechanism regardless of the eluent phase. Since the overall diffusion coefficient is significantly higher during gas injection, the mass transfer is faster. As N_2 pushed the aqueous sample through the membrane, the liquid boundary layer was never fully developed. After the sample passed through, the N_2 cleaned the membrane surface, which was "fresh" for the next sample. The reduction of liquid boundary layer results in much faster permeation across the membrane, and therefore a significantly shorter lag time.

Another issue with aqueous elution has been sample dispersion. It was reported that during aqueous elution in PIME, a 2ml sample was dispersed into 9ml volume at a flow rate of 1ml/min [27]. Similarly, a simulation of a membrane introduction mass spectrometry (MIMS) showed that a 15sec block input produced a 60sec dispersed profile [15]. Dispersion increases with the increase of aqueous eluent flow rate. As mentioned before, dispersion results in the increase in lag time and the decrease in analyte flux rate [15, 27]. The phenomena of dispersion in Flow Injection Analysis (FIA) have been studied [50-51]. The flow profiles here are similar to FIA, and the dispersion profiles are similar. The major causes of dispersion are convective and diffusive mixing of the sample with the carrier stream. Convection has been found to be the cause of tailing in the
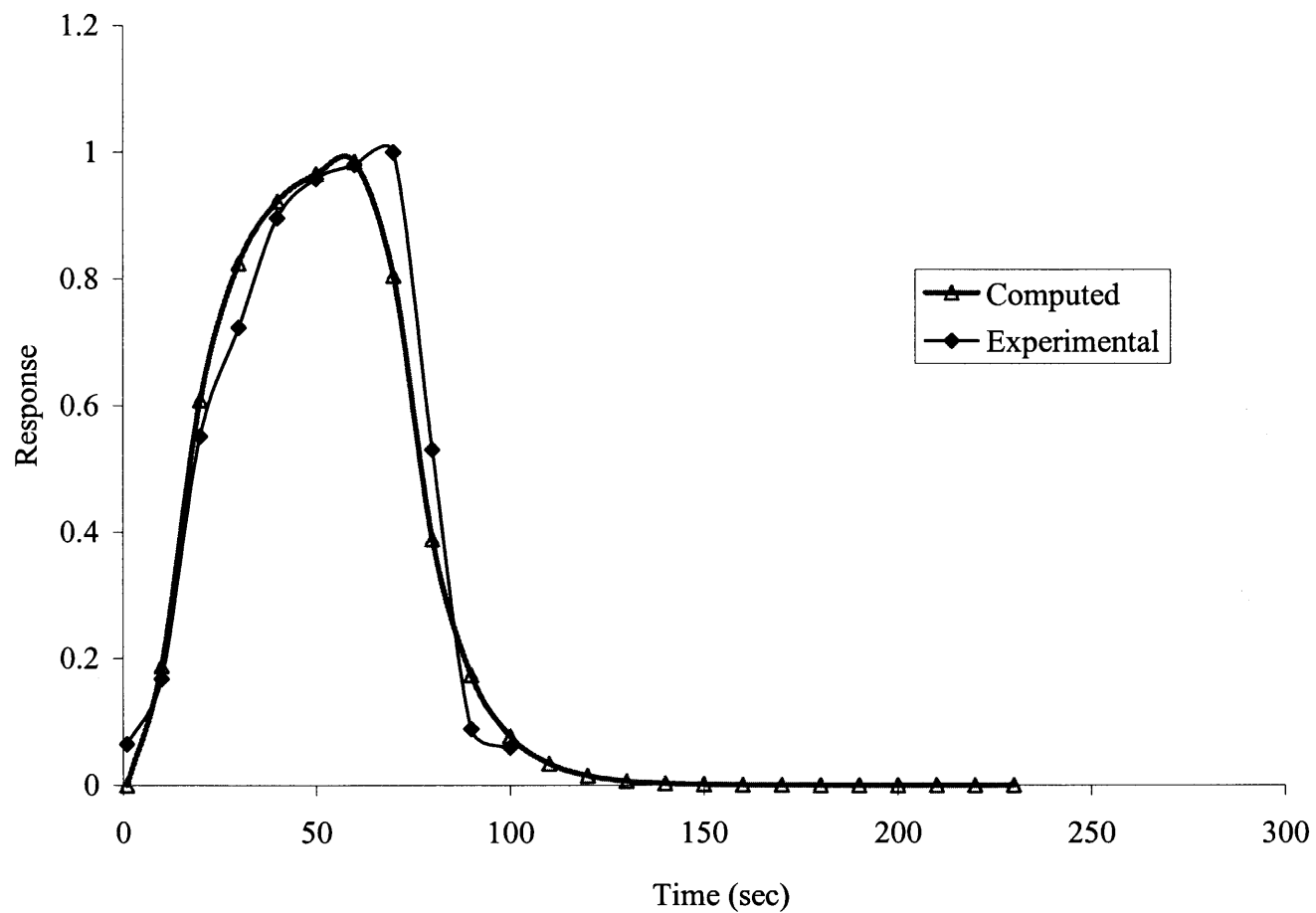
Figure 3.3 Experimental and computed permeation profiles for a 1ml, 500ppb benzene sample at a nitrogen flow rate of 1ml/min.

concentration profile. Diffusion is known to make minor contributions to the broadening

of the sample pulse and does not change its symmetric shape.

The long tailing in the permeation profile during aqueous elution shows strong

convective mixing between the eluent and the sample. On the other hand, the symmetric

shape of the permeation profile during GIME indicates that there was no convective

mixing with the N_2. The permeation profiles as a function of gas flow rate are shown in

Figure 3.4. Higher N_2 flow rates generated higher flux rates. The opposite was observed

during aqueous elution in PIME and MIMS, where the analyte flux rate decreased with

the increase of eluent flow rate [15, 27]. The drop of flux rate was due to increased

convective dispersion at higher flow rate. This difference further demonstrates the

elimination of dispersion by gas injection of aqueous samples.

In addition, GIME did not need a pump for eluent delivery. It also eliminated the

need for post-injection gas cleaning that had been used in PIME to break up aqueous

boundary layer. Therefore, gas injection resulted in simpler instrumentation and

operational procedures.

3.3.1 Effects of Process Parameters

Figure 3.5 shows that extraction efficiency increased with the increase in sample

residence time in the membrane. For a given sample volume, sample residence time

decreased as the N_2 flow rate increased. In other words, the lower the sample flow rate,

the higher was the extraction efficiency. Extraction efficiency is also a function of the

membrane-water partition coefficient of the analytes. According to Figure 3.5,

hydrophobic compounds such as benzene and toluene had much higher extraction
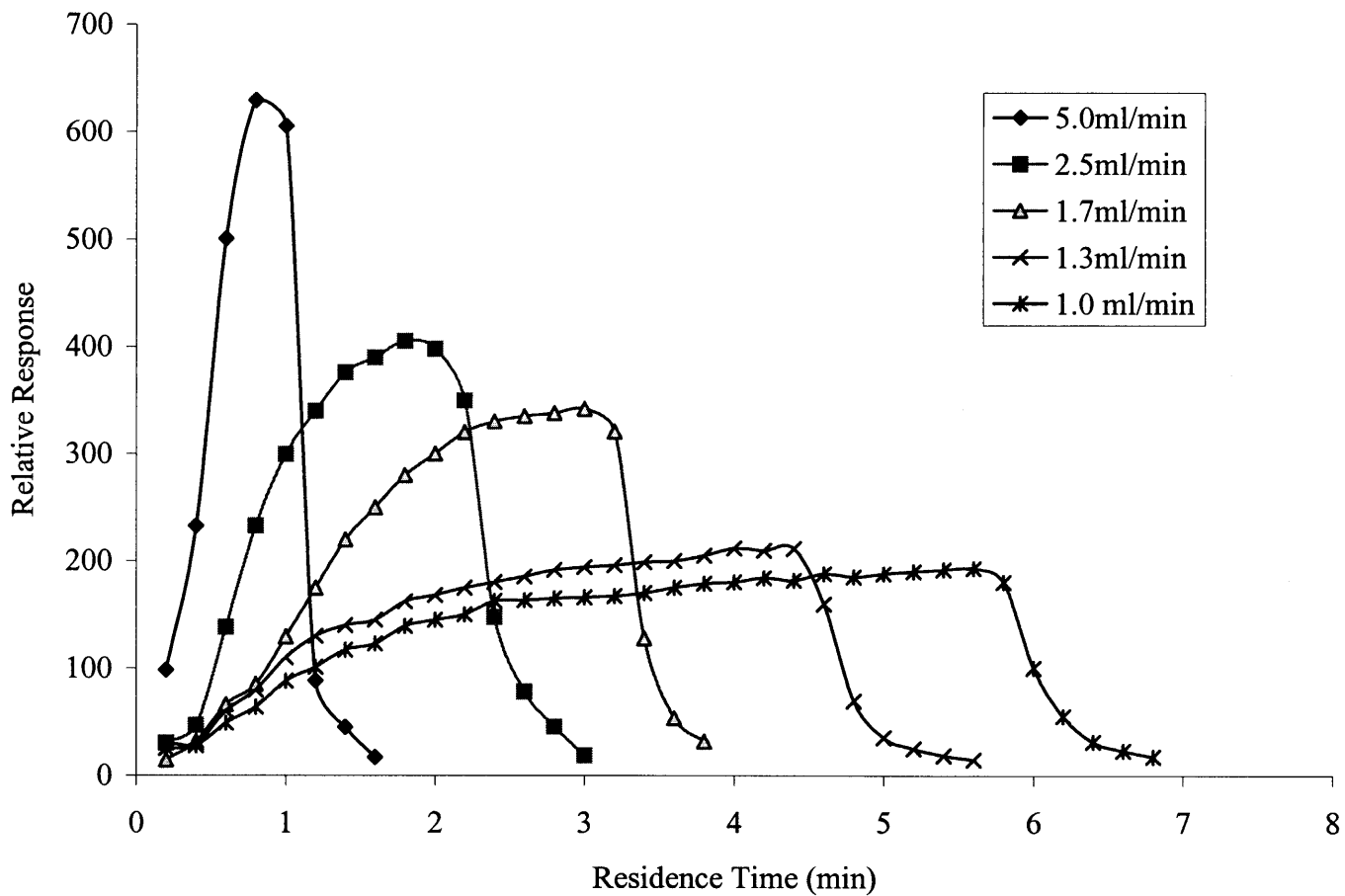
Figure 3.4 System response as a function of residence time for a 5ml, 100ppb toluene sample at different nitrogen flow rates.
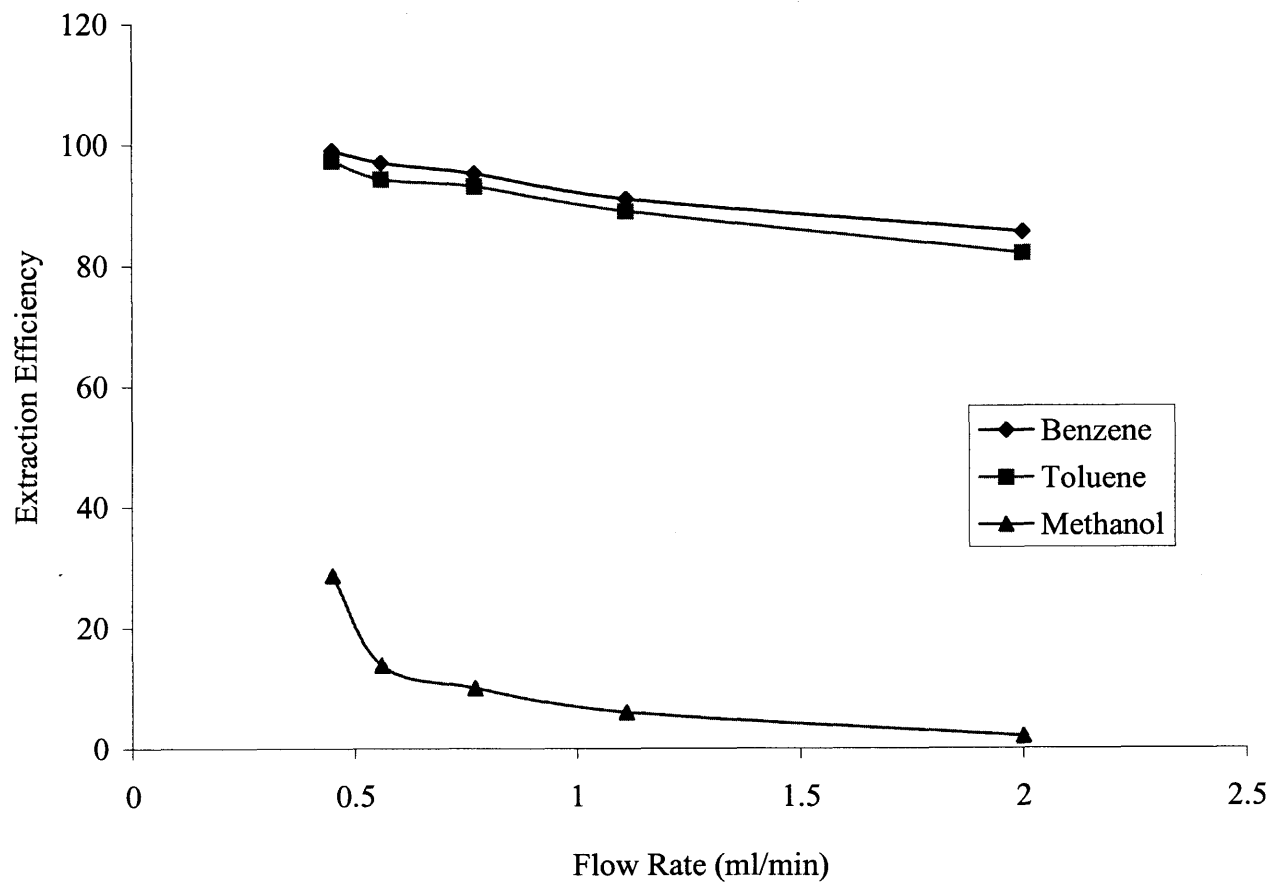
Figure 3.5 Extraction efficiency as a function of sample flow rate. A 5ml, 50ppm sample was used in each case.

efficiency than the polar, water-soluble methanol. Non-polar organics in general have a higher partition coefficient in the hydrophobic membrane used here.

Sample flow rate also affects lag time and analytical sensitivity. Figure 3.6 shows that higher flow rates resulted in shorter residence time in the membrane, which in turn reduced lag time. Figure 3.4 shows the permeation profiles for 5ml, 500ppb toluene samples at different N_2 flow rates. When the flow rate decreased, lower amounts of analytes were brought into the membrane per unit time, resulting in lower permeate flux rate. Figure 3.7 is a plot of instrument response as a function of flow rate. Despite lower permeate flux rate, the response increased with the decrease in flow rate. This was because lower flow rates resulted in longer residence times and higher extraction efficiencies. The system response was proportional to the cumulative flux. The response leveled off below the flow rate of 1ml/min, as the extraction was nearly exhaustive.

Sample volume is another important variable that affects lag time and sensitivity. With all other parameters remaining constant, the sensitivity was proportional to the sample volume, because a larger sample containing more analytes generated a higher detector response. On the other hand, a larger volume resulted in a longer lag time. The system response and lag time as a function of sample volume are shown in Figure 3.8. Both increased linearly with sample volume.

In summary, there was a compromise between the lag time and the sensitivity in GIME. Nevertheless, using the same sample volume and flow rate, gas injection was much faster than aqueous elution. This could significantly increase sample throughput if fast GC was coupled with GIME. If the analysis frequency in continuous monitoring
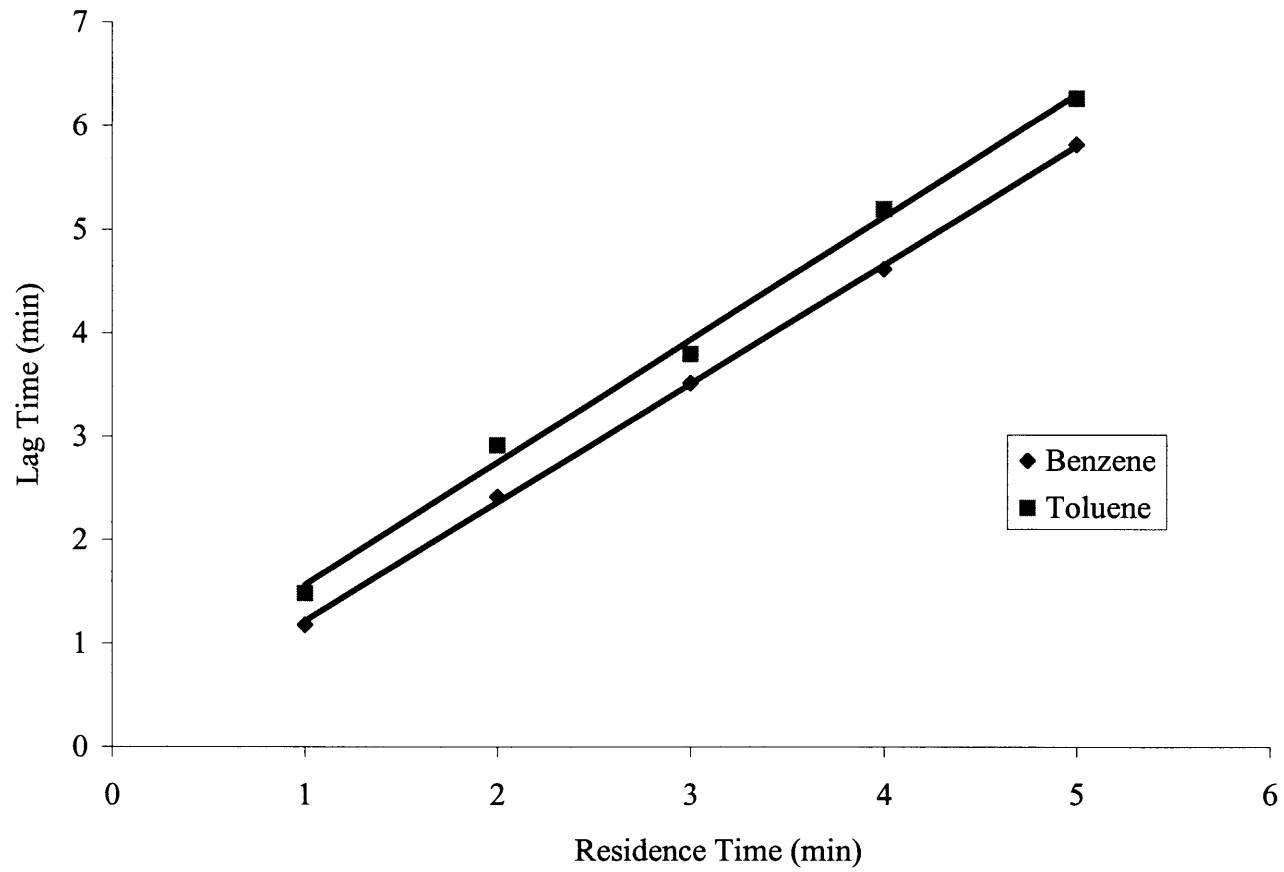
Figure 3.6 Lag time as a function of sample residence time. A 2ml sample at a concentration of 50ppm was used here.
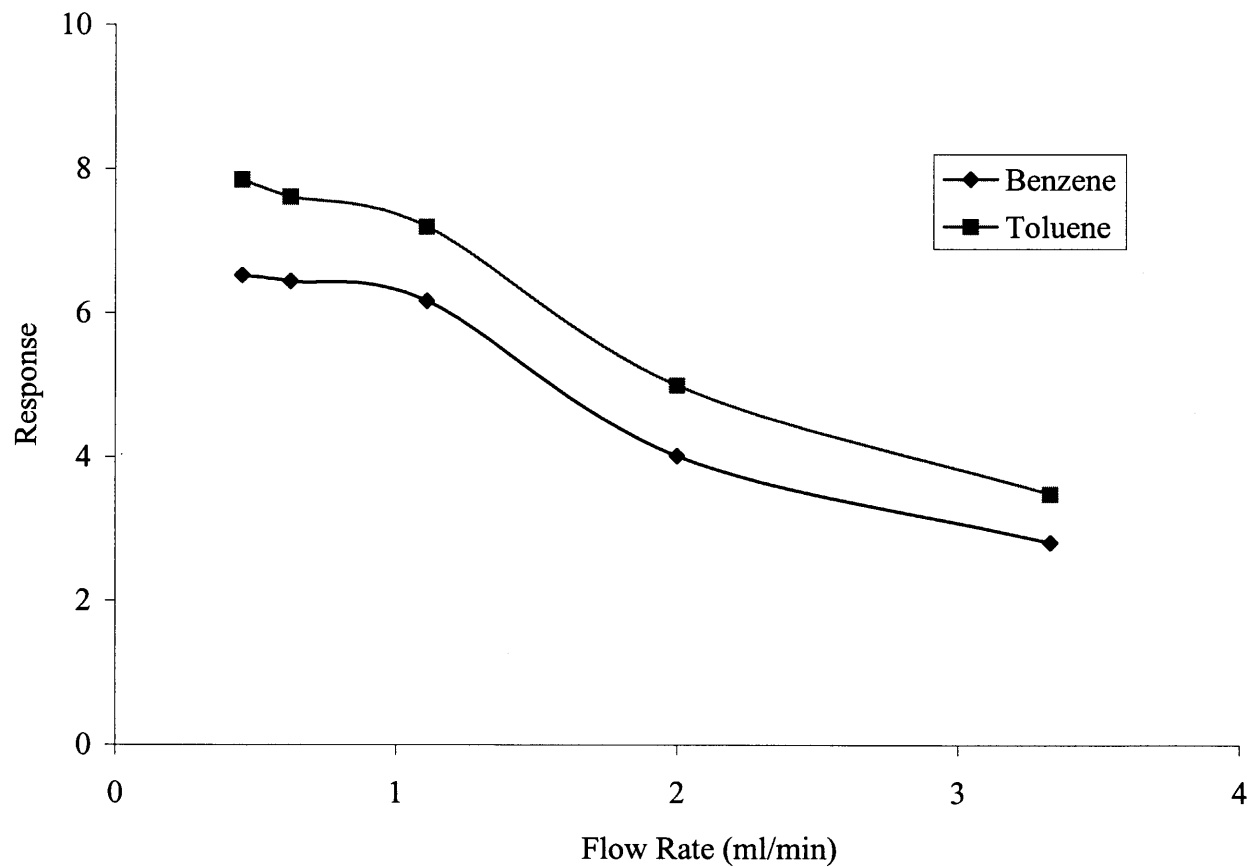
Figure 3.7 System response as a function of sample flow rate. Sample volume was 5ml, and concentration was 50ppb.
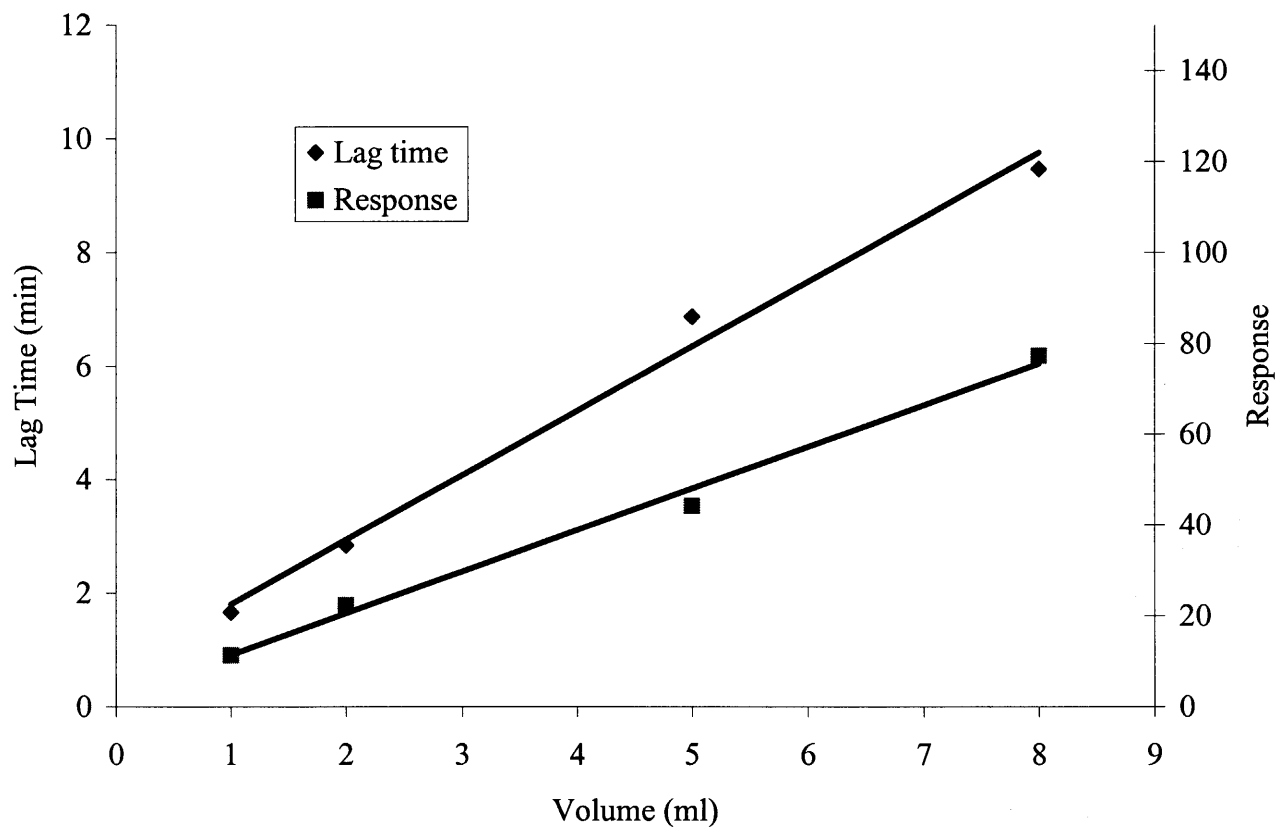
Figure 3.8 System response and lag time as a function of sample volume. 500ppb benzene samples were used at a nitrogen flow rate of 1ml/min.

were to be the same for aqueous elution and gas injection, a larger sample volume and a lower flow rate could be used in GIME to increase sensitivity.

3.3.2 Analytical Performance

In GIME, individual samples can be analyzed by discrete injections, and continuous monitoring can be carried out by sequential injections. Figure 3.9 shows a chromatogram of the seven aromatic compounds listed in EPA Standard Method 602 by GIME. The Method Detection Limits (MDLs) for benzene, toluene, and ethylbenzene were 0.1ppb, 0.1ppb, and 0.9ppb respectively using 2ml samples at a N_2 flow rate of 1ml/min. The MDLs were calculated using a standard EPA method [52]. The experiments were done with a portable GC fitted with a PID. This instrument was not as sensitive as the laboratory instruments. The direct comparison presented earlier indicated that the sensitivity by gas injection was comparable to that by water elution. Based on prior experiences [25-26], it is estimated that significantly lower detection limits could be achieved using a regular bench top GC/FID. In aqueous elution, the maximum volume that can be injected is limited by lag time [26-27]. Since permeation is much faster with gas injection, it is conceivable that the detection limits could be lowered by increasing injection volume. It should also be noted that MDLs depend on parameters such as membrane length, number of fibers, and the N_2 flow rate [26-27].

The Relative Standard Deviations (RSDs) obtained by seven replicate analyses of a 1ml, 10ppb sample were 1.7%, 2.3%, and 2.8% for benzene, toluene, and ethylbenzene respectively. The calibration curves in the 1 to 1000ppb concentration range were linear, and regression coefficients for benzene and toluene were 0.995 and 0.999.
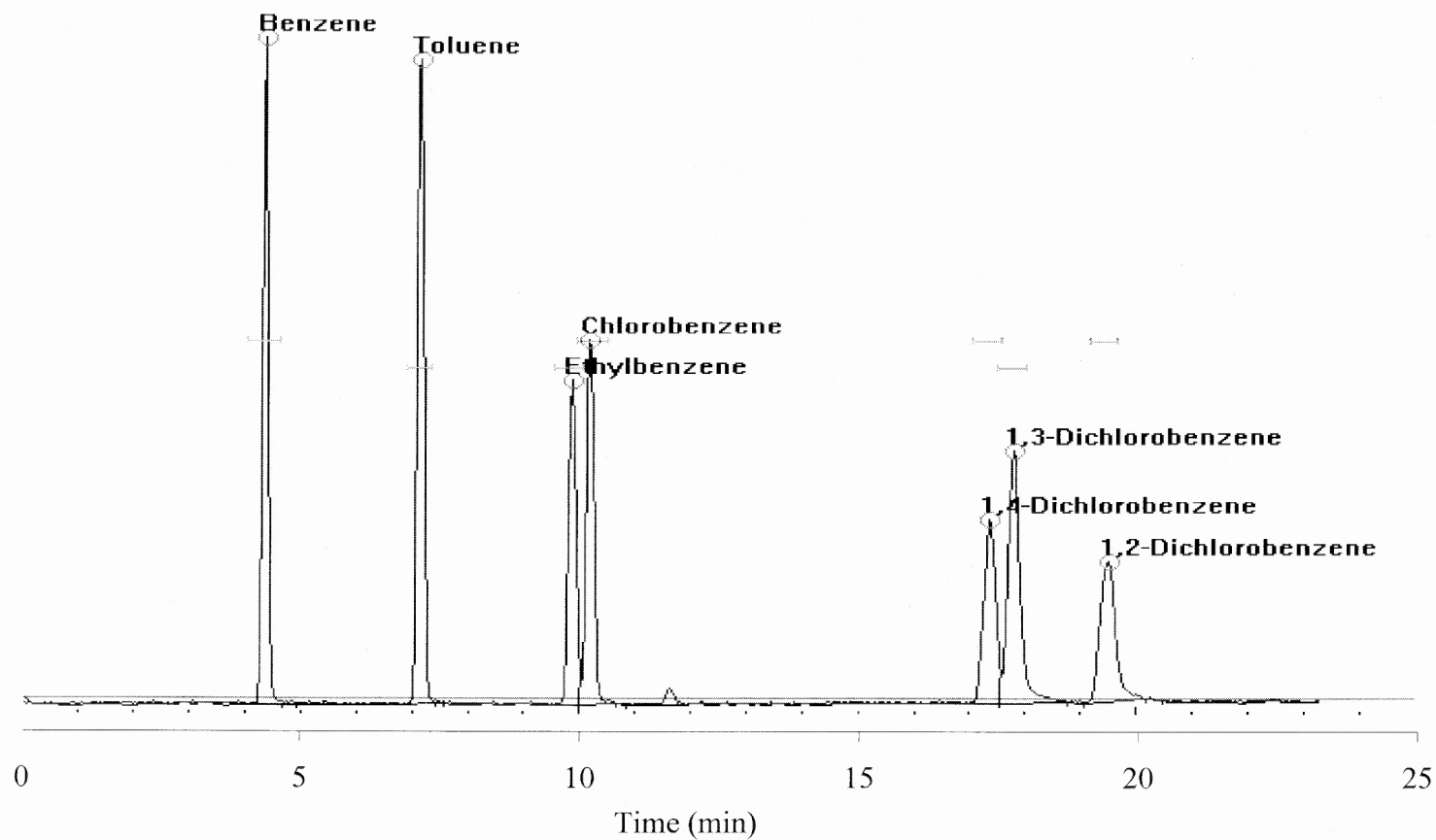
Figure 3.9 Chromatogram of an aqueous sample containing ppb level purgable aromatics as listed in USEPA Standard Method 602 by GIME.

3.4 Conclusion

Gas injection membrane extraction of aqueous samples was studied. Boundary layer effects and axial sample dispersion that are encountered during aqueous elution were significantly reduced. No pump was needed for the delivery of the aqueous eluent, nor was post-injection gas purging necessary. Most importantly, lag time was reduced and extraction speed was increased. The system showed high sensitivity, high precision, and fast response.

CHAPTER 4

SIMULTANEOUS EXTRACTION AND CONCENTRATION
WITH MEMBRANES DURING ON-LINE ANALYSIS

4.1 Introduction

The determination of trace-level pollutants in water usually involves three steps:
extraction of analytes from the sample, concentration of the extract, and analysis.
Conventional extraction techniques for semivolatile organics include Liquid-Liquid
Extraction (LLE) and Solid-Phase Extraction (SPE). Liquid-Liquid Extraction offers
good selectivity based on the choice of solvents, but solvent consumption is relatively
large. In addition, emulsion formation can occur and complicate phase separation. It is
difficult to couple LLE directly with an instrument for on-line analysis. Solid-Phase
Extraction uses less solvent, and has emerged as a widely used technique. Solid-Phase
Extraction has also been used as a method for semi-continuous automated online analysis
[53-54].

Membrane extraction has emerged as a promising extraction technique for both
volatile and semi-volatile organics [22-23, 25, 31, 56-57]. During the extraction of semi-
volatiles, water sample flows on one side (donor side) of the membrane. The analytes
migrate to the other side (acceptor side), where they are collected by an organic solvent
or an aqueous solution. Three types of membrane systems have been used: supported
liquid membrane (SLM), microporous membrane, and polymeric membrane. Supported
liquid membrane extraction is a three-phase (aqueous-organic-aqueous) system. The
membrane consists of a small amount of organic extractant held in a porous matrix by
capillary force. The water sample on the donor side is maintained at a certain pH, such

that the analytes are in their uncharged, molecular form, which can be extracted into the supported membrane liquid. On the acceptor side is an aqueous solution at a different pH, where the analytes are converted into the charged, ionized form and extracted. Supported liquid membrane offers excellent selectivity for ionizable analytes, but is not suitable for the extraction of neutral species [58-60]. Microporous membrane extraction is a two-phase (aqueous-organic) system. The water directly contacts the organic solvent at the membrane pores. It is virtually a micro system for continuous LLE, and can be used for the extraction of non-ionizable compounds [61-64]. Polymeric membrane extraction is a three-phase system, either aqueous-membrane-aqueous, or aqueous-membrane-organic, depending on the acceptor. It has been used for both ionizable and non-ionizable analytes, but the extraction efficiency is often low due to slow diffusion through solid polymer [65-66]. Moreover, Polymeric membranes are less flexible than supported liquid membranes. The former has fixed membrane material, while the latter can be easily changed by using a different membrane liquid.

Recently continuous, on-line membrane extraction coupled with HPLC had been demonstrated as a means of monitoring of semi-volatile organics in aqueous medium [57]. A composite membrane made of porous polypropylene coated with a thin siloxane film was used. The analytes that permeated through the membrane were collected by a solvent (such as acetonitrile) as the acceptor. A similar system has been reported for the extraction of phenols from crude oils and fuels [67-68]. Such a configuration provides several advantages over traditional LLE. It avoids formation of emulsion, consumes less solvent, and can be used for continuous, on-line extraction and analysis.

When the extract is dilute, a concentration step is needed between extraction and
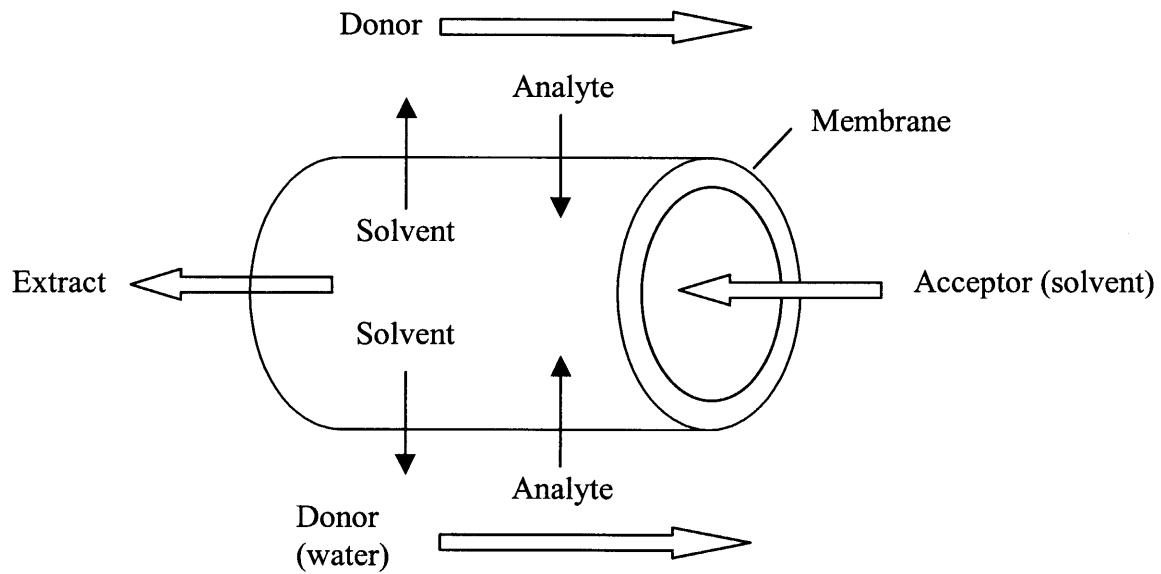
Figure 4.1 Simultaneous extraction and concentration across a hollow fiber membrane.

analysis to increase the concentration in the extract. Conventional approaches use Kuderna-Danish (K-D) condenser or nitrogen blowing. These methods are commonly used in the laboratory, but are not designed for on-line use. In this research, on-line simultaneous extraction and concentration of semivolatile compounds by hollow fiber membranes has been studied. The possibility of combining these two steps into one is demonstrated.

Figure 4.1 shows a schematic diagram of the simultaneous extraction and concentration process. As two fluids flow countercurrent on the acceptor and the donor sides of the membrane, two processes can occur simultaneously. One is the extraction of analytes into the solvent. The other is the two phases crossing over the membrane. The driving force for extraction is the partition of the analytes between the water and the solvent. The crossover can be caused by pressure difference between the two sides. If the water pressure is higher than a critical value ΔP_{cr}, called the Breakthrough Pressure, it can pass through the membrane to the other side [6]. In previous research, the intrusion of water into the acceptor solvent was reported [57]. This diluted the extract and decreased the enrichment factor. Similarly, if the pressure of the acceptor is higher than a certain value, the solvent can be squeezed through the membrane into the aqueous phase. Solvent can also enter the aqueous phase by dissolving in water. Solvent loss reduces the volume of the extract, resulting in the preconcentration of analytes before analysis. This increases the enrichment factor, and consequently lowers the detection limit. This chapter reports simultaneous extraction and concentration during on-line analysis of semivolatile organics in water. Important system parameters affecting solvent loss, analyte enrichment, and extraction efficiency are studied.
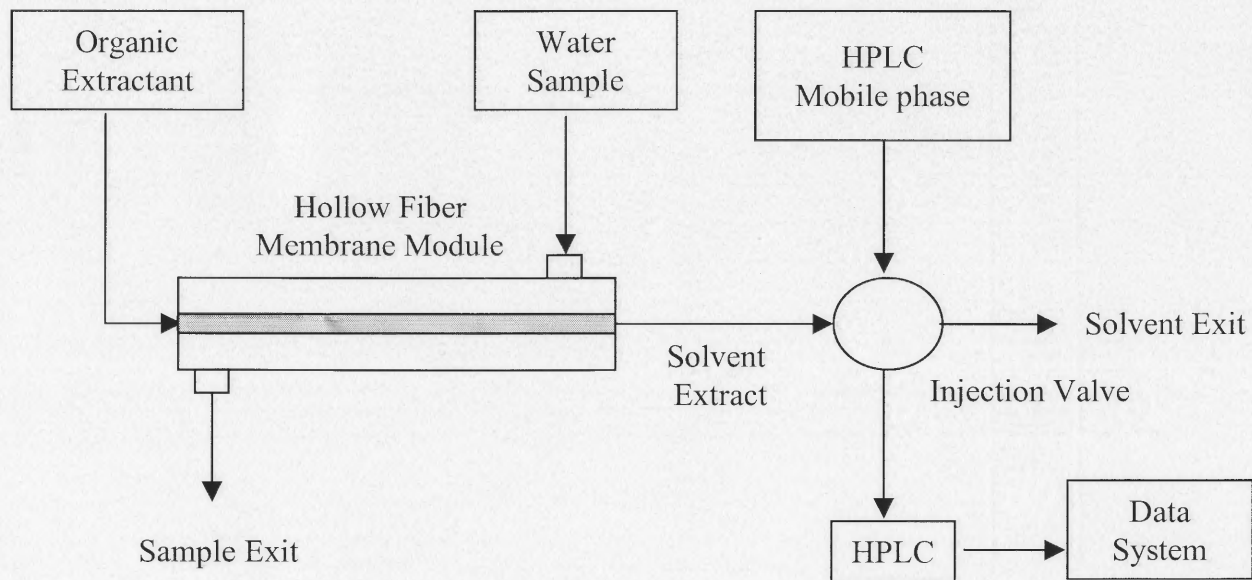
Figure 4.2 Schematic diagram of membrane extraction with an on-line HPLC.

4.2 Experimental

A schematic diagram of the membrane extraction system is shown in Figure 4.2. The water sample continuously flowed through the membrane module, which was made of multiple hollow fiber membranes in a shell-and-tube design. The water was on the shell side (donor side) of the membrane. The water pressure was kept at 50psi, which was at east 10psi higher than the solvent pressure. After extraction, the analyte-laden solvent was injected by a 10-port automatic injection valve into the HPLC for analysis. Corresponding to each injection, a chromatogram was obtained. Continuous monitoring was carried out by sequentially injecting the extract at preset frequency.

The membrane module was constructed with six 100 cm long hollow membrane fibers packed in a Teflon® tube. Two types of membranes were used: microporous membranes and composite membranes. The microporous membrane, Celgard X10 (Hoechst Celanese, Charlotte, NC), was made of polypropylene, with an i.d. of 0.240mm and an o.d. of 0.290mm. It had an average pore size of 0.03μm and porosity of 20%. The composite membrane had a 0.260mm o.d. and a 0.206mm i.d. (Applied Membrane Technology, Minnetonka, MN). It consisted of a 1μm thick homogeneous siloxane as the active layer deposited on a film of microporous polypropylene as the support. Each end of the Teflon® tube was connected with a "T" unit (Components & Controls Inc. Carlstadt, NJ). The space between the membrane and the "T" units were sealed with epoxy (Resin Technology Group, LLC, S. Easton, MA) in order to prevent the mixing between the water and the solvent.

The four solvents used in this study were: hexane, butyl acetate (BA), methyl isobutyl ketone (MIBK), and isopropyl acetate (IPA). The model compounds used as

analytes were pentachlorophenol (PCP), atrazine, and naphthalene. All the chemicals used in the experiments were analytical grade (Sigma Chemical Co. St. Louis, MO). The 10-port valve was purchased from Valco Instruments Co. Inc., Houston, TX. A reciprocating pump (Altex Model 110A) was used for water delivery, and a HPLC pump (Hewlett-Packard Model 1050) for solvent delivery. The analysis was carried out using a Hewlett-Packard 1050 HPLC with a Waters 486 Tunable Absorbance UV Detector at 254nm (Waters, Medford, MA). The HPLC column was a 3.9 ×150mm Nova-Pack C18 (Waters, Medford, MA) with 6μm packing. A mixture of 45:55 (v/v) acetonitrile-0.01M K_3PO_4 solution was used as the eluent at a flow rate of 2.0ml/min. Minichrom V. 1.62 software (VG Data Systems) was used for data acquisition and analysis.

4.3 Results and Discussion

4.3.1 Extraction Efficiency and Enrichment Factor

In membrane extraction where analytes are extracted from water into an organic solvent, the extraction efficiency (EE) is defined as:

$$EE = C_s F_{s,o} / C_{w,i} F_w \tag{4.1}$$

where C_s is the analyte concentration in the solvent extract, $F_{s,o}$ the flow rate of the solvent exiting the membrane, $C_{w,i}$ the analyte concentration in the water entering the membrane, and F_w the water flow rate. The mass balance for the membrane extraction is:

$$C_{w,i} F_w = C_{w,o} F_w + C_s F_{s,o} \tag{4.2}$$

Where $C_{w,o}$ is analyte concentration in the water exiting the membrane. The distribution coefficient of the analyte between the solvent and water is defined as:

$$K = C_s / C_{w,o} \tag{4.3}$$

The flow rate ratio of the water and the solvent is:

$$R = F_w / F_{s,o} \tag{4.4}$$

Combining Equations 4.1, 4.2, 4.3, and 4.4, and assuming equilibrium has been reached, the extraction efficiency can be written as:

$$EE = C_s F_{s,o} / (C_{w,o} F_w + C_s F_{s,o}) = 1/(1 + F_w / (KF_{s,o})) = 1/(1+R/K) \tag{4.5}$$

The enrichment factor (EF) in membrane extraction is defined as the ratio of analyte concentration in the solvent extract to that in the water entering the membrane:

$$EF = C_s / C_{w,i} \tag{4.6}$$

Combining Equations 4.2, 4.3, 4.4, and 4.6, enrichment factor can be written as:

$$EF = C_s / (C_{w,o} + C_s F_{s,o} / F_w) = 1 / (1/K + F_{s,o} / F_w) = 1/(1/K+1/R) \tag{4.7}$$

Equations 4.5 and 4.7 show that extraction efficiency and enrichment factors are determined by distribution coefficient and the flow rate ratio of the water to the solvent. As far as analytical performance is concerned, sensitivity is proportional to enrichment factor, not extraction efficiency.

Based on Equations 4.5 and 4.7, Figure 4.3 shows a simulation of the change in extraction efficiency (EE) as a function of K/R. If R is constant, EE increases with the increases in K, and the change is exponential. Initially, EE increases rapidly with K, and then the change becomes gradual. If K is constant, EE increases with the decrease in R, which can be achieved by using lower sample flow rate or higher solvent flow rate. When K/R>10, EE is approaching its maximum possible value, which is 100%. Further increasing K or decreasing R does not improve EE.

Figure 4.4 is a simulation of the change in enrichment factor (EF) as a function of K at a constant R. Enrichment factor increases with the increase in K, and the change is
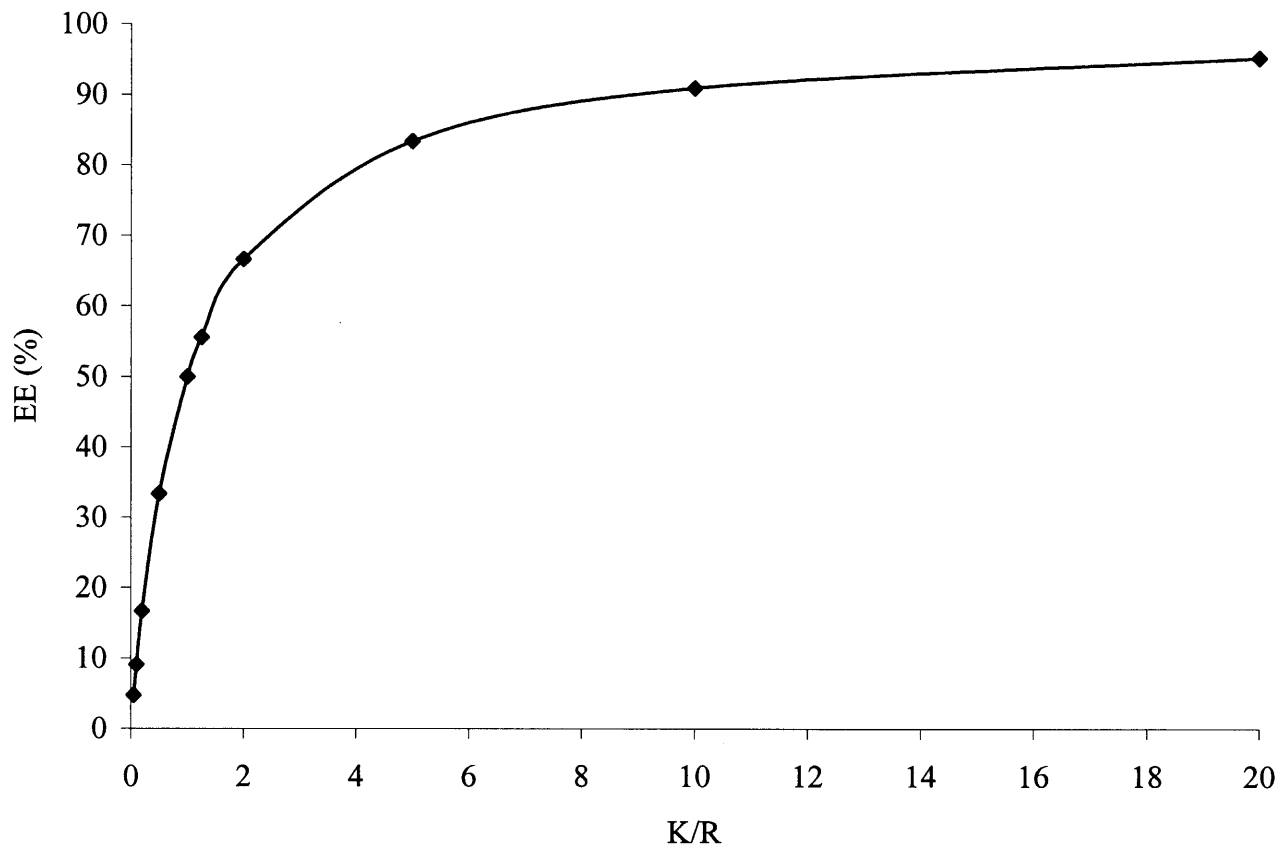
Figure 4.3 Extraction efficiency as a function of K/R.
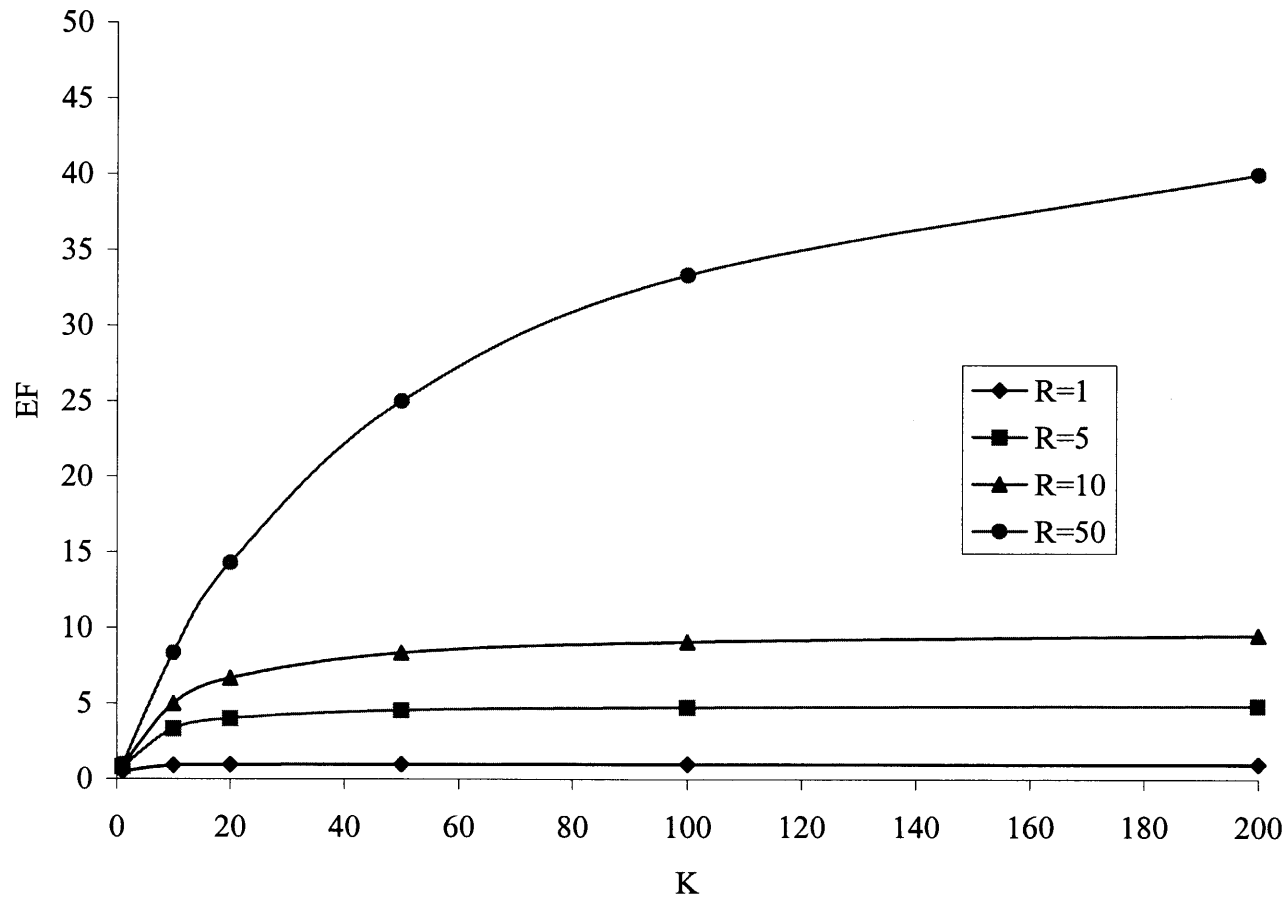
Figure 4.4 Enrichment factor as a function of K at a constant R.
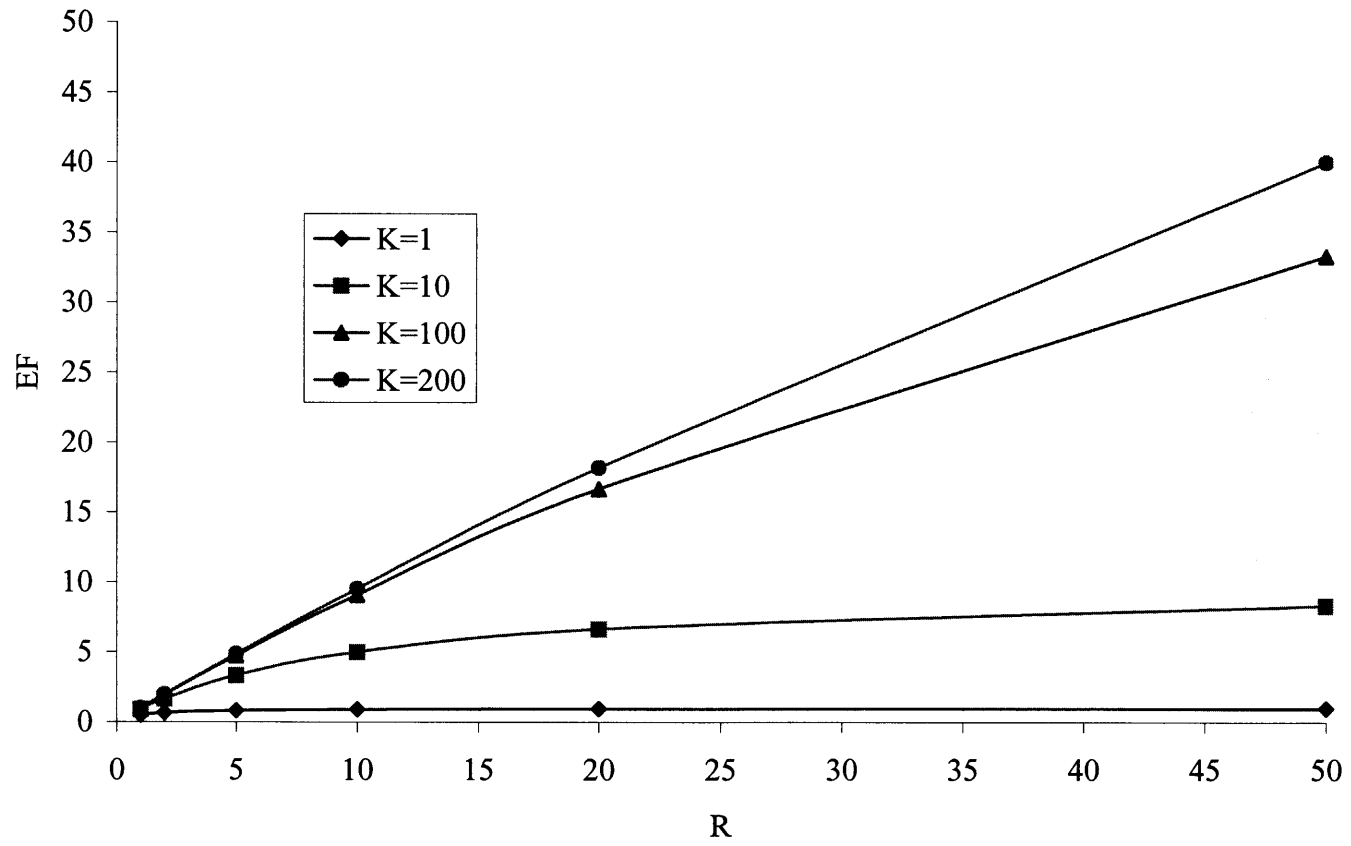
Figure 4.5 Enrichment factor as a function of R at a constant K.

exponential. The rate of change is:

$$d(EF)/dK = [R(R+K)-KR]/(R+K)^2 = [R/(R+K)]^2 = 1/(1+K/R)^2 \qquad (4.8)$$

The minimum $d(EF)/dK$ is equal to zero. This is possible when K is very high. The corresponding maximum EF in Equation 4.7 is R.

Figure 4.5 is a simulation of the change in enrichment factor (EF) as a function of R at a constant K. Enrichment factor increases with the increase in R, and this change is also exponential. The rate of change is:

$$d(EF)/dR = [K(R+K)-KR]/(R+K)^2 = [K/(R+K)]^2 = 1/(1+R/K)^2 \qquad (4.9)$$

The minumum $d(EF)/dK$ is equal to zero. This is possible when R is very high. The corresponding maximum EF in Equation 4.7 is K.

Therefore, the maximum EF is limited by K or R, whichever is smaller. In order to attain high EF, both K and R need to be large. From Figures 4.3, 4.4, and 4.5, it can be seen that the increase in K increases both EE and EF. However, the change in R has different impacts on EE and EF. A higher R gives a higher EF, but a lower EE at the same time. In other words, other factors being constant, higher sample flow rates results in higher EF but lower EE, while higher solvent flow rates results in lower EF, but higher EE.

4.3.2 Concentration via Solvent Permeation

The goal was to concentrate the extract by partially losing the solvent during membrane extraction. Solvent Loss is defined as:

$$L\% = (1 - F_{s,o} / F_{s,i}) * 100 \qquad (4.10)$$

Where L is percentage of solvent lost, and $F_{s,i}$ is the flow rate of solvent entering the membrane. Solvent loss resulted in the decrease in $F_{s,o}$. According to Equations 4.5 and 4.10, this should decrease EE and increase EF.

Table 4.1 Solvent Losses for Different Solvents

	K_{ow} (Log P) [69]	Solubility in Water at 20 ^{0}C [69]	Solvent Loss (%)*	
			Composite	Polypropylene
Hexane	3.90	9.5 mg/l	26.7	26.7
MIBK	1.31	19 g/l	88.9	87.5
BA	1.78	8.4 g/l	73.3	46.7
IPA	1.03	30.9 g/l	95	80
Acetonitrile	-0.34	Miscible	100	100
Methanol	-0.77	Miscible	100	100

*Solvent flow rate was 0.1 ml/min. Water flow rate was 3.9ml/min.

In this study, four different solvents with varying polarity and water solubility were used. Their octanol-water partition coefficients and solubility in water are presented in Table 4.1. Pressure differential could be used to manipulate solvent loss. However, high pressure could rupture or collapse the membrane. Moreover, precise pressure control was difficult. Considering all this, pressure was not chosen as the main variable. There are other factors contributing to the solvent loss. The first was the permeation of the solvent through the membrane, and second was the solubility of the solvent in the water. It was observed that solvent loss increased with its solubility in water. Table 4.1 shows the order of solvent loss. Hexane was the least soluble in water and suffered the least solvent loss. IPA, on the other hand, had the highest solubility in water and suffered the
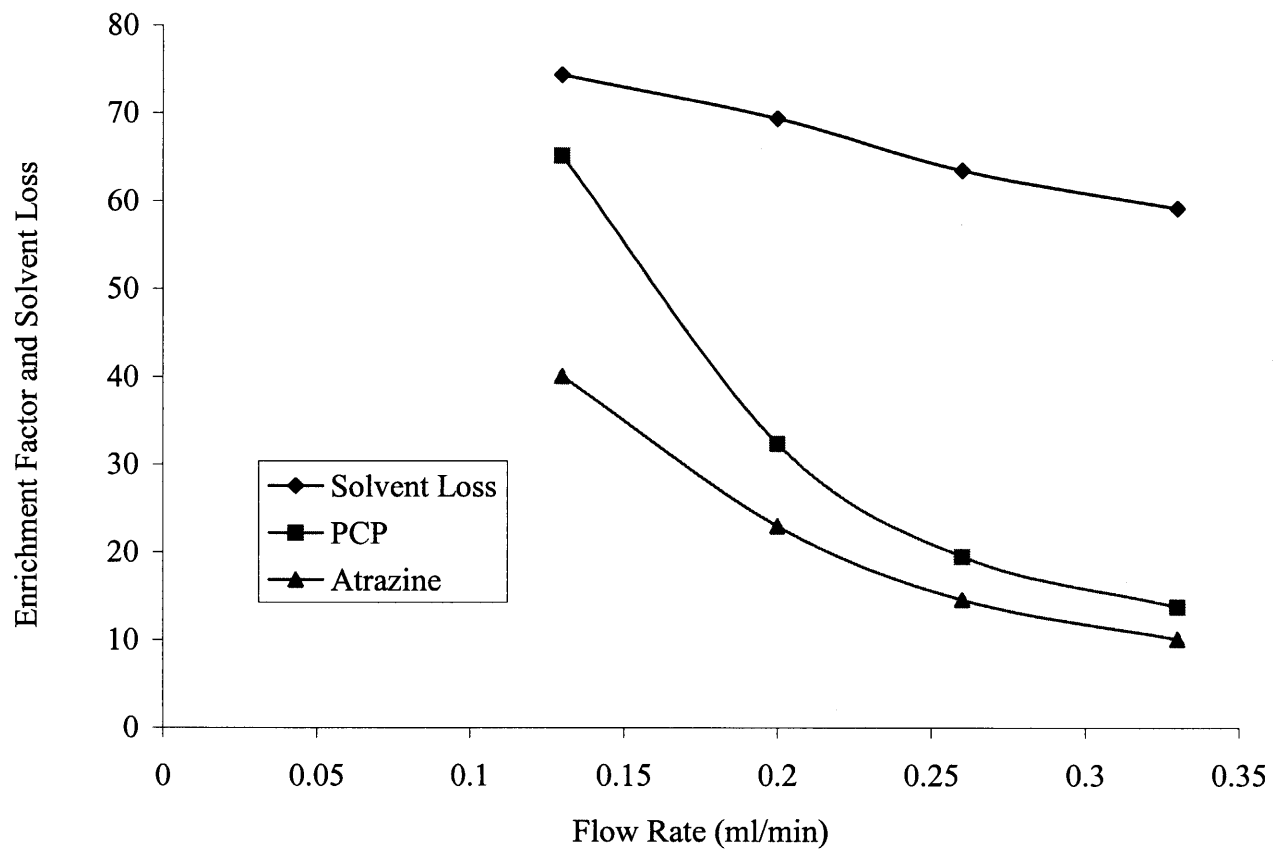
Figure 4.6 Enrichment factor and solvent loss as a function of solvent (IPA) flow rate .

maximum solvent loss. Experiments with highly water-soluble solvents such as methanol and acetonitrile resulted in extensive solvent loss to the point that there was none left. Consequently, these solvents could not be used.

Solvent loss was also affected by solvent flow rate. Figure 4.6 shows solvent loss was higher at lower flow rates. This was because the solvent residence time increased with the decrease in flow rate, and both permeation and solubility increased when contact time increased. Figure 4.6 also shows that the EF increased with the decrease in IPA flow rate, while water flow rate was constant. This is because lower solvent flow rate resulted in higher EF, which could be predicted from Equation 4.7. EF was further increased because more solvent was lost at lower flow rates. Figure 4.7 is a plot of EF as a function of solvent loss. This plot is empirical in nature, showing that EF increases with solvent loss. In reality, EF also depends upon K and residence time.

Table 4.2 Extraction Efficiency as a Function of Different Solvents
in Different Membranes

Extraction Efficiency (%)	K_{ow} (Log P)	Hexane		MIBK		BA		IPA	
		C	P	C	P	C	P	C	P
PCP	5.12	68.1	55.3	43.7	54.8	69.5	67.8	26.1	38.7
Atrazine	2.61	6.5	4.7	N/A	N/A	56.2	63.7	31.6	40.1
Naphthalene	3.30	46.3	68.1	33.9	19.5	81.3	60.1	37.4	20.2

C: composite membrane, P: polypropylene membrane. Solvent flow rate was 0.1ml/min. Water flow rate was 3.9ml/min. The concentrations of the three analytes were 6.67ppm each.

For the test compounds used in this study, Table 4.2 shows that under the same flow conditions of water and solvent, BA had the best extraction efficiencies, which were between 85% and 100 %. IPA showed the lowest extraction efficiencies, which were

40% and 60%. Some of the extracted analyte was lost back into the aqueous phase during solvent loss. This might have caused the lower extraction efficiency with IPA. Table 4.3 shows that the enrichment factors, exhibited a different trend. IPA, which had the lowest extraction efficiency, showed the highest enrichment factor. The order of enrichment factors in Table 4.3 is in line with the order of solvent loss in Table 4.1. The high solvent loss of IPA resulted in a preconcentration effect and consequently high enrichment factor. The data shows that solvent loss had a significant impact on extraction efficiency as well as enrichment factor. Since detection limit is ultimately determined by enrichment factor, solvent loss can be used effectively to enhance enrichment factor in membrane extraction. A more water-soluble solvent and a lower flow rate would increase preconcentration via solvent loss.

Table 4.3 Enrichment Factor as a Function of Different Solvents
in Different Membranes

Enrichment Factor	Hexane		MIBK		BA		IPA	
	C	P	C	P	C	P	C	P
PCP	36.3	29.4	153.3	171	101.6	49.6	203.4	75.5
Atrazine	3.5	2.5	N/A	N/A	82.2	46.6	246.6	78.3
Naphthalene	24.6	36.2	119	60.8	119	44	292	39.5

C: composite membrane, P: polypropylene membrane. Solvent flow rate was 0.1ml/min. Water flow rate was 3.9ml/min. The concentration of the three analytes was 6.67ppm.

The enrichment factor and the extraction efficiency also depend upon the analytes. Polar compounds have higher K in polar solvents, which result in higher extraction efficiency and enrichment factor. Similarly, non-polar compounds are extracted better with non-polar solvents. The K_{ow} of hexane is close to those of PCP and
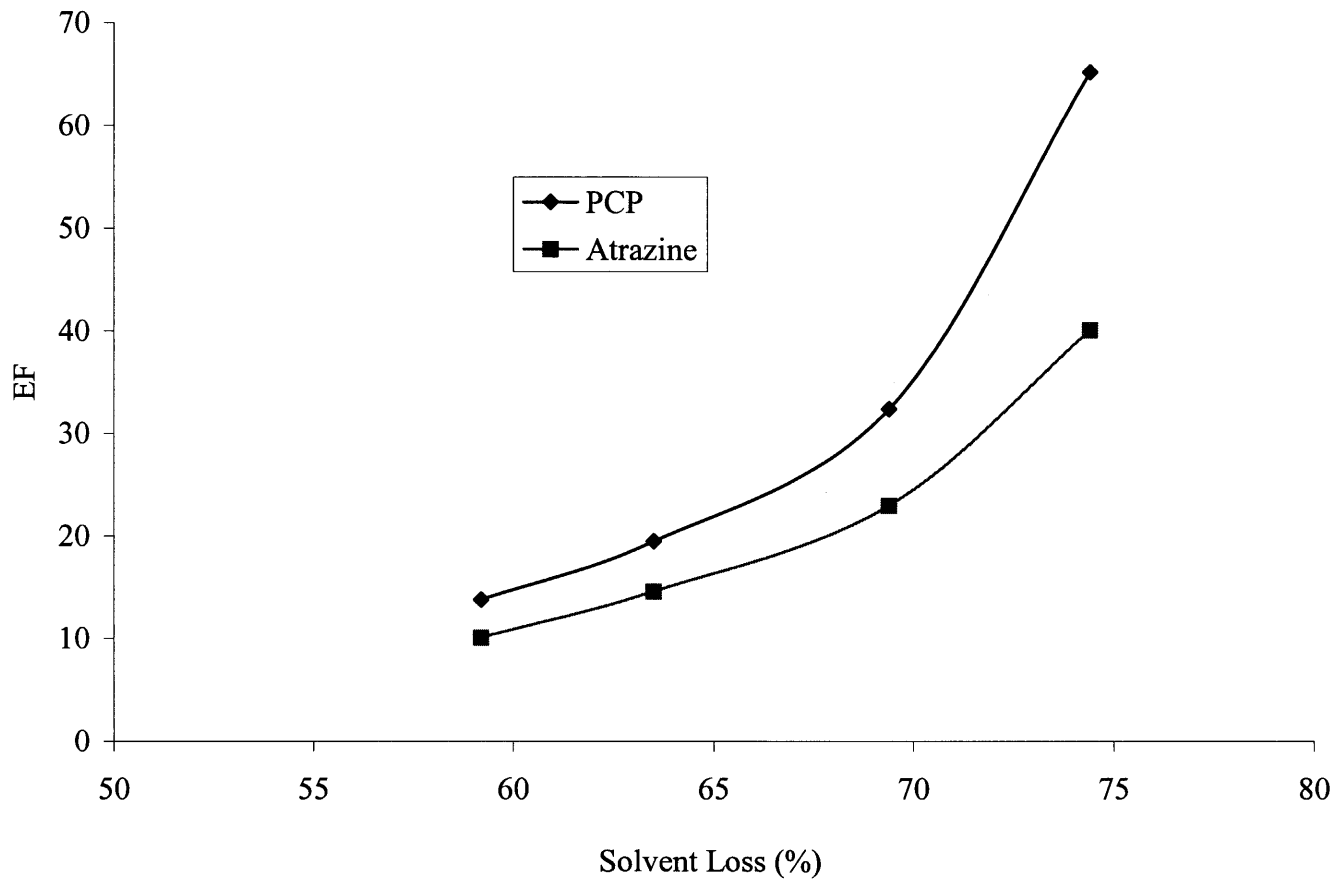
Figure 4.7 Enrichment factor as a function of solvent loss.

naphthalene, so it provided good extraction efficiency and enrichment factors for these compounds. On the other hand, the extraction efficiency of atrazine (which has a low K_{ow}) with hexane was quite low.

4.3.3 Effects of Membranes

Two membranes were tested in this study, a porous polypropylene membrane and a composite membrane consisting of a 1μm thin siloxane film on porous polypropylene. It had been expected that the microporous membrane would provide better enrichment factors, because the solvents had direct contact with the sample in the membrane pores. However, Table 4.3 shows that there was no significant difference in performance with hexane and MIBK as extractants. The EF was higher with the composite membrane when BA and IPA were used. Since the silicon-coated layer on the composite membrane was only 1μm, it tended to swell when in contact with solvents. Under these conditions, this layer no longer provided much resistance to permeation, and the composite membrane worked like a microporous membrane.

4.3.4 Analytical Performance

For atrazine, PCP, and naphthalene, the method detection limits were 0.5, 1, and 0.9ppb respectively, and the relative standard deviations were 4.6%, 7.8% and 6.3% based on seven replicate injections. The calibration curves were linear in the range of 10-1000ppb. A microporous membrane module was used. The water flow rate was 4.0ml/min, and the solvent (IPA) flow rate was 0.15ml/min. Figure 4.8 shows the chromatograms during continuous monitoring of these three compounds. As water flowed continuously through
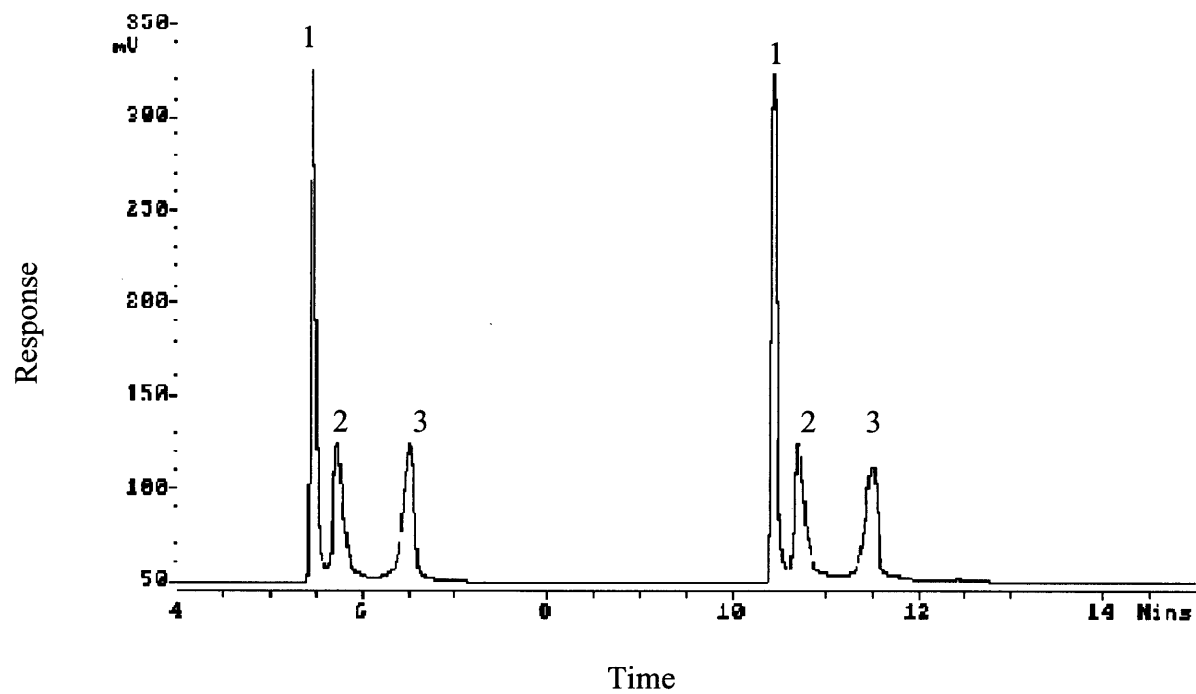
Figure 4.8 Continuous monitoring of water containing 2ppm of atrazine (1), PCP (2), and naphthalene (3). Water flow rate was 3.0ml/min, and IPA flow rate was 0.3ml/min. Injection was made every five minutes.

the membrane, injections were made every five minutes. Corresponding to each injection, a chromatogram was obtained.

4.4 Conclusion

Simultaneous extraction and concentration during on-line analysis using membranes was studied. The influences of distribution coefficient, solvent polarity, and solvent and water flow rates on enrichment factor and extraction efficiency were investigated. It was observed that solvent loss during extraction had significant impact on enrichment factor and extraction efficiency. Continuous on-line monitoring was demonstrated using this technique.

CHAPTER 5

SUPPORTED LIQUID MEMBRANE MICRO-EXTRACTION (SLMME) WITH ION-PAIR CHROMATOGRAPHY (IPC) FOR THE DETERMINATION OF NINE HALOACETIC ACIDS IN WATER

5.1 Introduction

Since the 1970s many disinfection by-products (DBPs) have been identified in chlorinated drinking water. These toxic, halogenated compounds are generated by the reaction of chlorine with natural organic matter (humic and fulvic compounds) and bromide (if present) in the source water. Trihalomethanes (THMs) are the major volatile DBPs, while haloacetic acids (HAAs) are the main non-volatile components [1]. Table 5.1 gives the names and acronyms of the nine HAAs. In addition to drinking water, HAAs have also been found in the swimming pools [70], rainwater [71], surface water [72-73], and seawater [74].

In the last few years, the adverse effects of HAAs on human health and the environment have been recognized. Haloacetic acids are toxic to humans, plants, and in particular to algae [75]. The USEPA has classified DCAA as a group B2 compound (probable human carcinogen), and TCAA as a group C (possible human carcinogen). Furthermore, decarboxlyation of HAAs contributes to the formation of THMs [76], which are also carcinogens. According to the current EPA DBP regulations [77], the Maximum Concentration Limit (MCLs) for the total of five HAAs (MCAA, MBAA, DCAA, BCAA, and DBAA) in drinking water should not exceed 60µg/L. The EPA Information Collection Rule (ICR) requires water utilities to monitor the concentration of six HAAs (the five HAAs mentioned above plus TCAA), and encourages the determination of the remaining three HAAs.

Table 5.1 Names, Acronyms, and Properties of Haloacetic Acids*

Full Name	Acronym	PKa	LogP
Monochloroacetic Acid	MCAA	2.87	0.22
Monobromoacetic Acid	MBAA	2.89	0.41
Dichloroacetic Acid	DCAA	1.26	0.92
Bromochloroacetic Acid	BCAA	1.39	1.14
Dibromoacetic Acid	DBAA	1.47	1.693
Trichloroacetic Acid	TCAA	0.51	1.33
Bromodichloroacetic Acid	BDCAA	1.09	2.31
Dibromochloroacetic Acid	DBCAA	1.09	2.907
Tribromoacetic Acid	TBAA	2.13	3.459

*The pKa and log P values of MCAA, MBAA, DCAA, and TCAA are from Ref. [69], the values of the other HAAs were calculated using Advanced Chemistry Development (ACD) Software Solaris V4.67.

The importance of HAAs calls for sensitive and reliable methods for their determination. The EPA method 552 and Standard Method 6251 for HAA analysis involve liquid-liquid extraction and derivatization, followed by GC detection [78-79]. Low method detection limits are attained at the cost of a lengthy, cumbersome extraction-derivatization procedure using diazomethane, which is toxic, carcinogenic and explosive. The EPA method 552.1 uses ion-exchange-derivatization, followed by GC. It consumes less solvent, but interference from anions cannot be prevented without sample dilution, which increases the detection limits [80]. The above methods can only determine six HAAs. The EPA method 552.2 uses acidic methanol instead of diazomethane for derivatization, and can be applied to the determination of nine HAAs [81]. However, it still follows the complicated liquid-liquid extraction-derivatization approach, with a GC run time of approximately 50 minutes.

Table 5.2 Detection Limits (μg/L) for Determination of HAAs by Different Methods

	RPLC [82]	Ion exclusion [84]	Ion exchange [84]	CE [87]	EPA 552.2 [81]
MCAA	200	70	8	5	0.273
MBAA	480*	85	21	5	0.204
DCAA	100	8	16	2	0.242
BCAA	N/A	N/A	N/A	N/A	0.251
DBAA	160*	90	30	3	0.066
TCAA	250	5	80	2	0.079
BDCAA	N/A	N/A	N/A	N/A	0.091
DBCAA	N/A	N/A	N/A	N/A	0.468
TBAA	350*	N/A	N/A	N/A	0.82

*Ref. [83]

In light of the limitations of the EPA methods, alternative techniques have been. Investigated. Some of these, such as GC-MS based methods, still require derivatization prior to analysis [70]. Methods do not require derivatization include liquid chromatography (LC) [82-83], ion chromatography (IC) [84-86], capillary electrophoresis (CE) [87], and electrospray ionization mass spectrometry (ESI-MS) [88]. ESI-MS provides excellent sensitivity and selectivity, but high price and limited availability of the instrument precludes its widespread use. With the reported sample preparation techniques, the detection limits of the LC, IC and CE methods are significantly higher than the GC methods. Table 5.2 shows the detection limits of LC, IC, CE methods, as well as the EPA method 552.2.Most of the alternative methods have been used for only five or six HAAs. A few were applicable for all nine HAAs. Recently, it

was reported that the three HAAs (BDCAA, DBCAA, and TBAA) made up a significant portion of the total HAAs and should not be overlooked [89].

Supported liquid membranes (SLM) have been used for the extraction of charged or ionizable compounds [90-91]. The membrane liquid is a small amount of organic extractant held by capillary force in a microprous membrane. The water sample on one side of the membrane is maintained at certain pH, such that the analytes are in their uncharged, molecular form, and can be extracted into the membrane liquid. On the other side is an aqueous solution at a different pH, where the analytes can be ionized and extracted from the organic solvent. Supported liquid membrane extraction offers high enrichment factors and excellent selectivity, and it can be used for on-line analysis. However, memory effects and relatively short membrane life have been the major concerns in SLM extraction.

The objective of this research is to develop a simple, inexpensive, and effective method for the analysis of all nine HAAs that does not require derivatization, or large amounts of organic solvents. A Support Liquid Membrane Micro-Extraction (SLMME) method is proposed for the extraction and preconcentration of HAAs. It provides very high enrichment factors, and the liquid membrane is inexpensive and easy to make. It uses only a few microliters of organic extractant per sample. Thus this method is both economical and environmentally friendly. A large number of samples can be extracted simultaneously to increase sample throughput. It is possible to use a new membrane for each extraction. This way, extraction is free of memory effects, and membrane life is not a problem. Similar configurations have been reported for the extraction of basic drugs

from biological fluids, as well as phenols from wastewater [92-94]. They provided enrichment factors in the range of 75 to 380.

Reverse phase ion-pair chromatography has been used to analyze six HAAs [82-83]. Such a method does not require derivatization. In this study, a new ion-pair chromatographic method with flow programming was developed. As mentioned before, high detection limits have been a major issue in LC, IC, or CE determination of HAAs. The high enrichment factor in SLMME can offset the lower sensitivities of these methods.

5.2 Experimental

The supported liquid membrane (SLM) used in this study was made by impregnating a segment of microporous hollow fiber with a membrane liquid for ten seconds. The membrane pores were automatically filled with the liquid. The excessive liquid was replaced by injecting micro liters of NaOH solution (the acceptor) into the membrane lumen. A schematic diagram of the SLMME system is shown in Figure 5.1. Two syringes were used to hold the membrane in place. One was used to inject (or withdraw) the acceptor into (or from) the membrane. The other served as a support. The liquid membrane was placed in a sample bottle that contains the water to be analyzed (the donor). The pH was lowered by adding concentrated sulfuric acid (H_2SO_4). Sodium sulfate was also added to increase the ionic strength. A magnetic stirrer was used to agitate the sample during extraction. After extraction, the acceptor solution was drawn into the syringe, and then transferred into a vial insert for HPLC analysis.

Two types of polypropylene microporous hollow fiber membranes were used to
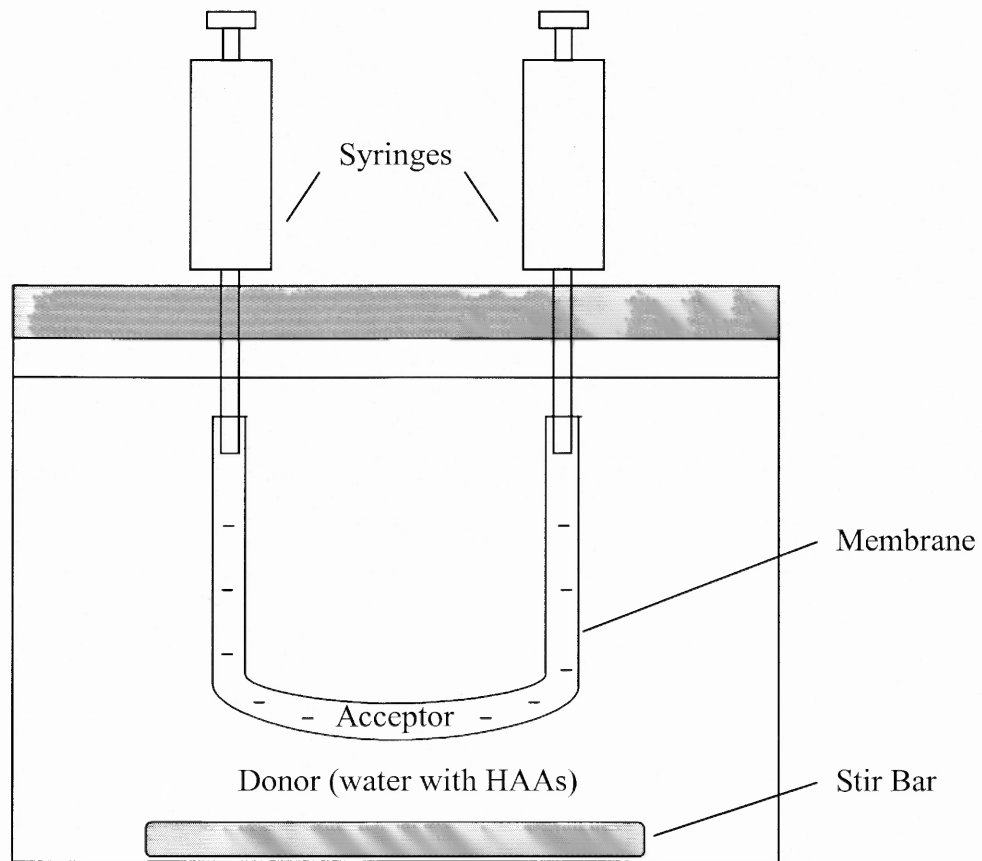
Figure 5.1 Schematic diagram of SLMME.

make the SLM. One was Celgard® X20 (Hoechst Celanese, Charlotte, NC). It had an i.d.
of 400μm and an o.d. of 460μm, with an average pore size of 0.03μm and porosity of
40%. The other was Accurel® PP Q 3/2 (Membrana GmbH, Wuppertal, Germany). It had
an i.d. of 600μm and a wall thickness of 200μm, with an average pore size of 0.2μm and
porosity of 75%. The membrane liquids tested were di (2-ethylhexyl) phosphate
(DEHPA) and di-hexyl ether (DHE). The effect of adding trioctylphosphine oxide
(TOPO) into DHE was also investigated.

Nine standard solutions were purchased from Supelco (Supelco Park, PA), each
of which contained an individual HAA. Other chemicals used in this study were all ACS
Reagent Grade (Sigma Chemical Co., St. Louis, MO). Deionized water was obtained
from a Milli-Q® water purification system (Millipore Co., Bedford, MA). The micro-
syringes were from Hamilton Co. (Reno, NV). The 150μl glass vial inserts were bought
from Fisher Scientific (Pittsburgh, PA).

A Hewlett-Packard 1050 HPLC system with an automated sample injector was
used for the analysis. The HPLC column was a 3.9 ×150mm Waters Resolve® C18 with
5-micron spherical packing. A Model 486 Tunable Absorbance UV Detector (Waters,
Medford, MA) was used at the wavelength of 210nm. A 0.4M ammonium sulfate
solution was the HPLC eluent. The flow rate was programmed as follows. It was held
constant at 0.5ml/min during the first five minutes, and then increased gradually to
2.0ml/min in the next three minutes. From 8 to 13 minute, the flow rate was kept constant
at 2.0ml/min. The sample injection volume was 20μl. Minichrom V. 1.62 (VG Data
Systems) software was used for data acquisition and analysis.
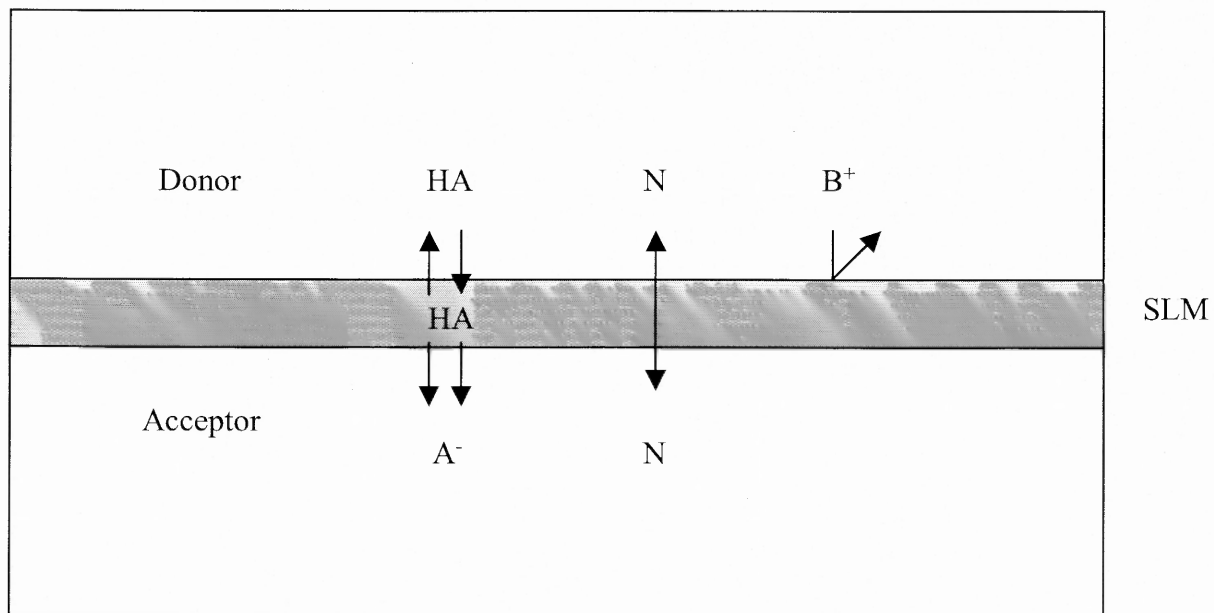
Figure 5.2 The concept of SLMME. HA, N, and B$^+$ represent acids, neutral species, and bases respectively.

5.3 Results and Discussion

Figure 5.2 illustrates the concept of Supported Liquid Membrane Microextraction

(SLMME). The acids first move from the bulk donor solution to the surface of the

membrane, and then partition into the membrane liquid. After migrating across the

membrane, they are back extracted into the acceptor through deprotonation. The two

processes take place simultaneously so that extraction is very efficient. The

concentrations of the neutral compounds are the same in both the donor and the acceptor,

which means no enrichment. Basic compounds are in the charged form in the donor and

excluded from the extraction. Therefore, SLMME provides both high enrichment and

high selectivity.

At equilibrium, the mass balance equation in SLMME can be written as:

$$C_I V_D = C_W V_D + C_M V_M + C_A V_A \qquad (5.1)$$

C_I is the initial analyte concentration in the donor prior to extraction; C_W, C_M, and C_A are

the equilibrium analyte concentrations in the extracted sample, in the membrane, and in

the acceptor respectively. V_D, V_M, and V_A are the volumes of the donor, the membrane,

and the acceptor respectively.

The analyte in the donor must be in the undissociated, molecular form to be

extractable. The analyte in the acceptor should be in the dissociated, ionized form so that

it cannot reenter the membrane. K_D is the partition coefficient between the membrane and

the donor, and K_A is the partition coefficient between the membrane and the acceptor.

$$K_D = C_M /(C_W * \alpha_D) \qquad (5.2)$$

$$K_A = C_M /(C_A * \alpha_A) \qquad (5.3)$$

K_D and K_A are of the same order, provided the ionic strength of the donor and the acceptor are not significantly different. α_D and α_A are the fractions of analyte in the undissociated form in the donor and acceptor phase. It is desirable to have α_D close to one, and α_A a very small number. For the extraction of weak acids, the donor pH must be at least 2 pH units lower than the pKa value of the acid in order to attain $\alpha_D > 0.99$. To achieve $\alpha_A < 0.0005$, the acceptor pH must be at least 3.3 pH units higher than the pKa value [42].

The extraction efficiency (EE) is defined as the fraction of analytes extracted, and is given as:

$$EE = C_A V_A / C_I V_D \qquad (5.4)$$

The enrichment factor (EF) is defined as the ratio of the analyte concentration in the acceptor phase to that in the initial water sample:

$$EF = C_A / C_I \qquad (5.5)$$

Combing Equations 5.1, 5.2, 5.3, and 5.4, the EE at equilibrium can be written as:

$$EE_{max} = 1 / [(\alpha_A V_D K_A)/(\alpha_D V_A K_D) + (\alpha_A K_A V_M)/ V_A +1] \qquad (5.6)$$

Combing Equations 1,2,3, and 5, the EF at equilibrium can be written as:

$$EF_{max} = 1 / [(\alpha_A K_A)/(\alpha_D K_D) + (\alpha_A K_A V_M)/ V_D + V_A / V_D] \qquad (5.7)$$

Because α_D is approximately 1, and if K_A and K_D are assumed to be similar, Equations 6 and 7 can be simplified to:

$$EE_{max} = 1 / [(\alpha_A V_D)/V_A + (\alpha_A K_A V_M)/ V_A +1] \qquad (5.8)$$

$$EF_{max} = 1 / [(\alpha_A + (\alpha_A K_A V_M)/ V_D + V_A / V_D) \qquad (5.9)$$

Equation 5.8 indicates that in order to achieve high EE, α_A should be small. Higher EE can be obtained by increasing the acceptor volume (V_A) or decreasing the donor volume

(V_D). According to Equation 5.9, small α_A is also necessary for a high EF. However, EF decreases with the increase in V_A, and increases with the increase in V_D. In other words, the donor and acceptor volumes have opposite effects on EE and EF. In analytical applications, the higher the EF, the lower the detection limit is. Therefore, the extraction should be optimized to provide the highest EF.

The time required to reach the maximum enrichment depends on several factors. The overall mass transfer resistance is the sum of mass transfer resistance in the bulk donor solution, the donor-membrane boundary layer, the membrane, the membrane-acceptor boundary layer, and the acceptor. Because the rate of deprotonation from the membrane to the acceptor is much faster than the mass transfer in other phases, the resistance on the acceptor side is generally negligible. The extraction speed is either donor-controlled, or membrane-controlled depending upon the conditions of each phase.

5.3.1 The Donor Conditions

Concentrated H_2SO_4 was added to the water sample to lower its pH to a level at which the HAAs were mostly in the uncharged, molecular form. The pKa values of the HAAs are listed in Table 5.1. When 6.0ml of H_2SO_4 was added into 100ml water, the sample pH dropped to about -0.3, which was only one unit below the pKa value of most HAAs. Further adding H_2SO_4 improved the EF, because at lower pH α_D was closer to one, and more HAAs existed in the extractable form. The EF almost doubled when the amount of H_2SO_4 added to 100ml water was doubled to 12.0ml.

The "salting-out effect" has been used in liquid-liquid extraction. It refers to increasing the ion-strength of an aqueous solution to lower the solubility of an organic
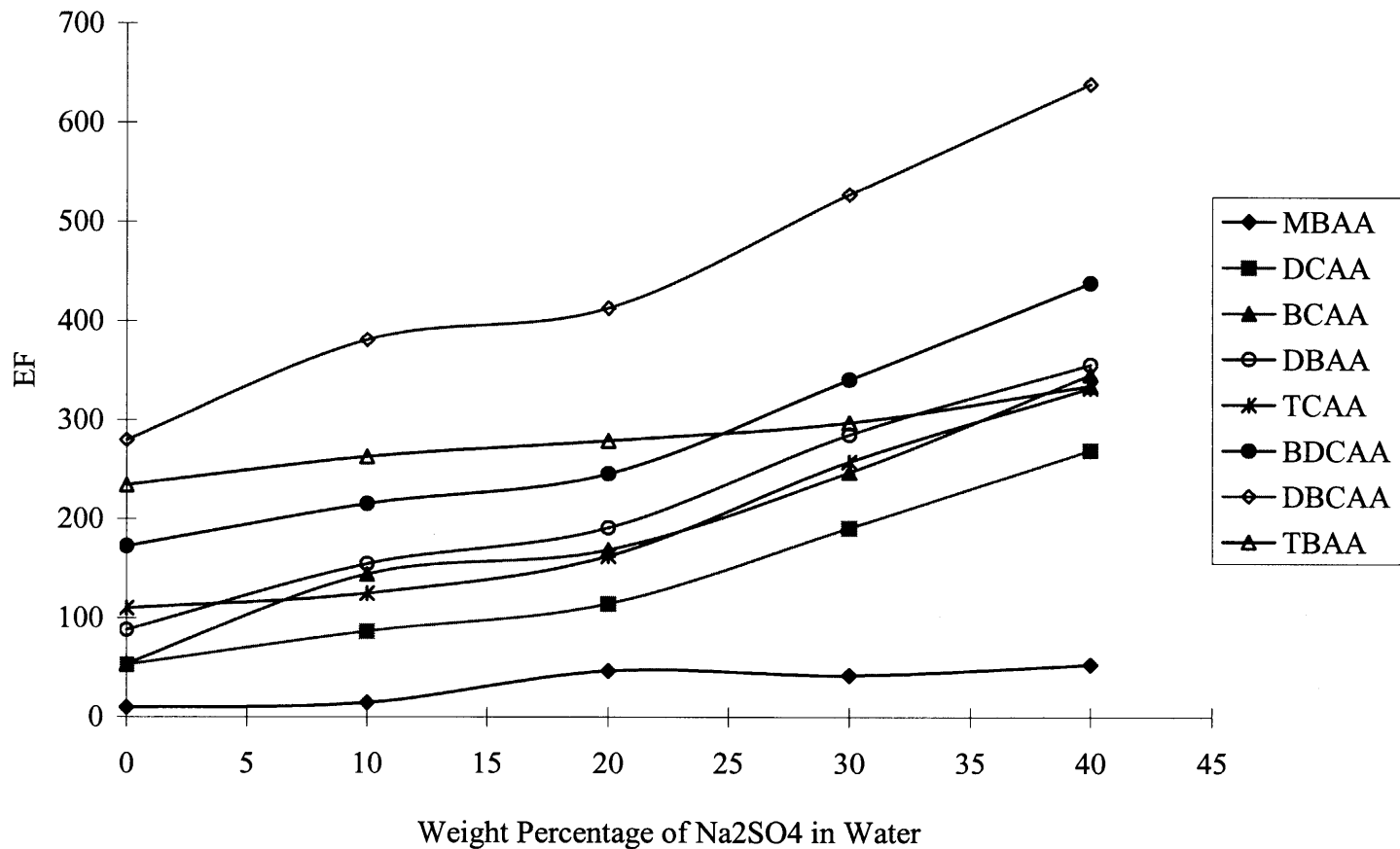
Figure 5.3 Enrichment factor as a function of Na2SO4 concentration. A 8.5cm of X20 membrane was used; the donor was 20ml of water containing 40-400ppb HAAs; the acceptor was 10ul of 0.01M NaOH; and the extraction time was 30 minutes at stirring setting 3.
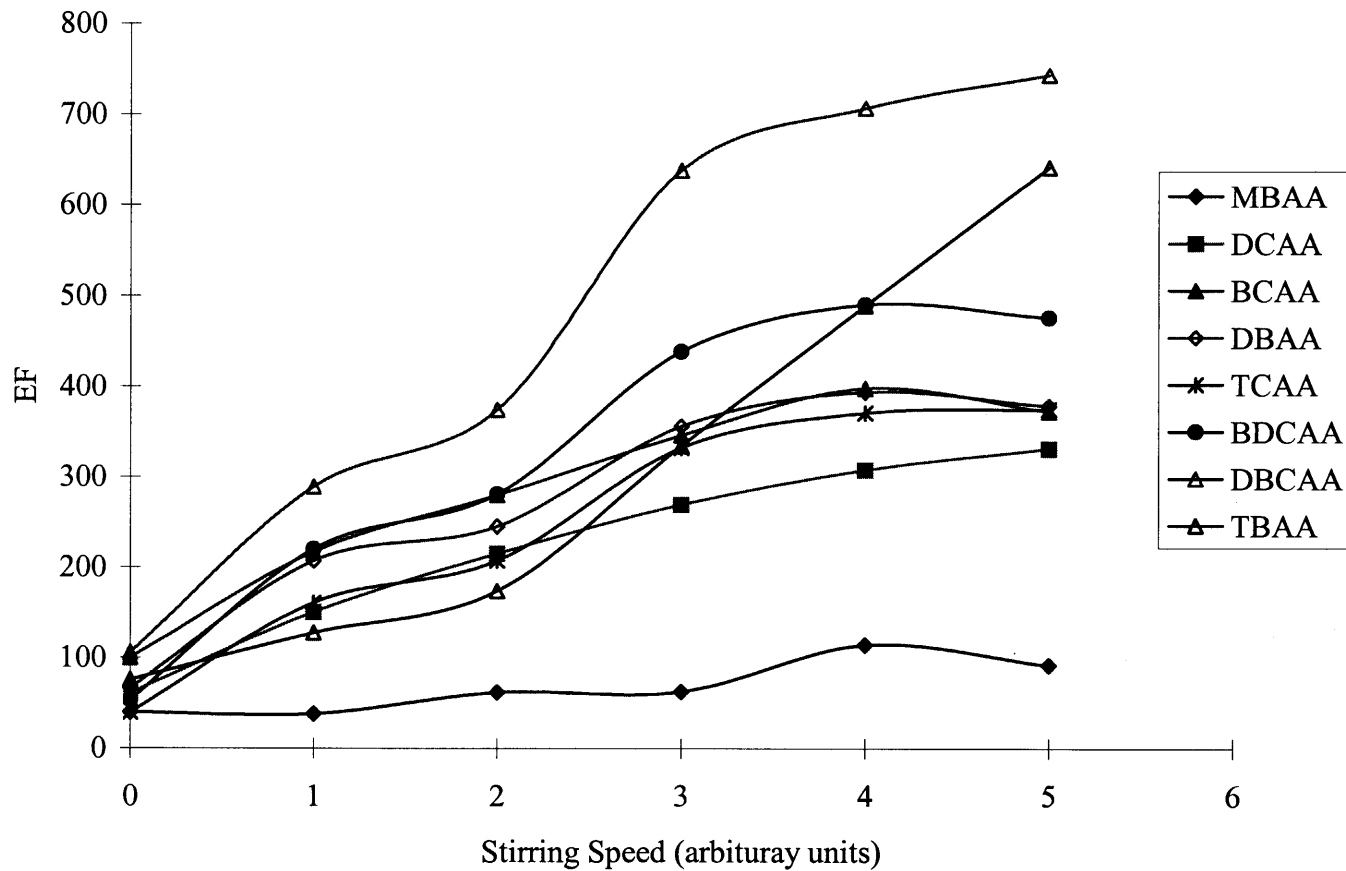
Figure 5.4 Enrichment factor as a function of stirring speed. A 8.5cm of X20 membrane was used; the donor was 20ml of water containing 40-400ppb HAAs and 40% Na2SO4; the acceptor was 10ul of 0.01M NaOH; and the extraction time was 30 minutes.

compound in water. This increases the partition coefficient (K_D). In this research, sodium sulfate was added to the water sample to "salt out" the HAAs. Salt concentrations from 0% to 40% (weight percentage) were tested. At 40%, the salt solution was near saturation. It was found that increasing salt concentration resulted in higher EF of HAAs. Figure 5.3 shows that the EF increased between two to six times (compound dependent), when the salt concentration increased from 0% to 40%.

Stirring improved extraction efficiency, because it increased the mass transfer coefficient in the donor phase. Figure 5.4 shows that EF increased about two to nine times for the HAAs, when the stirrer setting (arbitrary unit) increased from zero to five. The enrichment factor was a function of the donor volume. A larger volume sample contained more analytes, and resulted in higher EF. Under similar conditions, the EF obtained with a 210ml sample was approximately three times the EF with a 60ml sample. For drinking water analysis, sample availability is generally not an issue, and a larger volume can be used to obtain higher EF and consequently lower detection limits.

5.3.2 The Acceptor Conditions

The NaOH concentration in the acceptor from 0.002M to 0.2M was found to have little effect on the EF. This was because the pH of the lowest NaOH concentration was more than 3.3 units above the pKa values of the HAAs, and the corresponding α_A was smaller than 0.0005. NaOH concentrations higher than 0.2M might damage the HPLC column and was therefore avoided. The enrichment factor was directly related to the acceptor volume. The smaller the volume, the higher the EF was. An acceptor volume of 30μl was adequate for a 20μl HPLC injection, while providing high EF.

5.3.3 The Supported Liquid Membrane

Two types of microporous membranes were tested in this study. Under the same conditions, the EF of HAAs with the Celgard X20 membrane was found to be about twice that with the Accurel PP Q 3/2. When the acceptor volume was 30μl, the contact area between the membrane and the aqueous phases was approximately 130 mm^2 for a 25cm X20 membrane, and 200 mm^2 for a 12.5 cm Q3/2 membrane. The higher EF with X20 was attributed to its thinner membrane wall as compared to the Q3/2 membrane. The diffusion coefficient was larger in the thinner membrane, which in turn resulted in faster mass transfer. Therefore, the thinner membrane was preferable for faster extraction. However, the thicker membrane was mechanically stronger and less susceptible to bending. It was easier to work with, especially when the membrane was long.

Di-hexyl ether (DHE) and Di (2-Ethylhexyl) Phosphate (DEHPA) were tested as the membrane liquid. The enrichment factors for HAAs with DHE were an order of magnitude higher than those with DEHPA, so DHE was used in the rest of the study. It was reported that the addition of Trioctylphosphine oxide (TOPO) into the membrane liquid could increase the EE of polar analytes [91]. Figure 5.5 shows that the EF increased when the TOPO concentration was increased from 0 % to 5%. The degree of increase depended upon the polarity of the HAA. A more polar compound showed a larger increase in EF. When TOPO concentration increased from 5% to 10%, the EF of more polar (DCAA, BCAA, and DBAA) compounds continued to increase, while the EF of less polar compounds (TCAA, BDCAA, DBCAA, and TBAA) decreased. Moreover,
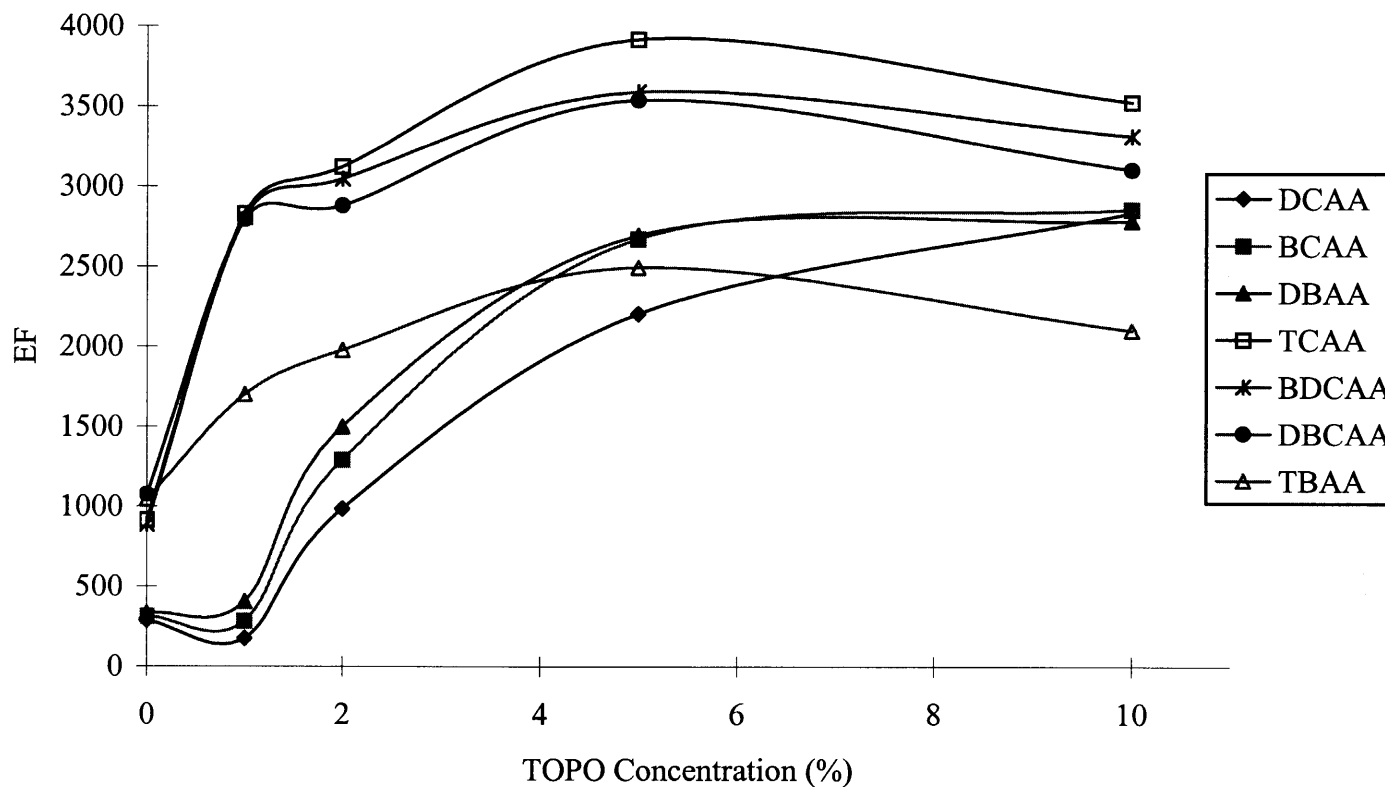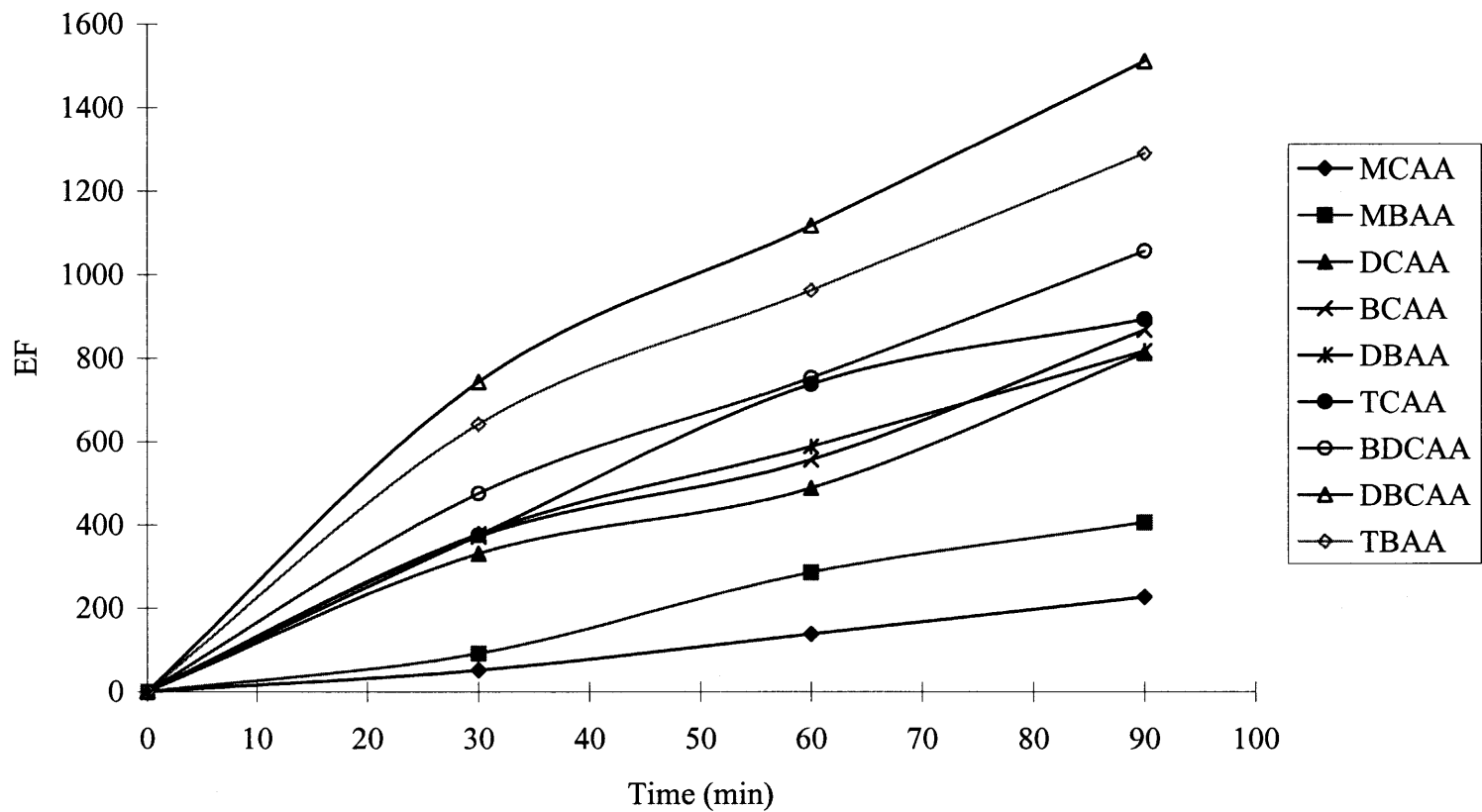
Figure 5.5 Enrichment factor as a function of TOPO concentration in the membrane. A 12.5cm of PP Q membrane was used; the donor was 230ml of water containing 5ppb HAAs; the acceptor was 30ul of 0.2M NaOH; and the extraction time was 60 minutes at stirring setting 9.

interferences in the chromatogram increased when TOPO concentration was higher than 5%. Therefore, 5% was chosen to be the optimum TOPO concentration in the membrane. The presence of TOPO significantly changed the behavior of the membrane. As mentioned before, the EF was not affected by the NaOH concentration in the range of 0.002 to 0.2M, when pure DHE membrane was used. However, when the membrane contained 5% TOPO, no HAAs could be extracted at a NaOH concentration lower than 0.05M. With 10% TOPO in the membrane, the minimum NaOH concentration was 0.2M. In other words, higher concentration of TOPO in the membrane required higher NaOH concentration in the acceptor. This is explained by the fact that TOPO is a very effective hydrogen-bonding reagent. A certain OH⁻ concentration is required to break the hydrogen bond between TOPO and HAAs, so that the acids could be released into the acceptor.

Moreover, with TOPO in the membrane, adding salt into the donor not only failed to increase the enrichment factor, but also had a negative effect. For example, when the membrane contained 5% TOPO and the acceptor concentration was 0.2M, increasing the Na_2SO_4 concentration in water to 40% (Na_2SO_4: H_2O, w/w) decreased the EF to 50% of what was obtained with no salt in the sample. Another interesting phenomenon was that with 1% of TOPO in the membrane, the EF remained unchanged when the sulfuric acid-to-water ratio doubled from 6:100 (v/v). This was also in contrast to the observation when a pure DHE membrane was used.

5.3.4 Extraction Time

The enrichment factor increased with time. The increase was almost linear. Figure 5.6 shows that the EF increased 2 to 4 times, when the extraction time was increased from 30

Figure 5.6 Enrichment factor as a function of extraction time. A 8.5cm of X20 membrane was used; the donor was 20ml of water containing 40-400ppb HAAs; the acceptor was 10ul of 0.03M NaOH; and the extraction was at stirring setting 5.

minutes to 90 minutes. Sixty minutes was taken as a compromise between a high

enrichment factor and a relatively short extraction time.

5.3.5 Ion-pair Chromatography with Flow Programming

An ion-pair chromatography (IPC) method with flow programming was developed for

the separation of all the nine HAAs within ten minutes. Ammonium sulfate at a

concentration of 0.4M was used as the ion-pairing agent in the mobile phase. Flow

programming rather than gradient elution was used because the former provided better

separation with less baseline drift. Figure 5.7 shows a chromatogram of a standard

solution containing nine HAAs at 1ppm each.

5.3.6 Analytical Performance

It was observed that the purity of the membrane liquid was critical for the precision and

accuracy of the analysis. Initially, DHE of 98.9% purity was used and the chromatogram

contained two interfering peaks. Since DHE is insoluble in water, it was assumed that the

interferences were caused by impurities. When DHE of 99.1% purity was tested, the

above assumption was confirmed. The higher purity ether showed less interference, and

the base line noise was also low. The purer DHE was then used in this study.

Figure 5.8 is a chromatogram after SLMME enrichment of a spiked water sample

containing ppb/sub-ppb level HAAs, obtained under the following conditions. The donor

was 210ml water mixed with 12.5ml concentrated sulfuric acid. The acceptor was 30µl of

0.05M NaOH solution. The membrane was 12cm PP Q3/2, with DHE containing 5%

TOPO as the supported membrane liquid. The extraction time was 60 minutes and the
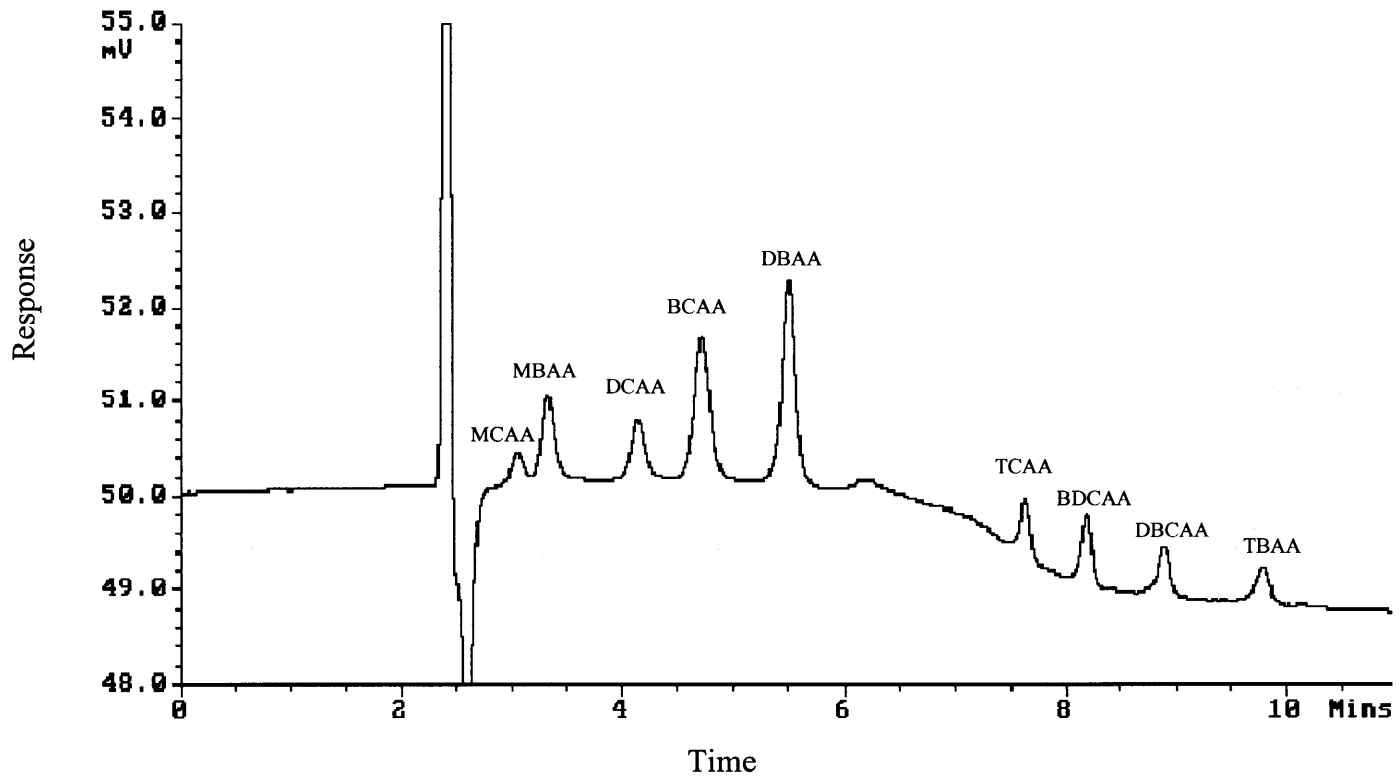
Figure 5.7 Chromatogram of nine HAAs in reagent water at a concentration of 1ppm each.
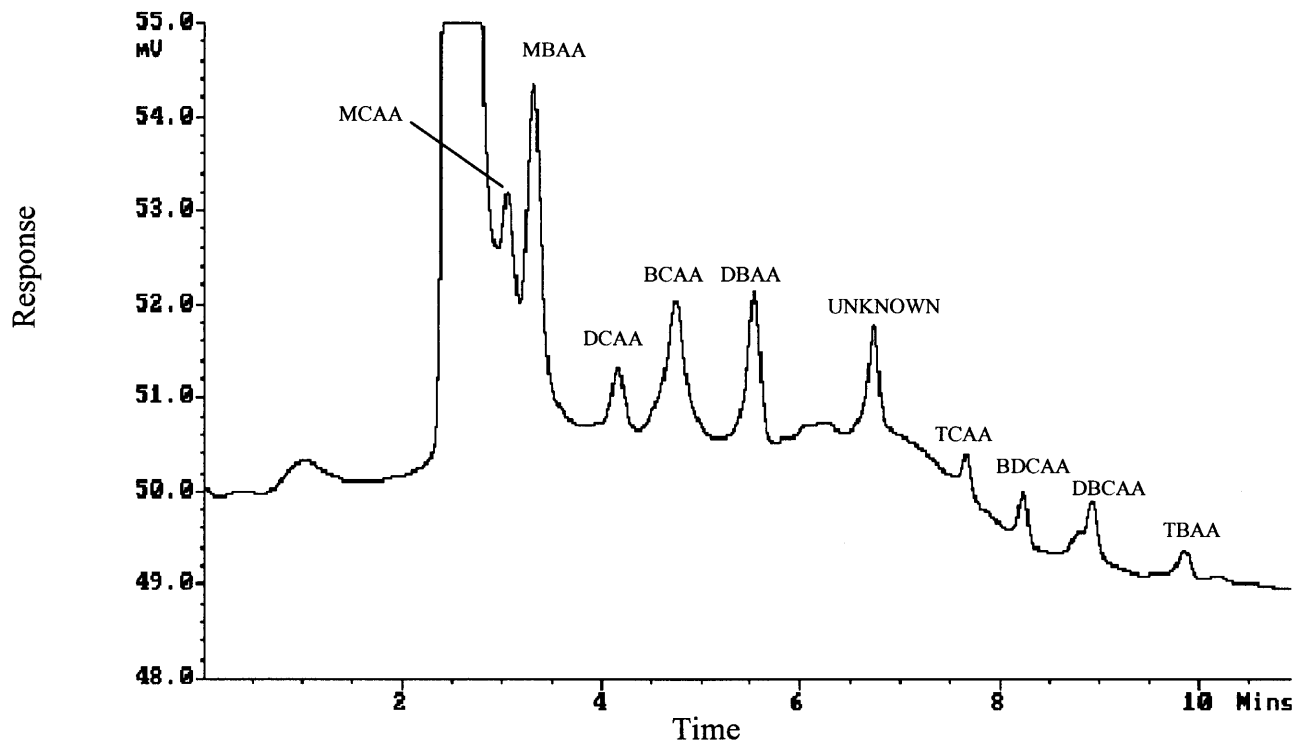
Figure 5.8 Chromatogram of nine HAAs in reagent water after SLMME. The concentrations were: MCAA at 40ppb, MBAA at 10ppb, DCAA at 0.8ppb, and the other six HAAs at 0.4ppb.

stirring speed was at setting 9. Compared with Figure 5.7, it represents an enrichment

factor as high as 3000, which demonstrates the effectiveness of SLMME. Table 5.3 lists

the method detection limits (MDL), linear dynamic range, and precision for HAA

analysis obtained under the same conditions as those for Figure 5.8. The MDLs were

lower than, or comparable to those of EPA method 552.2 for seven out of the nine HAAs.

The MDLs of MCAA and MBAA were higher than those of the EPA method. This is

because MCAA and MBAA are very polar compounds. Their octanol-water partition

coefficients (logP) are considerably lower than other HAAs (see Table 5.1).

Table 5.3 Analytical Performance of the Developed Method

	MDL (μg/L or ppb)*	Linear Dynamic Range (μg/L)	Linear Regression Coefficient	RSD**
MCAA	7.7	20-160	0.999	6.0
MBAA	2.0	10-80	0.998	6.9
DCAA	0.21	0.8-20	0.999	11.9
BCAA	0.09	0.4-20	0.999	6.6
DBAA	0.10	0.4-20	0.999	5.1
TCAA	0.05	0.4-20	0.999	2.6
BDCAA	0.13	0.4-20	0.999	7.1
DBCAA	0.12	0.4-20	0.999	5.7
TBAA	0.08	0.4-20	0.999	3.7

* The Method Detection Limit (MDL) was obtained following a standard EPA procedure [52].
** The Relative Standard Deviations (RSD) based on seven replications was obtained at concentrations of 40, 10, and 0.8ppb for MCAA, MBAA, and DCAA respectively, and the concentration was 0.4ppb for the rest of the HAAs.
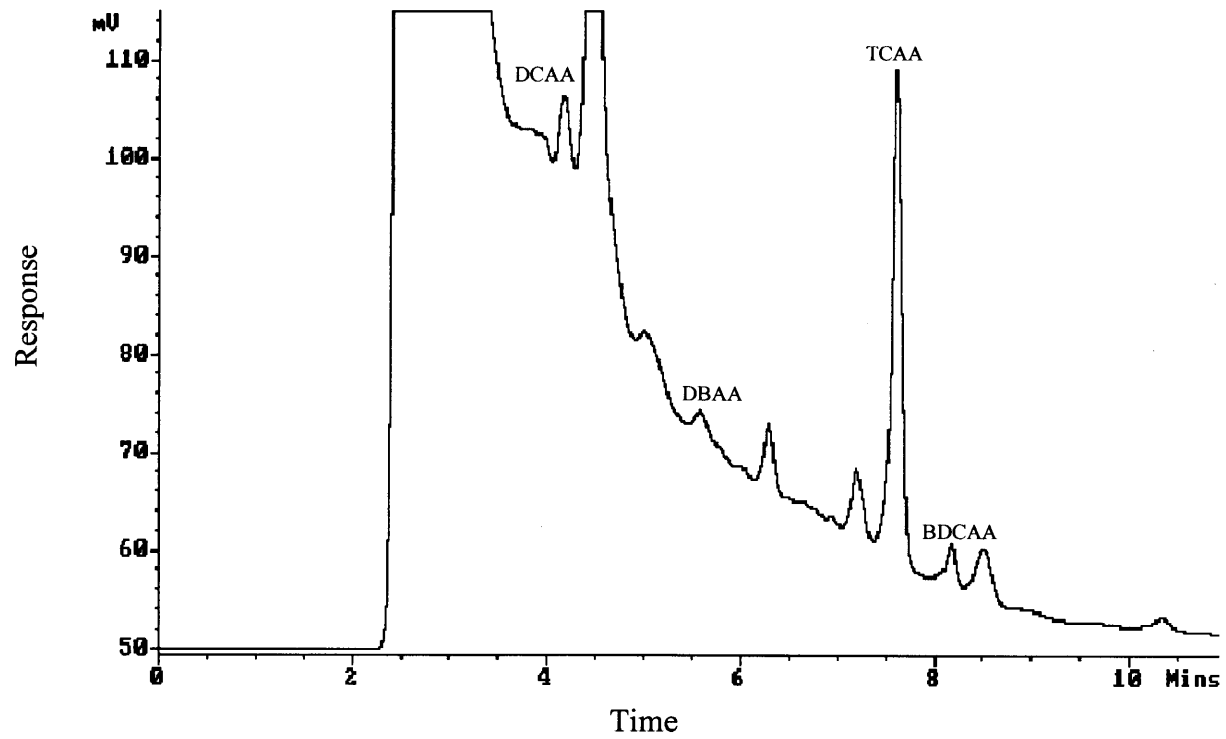
Figure 5.9 Chromatogram of tap water from Newark, NJ, obtained using the developed SLMME-IPC method.

5.3.7 Application

To test SLMME with Ion-pair chromatograph with real world samples, tap water from Newark, NJ was analyzed. Figure 5.9 shows a chromatogram obtained under the same conditions as those for Figure 5.8. Four HAAs, DCAA, DBAA, TCAA and DBCAA, were identified, and their concentrations were 9.82μg/L, 0.714μg/L, 25.3μg/L, and 2.21μg/L respectively.

5.4 Conclusion

Supported Liquid Membrane Microextraction followed by ion-pair chromatography was developed as a simple and effective method for the determination of nine HAAs in water. It did not require derivatization or large amounts of organic solvents. The SLMME device was easy to make and use. Enrichment factor as high as 3000 was obtained with 60 minute extraction. The extract was directly analyzed by IPC in ten minutes. This method showed excellent precision, and the detection limits of most analytes were lower or comparable to those by EPA standard method. The detection limits were significantly lower than other LC based HAA analysis methods. This method was also economical and environmental friendly because it used very little organic solvent. In addition, SLMME could also be used with IC or CE based HAA analysis methods, and was expected to significantly improve their sensitivity.

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